

SYNTHESIS OF NANOSIZED MULLITE FROM ALUMINOSILICATE PRECURSORS

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INTRODUCTION

The type of precursors used for the synthesis and processing of mullite plays a key role on the shape-forming characteristics, sinterability, and the final properties of the product. While particulate or macromolecular colloids are preferred in fiber processing, powders are the most common form used in the fabrication of bulk objects.

As it is found in our previous study [1], the controlled heating of ammonium-exchanged zeolite A resulted in the formation of an amorphous aluminosilicate, followed by desorption of water and ammonia. Except of bulginess formed on the particle surfaces as a result of the internal pressure of gas (NH_3) developed by thermal decomposition of NH_4^+ ions inside zeolite A micro-crystals, the resulting particles of the amorphous aluminosilicate kept the size and shape of the precursor micro-crystals (NH_4 -exchanged zeolite A). A prolonged heating of the amorphous aluminosilicate resulted in its transformation into a mixture of mullite (63.4 wt. %), amorphous SiO_2 (33.9 wt. %) and Na_2SiO_3 (2.7 wt. %). Resulting particles have the same size and shape as the particles of the starting amorphous aluminosilicate. The preserving of the particulate properties during the transformation processes led to the conclusion that each zeolite micro-crystal acted as a “closed” micro-reactor with a stable shell, and all relevant processes (crystal to amorphous transformation, nucleation and crystal growth of mullite from the amorphous aluminosilicate) occurred inside each single particle (crystal). This furthermore implied that mullite, SiO_2 and Na_2SiO_3 did not appear as separate particulate systems, but that all phases existed as their physical mixture inside each single particle (micro-reactor).

The intention of this study is to find a novel method for preparation of aluminosilicate-based ceramic materials by thermal treatment of amorphous aluminosilicates (zeolite precursors) as an alternative to conventional methods based on the thermal treatment of kaolin, feldspar, and other silicate, aluminosilicate and/or oxide mixtures, or by sol-gel method[2-6].

As the composition of the gel prepared for the synthesis of zeolite A is the same as the composition of the obtained crystalline product, and using the ability of the gel to exchange its hosts cations (sodium) with other cations from a solution as the zeolites did, in this study is used ammonium-exchanged gel as a precursor for preparation of mullite type ceramics.

EXPERIMENTAL

Two $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ amorphous gels having different Al /Si ratio were prepared by mixing the appropriate Na_2SiO_3 solution with NaAlO_2 solution at room temperature, followed by separation of the precipitated amorphous solid phase, then washed and dried. The original Na^+ ions from the starting gel precursors were exchanged with NH_4^+ from solution and were carried out by an already described procedure [7]. The resulting gels I: $(\text{NH}_4)_2\text{O}\bullet\text{Al}_2\text{O}_3\bullet 3.2 \text{ SiO}_2\bullet 1.94 \text{ H}_2\text{O}$ and II: $(\text{NH}_4)_2\text{O}\bullet\text{Al}_2\text{O}_3\bullet 2.6 \text{ SiO}_2\bullet 2.3 \text{ H}_2\text{O}$ (as

determined by the chemical analysis and TG technique) were heated isothermally at 1263 K for 3h, in a controlled-temperature chamber furnace (ELPH-2, Elektrosanitarij) to transform to a mixture of mullite and amorphous SiO₂.

The transition temperatures were determined by differential scanning calorimetry. The starting gels and the obtained ceramic material were characterized using combined information from differential scanning calorimetry (DSC), thermogravimetry (TG/DTG), X-ray powder diffraction (XRPD), IR spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS).

The weight fractions, f_a (I), of the amorphous phase obtained from gel(I) and f_a (II), of the amorphous phase obtained from gel(II), and f_{mul} (I) and f_{mul} (II) of mullite were calculated by Hermans-Weidinger method [8],

RESULTS AND DISCUSSION

FT-IR spectra of the prepared gels (fig.1) show the characteristic spectra for amorphous aluminosilicate gels with a slight band at about 581 cm⁻¹ characteristic for the zeolite structure.

