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Physicochemical Properties of TiO_2 (Anatase) Prepared by the Centrifugal Thermal Activation of Hydrated Titanium Dioxide

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Abstract—The physicochemical properties of titania (anatase) prepared from hydrated titanium dioxide by centrifugal thermal activation (CTA) at 140–700°C were studied. It was found that the microstructure and the texture parameters of anatase prepared by the above method were considerably different from those of the samples prepared by the traditional thermal decomposition of titanium hydroxide. The conditions of centrifugal activation exerted a considerable effect on the structure and the texture parameters of the resulting anatase. The crystal structure of anatase prepared at a temperature lower than 650°C was imperfect, and it approached a regular structure only at a temperature of >650°C. At temperatures higher than 300°C, the samples of TiO_2 prepared using CTA were characterized by higher specific surface areas, fine pore structures, and comparable mesopore volumes, as compared with the samples prepared by commonly used synthetic methods.

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INTRODUCTION

A new technology for the rapid thermal treatment of powdered materials in a centrifugal flash reactor (CEFLAR) to manufacture so-called centrifugal thermal activation (CTA) products was developed at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences in cooperation with the Design and Technology Division of the Lavrent'ev Institute of Hydrodynamics, Siberian Branch, Russian Academy of Sciences [1, 2]. This new technology is based on a short (0.5–1.5 s) contact of the initial reagent with a heated rotating surface followed by the rapid cooling of the resulting product. Two modifications of the CEFLAR systems with different configurations of the heated rotating surfaces (a cylinder [1] and a dish-shaped plate [2]) were developed. The heating rate of treated material particles in both of the reactors can be higher than 1000 K/s to exert a considerable effect on the formation of the phase composition of thermal decomposition products and on the microstructure, acid–base properties, and texture of these products. In this context, the physicochemical properties of substances prepared by this method can be highly specific and different from those of materials prepared by commonly used methods. Thus, the preparation of aluminum oxides and hydroxides based on the products of the rapid thermal decomposition of aluminum thrihydroxide (hydrargillite) in the CEFLAR system was studied previously [3–6]. It was found that the CTA of hydrargillite afforded an X-ray amorphous, highly reactive product with developed surface and porosity, and structurally different aluminum oxides can be formed from this product. Kul'ko et al. [5] demonstrated that, with the use of CTA products, the structure transformation of γ-Al_2O_3 to α-Al_2O_3 occurred at a lower temperature than that in the samples prepared by traditional methods, such as precipitation from a salt solution of aluminum nitrate. This was explained by a higher degree of crystal structure imperfection of γ-Al_2O_3 in the former case. In addition, Kul'ko et al. [6] found that the oxide with the γ-Al_2O_3 structure prepared by the CTA of hydrargillite was characterized by a higher acidity than that of γ-Al_2O_3 prepared from precipitated pseudoboehmite.

Note that the new technology for the treatment of powdered materials was mainly tested in the production of aluminum oxide. Up to now, other metal oxides, for example, titanium dioxide, which is also widely used in catalysis as a support for both environmental catalysts [7–9] and partial oxidation catalysts [10–12], have not been produced using the CTA method. Because of this, the use of CTA for the manufacture of a wider range of defect oxide materials is of considerable interest.

The aim of this work was to study the effect of the conditions of the CTA of hydrated titanium dioxide on the composition and physicochemical properties of the resulting products.

EXPERIMENTAL

Hydrated titanium dioxide, which was prepared by the thermal hydrolysis of a sulfuric acid solution of titanium in accordance with a commercial sulfuric acid technology [13], was used as a starting titanium compound. The initial sample as a fraction with a granule size of 200–400 μm, which was predried at 110°C for 12 h, was subjected to CTA for 1–1.5 s at a constant temperature of 140–700°C in the CEFLAR system with a heated rotating surface as a hollow thin-walled steel cylinder [1]. In the system used, the initial powder was supplied to the inner surface of the vertical rotating cylinder with an inner diameter of 200 mm and a height of 350 mm. Heating elements were arranged on the outside of the cylinder; in the course of thermal activation, the temperature of these elements (T_h) was kept constant. Calcined substrate particles helically moved in a downward direction being in contact with the hot surface due to centrifugal force for 1.0–1.5 s [2]. The rate of cylinder rotation was chosen in such a way as to prevent powder sticking to the working surface. From the hot zone of the reactor, the thermally activated material arrived at a water-cooled metal surface for quenching and then at a product collector. The setup was equipped with an exhaust ventilation system, because of which vapor released in the course of thermal decomposition was removed upwards.

