

# Nonhydrothermal Synthesis and Properties of Saponite-Like Materials

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INORGANIC SYNTHESIS  
AND INDUSTRIAL INORGANIC CHEMISTRY

Nonhydrothermal Synthesis and Properties  
of Saponite-Like Materials

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**Abstract**—Main features of nonhydrothermal synthesis of saponite-like materials containing Zn(II) and Mg(II) cations in octahedral networks were studied. Optimal conditions for the synthesis were determined. The influence exerted by the double-charged structure-forming cation on the rate of structure formation in the synthesized materials and also on their pore structure and thermal stability was studied.

Unique catalytic and adsorption properties of natural clay minerals are known and are a subject of numerous papers [1]. However, nonuniformity of the chemical composition and pore structure and a considerable content of impurities considerably limit their application in catalysis [2]. At the same time, synthetic clays have homogenous composition and structure, and their physicochemical properties can be controlled already in the stage of their preparation [2–4]. This fact, and also the possibility for the directional synthesis of materials having no natural analogs open new prospects for catalytic applications [5–8].

Synthetic clays are usually prepared under hydrothermal conditions (5–17 MPa, 423–773 K) [9] using special expensive autoclaves, which considerably limits applications of these materials. Therefore, it is urgent to develop alternative procedures for their preparation, among which the nonhydrothermal synthesis (synthesis under normal pressure) is the most promising [5]. The applicability of this procedure to obtaining saponite-like materials was shown in [5–8]. The key moment in the process is the use of urea as a hydrolyzing agent; its thermally initiated decomposition makes it possible to smoothly vary pH of the reaction medium [10] and thus to control the hydrolysis rate and hence the formation of the target material [5–7]. However, detailed information on the features of the nonhydrothermal preparation of synthetic clays is lacking.

Clay minerals included in the group of natural layered aluminosilicates are formed mainly from two structural fragments, namely, the networks of silicon-

oxygen tetrahedra  $\text{SiO}_4$  (*T*-network) and of aluminum–oxygen octahedra  $\text{Al}(\text{O}, \text{OH})_6$  (*O*-network) [11]. These networks are joined through  $\text{O}^{2-}$  ions into layers, which form the basis of the unit cell of the minerals. The structure of smectites, including saponite, is formed by layers separated by interlayer intervals, in which two *T*-networks are joined with an *O*-network lying between them (*T*–*O*–*T* minerals). The isomorphous substitutions, e.g.,  $\text{Al}(\text{III}) \rightarrow \text{Si}(\text{IV})$ , in the *T*-networks give rise to an excessive negative charge which is compensated by either positive charges localized in the *O*-networks or charges of cations arranged in interlayer spaces [1, 2, 11]. The idealized formula of saponite is  $\text{M}_{x/z}^{z+}[\text{Mg}_6](\text{Si}_{8-x}\text{Al}_x) \cdot \text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , where M are exchange (interlayer) cations; cations in the composition of the *O*-network are given in brackets; ions in tetrahedral networks are given in parentheses;  $x = 1.2$  [11]. This mineral is of considerable interest for heterogeneous acid catalysis [2, 5, 6], because its surface has enhanced acidity owing to the isomorphism  $\text{Al}(\text{III}) \rightarrow \text{Si}(\text{IV})$  in the *T*-networks.

The aim of this work was to reveal the main features of the synthesis of Zn- and Mg-containing synthetic analogs of natural saponite under nonhydrothermal conditions and to study their physicochemical properties.

