THERMAL BEHAVIOR OF MIXTURES BASED ON METAKAOLIN AND SODIUM HYDROXIDE

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The behavior of the mixtures $6Al_2Si_2O_7 : 12NaOH$ and $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$ during heat-treatment was studied by means of x-ray diffraction and simultaneous thermal analysis. It was shown that hydrated zeolite LTA forms after ultrasonic treatment and evaporation of a suspension, granulation of paste, and drying. It was determined that sodium aluminum silicate $Na_6Al_4Si_4O_{17}$ is synthesized at temperatures up to 700°C. Sodium aluminum silicate $Na_8Al_4Si_4O_{18}$, mullite, and nepheline were found in the systems after heat-treatment at temperatures above 800°C. It is shown that the calculations performed by Friedman's isoconversion method (differential) and the Kissinger–Akahir–Sunose (integral) method, for which the temperature interval 500 – 800°C is of interest, give close values of E. The growth of the apparent energy of activation with increasing degree of transformation attests a change in the reaction mechanism.

Key words: metakaolin, sodium hydroxide, zeolite LTA, Friedman analysis, Kissinger–Akahir–Sunose analysis.

Low modular zeolites (for example, LTA, SOD, and others) and feldspathoids possess close chemical composition (Si : Al ≈ 1 – 3, Me : Al ≈ 1 – 2, where ME = Na, K, and so on) but different crystalline structure [1]. So, zeolites comprise an aluminum-silicate frame with regular cavities. The elementary 'building' unit consists of T-atoms (T = Si^{4+}, Al^{3+}), which form the tetrahedra TO_4 [2]. These tetrahedra form β-cells, simple and double 4-, 6-, and 8-membered rings, a zeolite frame of one or another type is 'assembled' from other secondary 'building' structures. The crystal lattice of feldspathoids is also formed by TO_4 tetrahedra but possesses a different, closer packing, so that the final product of the heat-treatment of zeolites (in particular, LTA) is nepheline, crystallizing in a hexagonal system [3].

Usually, the raw material for synthesis of zeolite LTA is metakaolin [4], whose structure consists of a mixture of x-ray amorphous silicon and aluminum oxides [5]. To obtain granular zeolites the raw material components (kaolin, metakaolin, sodium hydroxide, and others) are formed and then subjected to heat-treatment at 500 – 800°C [6]. In the heat-treatment process not only does buildup of granule strength occur on account of the formation of ceramic bonds, but also a chemical interaction occurs between kaolin/metakaolin and sodium hydroxide. The phase transformations occurring at this stage have been studied quite well [7 – 9], but hardly any data on the kinetics of these processes have been published.

Non-isothermal methods are widely used to study the kinetics of solid-phase processes [10]. Under conditions with temperature rising linearly (β = $dT/d\tau$ = const) the reaction rate is described by the well-known general equation

$$dx/d\tau = \beta dx/dT = k_0 f(x) \exp(-E/RT), \qquad (1)$$

where x is the degree of transformation; $f(x)$ is a differential conversion function; and, k_0 is the pre-exponential factor in the Arrhenius equation.

The equation (1) is a fundamental expression for determining the kinetic parameters from thermogravimetric data by isoconversion methods [11]. An advantage of these methods is that there is no need to construct a kinetic model of the process. The methods are divided into differential and integral depending on how the data are calculated. Isoconversion methods have been successfully used to study the kinetics of thermal transformations of kaolin [12] and synthesis of gehlenite and anorthite [13] as well as nepheline [14].

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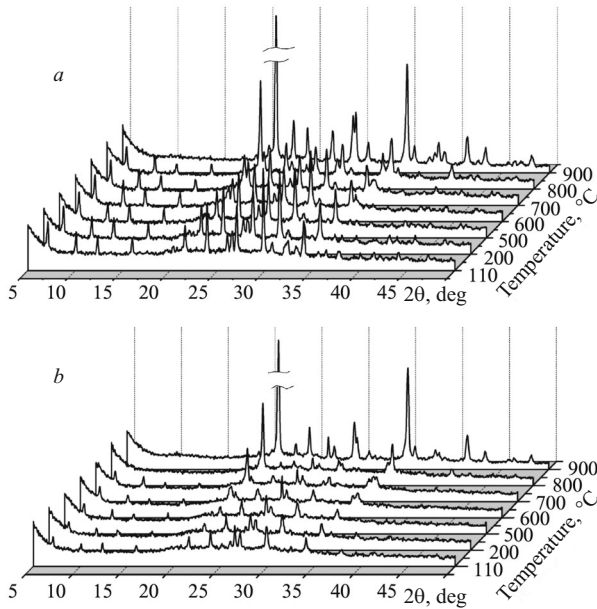
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Fig. 1. Diffraction patterns (CuK_α radiation) after calcination of the mixtures at different temperatures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$.

