

MORPHOLOGY OF ZEOLITE A CRYSTALS SYNTHESIZED AT DIFFERENT ALCALINITY

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ABSTRACT

The possibility to control particulate properties (particularly morphology) of the synthesized crystals can be implemented through several physico-chemical parameters. In this paper, we have studied the influence of the alkalinity of the system on the size and morphology of zeolite A crystals. Prepared hydrogels were heated at 80°C in reactors made of HDPE, under static conditions. Starting compositions were: 3.2/12.0 Na₂O × 2 SiO₂ × 1.1 Al₂O₃ × 300.0 H₂O. The characterization of the samples was performed using several analytical methods such as: X-ray diffraction (XRD), laser light scattering (LLS), optical microscopy (OM) and scanning electron microscopy (SEM). The analysis of the results show that the increase of alkalinity of explored system had two major effects: increase of the number of nuclei (crystals) in system and formation of crystals with more irregular shape.

Keywords: zeolite A, morphology, hydrothermal synthesis, crystal size distribution

INTRODUCTION

The morphology as well as the size of zeolite crystals could have important impact on their applications [1] as: absorbers (for gases and liquids), molecular sieves (membranes, purificators), cation exchangers (removal of Me cations from wastewaters, detergent ingredient) and catalysts (petrochemistry, environmental issues, fine chemicals, etc.).

Understanding of basic processes of zeolite crystals formation and growth enables prediction of their particulate properties at the end of crystallization process. This field, extensively studied several decades [2-4], still have unclear stages (events) concerning the processes of nucleation and crystal growth. A theory of autocatalytic nucleation [5,6] was developed on Zhdanov's observation that dissolution of gel also made "the structured blocks" free and in full contact with solution they can act as building units of growing crystals or as nuclei [7]. The consequence is that overall crystallization rate increases exponentially with time of crystallization and depend on amount of crystallized material. The main presumptions of autocatalytic nucleation is that the most of nuclei are generated during gel formation, hidden within gel matrix and can grow only in contact with solution.

The goal of the present study is to relate theory with practice and thus to reach a fine control of zeolite crystal size and morphology.

EXPERIMENTAL

Initial hydrogels were prepared by addition of clear silicate component into clear aluminate solution. Silicate solution was prepared by adding of appropriate amounts of waterglass (SiO₂ - 27% wt., Na₂O - 7.7% wt., Fluka) and sodium hydroxide (reagent grade NaOH, > 98% wt., Kemika) in demineralised water. Aluminate solution was prepared by dissolution of an appropriate amount of anhydrous sodium aluminate (Na₂O - 41% wt., Al₂O₃ - 54% wt., Riedel-de-Haën) in demineralised water. Starting composition of the system 1 (S1) was: 3.2 Na₂O × 2 SiO₂ × 1.1 Al₂O₃ × 300 H₂O. The only difference in system 2 (S2) is Na₂O

content - 12.0 instead of 3.2. The precipitated hydrogels were homogenised by stirring (magnetic bar stirrer) for 1 h, divided into HDPE reactors and put into convection oven at 80°C. At predefined crystallization times (t_c) reactors were taken out and samples were centrifuged to stop the crystallization process and separate the solid from liquid phase. The solid phase was dispersed in demineralised 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 the characterization.

Phase composition of the samples was determined by X-ray powder diffraction (XRD) with a Philips PW 1820 instrument (CuK α radiation, $2\theta = 5 - 50^\circ$). The size of the largest crystals (L_m) in the solid samples at various t_c was determined by the Zhdanov and Samulevichs' method [8], using OM (Meji equipped with Nikon Coolpix 990 digital camera) and SEM (Jeol 7000) for crystals smaller than 1.5 μm and for morphology comparison. Crystal (particle) size distribution (CSD) curves of the solid samples were determined by a Malvern Mastersizer 2000 LLS particle size analyzer. Specific number of crystals (N_s - number of crystals per gram of the zeolite) was calculated from corresponding particle size distributions, normalized to unit value of 1 g of zeolite A.

