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Synergistic Effect of Chemical and Thermical Treatment on the Structure and Sorption Properties of Natural and Chemically Modified Slovak Zeolite

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Abstract

The calcinated natural and chemically modified zeolite from the deposit Nižný Hrabovec (Slovak Republic) was studied. The changes of zeolite structure due to synergistic effect of temperature and chemical treatment were studied by DTA. The static radioindicatore method was used for studying the sorption of zeolite through the uptake of Cs and Co cations from model solutions. The results showed that the uptake of Cs and Co cations strongly depends on the modification of zeolite and on the higher temperature of calcination.

Key words: calcinations of chemically modified zeolite, thermochemical properties, DTA, sorption capacity, radioindicatore method

Introduction

Crystalline aluminosilicates – zeolites are an excellent example of anorganic type of natural ionexchange sorbent. The structure of zeolite is based on tetrahedral SiO_4 and AlO_4 units, which are connected by shared oxygen atoms. This kind of threedimensional structure has small pores where the exchangeable ions are located and where the ion exchange reaction takes place. Silicon is tetravalent and aluminium is trivalent and than the framework structure is negative charged. Thus each mole of aluminium produces one equivalent of cation exchange capacity for the zeolite framework. Zeolite has rigid pores and its exchange properties are mainly based on the charge density and pore size. Chemical modification of zeolite considerably increases its effectiveness for the sorption of multivalent and hydrated cations [1-6]. The influence of temperature on the natural zeolite is also well-known [7-10] and therefore our work described an assessment of the synergistic effect of temperature and chemical treatment on the structure and sorption quality of the Slovak zeolite.

Experimental

Natural zeolitic tuff from deposit Nižný Hrabovec, Slovak Republic [11] with a granularity from 1,5 to 2,5 mm was used. This type of zeolite mostly consists of the clinoptilolite (from 40 to 70%), quartz (2 to 5%), α - cristobalite (from 6 to 10%), feldspars (from 8 to 10%) and volcanic glass (from 13 to 30%) as is indicated by XRD-analysis. The purified material was converted to a near homoionic Na form by treatment at 80°C (for 4 hours) with 1, 2, 4 or 6 mol/l of the aqueous NaOH solution (1,2,4,6 M NaOH). The samples of natural and chemically modified zeolites were consequently calcinated at the temperature 20, 400, 600 and 800°C. DTA method was used for the studying of the influence of temperature on the studied samples. Thermal analysis was performed using a Derivatograph Q 1500D instrument in the temperature range 20-800°C and the heating rate 10°C /min.

Cation exchange properties so prepared zeolites were studied through the uptake of Cs and Co by static radioindicatore method. The tared amounts of samples (50 mg) were mixed with 15 ml of 5.10^{-2} mol/l CsCl labeled with ^{137}Cs, or 5.10^{-2} mol/l

$CoCl_2 . 6H_2O$ labeled with ^{60}Co, and slowly stirred for 24 hours. The radioactivity of 5 ml of the supernatant solution was measured by NaI(Tl) detector. These measurements enable to calculate isotherms.
From the linear parts of isotherms the sorption coefficients μ_{Cs} and μ_{Co} were calculated using the equation :

$$\mu = \alpha . m_{a+} / m_z . \nu$$

where α is the slope of the sorption curve, ma+ is the mass of cation in solution (mg), m_z is the mass of zeolite (g) and ν is the valence of cation.

