ESR ON SILVER CLUSTERS IN ZEOLITE A

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ABSTRACT

    The silver cluster formation in zeolite A with different loadings was studied by ESR. Depending on the reduction degree hyperfine spectra with seven and nine lines, a superoxide and a conduction electron spin resonance (CESR) line are observed. These signals could be assigned to the evolution in silver cluster formation in and outside the zeolite structure.
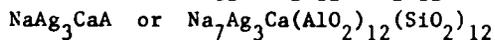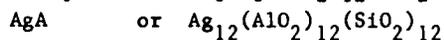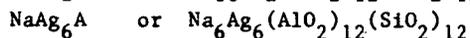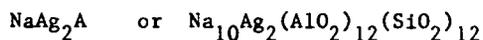
INTRODUCTION

    By cation exchange it is possible to incorporate various metals in zeolite structures dispersed as single cations. Reduction by molecular hydrogen leads to highly dispersed metal particles with important catalytic properties [1]. In order to explain the catalytic properties of metal-loaded zeolites it is necessary to know (i) the dimension of the metal clusters, (ii) the location of the metal clusters inside the zeolite structure and (iii) the reduction mechanism and cluster mobility. Metal particles in zeolites have been studied by X-ray diffraction [2], optical diffuse reflectance spectroscopy [3], fluorescence emission excitation [4] and temperature programmed ad- and desorption [5].

    In this paper we present ESR measurements on silver particles in zeolite A. There are several reasons to choose this silver-loaded system. Starting from NaA zeolite it is very easy to exchange the sodium cations by silver in any stoeichiometric amount [6]. The reduction of the silver ions is easily performed by reaction with molecular hydrogen; at room temperature the formation of silver particles inside the zeolite structure is expected [7]. Hermerschmidt and Haul [8] confirmed unambiguously the presence of Ag_6^{x+} clusters and submicroscopic silver crystallites by preliminary in-situ ESR measurements on AgA and AgX zeolites during the reduction process.

In zeolite A silver ions are located in the α- and β-cages and after reduction silver clusters are expected inside these cavities. The shaping of metal clusters by the zeolite structure is of interest for the study of the physical and chemical properties of small metal particles. Some theoretical predictions about the quantum size effect [9,10] for instance can be verified.

EXPERIMENTAL

Starting from NaA zeolite (Union Carbide, Linde Division) and by adding the necessary amount of 0.01 molar $AgNO_3$ solutions to the zeolites and exchanging in the dark overnight at room temperature we prepared the following silver samples :

$NaAg_2A$ or $Na_{10}Ag_2(AlO_2)_{12}(SiO_2)_{12}$

$NaAg_6A$ or $Na_6Ag_6(AlO_2)_{12}(SiO_2)_{12}$

AgA or $Ag_{12}(AlO_2)_{12}(SiO_2)_{12}$

$NaAg_3CaA$ or $Na_7Ag_3Ca(AlO_2)_{12}(SiO_2)_{12}$

The sodium-silver-calcium ratios are estimated from synthesis, and the samples were washed and dried. To avoid the ESR lines of Fe^{3+} present in commercial zeolite A we followed a chemical extraction procedure for iron impurities described by Derouane et al. [11]. The dehydration of the samples is done either by heating in vacuum or in a helium and oxygen gas flow at 700 K. The reduction of the samples is performed at room temperature by a pulse method or a flow method. The pulse reduction method consists of the admission of molecular hydrogen (10 p.p.m. O_2) at a certain pressure (3 mbar-1 bar) in the sample holder during a restricted time interval; after this activation the hydrogen gas was pumped off quickly and replaced by 1 bar helium (5 p.p.m. O_2). When severe reduction of the samples was needed a flow of hydrogen gas (1 cm^3/s) was used in the sample holder.

The ESR measurements were performed on a Bruker spectrometer (ER200 D-SRC) at 9.5 GHz and at room temperature.

RESULTS

For the sodium-silver samples the ESR results are independent of the Ag-loading. During the dehydration process the samples change their colour from white to yellow (500 K) and finally to brick red for AgA or yellow-brown for the other compositions. After dehydration we were able to detect in some cases a very weak seven line spectrum similar to that shown in figure 1A and due to Ag_6^{x+}. It is important to notice that these dried powder samples are light insensitive : the treatments and ESR measurements can be performed in day-light.

