On the variation in the composition of zeolite NaA crystals

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The conditions for crystallization of zeolite NaA, whose small cages are partially or completely (one molecule per unit cell) filled with $NaAlO_2$ molecules, were outlined. These molecules are occluded into cuboctahedra of zeolite NaA only during crystallization rather than during formation, aging, and modification of the initial aluminosilicate gels. Based on the data on the adsorption capacity for water in NaA zeolite samples, a small cage of this zeolite (cuboctahedron) adsorbs about four water molecules.

Key words: zeolite, aluminosilicate gels, aging of gels, crystallization, intermicellar liquid, small cage (β-cage, cuboctahedron).

According to the Lowenstein rule,[1] the minimum Si/Al ratio in zeolite crystals cannot be less than 1. However, the chemical composition of real zeolite NaA crystals varies with their SiO_2/Al_2O_3 ratio ranging from 1.83 to 2.01.[2] The authors[2] believe that these ranging can be related to either minor admixtures of amorphous aluminum hydroxide or sodium aluminate occluded in the crystalline lattice. For crystals with a SiO_2/Al_2O_3 ratio of 1.87, it was found[3] that excess Al_2O_3 was not washed out of them even after thorough (12 h) washing with hot water, and not all Na^+ cations in this sample can be exchanged with large cations, such as Tl^+. Based on these data, the authors concluded that excess aluminum exists as sodium aluminate occluded in the lattice and positioned inside the cuboctahedral cages in the sites inaccessible for exchange. To emphasize the presence of extra-framework alumina, it was proposed to indicate the zeolite composition as follows: $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 0.14NaAlO_2 \cdot 4.77H_2O$. It is accepted[3] that in zeolite NaA crystals with the limiting content of excess aluminum each small cage (cuboctahedron or β-cage) contains one $NaAlO_2$ molecule (in this case, the SiO_2/Al_2O_3 ratio should be 1.845). There is no crystallographic evidence in the literature for occlusion of $NaAlO_2$ by cuboctahedra.

In this work, we were able to outline conditions for crystallization of zeolite NaA with different concentrations of excess $NaAlO_2$. An attempt was also made to use adsorption measurements and data on recrystallization of zeolite NaA in a mother liquor as indirect evidence for the arrangement of $NaAlO_2$ molecules in the zeolite structure.

Experimental

To determine crystallization conditions of zeolite NaA, more than 30 syntheses were carried out in the aluminate region of compositions of the initial aluminosilicate gels ($SiO_2/Al_2O_3 \leq 2$) at 90 °C. Crystallization was accomplished by heating aluminosilicate gels formed by mixing solutions of sodium aluminate and silicate. The crystals were thoroughly washed with hot distilled water and dried at ~20 °C. In experiments on modification of aluminosilicate gels, the gels obtained by mixing of alkaline solutions of sodium silicate and aluminate were stored for 1—3 days at ~20 °C to form nuclei, then excess alkali was washed off, and an alkaline solution of sodium aluminate with a certain concentration was added to the washed gels. Subsequent crystallization was carried out at 90 °C. Intermicellar liquids were separated from gel frameworks by centrifuging, and each phase was analyzed (Table 1). Before separation of the intermicellar liquids for analysis, the aluminosilicate gels were stored for 1 day at ~20 °C to equilibrate the solid and liquid phases. A vacuum adsorption setup was used to measure adsorption. Before measurements, samples were evacuated at 400 °C.

The resulting zeolite phases were identified by X-ray diffraction, optical microscopy, and chemical analysis. The concentrations of Na_2O, Al_2O_3, and SiO_2 in crystals, aluminosilicate gels, and intermicellar liquids were determined by known procedures. X-ray diffraction patterns were detected on a D-500 diffractometer (Germany).

Results and Discussion

Areas of zeolite NaA formation from aluminosilicate gels under study in the $Na_2O—Al_2O_3—SiO_2—H_2O$ system, their compositions, and SiO_2/Al_2O_3 ratios in the zeolite crystals washed with water are shown in Fig. 1. In all cases, zeolite NaA free of admixtures of other phases is the crystallization product. In this system and at this temperature, zeolite NaA does not crystallize beyond the field studied.

