

SYNTHESIS AND PARTICULATE PROPERTIES OF ZEOLITE A

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ABSTRACT

Zeolites are materials with different applications. Every field of usage has special demands regarding zeolite particulate properties. Understanding the mechanisms of crystal formation enables control of these properties. After ageing at 25°C for $t_a = 0-209$ h hydrogels of 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 heated in reactor at 80°C under dynamic conditions. Optical microscopy and SEM images as well as particle size measurement provided data on crystal size and specific surface area of final products. Specific number of zeolite A crystals was calculated from particle size distributions. Observed effects were discussed on the grounds of the autocatalytic nucleation theory.

Keywords: zeolite A, hydrothermal synthesis, autocatalytic nucleation, specific number of crystals, hydrogel ageing

INTRODUCTION

In order to use certain material (powder) for specific application it is important to be able to control its particle shape, specific number of particles and their size distribution (particulate properties). Zeolites are widely used as: molecular sieves, catalysts, adsorbents, ion exchangers, etc [1]. Understanding of basic mechanisms of zeolite crystals' formation enables prediction of their properties. Zeolites are usually synthesized by hydrothermal treatment of (alumino)silicate amorphous hydrogel, which has been precipitated after mixing alkaline silicate and aluminate solutions. One of proposed models that describes the process of zeolite crystallization is the model of autocatalytic nucleation. It is based on the assumption that potential crystal nuclei are formed within the gel matrix during its precipitation and ageing. Nuclei can grow to crystals only when they are in contact with the reactive species from the solution. They are released to the solution during gels' dissolution [2].

Many physicochemical parameters influence the transformation of hydrogel into zeolite crystals [3]. Hydrogel ageing causes shortening of the reaction time and lowering the end product's size [4]. Our intention is to examine how the ageing of amorphous precursor affects the nucleation process.

EXPERIMENTAL

Aluminosilicate hydrogels having the batch 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 alkaline sodium silicate solution into alkaline sodium aluminate solution. Sodium silicate solution was prepared by dissolution of an appropriate amounts of fumed silica (99.8 wt. % SiO_2 ; Sigma) and sodium hydroxide (reagent grade, > 98 wt. % NaOH , Kemika) in demineralised water. Sodium aluminate solution was prepared by dissolution of an appropriate amount of anhydrous sodium aluminate (41 wt. % Na_2O , 54 wt. % Al_2O_3 , Riedel-de-Haën) in demineralised water. In order to remove impurities of the sodium aluminate solution, it was centrifuged and only clear solution was used for the preparation of hydrogels. Then, the precipitated hydrogels were homogenised by disperser and aged for $t_a = 0$ (freshly prepared hydrogel), 38 h, 66 h and 209 h at 25°C. After the appropriate time of ageing, the hydrogels (S1 – S4) were poured into stainless steel reaction vessel and stirred with a Teflon-coated

magnetic bar driven by a magnetic stirrer (dynamic conditions). The ageing time (t_A) is the time between the moment when two solutions were mixed and the moment when the hydrogel was put into the reactor. At predefined crystallization times (t_c) aliquots of the reaction mixture were drawn out and 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 (zeolite A) was determined by powder X-ray diffraction at Philips PW 1820 diffractometer, using $\text{CuK}\alpha$ radiation in the corresponding region of Bragg's angles ($2\theta = 5 - 50^\circ$). The size of the largest crystals (L_m) in the solid samples at various crystallization times (t_c) was determined by the Zhdanov and Samulevichs' method [5], using optical (Meji equipped with Nikon Coolpix 990 digital camera) and scanning electron microscope (SEM, Jeol 7000). Crystal (particle) size distribution (CSD) curves of the solid samples were determined by a Malvern Mastersizer 2000 laser light scattering particle size analyzer. Specific number of crystals (N_s - number of crystals per gram of the crystalline end product) was calculated from corresponding particle size distributions, normalized to unit value of 1 g of zeolite A.

$$N_s = \frac{1}{G\rho \sum (N_i(D_i)^3)}$$

where:

N_i - the number of the crystals within segment having size $D_i \pm \Delta D/2$ (sphere equivalent diameter), D_i - (average) particle diameter within segment, ρ - the density of zeolite A (2 g/cm³), and G - the geometrical shape factor (for sphere = 1).

