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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of Sulfate Anion Additions on the Phase Composition and Structure of Titanium Dioxide

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Abstract—Methods of X-ray diffraction analysis, electron microscopy, and microanalysis were used to examine the phase composition and structure of sulfate-anion-containing titanium dioxide samples into which a modifier was introduced by impregnation and by the sol-gel technique. It was demonstrated that the modification of titanium dioxide by the impregnation method results in that an ordered surface structure is formed, which is constituted by accreted crystallites 8–10 μm in size. In this structure, sulfate anions are stabilized at interblock boundaries. Titanium dioxide modified by the sol-gel method has the form of loosely packed coarse aggregates with sizes of about 30–32 μm. The appearance of the titanium tetrasulfide phase mostly situated on the surface was observed in its composition. The microstructural features and, in particular, enrichment of the surface of a sol-gel sample with sulfur and a decrease in dispersity are determined by the catalyst preparation conditions.

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Anion-modified ultradispersed catalytic systems based on zirconium and titanium oxides and aluminum oxide are widely used in the reactions of isomerization, hydroisomerization, alkylation, and cracking of hydrocarbons [1–8]. The promise exhibited by the development of catalysts of this kind is exemplified by sulfate-modified zirconium dioxide. This compound not only compares well in activity with the industrial chlorinated aluminum oxide, but is also more technologically convenient: being simple in preparation and having low cost, it exhibits a high activity, selectivity, and thermal stability [8].

The already accumulated experimental material demonstrates that the efficiency of sulfate-anion-modified oxide catalytic systems depends on several interrelated factors. These are (i) the method and conditions of introduction of the sulfate anion, which must favor the stabilization of the oxide support predominantly in a single particular phase and the formation of substitution solid solutions on its basis and (ii) also the amount of the sulfate anion being introduced and the calcination temperature of the catalyst. The last two factors affect how a multilayer coating is formed on the surface and, in the end, provide the maximum Brønsted and Lewis acidity [2, 8–10].

In [10], the evolution of the phase composition was examined and the crystallite size, specific surface area, and average size of mesopores in sulfated zirconium dioxide were determined in relation to the content of sulfate anions. Two concentration ranges were determined, between which the effects of SO_4^{2-} are different: at their low content (< 6 wt %), the largest specific surface area and the smallest mesopore size are observed and the crystallization of the nanosize tetragonal form of ZrO_2; the threshold concentration above which an abrupt transition to the crystallization of the predominantly tetragonal occurs was 2.5–3.0 wt %; at concentrations exceeding 7.7 wt %, sulfate anions hinder crystallization of both dioxide forms, to the point of stabilization of the X-ray-amorphous phase.

It was reported in a set of Lavrenov's publications [11–15] concerned with the structural, acidic, and catalytic specific features of sulfate-anion-containing oxides that modification of aluminum and zirconium oxides with sulfate anions makes it possible to obtain materials with strong Brønsted and Lewis acidity. It was noted that that the highest selectivity of isobutane alkylation with butenes is provided by sulfated zirconium dioxide having a mixed phase composition, in which the monoclinic modification of ZrO_2 is dominant over the tetragonal modification. It was shown that, when oxide supports $SO_4^{2-}/ZrO_2/Al_2O_3$ are formed in the course of a thermal treatment of mixtures of sulfated zirconium dioxide hydrate and pseudoboehmite at a temperature of 650°C, a chemical interaction occurs between the starting components to give sulfated aluminum oxide and sulfated solid solution ZrO_2/Al_2O_3. It was found that Lewis acid centers are dominant over Brønsted acid centers on the surface of bulk and supported catalysts SO_4^{2-}/ZrO_2.

Previously, the catalytic activity of sulfate-anion-modified titanium dioxide: industrial and that prepared by the sol-gel method has been studied. It was found that modification of titanium oxide definitely leads to a decrease in the specific surface area of the catalyst, but raises their catalytic activity in the isomerization of olefins [16, 17]. A comparative analysis of the catalytic and acid properties of catalysts demonstrated that the modification of titanium dioxide with sulfate anions raises both the Brønsted and Lewis acidity; however, it does so for the latter to a lesser extent. On the basis of the composition of the reaction products, the isomerizing activity of the sulfate-anion-containing titanium oxide was attributed to the cooperative involvement of three kinds of acid centers: Lewis and Brønsted acid centers and also superacid centers. Apparently, these specific features are related to the preparation method [18]. Titanium dioxide, including that containing sulfate ions, has been studied in sufficient detail [19, 20. Despite this circumstance, the specific features of how the impregnation method and the sol-gel method affect the physicochemical and structural features of sulfate-anion-modified titanium oxide samples differing in the preparation technique remained unexamined in [16, 17].

