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THE IMPEDANCE MEASUREMENTS OF METAL-SILICATE SYSTEMS

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ABSTRACT

During the dehydration of Ag-exchanged type-A zeolite at different temperatures a metal clusters Ag_n^{x+} are formed. The diffuse reflectance spectroscopy and impedance measurements were used to investigate this process.

INTRODUCTION

The autoreduction of silver ions by intrazeolitic water and lattice oxygen occurs during the vacuum thermal dehydration /1,2/. So produced Ag^o atoms migrate and interact with other Ag^o atoms or Ag^+ ions. As the result of this process silver metal clusters appear entrapped in the cages of zeolite's structure. The colour of zeolite changes from yellow to brick red, depending on the degree of dehydration and cluster formation/2/.

The usual methods of metal clusters investigation are reflectance spectroscopy, far - IR spectroscopy and X - ray diffraction /2,3/. Recently, the impedance measurements have been widely used in investigation of both electric condutivity of sold electrolytes and polarization phenomena at the electrode/electrolyte boundaries /4,5/. Expecting that the formation of metal clusters has an influence to the zeolites condutivity we used the method of electrochemical impedance accompanied with reflectance spectroscopy in order to investigate the process of cluster formation.

EXPERIMENTAL

The Ag-exchanged type-A zeolite was prepared by the process of ion exchange with the solution of 0.1M $AgNO_3$. The samples were washed and dried in the dark.

Reflectance spectra in the range 350 - 650 nm were recorded after gradual evacuation at different temperatures by Cary 17D equiped with reflectance unit. Ag-A zeolite was embeded in a quartz reflectance cell and a reflectance reference was MgO. All spectra were converted to the Kubelka - Munck function $F(R_\infty)$ vs. the wavelength. R_∞ is the ratio of light beam intensity reflected from sample to light beam intensity reflected from standard. $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$ and represents the ratio of apsorption to the scattering coefficient supposing that the investigated system represents a randomly distributed particles whose dimensions are much smaller than the system at all.

For impedance measurements Ag-A powder (100 mg) was pressed into pellets (diameter 8 mm). A good eletrical contact was provided by an additional pressing of silver powder as an tightly adjacent layer on both sides of pellets. The measuring cell was placed into a thermostated vacuum tube. Measuring device consisted of a potentiostat/galvanostat, lock - in analyzer and computer coupled together. Using the AC Impedance Software System V2 all experiments were controlled by the computer. By this experimental technique the investigated sample was perturbed by alternating voltage E_{ac} of small amplitude and different frequencies. The measured response is alternating current of the same frequency as E_{ac} but with different phase angle with respect to E_{ac}. Experimental results are presented in a complex plane, imaginary part of impedance being the function of real part of impedance /5/. The frequency range used, 10^{3} - 10^{5} Hz, doesn't cover the range in which polarization electrode/electrolyte boundary appears. Thus, equivalent circuit representing our system contains only the elements relating to the bulk effects i.e. geometric and intergranular capacitances and bulk and intergranular resistances.

RESULTS

Reflectance spectra show changes in zeolite behaviour upon thermal vacuum dehydration at different temperatures (figure 1). Thermal treatment at 523 K (3 hours) led to appearance of an absorption band at 450 nm, and zeolite got yellow colour. This band exist also at 623 and 723 K and its intensity increases. But there are some other changes at 623 and 723 K. At 623 and 723 K the new

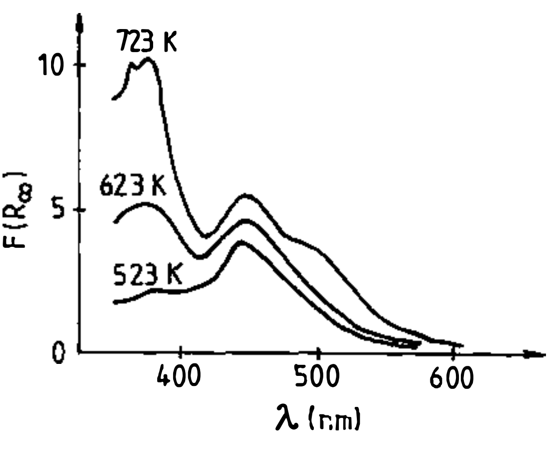

Figure 1. Reflectance spectra of vacuum dehydrated Ag-A at different temperatures

absorption band became evident appearing between 350 and 400 nm. The colour of Ag-A zeolite turned to orange - yellow. Finally at 723 K a new band at 500 nm appeared and the colour of sample changed to brick red (This band appears beyond 673 K).

