

Surface properties and photocatalytic activity of nanostructural films

V.I.Yatskiy, I.S.Petrik^{}, N.P.Smirnova^{*},
V.M.Granchak, A.M.Eremenko^{*}*

L.Pysarzhevsky Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 31 Nauky Ave., 03028 Kyiv-28, Ukraine

^{*}Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 General Naumov Str., 03164 Kyiv-164, Ukraine

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Glass-supported TiO₂ nanostructural films of various porosity have been prepared. The structure and sorption characteristics of the obtained coatings have been investigated by x-ray phase analysis, adsorption methods and transmission electron microscopy. The photocatalytic activity of prepared materials in the gas-phase oxidation of ethanol and acetone has been examined. Besides the specific photocatalytic activity of TiO₂ (anatase), photocatalyst sorption capacity defined by TiO₂ coating porosity was also found to exert a decisive influence upon efficient photooxidation in gaseous phase.

Получены наноструктурные пленки TiO₂ различной степени пористости, нанесенные на стеклянные подложки. Методами рентгенофазового анализа, адсорбции и трансмиссионной электронной микроскопии изучены структурно-сорбционные характеристики полученных пленок, исследована их фотокаталитическая активность в реакциях окисления ацетона и этанола в газовой фазе. Показано, что определяющее значение для эффективного газофазного фотоокисления, кроме собственной фотокаталитической активности TiO₂ (анатаза), имеет также сорбционная способность фотокатализаторов, которая определяется пористостью TiO₂-покрытий.

Numerous works have been devoted to study of photocatalytic activity of titanium dioxide in various redox processes [1, 2]. At present, development of high-efficient photocatalysts for commercial application in industry and ecology is one of the priority directions in this field. Obviously, besides high photocatalytic activity, such functional materials should have a combination of physico-mechanical properties (particle size, layer thickness and supported photocatalyst strength), thus ensuring their relatively simple, efficient and long-term operation. From this point of view, use of "classic" materials (i.e. powders, gels, sols, suspensions, TiO₂ colloids) as reported in many works [2] is not quite justified, sometimes problematic or even impossible. TiO₂-

based photocatalitically active films appear to be more promising for this purpose. Supported onto a hard base (i.e. ceramics, glass, porous matrix), the above films would find a wide application in the field of bactericide coatings [3], self-cleaning surfaces [4], systems for air purification [5]. This work is devoted to study of some peculiarities of structure and sorption properties of TiO₂ nanostructural films being characterized by a developed porosity as well as of their photocatalytic activity in heterogeneous gas-phase oxidation processes of acetone and ethanol.

Titanium dioxide was synthesized by sol-gel method involving hydrolysis of titanium tetraisopropoxide (TIPT) in isopropyl alcohol [8]. TiO₂ films were prepared by ex-

tracting ("dip coating") from the colloidal mother liquor; the corresponding TiO₂ powders were produced by drying of residual gels. The starting solutions were prepared using TIPT solution in isopropyl alcohol (iso-C₃H₇OH), acetic acid as a catalyst, α -terpineol as a viscous solvent [6] and PEG 300 (Loba Feinchemie) and PEG 1000 (Fluka) polymers as pore-forming agents. In order to obtain precursors of TiO₂ (300) and TiO₂ (1000) films (corresponding to the pore-forming agent used), two solutions were prepared: a) 0.34 mole TIPT, 4.57 mole isopropyl alcohol, 2.12 mole α -terpineol and a pre-specified amount of pore-forming polymer; b) 0.78 mole isopropyl alcohol, 1.11 mole H₂O and 0.37 mole glacial acetic acid (Table 1). The later was then added dropwise into the first one under intense stirring. The starting mass concentration of colloidal solutions in terms of TiO₂ was 4 %. The films were supported onto glass slides having smooth surface and etched by hydrofluoric acid (to increase their specific surface) which were previously deep cleaned (by ultrasonic cleaning, surfactant treatment, washing in deionized water, and drying). The slides were immersed into the starting precursor solutions, drawn out at a constant rate of 9 cm/min, dried and then calcined in air at 500°C for 1–3 h to result in transparent TiO₂-films being characterized by homogeneous surface and high mechanical strength.

