

SYNTHESIS OF ZEOLITE A CRYSTALS FROM HYDROGELS AGED AT ROOM TEMPERATURE

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INTRODUCTION

In chemistry of aluminosilicates, several physico-chemical parameters control the rate of synthesis (kinetics) and particulate properties of the end product (zeolite crystals) such as: pOH, temperature of gel formation, temperature of transformation, concentrations of reactive aluminate, silicate and alumino-silicate species, additives, templates, seed crystals, etc. One of very important factors is gel ageing that influences crystallization rate and particulate properties of the final product. Therefore, monitoring of the kinetic parameters and particle size distribution of the aged systems during crystallization, we can collect useful information on the nucleation process in the gel phase. Hydrothermal, solution mediated transformation¹ is general method widely used in zeolite synthesis.

EXPERIMENTAL

Alumino-silicate hydrogels having following molar composition: $3,2 \text{ Na}_2\text{O} \times 2 \text{ SiO}_2 \times 1,05 \text{ Al}_2\text{O}_3 \times 250 \text{ H}_2\text{O}$ 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 redistilled water. In order to remove impurities of the sodium aluminate solutions, they were centrifuged and only supernatant was used for preparation of hydrogels. Hydrogels were homogenised with a disperser and aged for 38 (System I) and 65.95 hours (System II) at room temperature, then were divided among needed number of HDPE reactors. Reactors were heated in the air convection oven at 80°C. Oven was preheated to 80°C, so the moment when reactors were put in was assigned to 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 predefined 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) and used for determination the concentrations of aluminium (C_{Al}) and silicon (C_{Si}) dissolved in solution. 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 particle size distribution.

The powder X-ray diffraction (XRD) patterns of samples were collected on Phillips PW 1820 diffractometer using CuK_α radiation in range $2\theta = 5\text{-}50^\circ$. Particle size distribution curves of solid samples were determined with Malvern Mastersizer 2000 laser light-scattering particle size analyzer. Concentrations of aluminium and silicon in the solutions separated from reaction mixtures at different crystallisation times were measured by PerkinElmer AAnalyst 200 atomic absorption spectrometer.

RESULTS AND DISCUSSION

Mixing of silicate and aluminate solutions causes precipitation of hydrogel. The optical micrographs of the solids formed during crystallization of the hydrogel in system I (Fig. 1), aged for 38 h, show that it was finished after 560 min at 80°C. The X-ray diffraction patterns (Fig. 2) show that complete transformation of the hydrogel, aged for 65.95 h, occurred after 340 min at 80°C. According to the reaction time, the first crystals observed by optical microscopy appear much earlier than the XRD can show. Detection limit for XRD method used in this research is around 4 % of crystalline phase within gel, while the detection limit for optical microscopy is determined with size of the crystals (above 400 nm) and does not depend on crystalline to amorphous phase ratio. On the other hand, lowest size of the crystals which can be detected by XRD is just few unit cells (cubes 2.5 nm) of ZA.

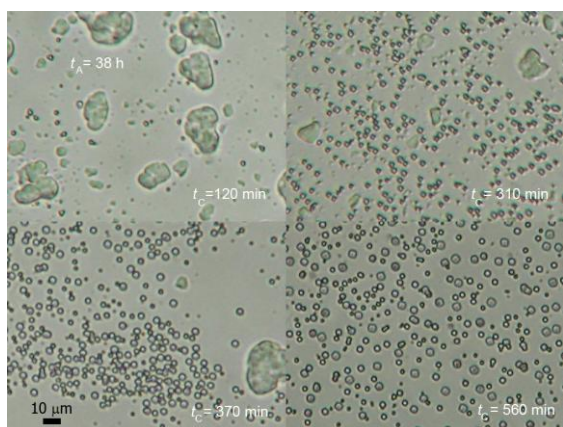


Fig. 1. Optical micrographs of samples taken during transformation of gels aged for 38 h.

