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Effect of amorphous seeds on the crystallization kinetics of Na—A zeolite

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The formation of crystal nuclei occurs when alkaline aluminosilicate gels are treated at temperatures below the crystallization temperature or during crystallization of gels rather than during precipitation of the gels. The linear growth rate of the crystals of Na—A zeolites yielded by alkaline aluminosilicate gels in the presence of amorphous seeds is a function of the product of the concentrations of the silicate and aluminate ions in the intermicellar liquid.

Key words: zeolites, crystallization; amorphous seeds, nucleation.

Recently, it has been stated that the linear growth rate of crystals (LGRC) from a particular gel is independent of the number of nuclei, and is solely a function of the composition of aluminosilicate gels and crystallization temperature for the period of constant linear growth.[1—4] On the other hand, another variable of crystallization kinetics, the rate of nucleation, is very sensitive to the previous history of the aluminosilicate gel. When the chemical composition of a gel is kept constant, the nucleation rate can be varied by changing the conditions employed for the thermal treatment or preparation of the gel. Treatment of aluminosilicate gels at different temperatures prior to crystallization has a significant effect on the nucleation of zeolites. Recently,[5—7] it has been shown that nucleation of Na—A and Na—X crystals occurs when alkaline aluminosilicate gels are treated at temperatures below the crystallization temperature (≤90 °C). In the temperature interval 0—90 °C, the plots showing the rates of nucleation against temperature are characteristically curves with maxima. The position of the maximum depends on the type of zeolite formed. The plot for Na—X shows a maximum at ~20 °C, whereas that for Na—A zeolite is at 45 °C. The difference between the temperatures of preferential nucleation of Na—X and Na—A zeolite can be related to the density of the framework of the zeolites. It appears that a more open Na—X zeolite structure requires less energy. The upper limits reported for the crystallization temperature of Na—A is 30 °C higher than that for Na—X zeolites (150 and 120 °C, respectively). This is probably also due to the more compact framework of Na—A zeolite, compared with the crystalline structure of Na—X.

An example for illustrating the variations in the form of the nucleation curves against temperature may be found in the increased nucleation rates of gels aged at ambient temperature. This effect can be ascribed to the Ostwald—Tomson process reported for colloidal systems.[3,8,9]

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The low-temperature growth of the crystal nuclei described previously for Na—A and Na—X zeolites at temperatures <0 °C [7] can apparently be explained by the phase separation that occurs in the liquid phases of gels on freezing.

The above data indicate that nucleation of zeolite crystals in alkaline aluminosilicate gels occurs when the gels are treated at temperatures below the crystallization temperature or during crystallization itself. The question remains, however, of whether the crystal nuclei appear when alkaline solutions of silicate and aluminate are mixed in at the instant of coagulation of aluminosilicate gels, which yield crystalline zeolites on further heating. Presumably, the crystal nuclei, which are aluminosilicate blocks, form during coagulation of hydrogel from alkaline solutions of sodium silicate and sodium aluminate. High rates of gelation, however seem to prevent considerable transformation of the gel into a structurally ordered species.

In order to get further insight into the mechanism of zeolite nucleation in alkaline aluminosilicate gels, a series of experiments was performed to outline the effect of amorphous seeds on the crystallization kinetics of type A zeolite.

Experimental

The aluminosilicate gels (ASG) studied were prepared by mixing alkaline solutions of sodium silicate and sodium aluminate. Three sets of experiments, designated as series I through III (Table 1), were performed. It was intended to measure the size of the largest crystals of A zeolite, to clarify the dependence of LGRC on the number of seeds introduced and, finally, to specify the instant of time at which nucleation commences. The composition of the initial ASG (samples *1*, *6*, and *10*) was $2.76Na_2O \cdot Al_2O_3 \cdot 1.91SiO_2 \cdot 409H_2O$. Aluminosilicate seed gel (SG) of composition $5.34Na_2O \cdot Al_2O_3 \cdot 0.34SiO_2 \cdot 143H_2O$ was added to this gel (samples *2* through *5*, *8*, *9*, *11*, and *12*). To prepare sample *7*, of composition $3.29Na_2O \cdot Al_2O_3 \cdot 1.91SiO_2 \times 409H_2O$, a solution of NaOH was added to the initial gel.

