ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 3, pp. 352–355. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © T.P. Maslennikova, E.N. Korytkova, I.A. Drozdova, V.V. Gusarov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 3, pp. 361–364.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Interaction of Potassium Chloride Aqueous Solution $Mg_3Si_2O_5(OH)_4$ with the Nanotubes Based on Magnesium Hydrosilicate

T. P. Maslennikova, E. N. Korytkova, I. A. Drozdova, and V. V. Gusarov

Grebenshikov Institute of Chemistry of Silicates, Russian Academy of Sciences, St. Petersburg, Russia

Received October 30, 2008

Abstract—Interaction of potassium chloride aqueous solution with the hydrosilicate nanotubes at 80°C is studied.

DOI: 10.1134/S1070427209030021

Inorganic nanotubes attract wide attention as the potential materials for nanoelectronics, photocatalysis, and nanolithography and for other areas of application [1–9]. For obtaining nanotubular forms compounds are promising with laminate type structure and clearly expressed anisotropy of interatomic interactions defined by conjunction of strong ionic and covalent bonds within the layers and weaker interactions of the type of hydrogen bonding and van der Waals interactions between the layers [10]. Such structural features are typical of many substances, e.g. of a series of hydroxides, oxyhydroxides, certain oxides and sulfides [11–14]. For the formation of rolled nanotubes the presence is significant of internal moment in the layer that forms substance with the structure of laminate type [15].

A great interest for practical application present hydrosilicate nanotubes varied by chemical composition and morphology [16–19]. These tubes are formed by rolling the layers of chemical compounds with laminate structure [15, 20–23] followed by growing the tubes due to recrystallization processes. Presence of cylindrical cavity in such nanorolls opens a possibility of preparation of new membrane nanomaterials with high selectivity and permeability [24]. Simultaneously, a possibility of filling the nanotubes with various substances creates conditions for immobilization and storage of these substances [25]. In this connec-tion, as show the results of a series of investigations of the features of composition, structure and properties of liquid substances in the space of nanometer size [24–27], certain systematic investtigations should be carried out.

Thus, it is actual to study the processes of redistribution of the components between bulk liquid and the liquid in a nanocanal of hydrosilicate nanotube, as well as the processes of transport of a substance in the nanotubes and its interaction with the nanotube wall.

EXPERIMENTAL

Synthesis of hydrosilicate nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ was carried out under hydrothermal conditions in aqueous solution of NaOH 1 wt % at the temperature 350°C and pressure 70 MPa along the procedure described in [19]. The nanotubes obtained were washed to neutral reaction, dried in air, then the phase composition of the samples, specific surface area, shape and size of the nanotubes were determined, and then were carried out further investigations.

For the study of the process of filling nanotubes with aqueous solution of potassium chloride the nanotubes were treated with 0.5 M solution of KCl according the following scheme. The initial weighted samples of nanotubes (0.04 g) were placed into identical glass vessels with caps, to each vessel was

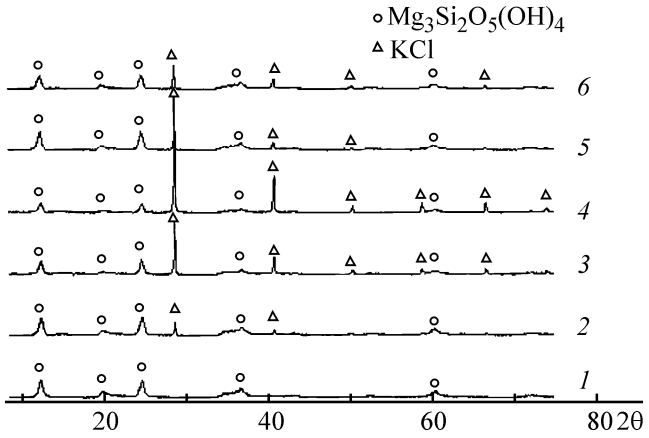

Fig. 1. X-ray diffractograms of initial nanotubes and those after keeping in 0.5 M solution of KCl at 80°C for various time periods. 2θ is Bragg angle, deg. Duration of thermostating, h: (*1*) 0, (*2*) 2, (*3*) 4, (*4*) 6, (*5*) 8, and (*6*) 10.

poured 8 ml of 0.5 M solution of KCl. The vessels were placed into a preliminary heated thermostat at 80°C for 2 to 10 h. After the thermostating, the vessels were cooled in air and the nanotubes were separated from the solution by decanting the latter. Then several times 40 ml of distilled water was added and nanotubes were kept under water at room temperature for 1 h. After each cycle of such treatment the liquid phase was decanted. The samples were treated with distilled water by different number of the cycles, from 0 to 7. Then the samples were dried in air at room temperature and their elemental compositions (by the method of energy-dispersion X-ray microspectral analysis with a microsound unit Oxford Link) and structural parameters were determined. An average error at the determination of the content of an element was 0.3 wt % [28].