By gradually reducing the samples at room temperature four kinds of ESR signals are successively seen. In a first stage and under mild reduction conditions (30 mbar H_2 during 60 s) we observe (fig. 1A) a growing seven line spectrum for all sodium-silver samples (g = 2.025 $\pm$ 0.003). The observed hyperfine splitting (a = 6.76 $\pm$ 0.07 mT) can be assigned to the hyperfine interaction of an unpaired electron with six equivalent silver nuclei (I = 1/2). The isotope effect (^{107}Ag, ^{109}Ag) is not resolved due to the small coupling constant and the large line width. This spectrum clearly indicates the presence of charged Ag_6^{x+} clusters; no information on the charge of the clusters is obtained from these ESR measurements (x = 5,3 or 1). This result is consistent with the findings of
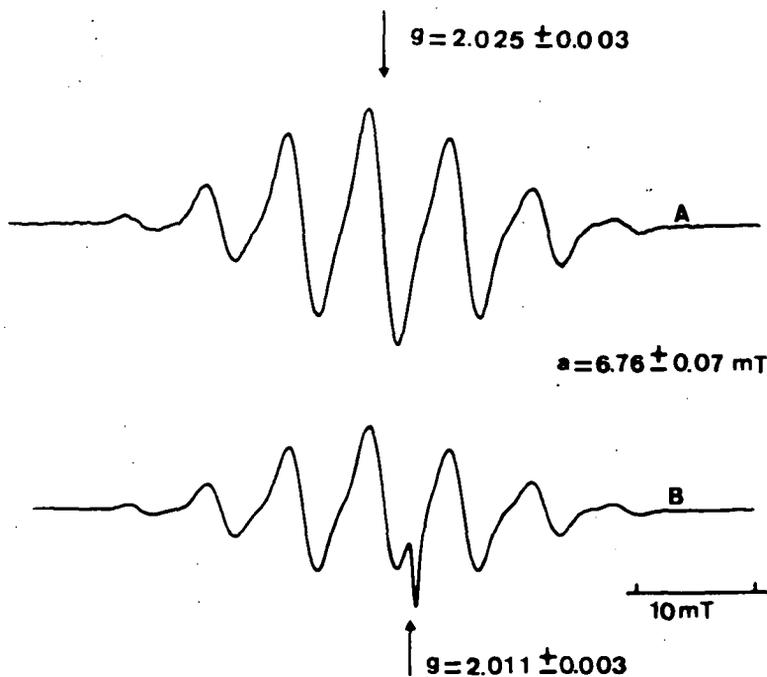
$g = 2.025 \pm 0.003$

$a = 6.76 \pm 0.07$ mT

A

B

10 mT

$g = 2.011 \pm 0.003$

Fig. 1. ESR of Ag_6^{x+} clusters in reduced $NaAg_6A$;
A : mild reduction, B : stronger reduction

