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Mechanochemical Synthesis of Organically Modified Magnesium Silicate

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Abstract—Magnesium silicate modified with hexadecyltrimethylammonium cations was synthesized by mechanochemical treatment of a mixture of magnesium hydroxide, silica xerogel, lithium fluoride, and hexadecyltrimethylammonium bromide. The X-ray diffraction analysis, scanning electron microscopy, and differential scanning calorimetry examinations and thermogravimetric analysis showed that variation of the synthesis conditions led to the formation of products differing both in the degree of structural order and in the particle size.

Keywords: organically modified magnesium silicate, mechanochemical synthesis, hexadecyltrimethylammonium bromide

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Layered silicates modified with cationic surfactants are promising sorbents for water and soil purification [1, 2] and precursors for preparation of mesoporous materials [3]. Organically modified layered silicates are currently used as rheological additives in drilling fluids and greases, as well as in the manufacture of inorganic polymer compositions, paints and varnishes, and cosmetics [2–5].

The classical synthetic route to organically modified layered silicates is based on replacement of the interlayer cations of natural or synthetic silicate by organic cations using liquid-phase ion exchange method [4, 6, 7]. Alternative methods of preparation of such systems are based on the use of mechanochemical [4, 7] or sol-gel processes [3, 6, 8]. Advantages offered by mechanochemical synthesis methods are the easy implementation and high performance at relatively low cost, as well as minimized, or absent, adverse environmental impact due to the fact that the process is run with the use of minimum amounts of solvent or under solvent-free conditions [9]. These advantages make mechanochemical technologies attractive for commercial applications.

Mechanochemical treatment of natural montmorillonite under solvent-free conditions in the presence of an organic modifier was carried out for the first time in 1989 [10]. A similar procedure was employed for modification of montmorillonites with n-alkylammonium halides in [11] and elsewhere. In 1995, mechanochemical treatment of bentonite with a quaternary ammonium salt was carried out in the presence of a minimum amount of solvent (water) in a high-shear mixer [12].

Mechanochemical synthesis of layered magnesium silicates [13–16] can be performed effectively by the soft mechanochemical route, where mixtures of solid compounds containing hydroxyl groups and bound water (hydroxides, acids, basic and acidic salts, crystal hydrates) are subjected to mechanical activation [17].

To date, there are no published reports on simultaneous mechanochemical synthesis of magnesium silicate and its modification by organic compounds. We carried out mechanochemical synthesis of magnesium silicate modified with a quaternary amine and characterized the resulting substance.

Discrete mechanochemical treatment of the initial mixture without water addition for 40 h (Fig. 1) leads to a decrease in intensity and broadening of the reflections from magnesium hydroxide (d_{001} = 4.76, d_{100} = 2.72, d_{101} = 2.36, d_{102} = 1.79, d_{110} = 1.57, d_{111} =

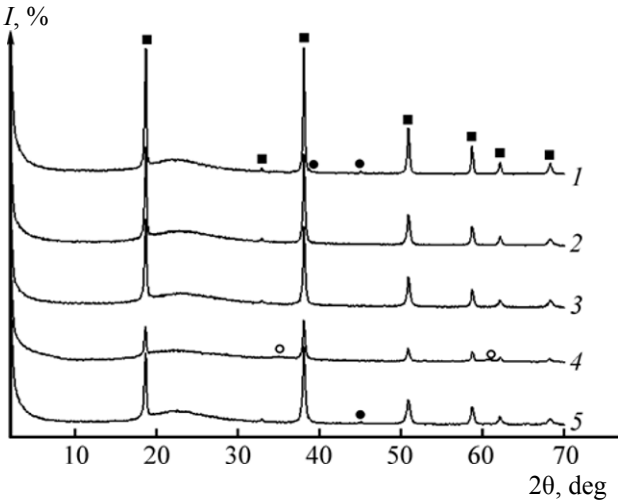

Fig. 1. X-ray diffraction patterns of (*1*) initial mixture and (*2–5*) products of mechanochemical discrete treatment of the component mixture (without water addition) for (*2*) 12, (*3*) 25, (*4*) 40, and (*5*) 65 h. (■) $Mg(OH)_2$, (○) synthetic hectorite, and (●) LiF.

