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Effect of aging temperature of alkaline aluminosilicate and silicate gels on the kinetics of crystallization of zeolite ZSM-5 and silicalite-1

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The temperature dependences of nucleation of zeolite ZSM-5 and silicalite-1 pass through extrema in the range from 110 °C to 120 °C. Despite having the same crystalline structures, zeolite ZSM-5 has a maximum and silicalite-1 has a minimum of nucleation in the temperature range mentioned. A method for preparation of single crystals of silicalite-1 up to 150 μm in size has been developed. The comparison of the curves of the temperature dependences of nucleation for zeolites Na—X, Na—A, and ZSM-5 shows that the positions of the maxima on these curves are determined by the type of the crystal structure of zeolite.

Key words: zeolite, silicalite, pentasils, nucleation, single crystals; crystallization, linear crystal growth rate.

The linear crystal growth rate (LCGR) of zeolites in alkaline aluminosilicate gels is determined by the gel composition and crystallization temperature. In the stationary period of growth, it is independent of either the crystal size or the number of nuclei.[1—6] Therefore, it can be suggested that nucleation rates in gels of the same compositions depend somewhat on the temperature. This dependence was observed in the study of the effect of aging temperature of gels on the nucleation rate of zeolites Na—A and Na—X. It is described by the curves with maxima in the temperature range from 0 to 90 °C, whose positions are determined by the structure of nuclei of zeolite crystals formed.[7—10] It also has been found that crystal nuclei of zeolites Na—A and Na—X are formed in alkaline aluminosilicate gels due to being kept at temperatures lower than the crystallization temperature or during the crystallization itself, and they are not formed at the moment of precipitation of gels when alkaline solutions of silicate and sodium aluminate are poured together.[10]

In this work, we studied the kinetic regularities of crystallization of zeolite ZSM-5 and silicalite-1 in aluminosilicate and silicate gels with organic cations, which were pre-aged at temperatures lower than the temperature of synthesis. The purpose of these studies is the determination of the temperature dependence of the nucleation rate of zeolites with the pentasil structure, which crystallize, unlike the previously studied zeolites, under conditions of autoclave synthesis (T > 100 °C).

Experimental

Zeolite ZSM-5 and silicalite-1 were crystallized from alkaline aluminosilicate and silicate gels in the presence of tetrapropylammonium bromide (TPA-Br). For the synthesis of

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ZSM-5, they were prepared by mixing silica sol (22.5 % SiO_2, 0.54 % Na_2O) with partially dissolved $NaAlO_2$ in a solution of TPA-Br and NaOH, and for the synthesis of silicalite-1, silica sol was mixed with a solution of TPA-Br. The gels obtained were of the following compositions: $6.72TPA\text{-}Br \cdot 4.94Na_2O \times$ $\times Al_2O_3 \cdot 67.1SiO_2 \cdot 1641H_2O$ (for ZSM-5) and $0.099TPA\text{-}Br \times$ $\times 0.026Na_2O \cdot SiO_2 \cdot 24.8H_2O$ (for silicalite-1). Samples of gels (2 g) were placed in autoclaves with Teflon shells, kept for 1 day at various temperatures (40, 70, 90, 115, and 135 °C in the case of zeolite ZSM-5 and 70, 90, 100, 115, and 130 °C in the case of silicalite-1), and crystallized at 180 °C. For comparison, initial gels were crystallized without preliminary thermal treatment. In certain intervals, the specimens were taken from the autoclaves, and the sizes of the largest crystals formed were determined by the procedure previously described.[1,4]

The histograms characterizing the size distribution of crystals in the final crystallization products were plotted for all samples on the basis of the measurements of sizes of 300 crystals in each sample. The times of the beginning of crystal growth of each mode were determined, and the curves characterizing the nucleation kinetics and an increase in the crystal mass in time were calculated from the histograms and the data on LCGR.[2,5] Sizes of crystals were measured on an Amplival optical microscope.

