

Surface layer composition of titania produced by various methods: the change of layer state under illumination

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Abstract. The comparative analysis of experimental data over titanium dioxide powders prepared by various ways under ambient air is carried out. The results over TiO₂ prepared by high-temperature heating of anatase, produced by burning of titanium micro particles and grinding of rutile crystal are used for that comparison. Water and carbon dioxide were the main products released from the surface of the titania powders. It was found that under UV irradiation absorbed by titania, in absent oxygen, water effectively reacts with lattice oxygen of titanium dioxide.

1. Introduction

The composition of solid surface layer influences over adhesive, corrosion-resistant and mechanical properties of solids. The corrosion rate of some metals depends on metal oxide film formed on metal surface under ambient air. Such films are created on surfaces zinc (ZnO), aluminum (Al₂O₃) and titanium (TiO₂). As subject of inquiry was selected titanium dioxide. Titania is used as paintwork pigment, plastic filler, photocatalyst for cleaning of water and air [1].

The oxides are affected by the gas components of the atmosphere, and primarily by the components having the higher partial pressure. The latter are water, carbon dioxide and nitrogen oxides. So, according to recent studies [2] for magnesia obtained from Mg(OH)₂ and exposed by the atmosphere for a long time, the amount of adsorbed compounds attained are: NO and N₂ (from nitrogen oxides) ca.1% of monolayer, CO₂ ca.10% of monolayer, H₂O ca. one monolayer. The total amount of the adsorbed compounds in this situation equals to 5 weight % (according to the data of derivatographic analysis).

Traditionally before performing experiments or using in various chemical processes, the surfaces of adsorbents and catalysts (including photoadsorbents and photocatalysts) are exposed to a rigid pretreatment of various kinds. The main goal of this pretreatment (e.g., in vacuum, in an appropriate gas environment, at a certain pressure and temperature, etc.) is usually to obtain either reproducible results, which are consistent with those of other researchers, or the maximum of adsorption or catalytic (accordingly, photoadsorption or photocatalytic) activity. However, it is essential that the rigid pretreatment of a surface may result in some sufficient changes of chemical composition of the adsorption layer, stoichiometry of the surface and near-surface layers of an adsorbent or a catalyst. Our purpose has been to study the surface chemical properties of titania samples produced by various ways under ambient air.



2. Experimental Part

A home-built static installation was used for the measurement of the rates of adsorption, desorption, catalytic oxidation in darkness and under irradiation. The experiments were performed in a high vacuum apparatus equipped with facilities of mass-spectrometer, Pirani gage and gas introduction. The base pressure of the apparatus was below about 10^{-7} Torr.

Water vapour did not get into the high-vacuum (measuring) part of the set-up, which allowed us to measure small (in comparison with water vapour) amount of adsorbates and products desorbed from the surface of oxides during the dark and photo processes.

The chemical composition during the course of the experiment was monitored with a mass spectrometer via their sampling through a leak valve. The mass spectrometer was made from a monopoly analyzer APDM-1. The kinetics of the observed processes was registered by measuring of the alteration in amplitude of the most intensive peak in the mass spectra of the corresponding substances.

The amounts of O_2 , N_2O , NO , CO and other products of desorption from the titania surface were determined using a Pirani gauge, which was calibrated with oxygen and carbon monoxide. A necessary correction was introduced for the sensitivity with respect to other gases.

To expose the oxides under UV radiation, an OSL-1 illuminator with a high pressure mercury lamp (DRSH-250, power 250 W), including a thermal water filter and UV filter, were used. The total radiation flux density, reaching the reactor's surface and recorded by an RTN-20S thermopile, was equal to ~ 1 milliwatt \cdot cm^{-2} for this filter. To separate monochromatic radiation, interference filters were used. The quantum yield of the photodesorption was found as the ratio of the quantity of photodesorbed molecules to the number of quanta passed through the reactor's frontal (transparent) wall.