Results and discussion

On the Fig.1 are shown DTA curves of not calcinated natural zeolite (20°C) and natural zeolite calcinated at 400, 600 or 800°C. On the Fig.2 are shown the DTA curves of the zeolite chemically modified with the 4 mol/l NaOH water solution (4M NaOH) and then calcinated by different temperatures (20, 400, 600 and 800°C).
The DTA curves of natural and natural calcinated zeolites represent also very similar DTA curves of zeolites modified with 1 mol/l NaOH solution and the DTA records of the zeolites chemically modified with 4 mol/l NaOH solution are very similar of DTA records of zeolites modified with 2 and 6 mol/l NaOH solution.
In the DTA of not calcinated natural zeolite there is the peak at 150°C which is associated with the dehydration of zeolite. Under this conditions the interlayer water weakly bonded to the surface of zeolite is released. Small peaks appearing at about 300°C have originated in a certain deformation in the structure of clinoptilolite. The changes of the unit cell parameters of this sample point to a tension in the clinoptilolite framework, which is due to the movement of tetrahydrally coordinated aluminium. Following peak at about 400°C indicated the dehydration of water molecules strongly bonded with cations and desorption of OH-groups. The peak about 600°C shows small dealumination and the initiation of the structural changes. At the temperatures above 700°C is the framework of clinoptilolite destroyed.
The DTA curves of natural zeolite calcinated at 400 and 600°C are approximate equal, small changes were caused by measurement conditions. The calcination of zeolite above 800°C refers to the gradual collapse of the zeolite structure and the transition to a glassy state.
Unlike the natural zeolite, the DTA record of not calcinated zeolite chemically modified with 4 mol/l NaOH solution shows endo peaks about 430 and 730°C. First peak indicates the dehydration of crystalline water and desorption of larger amount of OH-groups. The second one points to the breach of bonds between Na ion and the zeolite framework. Over 750°C the structural changes are started.
The DTA curve of zeolite chemically modified with 4 mol/l NaOH solution and calcinated at 400°C has broad peak about 730°C, i.e. the bonds Na-zeolite are the more destroyed. The calcination of this zeolite type above temperature 400°C causes the successive changes of zeolite structure and an increase of calcination temperature over 750°C leads eventually to the transition to the glassy state. The DTA curves of zeolite chemically modified with 4 mol/l NaOH solution and calcinated at 600 or 800°C show the loss of all characteristic clinoptilolite peaks and total destruction of the zeolite framework.
Finally, the changes in the structure of Slovak natural zeolite due to temperature treatment begin above 600°C. Synergistic effect of temperature and chemical treatment causes the structural changes in Slovak zeolite above 400 °C.
The most important results of the influence of the calcination on the sorption properties of zeolites are shown on figures 3 and 4. Figure 3 is a 3D plot showing the influence of the different calcination temperatures applied to the different type of chemically modified zeolites on theirs sorption coefficient for Cs.
Note that on one hand, the sorption of cesium (expressed in sorption coefficient) is at maximum for the zeolite modified with a 4 mol/l NaOH solution. Increasing concentration of the modifying medium has a negative influence on the sorption of Cs and sorption coefficient slowly decreases. On the other hand, the calcination of the zeolite up to 400°C does not affect on the Cs sorption; calcination above 400°C decreases the sorption of Cs and the calcination above 800°C reduces the sorption of Cs almost to minimum. Finally according to our results, the calcination of either chemically modified or natural zeolites at temperature up 400°C do not influence the sorption capacity of zeolite with regard to Cs.
Similarly to Fig.3, Fig.4 shows the sorption coefficient, this time for Co, as a function of the chemical modification of zeolite and as a function of the calcination temperature on the
zeolite. As can be seen, this Fig.4 shows that a non modified natural zeolite minimum sorbs the bivalent Co. Chemical modification of the zeolite increases the sorption of Co multiple times. The maximum of Co sorption is reached for zeolites chemically modified using 4 to 6 mol/l NaOH solution.
The influence of the calcination on the sorption of Co is not observable bellow the temperature of 400°C for zeolite chemically modified with 2 mol/l NaOH solution. The increase of the temperature of calcination yields a decrease of the sorption of Co that eventually reaches the minimal value. Zeolites modified using 4 or 6 mol/l NaOH

solutions and calcinated at 200°C rapidly loose theirs sorption capacity for Co so as finally reache the sorption of non modified natural zeolite.
Contrary to this observation, the sorption capacity of natural or chemically modified zeolite for Co is strongly influenced at lower temperatures. A very important decrease in the sorption (attaining eventually the negligible value) can be observed mainly for zeolites chemically modified with 4 or 6 mol/l NaOH solution. The explanation of this fact can be the fast closing of the zeolit surface so as the reducing size of surface pores.

