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Metal Phases in Zeolite Matrix: Electric and Electrochemical Properties

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Abstract: Thermal vacuum activation of hydrated silver zeolite forms leads to silver clusters formation in zeolite framework. The change in electrical conductivity of the Ag form of zeolites is a direct consequence of the appearance and formation of clusters. The electrochemical behaviour of samples points to the presence of several kinds of silver particles and also to their different location, inside and outside the zeolite. Electric and electrochemical measurements can be of practical importance in the investigation of metal clusters in zeolite structures.

1 INTRODUCTION

The replacement of some or all Na^+ ions in the zeolites $Na_{12}A$ or $Na_{85}X$ (where A and X represent the aluminosilicate part of zeolite) with Ag^+ ions, followed by the dehydration of zeolite, results in a partial reduction of Ag^+ ions and their association into clusters.[1–7] The formation of clusters in samples of Ag–A and Ag–X zeolites was established by X-ray structural analysis, transmission and diffuse reflectance spectroscopy.[2–7]

From data reported in the literature it follows that the dehydration of the Ag form of zeolites leads to the formation of silver clusters by one of the following mechanisms:[1,8]

autoreduction in the presence of zeolite water (25–250°C)

$$2(Ag^+ - Z - O^-) + H_2O \longrightarrow 2Ag^0 + \frac{1}{2}O_2 + 2Z-OH \quad (1)$$

and

autoreduction by oxygen from the zeolite lattice (127–380°C)

$$2(Ag^+ - Z - O^-) \longrightarrow 2Ag^0 + \frac{1}{2}O_2 + Z-O^- + Z^+ \quad (2)$$

The diffusion of silver atoms thus formed gives rise to the formation of silver clusters of the $Ag_n{}^{q+}$ type in the inside of zeolites, but at higher temperatures the formation of external silver particles is also possible.

In this paper the process of silver cluster formation was followed by electrochemical methods with the aim of widening our knowledge on silver clusters, their nature, mobility and position. The participation of electronic conductivity in the total electrical conductivity, as a consequence of Ag^0 existence, was also tested.

2 EXPERIMENTAL

The silver form of zeolites A and X with different Ag^+ contents were prepared by ion exchange of commercial zeolites Na–A and Na–X from Union Carbide with 0.1M $AgNO_3$ solution, as described in our previous papers.[9,10]

For conductivity and electrochemical measurements samples were pressed into pellets, 8–10 mm in diameter and 1–2 mm thick, under a pressure of 2.5 t/cm^2. The pellets were placed between silver and platinum plate electrodes and good contact was provided by means of a mechanical screw-clip. The electrode system was put into a suitable closed glass tube which could be evacuated up to 0.13 Pa, and heated in a suitable furnace under temperature control.

The conductivity of the samples was measured by using an alternating current of 1 kHz frequency, with an Iskra MA 5961 conductometer.

The electrochemical investigation was carried out using cyclic voltammetry and cyclic chronoamperometry with double potential jump. Measurements were carried out using two electrode systems in the range of silver deposition and dissolution, from +1.5 to −0.7V, with respect to a silver plate as the reference electrode, and using a flat Pt working electrode, in the temperature range 200–550°C. Samples previously dehydrated at 500°C in vacuum, designated as D, and thermally untreated samples, samples ND, were tested.

3 RESULTS AND DISCUSSION

3.1 *Electrical conductivity*

The electrical conductivity of zeolites is a function of the number of current carriers (in this case Na^+ and Ag^+ ions) and their mobilites, which depend on several factors. In an aluminosilicate matrix, the mobility of an ion depends on its position, size and charge. In silver exchanged forms of zeolites the conductivity was found to be lower than in the starting sodium forms. A partial exchange of Na^+ with Ag^+ ions is followed by a decrease in the electrical conductivity (Fig. 1). This may be caused by a decrease in the number and/or mobilities of ionic species, but both these phenomena are due to the process of cluster formation. This is evident from the behaviour of samples in the course of conductivity measurements. If conductivity measurements are carried out with samples previously heated at 500°C in vacuum and cooled, samples D, then the conductivity follows an Arrhenius behaviour with temperature (Figs 1 and 2). If, however, the conductivity is measured in the first heating cycle, samples ND, a significant distribution of points which do not converge to an Arrhenius behaviour is observed (Fig. 2). The fact is that with increasing temperature, due to thermal activation, the mobility of potential current carriers is increased, but, at the same time, with a increasing temperature the aforementioned processes of reduction and cluster formation occur within these samples, which will bring about a decrease in the electrical conductivity. These two processes have opposite trends and this is very clearly manifested in conductivity measurements with ND samples.