RESULTS AND DISCUSSION

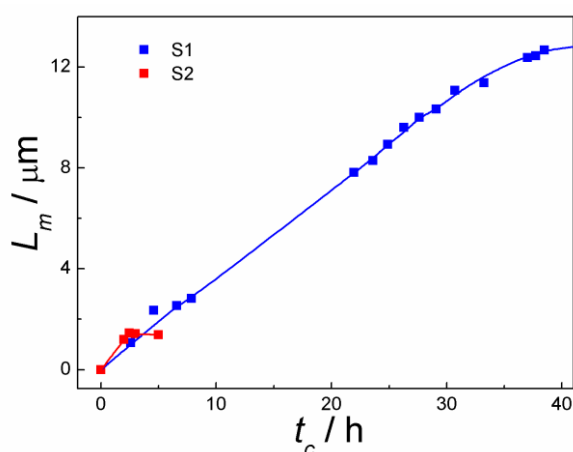


Figure 1. The dependence of the average size of largest crystals on the crystallization time. OM and SEM images are used for size measurements.

The curves of sizes of the largest crystals (Figure 1.) shows a linear crystal growth and an increase in crystallization rate with alkalinity (from 0.350 for S1 to 0.585 $\mu\text{m h}^{-1}$ for S2). Also, the largest crystals in S2 are about 7 times smaller than in S1. Taking into account that the amount of the starting material is the same in both cases, one can expect that the distribution by number will be strongly in favour to S2 (much smaller largest crystals). However, the curve of particle size distribution by number (Figure 2. left) has maxima at lower value in S1 than in S2 (around 0.6 and 0.7 μm , respectively).

In spite of that fact, the values for the specific number of the crystals (calculated from distributions by number) are in agreement with measurements of largest crystals and the theoretical assumption that higher alkalinity of the system generates larger number of nuclei within gel matrix. $N_s = 2.27 \times 10^{11}$ for S1 and $N_s = 9.40 \times 10^{11}$ for S2. The distribution by volume (mass) shows bimodal curve for S1 and narrower monomodal curve for S2, but both have the same starting point (0.47 μm). This means that the process of nucleation ends with large number of small crystals that appear in systems in time which corresponds to the crystallization time needed for dissolution of the most of the gel in both systems (over 90%).

On the other hand, large wide maxima of big crystals (7-27 μm) of S1 indicate slow appearance of nuclei. More precisely, it means that their release from gel matrix enables full contact with mother liquor, respectively with dissolved reactive low-molecular aluminate, silicate and aluminosilicate species, which is responsible for crystal growth (solution mediated growth). In contrast, faster appearance of larger number of nuclei in S2 from the beginning of

the reaction and faster gel dissolution (more OH⁻ ions present in system) causes increase of the crystallization rate.

