Study of structural transformations in potassium-exchanged zeolite A induced by thermal and mechanochemical treatments

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Thermal transformations of potassium-exchanged zeolite A and the X-ray amorphous material obtained by ball milling the potassium-exchanged zeolite A were investigated by different methods, such as differential thermogravimetric analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Controlled heating of crystalline, potassium-exchanged zeolite A causes a phase transformation in the sequence: $[0.22 \, Na_2O, 0.78 \, K_2O] \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3.48$ $H_2O \Rightarrow$ amorphous $\Rightarrow$ kalsilite + kaliophilite, while the heating of mechanochemically amorphous potassium-exchanged zeolite A results in its transformation into a mixture of kalsilite and kaliophilite. The differences in the pathways of the transformation processes are discussed in terms of the structural properties of the starting materials.

1. Introduction

Zeolites are crystalline aluminosilicates with open-framework structures. The fundamental building blocks of these structures are infinitely extended three-dimensional networks of SiO_4 and AlO_4 tetrahedra linked to each other through oxygen atoms [1]. Zeolites may be generally represented by the formula: $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is a cation of valence, n, that compensates the negative charge of the framework, $x \geq 2$ (depending on the type of zeolite) and y can vary from zero to ten. These framework structures consist of interconnected channels and cages that are occupied by the M cations and water molecules.

A very important property of zeolites is the ability to exchange the cations, M, located at specific sites in the channel/cage systems of zeolites by various cations from solution [2–4].

The thermal stability of the framework structure of zeolites varies considerably. Different types of non-framework cations may give rise to variations in thermal stability and in the types of transformation products obtained [5–7]. Thermal transformations of zeolites into other crystalline phases may happen directly, but are often preceded by formation of intermediate amorphous phases [5–8].

For instance, the original (sodium) form of zeolite A transforms at 900 °C into a mixture of carnegeite and nepheline [5]. At increased temperature (> 1000 °C) carnegeite completely transforms into nepheline [5]. On the other hand, thermal treatment of zeolite A in which the original sodium ions have been exchanged by potassium ions results in the crystallization of kalsilite [9] and kaliophilite [10]. Our

preliminary results show that the potassium-exchanged zeolite A transforms into an amorphous phase when heated at 960 °C for 30 min, and into a mixture of kalsilite and kaliophilite at prolonged heating at the same temperature.

High-energy ball milling of zeolites results in the formation of a truly amorphous aluminosilicate phase, if one uses a long enough milling time [11–13]. Hence, it can be assumed that a combined method of mechanochemical treatment and external heating would result in the formation of crystalline high-temperature phases at lower temperatures and/or shorter heating times.

In order to prove or disprove such an assumption, in this work we studied thermal transformations of crystalline and mechanochemically amorphous potassium-exchanged zeolite A.

2. Experimental procedure

Zeolite Linde 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) was used as the starting material.

Partial exchange of original Na^+ ions from zeolite 4A with K^+ ions from solution was carried out as follows. Some 10 g of powdered zeolite A was placed in a stainless steel reaction vessel containing 250 ml of 0.5 M solution of KCl preheated at 80 °C. The suspension was stirred for 1 h at 80 °C, and thereafter the solid phase was separated from the solution by filtration. The residue on the filter paper was redispersed in a fresh 250 ml portion of 0.5 M solution of potassium chloride and stirred again for 1 h at 80 °C. The exchange and separation procedure was carried out

three times in all. After final solid–liquid separation, the residue on the filter paper was rinsed with distilled water until reaction of the filtrate with $AgNO_3$ yielded a negative result, and then dried at $105\,^\circ C$ for 24 h. The exchanged zeolite was kept in a desiccator with saturated NaCl solution for 24 h before analysis.