Crystallization of the gel samples was conducted at 90 °C. As crystallization proceeded, the samples of the gels were withdrawn, and the sizes of the largest crystals were measured using the edge of the cubic crystals. The measurements were made with an Amplival optical microscope (Germany) using the procedure described earlier.[2,4]

The intermicellar liquids were analyzed for Na_2O, Al_2O_3, and SiO_2 by conventional methods.

Results and Discussion

It has been repeatedly reported that the introduction of amorphous seeds into aluminosilicate gels may strongly influence the crystallization kinetics of the zeolites that are formed from these gels, and may in many cases change the direction of crystallization.[10,11] It was therefore important to use a particular combination of the initial aluminosilicate and seed gels to obtain a particular type of zeolite, that is Na—A zeolite. Figure 1, *a* shows the results of measurement of the size of the largest crystals yielded on crystallization of the first series of ASG samples. It can be seen that both the LGRC and the rate of nucleation vary during crystallization. The linear growth rates increase with time and the time interval needed for complete crystallization decreases with the concentration of amorphous seeds. This pattern of behavior is like that often considered to arise when gels are allowed to age at room temperature. Increasing the aging period shortens the crystallization time of the gels, and increasing the number of seeds introduced in the gel reduces the crystallization time, and decreases the size of the crystals in the final products. Moreover, the data in Fig. 1, *a* also imply that the reduction in the crystallization time observed for the gels enriched in amorphous seeds can be attributed not only to the enhanced number of viable nuclei, but also to the increased LGRC. The latter proposal appears to contradict the literature data, which indicate that the LGRC is independent of the number of nuclei formed in the aging gels in the period of constant linear growth.[2—4] This apparent controversy may be explained by reasoning that the introduction of the amorphous seeds into the gel increases the total amount of NaOH in the reaction mixture. The LGRC is expected to increase strongly with increasing alkalinity[2—4] since highly alkaline intermicellar liquids are characterized by greater concentrations of silicate and aluminate ions.

Chemical analyses of the liquid phases of the gels pretreated at 90 °C for 5 h are given in Table 2. These data are supplemented by the kinetic parameters of crystallization. It is assumed that the time period of 5 h is sufficiently long for the concentrational equilibrium between the liquid and solid phases in the gels to be attained. The results in Table 2 make it possible to calculate the LGRC at 90 °C for Na—A zeolite as a function of the concentrational product of silicate and aluminate ions in the liquid phases of the gels (see

Table 1. Conditions used for preparing the gel samples investigated

Series	Sample	Concentration of SG (%)*	τ/h **	Pretreatment conditions
I	*1*	0	0	—
	2	0.5	24	—
	3	2.0	24	—
	4	5.0	24	—
	5	10.0	24	—
II	*6*	0	0	—
	7	0	0	—
	8	10.0	24	—
	9	10.0	24	Washed to pH 7
III	*10*	0	0	—
	11	10.0	0	Washed to pH 7
	12	10.0	24	Washed to pH 7

* Per 100 g of the initial gel. ** Duration of treatment of seed gel at ~20 °C.