The goal of our present study was to examine in detail the influence exerted by addition of sulfate anions on the composition, structure, and surface state of titanium dioxide. Combining the methods of X-ray diffraction (XRD) analysis and electron microscopy (SEM, TEM) will help in determining the reason for the difference in the manifested catalytic properties of sulfate-anion-modified titanium oxide.

EXPERIMENTAL

As starting substances served commercial titanium dioxide TiO_2 (Evonik Resource Efficiency GmbH, 90% anatase), tetraethoxyethane $Ti(OC_2H_5)_4$ (Merck), ethanol (98%), tetraethylammonium $(CH_3)_4NOH$, distilled water, and sulfuric acid (20%).

Four types of catalysts were taken for study: two untreated (industrial and produced by the sol-gel method) and two corresponding sulfated samples into which the sulfate anion was introduced via modification of titanium dioxide (by saturation of its moisture capacity, impregnation) and via sulfation of titanium dioxide in the stage of gelation (sol-gel synthesis) [21].

The XRD analysis was made on a Bruker D8 Advance instrument. The EVA software package was used to perform a semiquantitative estimation of separate phases with diffraction data from the CCD PDF-2 database. It is assumed in this analysis that all the phases are well crystallized and their sum is 100%.

The size of the coherent scattering region (CSR) was estimated by the Scherrer method [22].

The surface morphology, microstructure, and elemental composition of the catalyst samples under study was examined by scanning electron microscopy (SEM) [ESEM Quanta 400 FEG, FEI with built-in EDX analyzer EDS, Genesis 400 with Si(Li) detector], transmittance electron microscopy (TEM) on a JEM-2100 microscope with grid resolution of 0.14 nm at accelerating voltages of 100 and 200 kV. The catalyst samples for TEM measurements were fixed on carbon substrates mounted on a copper grid.

The specific surface area was determined by the method of capillary adsorption of nitrogen on a TriStar 3000 adsorption-structural analyzer.

RESULTS AND DISCUSSION

Figure 1 shows diffraction patterns of four titanium dioxide samples under study: unmodified industrial, modified industrial, titanium dioxide produced from alkoxide by the sol-gel method, and its modified analog. According to XRD data all the TiO_2 samples had predominantly the crystal structure of anatase (JCPDS 01-086-1156) (Table 1). The unmodified industrial titanium dioxide (Fig. 1a) is char-

