ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 5, pp. 751–755. © Pleiades Publishing, Ltd., 2011. Original Russian Text © B.N. Dudkin, O.A. Vasyutin, 2011, published in Zhurnal Prikladnoi Khimii, 2011, Vol. 84, No. 5, pp. 721–725.

> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of Magnesium Silicate by Heat Treatment of Sols and Mechanical Activation of Solid Components

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Received July 9, 2010

Abstract—A layered magnesium silicate, an analog to natural talc, was synthesized by mechanical treatment of a mixture of magnesium hydroxide and hydrated silicic acid powders, as well as by heat treatment of aqueous dispersions containing magnesium hydroxide particles and silica sols prepared from different precursors.

DOI: 10.1134/S1070427211050028

Naturally occurring layered silicates are represented by a mineral group that includes talcs, pyrophyllites, micas, montmorillonites, kaolinites, and closely related clay minerals. The structure of layered silicates is based on hexagonal networks of interconnected SiO_4 tetrahedra. All layered silicates exist as pseudohexagonal platyshaped particles [1].

Layered silicates find industrial applications as catalysts, adsorbents, and ion-exchangers and also are used in semiconductor manufacturing. Steadily growing demand for these mineral resources has motivated intense research efforts seeking to interrelate the composition, structure, and properties of the particle surface, based on the use of model colloid and chemical systems. Those studies have culminated in the development of hydrothermal synthesis procedures for layered silicates of different types and compositions [2–5].

Recent 20 years have witnessed an active development of a new application sphere for layered silicates, synthesis of organic-inorganic hybrid materials. Silicate–polymer hybrids are typically synthesized from layered silicates prepared by the sol-gel [6] or mechanochemical route. In the former case the synthesis procedure involves heat treatment [7], and in the latter, mechanical activation of the precursors [8]. Heat treatment or mechanical activation of layered silicates in the presence of organic macromolecules leads either to an organic-inorganic hybrid or, in the case of a sol-gel conversion, to a gel matrix incorporating the organic molecules. Such materials can be prepared by the sol-gel process solely [9, 10]. Synthesis of layered silicates from mechanically activated precursors follows a specific route which has its own peculiarities [11].

Here, we synthesized a layered magnesium silicate, an analog to natural tale, by heat treatment of aqueous dispersions and by mechanical treatment of a powder precursor mixture. Also, we determined the phase composition of the products obtained and examined how it changes during the aging process.

EXPERIMENTAL

Synthesis of a layered magnesium silicate by the heat treatment route in the liquid phase recycle mode was carried out in round-bottom flasks fitted with reflux condensers. In one experiment the flask was charged with a hydrated silicic acid ($SiO_2 \cdot nH_2O$) powder, and in the second and third experiments, with silica sols, of which one (sol I) was prepared by the ion-exchange route from a dilute solution of sodium metasilicate and KU-2 cation

exchanger [12] and the other (sol II), by hydrolysis of a dilute alcoholic solution of tetraethoxysilane (TEOS) at 25–50°C. The sols appeared as transparent, bluish in transmitted light, dispersed systems.

Magnesium hydroxide was prepared by the procedure described in [13]; the particle size analysis on an Analysette 20 Fritsch scanning photo sedimentograph showed that >90% of the magnesium hydroxide particles had sizes of less than 1 μ m,.

The required quantities of the precursors were calculated on the basis of the empirical formula of talc $Mg_3Si_4O_{10}(OH)_2$. The calculated volumes of sols I and II, together with an aqueous dispersion of silicic acid, were charged into the flasks fitted with reflux condensers. Subsequently, the reactors were heated to 60°C, and the appropriate amount of the freshly prepared ultradispersed magnesium hydroxide was added during the period of 30 min in small portions so as to avoid vigorous boiling up of the liquid phase and ejection of the reactants. The synthesis was run at 70°C under permanent stirring for 42 h; the optimal synthesis time was determined empirically. Upon completion of the synthesis the products were separated by centrifuging and placed into an exsiccator.