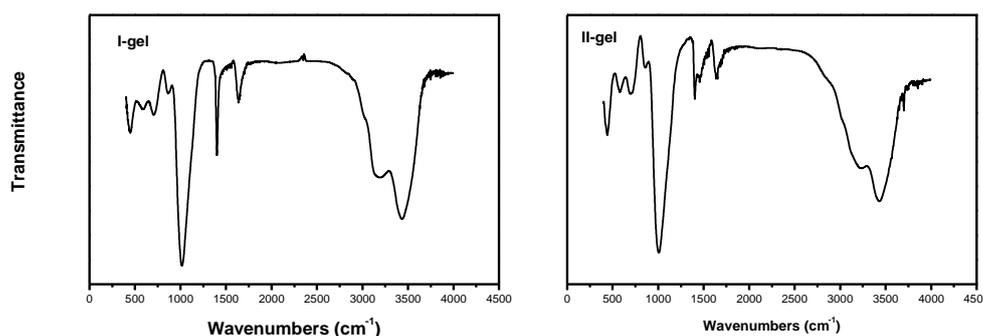
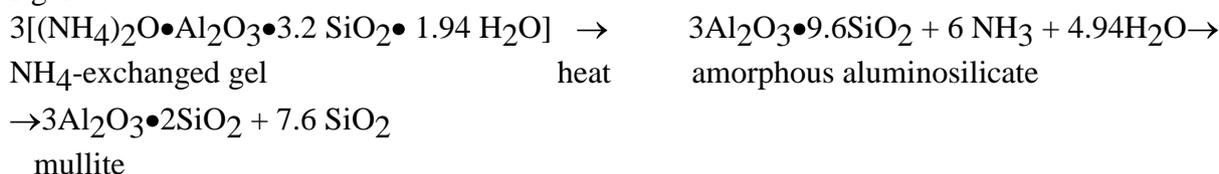


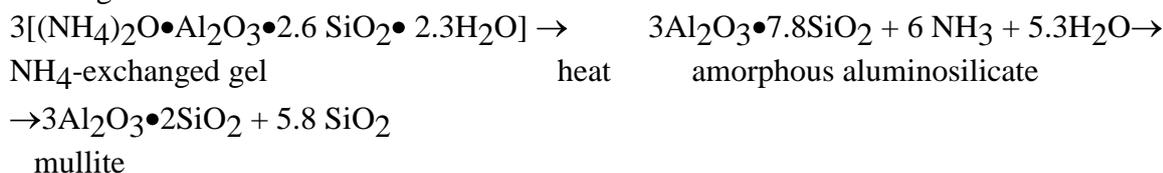
Figure 1. FT-IR spectra of the precipitated amorphous aluminosilicate precursors having SiO₂/Al₂O₃ ratio 3.2 (I-gel) and 2.6 (II-gel).

The processes that occurred during heating of the two gels may be presented as follows:

I-gel:



and II-gel:



The prepared NH₄-exchanged aluminosilicate gels, as described in the Experimental, contain more SiO₂ than it is necessary for the mullite composition. SiO₂ appears in the end product after thermal treatment as amorphous SiO₂. The amount of produced mullite is directly related to the amount of Al₂O₃ and the calcining temperature. The temperature at which the gels are treated is determined by differential scanning calorimetry. For both the gels the temperature of the exothermic peak was found to be (990°C) 1263 K, as it is presented in Fig. 2.

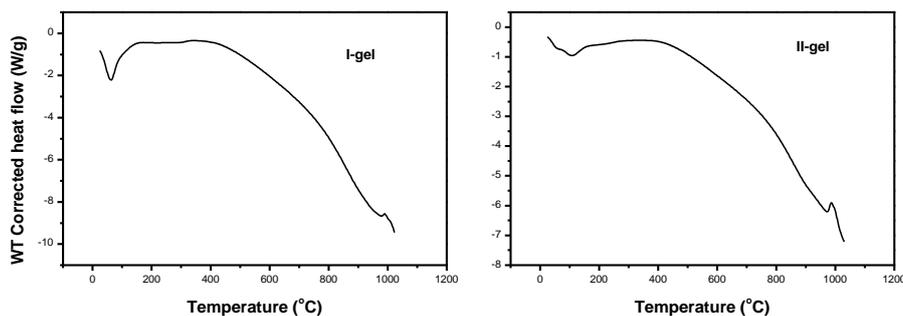


Figure 2. DSC curves of the precipitated amorphous aluminosilicate precursors having SiO₂/Al₂O₃ ratio 3.2 (I-gel) and 2.6 (II-gel).

The similarity in IR-spectra of the gels as well the same obtained temperatures of transformation and the close values of the measured external surfaces (BET for I-gel 50m²/g and 52 m²/g for II-gel) indicate that the two gels will follow the same mechanism of crystallization and will differ only in the percentage of the obtained mullite and SiO₂ because of the different Al/ Si ratio in the starting gels composition.