Results and Discussion

The curves presented in Fig. 1 describe the changes in sizes of the largest crystals of zeolite ZSM-5 and silicalite-1 upon crystallization at 180 °C in the gels studied after their preliminary exposure at various temperatures. All curves have the same shape and consist of three regions. The first region, whose slope determines LCGR at the stationary period of growth, at first transforms to an intercept of the nonstationary growth curve within which no increase in crystal sizes is observed. The existence of the initial linear region of all curves is evidence that during this period crystals in different samples grow with a constant linear rate, which is independent of the temperature of the preliminary treatment (aging), T_{tr}. The shift along the ordinate axis corresponding to T_{tr} = 135 °C in the case of zeolite ZSM-5 (see Fig. 1, *a*, curve *6*) is explained by the fact that the crystal growth rate considerably increases at higher temperatures, and the sizes of nuclei formed increase.[1,7–10] The fact that at the stationary period of crystal growth LCGR is independent of the aging temperature of gels has been mentioned previously[7,8] for zeolites Na—X and Na—A. At the same time, the effects of the temperature of preliminary treatment of the mixtures on sizes of the largest crystals in the samples (see in Fig. 1) and on the crystallization duration (τ) determined from the time of cessation of the visible crystal growth (marked by dotted vertical lines) are very distinct.

The curves presented in Fig. 1 are evidence that the crystallization more rapidly ceases to form finer crystals in gels of zeolite ZSM-5 exposed at 115 °C before crystallization and in gels of silicalite-1 exposed at 70 or 90 °C.