EXPERIMENTAL

The objects of this study were synthesized by a procedure close to that described in [5–8]. We used

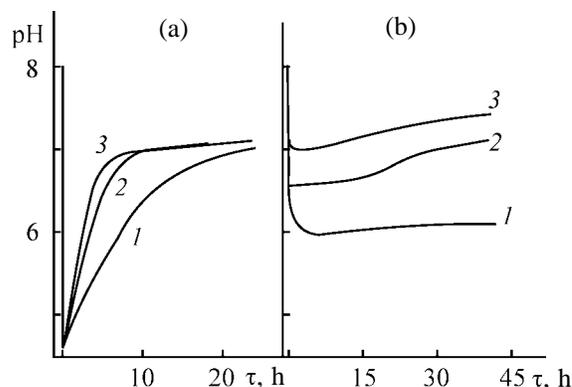
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  (27 wt %  $\text{SiO}_2$ ),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as sources of Si(IV), Al(III), and double-charged cations.

The synthesis procedure is described for a sample with the atomic ratio Si(IV)/Al(III) = 12 as example. An  $\text{Al}(\text{OH})_4^-$  sol was prepared by dissolution of 4.22 g (11.25 mmol) of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 2 M NaOH (28  $\text{cm}^3$ ). Then this sol was added in portions with vigorous stirring to a solution of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  (30.0 g, 0.135 mol) in 75  $\text{cm}^3$  of demineralized water. The resulting gel was kept at room temperature for 1 h without stirring, suspended with stirring in 600  $\text{cm}^3$  of  $\text{H}_2\text{O}$ , and heated to 363 K. Then 500  $\text{cm}^3$  of a separately prepared aqueous solution containing 32.60 g (0.109 mol) of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [or 28.1 g of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.109 mol)] and  $\text{CO}(\text{NH}_2)_2$  (0.15–0.80 mol) was added to the heated gel suspension. The addition rate was selected so that the temperature of the reaction mixture did not decrease by more than 10 K. This mixture was heated at 363 K for 3–72 h with continuous stirring. The resulting solid phase was separated by filtration, washed with five portions of distilled water, and dried for 12 h at 383 K. The samples containing Zn(II) and Mg(II) cations in octahedral networks are denoted as Zn-SP and Mg-SP, respectively.

The pH of the reaction medium was monitored with a CG804 (Schott–Gerade) pH-meter with automatic data recording. The  $^{27}\text{Al}$  NMR spectra were obtained in the magic angle spinning mode on a Bruker AMX 300 WB spectrometer (standard  $\text{ZrO}_2$  rotor, magnetic field frequency 78.20 MHz). The  $^{27}\text{Al}$  chemical shift was determined relative to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . The X-ray diffraction (XRD) patterns of the synthesized materials were taken on DRON-3 and Philips 1170 diffractometers ( $\text{CuK}\alpha$  radiation,  $\lambda = 0.154178$  nm, Ni filter). The adsorption–desorption isotherms of nitrogen (77 K) were obtained on an ASAP 2010 (Micromeritics) adsorption installation using samples preliminarily evacuated for 5 h at 473 K and a pressure of  $10^{-2}$  Pa. The IR spectra of samples prepared as pellets in thoroughly dried KBr (1 : 60) were recorded on Specord-M80 and FTIR Perkin–Elmer 2000 spectrophotometers.

The content of Mg(II), Zn(II), and Al(III) cations was determined by atomic absorption spectroscopy (Perkin–Elmer PE 3030 spectrophotometer). The cation-exchange capacity (CEC) of the synthesized materials was determined according to [12] by adsorption of a copper(II) ethylenediamine complex at pH 7.

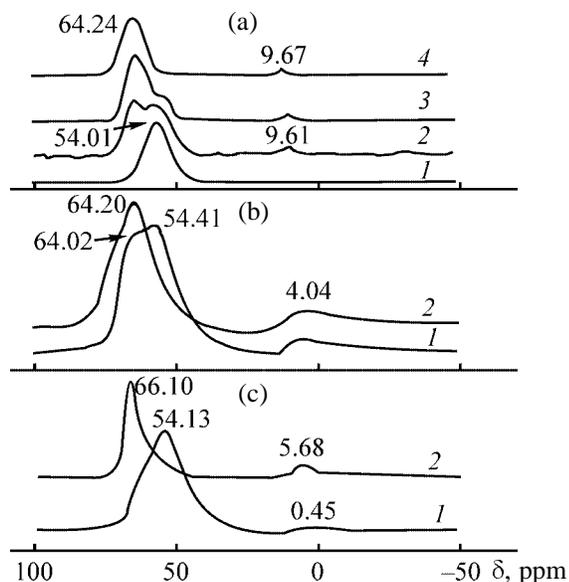
The experimental dependences of pH of the medium on the synthesis time (Fig. 1) have no pronounced