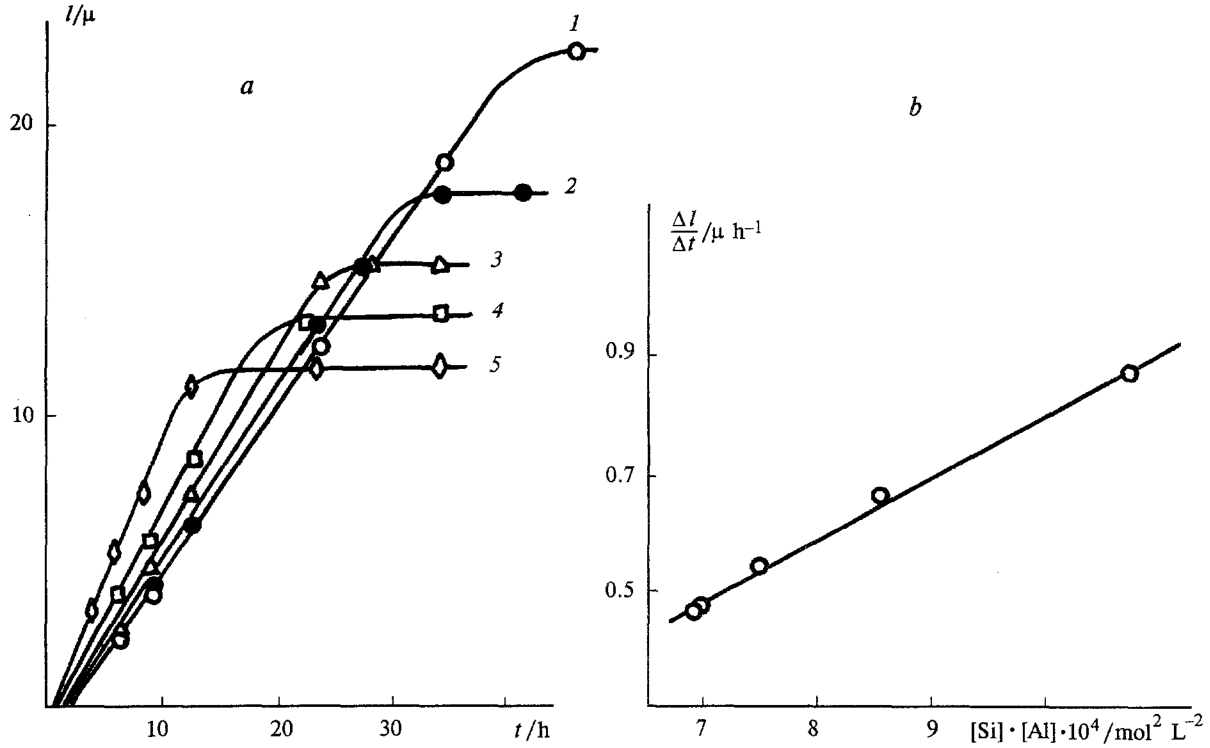

Fig. 1. *a.* Growth of crystals of Na—A zeolite from gels with different amounts of the amorphous seed (%) : 0 (*1*), 0.5 (*2*), 2 (*3*), 5 (*4*), 10 (*5*).
b. Linear growth rate for crystals of Na—A zeolite at 90 °C as a function of the product [Si] · [Al] in the liquid phase of the gels.

Fig. 1, *b*). Inspection of the data implies that both in the presence and in the absence of seeds in the gels, the growth rate of Na—A zeolite is a linear function of the product [Al] · [Si] in the liquid phase of the gels, and thus is related linearly to the concentration of silicate and aluminate ions. A similar relationship was reported earlier[12] for gels containing no amorphous seed.

Table 2 also gives the concentrations of nuclei for each gel related to the unit mass of the crystals (N_f). The data were derived using a method recently described.[7] The value of N_f per unit mass can be found from the relation

$$N_f = \frac{100}{V_{100}\,\rho},$$

where ρ is the density of the crystals, V_{100} is the volume of 100 crystals calculated from the histogram.

Histograms of the final size distribution can be used for calculating the N_f parameter because they are based on the LGRC which are assumed to be independent of the crystal size.[1] If this assumption is valid, the number of nuclei formed during crystallization of the gels can be defined by the number of crystals present in the final products of crystallization.

As can be seen from Table 2, the values of N_f increase with the enrichment of the gel with the amorphous seeds. Considering that aging time of SG is close to 24 h at ~20 °C, the increase in N_f supports our view that the formation of nuclei during gel aging at ambient temperatures is intense.