2.1. Preparation of samples

The TiO_2 monocrystal of the crystalline structure of rutile produced by the Czochralski method [3] was broken and ground in a corundum mortar ("crushing" TiO_2). The powder specific surface was 1.6 $m^2 \cdot g^{-1}$.

The titania powder of anatase crystalline modification was heated at 1273 K for two hours in air in order to obtain from the anatase phase (basically) the rutile phase (basically). After that treatment the titanium dioxide ("heating" TiO_2) was a rutile modification with a specific surface of 8 $m^2 \cdot g^{-1}$.

Next sample of powdery titanium dioxide was prepared by combustion of pyrotechnic mixture consisting of ammonium perchlorate, hydroxy-terminated polybutadiene and titanium particles (particle size from 60 to 90 μm) under ambient air [4]. The highly dispersed titanium dioxide powder ("burning" TiO_2) had the specific surface area of 6 $m^2 \cdot g^{-1}$. After a treatment of the oxide surface at temperature 625 K for 30 min in air the specific surface area was decreased to 4 $m^2 \cdot g^{-1}$.

A suspension of TiO_2 in the distilled water was supported on the internal wall of a quartz glass reactor, which was transparent for the light with wavelength longer than 185 nm. The TiO_2 layer was dried at room temperature in air. Then, without any additional treatment, the reactor was sealed to the high vacuum system for the photoadsorption experiments. The reactor was evacuated to 10^{-5} Pa at room temperature for several hours.

2.2. Absorption spectra

Titania samples with stoichiometric chemical composition are white powders. The absorption of light with energies below the band gap of titania in rutile modification ($E_g = 3.05$ eV) is minimal by all such powders (Figure 1, curves 1 and 2). This absorption corresponds to the impurity absorption bands for single crystals or surface absorption for finely dispersed powders.

According to these data (Figure 1), there is an inflection of absorption edge curve for powdered titania samples consisting from a mixture of anatase and rutile modifications. Such an inflection of curve is not observed for pure anatase or rutile (Figure 1, curve 1) samples. The absorption band edge

of anatase powder is shifted by 0.1-0.2 eV to shorter wavelengths compared to that of rutile powder (3.0 and 2.8-2.9 eV, respectively).

If the titania stoichiometry is changed due to partial reduction of Ti^{4+} to Ti^{3+} and formation of lattice oxygen vacancies during the oxide synthesis, the powders become colored and absorption in the surface band of the oxide appears.

The absorption properties of dispersed titania after storage in air for a long period of time and after activation by heating at 625 K in air for 30 min with respect to the light from different parts of the solar spectrum Figure 1, curve 3). The experiments with the samples contacted with the air for a long time are especially important for evaluating the prospects of titania prepared by this method for application in processes leading to purification of the environment during various man-caused catastrophes.

The absorption of titania powders prepared by combustion of pyrotechnic mixture containing titanium microparticles in the region before the TiO_2 intrinsic absorption edge (corresponding to the surface absorption region) depends on the synthesis method and after-treatment of the samples.

3. Results and their discussion

3.1. Composition of surface layer

The samples prepared under ambient air were deposited from water suspension in the form of thin layer on the walls of the reactor made from optical quartz. After soldering to high-vacuum set-up the sample was pumped out at room temperature to evacuate the most part of adsorbed CO_2 .

Titanium dioxide (“heating”) surface was cleaned from the adsorbed organic impurities, carbon dioxide, and water by long-time, high temperature, oxygen-vacuum treatment. The analysis of the products released upon heating from a rutile surface purified by on oxygen-vacuum treatment for 130 hrs shows the absence of CO_2 evolution and occurrence of water and oxygen evolution at about 450 K (H_2O alone) and above 800 K ($H_2O + O_2$). Increasing the time of oxygen-vacuum treatment to 300 hrs leads to the disappearance of the water thermodesorption peak at 450 K and, above 800 K, only small amount of oxygen evolve.

