

THERMAL TRANSFORMATIONS OF AMORPHOUS ALUMINOSILICATE PRECURSORS TO CERAMICS

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INTRODUCTION

Because of the wide application of ceramics materials is a growing need to purpose-tailor and control their desired performance. Beside that is a trend to track for cheaper raw materials which at the same time fulfill most of the desired property requirements. Introduction of zeolites as new materials for the preparation of ceramics from aluminosilicate-based precursors started something like twenty to thirty years ago and attracted the attention of global ceramic industries [1].

Zeolites have many advantages as precursors than the conventional ceramic precursors for example oxides. They are found to decompose and recrystallize to non-zeolitic ceramic materials at much lower temperatures comparing to α -alumina. The ability of zeolites to exchange their cations with other cations from a solution, and also their uniform and narrow particle size distribution give better chances for a microstructural homogeneity, compositional changes on the atomic level and for providing a better control over the microstructure of the products by a plant control of the particle size and changing the synthesis parameters of zeolite.

Changing certain variables in the synthesis of zeolites influences the properties of the resulted ceramic as: a) the increasing of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the gel that influence on the thermal stability, acid resistance and hydrophobicity, b) the decreasing of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio that enhanced the cation exchange capacity, c) the cation in the reaction mixture and d) the cation in the framework.

Ceramic materials from crystalline zeolites

The first step of the thermal transformation of zeolites is the formation of an amorphous aluminosilicate phase by thermally induced breaking of Si-O-Si and Si-O-Al bonds of zeolite framework [2-10]. The formed amorphous aluminosilicate has the same chemical composition as the original crystalline precursor (zeolite) [3, 6-10]. Prolonged heating of the amorphous aluminosilicate formed in the first step of transformation process, causes its spontaneous transformation into secondary crystalline phase (ceramic) [8-10]. The overall rate of transformation and the type of the secondary crystalline phase (ceramic) formed during the transformation depend on the type of zeolite used as precursor, type of compensation cation of zeolite framework structure and temperature of transformation [1, 3, 5-15].

Ceramic materials from amorphous aluminosilicate precursors

It is found in our previous studies, that the intermediate phase in the process of transformation of zeolite to ceramic material by thermal treatment is an X-ray amorphous phase. As it has the same composition as the starting zeolite that gave the idea to synthesize only the first step of the zeolite synthesis that means the gel at the room temperature and after certain treatment used it as starting material. Also using the ability of gels to exchange their cation with other cations similar to the zeolites behavior, gave us the possibility to yield different ceramic materials.

Further on, the influence of the starting sources of silicate and aluminate solution needed for the precipitation of the gel on the structural particularities of the gel also is reflected to the final product obtained by its thermal treatment. In this study will be presented the physico-chemical and “structural” properties of different amorphous Me-aluminosilicates (Me = Li, Na, K, Rb, Cs) obtained by (a) ion-exchange of Na⁺ ions from zeolitic Na-aluminosilicate gel with other Me⁺ ions and (b) direct precipitation from appropriate Me-aluminate and Me-silicate zeolitic solutions. 2. The study of the thermal transformations of the prepared amorphous zeolitic Me-aluminosilicates prepared as described above in order to see how the way of preparation of Me-aluminosilicate and the type of alkaline cation Me⁺, influence the crystal structure, chemical composition and particulate properties of the products of transformation - ceramics materials.

EXPERIMENTAL

Me-aluminosilicate hydrogels and the corresponding amorphous Me-aluminosilicate gels were prepared by two different procedures, as follows:

Procedure A: The aluminosilicate hydrogel having the molar oxide composition of $3.58\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2.264\text{SiO}_2\cdot 153.47\text{H}_2\text{O}$ was prepared by addition of the sodium silicate solution (prepared by the dissolution of Na₂SiO₃ in demineralised water) in to sodium aluminate solution (prepared by dissolution of NaAlO₂ in demineralised water), at ambient temperature. The prepared hydrogel was additionally stirred (for 5 min) at room temperature before the phase separation. The precipitated solid phase (amorphous Na-aluminosilicate precursor; Na-gel (A)) was separated by centrifugation and was washed until the pH was value 9- 10. The washed Na-gel(A) was dried at 105° C overnight and then was cooled down in a desiccator over dry silica gel. 10 g of the Na-gel(A), prepared as described above, was ion-exchanged in NH₄Cl solution by a known procedure [12, 15] and then part of it was re-exchanged in different MeCl solutions (Me = Li, K, Rb, Cs).