The crystalline structure of the resulted TiO₂ coatings was examined by x-ray phase

analysis (CuK α). Thickness and refraction index were measured by multiangular ellipsometry (LEF-3M, Russia, $\lambda = 632.8$ nm), transmission spectra were recorded by a Perkin-Elmer Lambda-35 spectrophotometer. The films microstructure was analyzed by transmission (TEM) and scanning (SEM) electron microscope (Philips CM 12 TEM/SEM) with 120 kV accelerating voltage. The porosity was defined according to Bruggemann equation describing porosity as changes in the refraction index of polycrystalline films as compared with TiO₂ single crystal [7], which is applicable for these systems as those comprising particles of indefinite shape and slight porosity. The samples sorption volume (VS) was determined for ethanol and acetone sorption by gravimetry [9]. Photocatalytic activity of the resulted films was studied in the reactions of gas-phase heterogeneous oxidation of acetone and ethanol (both analytical grade purity). The samples were exposed to light in the reactor at room temperature (25°C) and atmosphere pressure through a glass window using DRSh-1000 lamp, $\lambda > 310$ nm; the exciting light intensity as measured using a ferrioxalate actinometer was varied in the $0.54 \cdot 10^{-6}$ to $2.7 \cdot 10^{-6}$ Einstein/min range by using metallic gauzes. Reduction in concentration of the starting substances as well as accumulation of oxidation products were determined using a chromatograph [8].

The structure and sorption characteristics of all obtained TiO₂ coatings are presented in Table 2. The reported results

Table 1. Composition of precursors for nonporous titanium dioxide, TiO₂(300) and TiO₂(1000)

Film	Solution A (moles)					Solution B (moles)		
	TIPT	α -Terpineol	iso-Propanol	PEG300	PEG1000	iso-Propanol	CH ₃ COOH	H ₂ O
TiO ₂ (nonporous)	0.34	2.12	3.26	–	–	0.78	0.37	1.11
TiO ₂ (300)	0.34	2.12	3.26	0.19	–	0.78	0.37	1.11
TiO ₂ (1000)	0.34	2.12	3.26	–	0.06	0.78	0.37	1.11

Table 2. Structure and sorption characteristics of the studied nanostructural titanium dioxide films

Sample	Porosity, %	Thickness, nm	Crystallite mean size, nm	Powder spec. surface area, m ² /g	V _S , cm ³ /g (for ethanol)	V _S , cm ³ /g (for acetone)
TiO ₂ (300) smooth glass	40	130	12–13	105	0.055	0.033
TiO ₂ (1000) smooth glass	30	150	17–18	75	0.029	0.015
TiO ₂ etched glass	25	90	10–12	~50	0.019	0.011
TiO ₂ smooth glass	20	90	10–12	~50	0.012	0.007

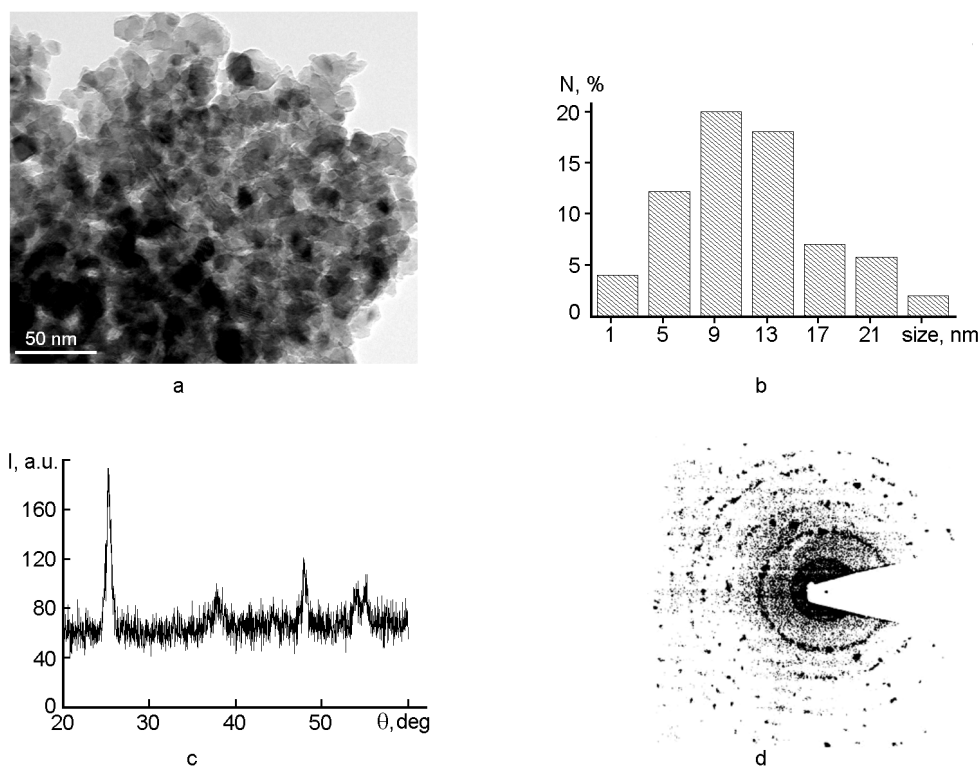


Fig. 1. Structure characteristics of porous TiO_2 films (TiO_2 300): (a) TEM image, individual crystals of 10 to 12 nm size; (b) particle size distribution histogram; (c, d) x-ray diffraction patterns, reflexes from anatase crystal structure.