The concentration of sulfate ions was determined by X-ray fluorescence spectrometry on a VRA-20 analyzer (Germany) with a tungsten anode. The water contents of the samples were found from the weight loss of the samples dried at 110°C and calcined at 850°C with consideration for the concentrations of sulfate ions.

X-ray diffraction experiments were performed on a URD-63 diffractometer (Germany) with a graphite monochromator using CuK_α radiation. X-ray diffraction patterns were obtained by point-by-point scanning with a 2θ step of 0.02° at an accumulation time of 20 s at each point. The lattice parameters of anatase were refined by the least-squares technique in accordance with a program [14] using three to seven lines depending on the degree of diffraction peak resolution in the angle range of 50°–70°. The size of the coherent-scattering regions of anatase crystallites (D_{CSR}) was calculated from the Selyakov–Scherrer equation using the half-widths of the (101) and (200) diffraction peaks [15]. The amount of anatase in the sample was determined from the (200) line using as an external reference standard titanium dioxide prepared in accordance with a published procedure [16] and calcined at 500°C.

The total specific surface area S (m^2/g) was measured on a SORBI-M instrument (META, Russia) using a traditional procedure of Ar thermal desorption based on four sorption equilibrium points. The pore-throat size distribution was calculated from the desorption branches of nitrogen adsorption isotherms using the classical Barret–Joyner–Halenda (BJH) method [17]. The isotherms of low-temperature (77 K) N_2 sorption were measured on a Micromeritics Digisorb 2600 instrument (United States). The samples were pretreated in a vacuum of 10^{-3} Torr at 200°C for 5 h.

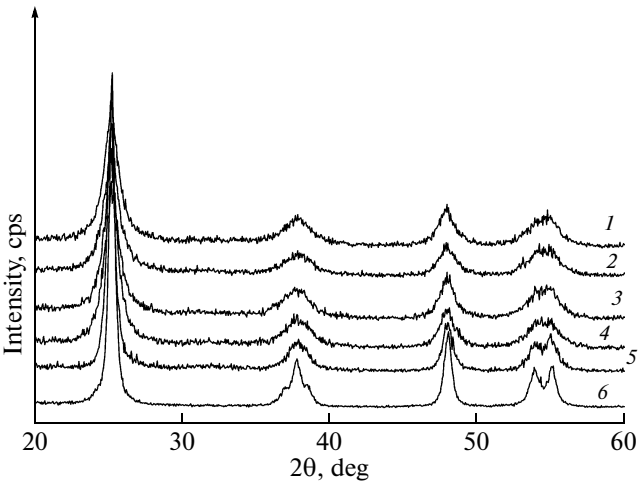

Fig. 1. X-ray diffraction patterns of titanium dioxide samples prepared by CTA over the temperature range of 140–700°C: (*1*) 140, (*2*) 200, (*3*) 300, (*4*) 400, (*5*) 650, and (*6*) 700°C.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction analysis data for the products obtained by the CTA of hydrated titanium dioxide over the temperature range of 140–700°C. It can be seen that all the samples contained only one crystalline phase of anatase, and no other crystalline phases were detected in the X-ray diffraction patterns.

According to published data [18], TiO_2 with a regular well-ordered anatase structure has a tetragonal structure with the parameters $a_0 = 3.785$ Å and $c_0 = 9.513$ Å. Table 1 summarizes the lattice parameters of anatase and the sizes D_{CSR} for titanium dioxide samples prepared by CTA depending on temperature. It can be seen that the treatment of hydrated titanium dioxide at a temperature lower than 650°C resulted in the formation of anatase with a considerably distorted crystal structure. At a treatment temperature of 650°C or higher, the lattice parameters of anatase became close to the lattice parameters of anatase with a regular structure.

According to chemical analysis data, the samples prepared contained the impurities of sulfate ions and water, the amount of which decreased with treatment temperature (Table 1). As found previously [19] (Table 2), the observed distortions in the anatase structure were due to the presence of structurally

Table 1. Crystallogrophic data for anatase depending on the CTA temperature

Sample	Chemical composition	Unit cell parameters		D_{CSR}, nm
		a_0, Å	c_0, Å	
TiO_2 (140°C)	$TiO_2 \cdot 0.55H_2O \cdot 0.019SO_4^{2-}$	3.791(3)	9.484(3)	7.5
TiO_2 (200°C)	$TiO_2 \cdot 0.53H_2O \cdot 0.018SO_4^{2-}$	3.791(4)	9.485(6)	7.0
TiO_2 (300°C)	$TiO_2 \cdot 0.50H_2O \cdot 0.017SO_4^{2-}$	3.783(4)	9.480(3)	8.0
TiO_2 (400°C)	$TiO_2 \cdot 0.46H_2O \cdot 0.016SO_4^{2-}$	3.789(2)	9.484(1)	7.5
TiO_2 (500°C)	$TiO_2 \cdot 0.41H_2O \cdot 0.014SO_4^{2-}$	3.788(2)	9.486(1)	8.5
TiO_2 (650°C)	$TiO_2 \cdot 0.18H_2O \cdot 0.010SO_4^{2-}$	3.787(5)	9.504(5)	15.0
TiO_2 (700°C)	$TiO_2 \cdot 0.10H_2O \cdot 0.007SO_4^{2-}$	3.785(2)	9.514(4)	26.0