Quantitative and qualitative analysis of the X-ray diffraction patterns (Fig. 3) gave the phases of the obtained product after thermal treatment [8].

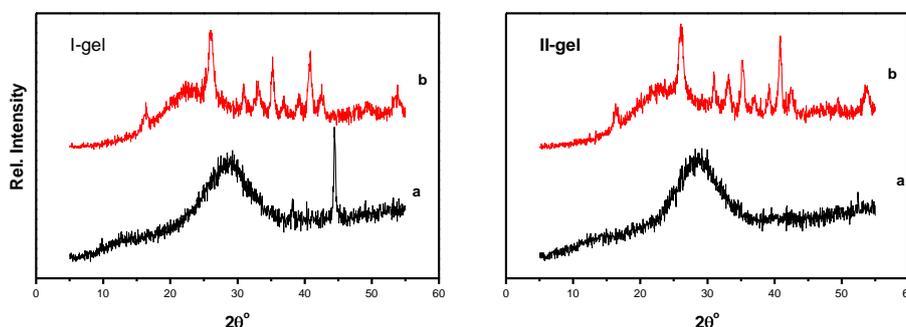


Figure 3. X-ray diffraction patterns of the precipitated amorphous aluminosilicate precursors (a) and the solids (b) obtained by isothermal heating of the precursors at (990°C) 1263 K.

In order to obtain pure mullite, another operation is needed to eliminate the formed amorphous SiO₂ that is well described in Ref.1.

Scanning electron micrographs of the obtained products are presented in figure 4. The size of the microcrystals does not exceed the value of 100 nm. The particles, due to the high temperatures used for the isothermal heating, form agglomerates and some of them are sintered.

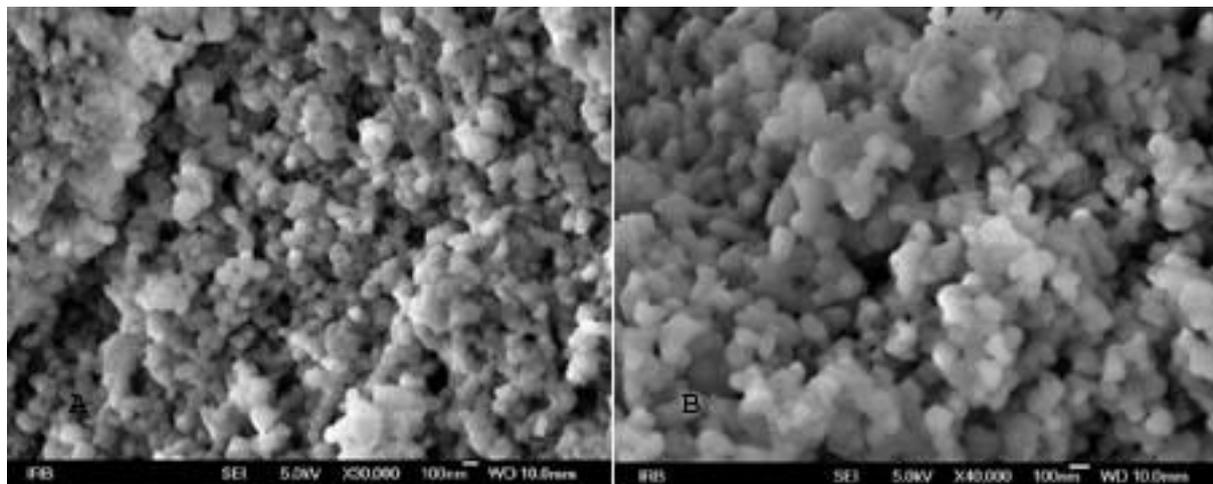


Figure 4. Scanning-electron micrograph of the samples obtained by isothermal heating of precipitated amorphous aluminosilicate precursors I-gel (A) and II-gel (B) at (990°C) 1263K for 3h.

CONCLUSION

Isothermal heating of precipitated amorphous aluminosilicates having Si/Al ratio 3.2 (I-gel) and 2.6 (II-gel) at (990°C) 1263 K for 3h results in a gradual transformation of the gels into a mixture of approximately 55% of mullite and 45% of amorphous SiO₂ which complies with the chemical composition of the precursors. Pure nano-sized mullite is obtained by further treatment.

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