show that all the samples are characterized by porous structure. For the films prepared of precursors not containing pore-forming polymer, the formation of porous structure may be attributed to forming of individual, different size and orientation, chaotic TiO_2 crystallites (globules) which are formed on glass surface in the course of deposition and subsequent annealing of films. Increasing in porosity of films supported onto glass base pre-etched with hydrofluoric acid is evidently attributed to their surface relief non-uniformity and, consequently, increased number of formed various centers of TiO_2 film crystallization. In other words, the "porosity" in the prepared TiO_2 -films is a consequence of "chaotic" mutual arrangement of the primary centres of TiO_2 particles (globulas) crystallization, while unfilled interglobular space appears in the role of "pores".

The films prepared from precursors containing pore-forming agents are characterized by a more ordered structure. The transmission electron spectroscopy pictures show that the crystallite size is mainly in 10–12 nm range (TiO_2 300) and the pore diameter about 10 nm (Fig. 1a, b). Diffrac-

tion patterns of the samples calcined at 500°C (Fig. 1,c,d) include all the peaks characteristic for the anatase crystalline structure. The crystallite size calculated using Scherrer formula agrees well with electron microscopy data.

The porosity (the morphology of support surface being the same) was found to increase in inverse proportion against increasing in molecular weight (carbon chain length) of the pore-forming polymer used. In our opinion, the primordial effect of the latter consists in coordination TIPT at the molecule ends owing to present free OH groups [10]. Longer carbon chain (as in the case of PEG 1000), first, contributes to more distant localization of coordinated TIPT molecules and, second, provides steric hindrances for TIPT interaction with water molecules in the starting sol. Hindered hydrolysis of Ti(IV) alkoxide leads to increasing mean size of TiO_2 crystallites (17–18 nm for TiO_2 1000 as compared with 12–13 nm for TiO_2 300), and their space isolation with organic phase confines the aggregation process in the course of the film coating formation. The sorption capacity of the films was found to increase with rising porosity of the supported coat-

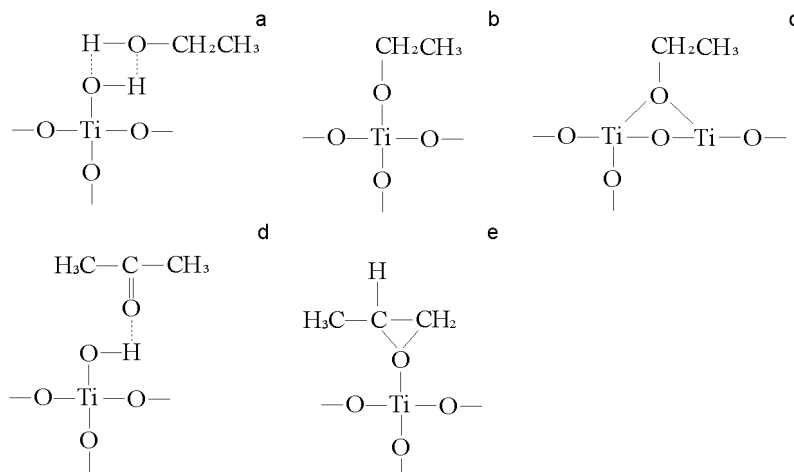
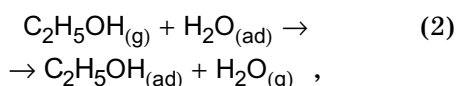
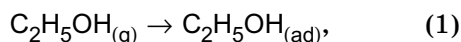


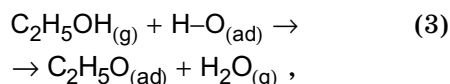
Fig. 2. Structures of adsorption compounds for ethanol (a, b, c) and acetone (d, e) on TiO_2 surface.

ings. The higher sorption capacity for ethanol in comparison with that for acetone is related most likely with actual distinctions of adsorption mechanism of these substrates on TiO_2 surface [11, 12].