Conclusion

The results of the DTA indicate the changes in the structure of Slovak natural zeolite due to temperature treatment begin above 600°C. Synergistic effect of temperature and chemical treatment causes structural changes in this zeolite even above temperature 400°C. The sorption properties of the calcinated natural and chemically modified zeolite show that maximum sorption of Cs is reached by zeolite chemically treated with 4M NaOH solution and calcinated up to 400°C. The increasing the temperature of calcination above 400 °C causes decreasing of sorption of Cs. The maximum of sorption of Co is reached by the zeolite chemically modified with 2M NaOH solution and calcinated up to 400°C . The sorption of Co by zeolites chemically treated with 4 or 6 M NaOH solution and calcinated up 200°C decreasing.
This results allow to tell that calcination of zeolite up to temperature 200°C generally does not affected sorption capacity of natural and chemically modified Slovak zeolite. These types of Slovak zeolite have good perspectives as adsorbents in exacting processes of pollutant removal.

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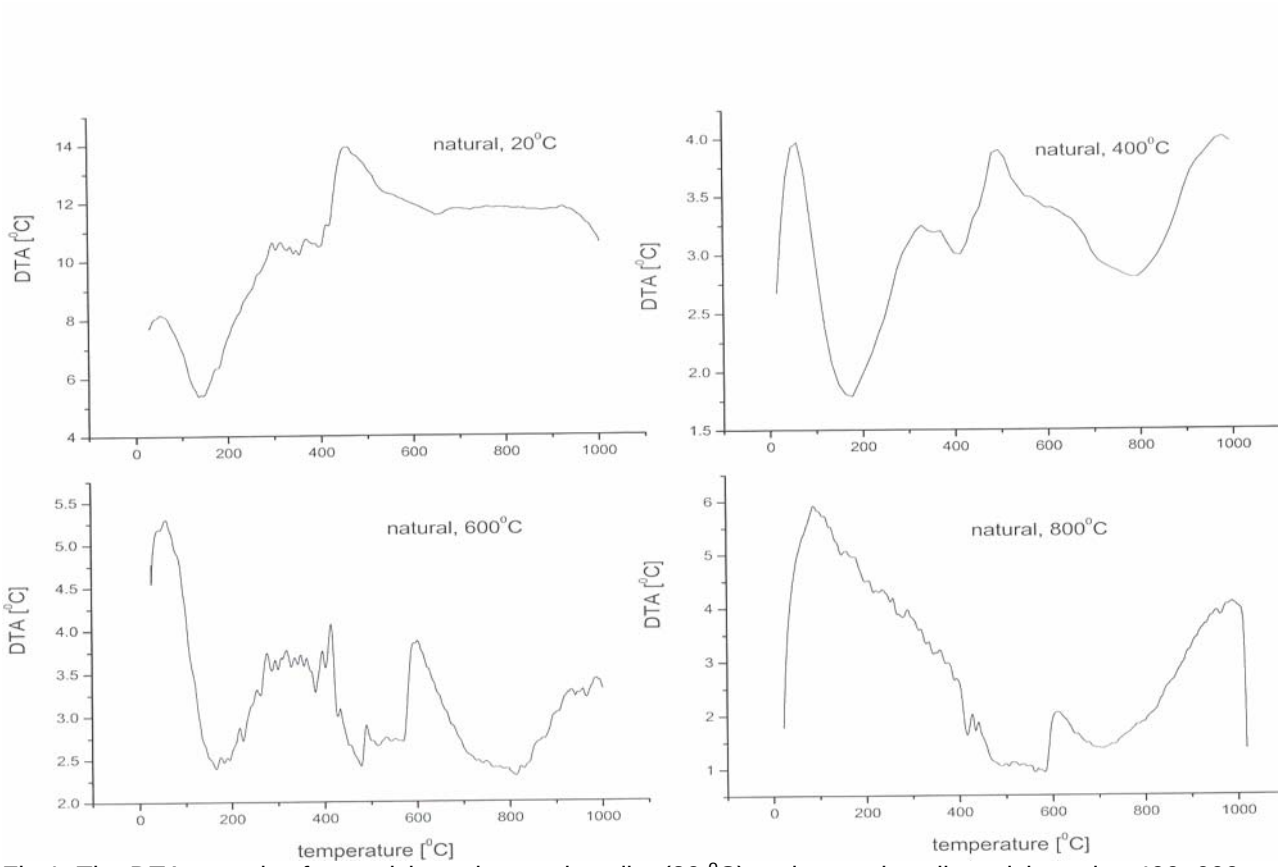

