ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2008, Vol. 53, No. 7, pp. 1065–1069. © Pleiades Publishing, Ltd., 2008.
Original Russian Text ©V.N. Krasil'nikov, A.P. Shtin, O.I. Gyrdasova, E.V. Polyakov, G.P. Shveikin, 2008, published in Zhurnal Neorganicheskoi Khimii, 2008, Vol. 53, No. 7, pp. 1146–1151.

Synthesis and Properties of Titanium Glycolate $Ti(OCH_2CH_2O)_2$

V. N. Krasil'nikov, A. P. Shtin, O. I. Gyrdasova, E. V. Polyakov, and G. P. Shveikin

Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences,
ul. Pervomaiskaya 91, Yekaterinburg, 620219 Russia

Received May 4, 2007

Abstract—A new efficient method for the synthesis of extended micro- and nano-sized crystals (whiskers, fibers) of titanium glycolate $Ti(OCH_2CH_2O)_2$ has been suggested. The method implies the reaction of hydrated titanium dioxide with ethylene glycol on heating in air. Thermolysis of $Ti(OCH_2CH_2O)_2$ in air gives titanium dioxide as anatase (400–500°C) and rutile ($T > 700$°C), the morphology of titanium glycolate crystals being inherited by the oxide. The pseudocrystals of the thermolysis product in an inert gas medium ($T = 500$–950°C) represent aglomeration of nano-sized titanium dioxide particles and amorphous carbon. At temperatures up to 1300°C, the formation of the $TiO_{2-x}C_x$ phase with a rutile structure is probable. In a wet air environment, titanium glycolate is partially hydrolyzed to give $TiO_x(OCH_2CH_2O)_{2-2x}(OH)_{2x} \cdot xH_2O$ ($0 \le x \le 1$) and on keeping in water at room temperature, ethylene glycol is completely displaced from the crystals. This process is also not accompanied by changes in the particle morphology.

DOI: 10.1134/S0036023608070152

Titanium dioxide is widely used in many fields of modern technology, the development of nanotechnology giving rise to its new promising applications. This refers to the production of special ceramics, pigment materials, membranes, sorbents, luminophores, catalysts, including materials for the photocatalytic oxidation of organic compounds [1–10]. In recent years, the attention of researchers has been focused on the search for and development of efficient methods for the synthesis of titanium dioxide as nano-sized extended (quasi-one-dimensional) objects—wires, fibers, whiskers, tubes, and rods—with unique electrical, magnetic, optical, and catalytic properties [2–10]. The most efficient known method for the synthesis of TiO_2 with extended particles is based on thermolysis of titanium glycolate $Ti(OCH_2CH_2O)_2$, which has a chain structure and, under certain conditions, can be obtained as about ~50 nm-thick crystals with a length of up to 40 μm [3, 4, 11]. Thermolysis of titanium glycolate in air is accompanied by transfer of the precursor morphology to the product. Currently, method for the synthesis of extended $Ti(OCH_2CH_2O)_2$ nanocrystals consists of many-hour hydrothermal treatment of mixtures of ethylene glycol (EG) and titanium alkoxides $Ti(OR)_4$ in a Teflon-lined autoclave at 160–180°C [1, 3, 4, 11]. A main drawback of this method hampering its wide use is high cost and environmental hazard of the alkoxides $Ti(OR)_4$ [12–14], which stimulates the search for alternative methods for the synthesis of titanium glycolate without the use of titanium alkoxides. In this paper, we report the results of studies dealing with formation conditions and properties of $Ti(OCH_2CH_2O)_2$ obtained by a basically new procedure based on the reaction of EG with hydrated titanium dioxide on heating under ambient conditions.