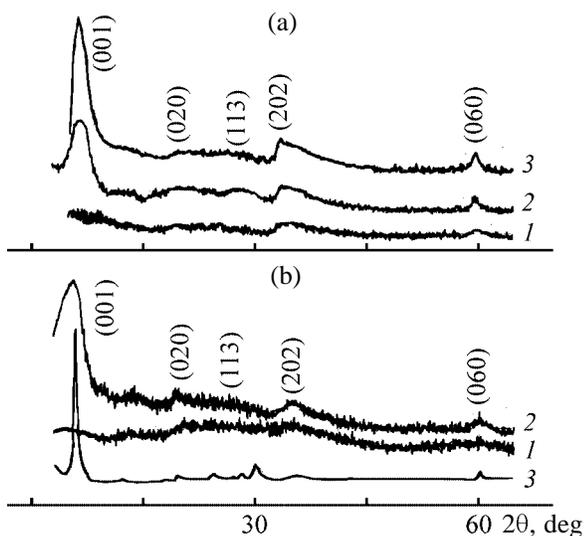
**Fig. 1.** Variation with synthesis time  $\tau$  of pH of the reaction medium at various urea concentrations. Sample: (a) Zn-SP and (b) Mg-SP; the same for Fig. 3.  $\text{CO}(\text{NH}_2)_2$  concentration, M: (1) 0.15, (2) 0.45, and (3) 0.80.

extrema, which suggests smooth nucleation and growth of particles of the synthesized materials. It is most probable that the decrease in pH observed in the initial moment of the reaction is due to the formation of  $\text{Zn}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  phases. A considerable difference in the initial pH values during the syntheses of Zn-SP and Mg-SP may be due to different solubility of these hydroxides, which is much higher in the case of  $\text{Mg}(\text{OH})_2$ .

The  $^{27}\text{Al}$  NMR spectra of the starting gels used for the synthesis of Zn-SP and Mg-SP contain a resonance of tetrahedrally coordinated Al(III) cations [Al(III)(tetr.)] with a chemical shift  $\delta$  about 54 ppm (Fig. 2). At the reaction time of 3 h, a signal of octahedrally coordinated Al(III) ( $\delta = 10$  ppm) and a shoulder with  $\delta = 64$  ppm assignable to Al(III)(tetr.) are observed in the spectrum of Zn-SP. The latter signal is characteristic of Al(III) cations localized in tetrahedral networks of smectites (Al–O–Si bonds) [13]. When the syntheses time increases to 12, and especially to 24 h, the intensity of this resonance considerably increases, which is accompanied by the disappearance of the signal with  $\delta = 24$  ppm (Fig. 2a). In this case, the change in the urea concentration within these limits affects the parameters of the  $^{27}\text{Al}$  NMR spectra only slightly. Nevertheless, the strongest signal of Al(III)(tetr.) was observed for a sample prepared in the presence of 0.45 mol of  $\text{CO}(\text{NH}_2)_2$ . The data obtained suggest that the incorporation of Al(III) cations into the crystal lattice of Zn-SP is practically complete within approximately 24 h. In the case of Mg-SP, this process is much slower, and a weak signal of Al(III)(tetr.) with  $\delta$  about 64 ppm was detected only at the reaction time of 30 h. Its intensity considerably increases as the synthesis time is increased



**Fig. 2.**  $^{27}\text{Al}$  NMR spectra of synthesized materials. ( $\delta$ ) Chemical shift. Sample: (a) Zn-SP and (b, c) Mg-SP; the same for Fig. 4. Synthesis time  $\tau$  (h): (a) (1) 0.5, (2) 3.0, (3) 12, and (4) 24; (b) (1) 30 and (2) 36; (c) (1, 2) 36.  $\text{CO}(\text{NH}_2)_2$  concentration, M: (a, b) 0.45 and (c) 0.80.