From the linear relation of log conductivity vs $1/T$, for samples D, the activation energy for the process of electrical conductivity was calculated; values are given in Table 1.

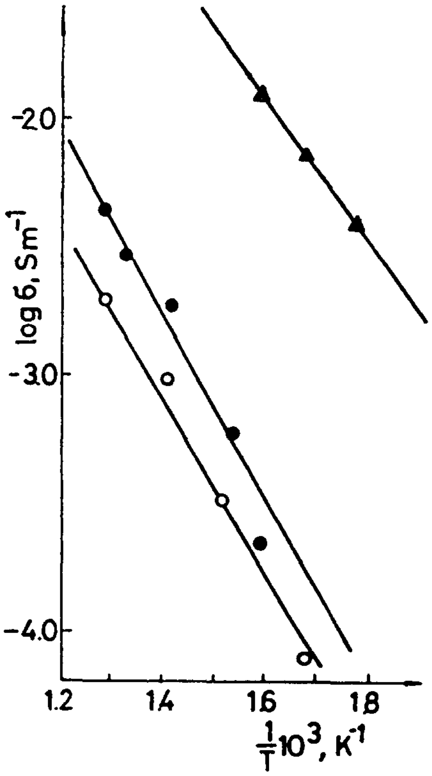

Fig. 1. Conductivity measurements in the form of an Arrhenius plot for zeolite Ag_xNa_{12-x}–A. D samples: x = 8.2(○), x = 11.8(●), x = 0(△) (from Ref. 9).

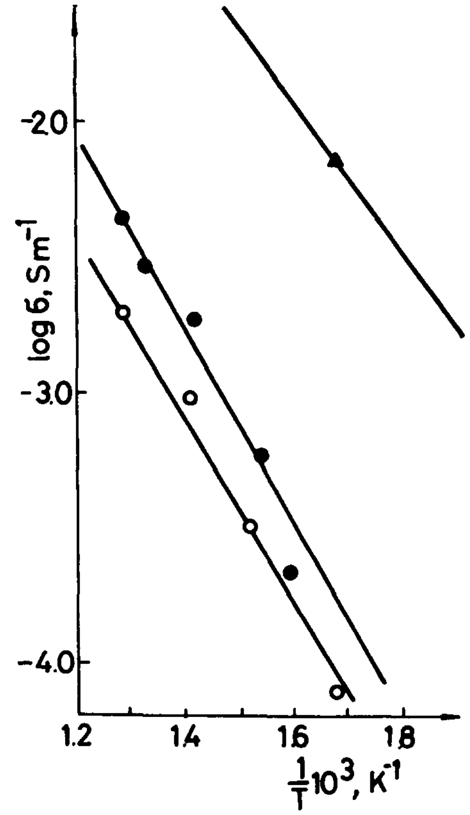

Fig. 2. Conductivity measurements in the form of an Arrhenius plot for zeolite Ag_xNa_{85-x}–X. D samples: x = 9.4(●), x = 20.1(△), x = 55.6(▲), ND samples; x = 9.4(■), x = 20.1(□).

Table 1. Activation energies for electrical conductivity, *E*, for different types of zeolites. The error of *E* is estimated to be ± 2 kJ mol^{-1}

Zeolite type	*E*, kJ mol^{-1}	Remarks
Na_{12}–A	52	Ref. 9
$Ag_{8.2}Na_{3.8}$–A	65	This work
$Ag_{11.2}Na_{0.2}$–A	61	This work
Na_{85}–X	52	Ref. 9
$Ag_{9.4}Na_{75.6}$–X	26	This work
$Ag_{20.1}Na_{64.9}$–X	59	This work
$Ag_{55.6}Na_{29.4}$–X	59	This work

In Fig. 3 it is shown that the conductivity of samples D depends considerably on the degree of $Na^+ \rightleftarrows Ag^+$ exchange. Namely, in zeolites of type A, as well as type X, the conductivity displays a minimum when the composition reaches about 0.3 mole fraction with respect to Ag^+; namely, at the latter composition the process of silver particle agglomeration is the most pronounced, whereas the participation of the charge carriers to the electrical conductivity process is the least.

