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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

A Study of Phase Transformations in the Surface Layer of Titanium Dioxide

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Abstract—The capabilities of the diffuse reflectance spectroscopy in a study of the state of the surface layer of anatase in anatase–rutile phase transformations in successive thermal treatments of anatase in the temperature range 200–900°C and in analysis of titanium dioxide of P25 brand (Degussa) containing anatase and rutile in a 80 : 20 ratio, respectively, are demonstrated for the example of dispersed titanium oxide.

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It is known that the composition, structure, and properties of solids predetermine their possible transformations in various technological processes [1]. An important factor determining the sorption, catalytic, and other properties of solids is their phase composition. In view of the important role of the surface in these materials, it is important to control not only the structure of the bulk phase, but also that of the surface layer to a depth of several tens of nanometers. However, as a rule, information about the phase composition traditionally refers to the bulk of solids and contains no data on the structure of their surface layers. At the same time, it is known that, for example, structural-phase transformations occur in the surface layer under thermal treatment at considerably lower temperatures, compared with transformations in the bulk [2].

A characteristic example is titanium dioxide. Owing to its chemical stability in acid and neutral liquid media, electrical conductivity, and photocatalytic activity, this compound is widely used in manufacture of fillers for composite polymeric materials, dielectric ceramics, ceramic films, and pigments for paint-and-varnish industry; in electronic devices, photoelectrochemical cells, photocatalysis, chemical sensors, solar cells, etc. [2, 3]. Depending on the crystalline modification, titanium dioxide (anatase, rutile, and brookite) exhibits different physicochemical properties. In the simultaneous presence of amorphous, anatase, and rutile constituents, the titanium oxide material has an increased photocatalytic activity, compared with a material composed of only a single crystallographic phase [4].

It is known that the formation of a TiO_2 modification is strongly affected by the mode of its thermal treatment, during which a phase transition in a solid begins with the lattice rearrangement in the surface layer at substantially lower temperatures [2]. For example, in calcination of amorphous titanium(IV) hydroxide at low temperatures (500–550°C), nanocrystalline anatase particles are originally formed. Further increase in temperature and treatment duration results in that rutile crystallites appear and the anatase–rutile phase transition occurs [3]. At the same time, the phase transition in titanium dioxide begins at the surface at a lower temperature, compared with the bulk [5], and can be characterized by a change in the composition of functional groups and in the total surface energy. In [5], the surface of titanium dioxide samples was studied by the potentiometric method. In this case, a transition from one phase state to another as a result of thermal treatment can be characterized by a change in the composition of adsorption centers and by the conditional adsorption potential for iron(III) ions.

Together with the method used in [5], there exist other ways to study the surface state of solids. These techniques are based, in particular, on adsorption of acid-base indicators [2] and probe molecules [7, 8], followed by identification by electronic and IR spectroscopies [9, 10, 11], pH measurements [12, 13], and ESR spectroscopy [14]. However, all these methods used for analyzing

Table 1. Selected properties of the titanium dioxide samples used in the study

Alloying additive (0.1 wt %)	T_{max} of indicated peak, °C (relative area, %)		
	peak I	peak II	peak III
–	160 (81.9)	320 (14.2)	200 (43.8)
Ce	120 (85.8)	350 (14.2)	
Sm	150 (78.8)	330 (21.2)	
(Ce + Ga)	120 (20.5)	160 (35.7)	

the state of a surface are rather labor-consuming and require special experimental conditions (deep vacuum, low temperatures, spectral-purity reagents) or involve measurements in liquid media.

In this study, the capabilities of diffuse reflectance spectroscopy (DRS) for analysis of the relationship between the state of the titanium dioxide surface and its phase composition identified by X-ray phase analysis (XPA) were demonstrated.

EXPERIMENTAL

We examined laboratory samples of nanocrystalline titanium dioxide (AK-1) with different phase ratios, produced as a result of its thermal transformations in the range 200–900°C, and commercial titanium dioxide products: P25 (Degussa), which contains 80 wt % anatase and 20 wt % rutile according to XPA data (Fig. 1), and white pigments based on anatase and rutile [GOST (State Standard) 98-08–84].

