NUCLEI DISTRIBUTION WITHIN MATRIX OF HYDROGELS AGED AT ROOM TEMPERATURE

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INTRODUCTION

Aluminosilicate zeolites are synthesized by hydrothermal transformation of the hydrogel prepared by mixing basic aluminate and silicate solutions. Some important processes that occur during this reaction are: precipitation of X-ray amorphous aluminosilicate (gel), formation of crystalline nuclei in the gel matrix, dissolution of gel and the growth of nuclei into much larger particles (crystals). Understanding of the mechanisms of these processes helps us in controlling of particulate properties of crystals and its phase composition.

Classical nucleation theories (homogeneous, heterogeneous and secondary) cannot explain the entire process of zeolite crystallization[1]. Therefore, we use the model of "autocatalytic nucleation" which is based on the hypothesis that the nuclei are formed in the gel matrix during its precipitation and/or ageing. This mechanism of "nucleation" assumes that the number of nuclei formed depends on the initial hydrogel composition, pH value, time and temperature of ageing as well as on the temperature of precipitation. As the gel dissolves nuclei are released and grow once they come in contact with the liquid phase[2,3]. It was first believed that nuclei were homogeneously distributed through gel matrix, but it was found that homogeneous distribution is just one rare example[4].

In this work, our intention is to examine the influence of the time of hydrogel ageing at room temperature on the distribution of nuclei in the gel matrix.

EXPERIMENTAL

In all experiments, starting aluminosilicate hydrogels have the following molar composition: $3,2 \, Na_2O \times 2 \, SiO_2 \times 1,05 \, Al_2O_3 \times 250 \, H_2O$. The gels were prepared by addition of the basic sodium silicate solution into the basic sodium aluminate solution. Both solutions were prepared by dissolving of appropriate amounts of fumed silica (Sigma, 99.8% SiO_2) or sodium aluminate (Riedel de Haën, 54% Al_2O_3; 41% Na_2O) with NaOH (Kemika, >98% NaOH) in double distilled water. In order to remove impurities of the sodium aluminate solutions, they were centrifuged and only clear solution was used for preparation of hydrogels. Reaction mixtures were homogenised with a disperser and divided among needed number of HDPE (high density polyethylene) reactors. After the preparation (precipitation and homogenization) of the first hydrogel (S1) it was put into the air convection oven at 80°C. Other two hydrogels (S2 and S3) were aged for 38 and 158 hours at room temperature and then put in the oven. Oven was preheated to 80°C, so the moment when reactors were put in was assigned as the zero time of crystallization (t_R). The ageing time (t_A) is the time between the moment when two solutions were mixed and the moment when reactors were put in oven.

At predetermined crystallisation times (t_C) reaction mixtures were taken from the oven, cooled to room temperature and centrifuged to stop the crystallisation process and separate the solid from the liquid phase. Clear liquid phase (supernatant) above the sediment was carefully removed without disturbance of the solid phase (sediment). After removal of the supernatant,

the solid phase was dispersed in redistilled water and centrifuged repeatedly until the pH value of the supernatant was about 9. The washed solid phase was dried at 105°C overnight, cooled to room temperature in desiccators over silica gel, weighted and then used for phase analysis and measuring of the particle size distribution.

The powder X-ray diffraction patterns (XRD) of samples were collected on Phillips PW 1820 diffractometer using CuK$_\alpha$ radiation in range $2\Theta = 5\text{-}50°$. Particle size distribution curves of solid samples were measured by Malvern Mastersizer 2000 laser light-scattering particle size analyzer.