The purpose of the present work is to study the kinetics of thermal solid-phase processes in mixtures of metakaolin and sodium hydroxide, intended for synthesis of zeolite LTA, as well as to determine the influence of excess aluminum oxide on the thermochemical processes.

The reaction mixtures were prepared using P-2 grade kaolin obtained from the Prosyanovksoe field and calcined at 700°C in order to obtain metakaolin $Al_2Si_2O_7$ (MK), solid NaOH (chemically pure grade), and Al_2O_3 obtained by calcining gibbsite at 550°C in 4 h. The mixtures $6Al_2Si_2O_7 : 12NaOH$ (*a*) and $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$ (*b*) were prepared for study. The ratio of MK and NaOH corresponds to stoichiometry of the synthesis reaction of zeolite LTA:

$$6Al_2Si_2O_7 + 12NaOH + 21H_2O \rightarrow$$
$$|Na_{12}(H_2O)_{27}|[Al_{12}Si_{12}O_{48}]. \tag{I}$$
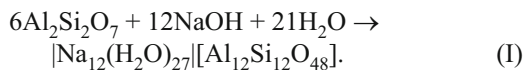
The mixtures were subjected to ultrasonic processing (USP) for 10 min in a water suspension (T : L = 1 : 5) in an UD-2 disperser (frequency 22 kHz, amplitude 8 μm). The conditions of preliminary treatment are optimal, which was established in [15]. Next, all suspensions were evaporated while mixing to optimal molding moisture content, which was equal to 20 – 22% (by weight). The obtained pastes were extruded into 3 mm in diameter granules. After drying at 110°C the granules were calcined at different temperatures.

The following methods of study were used in this work:

– x-ray phase analysis (XPA) of the powders was performed using a DRON-3M diffractometer and CuK_α radia-

tion ($\lambda = 0.15406$ nm, Ni filter); the ASTM database was used to identify the crystalline phases;

– a STA 449 F3 Netzsch simultaneous thermal analyzer with heating rates 5, 10, and 15 K/min in atmospheric air was used to obtain data for thermogravimetric (TG) analysis and differential scanning calorimetry (DSC).

For kinetics calculations the TG mass loss data must be converted into the degree of transformation:

$$dx / d\tau = \beta dx / dT = k_0 f(x)\exp(-E / RT), \tag{2}$$

where $m(\tau_s)$ is the signal at the initial moment in time τ_s; $m(\tau_j)$ is the signal at an intermediate time τ_j; and, $m(\tau_f)$ is the signal at the final moment in time τ_f.

For differential isoconversion analysis Friedman proposed using for non-isothermal conditions [16] the logarithm of the conversion rate $dx/d\tau$ as a function of the corresponding temperature:

$$\ln(dx / d\tau)\big|_{x=x_j} = \ln A - E / RT_{kj} + \ln f(x_j). \tag{3}$$

Since $f(x)$ in the last term of the expression (3) is constant for specified x_j, in the plot of Eq. (3) versus $1/T$ we have as a result a straight line with the slope $B = -E/R$.

The integral isoconversion methods of analysis of non-isothermal data are based on integration of Eq. (1):

$$G(x) = \int_0^\infty dx / f(x) = k_0 / b \int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT =$$
$$k_0 E/\beta R\, p(z), \tag{4}$$

where $z = E/RT$ and $p(z)$ is the so-called temperature integral. The employed methods are distinguished according to the approximation of this integral.

In the Kissinger–Akahari–Sunose method (KAS) [17, 18] the integral $p(z)$ is expressed by means of the approximation [19]

$$p(z) = \exp(-z)/z^2. \tag{5}$$

Substituting this expression into Eq. (4) and taking the logarithm we obtain

$$\ln(\beta_j/T_{kj}^2) = \ln(AR/E) - \ln(x_j) - E/RT. \tag{6}$$

It follows from Eq. (6) that for a series of measurements with heating rates $\beta_1 - \beta_j$ and fixed values of the degree of conversion $x = x_k$ the plots of the functions $\ln(\beta_j/T_{kj}^2) = f(1/T_{kj})$ give as a result a straight line. The term T_{jk} represents the temperatures at which the degree of conversion x_k is achieved with heating rate β_j. The slope of the straight lines is directly proportional to the activation energy.