The laboratory samples of nanocrystalline TiO_2 (AK-1) were produced by controlled hydrolysis of titanium tetrachloride, followed by drying and thermal treatment at 200°C:

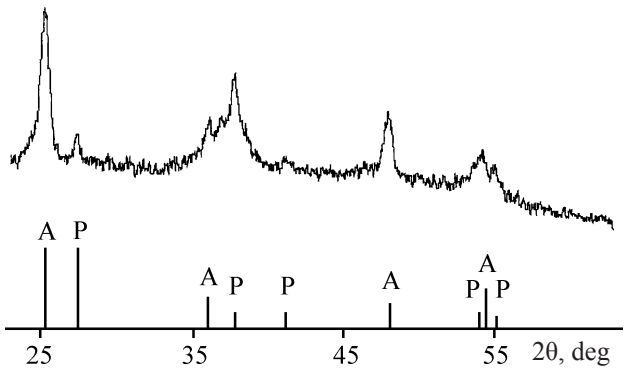

Fig. 1. X-ray diffraction pattern of P25 titanium dioxide (Degussa). (2θ) Bragg angle; the same for Fig. 4.

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \quad (1)$$

Selected characteristics of the TiO_2 samples studied are listed in Table 1.

The particle size was found from data on the specific surface area by the formula reported in [2].

The state of the surface of TiO_2 samples was analyzed by diffuse reflectance spectroscopy. DRS spectra were obtained with a Specord-M 40 instrument equipped with an attachment with an integrating sphere for reflectance measurements relative to an optical reference (MgO) in the ultraviolet and visible spectral ranges (200–900 nm). The position of the absorption edge in the spectra was determined by the tangent method [15, 16]. To find the inflection point in diffuse reflectance spectra more precisely, we performed their hardware differentiation, followed by decomposition into Gaussian components by the nonlinear regression method. The bulk phase composition of titanium dioxide was characterized by XPA.

The X-ray phase analysis was made with a Difray DRN-401 diffractometer (CuK_α radiation, $\lambda Cu K_\alpha^{av}$ = 1.5418 nm) at 2θ = 20–65°. The phase ratio in the composition of the samples under study was determined in accordance with GOST 9808–92. The crystallite sizes were estimated from the broadening of the 100% anatase lines by the Selyakov–Scherrer formula [17]

$$D = k\lambda/B\cos\theta, \quad (2)$$

where D is the size of the coherent scattering region (nm); B, full width at half-maximum of a diffraction reflection (rad); and k, constant equal to unity.

To analyze the state of the surface of thermally treated AK-1 samples, we measured diffuse reflectance spectra of the pigment anatase and rutile and P25 (Fig. 2). Table 2 lists the absorption edge positions for the samples under consideration.

The spectrum of the pigment rutile is shifted to longer wavelengths relative to that of anatase (Fig. 2), which is known to be due to differences in the energy gap and in the degree of distortion of the coordination polyhedron on which these modifications are based [18, 19]. Thus, the difference in the absorption edge positions in the DRS spectra makes it possible to indentify different titanium dioxide modifications. The DRS spectra of the

pigment anatase (Fig. 2, spectrum *1*) and P25 titanium dioxide (spectrum *3*) coincide at 320–360 nm. However, the absorption edge of sample P25 is shifted to longer wavelengths relative to anatase, which is apparently due to the simultaneous presence of the anatase and rutile titanium dioxide modifications in the sample being analyzed. Thus, the integral spectrum gives no way of reliably identifying different states of titanium and their ratio in a complex solid object.

Hardware differentiation of the DRS spectra of anatase and rutile yields curves with clearly pronounced peaks at 370 (3.3 eV) and 400 nm (3.1 eV), respectively (Fig. 3a, curves *1* and *3*).

The very first derivative of the spectrum of P25 sample shows, together with a peak at 390 nm, a clearly pronounced shoulder at 360–380 nm (Fig. 3a, curve *2*), i.e., analysis of the curve produced by hardware differentiation for P25 sample also demonstrates that titanium atoms are exist on its surface in two different coordination states related to the anatase and rutile modifications of titanium dioxide, simultaneously present in P25.