Based on the values of N_f obtained for the first two samples of Table 2, an increment of $1.2 \cdot 10^8$ crystal nuclei could be expected from the introduction of 0.5 g of SG. As the amount of GS added increases, some deviations from the rule can be observed and the actual N_f values tend to decrease. It appears that not every nucleus introduced by an amorphous seed can form a single germ of crystallization, and a number of nuclei can be consumed by the growing gel nuclei.

The series II ASG were prepared and examined to see whether the variations in the alkaline concentrations in the gels could be the only factor causing the increasing values of LGRC. Concentrations of components in the gels are given in Table 3.

The results obtained by measuring the size of the largest crystals formed during crystallization of the series II samples are collected in Fig. 2, *a*. As expected, the LGRC increases as [Na_2O] in the gel increases. The reason can be sought in the enhanced concentrations of aluminate and silicate ions in the intermicellar liquids caused by the increased alkalinity of the initial reaction mixture.

The LGRC of Na—A zeolite obtained from gels with the same alkalinities are similar. This is seen in Fig. 2, *a* (curves *1* and *4*, *2* and *3*) for gels prepared with and

Table 2. Compositions of liquid phases for different gel samples with amorphous seeds and kinetic parameters of crystallization

Sample	Concentration of SG (per 100 g of the initial ALG)	$[Na_2O]$*	$[Al_2O_3]$*	$[SiO_2]$*	$[Si] \cdot [Al] \cdot 10^4$ /$mol^2 L^{-2}$	$\Delta l/\Delta t$ /μh^{-1}	t/h **	$N_f \cdot 10^8$ /g^{-1}
1	0.0	0.270	0.0385	0.0090	6.93	0.46	48	2.1
2	0.5	0.275	0.0390	0.0090	7.00	0.47	38	3.3
3	2.0	0.290	0.0440	0.0085	7.50	0.54	28	4.8
4	5.0	0.330	0.0490	0.0088	8.60	0.66	24	9.4
5	10.0	0.410	0.0570	0.0095	10.8	0.87	18	23.0

* Concentration (in mol L^{-1}) in the liquid phases of gels. ** Duration of crystallization.

Table 3. Composition of aluminosilicate gels of series II and the corresponding concentrations of the crystal nuclei

Sample	$[Na_2O]$*	$[Al_2O_3]$*	$[SiO_2]$*	$N_f \cdot 10^{-8}$ /g^{-1}
6	23.3	13.8	15.5	2.3
7	31.9	13.8	15.5	3.4
8	31.9	16.0	14.9	17.0
9	23.3	—	—	33.4

* Concentrations in gel (in mg mL^{-1}).

without amorphous seeds. Figure 2, *a* indicates also that the finest crystals are yielded by sample *9*, which crystallizes more rapidly than the samples from the other three gels. The fact that the masses of the initial gel in samples *8* and *9* are nearly the same, indicates that gel *9* contains more crystal nuclei than gel *8*. The results collected in Table 2 suggest that the number of crystal nuclei present in gel *9* when related to the unit mass, is actually twice that present in gel *8*. Based on the nucleation rates depicted in Fig. 2, *b*, gel *9*, containing washed seeds,