EXPERIMENTAL

Titanium glycolate was prepared by an original procedure [15] based on a conditional reaction in which ethylene glycol serves as both a reactant and the reaction medium

$$\begin{aligned} &Ti(OH)_4 + 2HOCH_2CH_2OH \\ &= Ti(OCH_2CH_2O)_2 + 4H_2O\uparrow. \end{aligned} \quad (1)$$

Ethylene glycol was added to titanium hydroxide in the molar ratios $Ti(OH)_4 : HOCH_2CH_2OH = 1 : 20$, $1 : 30$, and $1 : 50$. The mixtures were placed in thermally stable conical flasks, heated under vigorous stirring to 170°C, kept at this temperature for 2–6 h, and cooled to room temperature. The products were separated from unreacted ethylene glycol by vacuum filtration using a glass filter, washed with acetone or acetonitrile, washed in a drying chamber at 50°C for 30 min, and placed into bottles with ground stoppers for storage. Mixtures with the composition $Ti_{1-x}Si_x(OH)_4 + 20HOCH_2CH_2OH$, where $x = 0.1$ and 0.2, were treated in a similar way. Titanium hydroxide was prepared by precipitation from a sulfuric acid solution of titanium containing 0.25 mol/L of $TiOSO_4$ and 0.57 mol/L of H_2SO_4. Ammonium hydroxide was added with vigorous stirring as the precipitating agent. The process was carried out at room temperature up to pH 7.5–8. The precipitate was separated from the mother liquor by filtering and washed by distilled water up to negative test for sulfate ions. Both wet and air-dry precipitates were used. Silicon-containing

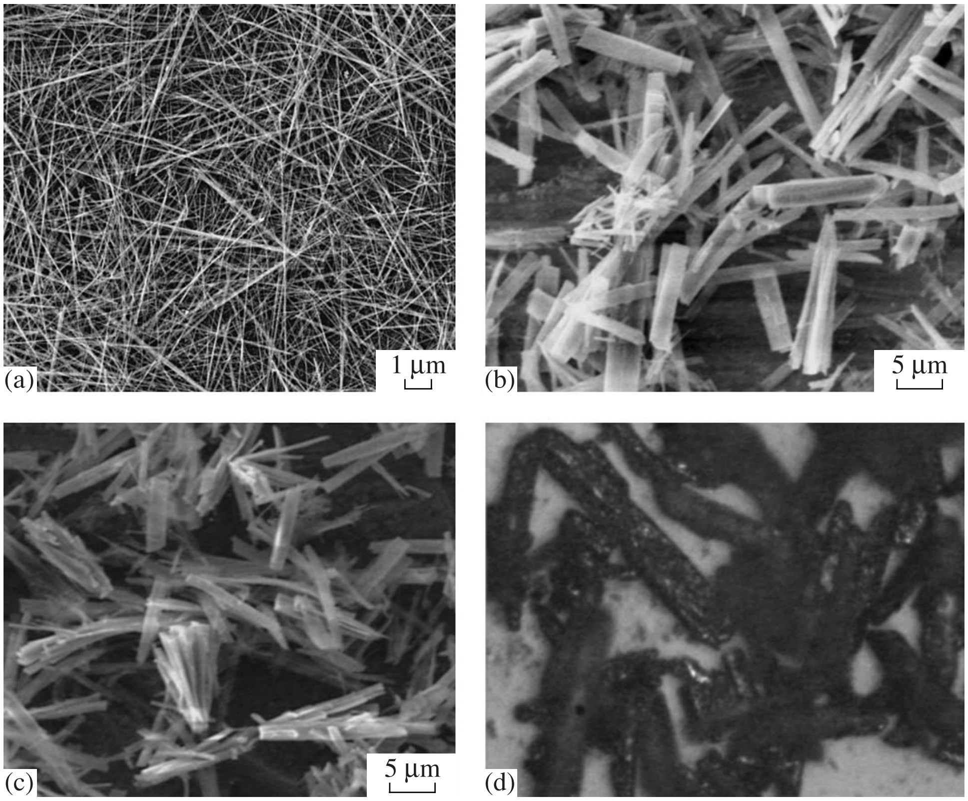

Fig. 1. SEM images of titanium glycolate and products of its thermolysis: (a) fibrous $Ti(OCH_2CH_2O)_2$; (b) thermolysis product of plate form of $Ti(OCH_2CH_2O)_2$ in air at 900°C; (c) thermolysis product of plate form of $Ti(OCH_2CH_2O)_2$ under argon at 900°C; (d) photographic image of the thermolysis product of plate form of $Ti(OCH_2CH_2O)_2$ annealed at 1300°C under argon.

