TEMPERATURE INFLUENCE ON THE ZEOLITE A CRYSTALLISATION PROCESS

Sanja Bosnar[1], Boris Subotić[1]
Ruđer Bošković Institute, Bijenička 54, Zagreb
E-mail: sbosnar@irb.hr

INTRODUCTION

Although generally rather simple, process of zeolite crystallisation comprises a range of complex and interconnected physical and chemical processes dependent on different factors like temperature, pH, source of silicate and aluminate etc. The type and properties of the final cristalline product (zeolite) depend on the crystallization conditions applied.

Temperature has direct influence on the reactions of polimerisation of reactive silicate, aluminate and aluminosilicate species, rate of gel dissolution and transformation, and consenquently rate of nucleation and crystal growth[1]. The temperature change influences transformation of metastable phases resulting in the formation of more stable but structurally different zeolites, as well as the morphology of zeolite crystals that is connected to the different activation energies of different crystal planes[1,2]. Generally, with temperature increase, rate of crystal growth accelerates and lenght of the induction period decreases.

Already during gel precipitation, because of high saturation of components, parts of the short ordered regions emerge inside gel matrix[3]. According to the assumptions of the autocatalitic nucleation[4] those regions are potential nuclei that can become active centres of crystallization, when, by dissolution of gel during the crystallisation process, they enter the liquid phase of the reaction mixture.

Although the rate of the nucleation and crystallisation, as well as properties of the final product depend on the crystallisation conditions (e.g. temperature in this investigation), particular properties, that means the specific number, the average size and size distribution of crystals of the final product do not, as it is postulated through the model of gel memory effect, that number and distribution of nuclei in the gel matrix depend only on the preparation conditions[3]. Under this assumption differences noticed in the results of the positron annihilation lifetime spectroscopy (PALS) of the differently prepared zeolite precursors can be ascribed to the different sizes of free volumes obtained in differently prepared precursors[5].

In order to determine influence of crystallization temperature on the rate of crystallisation of zeolite A and crystal size distribution, the change of the size of crystals, ratio of the crystalline phase were monitored during the process of crystallisation of two identically prepared systems but treated at different temperatures. The rate and activation energy of the crystal growth were also determined.

EXPERIMENTAL

The aluminosilicate precursor was prepared by mixing silicate and aluminate component in the same way for all investigated systems as described in Ref. 6. The reaction mixture contained the precursors with molar composition 1,03 Na_2O . Al_2O_3 . 2,38 SiO_2 . 1,66 H_2O dispersed in 1,2 M and 2 M NaOH solution. Crystallisation temperatures were 70, 75, 80, 85 and 90^oC. During the process of crystallisation aliquots of reaction mixture were taken and prepared for analyse on XRD, optical microscope, SEM and some of them for PALS.

RESULTS AND DISCUSSION

In all investigated systems the change of the fraction of crystalline zeolite during the crystallisation process can be described by S-shaped curves (Fig.1A; Fig 2A), as it is typical for most of zeolite syntheses. As it was expected the rate of crystallisation and crystal growth increase and the duration of entire process decreases with increase of temperature of the crystallisation.

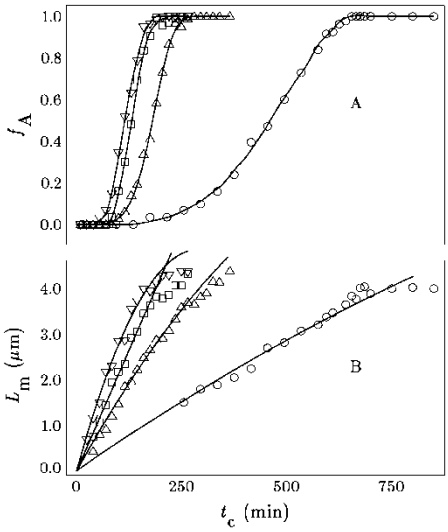

Figure 1. Changes of crystal fraction (A) and sizes of crystals (B) of zeolite A during crystallization process in systems with 1,2 M NaOH(○70°C, Δ 80°C, □ 85°C, v 90°C)