A mathematical decomposition of the hardware differentiation curve of the DRS spectrum of the P25 sample (Fig. 3b) revealed two clearly manifested dependences with extrema at 3.1 and 3.3 eV. Comparison of the values obtained with the positions of the extrema for the individual phases (Fig. 3a) with previously published data [15, 20] makes it possible to attribute the extrema in the dependences to electron transitions characteristic of titanium with a coordination environment in the rutile (E = 3.1 eV) and anatase (E = 3.3 eV) modifications. The area under the differential curves, which characterizes the relative amount of the corresponding titanium dioxide modification, indicates that the fraction of titanium in the coordination state characteristic of anatase is 69% of the amount of titanium dioxide present on the surface, whereas the fraction of the anatase phase in the bulk is 80% according to XPA data.

To estimate the anatase/rutile ratio in the bulk and at the surface in the course of structural-chemical transformations, we studied laboratory samples of AK-1 titanium dioxide, thermally treated at 200–900°C. It follows from the X-ray diffraction patterns of thermally treated TiO_2 (Fig. 4) that samples thermally treated at temperatures of up to 600°C are still composed of the anatase modification, similarly to samples treated at lower temperatures. It can be seen in the diffraction patterns of samples thermally treated at 700°C that, together with an increase in the intensity of the anatase reflections, which points to further crystallization of the amorphous component of the dioxide, there appear low-intensity peaks related to rutile. And only in the sample thermally treated at 800°C, the intensity of the reflection associated with anatase decreases, and that of the peak related to rutile becomes substantially higher. According to XPA data, the sample thermally treated at 900°C is composed of exclusively the rutile modification. It can also be seen in Table 3 that, at treatment temperatures of 200 to 600°C, the size of crystallites of the anatase phase of the dioxide somewhat increases. For a sample thermally treated at 700°C, the appearing rutile phase is characterized by a substantially smaller size of nucleating crystallites, compared with those of the already existing anatase modification. Further thermal annealing of AK-1 titanium dioxide at temperatures of 800–900°C is accompanied by an increase in the size of crystallites of the rutile phase.

Table 2. Absorption edge position of commercial titanium dioxide samples

Titanium dioxide	Absorption edge position λ, nm
Pigment anatase	380
Pigment rutile	410
P25	402

To determine how the coordination environment of

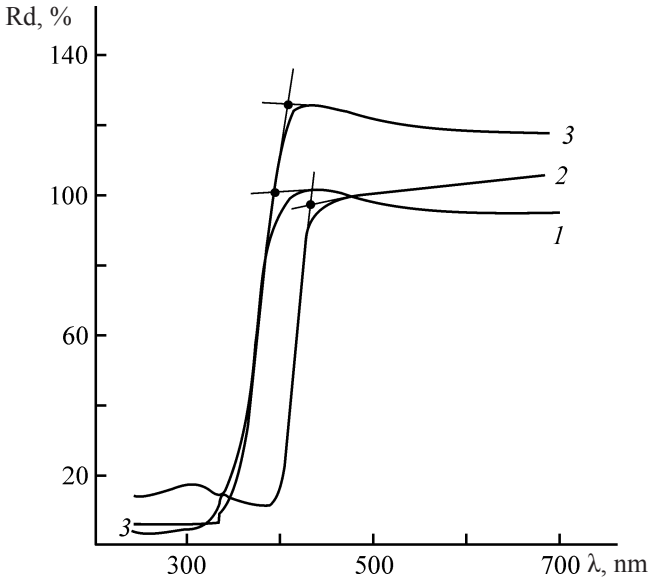

Fig. 2. Diffuse reflectance spectra of (*1*) pigment anatase, (*2*) pigment rutile, and (*3*) P25. (R_d) Diffuse reflectance and (λ) wavelength; the same for Fig. 5.