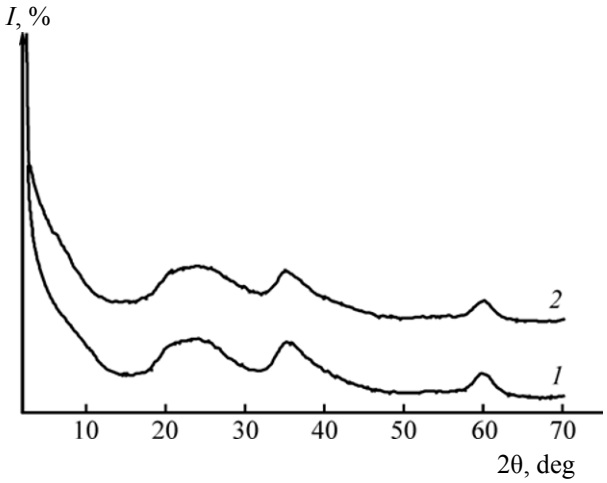

Fig. 2. X-ray diffraction patterns of the products of mechanochemical treatment of the component mixture (with water addition) in (*1*) discrete (70 h) and (*2*) continuous (50 h) modes.

1.49, d_{103} = 1.37 Å), the disappearance of reflections from lithium fluoride (d_{111} = 2.32, d_{200} = 2.01 Å), and the appearance of weak reflections from the magnesium silicate (synthetic hectorite) phase ($d_{130,200}$ = 2.53, d_{060} = 1.52 Å). With increasing treatment time the reflections from hectorite disappear, those from magnesium hydroxide increase in intensity, and a reflection from lithium fluoride appears as a consequence of degradation of the magnesium silicate phase. For the synthesis procedure in the continuous mode without water addition the same result was obtained, specifically, the onset of formation and subsequent complete degradation of the magnesium silicate phase. The formation of the hectorite phase during mechanochemical treatment of the reaction mixture without water addition proceeds as long as the system contains sorbed water. During further treatment the process is decelerated, and the intensity of the mechanical energy supplied proves sufficient for the degradation of the magnesium silicate phase to occur.

The (060) reflection from the samples mechanochemically synthesized in the discrete and continuous modes with water addition is indicative of the formation of a silicate layer proper (Fig. 2). In the X-ray diffraction pattern of the sample obtained in the discrete mode with water addition there is no clear reflection at small angles. At the same time, in the pattern of the sample prepared in the continuous mode there is a clear low-intensity reflection in the small-angle region, corresponding to d_{001} interplanar spacing of 14.57 Å, indicating that the silicate layers are stacked into "packets."

According to published data [4], certain values of d_{001} interplanar spacing for organically modified layered silicate correspond to particular orientations taken by the organic cations in the interlayer space of the silicates: 14 Å for the horizontal monolayer orientation, 18 Å for the horizontal bilayer orientation, and 22 Å for the pseudo-triple-layer orientation. The comparison of our results (d_{001} = 14.57 Å) with the published data (d_{001} = 14 Å) is indicative of the horizontal monolayer orientation of the hexadecyltrimethylammonium cations in the sample synthesized in the continuous mode with water addition. Certain difference between the interplanar spacing value determined by us and that reported in the literature is evidently due to the difference in the methods used for preparation of organically modified products.

The scanning electron microscopic examination showed that the samples synthesized in both the discrete and continuous modes are characterized by a homogeneous phase composition and consist of spherically-shaped particles, among which those measuring less than 1 μm dominate (Fig. 3). The sample synthesized in the continuous mode comprises particles that exceed in size (up to 4–5 μm) those of the sample obtained in the discrete mode (1–2 μm) (Fig. 3).