The compositions of the initial aluminosilicate gels (wt.%) used in syntheses are shown in Fig. 1 by circles, and the analytically determined SiO_2/Al_2O_3 ratios in the crystals are indicated by numbers at each point. The water

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Table 1. Compositions of the initial aluminosilicate gels, their liquid and solid phases, and related zeolite NaA crystals

Sample	Initial aluminosilicate gel[a]			Composition of aluminosilicate gels[b]					Composition of NaA zeolite crystals	
				Solid phase (framework)	Liquid (intermicellar) phase					
	SiO_2/Al_2O_3	SiO_2	Na_2O	SiO_2/Al_2O_3	$Al(OH)_4^-$	NaOH	SiO_2	$[Al]\cdot[Si]\cdot10^2$	SiO_2/Al_2O_3	$NaAlO_2$ [c]
		mol L^{-1}			mol L^{-1}					
1	0.33	0.133	2.07	2.2	0.466	3.44	0.030	1.40	1.86	0.90
2	0.33	0.184	1.74	2.6	0.800	2.80	0.026	2.08	1.84	1.00
3	0.33	0.239	1.44	2.8	1.096	2.40	0.027	3.96	1.85	0.97
4	1.00	0.270	2.15	2.6	0.218	3.52	0.054	1.17	1.95	0.31
5	1.00	0.510	1.50	—	0.434	2.34	0.018	0.78	1.92	0.50
6	1.00	0.620	1.23	3.0	0.570	1.54	0.011	0.63	1.95	0.31
7	2.00	0.710	1.58	2.3	0.066	2.22	0.062	0.41	1.98	0.12
8	2.00	0.770	1.16	2.8	0.064	1.42	0.023	0.15	2.00	0.00

[a] Composition of the initial mixtures taken for synthesis.

[b] Analysis data.

[c] Number of molecules per unit cell.

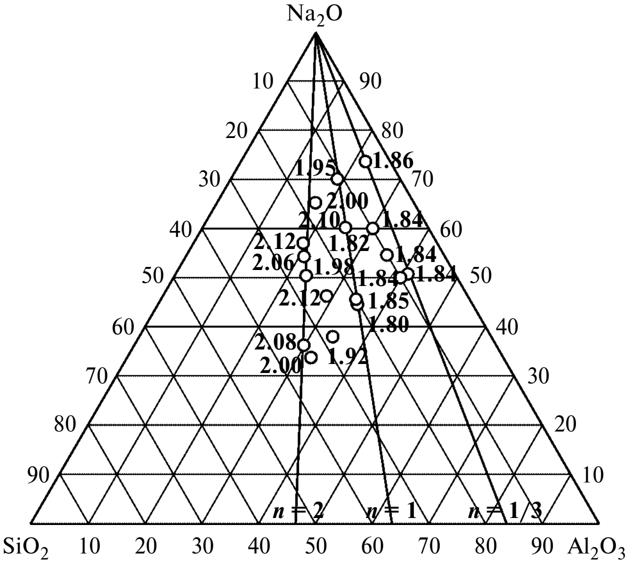

Fig. 1. Diagram illustrating the effect of compositions of the initial gels (wt.%) on the SiO_2/Al_2O_3 ratio in the zeolite NaA crystals; *n* indicate lines of equal SiO_2/Al_2O_3 ratios in the gels. See clarification in the text.

content in all gels studied varied from 80 to 95 wt.%. It follows from the data in Fig. 1 that the SiO_2/Al_2O_3 ratio in the zeolite NaA crystals is not constant and changes from 1.82 to 2.12.

In the zeolite NaA crystals, which crystallize from the gels with SiO_2/Al_2O_3 close to two, this ratio is also close to two. This ratio in the crystals decreases with an increase in the Al_2O_3 content in the initial gels. Correspondingly, the content of excess Al_2O_3 increases. The most aluminous samples with the ratio in the crystals $SiO_2/Al_2O_3 \approx 1.84$ crystallize from the aluminosilicate gels with the minimum ratio $SiO_2/Al_2O_3 \leq 1/3$.

The concentrations and ratios of components in the solid and liquid phases of some aluminosilicate gels in the region studied and compositions of the crystals obtained from these gels are presented in Table 1. Since the Si/Al ratios in the solid phases of the gels are restricted (Si/Al > 1), the liquid phases of the gels obtained from mixtures with the predominant Al_2O_3 content turned out to be more aluminous than the initial mixtures. The data in Table 1 indicate a sufficiently distinct dependence of excess sodium aluminate in the crystals on the composition of the intermicellar liquid within the same $n = SiO_2/Al_2O_3$ in the gels. The Si/Al ratio decreases and the number of excess $NaAlO_2$ molecules per unit cell (u.c.) in the crystals increases with an increase in the Al_2O_3 concentration and the product of concentrations [Si] • [Al] in the liquid phase.

