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Molten Zn-exchanged clinoptilolite – structural behaviour and properties at high temperature

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A molten exchange of $ZnCl_2$ in clinoptilolite is reported for the first time. The molten exchange occurs under solid state conditions and decreases significantly the time that is necessary for reaching a full exchange. This provides a potential alternative to the classical ion-exchange in liquids. The mechanism of the incorporation of Zn^{+2} cations in the channels of CPT-framework (their positions, Zn-content and movements along the channels) was evaluated at different temperatures by *in situ* high temperature (HT) X-ray diffraction. It is shown that molten exchanged Zn-CPT possesses a firm framework, which is thermally more resistant than natural CPT, due to the locations of Zn^{+2} cations in the eight-member channel.

Key words: clinoptilolite, zeolite, molten exchange, X-ray diffraction.

INTRODUCTION

The ion-exchange technique has been considered as an important method for improving technological properties of various natural zeolites by changing their cation content. In the ion-exchange process the cations easily exchange each other and the new ones integrate and adjust themselves in various positions into the system of pores and channels. The cation-exchanged zeolites commonly preserve their micro-porous structures unaffected. The process of ion-exchanging in zeolites is typically carried out by replacing Na^+ [1–3] with different ions, such as Ag^{2+}, K^+, Cs^+ and Sr^{2+} or through a pre-exchange of zeolite to its H-form [4] and further exchange the H-form with metal ions. Zinc-containing microporous materials (including natural zeolites) have drawn attention because of their antibacterial [5–7] and anti-tumor [8] properties. In contrast, formation of toxic ZnO-nanoclusters has been also reported [9]. Interestingly, results for ion-exchange of natural clinoptilolite (CPT) with Zn^{2+} salts, are almost missing [10–11] probably because of intrinsic difficulties of incorporation of Zn^{2+} in CPT structure at ambient temperatures (around 60–100 °C). Because of this, a classic liquid ion-exchange of Zn^{2+} in CPT commonly requires prolonged time for a sufficient high-rate Zn-exchange to take place. In this case, an alternative cation-exchange approach - the molten exchange was carried out. The molten exchange requires significantly less time – only a few hours [12, 13]. The major benefit of this approach is the improved stability of the initial CPT-structure at higher temperatures than the exchanged CPT-structure obtained by a common liquid ion-exchange [in preparation].

In this work, Zn-containing clinoptilolite (Zn-CPT) was produced by using a molten-exchange process. A NH_4^+ exchanged intermediate product (NH_4-CPT) was obtained from clinoptilolite rich tuff ("Beli plast", Khardjali) and $ZnCl_2$ was used as the Zn-source. The experimental results for the weight losses, the thermal stability of the CPT-structure under *in situ* heating, the unit cell variations and the diffusion of Zn^{2+} in clinoptilolite's structure are discussed below.

EXPERIMENTAL

Molten exchange

In our molten-exchange experiment, CPT was chosen as a substrate and $ZnCl_2$ (1:1 mass) - as the ion source. The CPT-substrate was subjected to preliminary removal of concomitant minerals such as quartz, plagioclase, mica, and then was NH_4^+ ex-

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changed in order to ensure the optimal exchange conditions. The molten-exchange temperature and the processing times were varied (360–400 °C and 30 to 360 minutes). Optimal temperature and time were found to be 380 °C and 240 minutes.

X-ray diffraction

The structural properties of the samples were analyzed with *in situ* HT X-ray powder diffraction (equipment: Bruker D2 Phaser, Cu-Kα radiation and Dron 3M, Co-Kα radiation). The *in situ* heating was conducted from room temperature (RT) to 800 °C using an in house temperature device. The heating scheme was: 100 °C step and 30 minutes retention time. Data collection was carried out at each HT-step with scan speed 0.02 °/sec. on a range from 5–35° 2-theta.

Rietveld Refinement

Rietveld analysis on the powder X-ray diffraction patterns was carried out with Topas v.3.0 [14] suite of programs. A pseudo-Voight profile function was used. Profile parameters (2θ zero correction, background, cell parameters) were refined first and then the positional parameters (locations and site occupancies) of Zn^{2+} cations at various temperatures: RT, 300 °C and 500 °C. Unit cell parameters for all samples (RT to 800 °C) were calculated primary by Pawley-extraction.