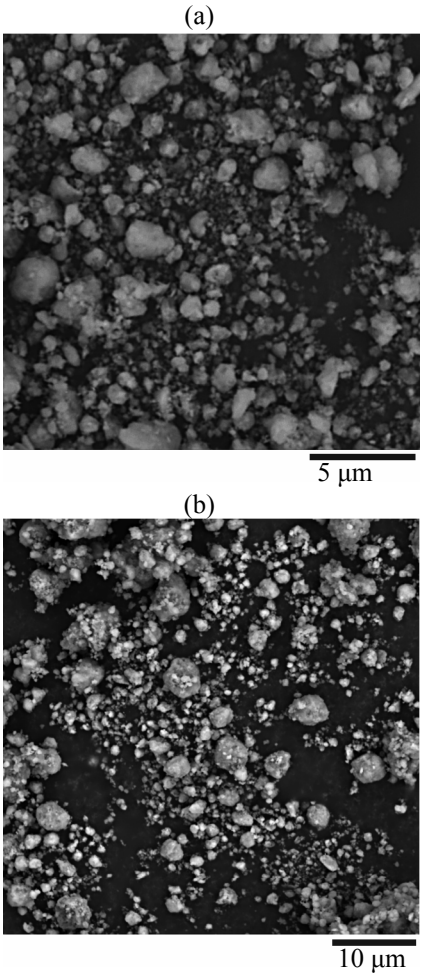

Fig. 3. Scanning electron microscopic images (produced by elastically scattered electrons) of the products of mechanochemical treatment of the component mixture (with water addition) in (a) discrete and (b) continuous mode.

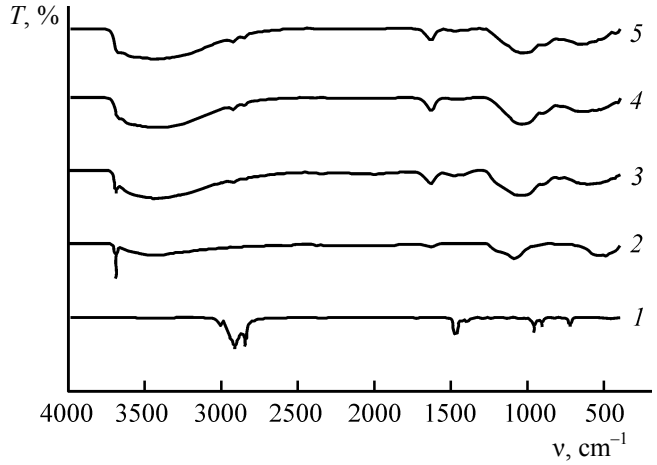

Fig. 4. IR spectra of (*1*) hexadecyltrimethylammonium bromide, (*2*) magnesium hydroxide-silica xerogel mixture, and (*3–5*) products of mechanochemical treatment of the component mixture (with water addition) in (*3, 4*) continuous mode for (*3*) 40 and (*4*) 50 h and (*5*) discrete mode for 70 h.

The position and number of bands in the IR spectrum of hexadecyltrimethylammonium bromide (Fig. 4) agree with the published data [18]. In the IR spectra of the products of mechanical treatment of the initial mixture the band associated with the stretching vibrations of the OH groups of magnesium hydroxide (3695 cm^{-1}) initially decreases in intensity and subsequently disappears completely, and this is paralleled by the appearance of the band corresponding to the stretching vibrations of structural hydroxyls (3674 cm^{-1}) in synthetic hectorite [19] (Fig. 3). The band associated with the Si–O stretching vibrations (1091 cm^{-1}) of silica [20] shifts to lower frequencies (1026 cm^{-1}) characteristic of the Si–O stretching vibrations of layered structures [21]. In parallel, the band corresponding to the Si–O–Si vibrations in silicon-oxygen tetrahedra (797 cm^{-1}) [20] decreases in intensity and subsequently disappears. Also, the bands appear associated with the Mg–OH bending vibrations (650 cm^{-1}) [22] and the Si–OH stretching vibrations (906 cm^{-1}) [14] in hydrated layered magnesium silicate. In the IR spectra of the activation products there are bands associated with the stretching (2962, 2926, 2854 cm^{-1}) and bending (1481 cm^{-1}) vibrations of methyl and methylene groups. The IR spectra of the samples synthesized in the discrete and continuous modes are identical (Fig. 4).

