

Structural and Morphological Transformations of the (NH₄, Na)-exchanged Zeolites 4A, 13X and Synthetic Mordenite by Thermal Treatment

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Thermal treatment of (NH₄, Na)-exchanged zeolites 4A and 13X results in the formation of an amorphous phase ($T < 1000$ °C) and a crystalline phase of mullite at temperatures above 1000 °C. No structural changes have been noticed for the (NH₄, Na)-exchanged synthetic mordenite treated under the same conditions. Scanning electron microscopy (SEM), X-ray powder diffraction, Fourier transform infrared (FT-IR) spectroscopy and particle size analysis were used to characterize the initial materials and the obtained products.

Key words: ion exchanged zeolites, thermal transformations, pseudomorphic transformation, mullite.

INTRODUCTION

In recent years considerable attention has been paid to the synthesis of mullite as a high-temperature engineering material.^{1–3} The composition of mullite is of the general formula Al_{2+2x}Si_{2–2x}O_{10–x} ($\approx 0.20 < x \leq 0.90$). Mullite structure consists of chains of edge-sharing AlO₆ octahedra running parallel to the crystallographic *c* axis. The chains are cross-linked by (Al, Si)O₄ tetrahedra forming double chains also running parallel to the *c* axis.⁴ The thermodynamically stable modification of mullite 3Al₂O₃ · 2SiO₂ is one of the most important ceramic phases with low thermal expansion, low thermal

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conductivity, excellent creep resistance, good chemical stability and high mechanical strength.⁴

Formation of mullite may take place directly from the amorphous phase or through a $\text{SiO}_2\text{-Al}_2\text{O}_3$ spinel phase as an intermediate phase. The criterion of the proceeding mechanism seems to be the degree of chemical homogeneity of the precursors of the starting materials. Formation of mullite through the amorphous phase is easier when the SiO_2 component is more miscible with the Al_2O_3 component.⁵

Mullite is produced from cheap natural raw materials such as kaolinite, sillimanite, ball clays, bauxites (gibbsite and diaspore), halloysite minerals and from synthetically produced materials such as γ -alumina, aluminum fluoride, aluminum hydroxide and α -alumina. The conventional way of making fine powders is to grind a bulk material and pass it through a fine sieve. The obtained fine powders are not always of uniform size because of the impurities involved in grinding. One method for preparing uniform-sized powders is the sol-gel process. This method offers a number of advantages over other techniques, such as better homogeneity due to mixing on the atomic scale, higher purity, uniform small particle size and lower temperature of preparation. The negative side is the high cost of raw materials, considerable shrinkage during processing, residual hydrolysis, residual carbon, health hazards of organic solutions and long processing times. In general, some of the raw materials used for the preparation of mullite by the sol-gel method are tetraethoxyorthosilicate (TEOS) and aluminum nitrate nonahydrate or dibutoxyethylacetoacetoaluminum ($\text{Al}(\text{OBU})_2(\text{AcAcEt})$),⁶ $\alpha\text{-Al}_2\text{O}_3$ and amorphous SiO_2 ,^{7,8} alkoxides (Al -butylate, TEOS) and alkoxides plus nitrates (TEOS , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$),⁹⁻¹¹ fumed or colloidal silica and boehmite sol (AlOOH),¹²⁻¹³ and TEOS and boehmite sol.¹⁴ Formation of mullite was detected at the temperatures ranging from 1000 to 1700 °C.

By controlling the hydrolysis of the reaction mixtures, the texture of the gels is affected producing single-phase or diphasic samples.^{12,15} The main process parameters are the gelation time, pH, temperature of hydrolysis and the water/alkoxide ratio.¹⁵⁻¹⁶

Surface areas of the resulting mullite powders derived from the sol-gel route varied depending upon the aging and/or drying conditions, due to the different agglomeration states of the primary particles, precipitated by hydrolysis of the precursor solutions. In the case of solvents with low dielectric constants, the obtained mullite powders have large surface areas. Mullite with smaller surface areas is obtained when solvents with high dielectric constants were used.¹⁷ The use of organic polydentate ligands such as ethylene glycol, 1,3-propanediol, 1,3-butandiol, 2-methyl-2,4-pentandiol, diethylene glycol monoethyl ether, ethoxyethanol, *etc.* make facilitate mullite formation.⁵

The ion-exchange ability of zeolites allows homogeneous compositional variation on an atomic scale. This advantage, coupled with their uniform particle sizes and a relatively low cost, makes zeolites very attractive precursors to aluminosilicate-based ceramics.