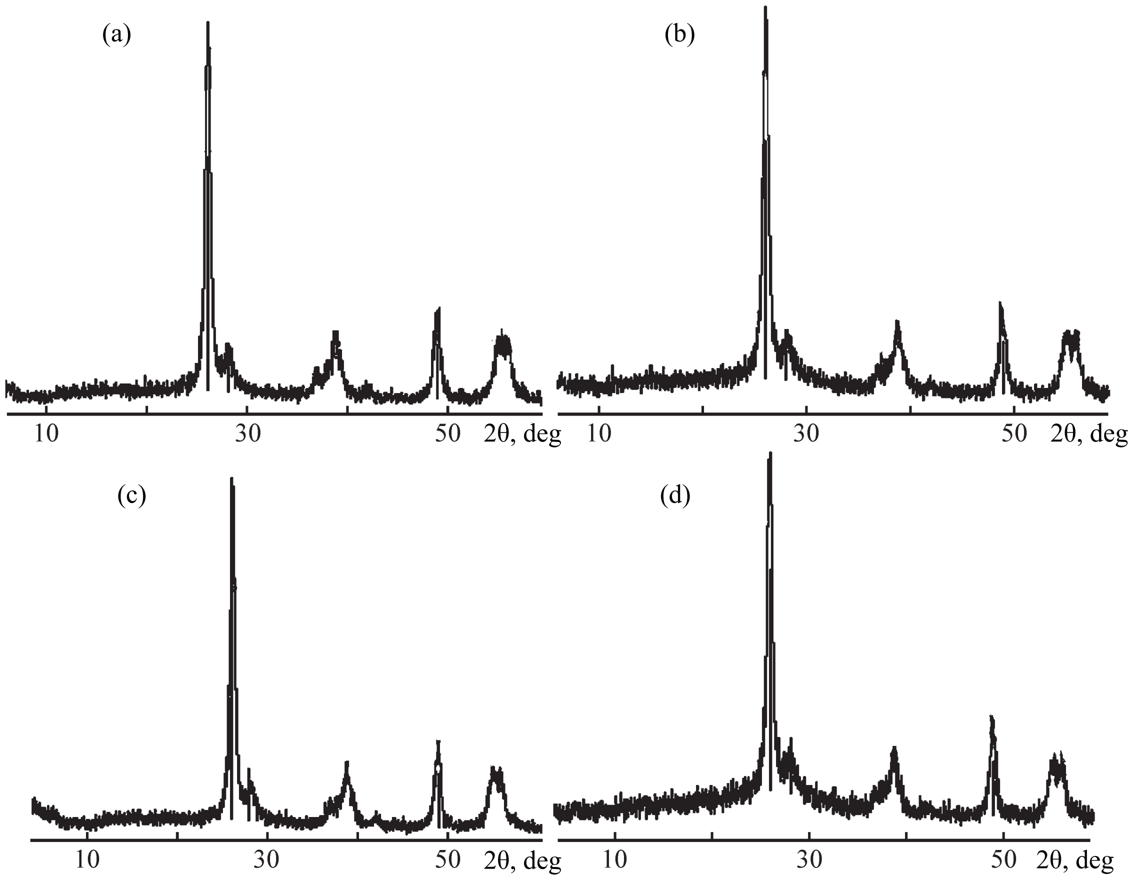

Fig. 1. X-ray diffraction patterns of unmodified titanium oxides and those promoted with sulfate ions. (2θ) Bragg angle. (a) Ti_{ind}, (b) SO_4/Ti_{ind}, (c) Ti_{alkox}, (d) SO_4/Ti_{alkox}.

acterized by high-intensity lines at 25.26, 36.05, 37.82, 48.08, and 54.01(86)°. The presence of an admixture in the form of the rutile phase is manifested by low-intensity lines at 27, 41, and 54° (JCPDS 01-078-4186).

After the sulfate anion is introduced into industrial titanium dioxide, the diffraction pattern changes due to the appearance of new reflections at 2θ = 29–32 and 43° and a broad halo at the same angles, which is presumably

Table 1. Characterization of the samples under study

Sample	Content of sulfate anions, wt %	Phase, wt %	Reflection position, deg	Interplanar spacing, Å	Height, mm	FWHM[a], deg	Integral intensity	Asymmetry	S_{sp}, $m^2 g^{-1}$	SCR
Ti_{ind}	–	Anatase	25.26	3.523	3647	0.57	3229	0.74	57	8.5
		Rutile	27.19	3.278	851.9	1.25	1113	0.99		
SO_4/Ti_{ind}	3.1	Anatase	25.42	3.502	2565	0.62	2240	1.31	53	18.5
		Rutile	27.54	3.236	642.5	1.23	687.7	1.31		
Ti_{alkox}	–	Anatase	25.34	3.512	3640	0.59	3344	0.81	170	11.2
		Rutile	27.35	3.258	751.9	1.29	731.5	0.96		
SO_4/Ti_{ind}	3.03	Anatase	25.28	3.520	3072	0.58	2962	0.64	146	19.6
		Rutile	27.31	3.262	659.4	1.70	888	1.34		

[a] FWHM is the full width at half-maximum.

due to the formation of a new amorphous titanium sulfate phase (Fig. 1b). In addition, the presence of the sulfate anion results in that the interplanar spacings decrease for both anatase and rutile and so do the heights, intensities, and halfwidths of reflections, but only for rutile (Table 1). Hence follows that the introduction of sulfate anions into industrial titanium dioxide by impregnation favored a growth of the coherent scattering region of the constituent crystallites, with the relative fraction of the impurity phase (rutile) reduced, but the relative content of the main component, anatase, preserved. Because the crystal structure of anatase is different: in particular, the ionic radius of titanium(IV) is substantially smaller than that of the sulfate anion, the stabilization of the latter in the crystal lattice of titanium dioxide is ruled out, but its possible place is at interblock boundaries between anatase particles. Just this behavior has been observed in modification of titanium dioxide with cerium, calcium, and silicon oxides [20, 23, 24].