RESULTS AND DISCUSSION

Few moments after mixing together silicate and aluminate solutions, the hydrogel precipitates and most of nuclei is formed within gel matrix. Since the nuclei can "normally" grow only in full contact with solution, they become active nuclei after their releasing from the gel matrix. Rising of the temperature of the system to 80 °C simultaneously accelerate both basic processes: gel dissolution (and thus, releasing of nuclei) and crystal growth. Growth of nuclei (crystals) takes place by incorporation of reactive species from the liquid phase on the surface of growing particles. Spending of the reactive species causes faster gel dissolution and more nuclei releasing closing the circle of autocatalytic effect until whole gel is dissolved. Crystal growth rate decreased after silicon and aluminium concentrations in liquid phase fall down to the value of zeolite A solubility. Kinetics of hydrothermal transformations of amorphous gels S1, S2 and S3 into crystalline zeolite A are shown in Fig. 1 (left). Pure zeolite A was only crystalline product. It is clear that crystallisation process accelerates with the ageing time.
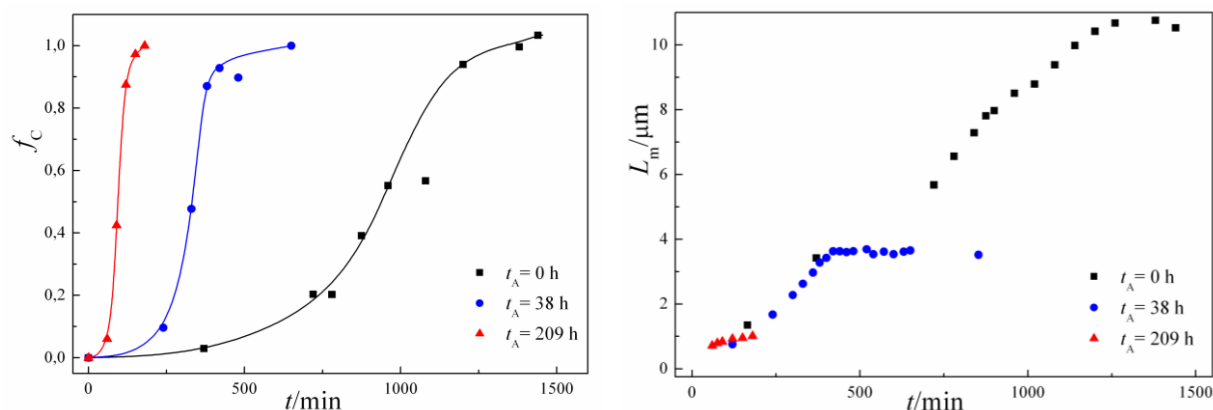

Figure 1. Changes of the fraction of crystalline phase (left) and dimension of largest crystals (right) during crystallization of the systems: S1 (squares), S2 (circles) and S3 (triangles).

Crystal growth rate was determined by Zhdanov-Samulevich[5] method using optical micrographs of samples taken during reaction. Dimensions of largest crystals formed during transformations are shown in Fig. 1 (right). It clearly shows how the size of largest crystals decreases inversely proportional to the ageing time. It also shows a constancy of the crystal growth rate within given crystallization conditions. It means that the number of nuclei and/or their distribution within gel matrix are responsible for the increase of crystallization rate with ageing time.

Fig. 2 shows particle size distributions (by number and volume, respectively) of the crystalline end products (zeoliteA) in the systems S1, S2 and S3. $D_{(0,5)}$ values listed in Table 1 are the values of size at which 50% of distribution fall below. These values give different information; $D_{(0,5)}$ values from distributions by volume are close to dimensions of largest crystals (see Fig. 2). As the time of ageing increases distribution curves get narrower. $D_{(0,5)}$ values from distributions by number become higher, while $D_{(0,5)}$ values from distributions by volume decrease with the time of hydrogel ageing.
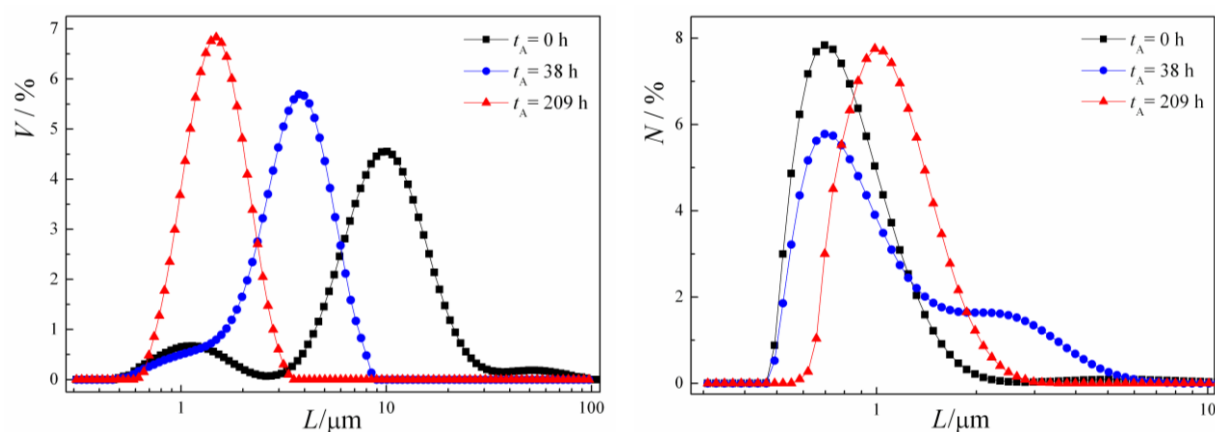

Figure 2. Particle size distributions by volume (left) and by number (right) of crystals at the end of crystallisation of all systems: S1 (squares), S2 (circles) and S3 (triangles).