After the stoichiometric mixture $6Al_2Si_2O_7 : 12NaOH$ was subjected to USP, evaporation, and drying low-intensity reflections belonging to the hydrated zeolite LTA were found in the diffraction pattern of the sample (Fig. 1*a*). Also present is a halo, which corresponds to unreacted ingredients.
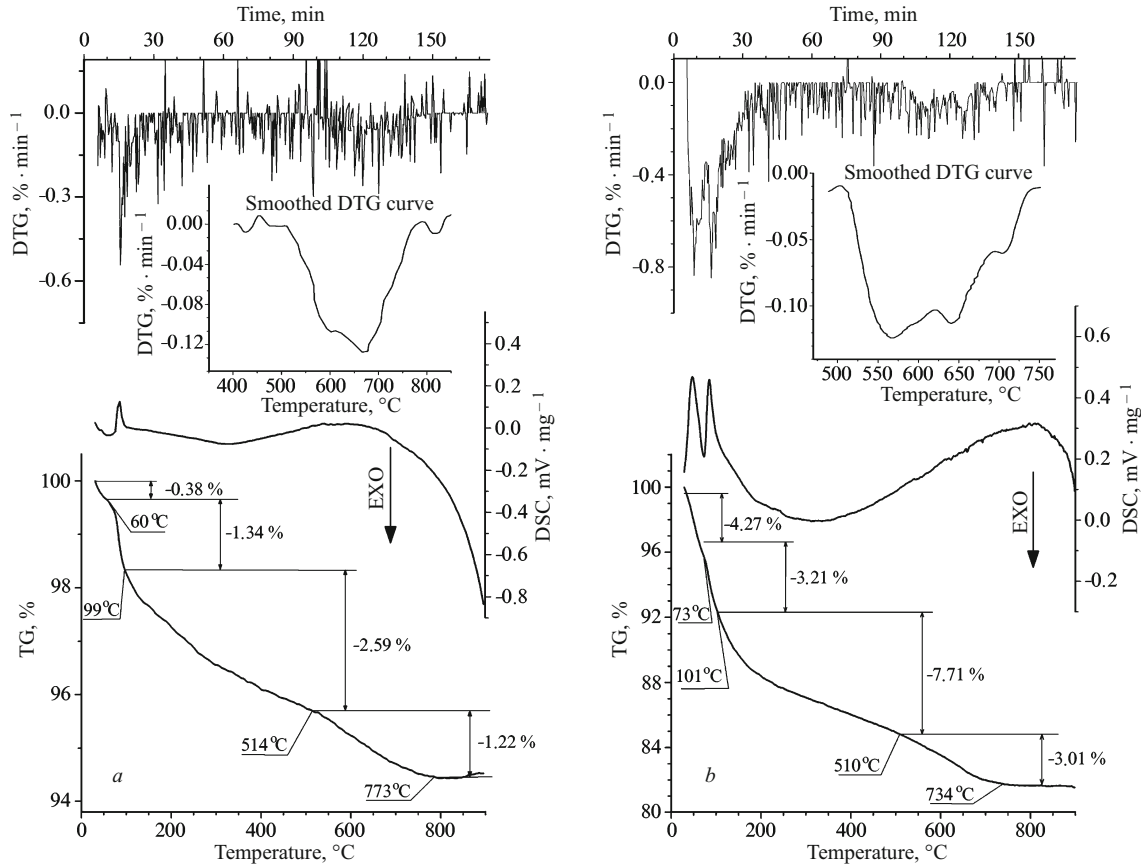
Fig. 2. Data from simultaneous thermal analysis of the mixtures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$; heating rate 5 K/min; TG — weight content, %.

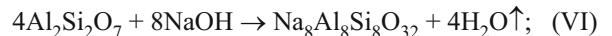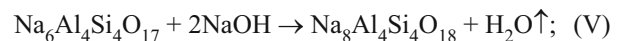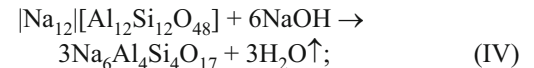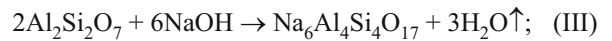The TG curve of the sample in this temperature interval possesses mass losses corresponding to an endo effect in the DSC curve (Fig. 2*a*). The observed processes are associated with removal of weakly bound adsorption water.