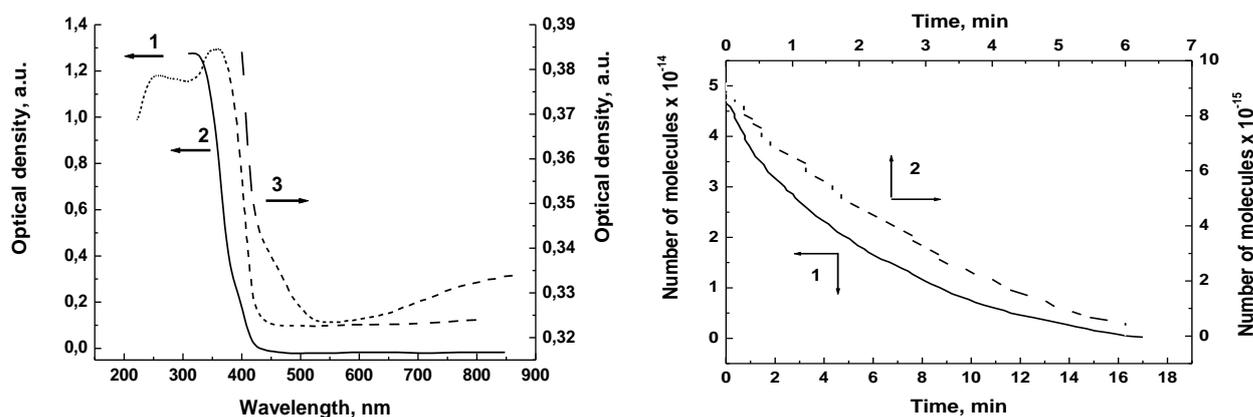


Figure 1. Diffuse reflection spectra of “crushing” (1), “heating” (2) and “burning” titania samples.

Figure 2. Kinetics of the desorption CO_2 from “crushing” TiO_2 surface. 1 – decrease of number of CO_2 molecules on TiO_2 surface (dark desorption); 2 - decrease of number of CO_2 (in addition to dark desorption) under illumination of TiO_2 surface through the UV filter (photodesorption).

3.2. Darkness processes

The presence of water vapour in the reactor was due to its desorption from the “crushing” TiO₂ after the connection of the reactor to the set-up. During evacuation, water vapour was frozen in trap cooled down to 173 K. Thus, water vapour was always present in the reactor. After pumping-out of the reactor through this trap, mainly NO evolved from the TiO₂ surface (fourfold greater than CO₂ accumulated inside the reactor).

It can be assumed that nitrogen oxide (II) is produced in a sufficient amount when grinding the TiO₂ crystal in air due to molecular nitrogen oxidation at centres formed at the break of the Ti–O bonds of the titanium dioxide lattice. The NO generation is also possible through the well-known reaction of N₂O decomposition at the electron donor centre of the metal oxide surface [5, 6]. In this case, N₂O is adsorbed from air like the carbon dioxide.

Prolonged evacuation of the reactor volume for 1 h in high-vacuum installation through a trap with the cooling liquid resulted in partial removal of carbon dioxide adsorbed on the titania surface. As a result, quasi-equilibrium filling of the surface with CO₂ was established. The kinetics of approaching to the equilibrium CO₂ pressure is shown in figure 2, curve 1. This kinetics is presented as the decrease of the amount of CO₂ molecules adsorbed on the titania surface (desorption). The kinetic curve follows the first-order equation with the time constant $\tau_1 \approx 6$ min. For comparison, the kinetics of CO₂ photodesorption, obtained after the attaining equilibrium of the dark adsorption, is also given in figure 2, curve 2.

No other gases except for CO₂ and H₂O were observed to be released in measurable amounts in the dark at room temperature from the surface of “burning” titania.

3.3. Processes under illumination

Surface photochemical reactions occur after absorption of radiation by compounds adsorbed on the surface of solid particles as they transform into the excited reactive state [7]. An example of such a reaction is photodecomposition of nitrous oxide adsorbed on the surface magnesia [8, 9]. The surface in this case plays the role of a “carrier” (substrate), changing the energy of excited state of the adsorbed compound, or role of stabilizer of the adsorbed compound in the state different from the state of molecules in the gas phase, for example, for such compounds as CO₃ complex, OH group, etc.