DTA/TG-MS

The weight losses were monitored by DTA/TG-MS on Setaram Setsys DTA/TG equipment coupled with a Thermo Scientific mass spectrometer for evolved gas analysis (EGA). The experiment was carried out by placing approximately 15–20 mg of the Zn-CPT sample into a corundum crucible and heating at a rate of 10 °C min^{-1} from ambient temperature to 700 °C under flowing (20 mL min^{-1}) high purity argon gas. Baseline curves measured under the same experimental conditions were acquired to account for buoyancy effects on the balance. The mass to charge ratios selected for analysis were 18, 35.5 and 65.4 amu. A one second acquisition time for each mass unit was set, thus requiring 0.13 min (or 1.3 °C) for each cycle. The chemical composition of the samples was determined by ISP-OES, apparatus Varian Vista MPX CCD simultaneous analyses.

Chlorine determination

One of the most widely used methods for the determination of chlorides at relatively low levels and where the error is in the range of 1–2% is the Mohr's method [15]. It is based on the reactions and the formation of hardly soluble precipitates with the condition that the reaction of precipitation is fast and that there is a true indicator that shows the end of the titration. To determine the concentration of chloride, samples were prepared as follows: the sample has been transferred into Erlenmeyer flask and diluted by distilled water (about 100 ml) and added 2 ml of 5% K_2CrO_4. Titration of the sample prepared in this way was carried out with standard solution of 0.0975 mol l^{-1} $AgNO_3$ under constant steering of the solution. Titration was completed when a reddish solution appeared. The obtained concentration for Cl^- was 11 (±0.09) g l^{-1}.

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 37 spectrometer at a resolution of 4 cm^{-1} accumulating 50 scans (in this case the samples were prepared in the form of KBr pellets).

RESULTS AND DISCUSSION

The chemical compositions of the starting NH_4-CPT and molten exchanged Zn-CPT are shown in Table 1. It is obvious that the amount of cations in the NH_4-CPT is very low with respect to the natural poly-cationic CPT [16]. Interestingly, the Zn^{2+} content in the molten exchanged CPT is 14.32 wt.% – a value significantly higher compared with the one in liquid ion-exchanged CPT-Zn (2.2 wt.%, 30 days at 100 °C [16]). The incorporation of Zn^{2+} in the channels of CPT structure causes visible changes in the intensities of some diffraction peaks in the pattern, which is another ultimate proof for the conducted cation exchange. A comparison of the powder diffraction patterns of Zn^{2+} CPT and non-exchanged CPT are shown on Figure 1. The changes on the XRD patterns are basically the same as previously established [16]: in Zn-CPT the 220 peak disap-

Table 1. Chemical composition (ICP-OES) of initial CPT and after molten exchange process

Oxides	NH_4-CPT	Zn-CPT
	wt.%	
SiO_2	68.19	57.08
Al_2O_3	12.51	10.32
CaO	0.06	0.20
Na_2O	0.09	0.09
K_2O	0.19	0.19
MgO	0.26	0.10
ZnO	–	14.32
LOI (1000 °C)	18.7	17.70

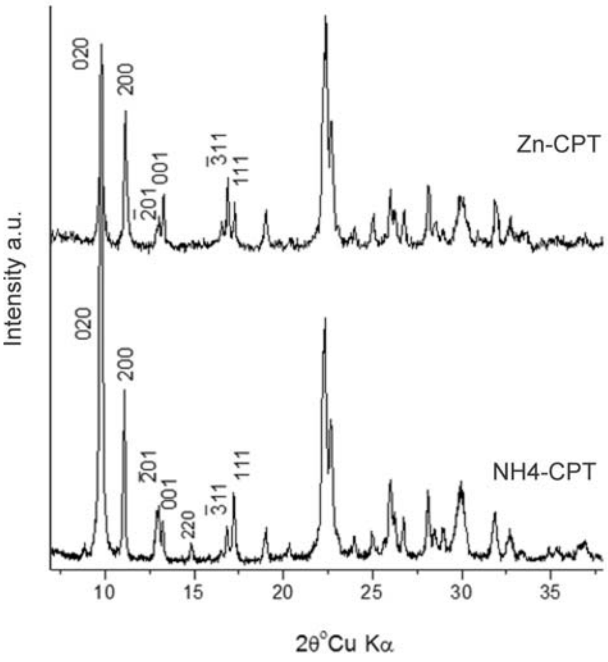

Fig. 1. XRD patterns of NH_4^+ and Zn exchanged CPT

pears, the intensities of 020, 311 and 001 increase while the intensity of 111 decreases. Our opinion is that the observed changes of the intensities of some diffraction peaks in Zn-CPT are due to the locations of the "heavy" Zn^{2+} cations in certain positions within the channels, which reasonably changes the structural factors of certain atomic plains (hkl).