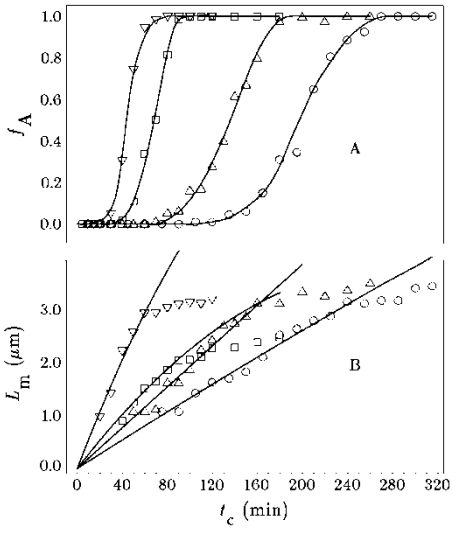

Figure 2. Changes of crystal fraction (A) and sizes of crystals (B) of zeolite A during crystallization process in systems with 2 M NaOH (○70°C, Δ75°C, □ 80°C, v90 °C)

The results from PALS measurements on the samples obtained during zeolite A synthesis at 80 °C (Table 3), show that the sizes of free volumes corresponding to the long Ps lifetimes are rather constant, but the sum of their relative intensities that can be connected to the concentration of those sites, is increasing and thus indicating more ordered structure emerging[7].

Table 3. Diameters of free volumes in samples taken during process of zeolite A crystallisation in system 2 M NaOH at 80 °C

Time min	R_3 nm	R_4 nm	I_3+I_4 %
0 (gel)	0,41	1,24	3,72
30	0,45	0,95	0,67
90	0,46	1,25	1,92
120	0,53	1,41	2,18
300	0,45	1,34	4,59

Crystal growth rates determined from the data shown in Figure 1B and 2B, are increasing with temperature. From the linear dependence of the crystal growth constant (log K) against temperature (1/T), as determined by Arrhenius law, activation energy for crystal growth is determined with value 81,4 J mol^{-1} for systems with 1,2 M NaOH, and 70,7 $Jmol^{-1}$ for systems with 2 M NaOH.

As all the investigated systems were prepared in the same way it was expected that the number and distribution of nuclei in the gel matrix will be rather same for all investigated systems. And in fact, the analyses of the results of the crystal size distribution (Fig.3) shows that sizes of crystals and their size distribution are rather same for all investigated temperatures in systems with 1,2M NaOH, but with exeptions in systems with 2M NaOH (Fig. 4). In those systems lower sizes and higher specific number of crystals were found (Table 2). On the basis of the previous results this could be explained by some additional processes of nucleation.

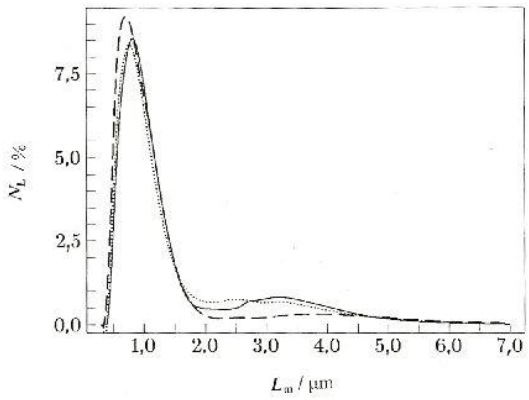

Figure 3. Crystal size distribution of zeolite A obtained in systems with 1,2M NaOH (70°C─, 80°C--, 90°C…)

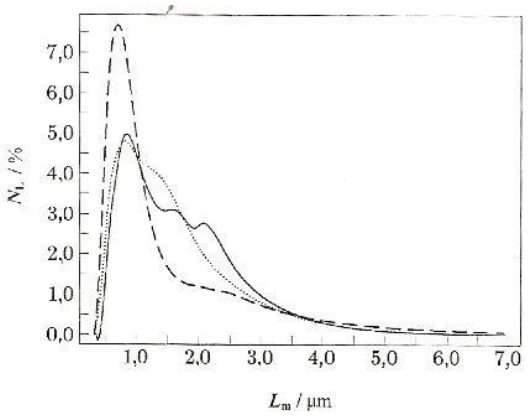

Figure 4.Crystal size distribution of zeolite A obtained in systems with 2M NaOH (70°C─, 80°C--, 90°C…)

Table 2. Average size *L* and specific number *N* of crystals of zeolite A obtained as the final product of crystallisation at different temperature in systems with 1,2 M and 2 M NaOH.

