CRYSTALLIZATION KINETICS OF ZEOLITE-LIKE PHOSPHATES AlPO₄-5 AND SAPO-5

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We show that the crystallization rate of isostructural zeolite-like phosphates AlPO₄-5 and SAPO-5 is considerably higher than for zeolites and polysilicates. We analyze the kinetic and energy parameters, taking into account the high structural lability of aluminophosphates, the effect of limiting processes of dissolution of the original pseudoboehmite and conversion of the intermediates, and also isomorphic inclusion of silicon atoms.

Major attention in the chemistry of zeolite-like phosphates has been directed toward synthesis of new varieties and characterization of already existing varieties, in connection with their practical utilization as sorbents and catalyst supports [1, 2]. However, relatively little attention has been paid to questions connected with the reactivity and mechanism of formation of zeolites in phosphate systems. Isolated papers [3, 4] are predominantly qualitative in approach. In a comparative study of zeolite formation, the considerably higher activity of phosphate systems compared with traditional silicate systems has become apparent. Accordingly, this research was directed toward determining the characteristic features of the crystallization kinetics of the isostructural phosphates AlPO₄-5 and SAPO-5 in aluminophosphate (AlP) and silicoaluminophosphate (SiAlP) systems.

The starting reaction mixtures were prepared according to the procedures in [1, 2], using pseudoboehmite, orthophosphoric acid, A-300 aerosil, and (as the organic template) tetraethylammonium hydroxide (TEAOH), containing 0.1 moles TEABr per 1.0 TEAOH. In the experiments, we used the following reaction mixtures, moles: 1.0 TEAOH, 1.0 Al₂O₃, 1.0 P₂O₅, 48 H₂O and 1.25 TEAOH, 1.0 SiO₂, 1.0 Al₂O₃, 1.0 P₂O₅, 60 H₂O with TEAOH/TO₄α = 0.25, H₂O/TO₄α = 12. The AlPO₄-5 and SAPO-5 were crystallized as in [1, 2] using a pulsed thermostat (polymethylsiloxane liquid as the heat-transfer agent, accuracy of temperature regulation ±0.3°C, heating rate of the autoclaves 7°C/min). The degree of crystallization (~,) was estimated from the intensity of the main diffraction lines (2θ about 7.5, 19.8, 21.0, and 22.5° for CuKα). The adsorption measurements were made by the gravimetric method and analyzed using the Dubinin-Radushkevich equation.

The experimental kinetic curves for crystallization of AlPO₄-5 (Fig. 1) and SAPO-5 (Fig. 2) are S-shaped, as is typical for zeolite crystallization [3, 5]. The analysis was performed using the A. N. Kolmogorov topokinetic equation [6]

\[ Z = 1 - \exp(kr^m), \]  

(\(Z\) is the fraction of crystalline phase at the moment of time \(r\); \(r\) is the time from the start of heating to \(T_r\); \(m\) and \(k\) are constants) and the G. V. Sakovich equation [7]

\[ K = mk^{1/m}, \]

(\(K\) is the crystallization rate constant), used in most work on studying crystallization characteristics of zeolites [3, 5], and also the analogous generalized equation for heterogeneous first-order reactions [8]. As in [8], the reaction rate constant was determined from the straight-line sections of the kinetic curves in the interval \(\alpha_{cr} = 0.1-0.5\) (for \(r_{cr} > 1\ h, \alpha_{cr} = 0.6-0.9\), using the equation...
Fig. 1. Kinetic curves for crystallization of AlPO₄-5 at 140°C (1), 150°C (2), and 156°C (3).

Fig. 2. Kinetic curves for crystallization of SAPO-5 at 140°C (1), 150°C (2), and 156°C (3).

\[ \lg Z = -Kr + \lg Z_0 \]  
(3)

where \( Z_0 \) is the fraction of crystalline phase at the initial moment of time. The experimental values of the crystallization rate constants for AlPO₄-5 suggest (Table 1) that formation of zeolite-like phosphates is a rather fast process compared with polysilicates and zeolites [5]. The induction period \( (\tau_{\text{ind}}) \) is no longer than a few minutes (at 156°C, there is practically no induction period, Fig. 1). One reason for this is obviously the high structure-forming activity of TEAOH (in the presence of triethylamine, for example, \( \tau_{\text{ind}} \) of AlPO₄-5 reaches 5 h [3]). The marked discrepancy between the values of the constants calculated using Eqs. (1), (2), and (3) may be connected with occurrence of accompanying processes: dissolution of pseudoboehmite and the reverse transition (degradation) of AlPO₄-5 to amorphous products. According to the ideas in [6], the coefficient \( m \) in Eqs. (1) and (2) characterizes the rate of formation of crystallization centers and the regularity of their development, and a value of \( m = 4 \) (Table 1) corresponds to a constant rate of formation of the centers over the course of the entire crystallization period at 140°C and 150°C. The decrease in \( m \) at 156°C suggests formation of nuclei at the onset of crystallization.

We should note that the calculations were done in the range of \( \alpha_{\text{cr}} \) values from 0.6 (\( \alpha_{\text{cr}} < 0.5 \) h). However, then in the second stage, \( \alpha_{\text{cr}} \) continues to slowly increase to 0.9 (\( \alpha_{\text{cr}} = 24 \) h). This may be a reflection of the process of crystal growth, which is supported by microscopic observations (visible region, \( \times 200-1000 \), polarizing light filters); the number of small round particles (similar to the original pseudoboehmite) obtained in the first stage markedly decreases, and considerably larger spherulites are formed.

Obviously in the first stage, on reaction of pseudoboehmite with \( H_3PO_4 \), formation of aluminum hydrophosphates and primary AlP-gel (like that described in [3]) occurs on the surface of the pseudoboehmite particles. On subsequent reaction with TEAOH and TEA-phosphate, formation of TEA-aluminophosphates is possible, and as a result of hydrolysis and condensation also TEA-aluminophosphate gel. We can assume that owing to inclusion of the template and its high activity, and also the high chemical and structural lability of the AlP framework, the gel formed has a zeolite-like skeleton (analogously to SAPO-37 [9]).