Synthesis of Nanoparticulate Anatase Sol from Tetrabutoxytitanium

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Abstract—Titanium oxyhydrate nanoparticles have been prepared via tetrabutoxytitanium hydrolysis. The addition of a stabilizing component (acetylacetone) to tetrabutoxytitanium prior to hydrolysis in a mixture of water and ethanol made it possible to sharply reduce the hydrolysis rate. Boiling at 100°C converted amorphous titanium oxyhydrate sol into nanocrystalline anatase with a crystallite size of 3.5 nm. According to scanning electron microscopy data, the TiO_2 particles were spherical in shape and ranged in size from 90 to 290 nm. The material was characterized by X-ray diffraction, simultaneous thermal analysis, electron microscopy, and dynamic light scattering.

INTRODUCTION

Nanoparticulate titania is of interest for applications in photocatalysis [1–4], sensors, solar cells, pigments, and self-cleaning coatings [4, 5]. At present, there is considerable effort to produce novel fine-particle and porous titania-based materials [4, 6]. Tetrabutoxytitanium (TBT) hydrolysis is one of the most attractive processes for the preparation of nanoparticulate TiO_2. The ability to control the size and shape of titania particles remains a challenging problem, because sol formation, gelation, and gel crystallization processes have not yet been studied in sufficient detail.

Beta-diketonates are known to be strong chelating ligands which form strong, hydrolysis-resistant complexes with multiply charged transition-metal cations [7, 8]. In particular, TBT forms strong complexes with acetylacetone (acac), which sharply reduce the rate and degree of TBT hydrolysis [6, 9].

Whereas TBT hydrolysis is rather often used for the preparation of titanium oxyhydrate [5, 10–12], TBT hydrolysis with the use of acetylacetone has been described in the literature for other solvents [13].

The purpose of this work was to study conditions for the preparation of TiO_2 nanoparticles from TBT using acetylacetone as a stabilizing component.

EXPERIMENTAL

In our preparations, we used analytical-grade TBT, acac, and ethanol (93%) and distilled water. The titanium content of TBT is 14.3 wt %; the major impurity is Fe (0.002 wt %). The uncertainty in solution compositions is within 2 vol %. A TBT + acac solution, ethanol, and water were prepared separately, and then sequentially mixed with each other. The components for synthesis were mixed in the following order: To 1 mL of TBT was added 0.2 mL of acac. After stirring, 33.3 mL of EtOH (93 vol %) was added, and the chemicals were again stirred. Next, to the resultant transparent solution was added 16 mL of water and the solution was vigorously stirred to give white sol. Part of the solid phase was removed by centrifugation (rotor rotation rate of 9000 rpm), and the remaining sol, stable to precipitation, was added to 150 mL of boiling distilled water and boiled for 1 h, while adding distilled water as the liquid vaporized.

After boiling, the sol was unstable and the forming precipitate was separated from the liquid by decantation, dried, and characterized by scanning electron microscopy (JEOL JSM-7001F) and X-ray diffraction (Rigaku Ultima IV).

The particle size of the sol before and after centrifugation was determined using dynamic light scattering (DLS) on a Microtrac Nanotrac Ultra 253 analyzer. After boiling, the precipitate was characterized by simultaneous thermal analysis (Netzsch STA 449C Jupiter).

RESULTS AND DISCUSSION

An important feature of the hydrolysis of a TBT + acac solution with an ethanol + water solution (93 wt % ethanol) at room temperature is precipitation, for a short time, of an opalescent sol of intermediate products, which then dissolve in the resultant solution. This points to a complex hydrolysis mechanism, which involves the formation of metastable, short-lived products.
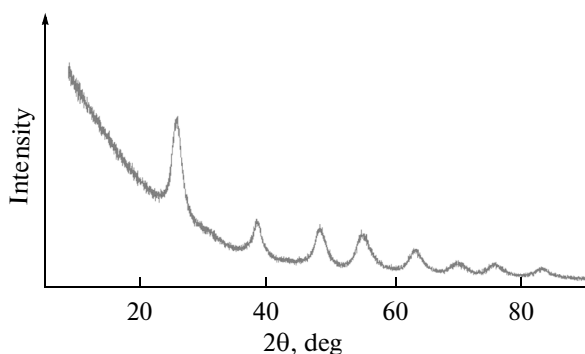
Fig. 1. X-ray diffraction pattern of the anatase sol after boiling at 100°C.