**Fig. 3.** Diffraction patterns of materials prepared at various synthesis times. ( $2\theta$ ) Bragg's angle. Synthesis time  $\tau$ , h: (a) (1) 3.0, (2) 12, and (3) 24; (b) (1) 5.0; (2) 36, and (3) natural saponite (Ballarat).

to 36 h (Fig. 2b). In this case, the amount of urea and hence the pH value crucially affect the course of Al(III) incorporation into the tetrahedral network of the synthesized material (Fig. 2c).

The increase in the Si(IV)/Al(III) atomic ratio in the reaction gel from 5 to 12 results in an appreciable decrease in the content of octahedrally coordinated

Al(III), with the content of Al(III)(tetr.) remaining virtually unchanged. Therefore, we can conclude that saponite-like materials with preferential Al(III) localization in the tetrahedral networks (a characteristic feature of this smectite [3, 5]) can be obtained under non-hydrothermal conditions only at  $\text{Si(IV)/Al(III)} \geq 12$ . Therefore, further experiments were performed using samples with the Si(IV)/Al(III) atomic ratio of 12 and Mg-containing materials synthesized in the presence of 0.80 mol of urea.

The X-ray diffraction analysis has shown that, in the case of Zn-SP, a certain amount of a saponite-like phase is formed within 3.0–3.5 h. As the synthesis time is increased to 12 h, its amount and the crystallinity of the resulting material increase (Fig. 3a), as indicated by the growth of the intensity of the long-range order basal reflections (020/110) and (113) [4, 6]. At the reaction time increased to 24 h, the X-ray peaks become narrower, and the intensity of the first basal reflection [ $d(001)$ ] considerably increases. At the synthesis time of 36 h the shape of X-ray diffraction patterns undergoes no significant changes, suggesting that the crystallization of Zn-SP is complete within 24 h. The macrostructure of this material is formed by crystallites with fairly large particles connected to each other predominantly by a plane–plane motif, as indicated by considerable intensity and symmetry of basal reflections [4, 5, 14, 15].

The X-ray diffraction patterns of Mg-saponite obtained at various synthesis times are given in Fig. 3b. They show that the structure of this material is formed much more slowly than that of Zn-SP. At a reaction time of 5 h only weakly pronounced reflections (060) and (201) are detected. The diffraction pattern of Mg-SP synthesized in 36 h contains all the basal reflections characteristic of saponite [4, 14]. However, the corresponding peaks remain fairly broad, with the value of  $d(001)$  being greater than for Zn-SP (Fig. 3b). Further prolongation of the synthesis (to 72 h) only slightly affects the intensity and width of the X-ray peaks. It should be noted that it is almost impossible to obtain X-ray patterns for Mg-SP using nonoriented samples. This fact suggests that the macrostructure of this material is formed by small particles, the majority of which are connected to each other by a plane–facet or facet–facet motif [4]. Such a structure is called “house of cards” or delaminated [2, 16]; its formation was noted earlier in the case of low-temperature syntheses of others trioctahedral Mg-containing clays [15].