The photodesorption kinetics is characterized by the fast desorption of carbon dioxide in the initial time of illumination (up to 3–5 min), followed by slow desorption with a constant rate. In the first case, probably, desorption of carbon dioxide is connected with classic photodesorption under illumination of the surface under quanta with energy from the fundamental absorption band of TiO₂ [10, 11]. In the second case, desorption is attributed to the photocatalytic reaction of the oxidation oxygen of an oxide of the by adsorbed carbon-containing compounds (for example, carbon oxide from air) followed by reducing the titanium dioxide surface [12]. During this process, as it follows from mass-spectrometric data, the magnitude of mass peak 44 increases by several times.

Measurements of the CO₂ photodesorption rate under illumination by monochromatic light at different wavelengths (via the use of interference filters) and light flux intensities allowed for the estimation of the quantum yield of the CO₂ photodesorption. The calculation results are given in figure 3 (curve 1). Curve 2 shows the diffusion reflection spectrum of the powder-like TiO₂ measured relative to magnesium oxide as the reference standard.

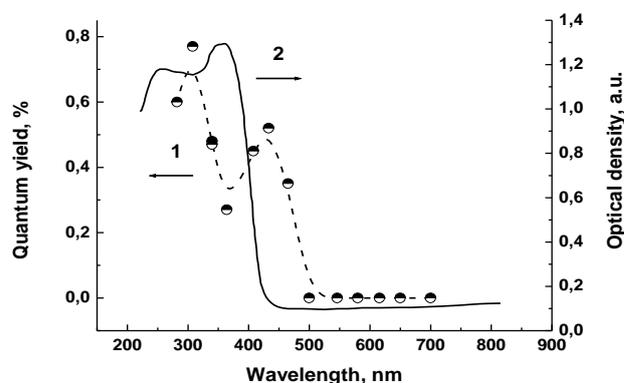


Figure 3. Spectral dependencies for the “crushing” TiO_2 : (1) the quantum yield of CO_2 photodesorption and (2) the optical density relative to MgO .

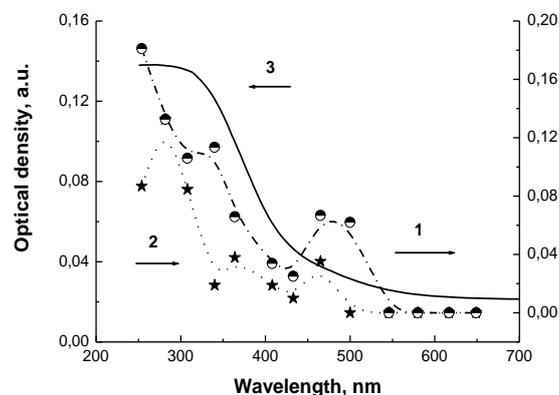


Figure 4. Spectral dependencies for “burning” TiO_2 . 1 – photodesorption CO_2 after first illumination; 2 - photodesorption CO_2 after the long-time illumination through the UV filter; 3 – diffuse reflection spectrum for TiO_2 which is the same as located on the wall of a reactor.

Much more processes take place on the titania surface under visible light illumination than in the dark. In addition to the dark desorption of CO_2 , its photodesorption was observed with the first-order kinetics similar to that of the dark desorption ($\tau_2 \approx 5$ min) by 20 times larger amount of desorbed CO_2 (Figure 2, curve 2). The photodesorption kinetics is presented as the decrease in the amount of CO_2 molecules adsorbed on the titania surface.

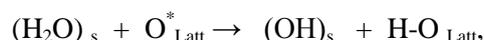
The measurement of the spectral dependencies of the CO_2 photodesorption quantum yield showed that the highest quantum yield was observed in the region of the TiO_2 intrinsic absorption (Figure 4, curves 1 and 2). A diffuse reflectance spectrum of the titania powder used in this study is shown for comparison (Figure 4, curve 3). If the time of the TiO_2 surface illumination was increased to several hours, the CO_2 photodesorption quantum yield decreased.