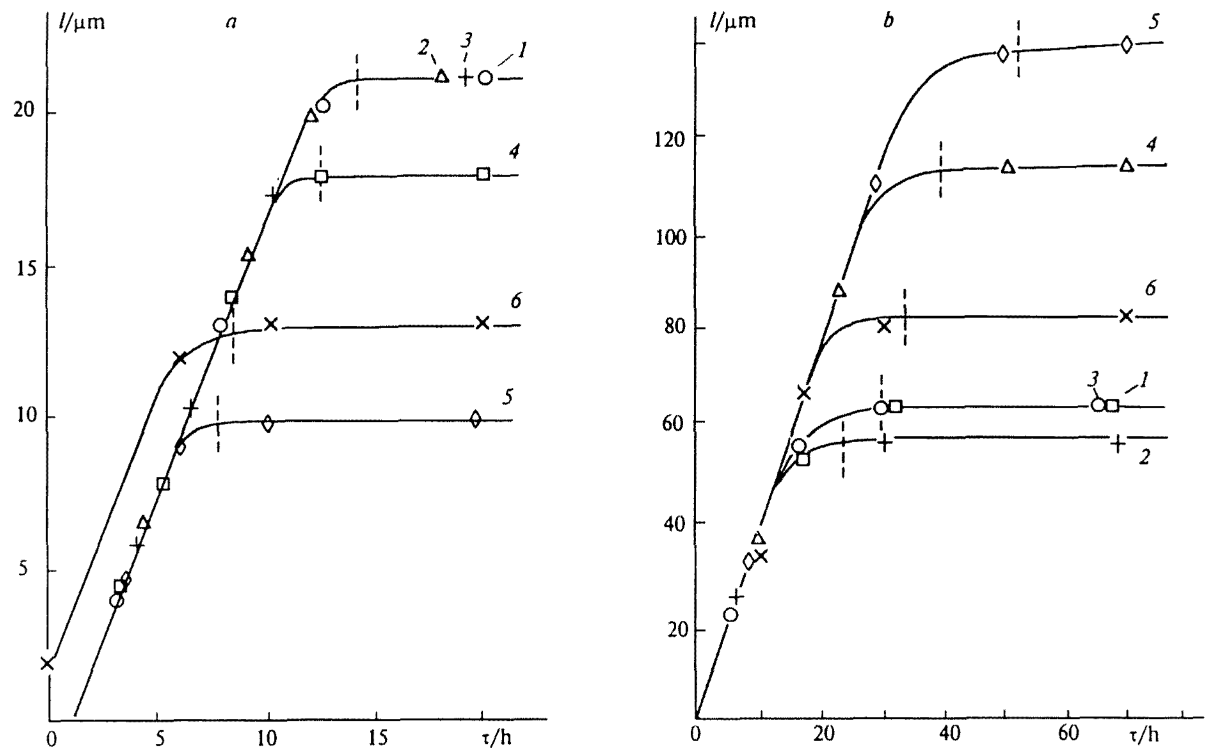

Fig. 1. Growth rates of largest crystals (l is the size of maximum crystals) of zeolite ZSM-5 (*a*) and silicalite-1 (*b*) in gels crystallized at 180 °C after their thermal treatment. Curves: *1*, samples were not thermally pretreated; *a*, T_{tr}/°C = 40 (*2*), 70 (*3*), 90 (*4*), 115 (*5*), and 135 (*6*); *b*, T_{tr}/°C = 70 (*2*), 90 (*3*), 100 (*4*), 115 (*5*), and 130 (*6*).

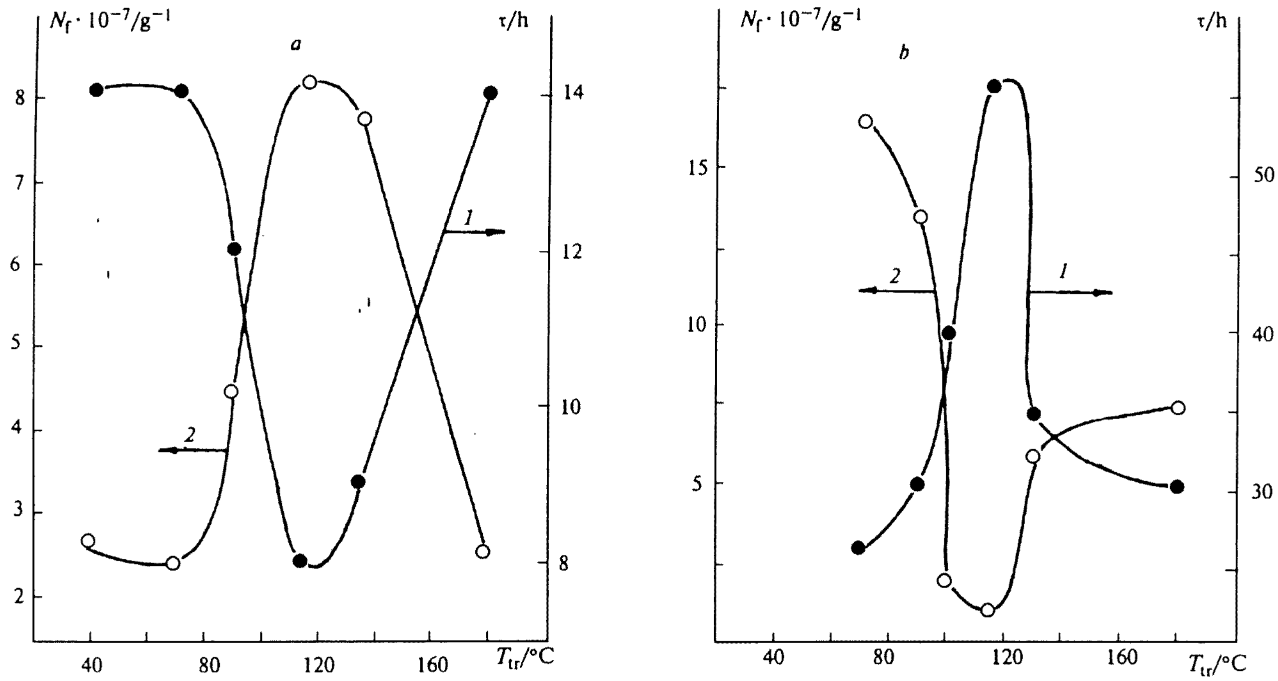

Fig. 2. Dependences of the crystallization time (curves *1*) and the total number of nuclei (curves *2*) on the temperature of preliminary treatment of gels for zeolite ZSM-5 (*a*) and silicalite-1 (*b*).