The average particle size of the sol obtained by adding 16 mL of water was 550 nm as determined by DLS. After part of the solid phase was separated by centrifugation, the average particle size of the remaining sol particles was 371 nm. This value is close to the size of spherical anatase particles observed by electron microscopy after boiling: 100−300 nm.

X-ray diffraction characterization of the sample obtained by boiling the sol showed that TiO_2 had the anatase structure (Fig. 1). From diffraction peak broadening, the TiO_2 crystallite size was estimated at 3.5 nm. Before boiling, the sol (the material separated by centrifugation) consisted of X-ray amorphous titanium oxyhydrate.

The morphology of the sample was examined by electron microscopy at magnifications of up to 200 000×. The sol particles had the form of regular spheres ranging in diameter from 100 to 300 nm (Fig. 2). The crystallite size evaluated from X-ray diffraction data was far smaller than the observed sphere size, which led us to assume that the larger spheres were composed of individual crystallites 3.5 nm in size. A similar structure was reported for 840-nm-diameter microspheres composed of anatase crystals about 12 nm in size, which were prepared by hydrothermal processing of titanyl sulfate in the presence of NH_4Cl [14].

Using simultaneous thermal analysis, we were able to assess the degree of TBT hydrolysis and the temperature at which the residual organics were removed (Fig. 3) during heating in air at a rate of 10°C/min. It follows from the thermal analysis data that the decomposition occurred in four steps: 100−255, 225−325, 325−390, and 390−1100°C. The total weight loss on heating to 1100°C was 40.2 wt %, with weight losses of 20.8, 12.9, 5.1, and 1.4 wt % in each step, respectively. Mass spectrometry data for gaseous decomposition products lead us to conclude that the predominantly released compounds are water, butanol, acac, and ethanol in the range 100−225°C and butanol, ethanol, and their decomposition products in the range 225−390°C (Fig. 4). The first two decomposition steps are accompanied by heat absorption, whereas the third step includes an exothermic event with a sharp peak at 386.5°C, due to the crystallization of the amorphous precipitate into anatase and the oxidation of organic molecules, as evidenced by the increase in the ion current of species with a mass number of 44 amu, corresponding to an increase in carbon dioxide concentration in the atmosphere over the sample. In the range 390−1100°C, a slight weight loss is observed (without significant thermal events), due to water release and the oxidation of organic residues.

Butanol is released in two steps. The first, lower temperature step, with a maximum at 146°C, is the vaporization of adsorbed butanol, which imparts a characteristic smell to the samples. This assumption is supported by the vaporization of water (not shown in Fig. 4) and ethanol, comparable in volatility to