It is well known from the literature that, after thermal treatment at appropriate temperatures for a defined period of time, ion-exchanged zeolites with different cations yield non-zeolitic structure ceramic materials. Thus, Ba⁺- and (Ba⁺, Li⁺)-exchanged precursors of zeolites 4A and 13X are transformed to a monoclinic celsian upon a proper thermal treatment.¹⁸

K, Rb and Cs ion exchanged zeolite Y gives, after calcining, leucit-pollucite ceramics that, depending on the temperature, may transform into a hexagonal structure modification or into a cubic high-leucite structure.¹⁹ Similar results were obtained by H. Mimura and T. Kanno²⁰ twenty years ago, using CsA, SrA and CsY, SrY as starting materials.

In this study, the starting materials are (NH₄, Na)-exchanged zeolite 4A and 13X, which are supposed to be suitable for mullite formation. The zeolite framework structure is composed of SiO₄ and AlO₄ tetrahedra, which allows for mullite formation through an amorphous phase.

EXPERIMENTAL

Materials

Well-shaped cubic crystals of zeolite NaA, sized between 10 and 20 μm, and well-shaped pyramidal crystals of zeolite 13X synthesized by a previously published method,²¹ were used as starting materials. Synthetic mordenite used as a starting material was a product of Union Carbide Corp.

Partial exchange of the original Na⁺ ions with NH₄⁺ cations from the starting zeolites was carried out by the already described procedure.²² The resulting ammonium-exchanged zeolite A [(0.05 Na₂O, 0.95 (NH₄)₂O) · Al₂O₃ · 1.98 SiO₂ · 2.12 H₂O], as determined by the chemical analysis, was heated at a rate of 10 °C/min to about 1000 °C, in a controlled-temperature chamber furnace (ELPH-2, Elektrosanitarij). The heating caused a transformation of (NH₄, Na)-exchanged zeolite A (NH₄A) into an X-ray and IR amorphous aluminosilicate of the same chemical composition as the starting NH₄A zeolite. After prolonged heating at about 1000 °C for one hour, the amorphous phase was transformed to a mixture of mullite and amorphous SiO₂. The same procedure was applied in the thermal treatment of (NH₄, Na)-exchanged zeolite X [(0.05 Na₂O, 0.95 (NH₄)₂O) · Al₂O₃ · 2.44 SiO₂ · 5.5 H₂O] and (NH₄, Na)-exchanged synthetic mordenite [(0.05 Na₂O, 0.95 (NH₄)₂O) · Al₂O₃ · 8.7 SiO₂ · 7.24 H₂O].

Analysis of Samples

Thermal analyses of the (NH₄, Na)-exchanged zeolites A, X and synthetic mordenite were performed on a Netzch STA 409 simultaneous thermal analysis apparatus.

tus. The heating rate was 10 K min^{-1} in a nitrogen atmosphere. The flow rate of nitrogen was $15 \text{ cm}^3 \text{ min}^{-1}$. The samples were heated in a platinum crucible. About 30 mg of sample was used in each run. Calcined kaolinite was used as a reference.

X-ray powder diffraction patterns were obtained with a Siemens 5000D diffractometer using $\text{Cu-K}\alpha$ radiation. Powder diffraction data were collected in the 2θ range from $4\text{--}80^\circ$ in the 2θ steps of 0.02° , with 1 s per step.

Infrared transmission spectra of the samples were measured by the KBr wafer technique. The spectra were recorded on a System 2000 FT-IR spectrometer (Perkin-Elmer).

Particle size distribution curves of the solid samples were taken by a Mastersize XLB (Malvern) laser light-scattering particle-size analyzer.

Scanning-electron micrographs of the samples were taken by a Philips SEM 515 scanning-electron microscope.

RESULTS AND DISCUSSION

DSC curves of the crystalline (NH_4, Na) -exchanged synthetic mordenite (a), zeolite 4A (b) and zeolite 13X (c) are shown in Figure 1. DSC curves of all the examined samples have the characteristic endothermic minimum below 200°C , caused by the thermally induced desorption of physically adsorbed water (moisture). The slight endothermic minima in the temperature