Procedure B: The aluminosilicate hydrogels having the molar oxide composition $3.58\text{Me}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2.264\text{SiO}_2\cdot 153.47\text{H}_2\text{O}$ were prepared by addition of 250 ml of Me-silicate solution (prepared by dissolution of fumed silica in MeOH solution) into a plastic beaker containing 250 ml of stirred Me-aluminate solution (prepared by dissolution of Al wire in MeOH solution), at ambient temperature.

Chemical compositions of the amorphous gels were determined by EDS technique using INCA Energy system attached to Zeiss SupraTM 3VP microscope

Table 1. Molar oxide compositions of the prepared Me-gels (Me = Li, Na, K, Rb and Cs) by procedure A and B

Molar oxide compositions of the gels obtained by Procedure A [Me-gels A].
$(0.033\text{Na}_2\text{O}, 0.980\text{Li}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 2.634\text{SiO}_2\cdot 4.1\text{H}_2\text{O}$
$1.03\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2.590\text{SiO}_2\cdot 4.074\text{H}_2\text{O}$
$(0.083\text{Na}_2\text{O}, 0.959\text{K}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 2.650\text{SiO}_2\cdot 3.285\text{H}_2\text{O}$
$(0.112\text{Na}_2\text{O}, 0.884\text{Rb}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 2.773\text{SiO}_2\cdot 4.151\text{H}_2\text{O}$
$(0.108\text{Na}_2\text{O}, 1.012\text{Cs}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 2.598\text{SiO}_2\cdot 3.603\text{H}_2\text{O}$
Molar oxide compositions of the gels obtained by Procedure B [Me-gels B].
$\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 10.255\text{SiO}_2\cdot 9.886\text{H}_2\text{O}$
$1.16\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3.307\text{SiO}_2\cdot 9.855\text{H}_2\text{O}$
$1.016\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3.307\text{SiO}_2\cdot 12.533\text{H}_2\text{O}$
$0.987\text{Rb}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 9.010\text{SiO}_2\cdot 12.533\text{H}_2\text{O}$
$1.246\text{Cs}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 5.178\text{SiO}_2\cdot 10.320\text{H}_2\text{O}$

The gels presented in Table 1. were isothermally heated in a chamber furnace with controlled temperature (ELPH-2, Elektrosanitarij) for 3 h and the starting gels as well the final products were characterized by several techniques such as X-ray powder diffraction (XRD), elemental analysis by X-ray dispersive spectroscopy (EDS), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), TEM, HR-TEM, AFM, Light and Polarizing microscopy and texture analysis (BET method).

RESULTS AND DISCUSSION

The differences in the chemical compositions (Table 1, experimental) between the two series are caused by the difference in the procedures of their preparation. The molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the Na-gel (A) does not change during the exchange of the host Na^+ ions with other Me^+ ions from solution (Table 1). This can be easily explained by the fact that hydrated Na^+ ions in the gel skeleton are simply replaced by the Me^+ ions from solution, without any chemical interactions. By the same reason, the exchange of the host Na^+ ions with other Me^+ ions do not considerably change either the BET surface area (Table 2) or the profile of X-ray powder diffraction patterns (Fig. 1.A) of the samples of Me-gels A.

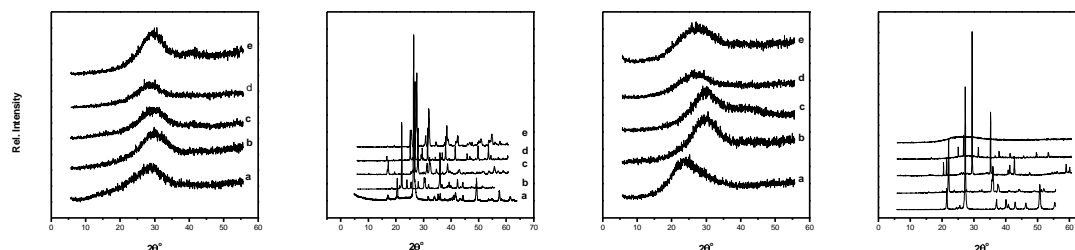


Fig.1 X-ray diffraction (XRD) patterns of the amorphous Me-aluminosilicate precursors obtained by Procedure A (a) as well the patterns obtained after their thermally induced transformations (b) and the corresponding ones obtained by procedure B (c) and (d) respectively.