Table 2. Crystallogrophic data for anatase depending on the temperature of thermal decomposition of titanium hydroxide under standard conditions according to Zenkovets et al. [19]

Sample	Chemical composition	Unit cell parameters		D_{CSR}, nm
		a_0, Å	c_0, Å	
TiO_2 (150°C)	$TiO_2 \cdot 0.55H_2O \cdot 0.017SO_4^{2-}$	–	–	–
TiO_2 (300°C)	$TiO_2 \cdot 0.47H_2O \cdot 0.014SO_4^{2-}$	3.793(3)	9.41(2)	8.0
TiO_2 (400°C)	$TiO_2 \cdot 0.39H_2O \cdot 0.012SO_4^{2-}$	3.790(1)	9.42(4)	12.5
TiO_2 (500°C)	$TiO_2 \cdot 0.16H_2O \cdot 0.008SO_4^{2-}$	3.789(1)	9.511(2)	19.0
TiO_2 (650°C)	$TiO_2 \cdot 0.09H_2O \cdot 0.003SO_4^{2-}$	3.787(3)	9.516(1)	39.0

Table 3. Texture parameters of TiO_2 on the temperature of treatment under CTA conditions

Sample	S_α, m^2/g	V_μ, cm^3/g	V_s, cm^3/g	D, nm
TiO_2 (200°C)	237	0.017	0.311	2.1
TiO_2 (300°C)	233	0.013	0.327	2.1
TiO_2 (400°C)	252	0	0.324	2.7
TiO_2 (650°C)	124	0	0.300	3.9
TiO_2 (700°C)	106	0	0.343	4.9

Note: S_α is the mesopore surface area; V_μ is the micropore volume; V_s is the limiting sorption space volume; and D is the dominant mesopore diameter.

bound sulfate ion impurities and hydroxyl groups. It is likely that the observed change in anatase lattice parameters for the resulting samples with increasing calcination temperature can be due to the fact that, in the anatase structure, the chains of vertex-connected TiO_6 octahedrons are arranged in the (001) planes along the [100] and [010] directions. The octahedrons from two parallel planes have shared edges, and the faces of these octahedrons form tetrahedrons (vacant in an ideal anatase structure) with A–O distances of 1.94 Å, where A is the center of the tetrahedron. The stabilization of the sulfur atom at a tetrahedrally coordinated position should result in a considerable decrease in the tetrahedron size and in the contraction of TiO_6 octahedrons from two different chains. As a consequence, the average Ti–O and O–O interatomic distances in the anatase structure decrease and the lattice parameter c_0 decreases because the chains of TiO_6 octahedrons belong to two parallel (001) planes. As found previously [19] by electron microscopy, the anatase structure containing sulfate ions is imperfect; statistically distributed defects in the cationic sublattice and a distortion in atomic rows were detected in this structure.

Table 3 summarizes the texture parameters of TiO_2 samples prepared by CTA. The resulting samples were characterized by high specific surface areas (Fig. 2). As

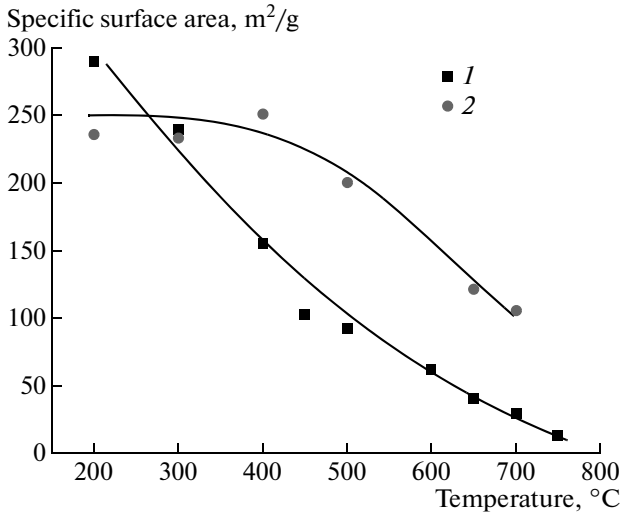

Fig. 2. Specific surface areas of titanium dioxide samples depending on temperature and synthetic procedure: thermal decomposition (*1*) in a muffle furnace and (*2*) in the CEFLAR system.