Table 1. $D_{(0,5)}$ values of the particle size distributions by volume and by number of the zeolite A crystals at the end products of each system.

Hydrogel	S1	S2	S3
$D_{(0,5)}$ by volume / μm	9,314	3,549	1,464
$D_{(0,5)}$ by number / μm	0,786	0,931	1,071
Ageing time / h	0	38	209

Kinetics of nucleation, shown in Fig. 3, were calculated using crystal growth rate and particle size distributions by number of the corresponding systems. Assuming that all nuclei are formed in the hydrogel during its precipitation plots f_N vs f_C in Fig. 3 (right) represent the distribution of nuclei within gel matrix[6]. Based on both figures it can be concluded that in the first hydrogel (S1) the most of the nuclei are positioned in the centre of the gel particles (they come out of gel matrix close to the end of the reaction, when the entire amount of gel was almost dissolved). This is the reason why the particle size distribution by volume of the system 1 (S1) is very wide. A small amount of nuclei that was released from the gel matrix in the beginning had enough time to grow into big crystals, but as the most of nuclei came out at final step of transformation, the particle size distribution shows presence of a large number of small crystals. The majority of nuclei in hydrogel aged for the longest time (S3) are close to surface of gel particles while the distribution of nuclei in gel aged for 38 hours shows higher density near centre of the biggest gel particles. It is obvious that nuclei distribution within gel matrix is heterogeneous in all systems and that ageing affects their re-arrangement. One of

possible explanations why ageing affects their distribution is that not all nuclei are formed during hydrogel precipitation but rather that some are formed at the interface hydrogel/solution (as the ageing time is longer more nuclei are formed closer to the surface of hydrogel).
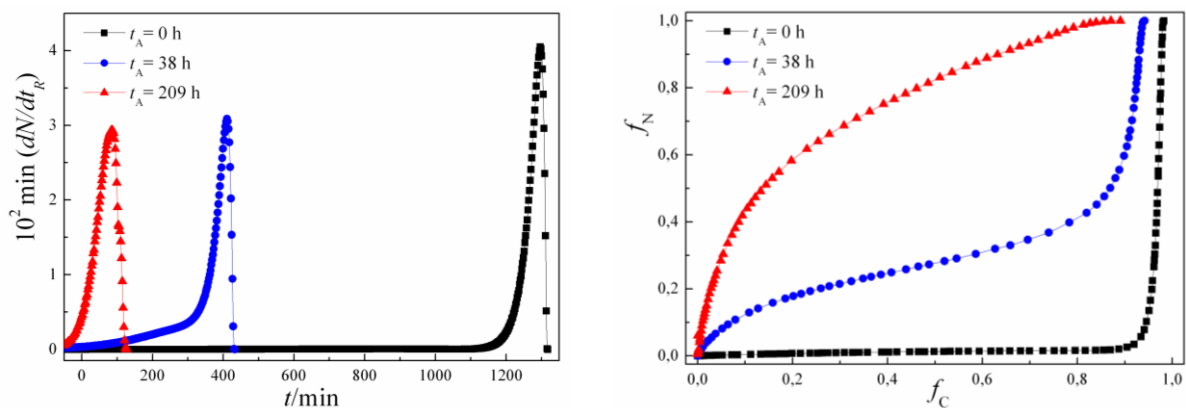

Figure 3. Kinetics of nucleation (left) and the distribution of nuclei within gel matrix (right) of the systems aged for: 0 h (S1, triangles), 38 h (S2, circles) and 209 h (S3, squares).

CONCLUSION

Ageing of hydrogel that transforms into crystalline zeolite A does not influence the growth rate of zeolite A crystals, but affects their size and size distribution. Crystal growth rate depends only on temperature of reaction and starting composition while particle size distribution depends on these factors as well as on nuclei distribution within gel matrix. It was shown that nuclei in freshly prepared hydrogel (S1) are mostly distributed around centre of the biggest gel particles. During ageing process, more and more nuclei are formed closer to the surface of hydrogel.

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