The chemical composition of the exchanged zeolite was determined as follows. A given amount (about 0.015 g) of the solid was dissolved in 1 ml of concentrated HNO_3, and then the solution was diluted with distilled water to the concentration ranges available for measuring the concentrations of silicon by atomic absorption spectroscopy. To determine the aluminium content in the exchanged zeolite, about 0.015 g of solid was dissolved in 1 ml of concentrated HF, and then the solution was heated in order to remove silicon by off-gassing of SiF_4. The solution was diluted by distilled water to the concentration ranges available for measuring the concentration of aluminium, sodium and potassium ions by atomic absorption spectroscopy. The concentrations of silicon, aluminium and sodium and potassium ions in the solutions obtained by the dissolution of the solids were measured by a Shimadzu AA-660 atomic absorption–flame emission spectrophotometer. The content of water in the solid sample was determined from the corresponding TGA curves. The chemical composition of the potassium exchanged zeolite A was $(0.22\,Na_2O, 0.78\,K_2O) \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3.48\,H_2O$.

A part of the potassium-exchanged zeolite A was milled in a planetary ball mill (Fritsch pulverisette type 7) at room temperature. For this purpose, a certain amount of each sample was put in an agate vessel containing ten wolfram carbide balls (dia. = 10 mm), and then the vessel was rotated (rotation speed, 3000 r.p.m.) until the crystalline storing powder was completely transformed into an X-ray amorphous material. Original crystalline samples of potassium-exchanged zeolite A, as well as amorphous samples obtained by the ball milling of the potassium-exchanged zeolite A were heated at appropriate temperatures for determined times (30 min and 3 h) in a chamber furnace with a controlled temperature (ELPH-2, Elektrosanitarij).

The starting crystalline powder (potassium-exchanged zeolite A), the sample obtained by its ball milling as well as the samples obtained by their thermal treatment were characterized as follows.

The X-ray diffractograms of the samples were taken by a Philips PW 1820 vertical goniometer with CuK_α radiation. The weight fractions of crystalline and amorphous phases were calculated by the external standard method using the integral value of the broad amorphous maximum, $2\theta = 17-39^\circ$ and the corresponding sharp peaks of crystalline phases. Because of overlapping of the strongest kalsilite (1 0 2 and 1 1 0) and kaliophilite (3 3 2 and 9 0 0) peaks, quantitative evaluations of crystalline kalsilite and kaliophilite fractions were performed by mixing method [14].

Thermal analyses of the samples were done by a Netzch STA 409 simultaneous thermal analysis apparatus. The heating rate was $10\,K\,min^{-1}$ in nitrogen atmosphere. The flow rate of nitrogen was $15\,cm^3\,min^{-1}$. The samples were heated in a platinum crucible (dia. = 6.8 mm, length = 26 mm). About 30 mg of sample was used in each run. Calcined kaolin was used as a reference.

Specific surface areas of the X-ray amorphous samples were determined by single-point nitrogen adsorption using a Micromeritics FlowSorb II 2300 instrument. Prior to measurements, the samples were outgassed for 1 h at $80\,^\circ C$.