Table 2. BET surface area of amorphous and crystalline phases, temperature and time of thermal treatment of the samples obtained by Procedure A and B.

BET (m^2g^{-1})	Li-gel	Na-gel	K-gel	Rb-gel	Cs-gel
Me-gels A	81	51	53	47	46
Me-gels B	193	36	183	170	134
Heated Me-gels A	1.1 (925°)	1.1 (990°) 0.3 (1250°)	0.2 (1250°)	0.7(1250°)	0.6(1250°)
Heated Me-gels B	40 (822°)	0.4 (990°) 0.3 (1250°)	2.9 (1037°) 0.2 (1250°)	0.6 (1250°)	0.2 (1250°)

High BET surface areas of the amorphous phases of Me-gels (A) (46 to 81 m^2/g) and Me-gels B (36 to 193 m^2/g) are the consequence of great internal surfaces of these amorphous phases caused by their porous nature. However, due to higher water content, the gels of series B are more porous than the gels of series A, and thus the BET surface area of the gels of series B is considerably higher (for factor 2 – 4) than the BET surface area of the gels of series A.

Gels prepared by the procedure B show a significant shift of their amorphous maximum in the X-ray patterns that indicated a difference in the gel structuring (Fig1 C). This is confirmed by TEM and AFM investigations done on sodium gel and potassium gel prepared by procedure B. TEM image (Fig.2A) shows that Na-gel B is consisted of 20-50 nm sized globular features (“shallow spherical features”); SAED pattern of the same sample shows few faint circles indicating a short range arrangement. HR-TEM (Fig. 2B) show material of different particle size than the one obtained for potassium gel (Fig. 3B). AFM images of the same sample (Fig. 2C, D) show that is consisted of unit particles, diameter 50-120 nm; height 8-20 nm; gradual transformation of amorphous particles to crystallites (700 nm) was visualized.

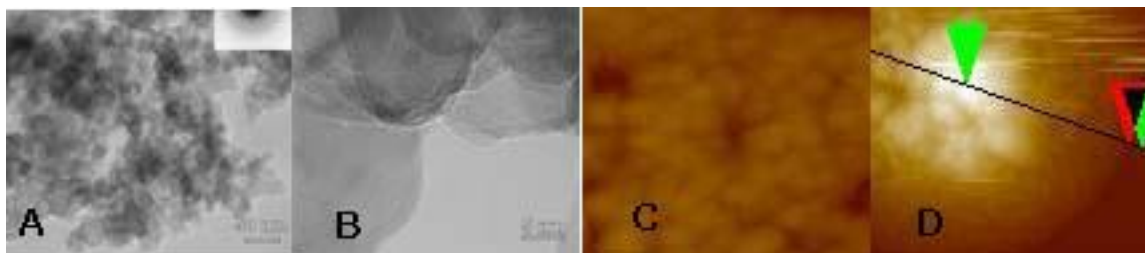


Fig.2 TEM image (A), electron diffraction pattern (inset in Fig.2A) and HRTEM image of the Na-gel[B] sample(B) as well AFM image (C, D) of the same sample on mica.

Contrary to sodium gel, potassium gel is found to be completely amorphous. TEM image (Fig. 3a) shows that the gel is consisted of 5-20 nm sized globular features. SAED pattern shows that no sign of short range ordered units are present which is confirmed by HR-TEM image (Fig3.b). AFM image shows that is consisted of unit particles; diameter 20-50 nm; height 3.5-8 nm.

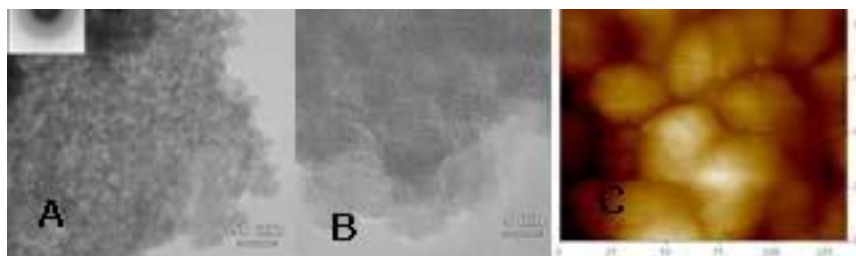


Fig.3 TEM image (A), electron diffraction pattern (inset in Fig.2A) and HRTEM image of the K-gel B sample (B) as well AFM image (C) of the same sample on mica.