Hermerschmidt et al. [8], although some differences in g-factor and hyperfine coupling constant a are found. After one reduction pulse the intensity of the ionic cluster spectrum reaches a constant value only after several hours indicating the mobility of silver atoms and ions during the cluster formation in the zeolite structure. If one applies a stronger reduction (a 60 s pulse of 1 bar H_2) a second ESR signal is superimposed on the ionic cluster signal (fig. 1 B). By further reducing the samples the Ag_6^{x+} spectrum disappears and the second ESR signal is clearly visible (fig. 2 A). This single line (g = 2.011 $\pm$ 0.003) has an asymmetric shape and is assigned to O_2^-. This is confirmed by the measurement at 110 K of the anisotropic g-value of O_2^- (g_{xx} = 2.007, g_{yy} = 2.012 and g_{zz} = 2.033). This O_2^- signal grows first and then decreases with further reduction. Superimposed on this signal a weak nine line hyperfine spectrum is sometimes seen in a further reduction stage (g = 2.025 $\pm$ 0.005; a = 5.2 $\pm$ 0.4 mT; figure 2 B). This nine line spectrum is due to Ag_8^{y+}. The deformed base line in figure 2 B is due to a broad signal which grows by still further reduction at the expense of the other signals. It results into a signal seen in figure 3; this CESR signal has a line width of 10 mT and the g-factor equals 1.981 $\pm$ 0.003. It vanishes when the reduction proceeds.
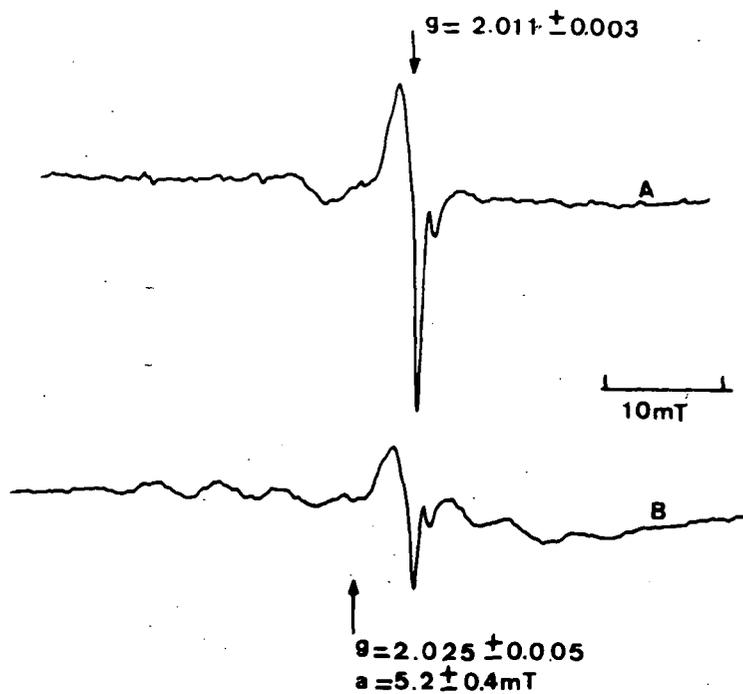
$g = 2.011 \pm 0.003$

A

10mT

B

$g = 2.025 \pm 0.005$
$a = 5.2 \pm 0.4mT$

Fig. 2. ESR of O_2^- and Ag_8^{y+} clusters in reduced $NaAg_6A$

$g = 1.981 \pm 0.003$

10mT
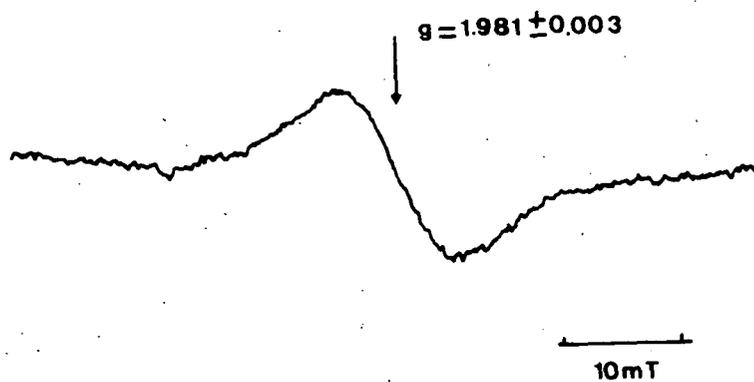
Fig. 3. CESR in severe reduced AgA (1 cm^3/s H_2 flow, 72 h)

This line was also seen by Hermerschmidt et al. but the nine line spectrum not [8]. It is important to notice that the four signals can be stabilized by pumping off the samples and keeping them under helium atmosphere.

In contrast to this, Hermerschmidt et al. detected their signals during a single complete reduction run. The ESR signals are also not affected by an oxygen flow treatment (600 s) at room temperature.

The results on the sodium-calcium-silver sample are somewhat different. Under mild reduction the ionic cluster signals are not observed; only after strong reduction (1 bar during 72 h) the asymmetric O_2^- line (g = 2.014 $\pm$ 0.003) is seen (fig. 4A); by further reduction the CESR signal (g = 1.976 $\pm$ 0.004; fig. 4 B) becomes apparent.