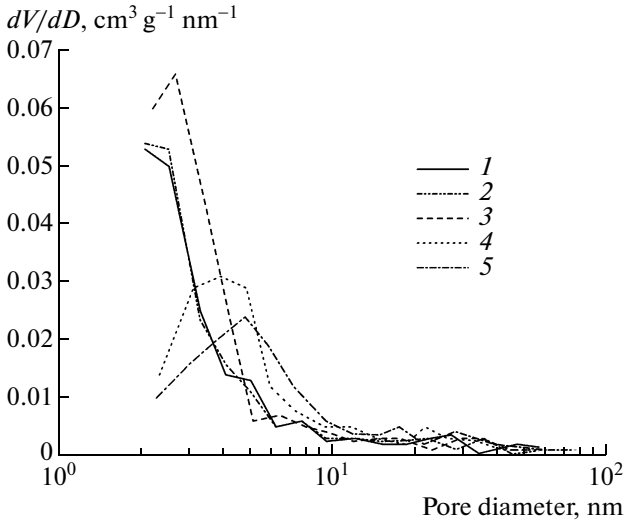

Fig. 3. Differential mesopore-size distribution curves for TiO_2 samples prepared by CTA at (*1*) 200, (*2*) 300, (*3*) 400, (*4*) 650, and (*5*) 700°C.

the treatment temperature was increased from 200 to 400°C, the specific surface area did not noticeably change, whereas a further increase in the temperature resulted in a decrease in the specific surface area. A comparison between the samples of titanium dioxide prepared by CTA and titanium dioxide prepared by the standard decomposition of titanium hydroxide in a muffle furnace showed that the CTA production of titanium dioxide at 200–700°C was accompanied by the formation of a higher specific surface area.

Table 3 indicates that the TiO_2 samples prepared by CTA and calcined at 300°C or lower contained micropores (V_μ), which disappeared as the calcination temperature was increased to 400°C (Fig. 3). Figure 3, which shows the mesopore size distribution, and Table 2 indicate that the mesopore size increased as the calcination temperature of the parent titanium hydroxide was increased; this increase was most strongly pronounced at temperatures higher than 400°C. From Fig. 3, it follows that, under these temperature conditions, the mesoporous portion of the xerogel underwent the most significant changes.

The occurrence of an insignificant micropore volume in the samples calcined at a temperature lower than 400°C suggests the occurrence of an amorphous TiO_2 phase under these conditions. At a higher temperature, complete crystallization occurred with a simultaneous rearrangement of the mesoporous part of the structure accompanied by a dramatic decrease in the specific surface area and an increase in the predominant mesopore size. A comparison of the pore structures of samples prepared by CTA with the pore structures of samples prepared by thermal decomposition under standard conditions [20] (Table 4) indicates that the samples prepared by CTA were characterized by a more finely porous structure over the entire test temperature range. Moreover, note that standard calcination did not result in the formation of micropores in TiO_2 even at a minimum temperature.

Thus, from the experimental data, it follows that defect products were formed upon the treatment of hydrated titanium dioxide, which was prepared by a commercial sulfuric acid technology, in the CEFLAR system. The chemical composition, microstructure, and texture parameters of these products considerably depended on the treatment conditions. The high rate of heat transfer to a granule was responsible for the dehydration of the starting material under nonequilibrium conditions to result in the formation of dispersed distorted anatase structures. Under these conditions, high-molecular-weight formations that formed structure regions with microporous properties are retained in the sample. At a treatment temperature lower than 650°C, anatase with a distorted crystal structure was formed; in addition, this was due to considerable concentrations of sulfate ion impurities and hydroxyl groups in its structure. Thermal treatment under more

Table 4. Texture parameters of TiO_2 on the temperature of treatment in a muffle furnace [21]

Sample	S_α, m²/g	V_s, cm³/g	D, nm
TiO_2 (300°)	239	0.316	2.5
TiO_2 (400°)	155	0.281	2.9
TiO_2 (450°)	103	0.302	4.8
TiO_2 (500°)	92	0.316	7.4
TiO_2 (650°)	41	–	–
TiO_2 (700°)	30	–	–

equilibrium conditions in a muffle furnace resulted in a decrease in the concentrations of sulfate ions and hydroxyl groups (Table 2). At a thermal activation temperature of 650°C or higher, anatase with a regular structure was formed. In addition, the samples prepared by CTA at corresponding treatment temperatures were characterized by higher specific surface areas and more finely porous structures, as compared with the samples prepared using the standard thermal decomposition of titanium hydroxide.

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