No new phases appear on subsequent calcination to temperature 500°C (see Fig. 1*a*). Only a change of intensity of already existing reflections is observed. Mass losses were observed in the TG curves in the considered range (see Fig. 2*b*). Taken together the observed phenomena are interpreted as dehydration of the zeolite LTA, which can be described by the gross reaction

$$|Na_{12}(H_2O)_{27}|[Al_{12}Si_{12}O_{48}] \rightarrow |Na_{12}|[Al_{12}Si_{12}O_{48}] + 27H_2O\uparrow. \quad (II)$$
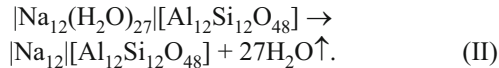
The formation of cubic sodium aluminate $Na_6Al_4Si_4O_{17}$ is observed in the mixture at temperatures above 500°C, which is attested by the appearance of reflections at the diffraction angles 2.16 and 34.65° 2Θ ({111} and {220} planes, respectively) (see Fig. 1*a*). After calcination at 800°C quite strong reflections are observed in the diffraction pattern at the angles 21.18 and 34.98° 2Θ, which correspond to reflections from the {111} and {220} planes of the cubic sodium aluminate with the composition $Na_8Al_4Si_4O_{18}$. Moreover, weak reflections due to mullite and silicon dioxide appear.

After calcination at 900°C strong reflections due to $Na_8Al_4Si_4O_{18}$ as well as reflections due to mullite and nepheline are present in the diffraction pattern. It should be noted that a reduction of the intensity of the reflections of zeolite LTA as well as a halo are observed in the course of the calcination; they completely vanish after treatment at temperatures above 800°C. The TG curves possess in the temperature range 500 – 800°C mass losses corresponding to the removal of water (see Fig. 2*a*). Summarizing, the following reactions can be supposed to occur in the system:

$$2Al_2Si_2O_7 + 6NaOH \rightarrow Na_6Al_4Si_4O_{17} + 3H_2O\uparrow; \quad (III)$$

$$|Na_{12}|[Al_{12}Si_{12}O_{48}] + 6NaOH \rightarrow 3Na_6Al_4Si_4O_{17} + 3H_2O\uparrow; \quad (IV)$$

$$Na_6Al_4Si_4O_{17} + 2NaOH \rightarrow Na_8Al_4Si_4O_{18} + H_2O\uparrow; \quad (V)$$

$$4Al_2Si_2O_7 + 8NaOH \rightarrow Na_8Al_8Si_8O_{32} + 4H_2O\uparrow; \quad (VI)$$

$$3Al_2Si_2O_7 \rightarrow Al_6Si_2O_{13} + 4SiO_2; \quad (VII)$$

$$2|Na_{12}|[Al_{12}Si_{12}O_{48}] \rightarrow 3Na_8Al_8Si_8O_{32}; \quad (VIII)$$

$$Na_8Al_4Si_4O_{18} + 2Al_2Si_2O_7 \rightarrow Na_8Al_8Si_8O_{32}. \quad (IX)$$
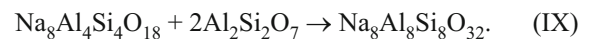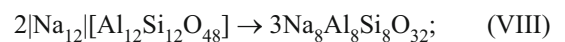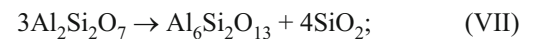
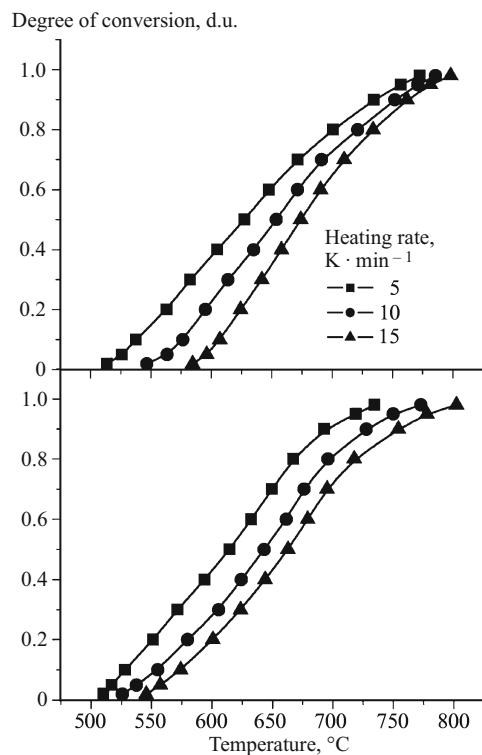**Fig. 3.** Degree of conversion versus temperature with different rates of heating for the mixtures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$; d.u.) dynamic units.