At the same time, the largest crystals of zeolite ZSM-5 grow in gels after aging at 40 or 70 °C, and those of silicalite-1 grow after aging at 115 °C. This indicates the substantial differences in the temperature dependences of nucleation rates of zeolite ZSM-5 and silicalite-1.

The dependences of the crystallization duration of gels of ZSM-5 and silicalite-1 at 180 °C on the pretreatment temperature are presented in Fig. 2. It can be seen that the form of the curve obtained for zeolite ZSM-5 is close to those of the corresponding curves for zeolites Na—X and Na—A (*cf.* Refs. 7—9). This curve is characterized by a minimum, but it is localized in the range of higher temperatures (110—120 °C) than that for zeolites Na—X and Na—A. Unlike all zeolites studied previously, the similar curve for silicalite-1 has a maximum in the same temperature range, in which the minimum is localized on the curve corresponding to zeolite ZSM-5.

This effect of the pretreatment temperature of alkaline aluminosilicate and silicate gels on the crystallization growth and sizes of largest crystals assumes a nonlinear dependence of the nucleation rate in gels.

To test this assumption using the equations presented in our previous works,[9,10] the amounts of the nuclei formed (N_f) were calculated:

$$N_f = 100/(V_{100}\rho),$$

where ρ is the crystal density and V_{100} is the volume of 100 crystals calculated from the histograms of the final crystallization products.

As indicated previously,[9,10] these calculations of N_f based on histograms of final crystallization products are possible when LCGR is independent of crystal sizes. In this case, the amount of nuclei in the sample is determined by the amount of crystals in the final crystallization product. The corresponding data are presented in Fig. 2. The maximum of nucleation for zeolite ZSM-5 and the minimum for silicalite-1 are distinctly manifested in the resulting curves in the temperature range from 110 to 120 °C. The unusual temperature dependence of the nucleation rate of silicalite-1 is likely related to the peculiarities of the gel formation at high temperatures in the systems with organic cations in the absence of aluminum.

The temperature of pre-treatment of silicate gels affects both the peculiarities of the size distribution of crystals in the final crystallization products (Fig. 3) and the course of the curves describing the growth of the mass of silicate-1 in mixtures after various thermal treatments (Fig. 4). The procedure for plotting curves of mass growth is presented in Refs. 3—5. The nonlinear character of the dependence of the mass growth (Z_T/Z_f) of silicalite-1 crystals on the temperature of gel aging before crystallization is illustrated in Fig. 4.

The mass of crystals increases more rapidly for the samples for which a higher nucleation rate is observed. Therefore, they contain more nuclei. The elucidated regularity of the dependence of the mass growth on the nucleation temperature means that an increase in the nuclei concentration (*i.e.*, N_f) increases the mass of the crystals formed for the same time.