Fig.1 The DTA records of not calcinated natural zeolite (20 °C) and natural zeolite calcinated at 400, 600 or 800 °C

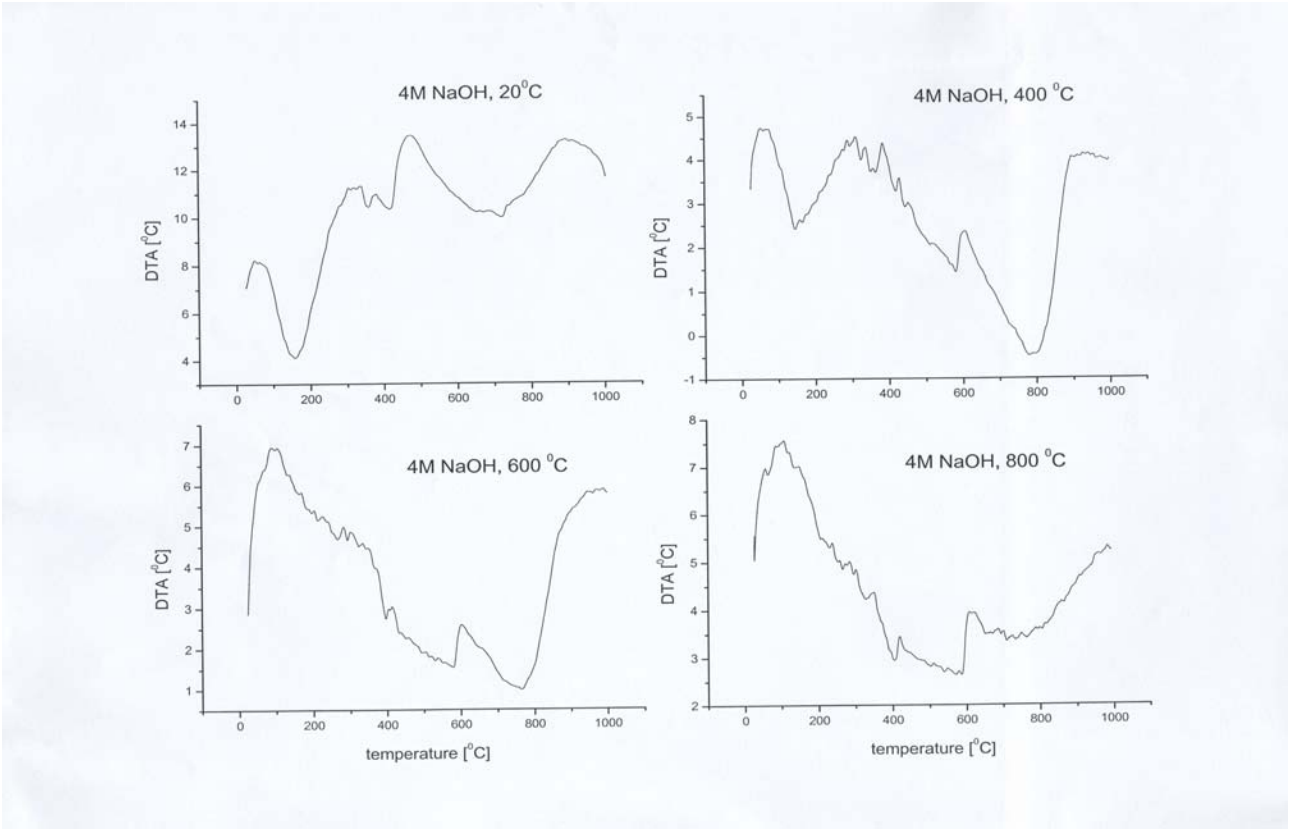

Fig.2 The DTA records of the zeolite chemically modified with the 4 mol/l NaOH water solution (4M NaOH) and then calcinated at 20, 400, 600 and 800 °C

