PARTICULATE PROPERTIES OF THE ZEOLITE CRYSTALS

Josip Bronić, Ana Palčić, Boris Subotić
[1]Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
E-mail: bronic@irb.hr

ABSTRACT

Zeolites particulate properties (crystal size distribution and crystals morphology) often have a very important role in use of zeolites in many applications: the mode and efficiency of their use as catalysts, adsorbents, cation exchangers, and molecular sieves.

The influence of physico-chemical parameters (reaction mixture starting chemical composition of liquid and solid phase, system alkalinity, reaction temperature, stirring conditions, way of components adding, template presence, etc.) which have impact on particulate properties of synthesized zeolites, are discussed. Special attention is given to the most important basic processes in zeolite crystallization - nucleation and crystal growth.

The collected knowledge about mentioned synthesis processes and crystallization parameters, helps us in their modeling as well as in the designing of the products (crystals) having desired phase and particulate properties, needed for specific applications.

Keywords: zeolite synthesis, particulate properties, nucleation, autocatalytic crystallization.

INTRODUCTION

Zeolites are very well defined crystalline materials in which Si atoms are connected via common oxygen atoms (tetrahedral coordination), forming three-dimensional rigid framework having caves and channels of defined size and shape. Some of the Si atoms are isomorphously substituted with Al causing negative charge of the framework, which is compensated by cation positioned nearby in crystal voids. Due to their structural and chemical characteristics, they are used in research and applications as: catalysts (some organic reactions, petrochemistry, biomass conversion) [1,2,3], adsorbents (liquids and gases adsorption and drying) [4,5], cation exchangers (removal of heavy metal and radioactive cations from wastewaters, in detergents for water softening) [6,7] and molecular sieves (membranes for gasses and liquids separation) [4,8,9].

Many parameters have influence on particulate properties of the synthesis final product. One of the most important is a total number of crystals at the end of crystallization. Generally, higher concentration of "reactive species" (low molecular silicate, aluminate, and alumo-silicate species) produces more gel phase and consecutively, more nuclei within gel matrix (increase of gel "density") [10]. More nuclei can also be formed (appeared) in synthesis system by increasing alkalinity of the starting hydrogel [11], than by ageing of the hydrogel at certain temperature [12], and by adding of seed crystals [13]. Source of active species also have influence to potential nuclei formation [14].

Kinetic of crystallization have a large influence on crystal morphology (also to the outer crystal surface "quality") and weak to the crystal (nuclei) number: fast crystallization produce more rounded defective crystals of rough surface, while low crystal growth rate can give crystals of well-defined planes and sharp edges [15].

RESULTS AND DISCUSSION

Every specific application has demands on crystal size distribution (CSD) and shape. To control particulate properties, one should be able to control the total number of nuclei (crystals) as well as the crystal growth rate. Knowledge about mechanism of nuclei formation and crystal growth (i.e., corresponding basic processes at molecular level) enable us to control

the number of nuclei, dynamics of their appearance (or release from gel matrix) in the system and rate of their growth.

Several method types (instruments) were used for measurement of particulate properties: microscopy (optical, SEM, TEM, AFM), mechanical (sieving), optical (laser light scattering) and combined methods (disc centrifuge-sedimentometry). Nowadays, only different types of microscopy and laser light scattering are still in use for research and quality control.

Here are some examples which show the most important kinetic parameters that can be measured or calculated, and how particulate properties of the final product (zeolite crystals) can be predicted by simulation of kinetic parameters using modified population density balance method [16].