The calculated from the chemical analysis formula of our molten exchanged Zn-CPT is:

$$Zn_{5.43}Na_{0.09}Ca_{0.11}K_{0.06}Mg_{0.08}Si_{29.33}Al_{6.25}O_{72} \times n.H_2O. \quad (1)$$

There are two remarkable features of this chemical composition:

1. Zn content is 5.43 APU, providing a theoretical positive charge of 10.86. This value is higher than the negative charge (from Al) of 6.25. However, "Cl^-" is not included in the above chemical formula as it was undetectable by ICP-OES.

2. The value of ~18 wt.% for the losses on ignition (LOI) is higher than the TG losses. Normally losses are associated with volatile compounds. In our case, such are: the water molecules located in the CPT channels, the residual NH_4^+ (the band at ~1400 cm^{-1} observed in the FTIR spectrum (Fig. 2.), and the Cl^- coming from $ZnCl_2$ source.

The results from the wet analysis (Mohr's titration) yield a presence of ~11% Cl. This value is quite close to one evaluated from the difference of the LOI-TG ($17.7_{LOI\ 1100°C} - 8.5_{TG\ 700°C} = 9.2$). Note that the humidity was not monitored and, therefore, the obtained value (for the "loss difference") is only an indicative one.

The DTA/TG-MS curves of the Zn-CPT sample are shown on Fig. 3. These curves show two distinct regions. Region 1 includes the data carried out from room temperature to 450 °C and Region 2 – above 450 °C. Each of these regions is characteristic of a mass loss step (TG), with combined mass losses of ~9%. The TG curve for Zn-CPT is plotted with a selected range of MS mass-to-charge ratio curves (in *amu*) on Fig. 3 for better visualization and characterization of each mass loss step.

Region 1 is linked to the evolution of water and/or NH_4^+ (18 *amu*) with peaks in the DTA curve observed at 68, 160, 213 and 314 °C. The maximum of the peak in the MS 18 *amu* curve is around 140 °C and continues up to ~ 400 °C. The observed DTA maxima may be accounted for different types of water-cations bonds and variations in water-framework molecular interactions.

Thermal decomposition of the analyzed Zn-CPT is not observed throughout the experiment.

Region 2 starts from ~500 °C and continues to 700 °C. The mass loss for Region 2 appears to be insignificant (~1%).

Remarkably, no Zn^{+2} or Cl^- could be detected up to 700 °C by TG-MS (the curves of the water/ammonium, Zn^{+2} and Cl^- mass-fragments have been shown for comparison) and no clear and pronounced decomposition (destruction) effect is observed on the DTA curve.

The diffraction patterns from *in situ*-HT XRD analysis are in good agreement with the DTA/TG-

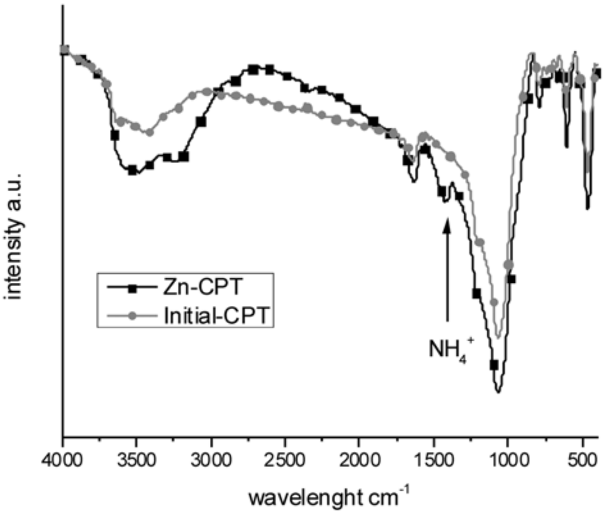

Fig. 2. FTIR for initial and Zn-CPT samples; the 1414 cm^{-1} mode is associated with NH_4^+ stretching