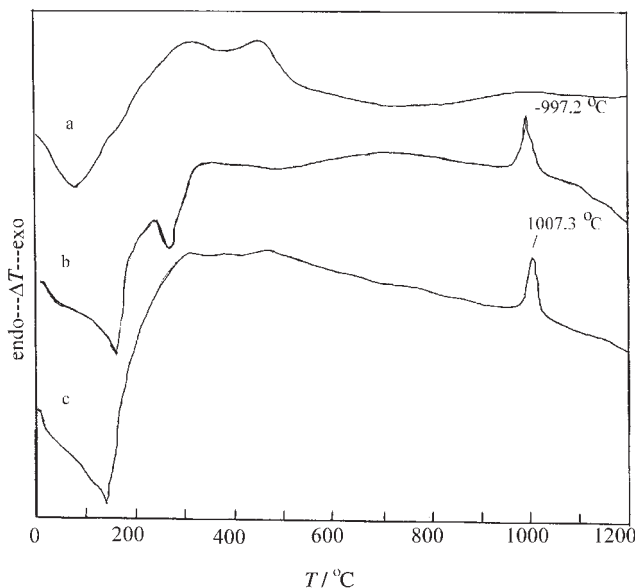


Figure 1. DSC curves of partially NH_4^+ -exchanged zeolites: synthetic mordenite (a), 4A (b) and 13X (c).

interval from 200 to 600 °C belong to the desorption of the remaining zeolitic water enclosed in the zeolitic matrix. Exothermic peaks in the DSC curves of (NH₄, Na)-exchanged zeolites 4A and 13X above 900 °C correspond to high-temperature solid-state transformations. The DSC curve obtained for (NH₄, Na)-exchanged synthetic mordenite does not show any exothermic peak up to 1200 °C, which indicates that no phase transformation has occurred. This result was confirmed by the X-ray powder diffraction analysis of the calcined (NH₄, Na)-exchanged synthetic mordenite; the X-ray powder diffraction pattern of the calcined sample (Figure 2A, a) is the same as the X-ray powder diffraction pattern of the starting (NH₄, Na)-exchanged synthetic mordenite. Also, the infrared spectrum of the calcined sample (Figure 2B, a) contains all the bands characteristic of synthetic mordenite.²³ This

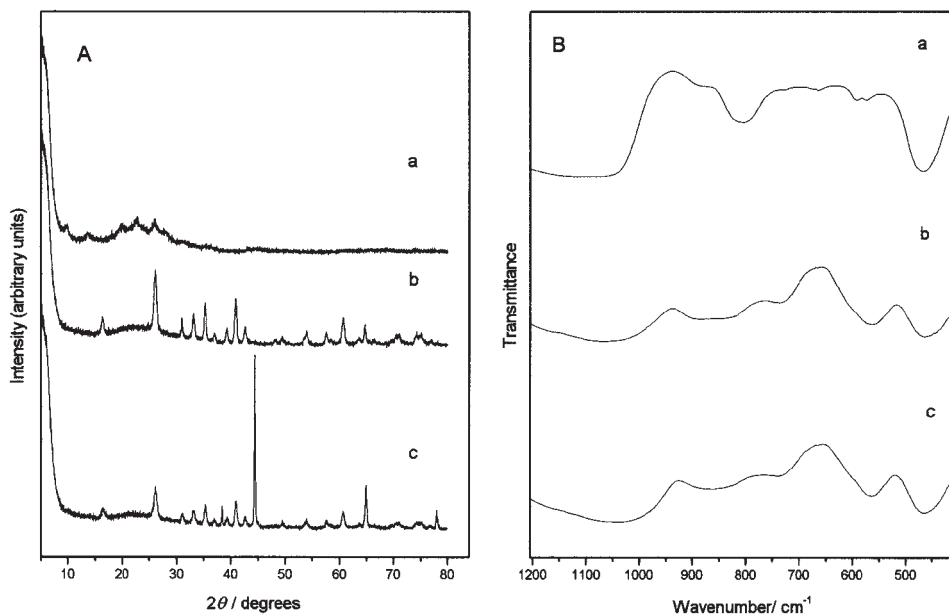


Figure 2. X-ray powder diffraction patterns (A) and FTIR spectra (B) of the partially NH₄⁺-exchanged zeolites 4A (a), 13X (b) and synthetic mordenite (c), calcined at a temperature about 1000 °C for 1 h.

indicates that the (NH₄, Na)-exchanged mordenite was initially transformed to an amorphous aluminosilicate which was then recrystallized to the starting crystalline material (synthetic mordenite) during prolonged heating.²⁴ For this reason, further investigations are carried on (NH₄, Na)-exchanged zeolites 4A and 13X only.

