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A novel synthesis of nano-sized mullite from aluminosilicate precursors

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ABSTRACT

A novel method was proposed for the preparation of aluminosilicate-based ceramic materials by temperature induced transformation 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.

Amorphous aluminosilicate gels that are usually used as precursors for the crystallization of zeolites after exchanging their host's cations (sodium) with ammonium cations from solution were thermally treated (at 1263 K for 3 h) and yielded a mixture of mullite and amorphous silica. Further chemical treatment of the mixture with sodium hydroxide solution yielded a pure mullite phase having particle size below 100 nm.

1. Introduction

High temperature inorganic materials with specific properties and stable chemical and physical characteristics and good mechanical properties, even at high temperature, are required as advanced materials in science and technology. Such demand leads to the need for new synthetic routes for preparation of a range of high purity synthetic (ceramic) inorganic compounds.

Mullite, $3Al_2O_3{\cdot}2SiO_2$ is one of the most important high temperature inorganic oxides. It is rarely found in nature because of its high temperature and low-pressure formation conditions [1]. The occurrence of mullite is a result of post-caledonian volcanic activities in which high temperature mullite phases are deposited when clay minerals are heated through contact with magma [2]. Mullite belongs to aluminum silicate family with an orthorhombic structure. The mullite crystal structure consists of a three-dimensional framework of alternate corner sharing of the AlO_6 octahedra and SiO_4 (or AlO_4) tetrahedra. The aluminum silicate crystal structure can be modified into various ortorhombic structures ranging from sillimanite $Al_2O_3{\cdot}SiO_2$ to $4Al_2O_3{\cdot}SiO_2$, achieved by substituting Si^{4+} ions with Al^{3+} ions in the tetrahedral sites of the alternating aluminum and silicon columns and the introduction of ordered oxygen vacancies [3].

Synthetic preparation of mullite is until now obtained using conventional methods based on the thermal treatment of kaolinite, feldspar and other silicate, aluminosilicate and/or oxide mixtures, or by sol–gel method [4–8]. 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. Production of mullite from clays, and in particular kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), showed them as very advantageous minerals for mullite synthesis, due to their low cost [9]. In order to use cheap precursors for the synthesis of mullite, we proposed zeolites as starting materials.

According to our previous findings [10–15], high temperature treatment of zeolites results in, either, (a) transformation of zeolite into X-ray amorphous phase and (b) nucleation and crystal growth of the secondary crystalline aluminosilicate ceramic phase; the particle size and morphology of thus formed phase do not change during the entire process (pseudomorphism). This implies that not only zeolites, but also amorphous gel precursors can be transformed into the secondary crystalline phases, which gives an additional importance to the study of the micro-structural studies of the gel precursors, relevant for the transformation pathways. In contrast to the impracticability of the study of the particulate properties during the high temperature transformation of zeolites caused by pseudomorphism, the high temperature transformations of the amorphous gel precursors enable to study the changes of both the structural and particulate properties during transformations.

Synthesis of mullite from zeolite precursor was obtained using ammonium-exchanged zeolite A [16]. 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,

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that is a result of the internal pressure of gaseous NH_3 developed during the 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 observed preservation 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 additionally implied that mullite, SiO_2 and Na_2SiO_3 did not appear as separate particulate systems, but they existed as physical mixture inside each single particle (micro-reactor).

By bear in mind that chemical composition of the crystalline product (zeolite A) is identical to the composition of initially used gel, as well as that the hosts cations (sodium) can be easily exchanged with other cations from a solution, the ammonium-exchanged gel is used in this work as a precursor for preparation of mullite type ceramics that contains exclusively constituent ions, silicon, aluminum and oxygen.

The intention of this study is to establish a novel method for preparation of aluminosilicate-based ceramic materials by temperature induced transformations of amorphous aluminosilicates (zeolite precursors) as an alternative to conventional used methods.