samples were precipitated by adding the required amount of sodium silicate Na_2SiO_3. The phase control was accomplished by a DRON-2 diffractometer (CuK_α radiation) and a POLAM S-112 transmission polarization microscope using the optical immersion control technique. Thermogravimetric analysis was carried out on a Q-1500D derivatograph in air at a heating rate of 10 K/min in the temperature range of 20–1000°C. The IR spectra were recorded on a Spectrum-One spectrophotometer in the range 4000–400 cm^{-1}. The particle size and shape of the samples were determined by scanning electron microscopy (SEM) on a Tesla BS-301 instrument. Elemental analysis of samples was carried out by standard procedures. All experiments were carried out under conditions either excluding or minimizing the effect of air moisture.

RESULTS AND DISCUSSION

According to powder X-ray diffraction, microscopic, thermogravimetric and elemental analysis, the reaction products comprised one chemical compound $Ti(OCH_2CH_2O)_2$. The weight loss on heating in air to 900°C estimated from the TG curve, taking into account the formation of TiO_2, corresponded to the theoretical value and was 52.56 wt %. By elemental analysis, the formation of mixed glycolate $Ti_{0.96}Si_{0.04}(OCH_2CH_2O)_2$ was established; the silicon concentration in all samples did not depend on its concentration in the initial mixture. According to SEM and optical microscopy data, all the synthesized samples were formed as extended crystals with linear dimensions decreasing with an increase in the EG concentration in the reaction mixture. Figure 1 shows the SEM image of the $Ti(OCH_2CH_2O)_2$ sample synthesized by heat treatment of the reaction mixture with $Ti(OH)_4$: $HOCH_2CH_2OH$ ratio of 1 : 50. At low titanium hydroxide concentrations in the initial mixture, $Ti(OCH_2CH_2O)_2$ is formed as thin filament crystals (Fig.1a) with diameters within 100 nm. At higher concentrations, the reaction gives flattened crystals with dimensions of 0.5–2 × 10–30 μm that tend to intergrow as crosses, bundles, or hedgehog type structures. Intergrowth and twinning along the direction parallel to crystal elongation are also possible. The longitudinal intergrowth of titanium glycolate fibers was observed by a high resolution electron microscope [3]. The presence of twinning is supported by inhomogeneous extinction of some flattened $Ti(OCH_2CH_2O)_2$ crystals oriented in the N_g–N_p section. Meanwhile, $Ti_{0.96}Si_{0.04}(OCH_2CH_2O)_2$ does not tend to undergo intergrowth or twining; this phase crystallizes as rods

~0.5–1 μm in diameter and up to 10–15 μm in length. The extinction of colorless $Ti(OCH_2CH_2O)_2$ crystals relative to their elongation is direct; the refractive indices are as follows: $N_g = 1.737 \pm 0.005$, $N_m = 1.689 \pm 0.002$, and $N_p = 1.676 \pm 0.002$.

According to published data [4], the chain quasi-one-dimensional structure of $Ti(OCH_2CH_2O)_2$ in which the zigzag chains are formed from TiO_6 octahedra connected by bridging $–OCH_2CH_2O–$ groups is readily transformed on heating in air into TiO_2 with retention of the crystal morphology of precursors. It can be seen from SEM images (Fig. 1) that particles of the thermolysis products of titanium glycolate synthesized at the ratio $Ti(OH)_4 : HOCH_2CH_2OH = 1 : 20$ retain the appearance of the initial crystals upon heating at 10 K/min to 900°C in air (Fig. 1b) or under argon (Fig. 1c). The powder obtained on annealing in air is colorless and, according to X-ray diffraction data, this is the high-temperature (rutile) modification of titanium dioxide and, after annealing under inert gas, the product becomes black (Fig. 1d). Examination under a transmission polarized light microscope shows black nontransparent extended objects pseudomorphous to the titanium glycolate precursor crystals.