The thermal treatment of (NH₄, Na)-exchanged zeolites 4A and 13X at a temperature about 1000 °C, for at least 1 h, yields the same product of about 60% crystalline mullite and about 40% amorphous SiO₂ as indicated by the X-ray powder diffraction analysis (Figure 2A; b, c) and FT-IR spectrometry (Figure 2B; b, c). The peaks at $2\theta = 44.41, 64.85, 77.96^\circ$ in the diffraction pattern 2A,c belong to the aluminum support of the sample holder. The infrared spectra b and c in Figure 2B are the same as the infrared spectrum of mullite.²⁵

Earlier studies of the thermal transformation of the sodium forms of zeolites A (4A) and X (13X) have shown that zeolite 4A transforms to a mixture of carnegieite and nepheline at 900 °C and that the mixture recrystallizes to nepheline at $T > 1000$ °C,^{20,24} while zeolite 13X transforms to an amorphous phase at 850 °C which recrystallizes to nepheline at $T > 1000$ °C.²⁰ Hence, it can be assumed that proportions of mullite and amorphous SiO₂ increase and the proportions of nepheline (in the case of zeolite X) and/or carnegieite + nepheline decrease with increasing the NH₄O/Na₂O ratio in starting zeolites. This is an unproved thesis so far, which will be evaluated in further investigations.

Scanning electron micrographs in Figure 3 show the same effects as in the case of the structural transformation of potassium-exchanged zeolite A,²⁶ namely, the particles of the starting zeolite (NH₄, Na)A (a), of the resulting X-ray amorphous (NH₄, Na)-aluminosilicate (b) and of the end product mullite have almost the same shape (cubes). Hence, the thermally induced amorphization of NH₄-exchanged zeolites and their recrystallization to another phase (mullite) represents a pseudomorphic transformation. Pseudomorphism of many natural and synthetic materials is well known in the literature, and it was recently observed in zeolite solid-state transforming systems.²⁶ However, smaller (Figure 3c) or larger »rounding« (Figure 4b) of the particles of the final product (mullite) relative to the original morphologies of NH₄-exchanged zeolite A (Figure 3a) and NH₄-exchanged zeo-

TABLE I

Changes in the geometric external specific surface area A , as well as the particle size D , of the NH₄-exchanged zeolite A, calcined NH₄-exchanged zeolite A^a and of the crystalline end product mullite

Samples	$D / \mu\text{m}$	$A / \text{m}^2 \text{g}^{-1}$
(NH ₄ , Na)-A	1.946833	0.08630
Amorphous (NH ₄ , Na)-A	2.676129	0.19734
Mullite	1.877443	0.08920

^a 1 h at 1000 °C.

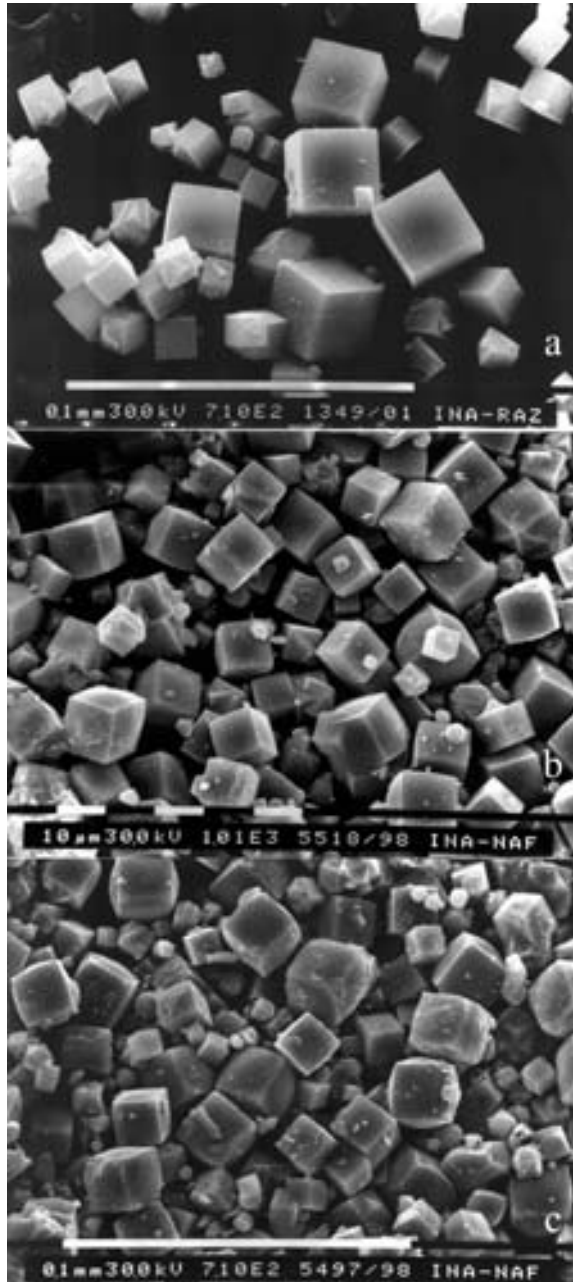


Figure 3. Scanning electron micrographs of the starting material zeolite A (a), the amorphous NH₄-aluminosilicate (b) obtained by heating (NH₄, Na)A at about 1000 °C and the end product mullite (c) obtained by prolonged heating at the same temperature.