2. Experimental

Two $Na_2O–Al_2O_3–SiO_2–H_2O$ 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 and subsequently washed and dried. The Na^+ ions from the starting gel precursors were exchanged with NH_4^+ from solution is as follows:

10 g of powdered gel was placed in a stainless-steel reaction vessel containing 250 ml of 0.5 mol dm−3 NH_4Cl solution preheated at 70 °C. The suspension was stirred for 1 h at 70 °C and thereafter the solid phase was separated from the solution by filtration. The residue was redispersed in a fresh 250 ml portion of 0.5 mol dm−3 solution of ammonium chloride and stirred again for 1 h at 70 °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 the reaction of filtrate with $AgNO_3$ yielded a negative result and dried at 105 °C for 24 h. The exchanged gels were kept in a desiccator with saturated NaCl solution for 24 h before analyses.

The resulting gels having composition:

I: $(NH_4)_2O·Al_2O_3·3.2SiO_2·1.94H_2O$ and
II: $(NH_4)_2O·Al_2O_3·2.6SiO_2·2.3H_2O$ (as determined by means of the chemical and TG analyses) were heated isothermally at 1263 K for 3 h, in a controlled-temperature chamber furnace (ELPH-2, Elektrosanitarij) in order to transform into a mixture of mullite and amorphous SiO_2.

The transition temperatures were determined by differential scanning calorimetry.

2.1. Dissolution procedure

Two grams of powdered material (mullite + amorphous SiO_2 obtained by thermal treatment of NH_4-gel) dried at 105 °C for 24 h were poured into a stainless-steel reaction vessel that contains 100 ml of 2 M NaOH solution preheated at 70 °C (mass concentration of the suspension was 20 g/dm^3). The reaction vessel was provided with a thermostated jacket and fitted with a water-cooled reflux condenser and a thermometer. The reaction mixture (suspension of the powdered material in 2 M NaOH solution) was stirred with a Teflon coated magnetic bar (L = 5 cm, Ø = 0.95 cm) driven by a magnetic stirrer at the speed of 510 rpm. At various time intervals, t_d, after the commencement of the dissolution process, aliquots of the suspension were drawn off to prepare samples for analyses. The moment when the powdered material was poured to the preheated NaOH solution was taken as the zero time ($t_d = 0$) of the dissolution process.

The starting gels and the obtained ceramic material were characterized using the following methods.

2.2. Thermal analysis

Thermogravimetric and differential thermogravimetric analyses (TG/DTG) of gels were performed on the SDT 2960 thermal analysis system (TA Instruments, Inc.). The measurements were carried out in nitrogen flow at heating rate of 10 °C/min.

2.3. X-ray powder diffraction (XRD)

The X-ray diffraction patterns of the samples were taken by an ItalStructures APD diffractometer with GD 2000 goniometer and Cu Kα graphite radiation. The scan step was 0.02 and the sampling time was 1 s per step.

The weight fractions, fa(I), of the amorphous phase obtained from gel(I) and fa(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 [17].

2.4. BET surface area

External specific surface area of selected powdered samples was determined by multiple BET method (Gemini 2360 Surface Area Analyzer, Micromeritics) using nitrogen as adsorbate at the temperature of liquid nitrogen (−195.6 °C). The relative pressure range was 0.05–0.3P/Po.

2.5. Fourier transform infrared spectroscopy (FTIR)

Infrared transmission spectra of the samples were made by the KBr wafer technique. The spectra were recorded on FTIR Spectrometer System 2000 FT-IR (PerkinElmer).

2.6. Chemical composition

The chemical composition of the gel (contents of Na, Al, Si) was determined using EDXS and thermal analysis (H_2O content). Energy dispersive X-ray analyser: FE-SEM linked to EDS/INCA 350 manufactured by Oxford Instruments Ltd. was used.

2.7. Scanning electron microscopy (SEM)

The scanning electron micrographs of the samples were taken by Philips XL 30 scanning electron microscope.

3. Results and discussion

There are several reasons why amorphous aluminosilicate gels were chosen to be the starting materials for the synthesis of mullite. First reason is their convenient chemical composition that is consisting of Na, Al and Si atoms. The sodium cation could be successfully removed by ion exchanging method introducing ammonium ion that could be easily disappeared in the form of NH_3 gas during the further temperature induced transformation. Second reason is their structural composition. The presence of "structure-forming" Na^+ ions in the reaction mixture was needed to enhance the formation of zeolite nuclei in the gel matrix [18–20]. Once the nuclei were formed it was possible to remove sodium without destroying the nuclei.

