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The study of the thermal behavior of solid mixtures of metakaolin and sodium hydroxide by isoconversional model-free analyzes

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ABSTRACT

Interactions in solid mixtures of $6Al_2Si_2O_7$: 12NaOH and $6Al_2Si_2O_7$: 12NaOH: $2Al_2O_3$ under thermal treatment were studied. Ultrasonic pre-treatment of suspensions with a frequency of 22 kHz was applied. X-ray phase analysis, scanning electron microscopy, and synchronous thermal analysis were used in this research. It was shown that after evaporation of the suspensions, the hydrated LTA zeolite and sodium hydroaluminate are synthesized. During thermal treatment up to 500 °C, the adsorption water is removed first and then the dehydration of the zeolite and hydroaluminate occurs. Calcination at temperatures above 500° C leads to the synthesis of $Na_6Al_4Si_4O_{17}$ and $Na_8Al_4Si_4O_{18}$ by the interaction of metakaolin and zeolite with sodium hydroxide. At temperatures above 700 °C, the formation of mullite and nepheline occurs in the temperature range of 500–800 °C. The kinetic parameters have been calculated using Friedman analysis (differential method), Kissinger–Akahira–Sunose and Ozawa-Flynn-Wall analyzes (integral methods). It was shown that all analyzes give similar dependences of the apparent activation energy vs the conversion extent and the values of E are in the range of 70–350 kJ mol^{-1}. It was established that ultrasonic pre-treatment allows to reduce the values of the apparent activation energy. It was discovered that the Al_2O_3 excess over the stoichiometry of the LTA zeolite synthesis is an inhibitor of the mullite and nepheline formation reactions.

1. Introduction

Zeolites are aluminosilicates of the family of microporous solid with regular cavities, called "molecular sieves" [1]. The crystal lattice of zeolites is formed by TO_4 tetrahedra (T = Si^{4+}, Al^{3+}, etc.). The excess charge (in the case of T = Al^{3+}) is compensated by metal cations (Na^+, K^+, Ca^{2+}, etc.). TO_4 tetrahedra form secondary building units (simple or double 4-, 6-, 8-membered rings, α- or β-cages, and others), of which the zeolites framework is assembled [2]. The types of zeolite framework and building schemes are also given on the web-site of the International Zeolite Association (IZA, http://www.iza-structure.org/).

The LTA (Linde Type A) zeolites are related to the low-silica zeolites with the Si:Al molar ratio close to 1 [2,3]. An empirical formula of the LTA zeolite is $|Me_x|[Al_{12}Si_{12}O_{48}]$, where Me is the metal cations. The structure of the LTA zeolite is formed from the simple β-cages which are composed of 24 T-atoms. The links of the β-cages appears through the double T4-rings D4Rs, and cavities in the zeolite framework (α-cages) are formed by the simple T8-rings S8Rs.

The atomic ratio of Si and Al in kaolin is the same as in the LTA zeolite and is about 1. For this reason, kaolin is widely used for the synthesis of LTA zeolite [4]. Under highly alkaline conditions, kaolin is not stable and is converted into various aluminosilicates. Usually cancrinite or other feldspathoids are the final products of the reaction [5,6]. LTA or SOD may be formed as intermediate products of the reaction [7]. For the zeolites synthesis, kaolin is usually converted by calcination to a more reactive phase of metakaolin ($Al_2Si_2O_7$) [8]. Metakaolin structure represents an amorphous mixture of silicon dioxides and aluminum trioxides [9]. Metakaolin is thermally stable up to 925 °C.

In the interaction of the metakaolin and NaOH solution, the LTA zeolite is synthesized [10]. This method allows to preparate zeolite only in powder form, which limits the use of zeolite in industry. To produce pellets, a binder (e.g., clay) should be added to the zeolite powder [11]. Of course, a binder will reduce the effectiveness of zeolite. Of course, a binder will reduce the effectiveness of zeolite application. To produce granular binder-free zeolites, kaolin or metakaolin is first moulded into balls or pellets, and then calcined at a temperature of 500–900 °C [12,13]. Subsequent hydrothermal crystallization in a solution of sodium hydroxide and sodium aluminate is characterized by multistage and long duration. The importance of thermal treatment during the formation of zeolites was also noted in Refs. [14,15]. However, all studies were

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Table 1
The composition of the starting mixtures.

Index	Substances, mol			Ratio		Substances, g/100 g		
	$Al_2Si_2O_7$	NaOH	Al_2O_3	SiO_2:Al_2O_3	Si:Al	$Al_2Si_2O_7$	NaOH	Al_2O_3
(i)	6	12	–	1:0.5	1:1	73.51	26.49	–
(ii)	6	12	2	1:0.67	1:1.33	66.07	23.81	10.12