Our diffraction pattern of the sol-gel titanium dioxide is nearly identical to that of the industrial titanium dioxide. The main difference consists in the larger fraction of anatase. This phase is manifested at angles of 25.26, 36.05, 37.82, 48.08, 54.01, and 54.86° (Fig. 1c) the presence of rutile was noted at 27.19, 41, and 54.46°.

The modification of the sol-gel titanium dioxide is accompanied by the appearance of new reflections at 2θ = 10–15 and 32–35°, with interplanar spacings of 8.33, 6.19, 5.71, 4.21, 2.72, and 2.51 Å. According to the JCPDS X-ray database, these values are related to titanium tetrasulfide (JCPDS 01-076-1715). The formation of this phase is in full agreement with the data on the ionic radii of Ti^{4+} and S^{3+}, equal to 0.62(0.64) and 0.37 Å. The presence of at once two crystalline phases, TiO_2 (tetragonal) and Ti_3S_4 (hexagonal) (Table 2) is accompanied by a shift of some lines attributed to anatase to larger angle, by the appearance of reflections at, respectively, 27.31, 36.74, 38.19, 41.41, 54.07, 55.01°, and by a shift of the reflection at 54.37° to smaller angles. Also observed for this titanium dioxide sample was a decrease in the interplanar spacings for all the reflections except those at 48.08, 54.07, and 54.37°.

Table 2. Change in unit cell parameters

Sample	Unit cell parameters, nm	
	a	*c*
Ti_{ind}	3.780(1)	9.39(4)
SO_4/Ti_{ind}	3.790(2)	9.41(1)
Ti_{alkox}	3.788(2)	9.515(6)
SO_4/Ti_{alkox}	3.43	11.44

These processes occur on the background of changes in the width of the diffraction lines: according to the values obtained, the highest dispersity state is characteristic of the anion-modified industrial titanium dioxide, despite that the most disperse among the unmodified samples was that produced by the sol-gel method. These results are well described in terms of the sol-gel mechanism by which mesoporous titanium dioxide is formed [25, 26]. According to this mechanism, the conditions of this synthesis ($H_2O : Ti \approx 3$) are accompanied by an insignificant decrease in the specific surface area and in the pore volume in titanium dioxide, which is due to the increased viscosity of the sol being formed.

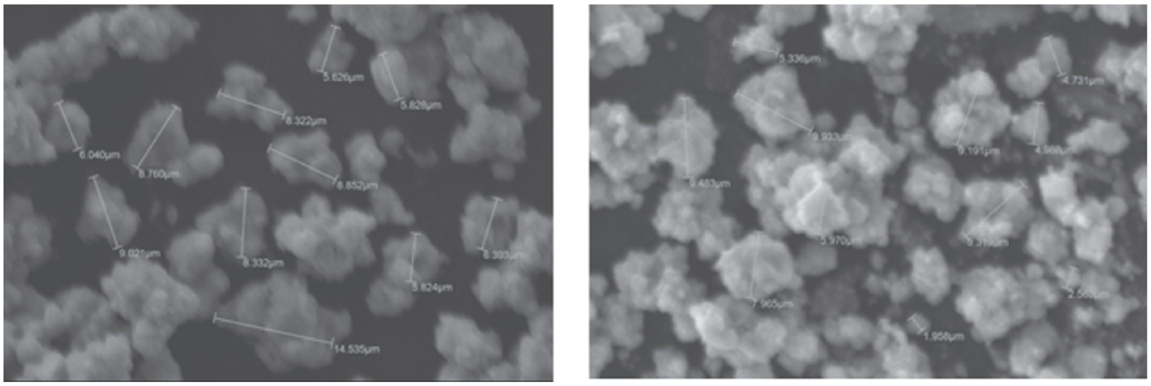
(a) (b)

Fig. 2. TEM image of (a) unmodified industrial and (b) sol-gel titanium dioxide.