The structure of such gels was examined by several methods [21] and especially AFM microscopy showed that they are consisting of three different types of nano-sized entities: (A) near-spheroidal-shaped particles (B) "transition", probably partially crystalline, features (particles of "quasi-crystalline" phase and (C) "pyramidal-shape" features which look like fully crystalline material. These "pyramidal" shape features are the formed nuclei that depending of the surrounding concentration of Al and Si transform to mullite and SiO_2.

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 zeolites structure that is an indication of the presence of long-range ordered aluminosilicate (partially or "quasi-crystalline") phase in the gel matrix. Prolonged heating of the gels at elevated temperatures resulted to the formation of mullite and SiO_2.

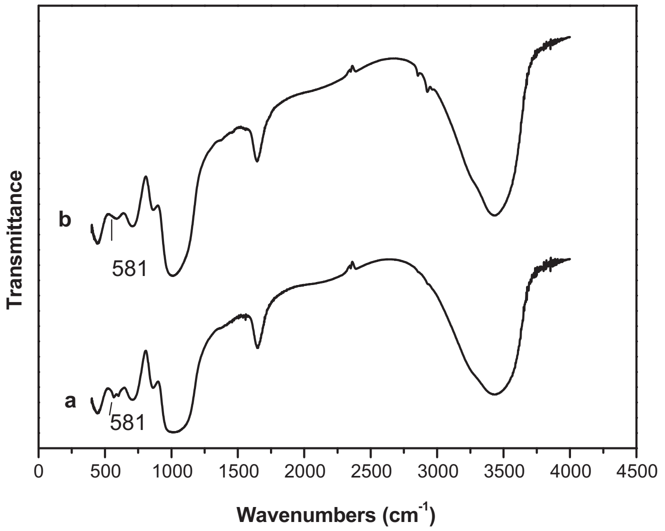

Fig. 1. FT-IR spectra of the precipitated amorphous sodium aluminosilicate precursors having SiO_2/Al_2O_3 ratio 3.2 (I-gel) (a) and 2.6 (II-gel) (b).

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

I-gel:

$$\overset{\text{NH}_4\text{-exchanged gel}}{3[(NH_4)_2O\cdot Al_2O_3\cdot 3.2SiO_2\cdot 1.94H_2O]}$$

$$\xrightarrow{\text{heat}}\overset{\text{amorphous aluminosilicate}}{3Al_2O_3\cdot 9.6SiO_2} + 6NH_3 + 8.82H_2O$$

$$\xrightarrow{\text{heat}}\overset{\text{mullite and amorphous silicon oxide}}{3Al_2O_3\cdot 2SiO_2 + 7.6SiO_2}$$

and II-gel:

$$\overset{\text{NH}_4\text{-exchanged gel}}{3[(NH_4)_2O\cdot Al_2O_3\cdot 2.6SiO_2\cdot 2.3H_2O]}$$

$$\xrightarrow{\text{heat}}\overset{\text{amorphous aluminosilicate}}{3Al_2O_3\cdot 7.8SiO_2} + 6NH_3 + 9.92H_2O$$

$$\xrightarrow{\text{heat}}\overset{\text{mullite and amorphous silicon oxide}}{3Al_2O_3\cdot 2SiO_2 + 5.8SiO_2}$$

The prepared NH_4-exchanged aluminosilicate gels contain more SiO_2 than it is necessary for the mullite composition. SiO_2 appears in the end product after thermal treatment as amorphous silicon oxide. The amount of produced mullite is directly related to the amount of Al present in the reaction mixture, as well as it is related to the calcining temperature. However, the question is if it is possible to produce mullite by following the same experimental procedure, but using exactly the stoichiometrical proportions of reactants: $2SiO_2$ (introduced as Na_2SiO_3 solution) and $3Al_2O_3$ (introduced as $NaAlO_2$). In order to find the answer, the gel was precipitated by using the respective amounts of the mentioned solutions. Unfortunately, the ion-exchange of the sodium cation with ammonium cation was not completely successful because of the structural nature of the formed gel. Namely, such prepared gel does not have the ability to exchange the cations, like the gels that are precursors for zeolite synthesis, as it was detected by EDXS analysis. Further thermal treatment of this gel resulted with a very small yield of mullite in a mixture with, predominantly, amorphous silicon oxide and carnegeite. The appearance of carnegeite was consequence of the presence of sodium cation remained in the gel.