In synthesis of a layered magnesium silicate by the "soft" mechanical treatment route (successfully tested earlier for various systems) we used magnesium hydroxide synthesized and hydrated silicic acid. A mixture of the components, preliminarily homogenized intimately by rubbing in an agate mortar for 15 min, was mechanically activated in a KM-1 colloid mill. The mechanochemical synthesis was run for 12 h, during which time the treatment intensity was gradually brought to the maximum permissible level. Treatment caused the mixture volume to decrease by nearly half; the resulting product was stored in an exsiccator.

The particle size distribution analysis of the products synthesized by the heat treatment and mechanical activation routes showed that 70% of the particles range in size from 20 to 100 μ m. The number of submicrometersized particles in the product formed by the latter route markedly exceeded that in the product obtained by the former route. A high content of <1 μ m particles in the mechanochemically synthesized product suggests the presence of magnesium hydroxide particles, which is due to the fact that the solid-phase synthesis reaction occurred to a certain extent only.

The IR transmission spectra of the products obtained were recorded at 4000–400 cm⁻¹ on a Shimadzu IR Prestige 21 Fourier-transform spectrometer (KBr pellets). The spectra show that the mechanochemically synthesized product contains free magnesium hydroxide, as suggested by a narrow band at 3690 cm⁻¹ which is lacking in the spectrum of the product resulted from heat treatment of a magnesium hydroxide–sol dispersion. The spectrum of the product obtained from sol II is virtually identical to that of the product obtained from sol I, except for the presence in the former of a low-intensity band at 3690 cm⁻¹ associated with free magnesium hydroxide (marked with an asterisk in Fig. 1).

The X-ray diffraction patterns of the products were recorded by the Debye procedure on a Shimadzu XRD 6000 DRON instrument ($Cu_{K\alpha}$ radiation, tube operated at



Fig. 1. IR transmission spectra of the samples synthesized by (a) mechanical treatment and (b) heat treatment of a sol. (T) Transmission, %, and (v) wavenumber, cm⁻¹.

30 kV, 30 mA, $2\theta = 2^{\circ}-60^{\circ}$, scanning speed 1 deg min⁻¹).

In the case of non-crystalline hydrated silicic acid we obtained an X-ray diffraction pattern typical for X-ray amorphous substances. Magnesium hydroxide has a layered structure of brucite in which the hydroxy groups form two parallel networks, with the sites between the layers occupied by magnesium atoms and the layers bound together by weak secondary chemical bonds [1].

The mechanochemically synthesized product exhibited an X-ray diffraction pattern due to overlap between the most intense reflections from crystalline magnesium hydroxide and the pattern obtained from hydrated silicic acid, represented by a broad halo (Fig. 2a). During aging of the sample for 2–6-month periods, the reflections from magnesium hydroxide tend to decrease in intensity, and low-intensity lines disappear. This is accompanied by broadening of the halo, which is indicative of a continuous synthesis reaction occurring at a not very high rate. Upon repeated mechanical treatment of the product for 30 h the medium-intensity reflections from magnesium hydroxide disappear in a discrete manner (Fig. 2b).

The X-ray diffraction pattern of the product resulted from heat treatment of the hydrated silicic acid–magnesium hydroxide dispersion is very similar to that of the mechanochemically synthesized product. Upon 2-month aging of the sample the reflections from magnesium hydroxide markedly decrease in intensity (Fig. 3a). The pattern recorded after 6 months of aging does not contain reflections from magnesium hydroxide; rather, it is represented by a set of broad asymmetric halos, which suggest formation of a layered silicate structure (Fig. 3b). The X-ray diffraction pattern of the 1–5-µm particle fraction isolated from the sample by the sedimentation procedure is typical for the layered silicate structures (Fig. 4); it is associated with diffuse X-ray scattering due to large interlayer spacings and small particle sizes [14].



Fig. 2. X-ray diffraction pattern of the mechanochemically synthesized product. (I/I_0) Relative intensity of the reflection, %, and (2 θ) Bragg's angle; the same for Figs. 3–5. Treatment: (a) primary and (b) repeated (after 2 months).



Fig. 3. X-ray diffraction patterns of the product resulted from heat treatment of a hydrated silicic acid–magnesium hydroxide dispersion, recorded upon (a) 3- and (b) 6-month aging.