3.2 Electrochemical behaviour

The electrochemical behaviour of representative samples displays all the properties characteristic of a solid ionic conductor based on silver salts (Figs 4 and 5). An increase in temperature leads to a higher mobility of Ag^+ ions with the deposition of silver according to $Ag^+ + e \longrightarrow Ag^\circ$. The deposited silver was oxidized under conditions of reversed polarization.

The presence of clusters in the aluminosilicate framework of zeolites is very clearly seen from a definite instability in the presence of a silver oxidation (anodic part of the curve); clusters also participate in the anodic process of dissolution.

More information on the electrode processes was obtained by analysing the polarization current changes with time in the course of 5, 10, 15 or 20 s, at a definite potential in the potential range of silver precipitation and dissolution (from −0.7 to +1.5V) (Fig. 5).

The shape of these curves depends on the potential given, as well as on the silver content of the investigated sample. In the case of samples with a lower silver content ($x_{Ag^+} \leqslant 0.5$ mole fraction), after a slight decrease the polarization current attains a constant value. This may point to a fast diffusion of the reducing species, but also to a considerable presence of electronic current.

Accordingly, the slope of the linear dependence $i = f(\log t)$, except for very small polarization values (0.0V), deviates considerably from 0.5, which indicates that Cotler's equation does not hold and excludes the diffusion as the limiting factor of the electrode process. In the case of samples with a higher silver content (diagram (b) in Fig. 5), the polarization current slightly increases at the beginning and then remains almost unchanged. These results indicate a considerable presence of the reducing species in the near-electrode layer which, under the influence of a direct electric field (potential given), is reduced on the electrode without any concentration polarization, and again oxidized at reverse polarization. The introduction of oxygen leads to a very abrupt increase in the polarization current (even after 1 min) and to disappearance of the instabilities observed on the polarization curves, due to rapid oxidation of clusters present. However, even after prolonged introduction of oxygen (several hours) the polarization current does not drop to the nullpoint. Such a behaviour may indicate a uniform distribution of metal clusters in the aluminosilicate framework, which oxygen molecules cannot reach very easily, (beta cages and hexagonal prisms), on account of their dimensions.

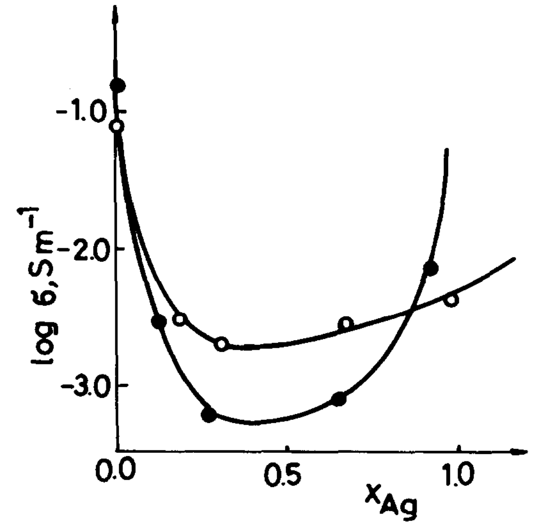

Fig. 3. Ionic conductivity as a function of composition for Ag_xNa_{12-x}–A zeolite (○) and Ag_xNa_{85-x}–X zeolite (●) at 400°C.

The correlation of electrical conductivity measurements and electrochemical measurements offer information on the location of clusters formed in the process of thermal dehydration of the silver form of zeolites. The fact that the polarization current does not decrease with time and that under an O_2 atmosphere there occurs an almost momentary oxidation of existing clusters suggest the presence of considerable external silver particles on zeolite crystallites, formed during heating at high temperatures (about 500°C) and/or under the influence of a direct electric field.