The temperature of transformation from one phase to another can be estimate by differential scanning calorimetry and is presented by the exothermic peak on the curve. For both the gels was found to lay about 1263 K (990 °C) (Fig. 2).

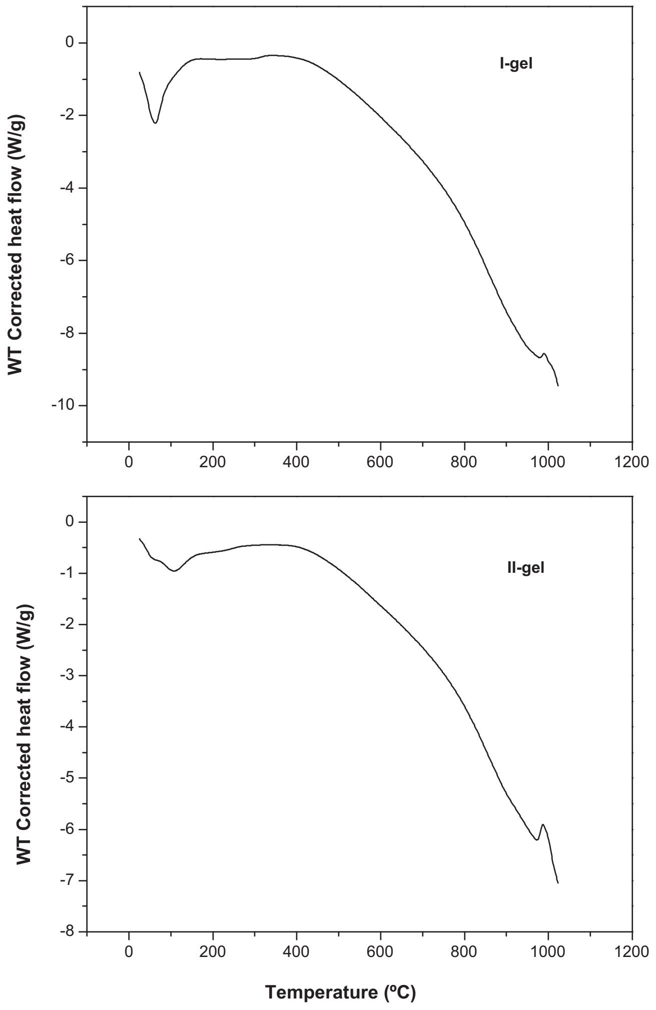

Fig. 2. DSC curves of the precipitated amorphous aluminosilicate precursors having SiO_2/Al_2O_3 ratio 3.2 (I-gel) and 2.6 (II-gel).

The similarity in IR-spectra of the gels (Fig. 1), identical temperatures of transformation, as well as the similar values of the measured external surfaces (BET for I-gel 50 m^2/g and 52 m^2/g for II-gel) indicate that the both gels followed the same mechanism of crystallization. The only difference was the content of the obtained mullite and SiO_2, as a consequence of the different Al/Si ratio in the starting gels composition. The proposed procedure of the pure mullite preparation is schematically shown in Fig. 3.