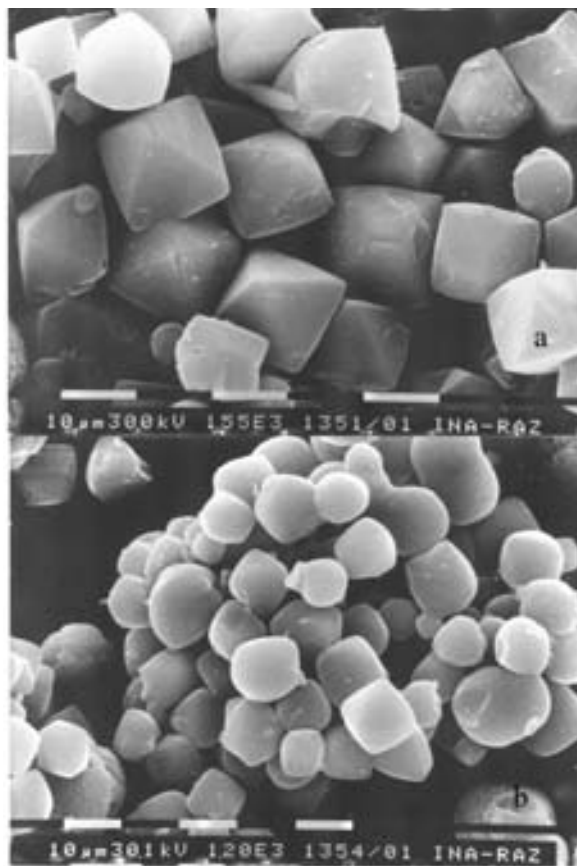


Figure 4. Scanning electron micrographs of the starting material zeolite 13X (a), and the end product mullite (b) obtained by heating $(\text{NH}_4, \text{Na})\text{X}$ at about 1000°C for a determined time.

lite X is probably caused by the internal pressure of gas (NH_3) developed by thermal decomposition of NH_4^+ ions inside zeolite microcrystals. Although the change in the particulate properties of zeolites (average crystal size, geometric external specific surface; see Table I) during their thermal treatment cannot be strictly explained at present; it is realistic to assume that this is connected with the morphological changes caused by NH_3 off-gassing.

CONCLUSION

Thermally induced transformations of the crystalline NH_4 -exchanged zeolite 4A and zeolite 13X (1 h at 1000°C) take place through the formation

of an intermediate amorphous phase and their recrystallization to a mixture of mullite (*ca.* 60%) and amorphous SiO₂ (*ca.* 40%). The obtained intermediate (amorphous aluminosilicate) and the final product (mullite) have the same shape as the precursor particles (NH₄-exchanged zeolites A and X). On the other hand, under the same conditions, NH₄-exchanged synthetic mordenite transforms into an amorphous aluminosilicate and recrystallizes to mordenite during prolonged heating.

NH₄-exchanged zeolites A and X may be used as precursors in the synthesis of mullite at temperatures much lower than in the synthesis with other starting materials. Owing to their uniform particle size and relatively low cost, zeolites have become very attractive raw materials for mullite preparation.

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SAŽETAK

Strukturne i morfološke promjene pri termičkoj obradbi (NH₄, Na)-zamijenjenih zeolita i sintetskog mordenita

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Pri termičkoj obradbi (NH₄, Na)-zamijenjenih zeolita 4A i 13X nastaje jedna amorfna faza (ispod 1000 °C) te kristalna faza mulita (iznad 1000 °C). Pri termičkoj obradbi (NH₄, Na)-zamijenjenog sintetskog mordenita nije došlo do strukturne promjene na temperaturama iznad 1000 °C. Za karakterizaciju početnih materijala i dobivenih produkata korištene su metode pretražne elektronske mikroskopije, rentgenske difrakcije, FT-IR spektroskopije i čestične analize.