(a)   10 nm   (b)   100 nm
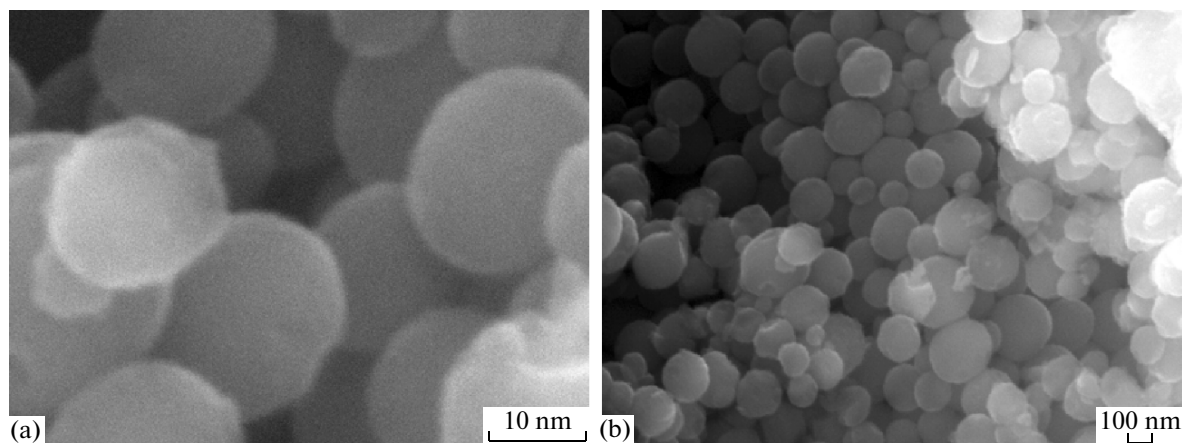
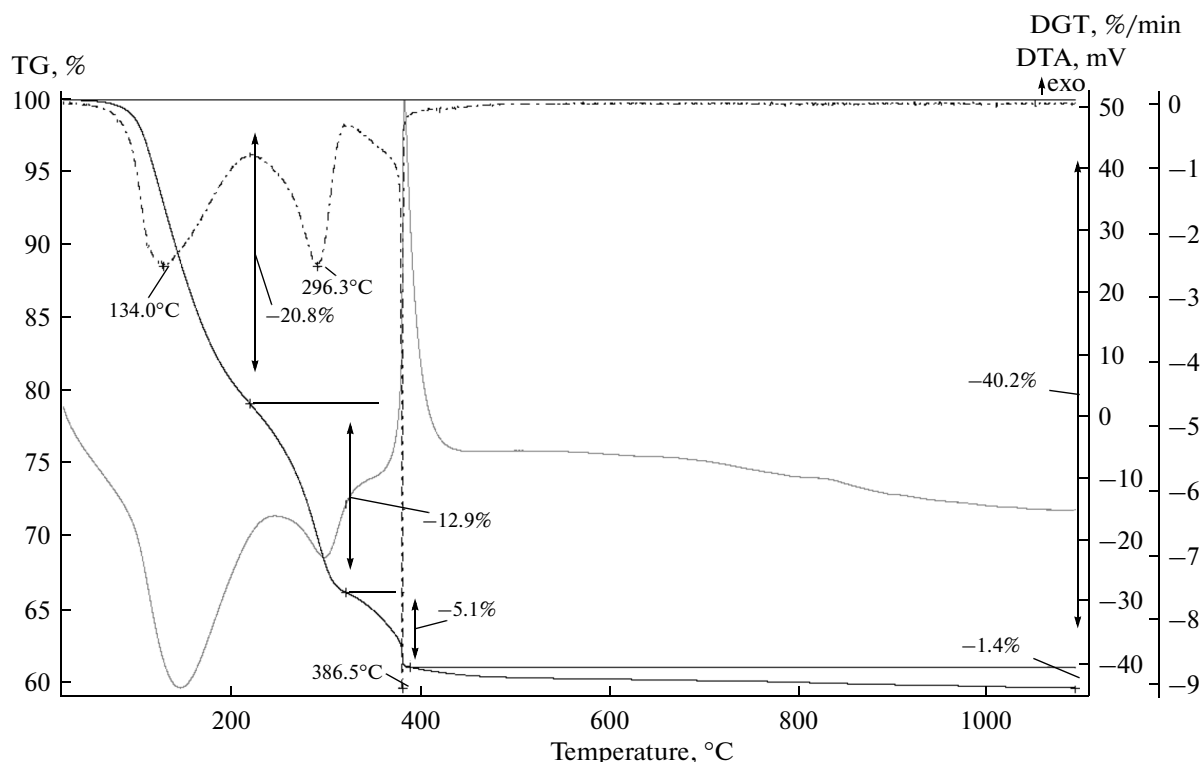**Fig. 2.** Morphology of the anatase sol.

Fig. 3. Thermal analysis data for the titanium oxyhydrate sol.

butanol, in the same temperature range (the boiling point of butanol is 117°C [15]). Similarly, acetylacetone, which has a higher boiling point (140°C [15]) has a release peak at a somewhat higher temperature: 192°C (Fig. 4). The second butanol release peak is centered at 302°C and is attributable to the decomposition of butoxy groups linked to titanium. At higher temperatures, a key role is played by oxidation accompanied by carbon dioxide release, with a maximum near 388°C. The thermolysis products of organic residues also show up as small peaks at larger mass numbers (67–120 amu), not attributable to the substances under consideration.

The second ethanol release peak, similar to the second butanol release peak, is most likely due to the decomposition of the ethoxy groups linked to the titanium. This assumption is consistent with the complex character of the hydrolysis, which shows up as temporal formation of an opalescent sol when a mixture of TBT and 15–30 vol % acac is added to a mixture of EtOH and 4–20 vol % water. The opalescent sol persists for several seconds or several days, depending on the temperature and the amounts of acac and water, and then completely dissolves. Thus, it is reasonable to assume partial substitution of ethoxy and hydroxy groups for butoxy groups in the course of interaction with the water–alcohol solution, which leads to the formation of unstable, insoluble intermediate species.