The capability to swell in polar media, in particular, in ethylene glycol vapor, is a characteristic feature

Pore structure parameters, elemental composition, and exchange capacity of synthetic saponite-like materials

Sample	$\tau,^* \text{ h}$	$S_{\text{BET}}, \text{ m}^2 \text{ g}^{-1}$	$V_{\text{lim}}$	$V_{\text{micro}}$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{M}^{2+}\text{O}$	CEC, $\text{mg-equiv g}^{-1}$
			$\text{cm}^3 \text{ g}^{-1}$		wt %			
Zn-SP	12	142.24	0.162	0.003	35.30	2.45	38.96	0.97
	24	218.72	0.183	0.004	35.25	2.49	38.86	1.20
Mg-SP	24	599.50	0.625	0.150	48.24	3.40	26.33	0.82
	36	592.14	0.323	0.280	48.20	3.43	25.10	1.25

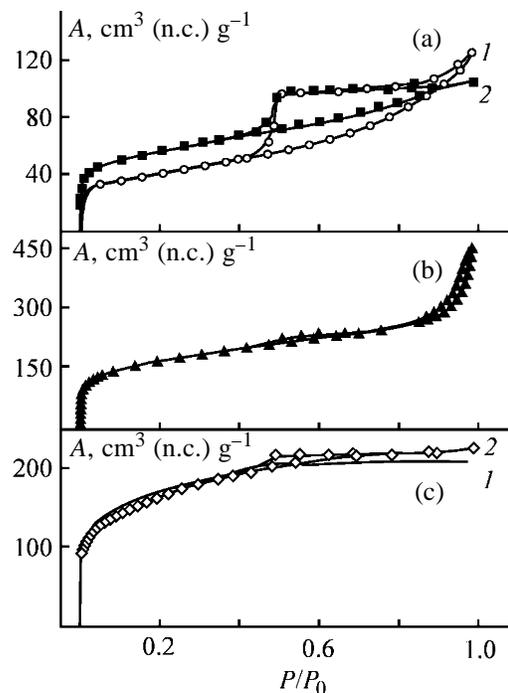
\* ( $\tau$ ) Synthesis time.

of smectites [1]. We found that Zn-SP samples synthesized in 3 or 24 h have this property, as seen from an increase in the size of their interlayer space  $\Delta d$ ; in the sample prepared in 24 h, this effect is more pronounced. Among the Mg-SP materials, the swelling was detected only for samples synthesized in more than 30 h. These observations agree with the assumption that the crystallization of Zn-containing saponite is practically complete in 24 h, whereas the formation of the Mg-SP structure requires a longer time. Furthermore, the nature of the structure-forming double-charged cation appreciably affects the value of  $\Delta d$ . In the case of Mg-SP samples, it is greater by 0.3–0.4 nm than that in their Zn-containing analogs. This may be due to the effect of a smaller size of Mg-SP crystallites and also to weaker electrostatic interaction of its silicate layers [14]. In view of these facts, we further studied the Zn-SP samples synthesized in 12 and 24 h and the Mg-SP samples synthesized in 24, 36, and 72 h.

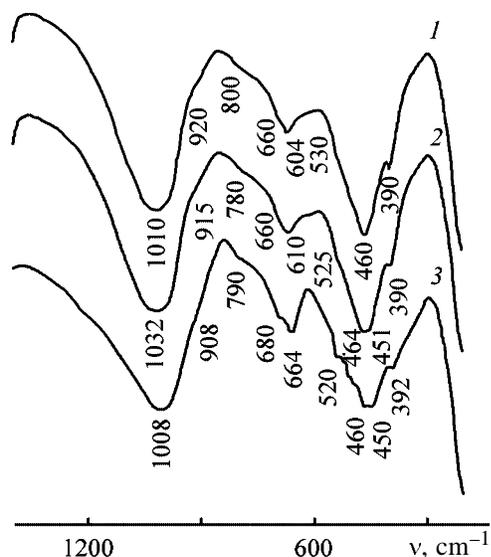
The isotherms of  $\text{N}_2$  adsorption–desorption for the Zn-containing materials (Fig. 4a) can be assigned to type IV according to the IUPAC classification [17]. This is indicative of the predominantly mesoporous structure [18]. The observed shape of the hysteresis loop (mixed type H4 + H2 [17–19]) is indicative of the presence of slit- and bottle-like pores [19]. The increase in the synthesis time from 12 to 24 h only slightly affects the shape of the isotherms and the parameters of the pore structure of Zn-SP samples (see table; Fig. 4a). In the case of Mg-containing materials, these parameters, as well as the shape of the isotherms of nitrogen adsorption, strongly depend on the synthesis time (see table; Fig. 4b). The sample obtained in 24 h is mainly mesoporous (type IIb isotherm [15]). Taking into consideration the NMR and XRD data, we can explain this fact by the presence of an amorphous phase. For materials prepared in a longer time (36–72 h), the adsorption isotherms differ insignificantly, and they can be assigned to distorted