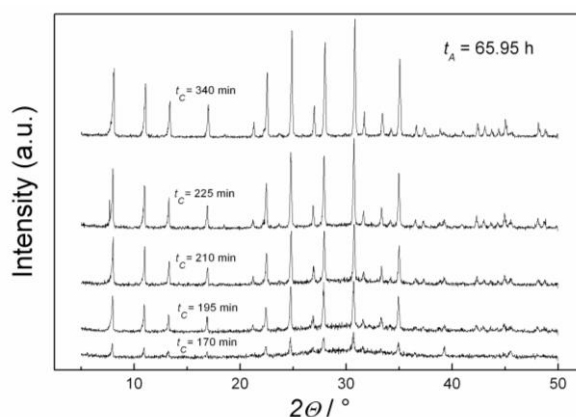


Fig. 2. XRD patterns of samples taken during transformation of gels aged for 65.95 hours

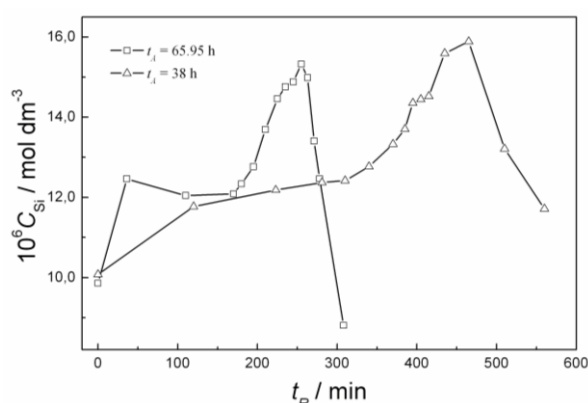
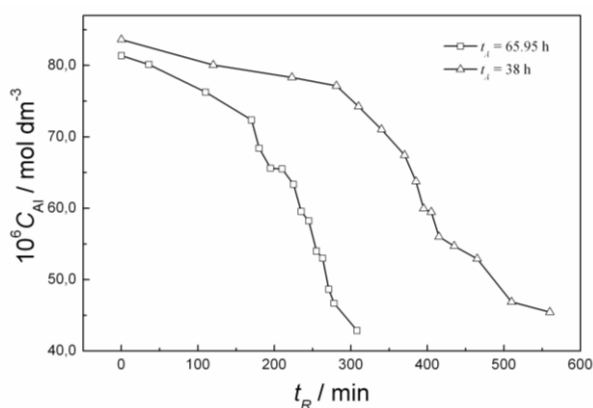


Fig. 3. Time dependence of aluminium (left side) and silicon (right side) concentrations in liquid phase of samples taken during hydrogels transformation.

Concentrations of aluminium and silicon in liquid phase (Fig. 3) at the beginning of the reaction depend on the Si/Al ratio of the aged gel and on its solubility in NaOH solution of a given concentration. A much higher concentration of aluminium in the liquid phase also means that the gel is richer in silicon. After the reaction temperature is reached, the concentration of silicon (Fig. 3, right side) is approximately constant (as the gel dissolves, nearly the same amount of silicon is built into zeolite). Process of gel dissolution is faster than ZA crystal growth, therefore slow change of the Si (increase) and Al (decrease)

concentrations before intensive crystal growth (around 300 min in System I and cca 170 min in System II) also means that amount of the dissolved gel (also crystallized ZA) was small. Stronger increase of the Si concentration and decrease of Al concentration causes constant supersaturation during the most of the reaction time (cca 450 min in System I, around 250 min in System II). Sudden decrease of Si concentration indicate complete gel dissolution and decrease of supersaturation down to the level which corresponds to the solubility of crystallised zeolite at given physico-chemical conditions. Dependence of measured concentrations of aluminium and silicon in the liquid phase on crystallization time shows that increasing time of the ageing speeds up crystallization process.

Crystals size distribution of the final product by volume (Fig. 4, left side) show almost normal distribution (symmetric curve of System II) and asymmetric (almost bimodal) distribution of the crystals in System I. Taking into account the fact that crystals (nuclei) can grow only in full contact with solution^{2,3}, it indicates faster release of nuclei in case of longer ageing and consequently non-uniform distribution of nuclei within gel matrix. It means that more nuclei were closer to the gel surface and they were faster released from gel matrix and start to grow⁴. Much wider distribution of crystals sizes for System I (0.4-8 μm) than for System II (1-5 μm) means also longer time of nuclei releasing from gel matrix.