Figure 5 shows the curves of complex thermal analysis of pure hexadecyltrimethylammonium bromide and of the organically modified sample synthesized in the continuous mode with water addition. The endothermic peaks with critical points at 80 and 115°C [23] observed for pure hexadecyltrimethylammonium bromide are not accompanied by mass losses and are evidently due to phase transformation. The mass loss (TG and DTG curves) in the 200–650°C range gives rise to a group of exothermic effects in the DSC curve, due to the oxidative thermal degradation of hexadecyltrimethylammonium bromide [23].

The mass loss in the first region (25–260°C) of the TG and DTG curves recorded for the organically modified sample (Fig. 5b) is accompanied by an endothermic effect in the DSC curve with the minimum at 112°C, which is due to the loss of adsorbed and interlayer water [24]. The mass losses of

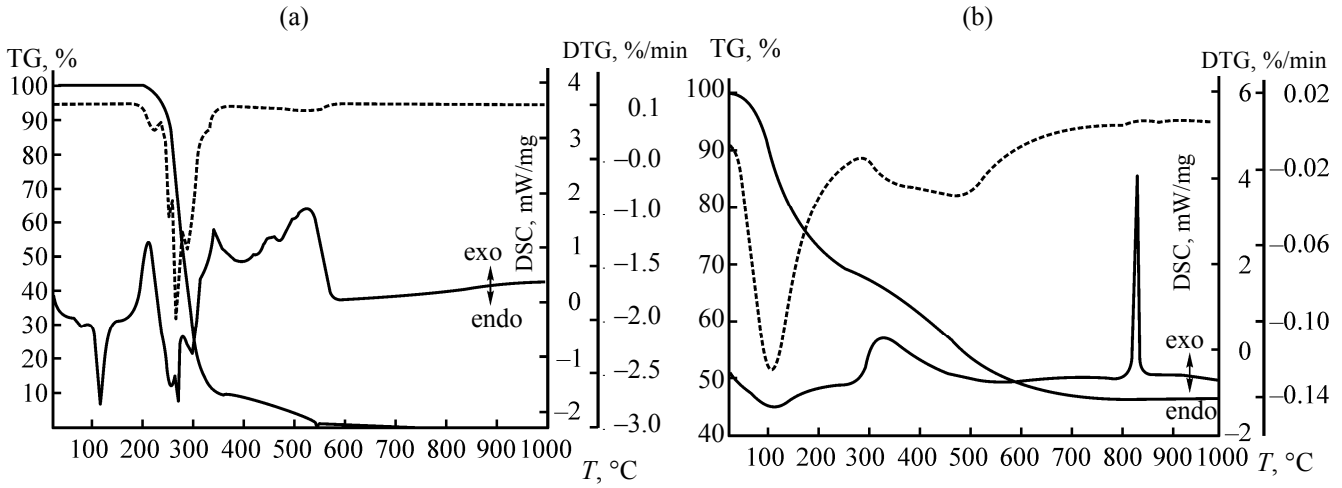

Fig. 5. DSC, TG, and DTG curves of (a) hexadecyltrimethylammonium bromide and (b) the product of continuous mechanochemical treatment of the component mixture (50 h) with water addition.

the sample in the 260–760°C range are associated with oxidative thermal degradation of hexadecyltrimethylammonium bromide and give rise to exothermic peaks of the DSC curve in the 280–440, 440–550, and 550–760°C regions.

The DTG data are indicative of the onset of oxidative thermal degradation of pure hexadecyltrimethylammonium bromide at 200°C (Fig. 5a), and of that of the organically modified sample at 294°C (Fig. 5b). A similar trend was found in the thermal analysis of organically modified natural montmorillonites obtained by the ion exchange method [25].

According to published data [26], the exothermic peak in the 280–440°C range is due to the oxidation of most of organic hydrogen with the formation of water, as well as to oxidation of a part of the carbon to carbon dioxide and of a part of the nitrogen to nitrogen dioxide.