Phase analysis of the samples and structural characteristics of the nanotubes were determined from the data of X-ray diffractometry. The diffractograms were taken on a X-ray diffractometer DRON-3 (CuK_α-radiation).

The nanotubes shape and size were measured using transmission electron microscopy (an EM-125 electron microscope with acceleration voltage $U_{acc} = 75$ kV).

Specific surface area of the samples was measured by means of nitrogen thermal desorption [29]. The error value was 5% or less.

The X-ray phase analysis of the samples obtained by hydrothermal treatment of a mixture of magnesium and silicon oxides showed that in the synthesis was magnesium hydrosilicate with the chrisotyle structure was formed (Fig. 1), whose morphology according to the data of electron microscopy is a uniform cylindrical nanotube with the following size: external diameter about 25 nm, internal diameter about 4 nm, tube length varied basically from 0.1 to 1 μm (Fig. 2). Specific surface area of the samples is 50–60 $m^2 g^{-1}$.

After keeping in aqueous solution of KCl and varied number of washing cycles molar content of potassium, sodium and chlorine were determined in the tubes per one unit corresponding to the formula $Mg_3Si_2O_5(OH)_4$ (Figs. 3 and 4). As follows from the data in Fig. 3, after two first washings sharp decrease occurs in the content of potassium and chlorine as compared with the nanotubes that were not kept in distilled water. Increase in the number of the cycles to 3–7 leads to insignificant decrease in potassium and chlorine content and the content becomes rather stable on a certain level. Obviously initially K^+ and C^- ions are removed adsorbed on the surface and then decrease in the content of K^+ and Cl^- in the nanotubes is defined by removing them from cylindrical canals and interlayer space. Therewith the plots of K^+ and Cl^- content in the nanotubes either on the number of the cycles of keeping in distilled water (Fig. 3) or on the

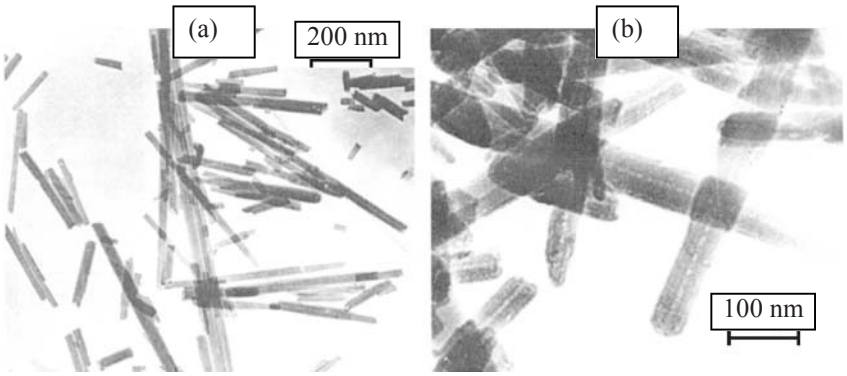

Fig. 2. Electron microphotographies of (a) initial nanotubes and (b) after treatment with KCl solution for 8 h.

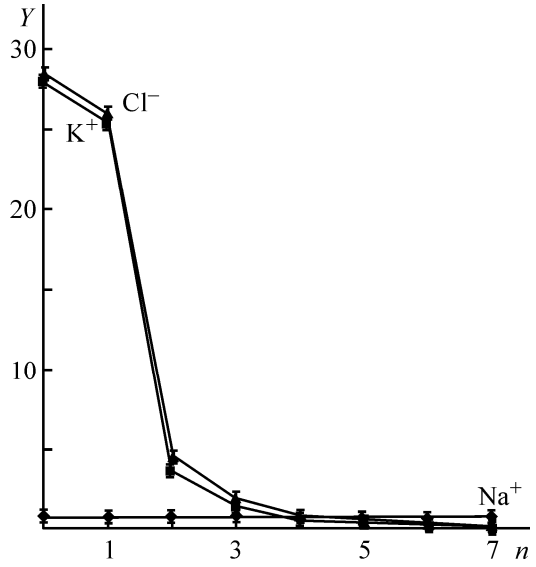

Fig. 3. Content *Y* (mol %) of potassium, chlorine and sodium in the nanotubes after keeping them in 0.5 M solution of KCl followed by *n*-fold washing up in distilled water.