Gel	Intermicellar liquid		Number of $NaAlO_2$ molecules per u.c.
	$Al(OH)_4^-$ /mol L^{-1}	$[Al]\cdot[Si]\cdot10^2$	
$n = 0.33$	0.446—1.096	1.40—3.96	~1
$n = 1.00$	0.218—0.570	0.63—1.17	~0.3—0.5
$n = 2.00$	0.064—0.066	0.15—0.41	0

As shown by our studies, excess $NaAlO_2$ is not washed from the zeolite NaA crystals by either cold, or hot water, and this can serve as an indirect evidence that excess $NaAlO_2$ exists in small zeolite cages, as some other authors believe as well.[3]

Zeolite NaS of the sodalite type, whose framework consists of cuboctahedra only, *i.e.*, closely packed small cages of zeolite NaA, does not crystallize with excess aluminate even from very concentrated aluminosilicate mixtures. For example, in the zeolite NaS crystals obtained from the most concentrated aluminosilicate gels with SiO_2/Al_2O_3 = 1/3 at the H_2O content equal to 60 wt.%, the ratio SiO_2/Al_2O_3 = 2.0. This means that the zeolite contains no excess $NaAlO_2$.

It has previously[4] been mentioned that upon prolong contact with a mother liquor the $0.96Na_2O \cdot Al_2O_3 \cdot 1.84SiO_2 \cdot 4.1H_2O$ crystals of zeolite NaA containing one $NaAlO_2$ molecule per u.c. recrystallize to form the $0.96Na_2O \cdot Al_2O_3 \cdot 2.00SiO_2 \cdot 2.4H_2O$ zeolite NaS containing no occluded sodium aluminate. The absence of excess aluminum in the zeolite NaS crystals indicates that cuboctahedral fragments formed could not trap $[NaAl(OH)_4]$ molecules from the mother liquor.

Small cages of zeolite NaA and cavities of zeolite NaS are structurally equivalent, they are ~6.6 Å in diameter with "windows" 2.2 Å. However, the cation density in a cuboctahedron of zeolite NaS is higher than that in zeolite NaA. Zeolite NaS contains six Na^+ cations in two cuboctahedra of u.c. At the same time, in the hydrated zeolite NaA an u.c. contains 12 Na^+ cations, which are located in the large cage of zeolite NaA, fall per u.c., whereas the cuboctahedron has almost no cations. It can be assumed that steric hindrances caused by a higher electron density in the cuboctahedra of zeolite NaS compared to that in NaA prevent occlusion of large $NaAlO_2$ molecules by the cuboctahedra of NaS zeolite.

Feldspathoids, with which sodalite is classified, contain excess cations, anions, and a minor amount of water in their cages. Unlike feldspathoids, in particular, basic sodalite, the cavities of zeolite NaS are filled with water only during synthesis, and after dehydration the zeolite can adsorb up to 18% H_2O.[5]

The absence of excess aluminum in the zeolite NaS crystals formed upon the recrystallization of zeolite NaA [4] can indicate that the $NaAlO_2$ molecules in zeolite NaA are occluded by the cuboctahedra. If zeolite NaA contains excess sodium aluminate as an admixture, it can be expected that the same admixture is present in zeolite NaS obtained by the recrystallization of zeolite NaA in a mother liquor under the same conditions. Due to steric hindrances, a $NaAlO_2$ molecule cannot pass through the cuboctahedron "window" 2.2 Å in size. An assumption remains that the $NaAlO_2$ molecules are occluded only during synthesis.

In which step of the synthesis of zeolite are the $NaAlO_2$ molecules occluded into its cuboctahedra? This can occur during gel formation, modification of the aluminosilicate gels by aging or changing the liquid phase composition, and, finally, directly during crystallization.

We have previously[6] shown that the aluminosilicate gels washed from alkali (skeletons of gels) have the ratio $SiO_2/Al_2O_3 > 2$, regardless of their initial composition. This is also seen from the data in Table 1. Evidently, during gel formation on mixing alkaline solutions of sodium silicate and aluminate, cuboctahedral cages are not formed due to a high gel formation rate or, if they are formed, they do not occlude the $NaAlO_2$ molecules.