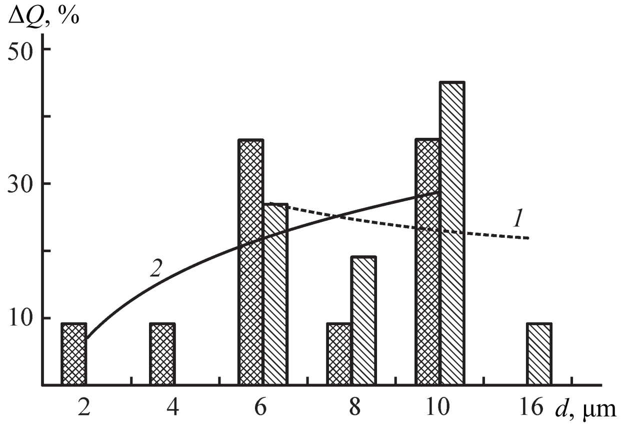

Fig. 3. Distribution ΔQ of particle size d distribution for (*1*) unmodified industrial and (*2*) sol-gel titanium dioxide.

Figure 2 shows electron-microscopic (TEM) images of samples of the starting, unmodified titanium dioxide. It can be seen that particles of both kinds of titanium dioxide have in the bulk a similar regular, nearly cubic structure and are combined into agglomerates. At the same time, it is noteworthy that the agglomerates being formed differ in nature. In the industrial sample with specific surface area of 57 $m^2 g^{-1}$, particles with average size of up to 3 μm are combined into ~10-μm agglomerates, whereas finer particles with average size of 1.96 μm, densely packed into ~8-μm agglomerates, are observed (Fig. 3) for the sample produced by the sol-gel method, with S_{sp} = 170 $m^2 g^{-1}$. Combined, these parameters and the specific surface area indicate that unmodified sol-gel samples are more highly dispersed.

An analysis of typical SEM images of titanium dioxide samples containing sulfate anions (Fig. 4) demonstrated that, morphologically, these samples retain specific features inherent in the unmodified samples, but certain differences also appear. It should be noted, for comparison, that modified industrial TiO_2 retains, as before (Fig. 2a), the structure of a quasi-homogeneous highly dispersed powder composed of aggregates 6–10 μm in size (Figs. 3 and 4a). At the same time, the structure of the modified sol-gel sample cardinally changes and becomes now composed of incoherently accreted particles forming large aggregates of nonuniform sizes. The TEM image of this sample in Fig. 4b shows single, both very fine and, in overwhelming majority, coarse particles.

The modification of titanium dioxide with sulfate anions was accompanied by a change of not only the microstructure, but also the texture of both types of samples. For example, the specific surface area of the sol-gel sample decreased by 14.15%, and that of the industrial sample by only 7.1% (Table 1). The decrease in the surface area of the modified titanium dioxide is in full agreement with the data of [20, 27], where it was shown that the transfer direction of low-molecular fragments of substance depends on the catalyst synthesis conditions, which are responsible for changes in the texture of the samples. The introduction of sulfate anions into the industrial sample by the impregnation method was accompanied by an insignificant decrease in the surface area, the granulometric composition being invariable. With these circumstances taken into account, it can be concluded that mostly the mechanism of surface-diffusion

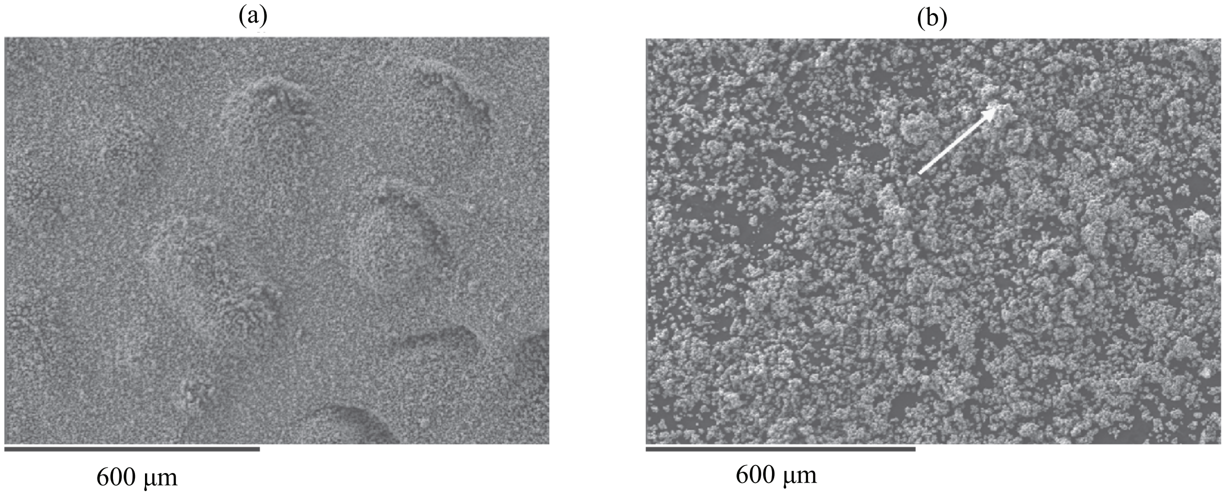

Fig. 4. TEM image of (a) unmodified industrial and (b) sol-gel titanium dioxide (the arrow shows the region of microanalysis).