The hydrolysis mechanism probably includes the formation of stable TBT tri- and tetramers in solution [7, 8, 16]. In particular, cryoscopic measurements of the average molecular weight of TBT dissolved in solvents weakly interacting with it demonstrate that, in dilute solutions, the average number of TBT molecules in the associates is three [16]. Later reports describe cyclic tetramer molecules [7]. In both cases, the coordination sphere of the titanium atoms is completed to an octahedron due to donor–acceptor (bridge) bonds with oxygens of neighboring TBT molecules.

Another factor influencing the equilibrium state and kinetics of the system is the formation of stable complexes of titanium with acetylacetone [7, 8]. At high acetylacetone concentrations, TBT hydrolysis in water is completely suppressed [7, 12], which is supported by the present results. Acting as a bidentate ligand, acac is capable of completing the TBT molecule to an octahedron and shielding titanium from water attack.

Acting at different rates, partial hydrolysis, re-esterification, complexation, and polymerization (cyclization) seem to be responsible for the primary formation of metastable precipitates, which then dissolve.

After boiling at 100°C, the differential thermal analysis (DTA) curve showed no peak attributable to anatase crystallization (Fig. 5), because all of the tita-
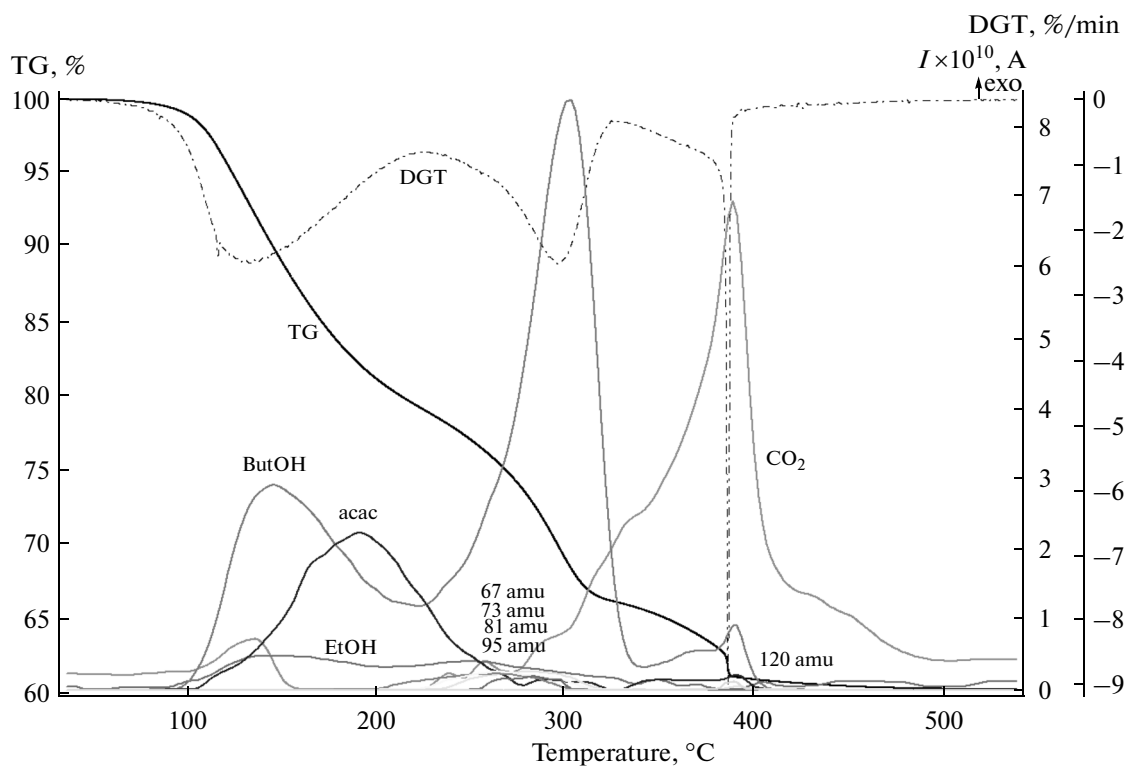
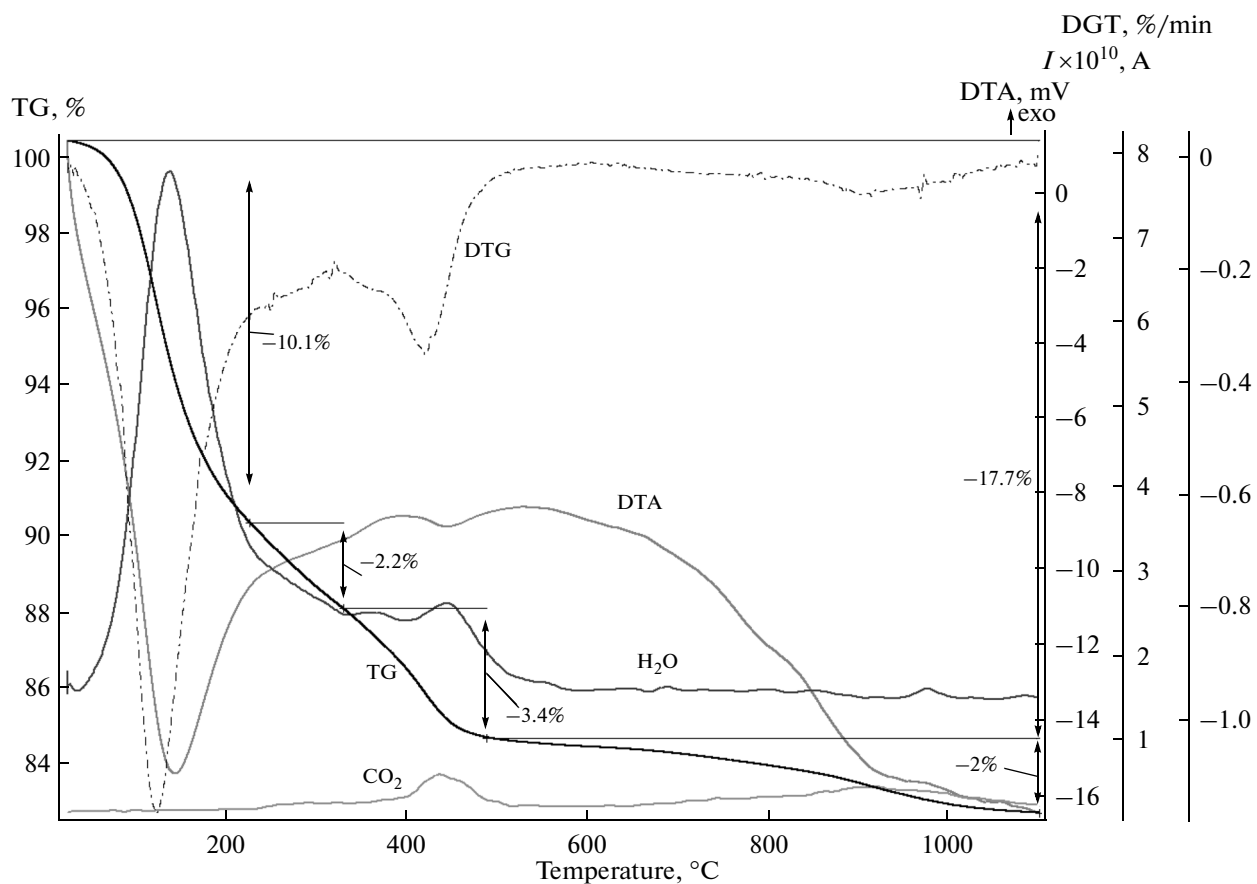**Fig. 4.** Composition of volatile components released during heating of the titanium oxyhydrate sol.

Fig. 5. Thermal analysis data for the anatase sol after boiling at 100°C.

nia was already crystalline (Fig. 1). A major component released when the sample was heated was water. The amount of released carbon dioxide was much smaller. Butanol, acac, and ethanol were missing in the mass spectrum, but the small amount of released carbon dioxide corresponds to the oxidation of their decomposition products.

CONCLUSIONS

Titanium oxyhydrate has been prepared via TBT hydrolysis in a mixture of water and ethanol. The addition of acetylacetone during hydrolysis made it possible to reduce the TBT hydrolysis rate and obtain a hydrolysis product in the form of spherical particles ranging in diameter from 100 to 300 nm. Boiling at 100°C converted the oxyhydrate sol into anatase with a crystallite size of 3.5 nm as determined by X-ray diffraction.

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