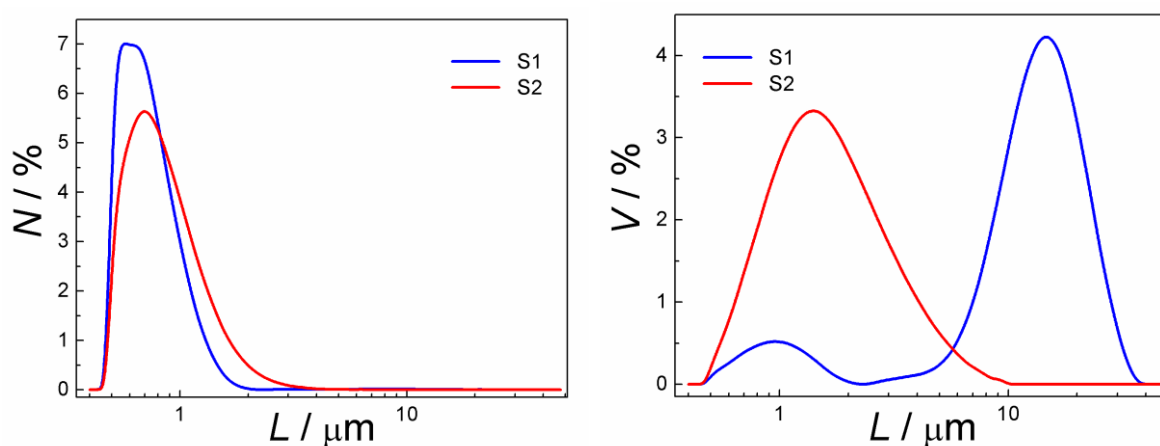


Figure 2. Particle size distribution curves of both systems at the end of crystallization of zeolite A by number (left) and by volume (right).

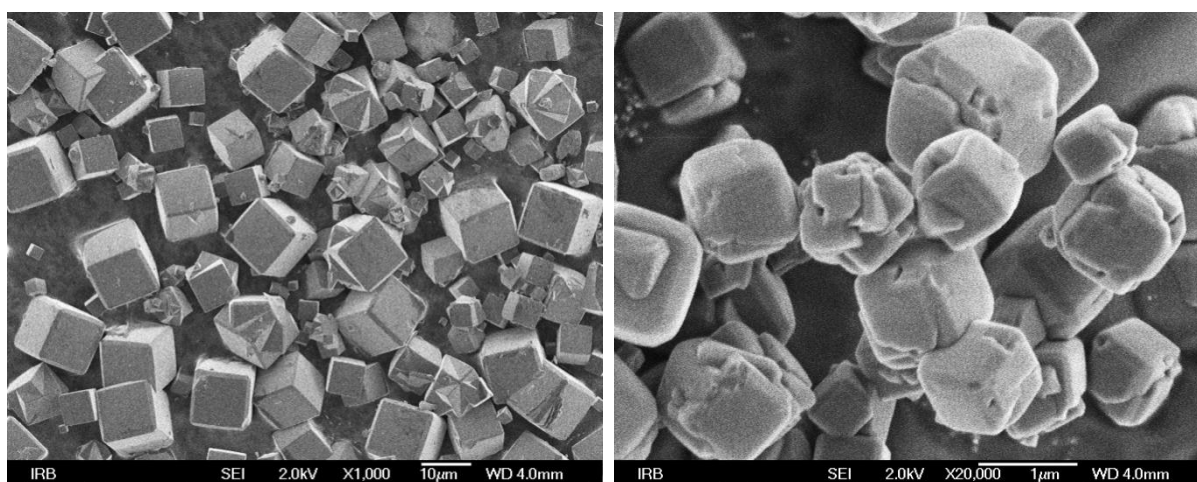


Figure 3. SEM photos of the zeolite A crystals at the end of the hydrothermal transformation of hydrogels S1 (left) and S2 (right).

Due to the higher alkalinity of S2, crystallization rate is higher as expected, but observed type of twin crystals (contact, penetration) is the same in both systems (Figure 3.). Cube of truncated edges is dominant crystal form in both systems. Crystals synthesized from S1 have nice well defined facets of sharp edges, while facets of crystals from S2 are more rounded, containing a lot of cracks, but still recognizable shape. Assemblies of several intergrowth crystals were not found.

CONCLUSIONS

Linear crystal growth of largest crystals is observed in both systems as well as an increase of the number of crystals with the raise of alkalinity of the gel.

Important consequence of the growth of higher number of nuclei from beginning of crystallization in S2 is the increase of crystallization rate, lower size of the largest crystals and more rounded morphology.

Large number of nuclei appears in both systems at the time of depletion of hydrogel, indicating concentration of nuclei close to the center of gel particles. At the same time, it also means inhomogeneous distribution of nuclei within gel matrix.

Increase of the alkalinity of the system has main impact on number of crystals (for more than 4 times) and on morphology of the crystals (rounded, defective crystal facets instead of very well defined, crystal planes with sharp edges).

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