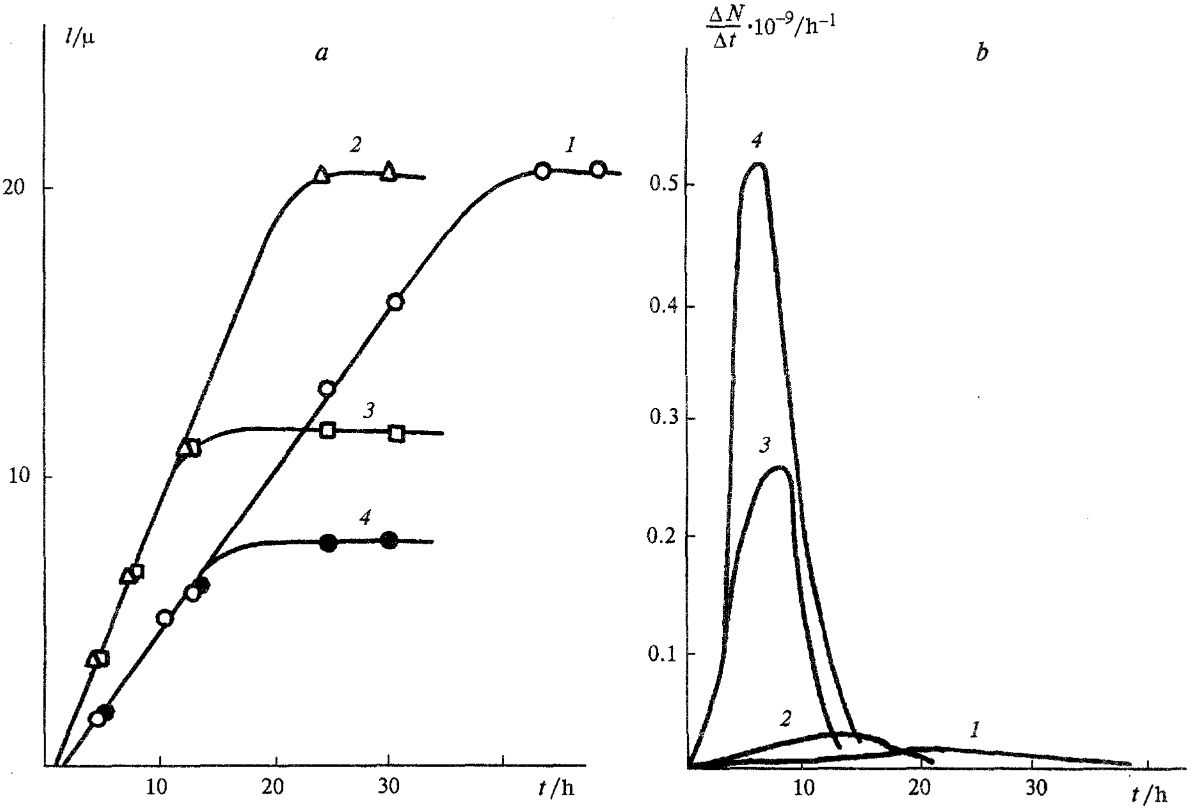

Fig. 2. *a.* Growth of crystals of Na—A zeolite at 90 °C from gels *6* and *7* with different concentrations of alkali and from gels *8* and *9* with added unwashed and washed amorphous seeds, respectively. Curves: *1,* sample *6*; *2,* sample *7*; *3,* sample *8*; *4,* sample *9*. *b.* The change in the nucleation rate during crystallization of Na—A zeolite at 90 °C from gels *6*, *7*, *8*, and *9*. Designation of the curves is the same as in Fig. 2, *a*.