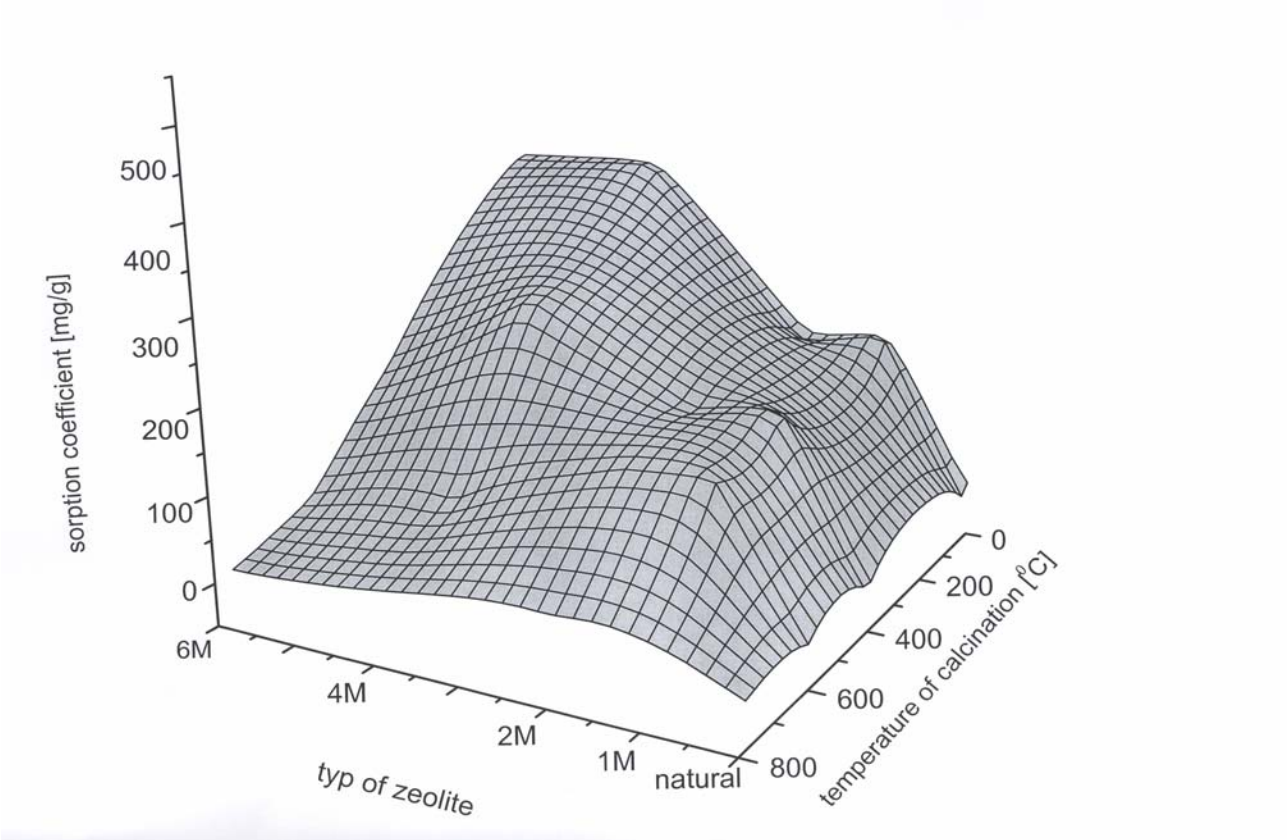

Fig.3. The three-dimensional plot showing the influence of the calcination temperature of the different types of chemically modified zeolites on the sorption coefficient for Cs.