Figure 2 shows the X-ray diffraction patterns of the products of thermolysis of titanium glycolate recorded after keeping under argon at 500, 900, and 1300°C for 2 h. It can be seen from Fig. 2 that heat treatment of $Ti(OCH_2CH_2O)_2$ at 500°C yields TiO_2 with the anatase structure. The sample heat treated, at 900°C contains two titanium dioxide modifications (anatase and rutile). A similar result is obtained upon heat treatment of titanium glycolate in air; however, in this case, titanium dioxide formed initially as anatase (400–500°C) is converted into rutile on heating to 700°C. As the temperature of annealing under argon increases, the sample becomes more and more X-ray amorphous. On the basis of reflections present in the X-ray diffraction pattern of the sample, one can suggest the presence of a rutile phase only with a high degree of admission. The image (Fig. 1d) obtained in the reflected light shows the pseudocrystals of the thermolysis product obtained by heating $Ti(OCH_2CH_2O)_2$ to 1300°C and keeping for 2 h under argon. The annealing of this sample in air does not change the particle morphology but its color becomes bluish-gray, which attests to incomplete removal of carbon or partial reduction of titanium to give, for example, nonstoichiometric oxide TiO_{2-x} [16]. According to powder X-ray diffraction, the sample contains titanium dioxide mainly as rutile with some anatase. It was shown [12] that heating of finely dispersed anatase mixed with carbon under argon does not induce its transformation into rutile even above 1000°C. The X-ray diffraction pattern of the sample heated to 1050°C showed new lines assigned to the oxycarbide TiC_xO_y.

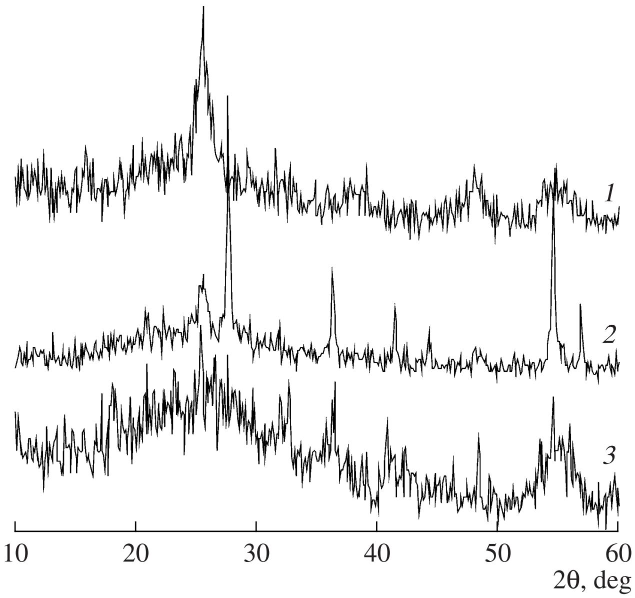

Fig. 2. X-ray diffraction patterns of thermolysis products of $Ti(OCH_2CH_2O)_2$ obtained under argon at (*1*) 500; (*2*) 900; (*3*) 1300°C.

Figure 3 demonstrates the TG and DTA curves of the (a) fibrous $Ti(OCH_2CH_2O)_2$ sample and (b) the same sample kept preliminarily at 600°C under argon for 2 h. Thermal decomposition of titanium glycolate occurs in two steps (Fig. 3a) and is completed by formation of TiO_2 (anatase) at ~500°C. The weight loss above 300°C and the corresponding exotherm in the DTA curve with a maximum at 405°C can be attributed to oxidation of the solid phase, preferably, amorphous

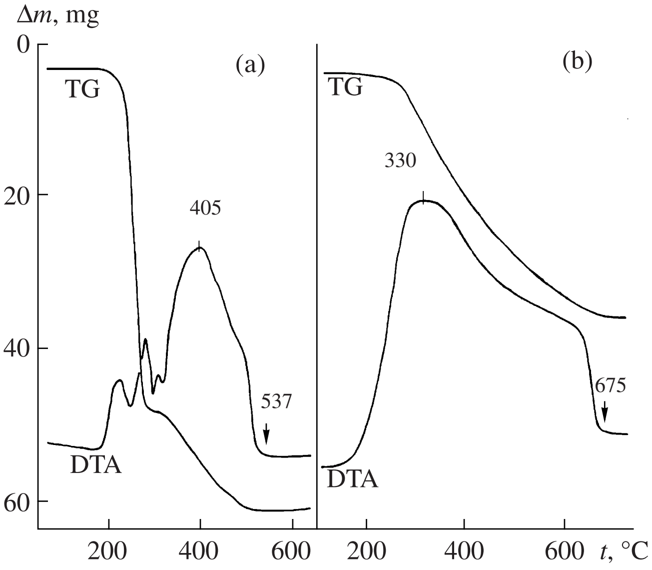

Fig. 3. TG and DTA curves of (a) titanium glycolate $Ti(OCH_2CH_2O)_2$ and (b) the same sample kept under argon at 600°C.