As is known [11, 12], ethanol may be sorbed on titanium dioxide surface via formation of hydrogen bond with hydroxyl groups (Fig. 2a) always present on TiO_2 surface [13]



where (g) — aggregated in gaseous phase, (ad) — adsorbed onto TiO_2 surface, or by dissociation,



with formation of mono- and bidentate Ti ethoxide compounds (Fig. 2b, c). The formation probability as well as thermal stability thereof are practically identical [11]. According to [14], adsorption of acetone on TiO_2 depends on its surface structure: for TiO_2/PVG samples (porous glass "Vycor"), adsorption occurs in two ways, i.e. due to hydrogen bonds (Fig. 2d) and also via chemical reaction to form surface bound epoxide $\text{CH}_3\text{CHCH}_2\text{O}$ (Fig. 2e). As to TiO_2 powders supported on ordinary glass, acetone is adsorbed predominantly in molecular form (i.e. in a reversible manner) whereas

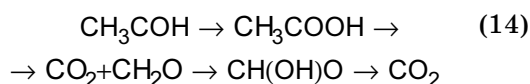
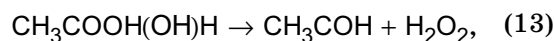
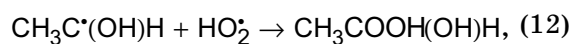
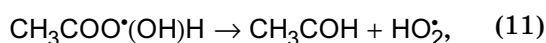
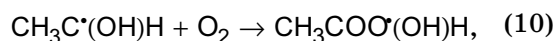
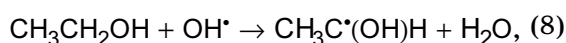
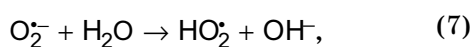
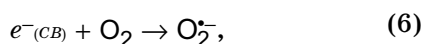
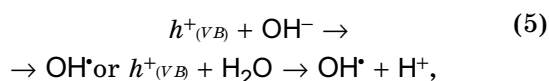
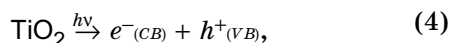
formation of surface epoxide complex occurs very slowly and with low efficiency [15]. Hence, a higher adsorptivity of the samples for ethanol as compared with that for acetone (Table 2) is attributed, first, to the structure steric factor (smaller molecular size) being manifested in the course of physical (molecular) adsorption of organic substrates owing to hydrogen bonds with hydroxyl groups located on titanium dioxide surface and, second, to more expressed ability of ethanol for irreversible dissociative adsorption with forming of stable ethoxide complexes on TiO_2 surface (Fig. 2).

When TiO_2 -films were exposed to light, reduction in concentration of oxidized substances in the reactor with simultaneous evolution of gaseous products was observed. While oxidation of acetone, no gaseous products other than CO_2 were observed. While oxidation of ethanol, the CO_2 evolution was not observed at the initial illumination stage (on average, for first 60 min), only reducing of ethanol concentration and acetaldehyde accumulation were fixed. But further illumination resulted in synchronous oxidation of alcohol to acetaldehyde and of the latter to CO_2 , similar to that described in [8]. CO formation was not observed in these reaction systems. Study of kinetic regularities of the photocatalytic oxidation of acetone and other substrates demonstrated the process efficiency to be almost independent of the starting reagent concentrations ranged from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-4}$ mol/l, that is a characteristic feature of the reactions occurring in adsorbed layer on semiconductor particle surface [1, 2]. It was also found

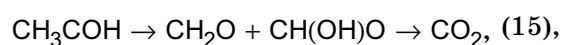
that the rate of these redox processes is in direct linear relation with light intensity, thus evidencing, in our opinion, the recombination rate constancy of photogenerated charges [16] and a rather long-term lifetime of active particles on TiO₂ surface [17].

The conversion degrees of organic substrates with all used photocatalysts are presented in Table 3. Taking into account that vapor adsorption of a reagent being oxidized on TiO₂ surface is an indispensable condition for photocatalytic redox-processes running in gaseous phase, the results reported here testify the direct proportional relationship between the samples sorption ability and the photocatalytic process efficiency. It is just the sorption volume (VS) being defined by the glass surface relief (for the films prepared without using of pore-forming agents) or by pore-forming polymer nature for TiO₂ (300) and TiO₂ (1000) that seems to be the crucial factor defining the rates of redox-processes. The differences in conversion degrees of organic compounds are obviously associated with their different chemical nature as well as different stability of complexes formed by adsorption on TiO₂ surface and diverse mechanisms of photochemical oxidation.