3. Results and discussion

Fig. 1 (diffractogram a) shows that partial exchange of the original sodium ions by potassium ions did not cause either the decrease of crystallinity or the change of framework structure of zeolite A. The FTIR spectrum of the sample (spectrum a, Fig. 2) contains all bands characteristic of zeolite A [15]: the broad band at $1000\,cm^{-1}$ is assigned to asymmetric stretching of internal $T–O$ (T = Al or Si) of TO_4 tetrahedra, the weak band at $670\,cm^{-1}$ is assigned to the symmetric stretch mode, the intense band at $558\,cm^{-1}$ is assigned to external vibrations related to double-four rings and the band at $456\,cm^{-1}$ is asssigned to the $T–O$ bend. The DTA curve of the potassium-exchanged zeolite A (curve a, Fig. 3) has a minimum at $\cong 170\,^\circ C$, which
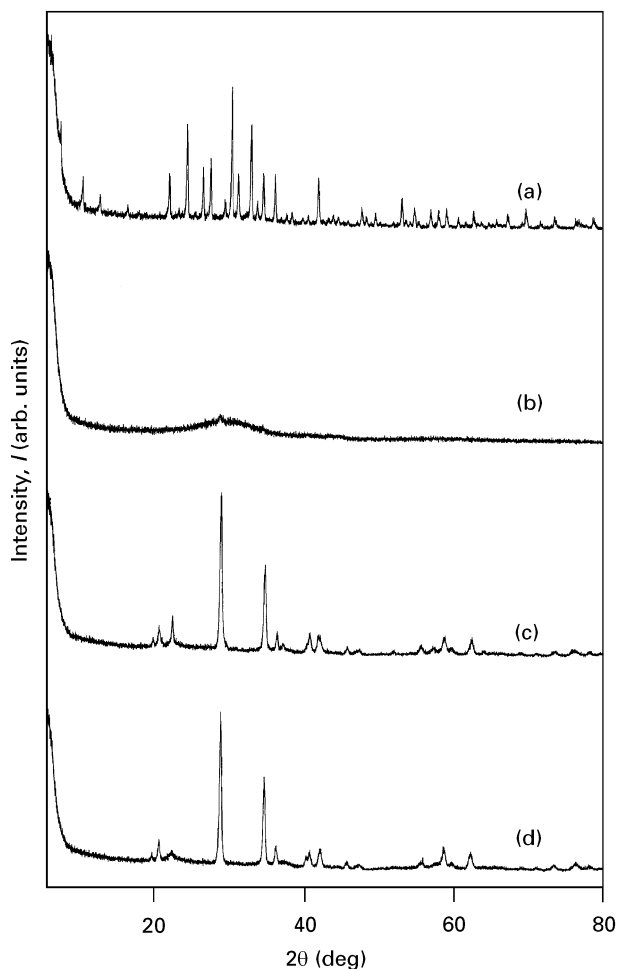

Figure 1 X-ray diffractograms of potassium-exchanged zeolite A (a) and the products obtained by heating of the potassium-exchanged zeolite A at $962\,^\circ C$ for 30 min (b), at $962\,^\circ C$ for 3 h (c), and at $1064\,^\circ C$ for 30 min (d).
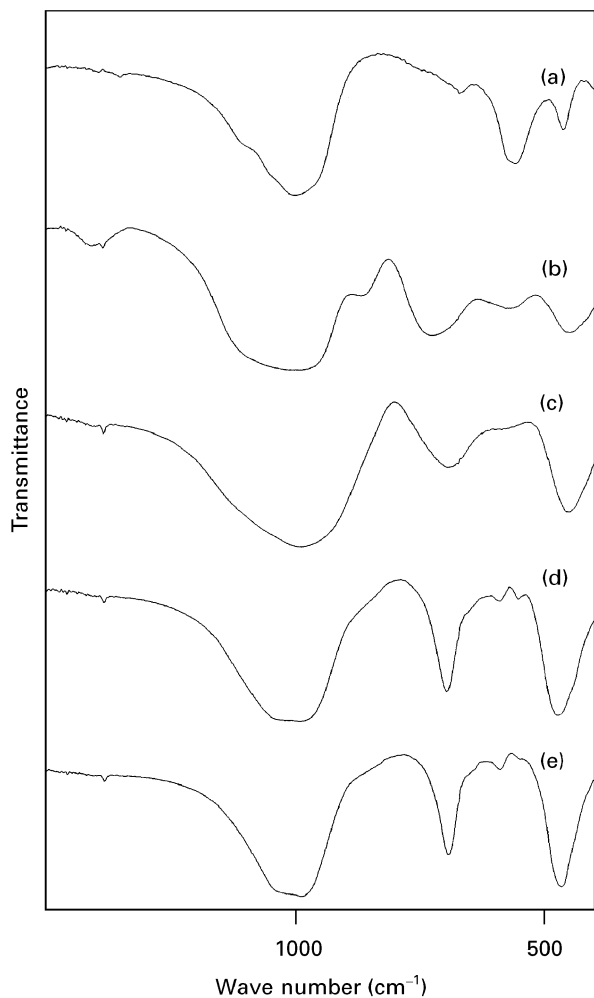
Figure 2 FTIR spectra of potassium-exchanged zeolite A (a) and products obtained by: ball milling of the potassium exchanged zeolite A (b), heating of the potassium-exchanged zeolite A at 962 °C for 30 min (c), ball milling of the potassium-exchanged zeolite A at and subsequent heating at 962 °C for 30 min (d), and ball milling of the potassium-exchanged zeolite A at and subsequent heating at 1064 °C for 30 min (e).
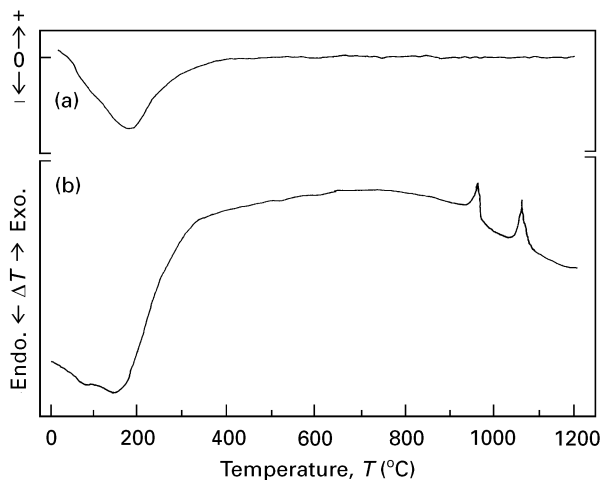