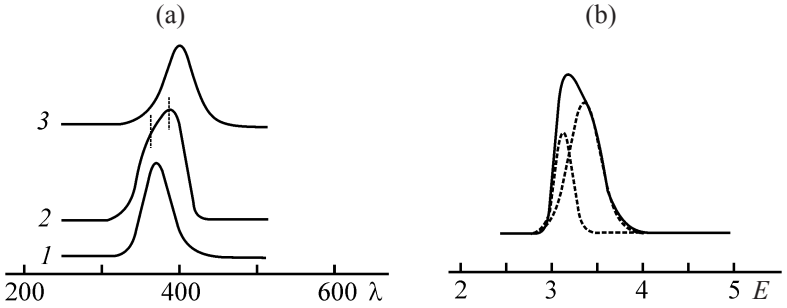

Fig. 3. Hardware differentiation spectra of the diffuse reflectance of commercial titanium dioxide. (λ) Wavelength and (*E*) electron transition energy.

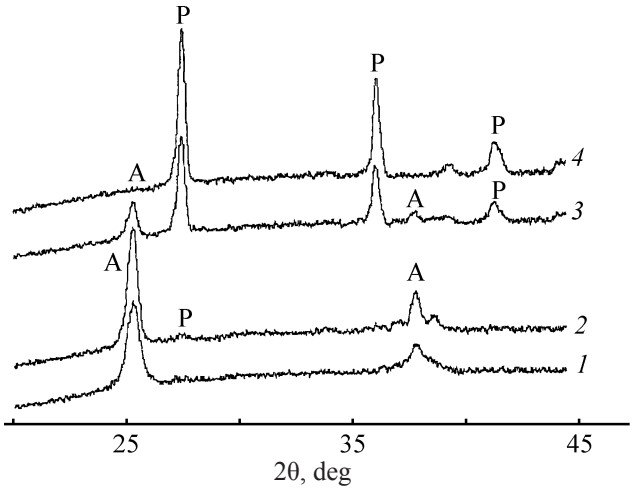

Fig. 4. X-ray diffraction pattern of titanium dioxide subjected to thermal treatment at various temperatures. Treatment temperature (°C): (*1*) 200–600, (*2*) 700, (*3*) 800, and (*4*) 900.

titanium in the surface layer changes in the course of the thermal annealing of TiO_2, we measured diffuse reflectance spectra shown in Fig. 5. The absorption edge positions are listed in Table 3. For a sample heated at 200°C (Fig. 5, spectrum *1*), the adsorption edge position is found to be at λ = 380 nm, which indicates that the coordination environment of titanium in the surface layer is characteristic of the anatase modification of titanium dioxide. Thus, according to XPA and DRS data, the sample of the nanodispersed titanium dioxide thermally treated at 200°C is homogeneous over the particle cross-section and contains the anatase phase both in the bulk of a particle and in its surface layer. As the annealing temperature of titanium dioxide is raised to 600°C, the absorption edge position in the spectra shifts to longer wavelengths (~420 nm), remaining unchanged in higher temperature treatments (Table 3). Thus, according to the absorption edge positions, thermal treatment of the samples under consideration gives rise to the rutile phase of titanium dioxide in the surface layer, beginning at 600°C.

An analysis of the dependences of the first derivatives of the DRS spectra (Fig. 6) demonstrated that the peaks in the curves are shifted to longer wavelengths on raising the thermal treatment temperature. For the sample treated at 200°C, the peak lies at λ = 370 nm. This suggests that titanium in the surface layer is in the coordination state characteristic of anatase. Raising the temperature to 600°C leads to a shift of the peak to longer wavelengths and, consequently, to a change in the coordination state of titanium. In addition, two features can be distinguished in curve *2* (Fig. 6) at 375 and 395 nm. This suggests that, at the given treatment temperature, structures with coordination environment close to anatase and rutile are simultaneously formed on the surface. At a treatment

Table 3. Phase composition, size of coherent scattering regions, and absorption edge position of thermally treated TiO_2 samples

Alloying additive (0.1 wt %)	Yield, g m^{-3}			Selectivity, %		Fractional composition of liquid hydrocarbons, %			α
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5~C_{10}	$C1_1$–C_{18}	C_{19+}	
–	21.5	79	14	18.1	66.5	47.5	43.2	9.3	0.8
Ce	20.2	79.2	11.2	17.0	68.2	41.7	45.1	13.2	0.82
Sm	27.5	81.9	13.8	20.0	59.3	61.6	31.9	6.5	0.77
(Ce + Ga)	26.5	48	59.2	17.0	36.0	33.1	54.9	12.0	0.83