Table 2. Influence of aging of the $2.2Na_2O \cdot Al_2O_3 \cdot 1/3SiO_2 \cdot 130H_2O$ aluminosilicate gel on the SiO_2/Al_2O_3 ratio in the gels and related zeolite NaA crystals

Sample	Duration of aging/day	SiO_2/Al_2O_3	
		gel	crystals
1	0	2.76	1.84
2	1	2.41	1.87
3	3	2.27	1.82

Let us consider the results of experiments on the modification of the aluminosilicate gels by aging and replacing the liquid phases (Table 2). The $2.2Na_2O \cdot Al_2O_3 \cdot 1/3SiO_2 \cdot 130H_2O$ aluminosilicate gel samples, from which zeolite NaA with cuboctahedra filled with sodium aluminate molecules crystallize at 90 °C under hydrothermal conditions, was subjected to aging for 1 and 3 days at ~20 °C, washed from alkali excess, dried, and analyzed. Experiments on crystallization of samples of these gels at 90 °C were carried out in parallel.

In all cases, zeolite NaA crystallizes with the same minimum SiO_2/Al_2O_3 ratio in the crystals. If all excess sodium aluminate exists as extra-framework species, *i.e.*, inside that sodalite cages, then this ratio corresponds to the maximum filling of the cuboctahedra with the $NaAlO_2$ molecules (1 $NaAlO_2$ molecule per u.c.). It is seen that during gel aging sodium aluminate molecules do not penetrate into the gel structure, because the ratio $SiO_2/Al_2O_3 > 2$ in all cases. Some decrease in the SiO_2/Al_2O_3 ratio in the aluminosilicate gels upon aging is common for all gels and related to a higher solubility of SiO_2 in the intermicellar liquid compared to that in Al_2O_3.

Let us consider the results of experiments on aluminosilicate gel modification made by the replacement of the liquid phases. These experiments were carried out on the gels from which low-silica zeolites NaX with SiO_2/Al_2O_3 = 2.30 and NaA with SiO_2/Al_2O_3 = 2.00 usually crystallize (Table 3). Gel samples were preliminarily stored for 1 day at ~20 °C to equilibrate the solid and liquid phases, then washed from alkali excess, and dried. An alkaline solution of sodium aluminate was added to the washed gels (skeletons of gels) in such a way that in each gel sample SiO_2/Al_2O_3 would be 1/3 and the gel composition would be in the aluminous field of compositions.

Zeolite NaA with SiO_2/Al_2O_3 = 1.82—1.87 crystallizes from the modified gels. This ratio corresponds to the maximum filling of the cuboctahedral cages with the $NaAlO_2$ molecules (1 $NaAlO_2$ molecule per cuboctahedron). The compositions of the crystals are determined by the composition of the modified mixture rather than the gel composition before modification with a solution

Table 3. Influence of modification of the liquid phases of the gels on the compositions of zeolites that formed

Gel or zeolite	Chemical composition (type of zeolite)	
Initial gel *I*	$3.84Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 145H_2O$	$2.9Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 200H_2O$
Zeolite crystallizing from gel *I*	$0.98Na_2O \cdot Al_2O_3 \cdot 2.3SiO_2 \cdot 4.9H_2O$ (NaX)	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.2H_2O$ (NaA)
Washed and dried gel *I* (gel *II*)	$0.92Na_2O \cdot Al_2O_3 \cdot 2.68SiO_2 \cdot 5.9H_2O$	$0.9Na_2O \cdot Al_2O_3 \cdot 2.78SiO_2 \cdot 6.48H_2O$
Modified gel *II** (gel *III*)	$1.87Na_2O \cdot Al_2O_3 \cdot 1/3SiO_2 \cdot 65H_2O$	$2.2Na_2O \cdot Al_2O_3 \cdot 1/3SiO_2 \cdot 130H_2O$
Zeolite crystallizing from gel *III*	$0.83Na_2O \cdot Al_2O_3 \cdot 1.82SiO_2 \cdot 4.24H_2O$ (NaA)	$0.93Na_2O \cdot Al_2O_3 \cdot 1.84SiO_2 \cdot 4.51H_2O$ (NaA)

* After a solution of sodium aluminate was added.

of sodium aluminate. It is most likely that the aluminosilicate gels contain no cuboctahedral blocks, which are formed upon neither aging, nor modification of the gels. The formation of cuboctahedral structural units of zeolite NaA and occlusion of the $NaAlO_2$ molecules occur, probably, only during crystallization. In this case, the gel skeleton is dissolved in the intermicellar liquid, and cuboctahedra are formed at the interface of the liquid and solid phases. This is also indicated by the above-presented data on the recrystallization of zeolite NaA in NaS in the mother liquor.