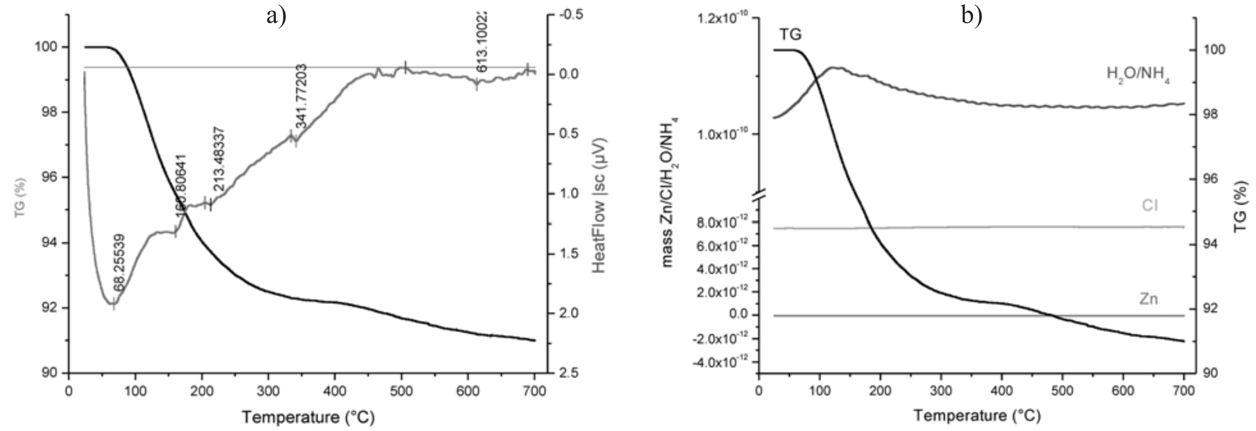

Fig. 3. (a) DTA/TG for Zn-CPT (b) TG-MS for Zn-CPT

MS results showing no collapse of the CPT structure up to 700 °C (Fig. 4). The diffraction patterns taken from heated Zn-CPT (from RT to 700 °C) clearly indicate that the overall structure remains unchanged up to 700 °C. Indeed, HT-diffraction patterns do not show any significant structural changes in the framework. As expected, there are some variations of the unit cell as a function of the temperature and they are shown on Fig. 5 and Table 2. It was found that the heating affects mainly *b* parameter, while *a*, *c* and *β* remain almost unchanged. The collapse of the Zn-CPT structure is not accompanied by a collapse of the B channel (Table 3). Some elongation of A-channel semi-major axis is observed but the values of the semi-axis for B-channel are basically unaffected. The variation of the eccentric-