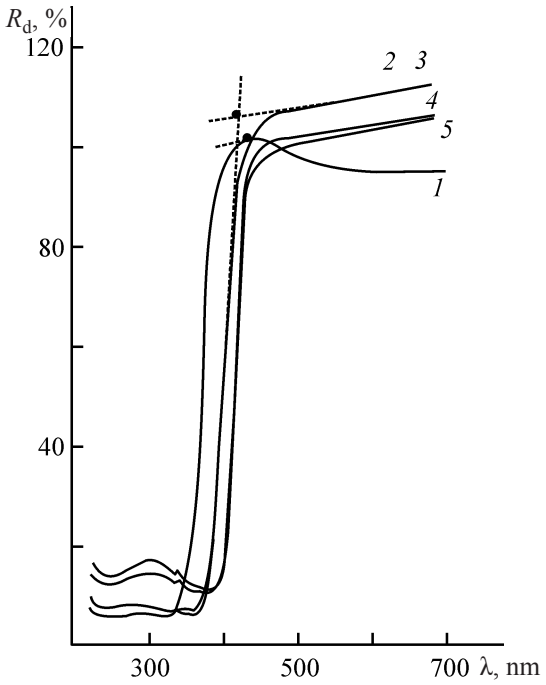

Fig. 5. Diffuse reflectance spectra of TiO_2 calcined at various temperatures. Treatment temperature (°C): (*1*) 200, (*2*) 600, (*3*) 700, (*4*) 800, and (*5*) 900.

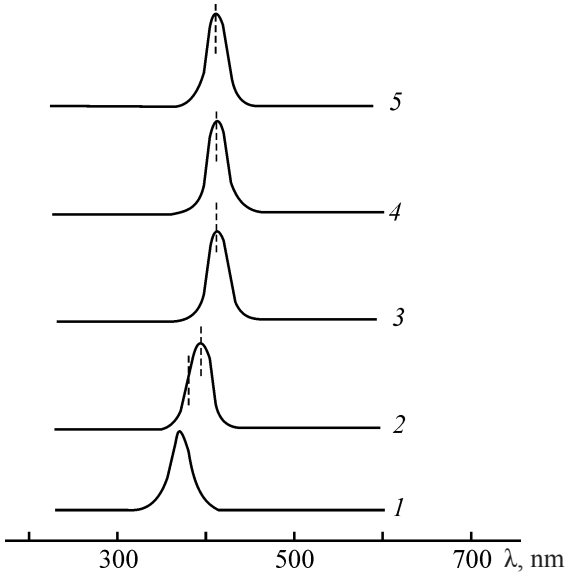

Fig. 6. Curves of hardware differentiation of DRS spectra of AK-1 titanium dioxide thermally treated at (*1*) 200, (*2*) 600, (*3*) 700, (*4*) 800, and (*5*) 900°C.

temperature of 700°C (Fig. 6, curve *3*), the peak lies at 405 nm, whereas upon further calcination (*T* 800 and 900°C) (Fig. 6, curves *4* and *5*), it is shifted to longer wavelengths to 415 nm. This means that, according to DRS data, titanium atoms in the surface layer of samples subjected to annealing at temperature of 700°C and higher are predominantly in the coordination state characteristic of rutile. At the same time, according to the results of XPA, the content of the anatase modification in samples thermally treated at 700 and 800°C is, respectively, 98 and 23%, and only the sample annealed at 900°C is fully composed of the rutile phase.

CONCLUSIONS

(1) It was demonstrated for the example of titanium dioxide that joint use of diffuse reflectance spectroscopy and X-ray phase analysis enables independent identification of the phase composition of the bulk and surface layer of disperse samples.

(2) It was found that P25 titanium dioxide (Degussa), which simultaneously contains the anatase and rutile phases according to X-ray phase analysis data, is 80% anatase in the bulk, whereas on the surface, the fraction of the anatase phase is 69% according to the results of diffuse reflectance spectroscopy.

(3) A comparative analysis of the nature of phase transformations occurring in calcination of TiO_2 of the anatase modification by DRS and XPA revealed an in-advance phase transformation of anatase to rutile in the surface layer, compared with the bulk.