Fig. 4. Plots for calculating the effective activation energy by Friedman's method using Eq. (3) for the mixtures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$; numbers on straight lines — degree of conversion, d.u.

On calcination of a mixture with excess aluminum oxide $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$ the qualitative changes of phase composition (see Fig. 1*b*) are similar to the transformations in a stoichiometric mixture (see Fig. 1*a*). Nonetheless, there are certain differences. In the first place the amount of formed sodium aluminates $Na_6Al_4Si_4O_{17}$ and $Na_8Al_4Si_4O_{18}$ at temperatures up to 800°C in a mixture with excess Al_2O_3 is less, which is attested by the weaker intensities of the corresponding reflections. Moreover, any significant reflections due to mullite and nepheline appear only at 900°C, and even in this case their intensity is lower than in a stoichiometric mixture. Another difference is that in the mixture $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$ the mass losses in the temperature range 500 – 800°C are much larger (see Fig. 2). This could be associated with the fact that the free Al_2O_3 at the stage of USP and evaporation can be hydrated and form sodium hydro aluminates. However, the low degree of crystallinity makes it impossible to record these phases in the diffraction patterns.

For isoconversion kinetic analysis we chose the temperature range 500 – 800°C, where the reactions (III) – (VIII) occur. Since several successive and parallel reactions with different heat effects, which are also coupled with other processes, occur in this range, it is impossible to accurately draw a baseline in the DSC curves and determine the precise temperatures of onset and completion of the process (see Fig. 2). After the onset and completion temperatures of the process
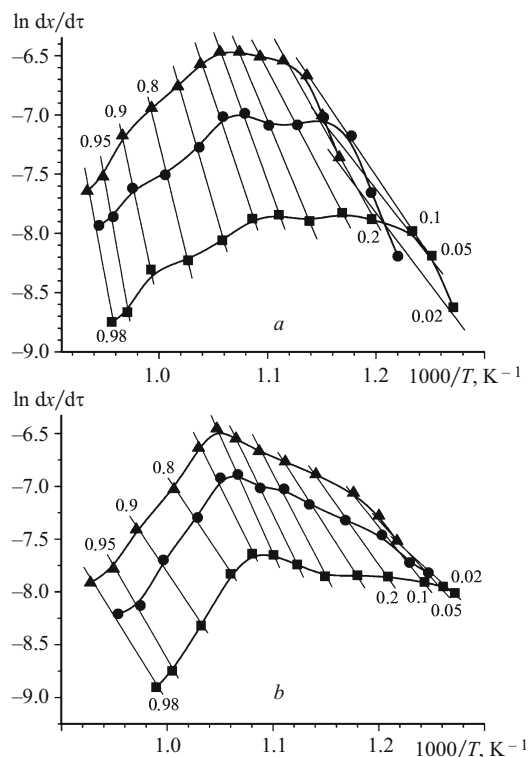
were determined using TG data Eq. (2) was used to calculate the transformation in terms of sodium hydroxide in the reactions (III) – (VI) for three heating rates (Fig. 3). A formal kinetic equation adequately describing the process could not be constructed. The data were processed by Friedman's differential method using Eq. (3) (Fig. 4) and the integral KAS method using Eq. (6) (Fig. 5).

The computational results for the effective activation energy versus the degree of conversion are presented in Fig. 6. Clearly, the differential and integral methods of analysis both give close results.

For a stoichiometric mixture, as the reactions proceed, for all values of the degree of conversion the effective activation energy changes very little and lies in the range $70 – 150 \, kJ \cdot mol^{-1}$ (see Fig. 6, *1a*, *2a*). This could attest that the process proceeds without a change of the mechanism.