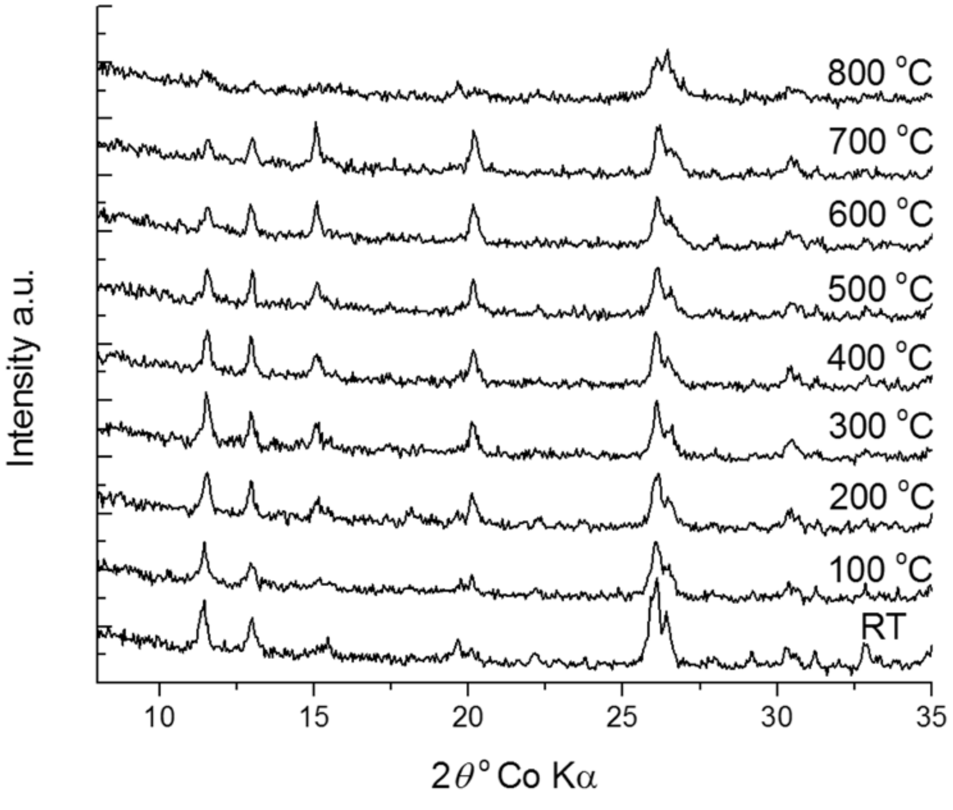

Fig. 4. Zn-CPT diffraction patterns from *in situ*-HT XRD analysis (RT –800 °C)

Table 2. Unit cell parameters for all samples (RT to 800 °C) calculated by Pawley-extraction[1] and by Rietveld method[2] along with R_{wp} value

°C	*a*	*b*	*c*	*ß*	V	R_{wp}
RT[1]	17.664(12)	17.999(13)	7.404(3)	116.109(25)	2111.60(2.4)	11.136
RT[2]	17.642(15)	17.978(16)	7.401(4)	116.078(38)	2108.49(3.0)	11.201
100[1]	17.660(21)	17.941(23)	7.398(6)	116.162(41)	2104.12(2.3)	11.723
200[1]	17.685(10)	17.873(12)	7.405(3)	116.073(31)	2103.22(2.2)	12.821
300[1]	17.681(14)	17.900(17)	7.405(4)	116.049(33)	2105.53(2.6)	12.333
300[2]	17.688(16)	17.863(15)	7.401(4)	116.134(42)	2099.33(3.0)	11.351
400[1]	17.679(10)	17.850(15)	7.399(3)	116.103(33)	2096.92(2.5)	11.301
500[1]	17.659(12)	17.847(13)	7.395(4)	116.074(35)	2093.55(2.5)	12.192
500[2]	17.658(17)	17.823(21)	7.383(5)	116.08935)	2086.65(3.2)	12.981
600[1]	17.658(14)	17.815(18)	7.391(4)	116.161(32)	2086.72(3.1)	11.643
700[1]	17.639(17)	17.758(15)	7.391(4)	116.240(41)	2076.92(2.9)	12.176

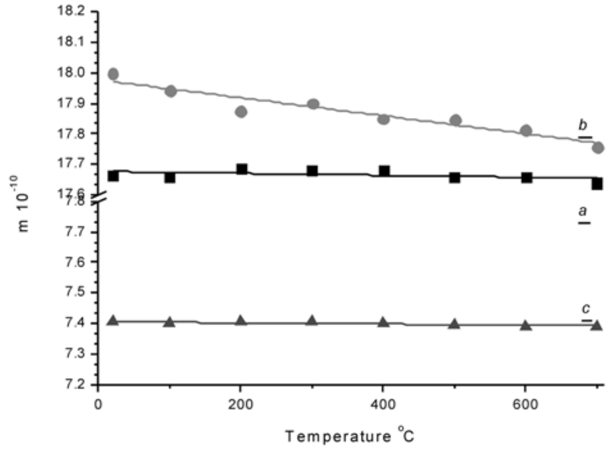

Fig. 5. Variations of the unit cell parameters of Zn-CPT in function of the temperature

ity is different for both channels: for A-channel it increases towards a value of 1 – thus, the shape is more compressed (elongated) along the semi-minor axis, while for B-channel the decrease leads to more spherical shape of the channel. Similarly to ref. [17], we could not associate a collapse phase or trend unit cell/channel shape to the collapse of the structure. However, as both *in situ*-HT XRD and DTA data have been collected for a relatively short period of time (4 hours of total heating time), the effect may have not been well expressed. One reason could be that the structure was not allowed to "relax" due to insufficient time.