The CO_2 photodesorption in the region of the TiO_2 intrinsic absorption (including the 308 nm filter) is apparently caused by deep oxidation of adsorbed hydrocarbons with the oxygen from the air [13]. The processes predominating in the region of the surface absorption are related to the electron transfer from the oxide valence band to the surface and discharging of the surface compounds (e.g. CO_3^- , CO_2^-) with the electron transfer to the conduction band. In the former case, the CO_2 photodesorption results from discharging of the surface carbonate and carboxylate groups [14] with a mobile hole of the valence band. In the latter case, the CO_2 photodesorption to the gas phase is related to direct discharging of these compounds. The efficiency of the absorption with the formation of electron-hole pairs is substantially higher than that in the surface absorption band. The quantum yield of photodesorption in the region of the oxide intrinsic absorption is also much higher than in the surface absorption region (Figure 4).

It is known that the surface of the commercial (initial) TiO_2 material is reduced during heating in a vacuum, an inert gas, or hydrogen at high temperatures. This treatment can vary the color of the TiO_2 powder from slightly gray to dark blue depending on the degree of reduction of the sample [15, 16]. After high temperature oxygen–vacuum treatments of starting TiO_2 , the degree of reduction of its surface by high temperature heating in a vacuum or illuminating decreases. The dark adsorption of oxygen on such a sample is not observed [17]. In light of the foregoing, it can be assumed that

adsorbed water plays the key role in the reduction of the surface of hydrophilic titanium dioxide in a vacuum, inert gas, or hydrogen atmosphere, interacting with the lattice oxygen of the oxide.

Long-term illumination of the surface of TiO₂ particles in a water vapor atmosphere (in the reactor space) results in the reduction of the particle surface, which is detected both visually and by the diffuse reflectance spectrum of the sample in air. This is evidence for the effective photoreduction of titanium dioxide by water molecules, i.e., the oxidation of water by the titania lattice oxygen under the action of UV radiation. Under the given experimental conditions, as water, the hydrogen peroxide produced is frozen out into the trap with a cooling mixture. After thawing the trap to room temperature, oxygen is generated in the closed reactor volume; the amount of oxygen is measured with the Pirani gauge and the mass spectrometer. The oxygen produced is not adsorbed in the dark on the titanium dioxide surface. Thus, by the action of UV radiation and the subsequent storage, the titanium dioxide is reduced by the adsorbed water in the reactor space to produce an intermediate peroxide compound via the reaction:



where O_{Latt}^* is the surface lattice oxygen activated by the free mobile “hole” of the valence band [13]. Some confirmation for this assumption is the STM data by Du et al. [18], who showed the formation of hydroxyl groups by the reaction of water with oxygen atoms formed during the adsorption of molecular oxygen on the (110) face of reduced TiO₂. The subsequent long-term holding of the sample in the reactor in the dark resulted in the release of molecular oxygen into the gas phase. For the TiO₂ sample prepared by grinding (dispersing) of the rutile crystal in air, the amount of oxygen formed after a 30-min exposure to light in water vapor and holding in air in the dark was greater than that corresponding to the monolayer coating of the surface of the titania sample.

Over a long period of illumination time by all radiation of OSL-1 illuminator in atmosphere of various gases (halogenorganic compounds, acetone) the titania surface is reducing as the result of lattice oxygen consumption for the carbon dioxide formation in the gas phase. At that, the formation of nonstoichiometric Ti³⁺ is detected by ESR method and by the absorption of light quanta with the wavelength more 400 nm and even by sight. Moreover, the darkness adsorption of oxygen is observed on reduced titania surface.

4. Conclusions

Water and carbon dioxide were the main products released from the surface of the titania powders. During exposure under UV light, which is absorbed by titania water interacts efficiency with the metal oxide lattice oxygen to subsequently release oxygen in darkness to gas phase, reduce titanium dioxide and form lattice oxygen vacancies.

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