The oxidative thermal degradation of the organic substance on the external surface of the silicate layers gives carbon that is stable at low temperatures, while the same process inside the interlayer space of the silicate leads to the formation of carbon that is oxidized at significantly higher temperatures compared to the pure organic compound [26]. Oxidation of the carbon residues, stable at low and high temperatures, gives rise to exothermic effects in the 440–550 and 550–760°C ranges.

The endothermic effect at the critical point of 792°C corresponds to the loss of structural hydroxyls of the silicate, and the exothermic effect at the critical point of 835°C, to the crystallization of the enstatite phase. These effects are accompanied by the mass loss in the 760–920°C range. The curves of the comprehensive thermal analysis of the sample synthesized in the discrete mode have similar appearance.

Thus, one-step mechanochemical synthesis of organically modified (with hexadecyltrimethylammonium cations) magnesium silicate under different conditions allows obtaining products differing in the degree of structural order and the particle size. The hexadecyltrimethylammonium cations are localized both on the silicate layer surface and in the interlayer space of the silicate. In the interlayer space of the organically modified product mechanochemically synthesized in the continuous mode the hexadecyltrimethylammonium cations take the horizontal monolayer orientation. Mechanochemical synthesis of organically modified magnesium silicate proceeds only in the presence of water, which confirms the previously proposed schemes of the formation of the structure of layered magnesium silicate [16] and the organically modified magnesium silicate [8].

EXPERIMENTAL

Magnesium hydroxide was synthesized by the procedure described in [27]. A silica sol was prepared by ion exchange of sodium metasilicate on KU-2 ion exchange resin, and after drying at 25±3°C in air it was ground to obtain silica xerogel. According to the gravimetric analysis data, the silica xerogel contained 33 wt % water.

Synthesis was carried out in a MLW KM-1 vibratory ball mill (Germany) at the vibration intensity (on the relative scale of the mill) of 17, in the discrete and continuous modes for 50–70 h. The discrete mode included 7 cycles, each consisting of 10 h of treatment and 14 h of "rest." The mechanical treatment of the reaction mixture (2.74 g) was performed (a) without and (b) with solvent (water) added in small amounts. The molar ratio of the initial components used in this study is presented below.

	MgO	SiO_2	LiF	$C_{16}H_{33}(CH_3)_3NBr$	H_2O
(a)	1	1.34	0.05	0.016	–
(b)	1	1.34	0.05	0.016	21

The samples obtained were rinsed with water until no presence of halide ions was detected in the washings (as tested with aqueous silver nitrate) and dried at 60°C to a constant weight.

The IR spectra were recorded in the 4000–400 cm^{-1} range on a Shimadzu IR Prestige 21 Fourier transform spectrometer (KBr pellets). The X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer (CuK_α radiation, 2θ range 2°–70°, recording rate 1 deg/min). Thermogravimetric analysis and differential scanning calorimetry measurements were performed on a Netzsch STA 409 PC/PG simultaneous thermal analyzer in platinum crucibles at the heating rate of 10 deg/min in air. Scanning electron microscopy examination of the samples was performed on a VEGA3 TESCAN scanning electron microscope.