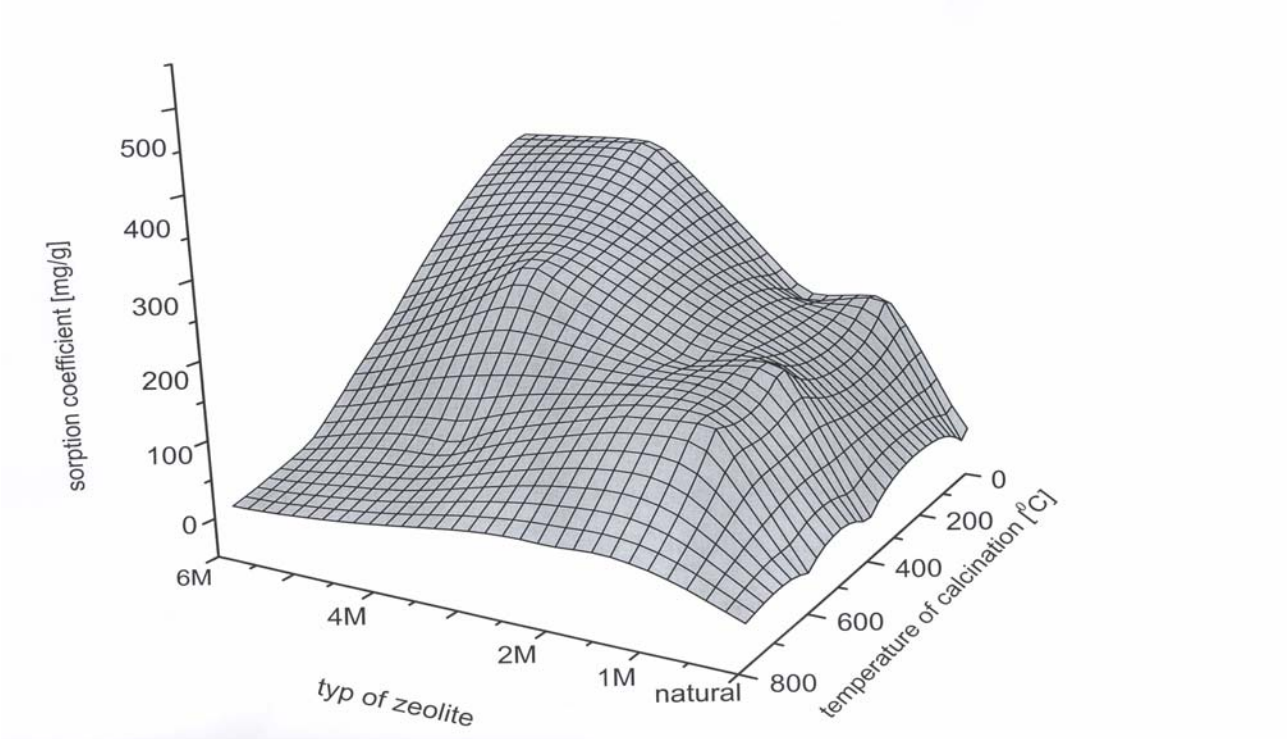

Fig.4. The three-dimensional plot showing the influence of the calcination temperature of the different types of chemically modified zeolites on the sorption coefficient for Co.