For a mixture with excess Al_2O_3 and degree of conversion increasing to about 0.8 the values of the effective activation energy increase from 70 – 100 to 250 – 350 $kJ \cdot mol^{-1}$ (see Fig. 6, *2a*, *2b*). The values of E remain practically unchanged as the process proceeds ($x > 0.8$). This character of the dependence of E on x attests a change in the mechanism of the process as the process proceeds. In our view, this is associated with the presence of free Al_2O_3 in the system. As already mentioned, less mullite and nepheline are formed in
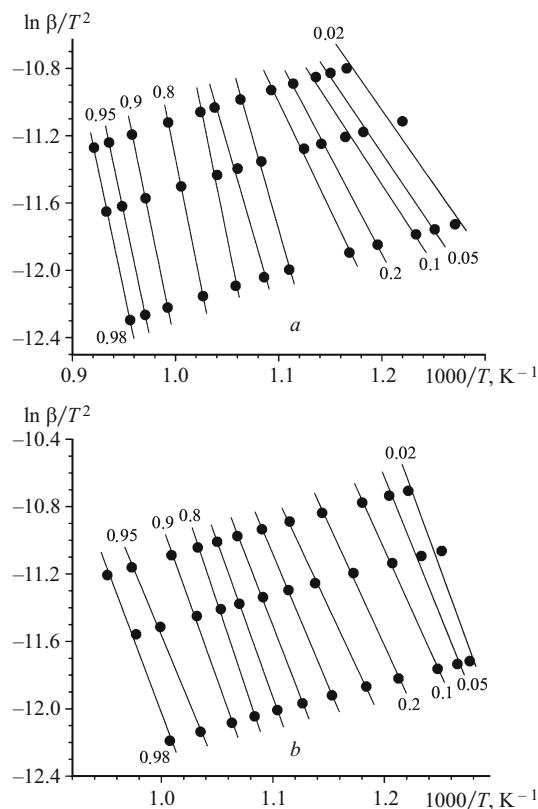
Fig. 5. Plots for calculating the effective activation energy by the KAS method using Eq. (6) for the mixtures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$; numbers on straight lines — degree of conversion, d.u.
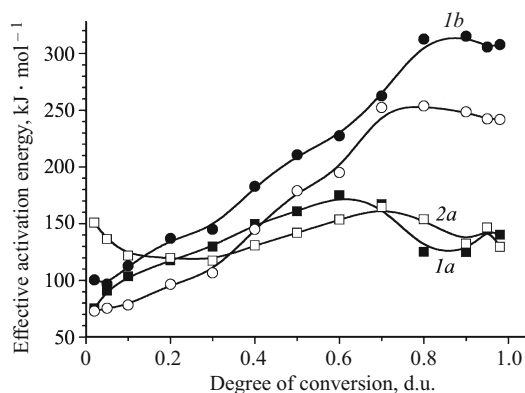

Fig. 6. Effective activation energy versus the degree of conversion, calculated by Friedman's (*1*) and KAS (*2*) methods, for the mixtures: *a*) $6Al_2Si_2O_7 : 12NaOH$; *b*) $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$.

synthesized upon heat-treatment above 500°C. As temperature rises above 700°C mullite and nepheline are formed, which is accompanied by vanishing of the zeolite LTA.

The values of the effective activation energy in the temperature range 500 – 800°C were calculated by the methods of Friedman and Kissinger–Akahari–Sonose on the basis of the data obtained from simultaneous thermal analysis. It was shown that both methods give close values of *E*. It was determined that excess Al_2O_3 above stoichiometry of the synthesis reaction of zeolite LTA causes the amount of formed mullite and nepheline to decrease and the values of the effective activation energy to increase, which made it possible to conclude that Al_2O_3 has an inhibiting effect in terms of undesirable reactions.

this mixture than in a stoichiometric one (see Fig. 1). Moreover, the values of the effective activation energy for the mixture $6Al_2Si_2O_7 : 12NaOH : 2Al_2O_3$ with $x > 0.5$ become greater than for the mixture $6Al_2Si_2O_7 : 12NaOH$ (see Fig. 6). Thus, it can be concluded that the presence of Al_2O_3 is a factor inhibiting the formation of mullite and nepheline. Since mullite and nepheline are the final products of thermal transformations in a mixture of MK and NaOH, and in contrast to $Na_6Al_4Si_4O_{17}$ and $Na_8Al_4Si_4O_{18}$ they cannot be converted into zeolites at the next stage of the hydrothermal crystallization, there is no doubt that their presence in the systems for synthesis of zeolites is extremely undesirable. Therefore, excess Al_2O_3 makes it possible ultimately to increase the yield of zeolites, as is indicated in [15, 20].

CONCLUSIONS

The phase transformations occurring during heat-treatment and the kinetics of the solid-phase processes in mixtures of metakaolin and sodium hydroxide were investigated. It was shown that on heating to about 500°C the zeolite LTA synthesized at the preceding stages of ultrasonic processing of suspensions and their evaporation undergoes degradation. It was determined that $Na_6Al_4Si_4O_{17}$ and $Na_8Al_4Si_4O_{18}$ are

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