However, in order to obtain the mullite as pure as possible, the additional process for amorphous SiO_2 removal was necessary. Thus, the dissolution and removal of SiO_2 was performed by using sodium hydroxide solution. Fig. 4 shows the XRD diffractograms of the samples obtained by calcination and subsequent dissolution of I-gel (Fig. 4Ab) and II-gel (Fig. 4Bb): the presence of only mullite's diffraction peaks, as well as a distinct amorphous "hump" indicates that the formed silicon dioxide is amorphous [17]. The calculated composition of the calcined samples shows approximately 50% of mullite and 50% of amorphous SiO_2, which complies with the chemical composition of the used precursors. Theoretically, temperature induced transformation of I-gel yields to a mixture of 48.27% mullite and 51.73% amorphous SiO_2, while the treatment of II-gel yields to a mixture of 55.01% mullite and 44.99% amorphous SiO_2 that is in a good agreement with the findings of X-ray diffraction analyses. Further on, the diffraction pattern c, Fig. 4(Ac and Bc) recorded for

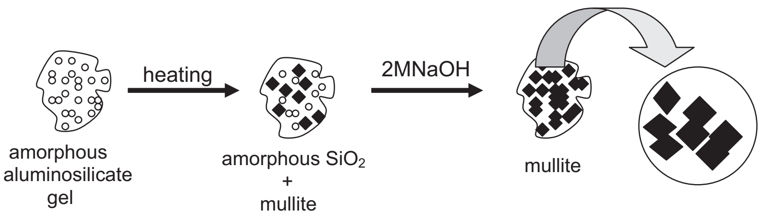

Fig. 3. Schema of the whole production process for the preparation of pure mullite using amorphous aluminosilicate gel as starting material.

the sample obtained after the dissolution of the amorphous SiO_2 in 2 M NaOH solution, at 343 K, in a period of 3 h, is showing according to database [23] the pattern of pure mullite.

FTIR spectroscopy was also used to study the mullite formation from gel precursors.

The IR spectra of the starting amorphous sodium aluminosilicate gels were presented in Fig. 1. Both gels, in sodium form, show the characteristic bands of amorphous aluminosilicate gels: a band at 430 cm^{-1} is assigned to TO (T = Al, Si) [22,24] bending mode, the weak broad band in the frequency range between 510 cm^{-1} and 650 cm^{-1} with a minimum at 581 cm^{-1} is ascribed to the symmetric stretching modes of OTO (T = Al, Si) [22,25] while the band at 830 cm^{-1} is assigned to the asymmetric stretching of Al–O mode [25]. The bands in the region between 1000 and 1100 cm^{-1} are identified as Si–O–Si and Si–O–Al stretching frequencies [22,26]. The cation exchange of the sodium cation with ammonium cation does not cause changes in the gel structure as it is found by our previous studies [27]. The extra band that appears at 1400 cm^{-1} in the spectra obtained for the ion-exchanged gel with ammonium ion (Fig. 5Aa) and Ba) is assigned to the valence and deformation vibrations of the NH_4^+ ion [28]. The next synthesis step was