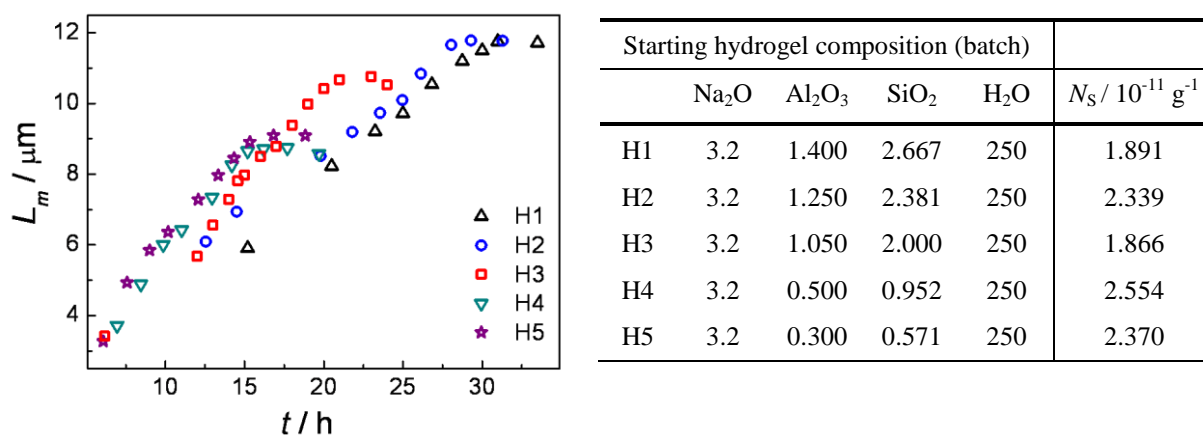| Starting hydrogel composition (batch)					
	Na_2O	Al_2O_3	SiO_2	H_2O	N_S / 10^{-11} g^{-1}
H1	3.2	1.400	2.667	250	1.891
H2	3.2	1.250	2.381	250	2.339
H3	3.2	1.050	2.000	250	1.866
H4	3.2	0.500	0.952	250	2.554
H5	3.2	0.300	0.571	250	2.370

Fig. 1. Growth rate of zeolite A crystals obtained from hydrogels of different "density" and corresponding starting chemical composition as well as specific number of crystals. (Adopted from ref. 10.)

Changes of the starting composition of the dense hydrogel affects only amount of Si (Al also, keeping the same Si/Al ratio) in the system as it is shown in Fig. 1. The crystal growth rate (the slope of the linear part of curves, calculated by Zhdanov-Samulevich's method) increases with decreasing density of hydrogel.
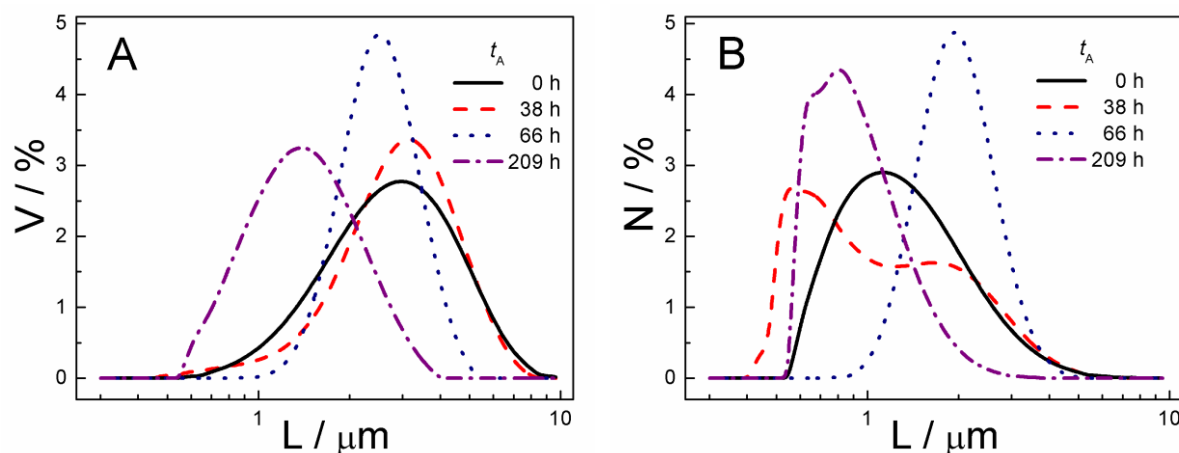

Fig. 2. Particle size distribution curves of the final product (crystals of zeolite A) by volume (A) and by number (B) for given ageing time of the hydrogel at 25 °C. All used systems have the same starting chemical composition: (Adopted from ref. 17.)