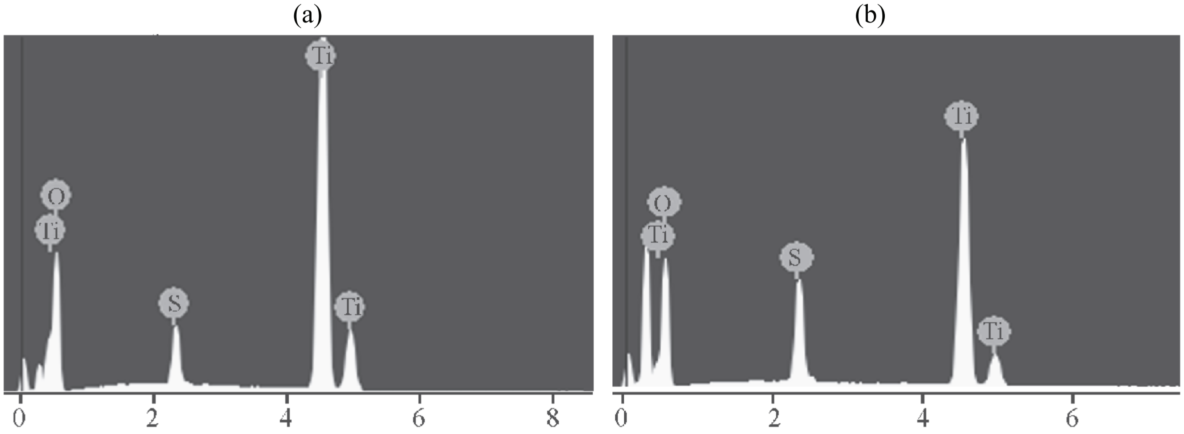

Fig. 5. EDX microanalysis data for modified sol-gel titanium dioxide sample at accelerating voltage of (a) 200 and (b) 100 kV.

sintering is operative under the given conditions. With consideration for the above-noted structural specific features of sol-gel samples into which sulfate anions were introduced in the gelation stage (substantially smaller surface area, larger agglomerates) and for the whole set of synthesis conditions, the sintering by the bulk-viscous flow is the most probable mechanism responsible under the given conditions for the occurring structural changes.

The results of a microanalysis of the modified sol-gel sample (Fig. 5) at various accelerating voltages suggest that the surface of this sample is enriched in sulfur. This enrichment is presumably due to the formation of the titanium tetrasulfide phase, found by the XRD method (Fig. 1b). That this phase is mostly concentrated in the surface layer of coarse agglomerates is evidenced by the increase in the intensity of the signal from sulfur ions with decreasing accelerating voltage.

CONCLUSIONS

The whole set of the experimental data obtained in the study indicates that the extent and nature of the influence exerted by sulfate anions on the structure and phase composition of titanium dioxide depend on the method by which the samples are obtained. The slight decrease in the surface area on the background of the invariable granulometric composition of industrial titanium dioxide 3%-sulfate-modified by the impregnation method suggests that sulfate anions are stabilized under the given conditions outside the crystal lattice of anatase, most probably at interblock boundaries. Presumably, this stabilization also hinders sintering of titanium dioxide particles and favors preservation of a developed surface. The catalyst being formed is a quasi-homogeneous highly dispersed powder constituted by aggregates 6–10 μm in size.

According to XRD and microanalysis data, the synthesis of the 3%-sulfate-anion-modified titanium dioxide by the sol-gel method yields a new phase, titanium tetrasulfide, which is contained, together with anatase, in the coarse surface agglomerates (30–32 μm) being formed. Presumably, the lowered activity of the sol-gel sample may be due both to a change in the phase composition and to a decrease in the dispersity of catalyst particles.

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