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 Na2O, 0.78 K2O]·Al2O3·2SiO2·3.48 H2O ↔ amorphous ↔ 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 SiO4 and AlO4 tetrahedra linked to each other through oxygen atoms [1]. Zeolites may be generally represented by the formula: $\text{M}_n\text{O}·\text{Al}_2\text{O}_3·x\text{SiO}_2·y\text{H}_2\text{O}$, where $M$ is a cation of valence, $n$, that compensates the negative charge of the framework, $x ≥ 2$ (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 carnegiite and nepheline [5]. At increased temperature (> 1000 °C) carnegiite 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 (Na2O·Al2O3·2SiO2·4H2O) 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 AgNO₃ yielded a negative result, and then dried at 105 °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 HNO₃, 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 SiF₄. 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 (0.22Na₂O, 0.78K₂O)·Al₂O₃·2SiO₂·3.48H₂O.

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 CuKα 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, 2θ = 17–39° and the corresponding sharp peaks of crystalline phases. Because of overlapping of the strongest kalsilite (10 2 and 1 10) 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 cm³ 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 °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 TO₄ tetrahedra, the weak band at 670 cm⁻¹ is assigned to the symmetric stretching 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 assigned to the T–O bond. The DTA curve of the potassium-exchanged zeolite A (curve a, Fig. 3) has a minimum at ≈ 170 °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 °C for 30 min (b), at 962 °C for 3 h (c), and at 1064 °C for 30 min (d).]