General and Inorganic Chemistry

Study of the stability of zeolites Na—A and Na—X in mother liquors

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It was shown that Na zeolites of A and X types are unstable under the conditions of hydrothermal synthesis and are easily recrystallized to form other zeolites with more compact crystal structures and higher Si/Al ratios. Zeolite X is recrystallized to phillipsite (zeolite P), and zeolite A is recrystallized to phillipsite from gels with the SiO_2/Al_2O_3 ratio equal to 2 and to sodalite from gels with $SiO_2/Al_2O_3 < 2$ (zeolite J). The nucleation of secondary zeolite phases occurs as the result of rearrangement and decomposition of the lattice of primary crystals.

Key words: stability, recrystallization; aluminosilicate gels; intermicellar liquids; zeolites.

The properties of zeolites crystallizing in aqueous alkaline aluminosilicate systems under hydrothermal conditions depend on the conditions of preparation of the initial mixtures, the intensity of stirring, seeding, and other factors. This demonstrates that these heterogeneous systems, after formation of primary crystals of zeolites, do not reach thermodynamic equilibrium. Under certain conditions of synthesis, storage of zeolite crystals in contact with mother liquors for 2—3 h and longer does not lead to phase transformations, which is evidence of the relative stability of the crystals under the conditions of their formation. However, as a rule, synthetic zeolites are not true equilibrium phases and can be isolated in the pure state.

It was shown previously[1] that prolonged contact of zeolite A with the mother liquor results in its recrystallization into phillipsite in less alkaline solutions, while it is transformed into basic sodalite in more alkaline solutions. It was also reported that the primary phases of all zeolites studied are recrystallized either into phillipsite or sodalite.[2] There are published data[3—5] indicating that recrystallization of synthetic and natural zeolite phases is possible on treatment with alkaline solutions.

The purpose of this work is to study the conditions of the stability of zeolites Na—A and Na—X in mother liquors in a sufficiently wide range of compositions of the initial aluminosilicate gels, which makes the preparation of widely used zeolite pure phases possible.

Experimental

To study the recrystallization of primary zeolite phases formed on heating of aluminosilicate gels, 15 series of experiments with prolonged storage of crystals of zeolites A and X in contact with the mother liquor were performed at 90 °C (Table 1). The compositions of the aluminosilicate gels obtained by mixing of alkaline solutions of sodium silicate and aluminate were chosen in such a way that the zeolite would be obtained in a maximum and almost total yield and without impurities of other phases. In each series of experiments, 4—5 samples of the same composition were studied parallelly. In one experiment of each series, the primary zeolite phases were separated from the mother liquors immediately after

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2415—2418, October, 1996.

Table 1. Composition of initial aluminosilicate gels and character of the primary crystalline phases and products of their partial and total recrystallization

Sample series	Initial gels		Primary phase	Duration (days) of contact of the primary crystalline phase with the mother liquor at 90 °C and phases formed					
	Na_2O /mol L^{-1}	$\frac{SiO_2}{Al_2O_3}$		5	10	15	20	30	40
1	2.00	0.33	A	A + J	J	J	J	J	—
2	2.20	0.50	A	A + J	J	J	J	J	—
3	0.50	0.50	A	A	A	A	A	A	A
4	1.70	0.60	A	A	A + J	J	J	J	—
5	1.70	1.00	A	A	J	J	J	J	—
6	2.00	1.00	A	J + A	J	J	J	J	—
7	1.34	2.00	A	A	A + P	P	P	P	—
8	1.50	2.00	A	A	A + P	P	P	P	—
9	1.60	2.00	A	A	A + P	P	P	P	—
10	2.00	2.00	A	A	A + P	P	P	P	—
11	1.40	2.70	X	X	X	X	X	X	X + P
12	1.60	2.70	X	X + P	X + P	P	P	P	—
13	1.50	3.00	X	X + P	P + X	P	P	P	—
14	1.00	3.00	X	X + P	P + X	P + X	P + X	P + X	—
15	1.10	5.00	X	X + P	X + P	P + X	P + X	P + X	—