Figure 3 (a) DTA and (b) DSC curves of crystalline, potassium-exchanged zeolite A.

corresponds to the desorption of "zeolitic" water, i.e. dehydration of the hydrated sodium and potassium ions located in the channel/cage system of the zeolite A framework [16]. On the other hand, the DSC curve of the same sample (curve b, Fig. 3) has an endothermic shoulder at 95 °C, broad endothermic minimum at $\cong 170$ °C, and two exothermic peaks at 962 and 1064 °C, respectively. The endothermic shoulder is probably connected with the desorption of loosely held moisture from within the solid microstructure [16], while the position of the endothermic minimum corresponds to the position of the minimum in the DTA curve, and thus can be attributed to the dehydration of non-framework sodium and potassium ions. The exothermic peaks at 962 and 1064 °C are probably connected with the solid-state transformations at peak temperatures. In order to prove or disprove such an assumption, crystalline powder of the potassium-exchanged zeolite A was heated at 962 °C for 30 min and 3 h, and at 1064 °C for 30 min. The products obtained by the heating were characterized by XRD and FTIR spectroscopy. Heating of the sample at 962 °C for 30 min resulted in the destruction of the long range order, breaking and rearranging Si–O–Si and Si–O–Al bonds of the zeolite framework [8, 17] [as indicated by the disappearance of the bands at 558 and 670 cm^{-1} in the FTIR spectrum of the heated sample (spectrum c, Fig. 2)], and formation of X-ray amorphous phase (diffractogram b, Fig. 1). Very weak peaks at $2\theta = 28.84$ and $34.64°$, superimposed on the broad amorphous X-ray curve (diffractogram b, Fig. 1) and on the FTIR broad band at 690 cm^{-1} (spectrum c, Fig. 2), indicate an early stage of crystallization of kalsilite inside the amorphous aluminosilicate matrix. Heating of the crystalline, potassium-exchanged zeolite A at the temperature of the second exothermic peak (1064 °C) results in simultaneous crystallization of kalsilite and kaliophilite, so the product contains 73% kalsilite and 27% kaliophilite (see Table I; diffractogram c, Fig. 1) after heating for 30 min. This could be an indication that 1064 °C is the temperature of transition of amorphous to crystalline phases (kalsilite + kaliophilite). However, the complete transformation of amorphous to crystalline phases (82% kalsilite and 18% kaliophilite), after heating at 962 °C for 3 h (see Table I; diffractogram c, Fig. 1), indicates that the crystallization of kalsilite and kaliophilite from an amorphous aluminosilicate precursor is a time-consuming process that takes place at the first transition temperature (962 °C) that is characteristic of the transformation of potassium-exchanged zeolite A to amorphous aluminosilicate. Hence, it can be concluded that the appearance of the second exothermic maximum at higher temperatures (1064 °C) is a consequence of the relatively slow process of transformation at temperatures < 1064 °C, and that the rate of transformation at temperatures ≥ 1064 °C is high enough to cause energetic changes needed for recording the exothermic effect in the DSC curve (curve b, Fig. 3) at a heating rate of 10 K min^{-1}. Consequently, it can be assumed that the transformation of amorphous to crystalline phases (kalsilite + kaliophilite) can occur at temperatures ≥ 962 °C, and that the position of the second exothermic peak depends on the heating rate, i.e. the second exothermic peak will appear at a lower temperature in the case of a lower heating rate and vice versa.