RESULTS AND DISCUSSION

Optical micrographs of the crystals obtained at end of the crystallization of hydrogels aged for $t_A = 0$ h, 38 h and 66 h, were shown in Figure 1. It is evident that the ageing process affects final product's size - particles of the system S1 are larger than the particles of the systems S2 and S3. Since diffraction halo of visible light around the particles smaller than 1,5 μm gives overestimation of their size, only SEM images of the end products of the hydrogel aged for 209 h were taken (S4). The values of the sizes of the largest crystals, L_m , observed in each system by optical and scanning electron microscope (Table 1.), indicate that the crystal size of the end products of aged hydrogels becomes smaller with the ageing time (4,89 μm from freshly prepared hydrogel to 1,19 μm from hydrogel aged for $t_A = 209$ h).

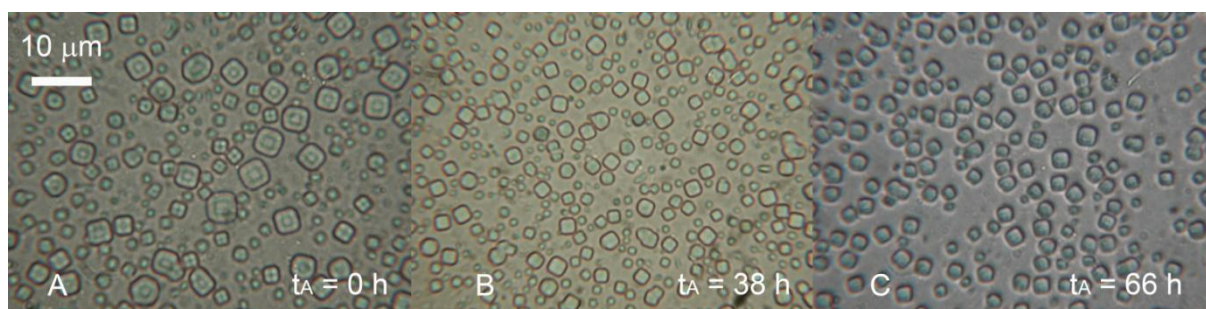


Figure 1. Optical micrographs of the zeolite A crystals formed during the hydrothermal transformation of hydrogels aged for $t_A =$ A) 0 h, B) 38 h and C) 66 h.

Crystal size distributions by volume and number of the final products (Figure 2) show that the particles obtained from fresh hydrogel are the largest (also widest distribution), while the particles obtained from the hydrogel aged for 209 h are the smallest (also narrowest distribution) which is in good agreement with the L_m measurements.

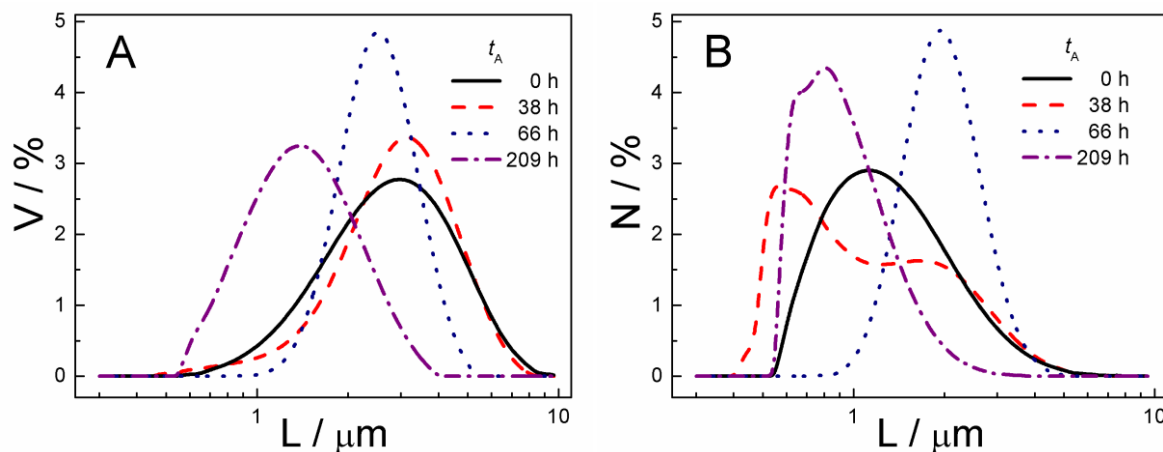


Figure 2. Particle size distribution curves at the end of crystallization of zeolite A by volume (A) and by number (B) for $t_A = 0$ h (full line), 38 h (dashed line), 66 h (dotted line) and 209 h (dash-dotted line).