Note. A and X are zeolites Na—A and Na—X, respectively; J is basic sodalite; P is phillipsite; the sum means the mixture of the phases (the first term is greater than or equal to the second one).

precipitation of the crystals. In the other experiments, crystals of the primary phase remained in contact with the mother liquor for 5—40 days. The experiments were carried out in Teflon vessels. The zeolite phases obtained were studied by X-ray diffraction analysis and optical microscopy, and in some cases, the adsorption properties were studied on a vacuum adsorption setup.

Mother liquors were separated from crystals by filtration, and intermicellar liquids were separated from the gel frameworks by centrifugation. Before centrifugation, the gels were stored for 6 h at the crystallization temperature of 90 °C to attain equilibrium between the solid (gel frameworks) and liquid (intermicellar liquids) phases. The content of Na_2O, Al_2O_3, and SiO_2 in the mother liquors, intermicellar liquids, and crystals was analyzed by the well-known procedures.

Results and Discussion

The compositions of the initial aluminosilicate gels, the character of the primary phases obtained, and the change in the phase composition due to recrystallization are presented in Table 1 (the data were obtained by X-ray diffraction analysis). Table 1 shows that zeolites of the A type crystallizing from aluminosilicate gels with a ratio of $SiO_2 : Al_2O_3 < 2$ (samples *1*, *2*, *4*, *5*, and *6*) even after 5—10 days of the storage in the mother liquor begin to recrystallize into basic sodalite (zeolite J), and recrystallization ceased after 10—15 days at 90 °C.

On the other hand, samples of zeolite A crystallizing from silicoaluminogels with $SiO_2 : Al_2O_3 = 2$ stored in the mother liquor recrystallize to phillipsite (zeolite P) (samples *7*—*10*). No changes in the X-ray-patterns are observed when these samples are further stored for up to 30 days.

The recrystallization of zeolite A into basic sodalite and phillipsite is confirmed by the change in the adsorption properties of the crystals, which is confirmed by the existing data on the adsorption capacity with respect to water for zeolites of these types (Table 2).

It is difficult to follow phase transition $A \rightarrow J$ by microscopic analysis because of the very small sizes of the crystals. Transition $A \rightarrow P$ can be observed with a microscope, because zeolite A is crystallized as small

Table 2. Data from chemical analysis of the primary (A and X) and final (J and P) phases and their adsorption capacities

Sample series	Primary phase	Final phase	Chemical composition of crystals	Adsorption of H_2O/cm^3 g^{-1} (p/p_s = 0.5 and T = 18 °C)
2	A	J	$0.96Na_2O \cdot Al_2O_3 \cdot 1.84SiO_2 \cdot 4.1H_2O$	0.265
			$0.96Na_2O \cdot Al_2O_3 \cdot 2.00SiO_2 \cdot 2.4H_2O$	0.075
10	A	P	$0.96Na_2O \cdot Al_2O_3 \cdot 1.98SiO_2 \cdot 4.16H_2O$	0.267
			$0.94Na_2O \cdot Al_2O_3 \cdot 3.16SiO_2 \cdot 3.96H_2O$	0.200
12	X	P	$0.98Na_2O \cdot Al_2O_3 \cdot 2.17SiO_2 \cdot 5.06H_2O$	0.320
			$0.96Na_2O \cdot Al_2O_3 \cdot 3.45SiO_2 \cdot 4.23H_2O$	0.205

crystals 1—3 μm in size, and zeolite P forms large spheres up to 20 μm in diameter.