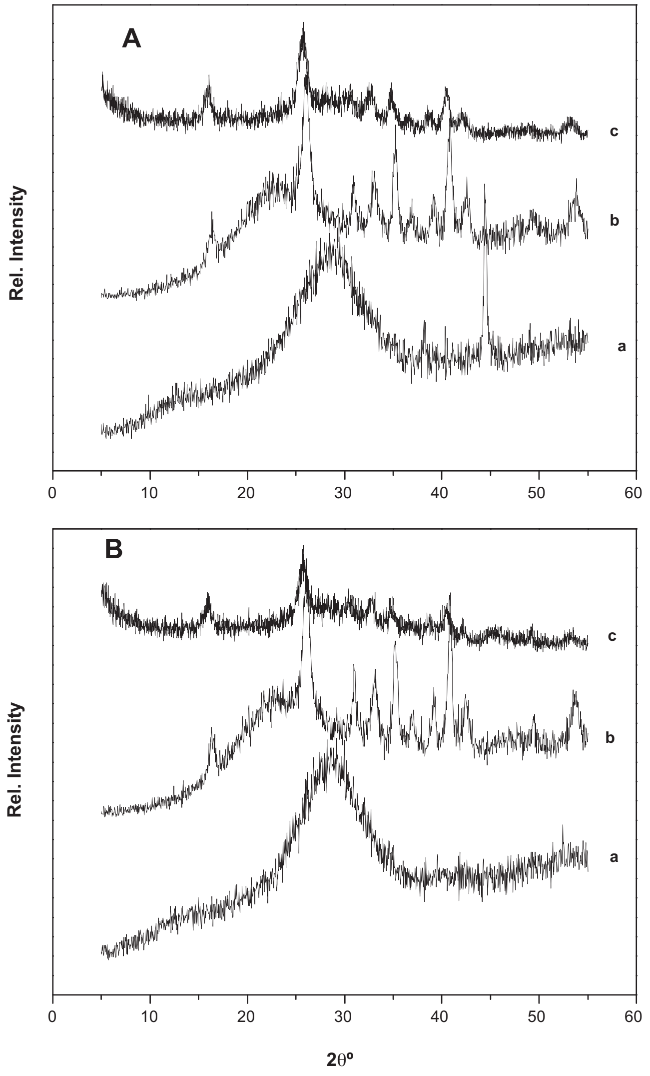

Fig. 4. X-ray diffraction patterns of the precipitated amorphous aluminosilicate precursors (Aa and Ba) and of the solids (Ab and Bb) obtained by isothermal heating of the precursors at 1263 K and (Ac and Bc) obtained after their dissolution in 2 M NaOH solution at 343 K for t = 3 h, respectively.

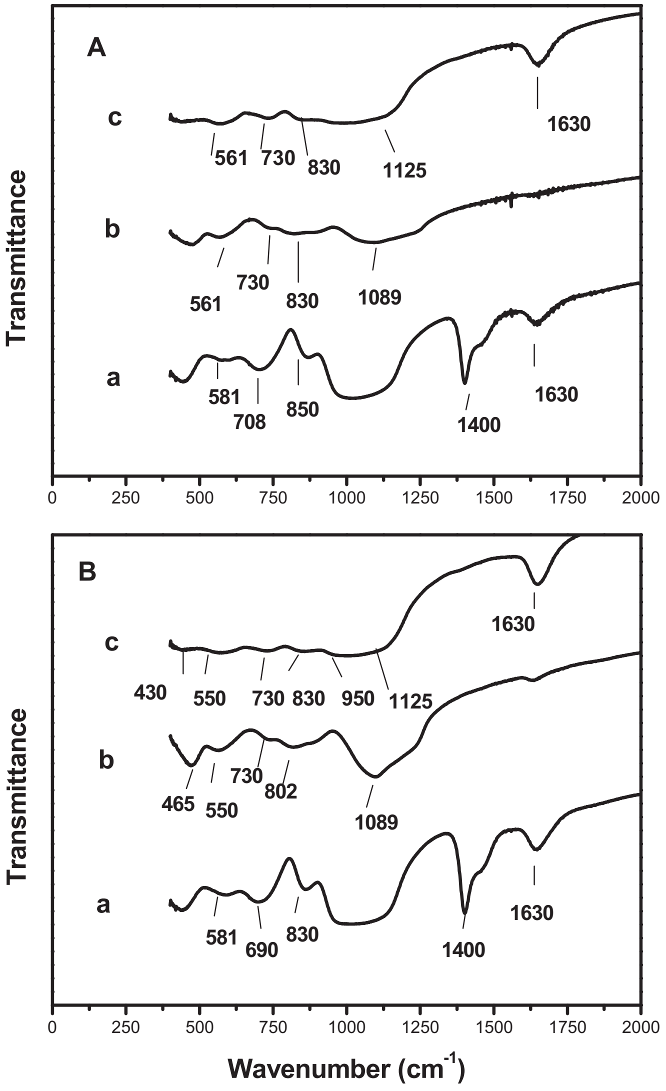

Fig. 5. FT-IR spectra of the ammonium aluminosilicate I-gel (Aa) and II-gel (Ba), of the solid obtained by isothermal heating of the precursors at 1263 K I-gel (Ab) and II-gel (Bb) and of the solid residue obtained after dissolution in 2 M NaOH solution at 343 K for t = 3 h of the calcined samples of I-gel (Ac) and II-gel (Bc).