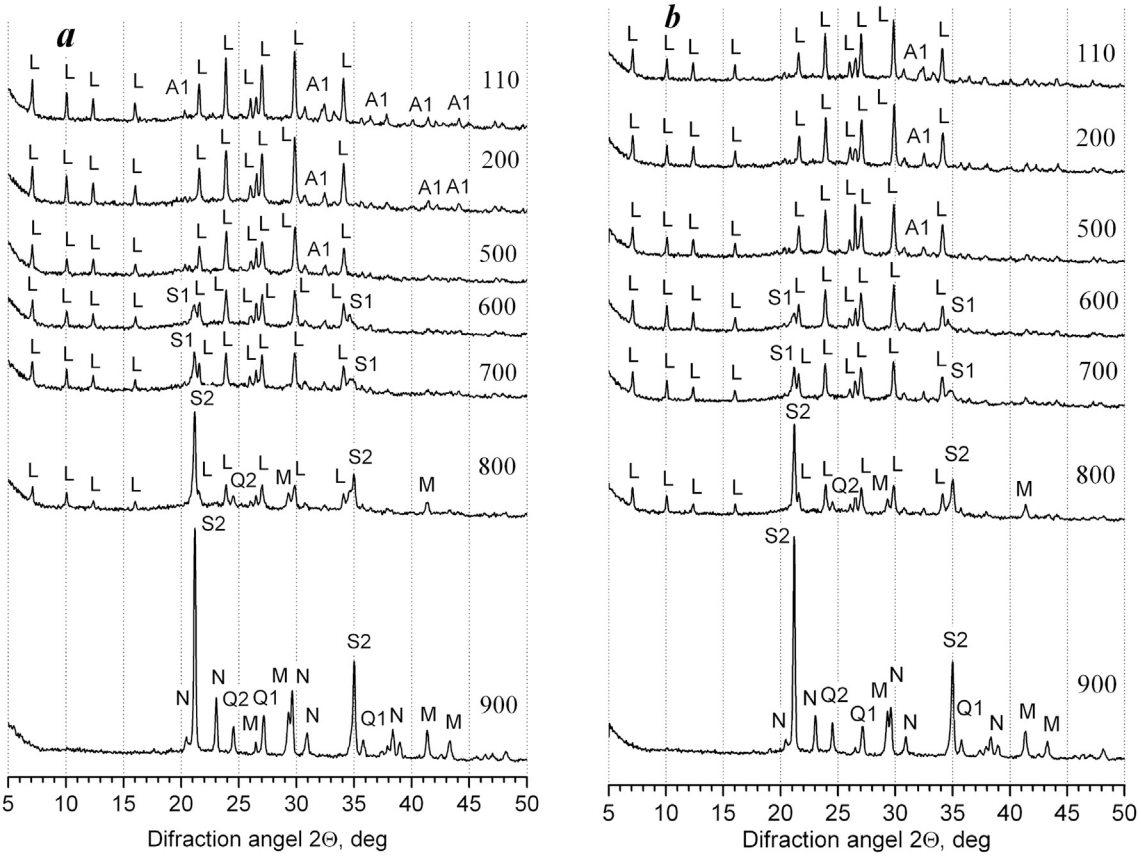

Fig. 1. XRD patterns of the mixture (i) $6Al_2Si_2O_7$: 12NaOH. Pretreatment: *a*) WPT; *b*) UST. The numbers about the diffractograms are the temperatures of the thermal treatment (°C). A1 is sodium hydroaluminate $Na_2Al_2O_4{\cdot}(H_2O)_{2.5}$ (ASTM PDF #410638); L is LTA zeolite $|Na_{12}(H_2O)_{27}|[Al_{12}Si_{12}O_{48}]$ (IZA database); M is mullite $Al_6Si_2O_{13}$ (ASTM PDF #021160); N is nepheline $NaAlSiO_4$ (ASTM PDF #191176); Q1 is quartz SiO_2 (ASTM PDF #791912); Q2 is silicon dioxide SiO_2 (ASTM PDF #821574); S1 is sodium aluminosilicate $Na_6Al_4Si_4O_{17}$ (ASTM PDF #100033); S2 is sodium aluminosilicate $Na_8Al_4Si_4O_{18}$ (ASTM PDF #762386).

Table 2
a parameters (Å) of unit cell of the LTA zeolite depending on the temperature.

Temperature, °C	(i) $6Al_2Si_2O_7$: 12NaOH		(ii) $6Al_2Si_2O_7$: 12NaOH: $2Al_2O_3$	
	WPT	UST	WPT	UST
110	24.680	24.671	24.693	24.648
200	24.665	24.626	24.675	24.641
500	24.639	24.657	24.675	24.660
600	24.665	24.662	24.683	24.668
700	24.675	24.680	24.697	24.679

focused on the change in composition of the solid phase only.

Granular binder-free zeolites were also synthesized from a mixture of metakaolin and solid sodium hydroxide [16,17]. For the intensification of solid-phase processes, mechanochemical activation and ultrasonic treatment were applied. Here the thermal treatment stage of the pellets was also used. At this stage, the strength of the pellets increases, and precursors for the following synthesis of zeolites are formed. However, only the optimal conditions for thermal treatment were determined, but no detailed study of the thermochemical processes was carried out. In Refs. [18,19], the routes of transformation of zeolites under heat treatment was investigated. It was shown that hexagonal nepheline and monoclinic trinephrine are formed upon temperatures above 950 °C.

Nonisothermal methods have found wide application for studying the kinetics of processes in solid [20]. In conditions with a linear regime of temperature increase in time:

$$\beta = dT/d\tau = constant, \quad (1)$$

where β is the heating rate; T is the temperature; τ is the time.

Then the reaction rate in the solid is described by a well-known general equation [21]:

$$dx/d\tau = \beta dx/dT = Af(x)\exp(-E/RT), \quad (2)$$

where x is the conversion extent; $f(x)$ is the differential conversion function; A is the pre-exponential factor in the Arrhenius's equation; E is the activation energy; R is the gas constant.

The conversion extent according to thermogravimetric measurements can be calculated as:

$$x_j = \big(m(\tau_s) - m(\tau_j)\big)/\big(m(\tau_s) - m(\tau_f)\big), \quad (3)$$