TABLE I Products obtained by heating of crystalline potassium-exchanged zeolite A (CP) and amorphous phase formed by ball milling of CP (AP) at 962 °C (30 min and 3 h) and 1064 °C (30 min)

Time of heating (min)	Temperature of heating (°C)	CP	AP
30	962	amorphous phase + traces of kalsilite	67% kalsilite + 33% kaliophilite
180	962	82% kalsilite + 18% kaliophilite	100% kalsilite + traces of leucite
30	1064	73% kalsilite + 27% kaliophilite	100% kalsilite

Mechanical treatment (ball milling) of potassium-exchanged zeolite A causes a loss of its crystallinity and the formation of an X-ray amorphous phase (see diffractogram a, Fig. 4) with the same chemical composition as the original crystalline compound [18]. The loss of crystallinity is followed by the disappearance of the band at 558 cm^{-1}, which is sensitive to the framework structure, and of the weak band at 670 cm^{-1}; broadening and shifting (to lower wave numbers) of the band at 456 cm^{-1}; and the appearance of a new broad band at 710 cm^{-1} and a shoulder at 854 cm^{-1} (compare spectra a and b, Fig. 3). The weak broad band with a minimum at 558 cm^{-1} in spectrum b is probably caused by the presence of residual nanometre sized quasicrystalline particles (short-range ordering of Si and Al atoms inside amorphous regions) as was experimentally observed earlier by different methods [18–22]. Analyses of particulate and structural changes of the solid phase (zeolite) during its ball milling show that the loss of crystallinity is caused by structural changes on the molecular level (breaking of the Si–O–Si and Si–O–Al bonds and collapse of the original crystal structure under the action of an intensive mechanical force, and/or by very localized heating created by the mechanical treatment) rather than by lowering of the crystal size below the X-ray detection limit [11–13]. Such a process leads to the formation of a "true" amorphous aluminosilicate precursor (see spectrum b, Fig. 3), similar to that obtained by precipitation from alkaline and aluminate solutions [11].