Temperature °C	$L_{(1,2MNaOH)}$ μm	$L_{(2MNaOH)}$ μm	$N_{(1,2\ M\ NaOH)}$ g^{-1}	$N_{(2\ M\ NaOH)}$ g^{-1}
70	1,541	1,152	$3{,}38 \times 10^{10}$	$4{,}22 \times 10^{10}$
75		1,193		$3{,}89 \times 10^{10}$
80	1,522	1,090	$3{,}18 \times 10^{10}$	$4{,}33 \times 10^{10}$
85	1,533		$3{,}13 \times 10^{10}$	
90	1,526	1,382	$2{,}94 \times 10^{10}$	$3{,}26 \times 10^{10}$

The scanning elecron micrographs of zeolite samples obtained at different temperatures, at 70°C and 90°C in the same 1,2 M NaOH system, (Fig 5) show slight change in morphology of the crystals.

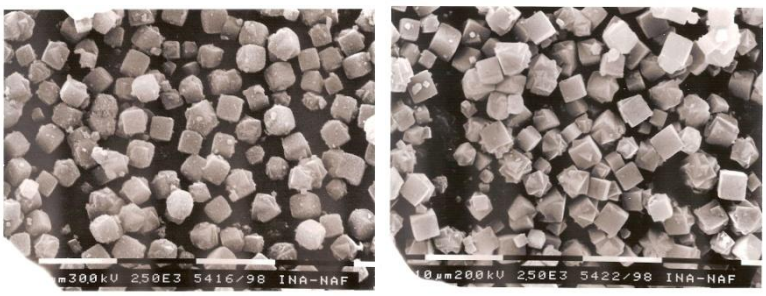

Figure 5. Scanning electron micrographs of zeolite A crystals obtained in 1,2 M NaOH at 70 ^{o}C (left) and 90^{o}C (right).

CONCLUSION

The rate of the crystal growth and crystallisation generally are increasing with temperature. On the contrary, crystal size distribution, as well as their mean size and specific number are rather the same for samples obtained at different crystallisation temperature, that is in agreement with models of autocatalytic nucleation and gel memory effect. The exceptions found in more alkaline systems can be explained by additional processes of nucleation.

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UTJECAJ TEMPERATURE NA PROCES KRISTALIZACIJE ZEOLITA A

Sanja Bosnar[1], Boris Subotić[1]
Institut „Ruđer Bošković“, Bijenička 54, Zagreb
E-mail: sbosnar@irb.hr

SAŽETAK

U cilju određivanja utjecaja temperature na proces kristalizacije zeolita A, praćena je promjena udjela kristalne faze, te veličine najvećih kristala u reakcijskom sustavu tijekom procesa kristalizacije u sustavima s 1,2 M i 2 M NaOH u temperaturnom rasponu 70 do 90^{o}C.

Povećanje brzine kristalizacije, rasta kristala, te skraćivanje indukcijskog perioda s povišenjem temperature uočeno je u svim istraživanim sustavima. Grafičkim prikazom ovisnosti konstante brzine o temperaturi, prema Arrheniusovom zakonu, određena je i energija aktivacije kristalnog rasta: 81,4 J mol^{-1} u sustavima s 1,2 M NaOH, te 70,7 J mol^{-1} u sustavima s 2 M NaOH. Čestična svojstva konačnih produkata su slična u većini ispitivanih sustava pri svim temperaturama kristalizacije, što je u skladu s principima autokatalitičke nukleacije i „učinka pamćenja“ gela. Razlike uočene u alkalnijem sustavu se mogu objasniti dodatnim procesima nukleacije.

Ključne riječi: zeolit A, temperatura, energija aktivacije, kristalni rast