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REFERENCES

1. Tret'yakov, Yu.D. and Putlyaev, V.I., *Vvedenie v khimiyu tverdofaznykh materialov* (Introduction to Chemistry of Solid-Phase Materials), Moscow: Nauka, 2006.
2. Kiselev, V.F. and Krylov, O.V., *Adsorbtsionnye protsessy na poverkhnosti poluprovodnikov i dielektrikov* (Adsorption Processes on the Surface of Semiconductors and Insulators), Moscow: Nauka, 1978.
3. Shabanova, N.A., Popov, V.V., and Sarkisov, P.D., *Khimiya i tekhnologiya nanodispersnykh oksidov: Uchebnoe posobie IKTs* (Chemistry and Technology of Nanodispersed Oxides: IKTs Textbook), Moscow: Akademkniga, 2006.

4. Artem'ev, Yu.M. and Ryabchuk, V.K., *Vvedenie v geterogennyi fotokataliz* (Introduction to Heterogeneous Catalysis), St. Petersburg: SPb Gos. Univ., 1999.
5. Bogatyrev, M.Yu. and Korsakov, V.G., *Formirovanie i svoistva vysokodispersnykh sistem* (Formation and Properties of Highly Dispersed Systems), Leningrad: Len. Tekhnol. Inst., 1989, pp. 108–117.
6. Tanabe, K., *Solid Acid and Bases. Their Catalytic Properties*, Tokyo: Kodansha, 1970.
7. Golubev, V.B., Lunina, E.V., Selivanovskii, A.K., and Luk'yanov, D.B., *Zh. Fiz. Khim.*, 1979, no. 5., pp. 1327–1330
8. Blagoveshchenskii, V.V., Zakharova, M.N., Lunina, E.V., and Kholmogorov, V.E., *Primenenie fluorestsentnogo zonda dlya issledovaniya aktseptornykh tsentrov oksida alyuminiya* (Use of a Fluorescent Probe for Analysis of Acceptor Centers in Aluminum Oxide), Available from VINITI, 1985, Moscow, no. 4607-85.
9. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (IR Spectroscopy in Heterogeneous Acid-Base Catalysis), Novosibirsk: Nauka, 1992.
10. Radionova, T. A, Tsyganenko, A.A., and Filimonov, V.N., *Adsorbtsiya i adsorbenty* (Adsorption and Adsorbents), Kiev: Naukova dumka, 1982, issue 10, pp. 33–42.
11. Shepot'ko, M.L. and Davydov, A.A., *Zh. Fiz. Khim*., 1992, no. 9, pp. 2486–2492.
12. Nechiporenko, A.P. and Kudryashova, A.I., *Zh. Prikl. Khim*., 1987, vol. 60, no. 9, pp. 1956–1961.
13. Nechiporenko, A.P., Vlasov, E.A., and Kudryashova, A.I., *Zh. Prikl. Khim*., 1986, vol. 59, no. 3, pp. 689–692.
14. Markaryan, G.L. and Lunina, E.V., *Zh. Fiz. Khim*., 1992, vol. 66, no. 9, pp. 2480–2485.
15. Pak, V.N., *Zh. Fiz. Khim.,* 1976, vol. 50, no. 5, pp. 1266–1268.
16. *Praktikum po khimii tverdykh veshchestv: Uchebnoe posobie* (Practical Course of Solid-State Chemistry: Textbook), Kol'tsov, S.I., Korsakov, V.G., and Smirnov, V.M., Eds., Leningrad: Len. Gos. Univ., 1985.
17. Kachanov, N.N. and Mirkin, L.I., *Rentgenostrukturnyi analiz* (X-ray Phase Analysis), Moscow: Mashgiz, 1960.
18. Pak, V.N. and Ventov, N.G., *Zh. Fiz. Khim*., 1975, vol. 49, no. 10, pp. 2535–2537.
19. Marfunin, A.S., *Vvedenie v fiziku mineralov* (Introduction to Physics of Minerals), Moscow: Nedra, 1974.
20. Luo, H., Takata, T., and Lee, Y., *Chem. Mater.,* 2004, no. 16, pp. 846–849.