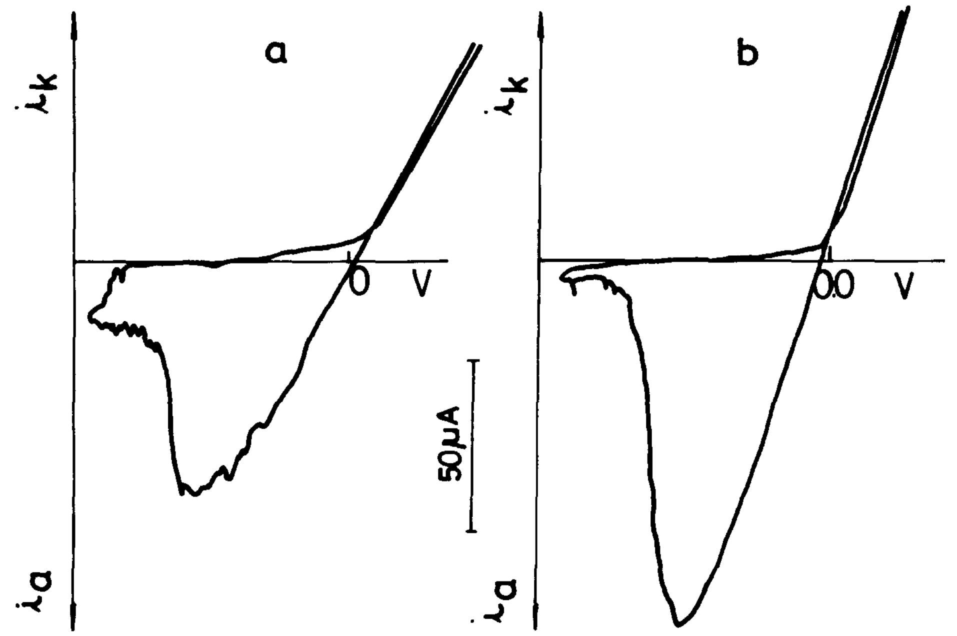

Fig. 4. Cyclic voltamograms of $Ag_{3.8}Na_{8.2}$–A at 500°C: sweep rate 50 mV/s from +1.5V to −0.7V; (a) in vacuum, and (b) in O_2.

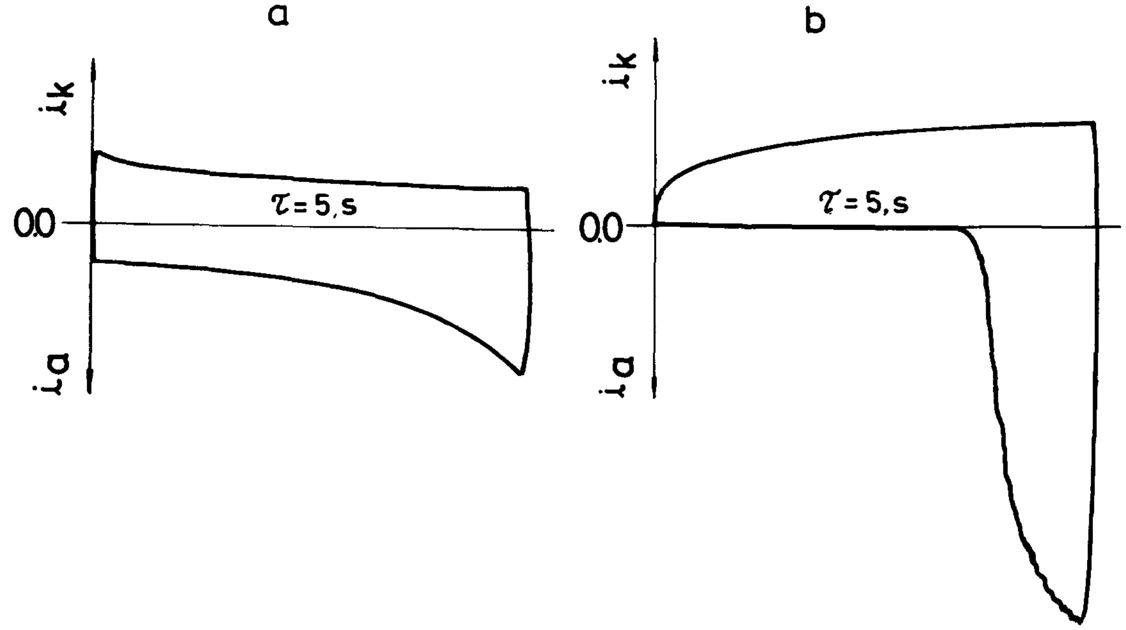

Fig. 5. Chronoamperograms of double potential step: (a) for $Ag_{3.8}Na_{8.2}$–A at 336°C from +1.5V to −0.3V; (b) for $Ag_{55.6}Na_{29.4}$–X at 500°C from +1.5V to −0.4V.

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