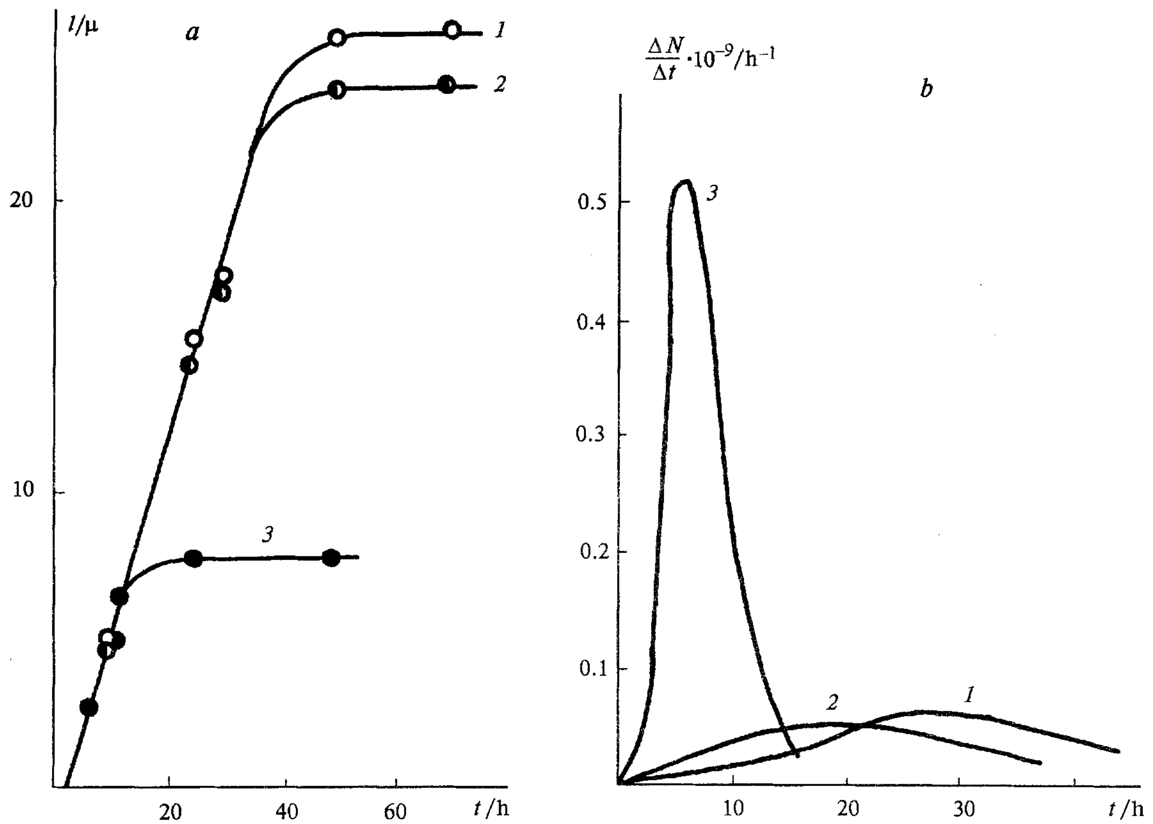

Fig. 3. *a*. Growth of crystals of Na—A zeolite at 90 °C from the initial gel (*10*), from gel containing washed amorphous seeds prepared without aging (*11*), and from gel containing washed amorphous seeds prepared with aging at ~20 °C for 24 h (*12*). Curves: *1*, sample *10*; *2*, sample *11*; *3*, sample *12*.
b. The change in the nucleation rate during crystallization of Na—A zeolite at 90 °C from the initial gel *10* and from gels *11* and *12*. Designation of the curves is the same as in Fig. 3, *a*.

exhibits the highest rate of nucleation during the initial period of crystallization.

Comparison of gels *8* and *9* suggests that the higher rate of nucleation observed for gel *9* is related to the different fractions of the structurally ordered aluminosilicate blocks in a unit mass of the washed and untreated SG. These blocks could not be removed by washing, and function then as germs of the crystals. Doubled 4-membered rings can be regarded as such aluminosilicate blocks in the case of Na—A zeolite. It is also possible that washing is accompanied by the hydrolysis of the terminal groups in the aluminosilicate blocks that are regarded as the germs of future crystals, and thus the washed gels contain more viable nuclei.

The increase in the nucleation rates and the enhanced values of LGRC observed for the gels enriched in alkali appear to support the view that the mechanism for crystallization of aluminosilicate gels involves the liquid phase in the gels. It appears that introducing amorphous seeds increases the alkalinity of the initial gel. The gel material dissolves more rapidly in these cases and the dissolved species are accumulated in the liquid phase of the gels. The net result is the more rapid transportation of the crystal nuclei from the gel to the growing crystals and to the surface of the amorphous globules and, finally, increased rates of nucleation and enhanced values of LGRC.

The question of whether the crystal nuclei of zeolites are formed directly when alkaline solutions of sodium silicate and sodium aluminate are mixed or if they appear either when the gel is treated at ambient temperatures or during its crystallization is very important for understanding the crystallization mechanism. The variety of opinions on this subject emphasizes the importance and sophistication of the problem.