The DTA curve of the amorphous sample obtained by ball milling of the potassium-exchanged zeolite A (see curve a, Fig. 5) is almost the same as the DTA curve of the amorphous aluminosilicate gel precipitated from potassium silicate and potassium aluminate solutions (see Fig. 3 in [16]). The minimum at 83 °C in the DTA curve corresponds to the desorption of loosely held moisture from within the solid microstructure of the amorphous aluminosilicate [16]. The endothermic minimum at 83 °C in the DSC curve (curve b, Fig. 5) can be attributed to the same process. Absence of minima at ≈ 170 °C in the DTA and DSC curves of the amorphous aluminosilicate indicate that the channel/void system of zeolite A is almost completely destroyed during ball milling and that the hydrated cations (Na$^+$, K$^+$) are located in a new system of macro-, micro- and meso-pores formed by destruction of the original zeolite structure [11, 18]. No high-temperature endothermic or exothermic effects were observed in the DSC curve of the amorphous precursor. However, heating of the amorphous precursor at 962 °C resulted in transformation of the
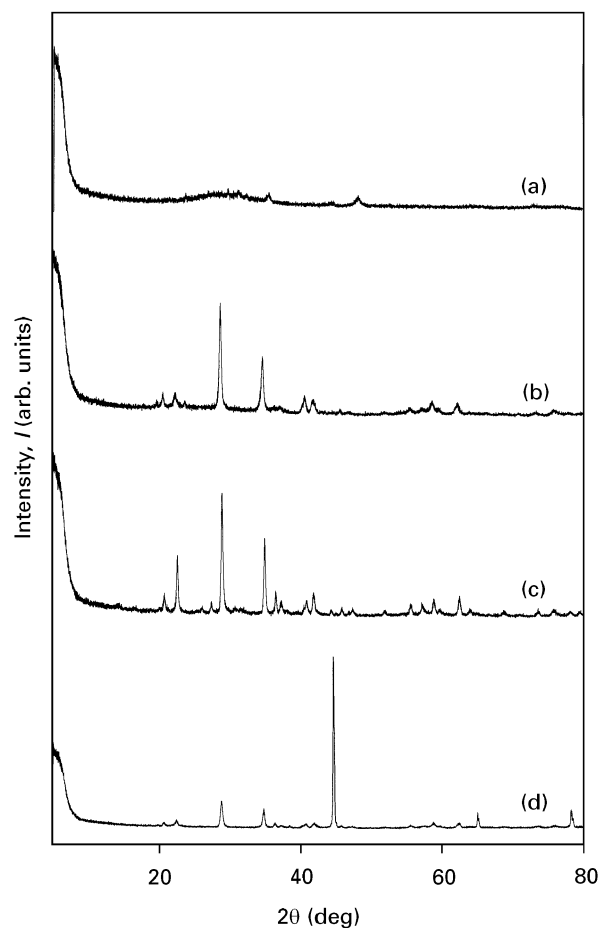

Figure 4 X-ray diffractograms of the potassium-exchanged zeolite A made amorphous by ball milling (a) and amorphous samples heated at 962 °C for 30 min (b), 962 °C for 3 h (c), and 1064 °C for 30 min (d).
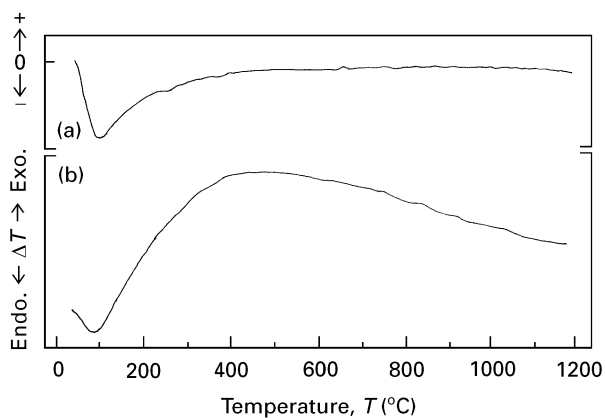

Figure 5 (a) DTA and (b) DSC curves of the amorphous phase obtained by ball milling of the crystalline, potassium-exchanged zeolite A.

amorphous phase into kalsilite and kaliophilite, so that the product contained 60% kalsilite, 30% kaliophilite and 10% untransformed amorphous phase after heating for 30 min (see Table I; diffractogram b, Fig. 4; spectrum d, Fig. 2). Prolonged heating at the same temperature caused complete transformation of amorphous into crystalline phases, and additionally, transformation of kaliophilite into kalsilite, so that the product obtained by heating at $962\,^{\circ}C$ for 3 h contained only kalsilite with traces of leucite (see Table I; diffractogram c, Fig. 4). Heating of the amorphous aluminosilicate precursor at $1064\,^{\circ}C$ for 30 min resulted in crystallization of pure kalsilite (see Table I; diffractogram d, Fig. 4; spectrum e, Fig. 2). The peaks at $2\theta = 45.66$ and 78° belong to the aluminium support of the sample holder (diffractogram d, Fig. 4).