The aluminosilicate gels chosen for the study of recrystallization of zeolite X crystallized for 2—4 days to form zeolite X as the primary phase. As can be seen from Table 1, zeolite X recrystallized into phillipsite (zeolite P) in all cases studied. When crystals of zeolite X are stored in the mother liquor, the lines of phillipsite appear in the X-ray patterns even after 5 days, their number increases in time, and after 30 days the product is pure phillipsite or phillipsite with a small amount of zeolite X. An exception is sample *11*, in which the first lines of phillipsite appeared only after storage in the mother liquor for 40 days. The reasons for this stability are not clear enough, but they are likely caused by the composition of the initial gel (a low concentration of alkali for a small ratio of $SiO_2 : Al_2O_3$ in the initial gel).

It follows from the data in Table 1 that recrystallization of zeolites Na—A and Na—X occurs more rapidly with a high concentration of alkali in the initial gel. In dilute mother liquors, recrystallization occurs for a longer time (samples *3* and *11*).

Recrystallization of zeolite X to phillipsite can be easily controlled by changing the size and habitus of crystals X and P (as described in the case of zeolite A). The corresponding changes in the adsorption capacity with respect to water for the primary and secondary phases indicated in Table 2 also indicate recrystallization. The data on the chemical analysis of the primary and final phases as well as their adsorption capacities with respect to water for $p/p_s = 0.5$ and 18 °C are presented in Table 2.

The comparison of the $SiO_2 : Al_2O_3$ ratios for the primary and final phases of sample *2* (see Table 2) makes it possible to conclude that the lattice of zeolite Na—A decomposes during its recrystallization to basic sodalite. As follows from the composition of crystals of zeolite Na—A ($SiO_2 : Al_2O_3 = 1.84$), each cubic octahedron contains one molecule of $NaAlO_2$,[6] and the secondary phase in the crystals has a ratio of $SiO_2 : Al_2O_3 = 2$ and, hence, it consists of cuboctahedrons without $NaAlO_2$ molecules. Due to steric factors, $NaAlO_2$ can enter the cuboctahedrons only during synthesis, therefore, one can draw a conclusion that the decomposition of the cuboctahedral structural elements of zeolite Na—A during recrystallization results at least in the formation of double four-membered rings.[7] Similar conclusions about the decomposition of the structure of the primary phases during their recrystallization can be also made for the other phase transitions A → P and X → P. It is difficult to imagine that an increase in the $SiO_2 : Al_2O_3$ ratio in crystals of secondary phases could occur without the decomposition of cuboctahedral units of zeolites Na—A and Na—X.

Thus, the changes in the size, shape, and chemical composition of crystals observed during recrystallization indicate that the phase transitions in long contact of the primary phases with the mother liquors occur due to rearrangement and decomposition of the lattice of the primary crystals. As follows from the data in Table 2, the secondary phases formed are more compact, have a lower adsorption capacity and a higher $SiO_2 : Al_2O_3$ ratio than the primary phases.

The conclusion about the higher SiO_2/Al_2O_3 ratio in crystals of the final phase compared to those in the initial phase agree with our concepts on the mechanism of crystallization of zeolites.[8] It is known that crystallization of the primary phase occurs with direct participation of the intermicellar liquid (liquid phase in contact with the amorphous phase), and the final phase is crystallized from the mother liquor (the liquid phase in equilibrium with crystals). The compositions of the liquid phases determine to a considerable extent the composition of crystals of both phases. The data on analysis of the intermicellar liquids and mother liquors for parallel samples of the same gels are presented in Table 3. It follows from Table 3 that the concentrations of the components (especially of SiO_2 and Al_2O_3) in intermicellar liquids of the corresponding mother liquors differ substantially. In the case of gels in which $SiO_2 : Al_2O_3 < 2$, this ratio is lower in the mother liquors than in the intermicellar liquids. By contrast, when aluminosilicate gels with $SiO_2 : Al_2O_3 \geq 2$ are crystallized, the values of $SiO_2 : Al_2O_3$ in the mother liquors are greater than in the corresponding intermicellar liquids. Based on these data, we can assume that the secondary phase crystallizing from gels with $SiO_2 : Al_2O_3 \geq 2$ should be more siliceous than the primary phase. Phillipsite with a higher $SiO_2 : Al_2O_3$ ratio than in the primary phases of zeolites Na—A or Na—X is always crystallized from these gels as the secondary phase (see Table 2). This conclusion contradicts the statement of the authors of Ref. 9 that phillipsite less siliceous than the primary phase is formed in recrystallization of zeolite Y.