The results obtained by the two fundamentally different methods are surprisingly in accord taking into account the sample preparation procedure and imaging conditions. TEM requires dehydrated sample (ethanol) and imaging under vacuum. In contrast, sample for AFM was suspended in water prior to the deposition on mica while imaging was performed under ambient conditions (50% humidity and normal pressure). The shrinkage (dehydration) of unit particles (globular features) in TEM experiments causes the observed difference in particle size. The Na-gel B and K-gel B may be described as clusters of elemental particles. The two gels differ in elemental particle size, and in the level of crystallinity.

The crystalline phases obtained by thermal treatments of Me-gels A and Me-gels B are shown in Table 3. The phase transformations are refined from the X-ray diffraction patterns (Fig. 1 B, C).

Table 3. Phase transformations of the samples obtained by Procedure A [Me-gels A] and Procedure B [Me-gels B], respectively, Me = Li, Na, K, Rb and Cs, after thermal treatment at the appropriate temperature for 3h.

Sample [Me-gel A]	Temperature (°C)	Time (h)	Phase
Li-gel	925	3	Lithium aluminum silicate (LiAlSiO ₄) + (Al ₂ (Al _{2.8} Si ₂)O _{9.6}) aluminum silicon oxide
Na-gel	950, 1250	3	Low carnegieite (NaAlSiO ₄)
K-gel	1250	3	Leucite (KAlSi ₂ O ₆)
Rb-gel	1250	3	Rubidium aluminum silicate (Rb(AlSi ₂ O ₆))
Cs-gel	1250	3	Synthetic pollucite (CsAlSi ₂ O ₆)
Sample [Me-gel B]			
Li-gel	822	3	Low quartz (LiAlSiO ₄)
Na-gel	990	3	Low carnegieite (NaAlSiO ₄)
K-gel	1250	3	Kalsilite (KAlSiO ₄)
Rb-gel	1250	3	Amorphous glassy material
Cs-gel	1250	3	Cesium aluminum silicate, pollucite syn. (Cs(AlSiO ₆)) + amorphous silicon oxide

Heating of all gels of series A and the Li-, Na-, K- and Cs-gel B at appropriate temperatures (925 – 1250° C) for 3 h resulted in their transformation to crystalline Me-aluminosilicates; whereas Rb-gel B was melted to amorphous glassy material at 1250°C. While the chemical composition of the aluminosilicate part of all the crystalline phases obtained by thermal treatment of gels are of type Me-(AlSiO₄) or Me-(AlSi₂O₆), respectively. The type (crystal structure) of the obtained crystalline materials strongly depends on the compensating cation Me⁺.

All the transformations are accompanied with drastic decrease in the surface area (Table 2) caused by the transition of porous amorphous Me-aluminosilicates into more dense, non-porous crystalline phases (having the crystal size in the micrometer or even nanometer range) or into amorphous glassy material (rubidium aluminosilicate obtained by thermal treatment of Rb-gel B).

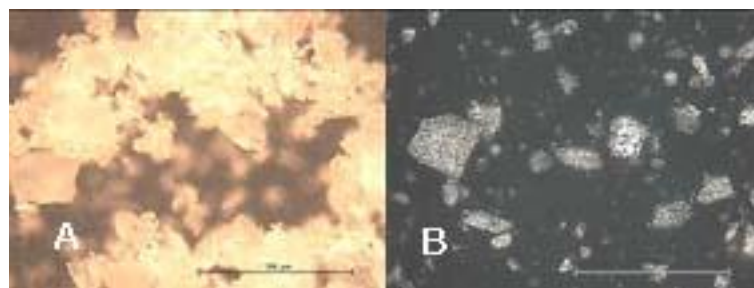


Fig.4. Kalsilite pictures obtained by Polarizing microscope without (A) and in cedar oil (B).

The obtained crystalline materials are nano-sized. Fig. 4 shows the nanosized crystals of the sample K-gel A treated isothermally at 1200 °C for 3h as it is recorded by Polarizing microscope as a pouter and in cedar oil.

CONCLUSION

Thermal transformations of the amorphous aluminosilicate precursors enable the formation of pure ceramic materials. The synthesis route is simple and relatively cheaper than the conventional procedures. The kinetics and optimization of each process will be the goal of our next investigation.

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