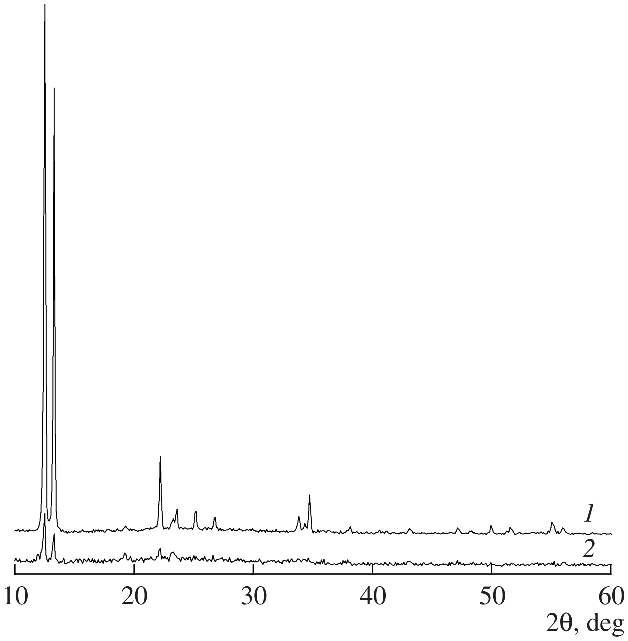

Fig. 4. X-ray diffraction patterns of fibrous $Ti(OCH_2CH_2O)_2$ (*1*) before and (*2*) after keeping in a closed desiccator over water.

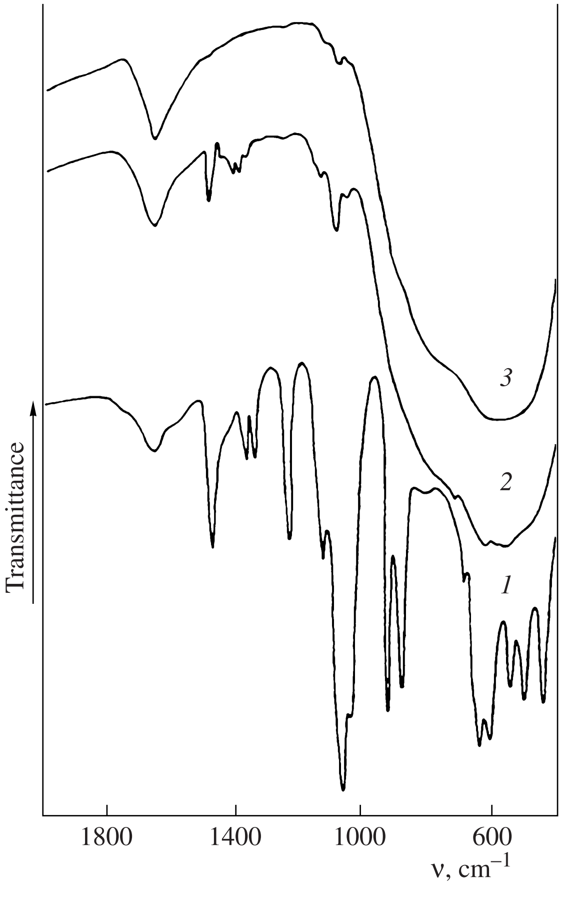

Fig. 5. IR spectra of $Ti(OCH_2CH_2O)_2$samples kept (*1*) in air, (*2*) in a desiccator over water, or (3) in water.

carbon. The TG curve of the sample kept under argon shows the weight loss of up to 20 wt % accompanied by an exotherm with a maximum at 330°C in the DTA curve. Complete removal of the combustible components is accompanied by the formation of titanium dioxide with rutile structure. Since the particle morphology remains unchanged during all operations, the pseudocrystals formed upon thermolysis of $Ti(OCH_2CH_2O)_2$ under inert gas atmosphere can be considered as containers incorporating separate nanoparticles of titanium dioxide and amorphous carbon. It is quite probable that the above-noted amorphization of the thermolysis product at 1300°C under argon is due to the reaction of TiO_2 particles and carbon to give phases like $TiO_{2-x}C_x$ with a structure similar to that of rutile, which is converted into rutile upon maintenance in air at 450°C.