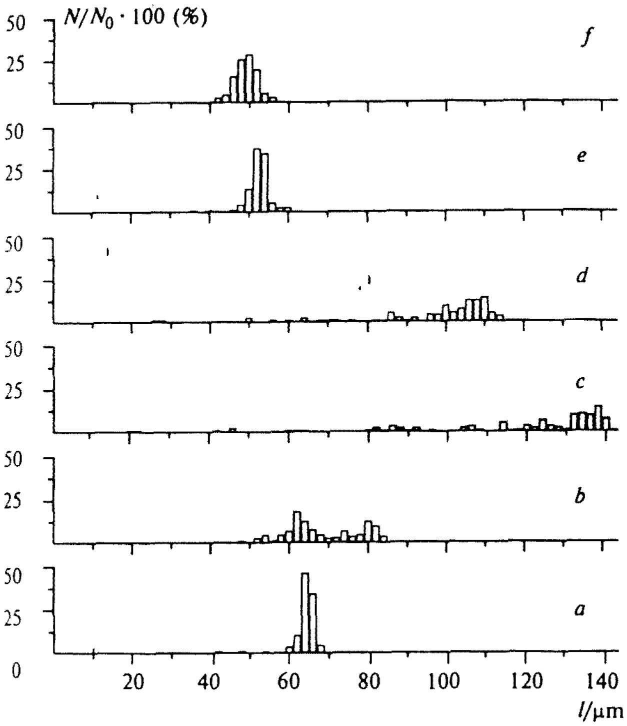

Fig. 3. Histograms of final products of crystallization at 180 °C of silicalite-1 samples, which were not thermally pretreated (*a*) and after aging of initial gels at various temperatures: T_{tr}/°C = 130 (*b*), 115 (*c*), 110 (*d*), 90 (*e*), and 70 (*f*).

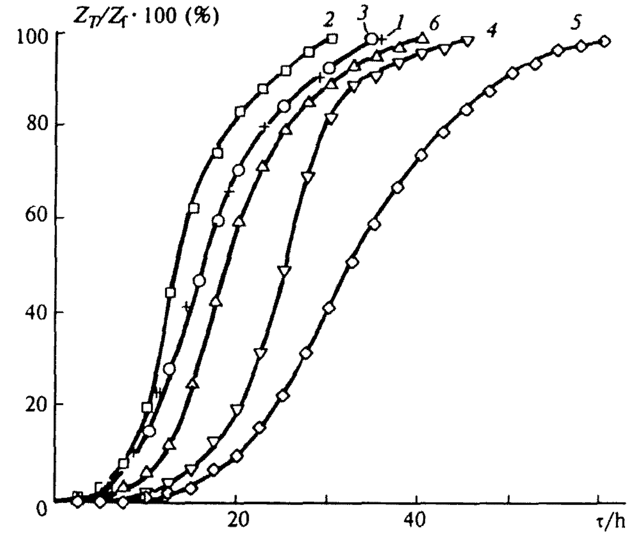

Fig. 4. Curves of the mass growth of silicalite-1 crystals (Z_T/Z_f) in the isothermal crystallization of gels at 180 °C after their treatment at temperatures lower than the crystallization temperature. Curves: *1*, sample was not thermally pretreated; T_{tr}/°C = 70 (*2*), 90 (*3*), 100 (*4*), 115 (*5*), and 130 (*6*).

The histograms presented in Fig. 3 testify to the different degrees of dispersity of crystals in the samples exposed at different temperatures before crystallization: the smaller is the number of crystal nuclei N_f, the larger are the crystals. On the basis of the studies performed, the method for growing single crystals of silicalite-1 up to 150 μm in size can be suggested.

The peculiarities of nucleation of silicalite-1 related to the existence of the minimum on the curve of the temperature dependence of the nucleation rate remain difficult to explain. For all other zeolites Na—A, Na—X, and ZSM-5 studied, these dependences pass through maxima at temperatures higher than 0 °C and lower than their crystallization temperatures. The position of the nucleation maximum is determined by the structure of zeolite formed, and there is a certain regularity: the lower is the possible crystallization temperature of this zeolite, the lower is the temperature at which the nucleation maximum is localized. The comparative data for zeolites Na—A, Na—X, and ZSM-5 are presented in Table 1.

Table 1. Temperatures of maximum nucleation (T_f^{max}) and limiting crystallization temperatures (T_{cr}) for zeolites Na—X, Na—A, and ZSM-5

Zeolite	T_f^{max}/°C	T_{cr}/°C
Na—X	~20	120
Na—A	40—45	150
ZSM-5	110—120	200

This dependence can be explained, if the density of the zeolite structure of each type is taken into account. Zeolite Na—X, whose structure is the most open of those considered above, has the lowest temperatures of limiting crystallization (120 °C) and nucleation (20 °C). On the contrary, a zeolite of the type of pentasil ZSM-5 with the densest structure crystallizes up to 200 °C, and its nucleation maximum is observed at $T > 100$ °C. Zeolite Na—A occupies an intermediate position between Na—X and ZSM-5.

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