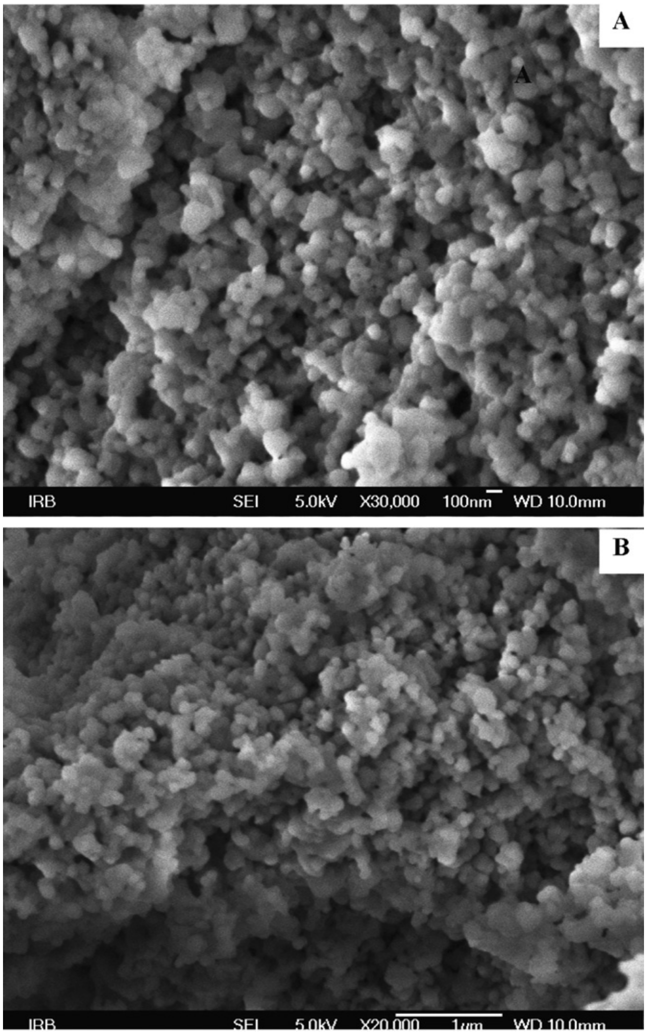

Fig. 6. Scanning electron micrograph of the samples obtained by isothermal heating of precipitated amorphous aluminosilicate precursors I-gel (A) and II-gel (B) at 1263 K for 3 h.