Previously [3, 4, 11], in order to remove EG impurity from the synthesized titanium glycolate precipitate, the samples were washed with distilled water and then with ethanol. In our experiments, we found that the $Ti(OCH_2CH_2O)_2$ crystals can sorb atmospheric moisture, the fibrous crystals being most hygroscopic. Keeping nano-sized titanium glycolate fibers in a desiccator over water transforms them into an amorphous gel-like material. Figure 4 shows the X-ray diffraction patterns of $Ti(OCH_2CH_2O)_2$ and the sample obtained by keeping this compound in a closed desiccator over water for a week at room temperature followed by washing by acetone and drying at 50°C. Comparison of X-ray diffraction patterns unambiguously attests to degradation of titanium glycolate caused by the action of water vapor. This occurs as a result of EG displacement from $Ti(OCH_2CH_2O)_2$ crystals by water. It is important that, in this case too, the change in the sample composition does not affect the particle morphology, which remains invariable throughout all stages of hydration; the morphology remains the same even after almost complete removal of EG by keeping the $Ti(OCH_2CH_2O)_2$ sample in distilled water for 2 weeks. Annealing in air at 350–500°C affords titanium dioxide with the anatase structure and with particles that inherited the precursor morphology.

The IR spectra of titanium glycolate treated with water vapor in an open vessel in air or in a closed desiccator over water, and those kept directly in water are presented in Fig. 5. The IR spectrum of the sample kept in air differs from the spectrum of the initial titanium glycolate by the presence of new bands in the vibration frequencies of water molecules [17]. The $\nu(H_2O)$ stretching vibrations are responsible for a broad band with an absorption peak at 3285 cm^{-1} and the $\delta(H_2O)$ bending vibrations are responsible by one more broad band at 1646 cm^{-1}. In the IR spectra of samples that have been kept in the desiccator over water and in water, these bands are more clear-cut and, in addition, they are shifted to lower frequencies (3230, 3190 cm^{-1}

and 1638, 1633 cm^{-1}). The bands corresponding to $–OCH_2CH_2O–$ group vibrations are absent from the IR spectrum of the sample kept in water, indicating complete displacement of EG from the titanium glycolate crystals. After annealing at 900°C under argon, this sample remained colorless, while the samples kept preliminarily in desiccator over water or in water became black or bluish-gray, respectively, which is related to different contents of carbon in them. Thus, washing of titanium glycolate with water followed by heat treatment under an inert gas or in air can be used to control the carbon content in the extended pseudocrystals thus formed, which is quite significant for the formation of titanium dioxide-based catalysts photoactive in the visible region [18–20]. The presence of rather broad $\delta(H_2O)$ band with an absorption peak at 1647 cm^{-1} in the IR spectrum of $Ti(OCH_2CH_2O)_2$ kept in air (Fig. 5) is indicative of a complicated route of its reaction with water vapor differing from the mere substitution of OH groups for the $–OCH_2CH_2O–$ groups. In the IR spectra of samples kept in an atmosphere of saturated water vapor and in water, the $\delta(H_2O)$ band becomes more intense; in addition, these spectra exhibit a very intense broad band at ~1000–500 cm^{-1}, which is usually attributed to Ti–O and Ti–O–Ti vibrations and OH bending vibrations [14, 17, 21]. The IR spectra recorded for intermediate periods of keeping the samples in water represent superpositions of bands observed for the initial titanium glycolate and for hydrated titanium dioxide [14, 21], the contribution of the band at ~1000–500 cm^{-1} regularly increasing and that of the bands for $–OCH_2CH_2O–$ regularly decreasing. Correspondingly, the intensity of the exotherm with DTA maximum at ~400°C also decreases (see Fig. 3a). Thus, on the basis of IR spectroscopy data, the products of titanium glycolate hydration can be represented as $TiO_x(OCH_2CH_2O)_{2-2x}(OH)_{2x} \cdot xH_2O$, where $0 \le x \le 1$.