The results presented show that heating of both the original, crystalline potassium-exchanged zeolite A and the amorphous phase obtained by its ball milling resulted in the crystallization of kalsilite and kaliophilite. The sequence of transformation (crystalline phase $\Rightarrow$ amorphous phase $\Rightarrow$ kalsilite + kaliophilite) indicates that the transformation does not occur by a direct way, i.e. by reorganization (rotation, translation) of primary and secondary building units of the zeolite framework into other crystalline phases (kalsilite and kaliophilite), but that nucleation and crystal growth of kalsilite and kaliophilite take place by reaction of primary building units (SiO_4 and AlO_4 tetrahedra) of the amorphous phase. A possible reason for such a pathway of the transformation process is that the activation energy of the breaking of Si–O–Si and Si–O–Al bonds of the zeolite is lower than the activation energy of the appropriate rotation and translation of primary and secondary building units of the zeolite framework.

The results presented also show that the rate of transformation of the amorphous precursor obtained by ball milling of the crystalline phase is considerably higher than the rate of transformation of the amorphous phase obtained by thermal treatment (30 min at $962\,^{\circ}C$) of the crystalline phase. This is probably caused by differences in the structural (see spectra b and c, Fig. 2) and particulate properties of the two amorphous phases. Taking into consideration that mechanical amorphization is a complex process that includes mechanical fragmentation of original zeolite crystals, aggregation and deaggregation of smaller particles of crystalline and amorphous phase, comminution of the particles of the fully amorphus phase, their aggregation to larger particles by the compression of material between balls and walls of the vessel as well as between the balls themselves, and deaggregation of such formed aggregates [13], it is really to be expected that the total (internal plus external) surface area of the mechanochemically amorphous material ($13.4\,m^2\,g^{-1}$) is considerably higher than the total surface area of the thermally amorphous material ($3.9\,m^2\,g^{-1}$). Additionally, it can be assumed that the number of "free" primary building blocks (SiO_4 and AlO_4 tetrahedra) needed for nucleation and crystal growth of kalsilite and kaliophilite is higher in the mechanochemically amorphous material than in the thermally amorphous material. Hence, it can be assumed that the higher rate of transformation of the mechanochemically amorphous material compared with the rate of transformation of the thermally amorphous material can be explained by the higher internal surface area at which the process occurs and by the higher number of active primary building blocks in the mechanochemically amorphous material. However, at present this is an unproved thesis that should be confirmed or rejected in a separate study.

Finally, the production of pure kalsilite during the heating of a mechanochemically amorphous zeolite at $1064\,^{\circ}C$ as well as by prolonged heating at $962\,^{\circ}C$ (see Table I) indicates that kaliophilite is an unstable phase relative to kalsilite and that there is a spontaneous direct transformation of kaliophilite into kalsilite under given conditions.

4. Conclusions

Both heating at $962\,^{\circ}C$ for 30 min and ball milling for 3 h of the potassium-exchanged zeolite A resulted in the formation of an X-ray amorphous aluminosilicate precursor. Subsequent heating at peak DSC temperatures, (962 and $1064\,^{\circ}C$) of the amorphous precursors resulted in their transformation into a mixture of kalsilite and kaliophilite or into pure kaliophilite.

Formation of an amorphous phase before subsequent transformation into kalsilite and kaliophilite leads to the assumption that the transformation does not occur in a direct way, i.e. by the reorganization (rotation, translation) of primary and secondary building units of the zeolite framework into other crystalline phases (kalsilite and kaliophilite), but that nucleation and crystal growth kalsilite and kaliophilite take place by reaction of primary building units (SiO_4 and AlO_4 tetrahedra) of the amorphous phase.

The considerably higher rate of transformation of the mechanochemically amorphous sample compared with the rate of transformation of the thermally amorphous sample is probably caused by the difference in structural and particulate properties of the two amorphous phases, i.e. by higher "concentrations" of primary building units in the mechanochemically amorphous material.

Kaliophilite is an unstable phase in relation to kalsilite, so that spontaneous transformation of kaliophilite into kalsilite occurs during prolonged heating of the mixtures of kaliophilite and kalsilite.

The findings described in this paper offer interesting possibilities for a parallel study of the kinetics of transformation of crystalline and amorphous precursors into kalsilite and kaliophilite and subsequent transformation of kaliophilite into kalsilite. This will be the subject of our further investigation in this field.

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