type I [20], which is characteristic of microporous substances [18–20]. A narrow hysteresis loop (Fig. 4b) close to the H4 type [18] points to the presence of slit-like pores. Similar isotherms were obtained for synthetic laponite, a mineral with a delaminated structure [20]. Therefore, we can suggest that the macrostructures of Mg-SP and laponite are similar to each other, which also agrees with the above-given XRD data. Thus, we can conclude that the formation of the pore structure of Mg-containing saponite is complete in 36 h.

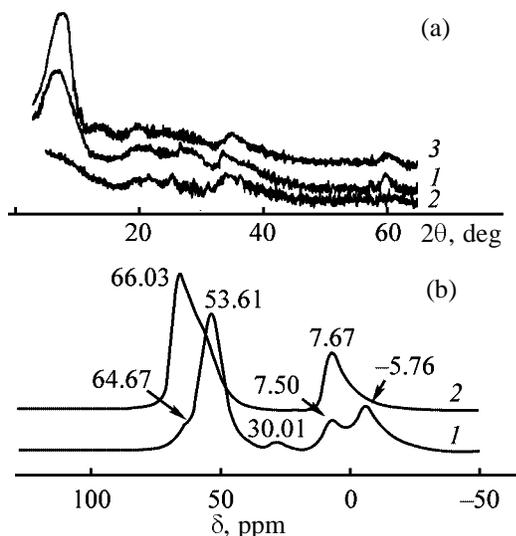
The nature of double-charged cations strongly affects the size and volume of pores and the specific surface area of the synthesized clays (see table). Sam-



**Fig. 4.** Nitrogen adsorption–desorption isotherms. (A) Sorbed volume and ( $P/P_0$ ) relative pressure. Synthesis time  $\tau$ , h: (a) (1) 12 and (2) 24; (b) 24; (c) (1) 36 and (2) 72.



**Fig. 5.** IR spectra of samples. ( $\nu$ ) Wave number. Sample: (1) Zn-SP, (2) Mg-SP, and (3) natural saponite (Ballarat).



**Fig. 6.** (a) Diffraction patterns and (b)  $^{27}\text{Al}$  NMR spectra of calcined samples. ( $2\theta$ ) Bragg's angle and ( $\delta$ ) chemical shift. Sample: (a) (1, 2) Zn-SP and (3) Mg-SP; (b) (1) Zn-SP and (2) Mg-SP.  $T$ , K: (a) (1) 673, (2) 773, and (3) 873; (b) (1) 773 and (2) 873.

ples of Zn-SP are mainly mesoporous, whereas Mg-containing saponite-like materials are microporous.