According to the $D_{(V,0.5)}$ values (50 % of the particles have the volume under this value) in the Table 1, system aged for 38 h shows anomaly. Due to the correlation between volume and number size distributions of the same sample, it is normal that $D_{(0.5)}$ value for number distribution is shifted towards lower value than for volume distribution. A large number of small crystals in systems S4 and S2 show strong maxima at 0.4-0.6 μm and causes significant shifting of $D_{(0.5)}$ value, and even bimodal distribution of S2 (Fig. 2B).

Table 1. Numerical values of measured and calculated parameters relevant for describing crystals of zeolite A formed from aged hydrogels in dynamic conditions: t_a – time of gel ageing, L_m – the size of the largest crystals determined by Zhdanov-Samulevich method, $D_{(V,0.5)}$ - value in μm under which 50% of particles lie in CSD by volume, $D_{(N,0.5)}$ - value in μm under which 50% of particles lie in CSD by number, a_s (m^2g^{-1}) – specific surface area of crystals, and N_s - specific number of crystals, both obtained from particle size distribution by volume.

System	t_A / h	L_m / μm	$D_{(V,0.5)}$ / μm	$D_{(N,0.5)}$ / μm	a_s / m^2g^{-1}	N_s / $\#\text{g}^{-1}$
S1	0	4,89	2,832	1,286	2,46	$2,053 \times 10^{11}$
S2	38	2,78	3,035	1,050	2,32	$2,074 \times 10^{11}$
S3	66	2,62	2,555	1,988	2,45	$2,702 \times 10^{11}$
S4	209	1,20	1,418	0,902	4,56	$9,493 \times 10^{11}$

Data of the specific surface area (column a_s in Table 1) show significant difference between the system aged for $t_A = 209$ h and other systems. While a_s has nearly the same value for systems S1-S3 (2,32 – 2,46 m^2g^{-1}), in the S4 system it becomes almost two times higher (4,56 m^2g^{-1}). This fact is a consequence of much smaller crystals (higher specific number of crystals) than in other systems. (Relationship between particle size and its area is square.)

Specific number of particles in studied systems is the number of zeolite A crystals present in 1 g of the material obtained at the end of transformation. The values calculated from corresponding crystal size distributions are listed in Table 1. Specific number increases with ageing time ($2,053 \times 10^{11}$ - $9,493 \times 10^{11}$). This behavior is expected by the model of autocatalytic nucleation and is in accordance with findings of Cundy et. al., on silicalite-1 and

titanosilicalite-1 [6]. These results confirm the predictions of the autocatalytic nucleation theory: crystal nuclei are formed during hydrogel precipitation and during ageing due to reactions of reactive species from solution with the surface and subsurface area of gel particles. Since the nuclei can grow only in contact with solution, they need to be released from gel matrix. Increasing the ageing time more nuclei were formed and quickly released to solution from gel matrix at the beginning of the crystallization. Therefore, overall reaction is faster and crystals are smaller. It is in accordance with above presented results, since all prepared hydrogels have the same chemical composition, but more crystals are formed in systems of longer ageing time.

CONCLUSION

Data obtained by particle size measurements and optical and scanning electron microscopy indicate that the size of zeolite A crystals formed by transformation of hydrogels aged for longer time is lower than ones aged for shorter time.

Nuclei are formed during hydrogel formation, but also during its ageing at the interface between the solution and gel particles. As the ageing time increases, more nuclei are formed due to longer time of the reaction on the gel surface.

Larger number of nuclei, quickly released from the gel matrix at beginning of transformation, indicates a formation of new nuclei during ageing time, just as it was predicted by the autocatalytic nucleation theory.

Specific surface area as well as the specific number of prepared zeolite A crystals strongly depends on their size distribution.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Science, Education and Sport of Republic of Croatia within basic project 098-0982904-2953 and bilateral Croatian-French program COGITO .

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