REFERENCES

1. Lee, S.M. and Tiwari, D., *Appl. Clay Sci*., 2012, vols. 59–60, p. 84. DOI: 10.1016/j.clay.2012.02.006.
2. He, H., Ma, L., Zhu, J., Frost, R.L., Theng, B.K.G., and Bergaya, F., *Appl. Clay Sci*., 2014, vol. 100, p. 22. DOI: 10.1016/j.clay.2014.02.008.
3. Carrado, K.A., *Appl. Clay Sci*., 2000, vol. 17, p. 1. DOI: 10.1016/S0169-1317(00)00005-3.
4. de Paiva, L.B., Morales, A.R., and Diaz, F.R.V., *Appl. Clay Sci*., 2008, vol. 42, p. 8. DOI: 10.1016/j.clay.2008.02.006.
5. Lomakin, S.M. and Zaikov, G.E., *Polymer Sci., Ser. B*, 2005, vol. 47, p. 9.
6. Pomogailo, A.D., *Polymer Sci., Ser. C*, 2006, vol. 48, p. 85.
7. *Handbook of Clay Science*, Bergaya, F., Theng, B.K.G., and Lagaly, G., Eds., Amsterdam: Elsevier, 2006, vol. 1, p. 309. DOI: 10.1016/S1572-4352(05)01010-X.
8. Loukhina, I.V., Dudkin, B.N., and Bugaeva, A.Yu., *Russ. J. Appl. Chem*., 2013, vol. 86, no. 10, p. 1465. DOI: 10.1134/S1070427213100017.
9. Yoshimoto, S., Ohashi, F., and Kameyama, T., *Macromol. Rapid Commun*., 2005, vol. 26, p. 461. DOI: 10.1002/marc. 200400529.
10. Ogawa, M., Kato, K., Kuroda, K., and Kato, C., *Chem. Lett*., 1989, vol. 9, p. 1659. DOI: 10.1246/cl.1989.1659.
11. Ogawa, M., Kato, K., Kuroda, K., and Kato, C., *Chem. Lett*., 1990, vol. 19, no. 1, p. 71. DOI: 10.1246/cl.1990.71.
12. Breakwell, I.K., Homer, J., Lawrence, M.A.M., and McWhinnie, W.R., *Polyhedron*, 1995, vol. 14, no. 14, p. 2511. DOI: 10.1016/0277-5387(95)00053-U.
13. Liao, J. and Senna, M., *Thermochim. Acta*, 1992, vol. 210, p. 89. DOI: 10.1016/0040-6031(92)80280-A.
14. Temuujin, J., Okada, K., and MacKenzie, K.J.D., *J. Solid State Chem*., 1998, vol. 138, p. 169. DOI: 10.1006/jssc.1998.7768.
15. Karakchiev, L.G., Avvakumov, E.G., Gusev, A.A., and Vinokurov, O.B., *Khim. Inter. Ust. Razv*., 2009, vol. 17, p. 591.
16. Dudkin, B.N. and Vasyutin, O.A., *Russ. J. Appl. Chem*., 2011, vol. 84, no. 5, p. 751. DOI: 10.1134/S1070427211050028.
17. Avvakumov, E., Senna, M., and Kosova, N., *Soft Mechanochemical Synthesis: a Basis for New Chemical Technologies*, Boston: Kluwer Academic, 2001.
18. Smith, A.L., *Applied Infrared Spectroscopy*: *Fundamentals*, *Techniques*, *and Analytical Problem-Solving,* New York: Wiley, 1979.
19. Plyusnina, I.I., *Infrakrasnye spektry silikatov* (Infrared Spectra of Silicates), Moscow: Mosk. Gos. Univ., 1967, p. 73.
20. Plyusnina, I.I., *Infrakrasnye spektry mineralov* (Infrared Spectra of Minerals), Moscow: Mosk. Gos. Univ, 1976, p. 51.
21. Lazarev, A.N., *Kolebatel'nye spektry i stroenie silikatov* (Vibrational Spectra and Structure of Silicates), Leningrad: Nauka, 1968, p. 163.
22. Farmer, V.C., *Clay Miner*., 1968, vol. 7, p. 373.
23. He, H., Ding, Z., Zhu, J., Yang, P., Xi, Y., Yang, D., and Frost, R.L., *Clays Clay Miner*., 2005, vol. 53, no. 3, p. 921. DOI: 10.1346/CCMN.2005.0530308.
24. Lapides, I., Borisover, M., and Yariv, S., *J. Therm. Anal. Calorim*., 2011, vol. 105, p. 921. DOI: 10.1007/s10973-011-1304-4.
25. Park, Y., Ayoko, G.A., Kristof, J., Horvath, E., and Frost, R.L., *J. Therm. Anal. Calorim*., 2012, vol. 107, p. 1137. DOI: 10.1007/s10973-011-1568-8.
26. Yariv, S., *Appl. Clay Sci*., 2004, vol. 24, p. 225. DOI: 10.1016/j.clay.2003.04.002.
27. *Handbuch der präparativen anorganischen Chemie,* Brauer, G., Ed., Stuttgart: Enke, 1978.