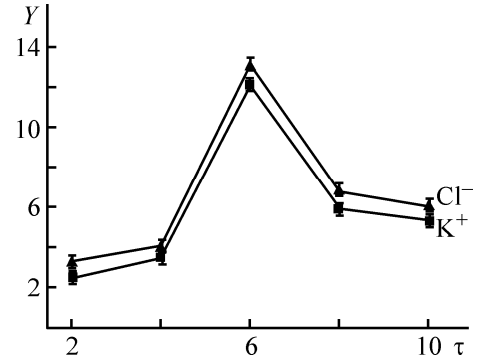

Fig. 4. Dependence of potassium, chlorine and sodium content in nanotubes *Y* (mol %) on the duration of treatment τ (h) in KCl.

duration of keeping in KCl solutions (Fig. 4) are practically coinciding that points to existence of K^+ and Cl^- in the nanotubes in the form of potassium chloride.

On the plot of dependence of K^+ and Cl^- ions content in the samples of nanotubes after their keeping in 0.5 M aqueous KCl at 80°C on the keeping duration (Fig. 4) is registered a stepwise increase in the content that achieves maximum after keeping for 6 h. At the longer action of aqueous KCl on the hydrosilicate nanotubes the content of K^+ and Cl^- ions in the tubes falls. Probably this can be explained by redistribution of the solution components after filling the nanotubes with the KCl solution between the bulk liquid phase and the liquid phase inside the nanotubes that leads to decrease in the KCl content in the nanotubes.

Effect of duration of keeping nanotubes at the temperature 80°C in KCl solution and in water on the interlayer distance

Keeping duration, h	Solution of KCl, H_2O	*d/n* , Å
0 (initial sample)	–	7.20
2	KCl	7.26
4	KCl	7.26
6	KCl	7.30
8	KCl	7.30
10	KCl	7.30
10	H_2O	7.21

Note that from the data of electron microscopy (higher contrast of image owing to heavy potassium and chlorine atoms) one can conclude that K^+ and Cl^- are localized not only in the nanotube canal but also in the interlayer space (Fig. 2). This is confirmed by the results of X-ray studies of the samples that attests increase of interlayer space in the structure of the hydrosilicate samples (see the table).

Analysis of dependence of the nanotubes external diameter on the duration of keeping them in KCl solution carried out using the data of electron microscopy (acquisition over 50 nanotubes) showed small increase in the outer diameter, the most significant at 8–10-h keeping of the nanotubes in 0.5 M KCl solution at 80°C. Hence, after filling the nanotubes with the solution of KCl occurs certain structural transformation. However, under the applied conditions does not occur destruction or morphological degradation of the nanotubes unlike the action of aqueous KOH solution on the nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ at the same temperature – duration parameters as in the case of chemical reaction of KOH solution with internal walls of the nanotubes that led to their damage [27].

CONCLUSIONS

(1) It is established that at the thermal keeping of nanotubes of $Mg_3Si_2O_5(OH)_4$ composition in aqueous solution of KCl proceeds filling of internal canal of the nanotubes and of interlayer space in the structure of hydrosilicate by potassium chloride at the considered temperature–duration parameters.

(2) Filling of nanotubes with KCl solution results in small structural and morphological transformation that appears as increase in the interlayer space but not leads to destruction and morphological degradation of the nanotubes under the applied conditions.

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (grant RFBR no. 08-03-00456-a).