Rietveld method was applied mainly for evaluating unit cell parameters and locating the atoms in the CPT channels. The performed Rietveld refinement of the XRD patterns locates water molecules in heated samples up to 200 °C. The location of water molecules by XRD cannot be evaluated correctly because most of the positions are not fully occupied and the heating increases their thermal displacement/diffusion inside the CPT channels. As a result, the electron density associated with water molecules is very shallow and is not clearly visible on the [F_o-F_c] difference map. On the other hand, as Zn^{+2} cation possesses more electrons than Si^{+4} and Al^{+3} (the main building units of the CPT framework), we expected its main locations in the CPT channels to be accessed by Rietvled analysis. The total amount of Zn located in the CPT channels is in agreement with the ICP-OES data (5.43 from ICP vs 5.64 at RT, 5.44 at 300 °C and 5.47 at 500 °C). The positions of Zn^{+2} cations, in both A- and B-channels as they were assigned from Rietveld refinement are shown on Fig. 6 and Table 4.

At ambient conditions (RT) four different Zn^{+2} positions are found: three in A-channel ("Zn1", "Zn2" and "Zn3") and one in B-channel ("Zn4"). The "Zn4" position in B-channel sits close to the well established Ca^{2+} (M2) position in natural clinoptilolite [18]. Two of the positions in A-channel, "Zn1" and "Zn2", are located close to its center. The "Zn1"

Table 3. Variation of major (h index) and minor (v index) semi-axes for A- and B-channels

Temperature [°C]	size [Å]			
	$A1_h$	$A2_v$	$B2_v$	$B1_h$
20 (RT)	9.08	6.02	6.07	6.44
300	9.45	5.99	6.34	6.43
500	9.49	5.95	6.31	6.45