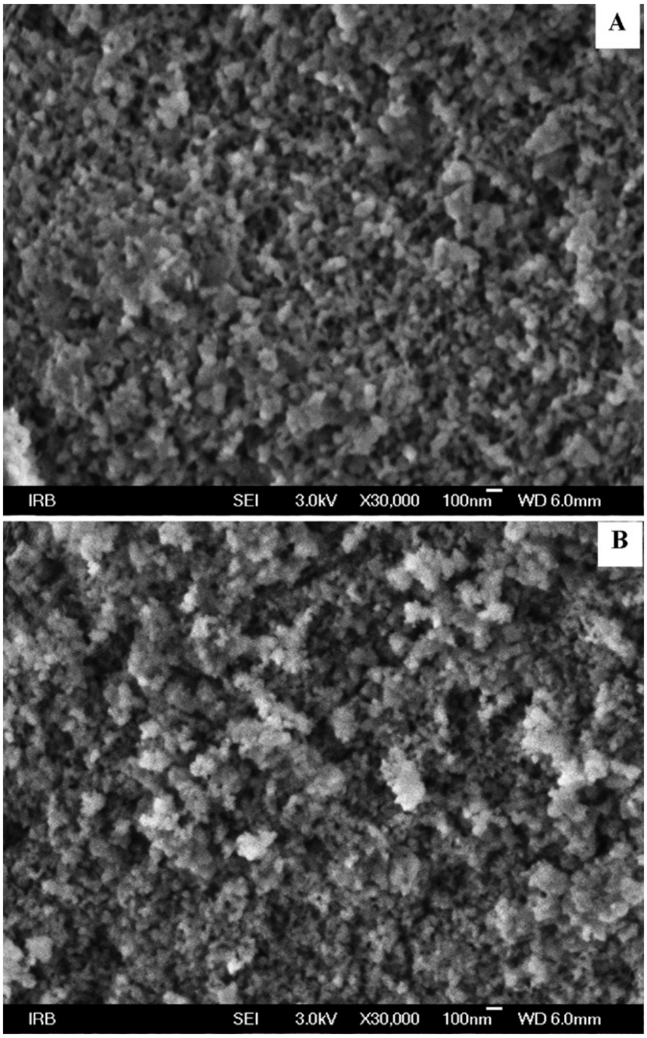

Fig. 7. Scanning electron micrograph of the samples obtained after alkaline treatment (3 h, 70 °C 2 N NaOH solution) of the samples obtained by isothermal heating of precipitated amorphous aluminosilicate precursors I-gel (A) and II-gel (B) at 1263 K for 3 h.

the thermally induced transformation of the ammonium-exchange aluminosilicate gels.

The recorded IR spectra of the samples show the characteristic bands for mullite form as well of the formed silicon dioxide (Fig. 5Ab and Bb). The band that belongs to Si–O bending at about 800 cm^{-1} is common for both the products (mullite and silicon oxide) but the Si–O–Si stretching at about 1083–1089 cm^{-1} by the shape and the position of the band is assigned to a stoichiometric silicon dioxide structure. This band disappears from the spectra of the samples obtained after dissolution of amorphous SiO_2 in NaOH solution (Fig. 5Ac and Bc). The recorded spectra contain only the characteristic bands of mullite (Fig. 5Ac and Bc). These bands are identified as Si–O stretching frequencies in the region of 1125–1165 cm^{-1} as well in the region of 950–988 cm^{-1}. The band in the region of 830–909 cm^{-1} is identified as a tetrahedral Al–O stretch, the band at 730 cm^{-1} as a tetrahedral (Al or Si) stretch, the band at 550 cm^{-1} as an octahedral Al–O stretch and the band at 430 cm^{-1} as Si–O stretch thus confirming that the obtained mineral form is mullite. The band that appears at about 1630 cm^{-1} at some spectra is assigned to C–O bending.

Scanning electron micrographs of the obtained products of mullite and amorphous SiO_2 are presented in Fig. 6. The linear dimension of the particles does not exceed the 100 nm, but they form agglomerates as a consequence of the high temperature at which the samples were isothermally heated.

BET surface area analysis of the samples obtained after thermal treatment of I-gel and II-gel showed that they are slightly porous, having BET surface areas of 11 $m^2 g^{-1}$ and 24 $m^2 g^{-1}$, respectively. After the dissolution of amorphous SiO_2 BET surface analysis of both samples showed an increase of the surface area to $s = 51\ m^2 g^{-1}$ and $s = 47\ m^2 g^{-1}$, respectively that indicate the nano sized nature of the primary particles. This is additionally evidenced by scanning electron micrographs, recorded for the final products and presented in Fig. 7. The presence of Al, Si and O in the samples was determined by the EDXS analysis, thus confirming their mineralogical composition (mullite), obtained by X-ray diffraction (Fig. 4c).

The proposed procedure enables the preparation of nano sized mullite, using two different gel precursors as starting materials. Depending on the initial Al_2O_3 content, the coefficient of utilization was found to proportionally increase.

4. Conclusion

Isothermal heating of precipitated amorphous aluminosilicates having Si/Al ratio 3.2 (I-gel) and 2.6 (II-gel) at 1263 K (990 °C) for 3 h, results in a gradual transformation of the initially formed gels into a mixture of approximately 50% of mullite and 50% of amorphous SiO_2 which complies with the chemical composition of the precursors.

Since the solubility of amorphous SiO_2 in 2 M NaOH solution, at 343 K (70 °C), is considerably higher than the solubility of mullite under given conditions, the respective treatment of the samples obtained after isothermal treatment resulted in formation of nanosized mullite.

The use of amorphous aluminosilicate gels, instead of crystalline zeolites or other materials regularly used for mullite preparation (kaoline, clays) reduced the number of process steps, lower the temperature and shortened the time of thermal treatment.

Acknowledgements

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