Ageing of the hydrogel at certain temperature induces additional nucleation at hydrogel surface and subsurface regions. The direct consequence is decrease in the size of crystals with ageing time as well as narrower crystal size distribution (Fig. 2).
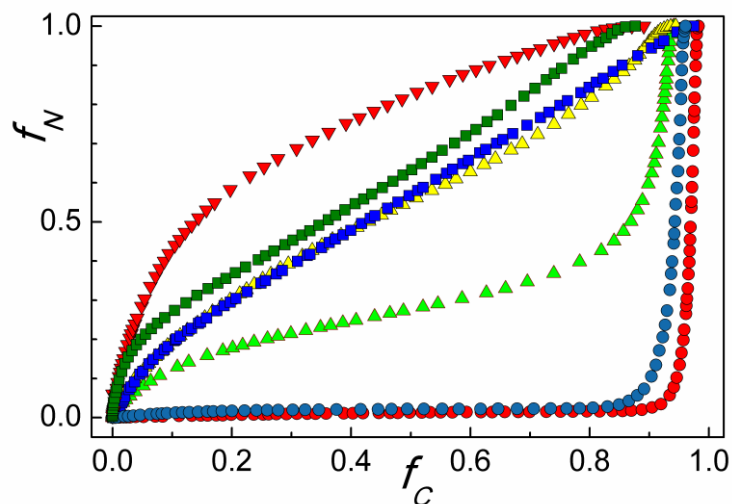
Fig. 3. Distributions of nuclei in gel matrixes after ageing at 25 °C for (from right to left): $t_a = 0$ h (freshly prepared hydrogel, ●), 10 h (●), 38 h (▲), 66 h (▲), 113 h (■), 158 h (■) and 209 h (▼). (Adopted from ref. 18.)

The distribution of the nuclei within gel matrix (calculated from nucleation and crystal growth curves, Fig. 3) of the systems aged before crystallization confirms that more nuclei is positioned at surface and subsurface of gel. The hydrogel put at transformation temperature (80 °C) have the nuclei which are in contact with liquid phase and start to grow. The most of nuclei, in freshly prepared system (also the one aged for 10 h), is positioned close to the center of the gel particles and released from gel matrix when more than 90% of the zeolite mass has been crystallized! Increase of the ageing time to 66 h gives quasi-homogeneous distribution of the nuclei within gel matrix. Further increase of the ageing time to the 158 h (or more), clearly shows a presence of the large number of the growing nuclei at beginning of the gel transformation (green squares and red triangles in Fig. 3). Therefore, by ageing of the starting hydrogel it is possible to reduce the size of the synthesized crystals, increase their specific number and decrease the overall crystallization time.
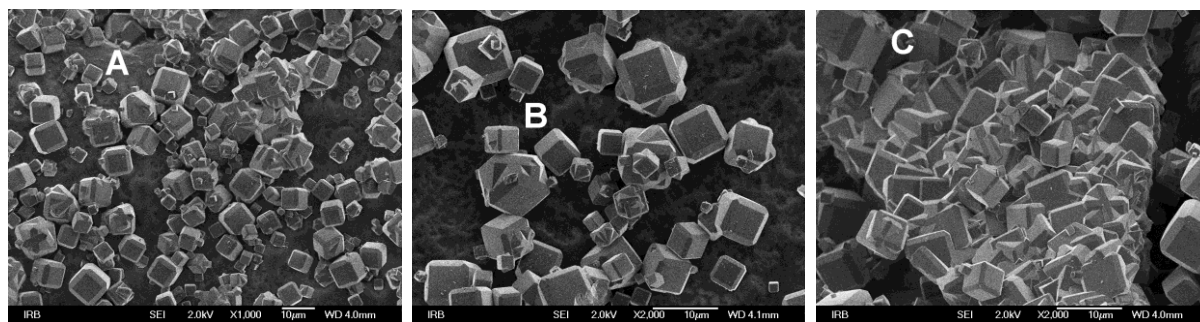

Fig 4. SEM photographs of the zeolite A crystals obtained from fresh hydrogel: (A) single and twin crystals, (B) higher magnification shows sharp truncated edges of ZA cubes and different types of twin crystals (contact, penetration), and (C) an example of compact assembly of many intergrowth crystals. (Adopted from ref. 18.)

High crystal growth rate, induced by higher alkalinity of the system, may causes crystals rounding and structural defects. Even well-defined crystals (nice cubes with sharp edges) can grow into compact assembly of many intergrowth crystals (Fig. 4C), but only in the systems which are not stirred.

CONCLUSION

Particulate properties of zeolite crystals (particles size and morphology) have large importance in many applications. Therefore, the control of synthesis parameters which determine particulate properties of the product (zeolite crystals) is necessary.

The most important things are the control of: the total number of the crystals (nuclei) in the system, dynamics of nuclei appearance (nucleation curve), and crystal growth rate.

Among many physico-chemical parameters that affect the course of reaction, the strongest effects are presented through three typical examples: influence of gel density on crystals' number and growth rate (it increases with decreasing density of hydrogel); influence of gel ageing on nuclei number and distribution within gel matrix and consecutively to the particle size distribution curves (increasing of the ageing time shows more nuclei at gels (sub)surface regions, decreasing crystals size and narrower CSDs'); and influence of the mode of crystallization on crystals' morphology (unstirred systems can produce compact assemblies of many intergrowth crystals).

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