$\downarrow$ g = 2.014 $\pm$ 0.003
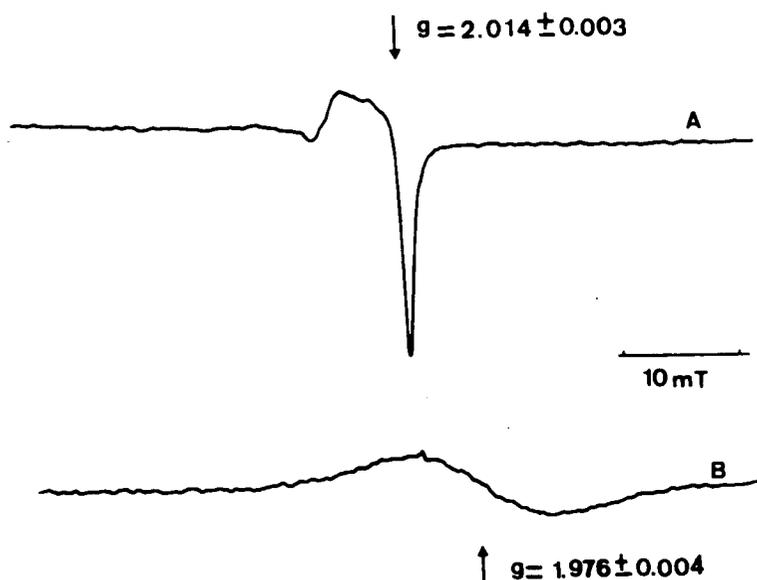
A

10 mT

B

$\uparrow$ g = 1.976 $\pm$ 0.004

Fig. 4. The O_2^- and CESR line in NaAg$_3$CaA

DISCUSSION

These ESR experiments prove that certain stages of cluster formation in silver-loaded zeolite A can be followed.

First of all, a very weak signal due to Ag_6^{x+} has been found after dehydration. Ag_3^{x+} and Ag_6^{x+} clusters have been found with X-ray diffraction, but the number of clusters detected by ESR is orders of magnitude smaller than the number expected on the basis of the X-ray diffraction data [2].

The comparison of the results of NaAgA zeolites and NaCaAgA allows us to conclude indirectly that the charged clusters, Ag_6^{x+} and Ag_8^{y+}, are located in the sodalite cages. Indeed, according to recent X-ray diffraction studies NaAgA zeolites have part of their Ag^+ ions in the sodalite cages, while NaCaAgA have the Ag^+ ions in the sixrings [2,12]. Thus, in the former case reduction of Ag^+ in the sodalite cages leads to clustering and stabilization of Ag_6^{x+}, and eventually Ag_8^{y+}, inside the cubooctahedron. Reduction of Ag^+ in NaCaAgA gives Ag atoms in the supercages, which agglomerate to metal particles inside the supercages. The dimensions of the supercages are probably too large to stabilize small, well-defined clusters. In NaAgA the charged clusters are decharged by further reduction; the electrostatic interaction with the lattice becomes zero and the Ag atoms migrate inside the supercages and agglomerate into supercage metal particles. The presence of these metal particles are indirectly detected by the appearance of an O_2^- signal. This superoxide line in the spectrum after reduction is coming from adsorbed oxygen on the surface of the very small metal particles located in the α-cage and from the resulting electron transfer from the metal particle surface to the adsorbed oxygen molecules [13]. The relatively narrow signal can not be assigned to the metal particles in the supercages as stated in a previous paper [14]. The O_2 molecules are present as impurities in the H_2 or He gases. Indeed, it is possible to prepare Ag_6^{x+} without the O_2^- by static reduction with H_2, followed by evacuation (instead of He-flushing).

The g-value of the broad CESR line of figure 3 is 1.983, exactly the value of bulk silver [15,16]. We assign this signal and that of figure 4B to larger metal particles in the supercage or on the external surface. The CESR signals exhibit the features of the quantum size effect of small metal particles, for instance the appearance of the signal at room temperature and the Lorentz shape [9,10]. Work is in progress to obtain valuable experimental data concerning the quantum size effect.

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