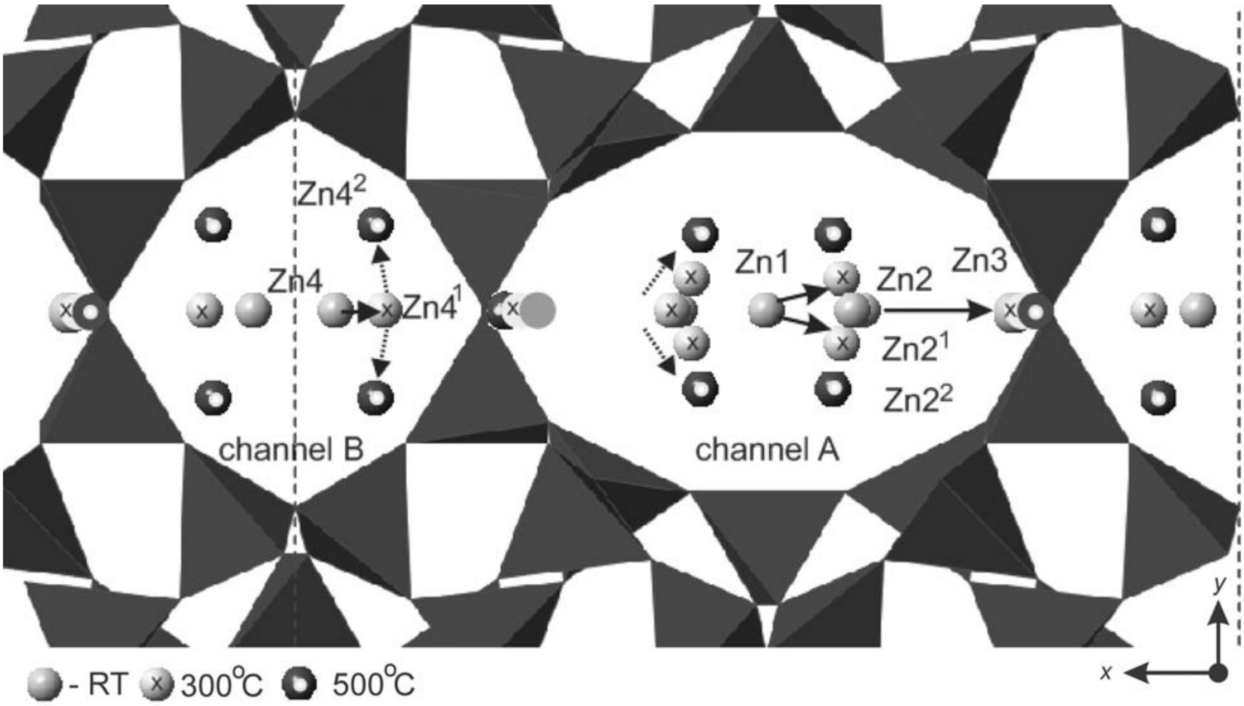

Fig. 6. The positions of Zn^{+2} cations in both A- and B-channels as they were assigned from Rietveld refinement. The positions of Zn at RT are shown in green/full circles; in yellow/x at 300 °C; and in red/● at 500 °C (colors are available in the online version of the manuscript)

Table 4. Positions of Zn sites for Zn-CPT at RT and heated at 300 and 500 °C

Zn positions	Atomic coordinates								
		RT			300 °C			500 °C	
A channel									
Zn1	0	0	0.5		–			–	
Zn2	0.092	0	0.464	0.1	0	0.444		–	
Zn2^1		–		0.580	0.468	0.104		–	
Zn2^2		–			–		0.070	0.072	0.76
Zn3	0.234	0.5	0.035	0.220	0.5	0.151	0.217	0.5	0.084
B channel									
Zn4	0.043	0.5	0.27		–			–	
Zn4^2		–		0.095	0.5	0.16		–	
Zn4^2		–			–		0.085	0.420	0.09

position is sited exactly in the center of the channel taking the position of Mg^{2+} [17]. The other centered position, "Zn2", corresponds to the one designated by Dimowa for ion-exchanged Zn-CPT [15]. The third position, "Zn3", is located very close to the intersection of A- and B-channels and matches the known "M3" position in non-exchanged clinoptilolite [18]. The estimated amounts of Zn^{+2} cations in A- and B-channel are 3.92 vs 1.72 respectively.

It was expected that at higher temperatures the Zn^{+2} cations will move (diffuse) and change their initial positions due water molecules expelling from the structure, which causes re-location of the cations to maintain the initial charge balance. This was confirmed by the performed Rietvled analyses on the diffraction patterns at various temperatures.

At 300 °C the Zn^{+2} cations are also located in four positions, but some of them change from the intial RT positions. Namely, "Zn1" position disappeared, "Zn2" position slightly shifts along *a* allowing the appearance of a new "Zn2^1" position. The "Zn3" position also shifted along *a* towards the B-channel.

The disappearance of "Zn1" [17] is associated with the loss of the coordination water surrounding the hydrated Zn^{+2} cations at RT. Zn4 position (B-channel) shifts along *c*, closer to the negatively charged framework producing Zn4'. A more general comparison of the positioning of the Zn atoms in the channels at RT and 300 °C shows that all Zn sites are located closer to the Si/Al framework. In order to compensate its surcharge, the Zn^{+2} shifts towards the negatively charged framework preserving the initial charge balance. At 300 °C, the distribution of Zn^{+2} cations in A and B-channel is 3.52 vs 1.92 APU respectively. The distribution of the Zn sites indicates a slight positive "shift" of the compensating charges towards the B-channel.

At 500 °C Zn^{+2} is found in three sites in the CPT framework. The already modified at 300 °C "$Zn2^1$" position in A-channel moves now closer to the CPT framework – "$Zn2^2$" position. The "Zn3" position situated at the intersection of the two channels is almost unchanged, but slightly migrates towards the B-channel. Finally, a new "$Zn4^2$" position appears as a result of the shift and splitting of $Zn4 \rightarrow Zn4^1 \rightarrow Zn4^2$ positions. At 500 °C the distribution of the Zn atoms in A and B channel is 2.55 vs. 2.92 APU respectively. Thus, the charge transfer from A to B channel, already noticed at 300 °C, is even more pronounced. Similarly to "RT vs. 300 °C" the "300 vs. 500 °C" general comparison of the Zn sites in the channels shows further displacement of the cations towards the framework. The distribution and Zn amounts in the channels, described above is shown on Fig. 7. The results indicate that there is a diffusion of Zn^{+2} from A to B-channel. The "Zn3" position is serving as a bridge between the channels [15]. On the other hand, the loss of Zn^{+2}-coordination seems to occur first in the A-channel (associated with the disappearance of "Zn1" site) and thus further promotes the diffusion of Zn^{+2}. The occupancy of the "Zn3" site in A-channel diminishes in favor of the Zn4/Zn4' and Zn4" located in the B-channel. As the amount of Zn remains the same at RT, 300 °C and 500 °C the observed changes and shifts of the Zn-sites are associated with the increased mobility (thermal motion) of the cations inside the channels.