Table 3. Concentrations of components (mol L^{-1}) in liquid phases of gels and in mother liquors over crystals of zeolites A and X formed from these gels

Sample	$SiO_2:Al_2O_3$ ratio in initial gels	Na_2O	Al_2O_3	SiO_2	$\frac{SiO_2}{Al_2O_3}$	Phase
			Intermicellar liquids			
1	0.33	1.720	0.2340	0.0298	0.127	A*
6	1.00	1.760	0.0643	0.0610	0.950	A*
5	1.00	1.170	0.2170	0.0176	0.081	A*
7	2.00	0.713	0.0323	0.0229	0.710	A*
15	5.00	0.720	0.0100	0.5470	54.70	A*
			Mother liquors			
1	0.33	1.780	0.2200	0.011	0.051	J**
6	1.00	1.780	0.0910	0.013	0.140	J**
5	1.00	1.330	0.2100	0.015	0.070	J**
7	2.00	0.720	0.0108	0.033	3.040	P**
15	5.00	0.764	0.0020	0.683	341.0	P**

* Primary. ** Secondary.

Table 4. Crystallization of zeolites from intermicellar liquids and mother liquors at 90 °C

Experiment	Concentration in the liquid phase /mol L^{-1}			$\frac{SiO_2}{Al_2O_3}$ in the liquid phase	Ratio of components in crystals			Type of zeolite formed
	Na_2O	Al_2O_3	SiO_2		Na_2O	Al_2O_3	SiO_2	
				Intermicellar liquids				
1	1.46	0.0184	0.460	25.0	0.95	1.0	2.60	X
2	1.41	0.0177	0.426	24.1	1.00	1.0	2.58	X
				Mother liquors				
1	1.41	0.0097	0.485	50.0	0.95	1.0	2.85	P
2	1.38	0.0123	0.455	37.0	0.97	1.0	2.67	P

As shown above, zeolite J of the sodalite type with the same Si : Al ratio in the framework as in the primary phase is crystallized from aluminosilicate gels with $SiO_2 : Al_2O_3 < 2$, since in crystals it cannot be less than 1.[10] Based on the data on the overall chemical composition, the secondary phase also has a higher Si : Al ratio than the primary phase (see Table 2) due to the absence of $NaAlO_2$ molecules in the cuboctahedrons of sodalite.

The study of crystallization of the intermicellar liquids separated from gels and of the mother liquors filtered off from crystals are of special interest. The data on crystallization of the liquid phase of gels of $8.9Na_2O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 300H_2O$ composition and mother liquors of the same gels after separation of the primary crystalline phases at 90 °C are presented in Table 4. The initial alkaline aluminosilicate gel from which the liquid phases studied were isolated crystallized reproducibly to form zeolite X of the $Na_2O \cdot Al_2O_3 \cdot 2.6SiO_2 \cdot 6.1H_2O$ composition. It is seen from the data presented in Table 4 that zeolite of the same structure and chemical composition as for normal crystallization of the initial gel is obtained from the intermicellar liquid in parallel experiments. Phillipsite (zeolite P) with a higher $SiO_2 : Al_2O_3$ ratio in crystals than in primary phase X is crystallized from the mother liquor.

The studies show that sodium zeolites A and X are unstable phases under the conditions of their normal synthesis; they are crystallized to transform into zeolites of other types with a more compact structure and a higher Si : Al ratio.

This work was financially supported by the International Science Foundation and the Government of the Russian Federation (Grant J52 100).

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Received March 29, 1996