Aluminosilicates are, essentially, cationic condutors /6,7/, so formation of silver particles during vacuum thermal dehydration must have the influence on their conductivity.

The impedance measurements were performed at the similar temperatures 541, 619 and 688 K. Starting at 541 K we observed change of ohmic resistance with time. Time dependence of resistance was observed at two other temperatures too. In the figure 2 time dependence at 688 K is presented.

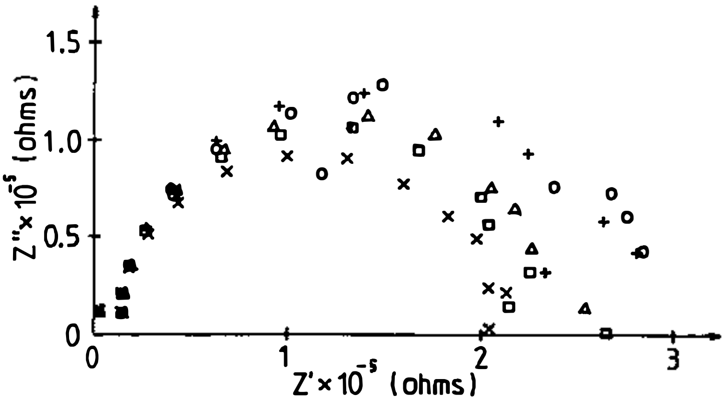

Figure 2. Time dependence of the impedance at 688 K :
x - 0min (the moment of achieving 688 K),
□ - 130min, Δ - 250min, o - 370min,
+ - 495min
Low frequency Z' axis intercepts represent the sum of bulk and intergranular resistance of a sample

Ohmic resistance increases at all temperatures with time, but the rate of resistance change decreases at higher temperatures (figure 3). The higher rate of resistance increase at lower temperatures is atributed to metal cluster formation, and its lower values at higher temperatures, where the cluster formation should be favoured, points out to the process of agglomeration. Such an interpretation is in accordance with reflectance studies where appearance of a new bands at 623 K and beyond 673 K points out to the process of agglomeration too.

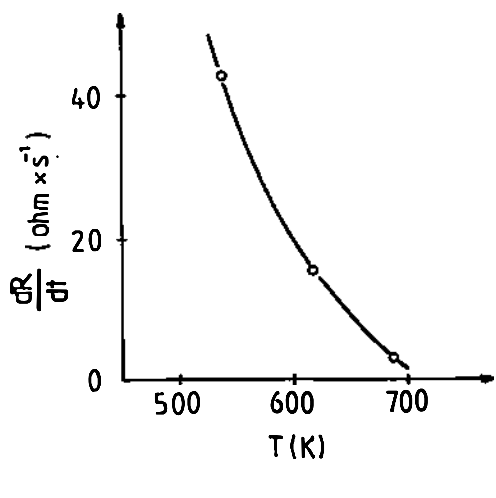

Figure 3. The rate of overall resistance increase ploted versus temperature

CONCLUSION

Thermal treatment of Ag - exchanged A - type zeolite causes the reduction of Ag^{+} cations and further agglomeration of Ag atoms. This process is accompanied by the change in reflectance spectra consisting in an increase of the intensity of allways present 450 nm band as well as in appearance of new bands at 375 and 500 nm.

Temperature induced impedance changes one can consider to be in accordance with the changes in reflectance spectra.

The impedance at constant temperature shows the time dependence, what means that the process of cluster formation appears to be kineticaly controlled.

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