To shed some light on the problem, the series III experiments were conducted with the results shown in Fig. 3, *a*. It can be easily recognized that all the gels investigated are characterized by similar LGRC. This result is not unexpected since both the concentration of alkali and crystallization temperature were maintained constant in all experiments. Crystallization from gels *10* and *11* requires nearly the same time and the crystals formed have a similar size distribution. However, gel *12* loaded with seeds aged at the ambient temperature, crystallizes much more rapidly than gels *10* and *11* to yield the finest crystals of Na—A zeolite.

By comparing the rates of nucleation calculated for these products from the LGRC and the histograms of the final crystal size distribution (see Fig. 3, *b*) it is evident that during the initial crystallization, nuclei are present only in gel *12* and are essentially absent in gels *10* and *11*. It can be thus inferred that nucleation does not occur when alkaline solutions of sodium silicate and sodium aluminate are mixed to yield aluminosilicate. Assuming the simultaneous formation of aluminosilicate gel and crystal nuclei it can be expected that gel *11*, containing washed seeds from the freshly-prepared gel, would crystallize more rapidly and yield finer crystals than gel *10*. Hence, crystal nuclei of Na—A zeolite appear in the alkaline aluminosilicate gels as the result either of crystallization or treatment at temperatures lower than the crystallization temperature. The nuclei cannot, however, be yielded simultaneously with the formation of alkaline aluminosilicate gels.

The results outlined above are consistent with the view[13] that structural units or nuclei of L zeolites and erionite form only when aluminosilicate gels are treated at ambient temperatures and not when aluminosilicate gels are precipitated from alkaline silicate and aluminate solutions. The conclusion that crystal nuclei form when gels are aged at temperatures below the crystallization temperature can be apparently extended to crystallizations of other types of zeolites yielded by alkaline aluminosilicate gels.

References

1. S. P. Zhdanov, in *Molecular Sieve Zeolites-1*, Am. Chem. Soc., Washington, 1971, 20.
2. S. P. Zhdanov and N. N. Samulevich, in *Proc. 5th Intern. Zeolite Conf.*, Ed. L. V. C. Rees, Heyden, London, 1980, 75.
3. S. P. Zhdanov, S. S. Khvoshchev, and N. N. Samulevich, *Synteticheskie tseolity* [*Synthetic Zeolites*], Khimia, Moscow, 1981 (in Russian).
4. S. P. Zhdanov, S. S. Khvoshchev, and N. N. Feoktistova, *Synthetic Zeolites*, **1**, Gordon and Breach Sci. Publ., New York, 1990.
5. S. P. Zhdanov, N. N. Feoktistova, and E. Ian′, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1720 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1561].
6. N. N. Feoktistova and L. M. Vtyurina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 727 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 617].
7. S. P. Zhdanov, N. N. Feoktistova, and L. M. Vtyurina, in *Proc. of Zeocat 90 (Leipzig, August 20—23, 1990)*, Elsevier Sci. Publ. B.V., Amsterdam, 1991, 287.
8. D. W. Breck and E. M. Flanigen, in *Molecular Sieves*, Soc. Chem. Ind., London, 1968, 47.
9. S. P. Zhdanov, in *Proc. 3rd Intern. Conf. on Molecular Sieves*, Louven Univ. Press, Louven, 1973, 25.
10. US Pat. 3671191b, 1972.
11. Ia. V. Mirskii, N. F. Meged′, L. M. Ishchenko, *et. al.*, in *Adsorbenty, ikh svoistva, poluchenie i primenenie* [*Adsorbents, their Properties, Manufacturing, and Application*], Nauka, Leningrad, 1985, 32 (in Russian).
12. S. P. Zhdanov and N. N. Samulevich, in *Adsorbenty, ikh svoistva, poluchenie i primenenie. Trudy IV Vses. soveshch. po adsorbentam* [*Adsorbents, their Properties, Manufacture and Application. Proceedings of the IVth All-Union Conference on Adsorbents*], Leningrad, 1978, 10 (in Russian).
13. S. P. Zhdanov, M. A. Shubaeva, and M. M. Piryutko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1949 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1764].

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