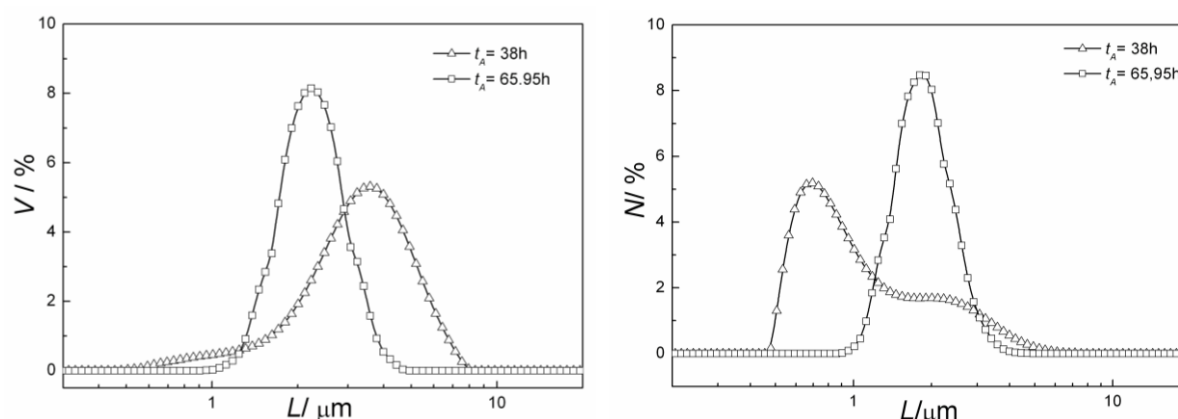


Fig. 4. ZA crystal size distribution by volume (left side, $D_{(0.5)} = 3.239$ and $2.216 \mu\text{m}$) and by number (right side, $D_{(0.5)} = 0.894$ and $1.825 \mu\text{m}$) at end of the crystallization of System I (triangles) and System II (squares).

Moreover, larger number of smaller particles at the end of crystallization of System I (aged for 38 h, Fig. 4, right side) in bimodal shape of the size distribution by numbers causes large shifting of the $D_{(0.5)}$ value to the $0.894 \mu\text{m}$. That also indicate inhomogeneous distribution of the nuclei within volume of gel matrix, but inhomogeneity is lower than in System II.

CONCLUSION

- ageing of the hydrogel at room temperature for longer time (65.95 instead of 38 h) speeds up crystallization process (from 560 to 310 min),
- the inhomogeneous distribution of nuclei in hydrogel increases with ageing time (nuclei are closer to the surface of the gel particles)
- gel aged for shorter time gives wider crystal size distribution at the end of crystallization process,

- large number of small crystals in System I at the end of crystallization causes unusual shifting of $D_{(0,5)}$ value below $1 \mu\text{m}$ ($0.894 \mu\text{m}$).

ACKNOWLEDGEMENT

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SINTEZA KRISTALA ZEOLITA A IZ HIDROGELOVA STARENJIH NA SOBNOJ TEMPERATURI

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SAŽETAK

Posredstvom tekuće faze odvija se proces sinteze zeolita iz priređenog hidrogela. Na brzinu rasta kristala i njihova čestična svojstva utječu razni fizičko-kemijski parametri kao što su: pOH, temperatura geliranja, temperatura reakcije, koncentracije reaktivnih čestica (aluminata, silikata i alumo-silikata), dodaci, templati, kristalno cjepivo, itd. U ovom radu je studiran utjecaj starenja hidrogela na kinetiku pretvorbe gela u zeolit A kao i na čestična svojstva produkta nakon potpune transformacije. Na osnovi praćenja koncentracija Si i Al u tekućoj fazi, tijekom kristalizacije ZA iz gela starenog 38 i 65,95 h, zatim analize kristala ZA pomoću optičke mikroskopije, difrakcije rendgenskih zraka na prašku i raspodjela veličina čestica dobivenih dinamičkim raspršenjem laserskog svjetla, zaključeno je slijedeće: dužim starenjem se ubrzava pretvorba gela u zeolit, dužim starenjem se povećava nehomogenost raspodjele nukleusa u matrici gela, kraćim vremenom starenja povećano je vrijeme izlaska nukleusa iz matrice gela, a dobivena bimodalna raspodjela veličina kristala ZA uzrokuje pomak prosječne veličine čestica ($D_{(0,5)} = 0,894 \mu\text{m}$) k nižoj vrijednosti.

Ključne riječi: hidrotermalna sinteza, nukleacija, raspodjela veličina čestica, starenje, matrica gela