Basing on the results obtained and literature data reported [18–20], the photocatalytic oxidation mechanism of ethanol vapor on TiO₂ surface can be described by the following stages:



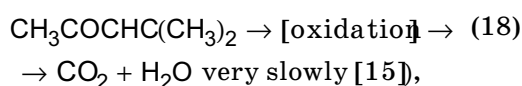
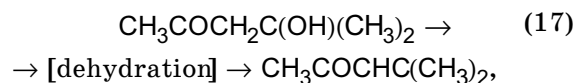
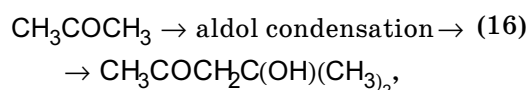
or



where $e^-(CB)$ — electrons in conduction band, $h^+(VB)$ — holes in semiconductor valence band.

Photocatalytic oxidation of acetone also can pass in two ways depending on the structure of TiO₂ active surface [15]:

(a) for molecular adsorption of acetone (Fig. 2d)



or

(b) for ethoxide coordination of acetone on TiO₂ surface (Fig. 2e)

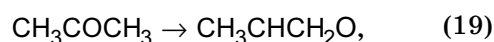
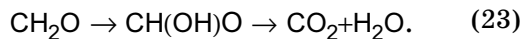
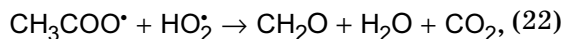
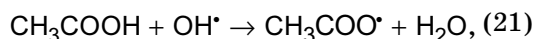
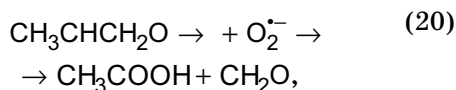


Table 3. Photocatalytic conversion degree of organic vapors on TiO₂ film materials

Film	Photocatalytic conversion (%) during 90 min for:		
	acetone	ethanol	acetaldehyde (intermediate)
TiO ₂ (300)	37	64	62
TiO ₂ (1000)	29	58	55
TiO ₂ smooth glass	24	52	50
TiO ₂ etched glass	18	46	42

$$I = 2.7 \cdot 10^{-6} \text{ Einstein/min}, C_{\text{starting}} = 5 \cdot 10^{-4} \text{ mol/L}$$



Obviously, the apparent total rate of these redox-processes passing through either of above described mechanisms should be defined by the efficiency of intermediate stages 16, 17, and 19, respectively. A low reaction rate at these intermediate stages is attributed most likely, first, to retarded surface diffusion and mutual orientation of adsorbed acetone molecules preceding the aldol condensation (stage 16) and, second, to additional energy required for the dehydration of intermediate surface complexes (stage 6a) or epoxide coordination (stage 19) of CH_3COCH_3 on TiO_2 surface. Hence, the more slow photocatalytic oxidation process of acetone (as compared to that of ethanol) may be, most likely, related with low restructurization stage rate of acetone adsorption complexes on TiO_2 surface.

Thus, in the course of this work, a series of titanium dioxide nanostructural films with different porosity degrees were prepared. The obtained results evidence interrelations between the structure and sorption characteristics of the prepared films and their photocatalytic activity. Alongside with TiO_2 intrinsic photocatalytic activity, the sample developed surface and its porosity were found to influence cardinaly the photooxidation efficiency of organic substrates in gaseous phase. The prepared nanostructural TiO_2 films characterized by an appreciable sorption capacity are very promising

functional materials to be applied in systems for gas phase photocatalytic oxidation of volatile organic compounds (as possible air pollutants).

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Властивості поверхні та фотокаталітична активність наноструктурних плівок на основі TiO_2

***В.І.Яцьків, І.С.Петрик, Н.П.Смірнова,
В.М.Гранчак, А.М.Єременко***

Одержано наноструктурні плівки TiO_2 різного ступеня пористості, нанесені на скляні підкладки. Методами рентгенофазового аналізу, адсорбції та трансмісійної електронної мікроскопії досліджено структурно-сорбційні характеристики одержаних плівок, вивчено їх фотокаталітичну активність в реакціях окислення ацетону та етанолу у газовій фазі. Показано, що визначальний вплив для ефективного газофазного фотоокислення, окрім власної фотокаталітичної активності TiO_2 (анатазу), має також сорбційна здатність фотокаталізаторів, яка визначається пористістю TiO_2 -покривів.