The IR spectra of Zn-SP and Mg-SP samples in the region of lattice vibrations are given in Fig. 5. It is seen that the nature of the structure-forming double-charged cation affects the position of the maximum of the strong band near  $1020\text{ cm}^{-1}$  (Si–O–Al bending vibrations [13, 21]). Less intensive absorption bands at  $915\text{--}920$ ,  $800\text{--}780$ , and  $660\text{--}620\text{ cm}^{-1}$  are assignable to the Si(Al)–O, Si–O–Al, Al–OH–Mg, and Si–

O–Mg vibrations, respectively [11, 18]. The bands of the Mg(Zn)–OH, Si–O–Mg, or Si–O–Zn vibrations ( $550\text{--}527$  and  $460\text{--}440\text{ cm}^{-1}$ ) are also present in the IR spectra [13, 22]. All these absorption bands are characteristic of lattice vibrations of trioctahedral smectites [21, 22], including natural saponite (see spectrum of the reference sample). The chemical compositions of the synthesized materials and their cation–exchange capacities (see table) also agree with the corresponding published data for this clay mineral [14, 22].

Summarizing the data obtained, we can conclude that the optimal parameters of the Zn-SP synthesis are the time of 24 h and the urea concentration in the reaction mixture of 0.45 M, whereas for the synthesis of its Mg-containing analog these are 36 h and 0.80 M, respectively.

The thermal stability is one of the major characteristics of heterogeneous catalysts [23]. As the substances studied in this work can be potentially used in high-temperature catalytic reactions [4–8], it seemed important to study the stability of their structure at elevated temperatures. We heated the samples stepwise in an air flow in the range  $298\text{--}1073\text{ K}$  at a rate of  $5\text{ deg min}^{-1}$ , with keeping at selected temperatures for 18 h. The structural transformations were monitored by XRD and  $^{27}\text{Al}$  NMR.

The results obtained are shown in Fig. 6. It is seen from the X-ray patterns (Fig. 6a) that the calcination of Zn-SP at  $623\text{ K}$  makes its structure amorphous to a considerable extent, and at  $773\text{ K}$  its crystallinity is virtually fully lost. The NMR spectrum appreciably changes in the process (Fig. 6b). The signal at  $\delta = 64\text{ ppm}$  [Al(III)(tetr.)] becomes considerably less symmetric. The computer resolution of this signal has shown that it is a superposition of two signals with  $\delta 62$  and  $56\text{ ppm}$ . The latter signal is assignable to the Al(III)(tetr.) resonance in an amorphous phase. Simultaneously, a weak signal appears in the NMR spectrum near  $30\text{ ppm}$ , which is assignable to the resonance of five-coordinate Al(III) [24]. In the case of Mg-SP, the calcination at temperatures of up to  $873\text{ K}$  does not make its structure amorphous to a noticeable extent (Fig. 6a), and the shape of the  $^{27}\text{Al}$  NMR spectra does not change appreciably (Fig. 6b). As the temperature is increased further to  $973\text{ K}$ , the Al(III)(tetr.) signal becomes less symmetric, suggesting partial degradation of the crystal structure. Thus, Mg-SP is more thermally stable than its Zn-containing analog. This may be due to the effect of the size of the double-charged cation forming the octahedral networks of synthetic saponite. It was

shown in the case of trioctahedral micas that the minerals containing structure-forming cations with large ionic radii have a lower thermal stability [25].

It should be specially noted that the temperatures at which the structures of the synthesized materials degrade are higher than those known for natural saponites. This fact once again demonstrates prospects for using synthetic clays as heterogeneous catalysts.

### CONCLUSIONS

(1) Experiments on optimization of the conditions for preparing of Zn- and Mg-containing synthetic analogs of natural trioctahedral smectite (saponite) under conditions of nonhydrothermal synthesis showed that the preferential localization of Al(III) cations in the tetrahedral networks of these materials is possible only at the atomic ratios Si(IV)/Al(III)  $\geq 12$ .

(2) The rate of formation of the structure of M(II)-containing synthetic saponites [the process is complete in 24 h for Zn(II) and 36 h for Mg(II)], the parameters of their pore structure, and the macrostructure and thermal stability depend on the nature of the structure-forming cation [Zn(II) or Mg(II)]. Synthetic Mg-saponite has a large specific surface area ( $650 \text{ m}^2 \text{ g}^{-1}$ ) and a high thermal stability (up to 973 K).

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