Thus, the mechanism of zeolite formation, which is based on crystallization from the liquid phase, is confirmed. The same mechanism is indicated by a fairly clear dependence of the chemical composition of the crystals on the composition of the intermicellar liquids (see Table 1).

Taking into account errors of chemical analyses and assuming that excess $NaAlO_2$ is occluded in the cuboctahedra, we can see that the changes in SiO_2/Al_2O_3 in the zeolite NaA crystals (see Table 1) correspond to different degrees of filling of the cuboctahedra with the $NaAlO_2$ molecules (from 1.0 at $SiO_2/Al_2O_3 = 1.84$ to 0 at $SiO_2/Al_2O_3 = 2.00$).

Regardless of the localization of excess $NaAlO_2$ in the framework of zeolite NaA, it should decrease the adsorption capacity of the crystalline phase. Figure 2 shows the adsorption isotherms of water for two samples of zeolite NaA with the $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.6H_2O$ (isotherm *1*) and $Na_2O \cdot Al_2O_3 \cdot 1.84SiO_2 \cdot 4.5H_2O$ (isotherm *2*) crystal compositions. The differences in water adsorption observed for these samples can be explained by different accessibilities of small cages for H_2O molecules. Each cuboctahedron in sample *2*, as follows from the composition, contains one $NaAlO_2$ molecule. Since the isotherms describe the equilibrium adsorption, it can be considered that the decrease in the adsorption capacity for water for sample *2* is related to the fact that the cuboctahedra filled with the $NaAlO_2$ molecules are inaccessible for water molecules. In this case, the difference in adsorption capacity is a volume of H_2O adsorbed by small cages of sample *1*. The data on the adsorption capacity for water for these zeolite NaA samples (at $p/p_s \approx 0.5$) show that a small cage of this zeolite (cuboctahedron or β-cage) adsorbs about four H_2O molecules.

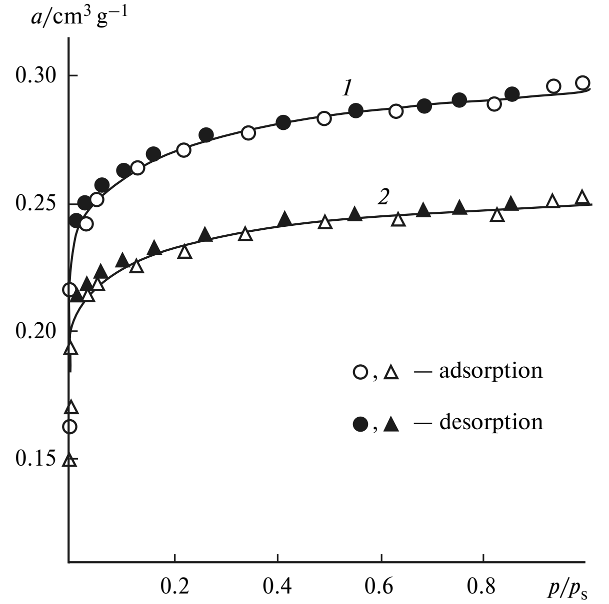

Fig. 2. Adsorption isotherms of H_2O vapor at 18 °C for the zeolite NaA samples with free cuboctahedra (*1*) and those filled with $NaAlO_2$ molecules (*2*).

This value corresponds to the ratio of large to small cages of zeolite NaA [7] and almost coincides with the adsorption capacity for water of zeolite NaS, whose structure consists of cuboctahedra only.[5]

Thus, the calculated data on the water content in small cages of zeolite NaA (~4 H_2O molecules per sodalite unit) and a possibility to recrystallize zeolite NaA with $SiO_2/Al_2O_3 = 1.84$ to form zeolite NaS without excess $NaAlO_2$ ($SiO_2/Al_2O_3 = 2.00$) indicate that the $NaAlO_2$ molecules are occluded by small cages (cuboctahedra) of zeolite NaA.

When zeolite NaA is produced under industrial and laboratory conditions, it is important to choose the composition of the initial gels, because the presence of excess sodium aluminate in crystals always decreases their adsorption activity. The compositions of the initial aluminosilicate gels in which the SiO_2/Al_2O_3 ratio is close to two is optimum for syntheses of zeolites with a minimum $NaAlO_2$ content.

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