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The product obtained with the use of sol (I) exhibited a set of broad asymmetric lines with diffraction lines from magnesium hydroxide lacking in the X-ray diffraction pattern (Fig. 5a). Within the $2\theta = 2-6^{\circ}$ range, a resolved peak (marked with an asterisk in Fig. 5a) is observed in the position associated with the basal reflection plane d₀₀₁ corresponding to the interlayer spacing of ~1.7 nm.

The difference between the X-ray diffraction patterns of the product synthesized with the use of sol (II) (Fig. 5b) and sol (I) consists in that, in the former, the broad asymmetric halos associated with the silicate structure are superimposed by low-intensity diffraction lines associated with residual magnesium hydroxide. Within 1-month aging of the sample the formation of the layered silicate lattice is complete; the reflections from magnesium hydroxide disappear from the diffraction pattern of the product, and the diffraction curve shows an inflection point at small angles, which corresponds to the interlayer spacing of ~1.5 nm.

In view of the fact that a not very large dose of energy is supplied to a substance during mechanical treatment by the soft route, the formation of a layered structure of silicate during its treatment and aging is a lengthy process which, presumably, follows the diffusion mechanism.

Additional mechanical treatment of the primary product, which destroys the microstructure of the silicic acid particles and leads to appearance of water in the system, further promotes formation of the layered structure. Temuujin et al. [8] monitored formation of a layered silicate structure during 6-month aging of the mechani-



Fig. 4. X-ray diffraction pattern of the $1-5-\mu m$ particle size fraction. The fraction was isolated from the product obtained by heat treatment of a hydrated silicic acid–magnesium hydroxide dispersion.

cally activated mixture and presumed that water resulted from the treatment which destroys the structure of the precursors is essential for the dissolution of silica in the alkaline environment of the magnesium hydroxide, so that a silicate is formed.

Heat treatment of an aqueous dispersion of magnesium hydroxide and hydrated silicic acid under water excess conditions at 70°C is a route that satisfies all the criteria for the above-mentioned scheme. However, complete formation of a silicate structure is not achieved even after 3 months of aging of the sample (Fig. 3b).

Golubeva et al. [15] suggested adsorption of the SiO_4 units of silica from the hydrothermal solution onto the brucite layers of magnesium hydroxide as the most plausible mechanism which underlies the formation of the layered silicate structure under hydrothermal synthesis conditions.



Fig. 5. X-ray diffraction patterns of the products resulted from heat treatment of (a) magnesium hydroxide–sol (I) and (b) magnesium hydroxide–sol (II) dispersion.

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SYNTHESIS OF MAGNESIUM SILICATE BY HEAT TREATMENT

The presence of water in the reaction space is of much significance for the layered silicate structure formation, as confirmed by the experiments both with heat treatment of magnesium hydroxide–silica dispersions differing in the compositions of the dispersion medium and with mechanical treatment of the components.

Heat treatment of a magnesium hydroxide dispersion with sol(I) under water excess conditions enables complete formation of a layered silicate structure. This is strongly favored by a loose, fractal structure of the silica sol particles as comprised of SiO_4 tetrahedral networks. Assisted by water which acts as a transporting agent, the hydrated magnesium ions evidently experience weaker steric hindrance to incorporation into the tetrahedral networks of silica from the liquid phase.

As to the synthetic route with the use of sol(II), the reaction does not occur to the full extent. Considering the identical physical conditions of syntheses and the difference in the compositions of the dispersion media for sols(I) and (II), this finding may be associated with the specific composition of the dispersion medium in the case of sol(II), which is essentially an aqueous alcoholic solution. A poorer solubility of magnesium hydroxide and a lower mobility of magnesium ions in this medium [16] affect the performance of water as an agent transporting the magnesium ions into the structural units of silica.

CONCLUSIONS

(1) Synthesis of a layered silicate in all the examined systems proceeds with participation of water which acts as an agent transporting the magnesium ions into the structural units of silica.

(2) Another factor that favorably affects the layered silicate structure formation is the density (looseness) of the microstructure of the silica particles, which limits the penetration of the hydrated magnesium ions into the SiO_4 tetrahedral networks of silica.

ACKNOWLEDGMENTS

This study was financially supported by the Program

of Joint Studies by Institutes of the Ural and Siberian Divisions, Russian Academy of Sciences.

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