Thus, it was found that the proposed synthetic procedure based on the reaction of hydrated titanium dioxide with ethylene glycol allows the preparation of $Ti(OCH_2CH_2O)_2$ as either micro- or nano-sized extended crystals. The shape and the linear dimensions of the sample particles depend on the chosen reaction conditions. On heating in oxidative air atmosphere or in an inert gas, the morphology of the $Ti(OCH_2CH_2O)_2$ precursor particles is imparted to the products of its thermolysis. The same takes place in the hydrolysis of titanium glycolate on contact with water. The $Ti(OCH_2CH_2O)_2$ samples, especially as nanofibers, should be stored under conditions that rule out contact with water or water vapor.

ACKNOWLEDGMENTS

This work was carried out under the State contract no. 2007-2-13-03-24-01-595 and partially supported by the Council for Grants of the President of the Russian Federation for support of Scientific Schools (grant no. NSh-8380.2006.3.

REFERENCES

1. N. Phonthammachai, T. Chairassameewong, E. Gulari, et al., Microporous Mesoporous Mater. **66**, 261 (2003).
2. Congkang Xu, Yongjie Zhan, Kunquan Hong, and Guanghou Wang, Solid State Commun. **126**, 545 (2003).
3. Xuchuan Jiang, Yuliang Wang, Thurston Herricks, and Younan Xia, J. Mater. Chem. **14**, 695 (2004).
4. Dan Wang, Ranbo Yu, Yunfa Chen, et al., Solid State Ionics **172**, 101 (2004).
5. Hongrui Peng, Guicun li, and Zhikun Zhang, Mater. Lett, **59**. 1142 (2005).
6. B. Neppolian, H. Yamashita, Y. Okada, et al., J. Catal. Lett. **105** (1–2), 111 (2005).
7. M. Calatayud and C. Minot, Top. Catal. **40** (1–4), 17 (2006).
8. Ye Sheng, Bing Zhou, Yanhua Liu, et al., Mater. Lett. **60**, 1327 (2006).
9. O. P. Ferreira, A. G. S. Filho, J. M. Filho, and O. L. Alves, J. Braz. Chem. Soc **17** (2), 1 (2006).
10. Jung-Chul Lee, Kyung-Soo Park, Tae-Geun Kim, et al. Nanotechnol. **17**, 4317 (2006).
11. Wang. Dan, Yu. Ranbo, N. Kumada, and N. Kinomura, Chem. Mater. **11** (8), 2008 (1999).
12. Y. Gotoh, K. Fujimura, M. Koike, et al., Mater. Res. Bull. **36**, 2263 (2001).
13. S. J. Lee and C. H. Lee, Mater. Lett. **56**, 705 (2002).
14. R. Campostrini, M. Ischia, and L. Palmisano, J. Therm. Anal. Cal. **75**, 25 (2004).
15. V. N. Krasil'nikov, A. P. Shtin, O. I. Gyrdasova, and G. P. Shveikin, *Proceedings of the 6th International Conference "Solid State Chemistry and Advanced Micro- and Nanotechnologies"* (Kislovodsk, 2005), p. 70.
16. I. Tsuyumoto and H. Uchikawa, Mater. Res. Bull. **39**, 1737 (2004).
17. K. Nakamoto, *Infrared and SEMan Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1986; Mir, Moscow, 1991).
18. G. Colon, M. C. Hidalgo, M. Macias, and J. A. Navio, Appl. Catal. A **259**, 235 (2004).
19. C. Valentin, G. Pacchioni, and A. Selloni, Chem. Mater. **17** (26), 6656 (2005).
20. Ming Shen, Zunyi Wu, Hui Huang, et al., Mater. Lett. **60**, 693 (2006).
21. L. I. Biryuk, Ya. G. Goroshchenko, and A. M. Kalinichenko, Ukr. Khim. Zh. **37**, 1063 (1971).