REFERENCES

1. Pokropivnyi, V.V., *Poroshkovaya Metallurgiya*, 2002, no. 3/4, p. 13.
2. Tenner, R. and Rao, C.N.R., *Phil. Trans. Royal, Soc. London*, 2004, vol. A362, pp. 2099.
3. Tenner, R. and Zettl, A.K., A, *Topics Appl. Phys*., 2001, vol. 80, p. 81.
4. Enyashin, A.N., Ivanovskaya, V.V., Makurin, Yu.N., et al*., Chem. Phys. Lett.,* 2004, vol. 392, p. 555.
5. Ma, R., Bando, Y., Zhu, H., et al*., J. Am. Chem. Soc.,* 2002, vol. 124, p. 7622.
6. Chen, J., Kuriyma, N., Yuan, H., et al*., J. Am. Chem. Soc*., 2001, vol. 123, p. 11813.
7. Zhu, H., Yuan, D., and Zhang, H., *Neorgan. Materialy*, 2006, vol. 42, no. 11, p. 1325.
8. Yudin, V.E., Gladchenko, S., Otaigbe, J., et al., *Polymer*, 2007, vol. 48, pp. 1306–1315.
9. Gofman, I.V, Svetlichnyi, V.M., Yudin, V.E*.,* et al*., Zh. Obshch. Khim.,* 2007, vol. 77, no. 7, p. 1075.
10. Ivanovskii, A.L., *Kvantovaya khimiya v material-lovedenii: Nanotubulyarnye formy veshchestva* (Quantum Chemistry in Materials Technology: Nanotubular Forms of a Matter), Ekaterinburg: UrO RAN, 1999.
11. Rao, C.N.R. and Nath, M., *Dalton Trans.*, 2003, p. 1.
12. Grigor'eva, A.V., Anikina, A.V., Tarasov, A.B*.,* et al*., Dokl. Akad. Nauk*, 2006, vol. 410, no. 4, p. 482.
13. Ivanovskii, A.L., *Uspekhi Khimii*, 2002, vol. 71, p. 203.
14. Zakharova, G.S., Volkov, V.L., Ivanovskaya, I.I., and Ivanovskii, A.L., *Uspekhi khimii*, 2005, vol. 74, no. 7, p. 651.
15. Chivilikhin, S.A., Popov, I.Yu., and Gusarov, V.V*., Dokl. Akad. Nauk,* 2007, vol. 412, no. 2, p. 201.
16. Korytkova, E.N., Maslov, A.V., Pivovarova, L.N*.,* et al*., Neorgan. Materialy*, 2005, vol. 41, no. 7, p. 849.
17. Korytkova, E.N., Pivovarova, L.N., Drozdova, I.A., and Gusarov, V.V., *Fizika Khimiya Stekla*, 2005, vol. 31, no. 6, p. 1099.
18. Korytkova, E.N., Pivovarova, L.N., Drozdova, I.A., and Gusarov, V.V*., Zh. Obshch. Khim.,* 2007, vol. 77, no. 10, p. 1600.
19. Korytkova, E.N., Maslov, A.V., Pivovarova, L.N*.,* et al*., Fizika Khimiya Stekla*, 2004, vol. 30, no. 1, p. 72.
20. Yada, K., *Acta Crystal*., 1967, vol. 23, p. 704.
21. Yada, K., *Acta Crystal*. *A*, 1971, vol. 27, p. 659.
22. Yada, K., *Am. Mineralogist.*, 1977, vol. 62, p. 958.
23. Chivilikhin, S.A., Popov, I.Yu., Blinova, I.V. et al*., Fizika Khimiya Stekla*, 2007, vol. 33, no. 4, p. 442.
24. Kononova, S.V., Korytkova, E.N., Romashkova, K.A. *et al., Zh. Prikl. Khim.,* 2007, vol. 80, no. 12, pp. 2064–2070.
25. Maslennikova, T.P., Korytkova, E.N., and Gusarov, V.V., Abstracts of Papers, *VII Mezhdunar. nauch. konf. "Khimiya tverdogo tela i sovremennye mikro- i nanotekhnologii"* (7th Int. Sci. Conf. on Chemistry of Solids and Modern Micro and Nano Technology), Kislovodsk, 2007, p. 186.
26. Chernysheva, M.V., Kiseleva, E.A., Eliseev, A.A*.,* et al*., Al'ternativnaya energetika i ekologiya* (Alternative Energetics and Tevhnology), 2008, p. 22.
27. Maslennikova, T.P., Korytkova, E.N., Gusarov, V.V., *Zh. Prikl. Khim.,* 2008, vol. 81, no. 3, p. 389.
28. Goldstein, J., Newbury, D.E., Echlin, P., Joy, D.C., and Lyman E., *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum, 1984.
29. Deryuzhkina, V.I. and Buzanova, G.N., *Metody opredeleniya udel'noi poverkhnosti katalizatorov* (Methods of Determination of Specific Surface of Catalysts), Leningrad: LTI im. Lensoveta, 1987.