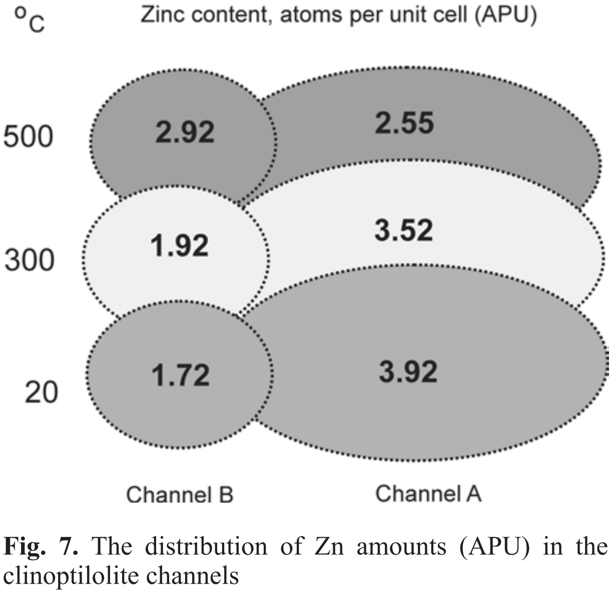

Fig. 7. The distribution of Zn amounts (APU) in the clinoptilolite channels

The saturation of the $Zn4^2$ position (leading to the presence of 2.92 Zn APU in B channel at 500 °C) is probably responsible for the stabilization of the CPT framework. If we consider the systems of channels acting like interconnected vessels one can assume that the transfer of Zn to B-channel rigidifies it and preventing its structural deformation. This enhanced stability of B-channel also inhibits the deformation of A-channel (interconnected vessels).

The enhanced thermal motion and diffusion of both the CPT framework and cations profits the mutual compensation of the charges and prohibits the release of the cations. Thus, the overall effect is a relative stabilization of the CPT structure at high temperatures.

CONCLUSIONS

Molten exchange of $ZnCl_2$ in NH_4^+ exchanged clinoptilolite is reported. The amount of Zn incorporated in the CPT structure after four hours molten exchange is about five times greater than that one of the liquid ion-exchanged Zn-CPT for 30 days. The temperature of 380 °C required for the molten exchange does not affect the structural ordering. Instead, it was found out that Zn^{+2} presence in the channels improves the overall thermal stability of CPT structure. The stabilization occurs through a diffusion of Zn^{+2} cations from A to B-channel, which prevents the deformation of B channel. The CPT system of channels acts as interconnected vessels and the rigidified B-channel hampers the deformation of A-channel. The higher amount of Zn-cations achieved in the molten- exchange process and their locations and transport through the channels in CPT-structure at elevated temperature play an important role for this stabilization.

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ОБМЕН НА КЛИНОПТИЛОЛИТ ОТ СТОПИЛКА $ZnCl_2$: СТРУКТУРНИ ОСОБЕНОСТИ И СВОЙСТВА ПРИ ВИСОКА ТЕМПЕРАТУРА

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(Резюме)

За първи път е направен обмен на стопилка $ZnCl_2$ в клиноптилолит (Zn-CPT). Обменът се осъществява в твърдо-течно състояние и намалява значително времето, което е необходимо за постигане пълен цинков обмен в клиноптилолита. Методът е потенциална алтернатива на класическия йонен обмен от разтвор. Механизмът на включването на Zn^{2+} катиони в каналите на клиноптилолита структура е изследван с различни методи, като високо температурна рентгенова дифракция, инфрачервена спектроскопия, диференциално термичен анализ, и др. Показано е, че обмененият на Zn клиноптилолит е термично по-устойчиви от природния, поради насищане на осем членния Б-канал на Zn^{2+} катиони.