CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2021,
Vol. 15, No. 4, pp. 465–474

Chemistry

CHARACTERIZATION AND PROPERTIES OF TITANIUM(IV) OXIDE, SYNTHESIZED BY DIFFERENT ROUTES

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https://doi.org/10.23939/chcht15.04.465

Abstract. The article considers the influence of precursor type and sol-gel synthesis conditions of TiO_2 on its properties. The obtained TiO_2 samples were characterized by X-ray diffraction methods, electron microscopy, as a result of which it was found that all the obtained TiO_2 powders have the crystallite size in a nanorange of 2.5–17 nm. It was shown that sorption-photocatalytic properties of TiO_2 significantly depend on a phase composition, surface acidity, specific surface area and porosity. It was found that the amorphous TiO_2 has improved adsorption properties, while crystalline TiO_2 is characterized by enhanced photocatalytic properties. Determined acidic nature of the TiO_2 surface explains the better sorption and photocatalysis relative to the cationic dye.

Keywords: titanium(IV) oxide, sol-gel method, structural-adsorption characteristics, sorption, photocatalysis.

1. Introduction

Titanium(IV) oxide (TiO_2) has a great potential for use in various chemical processes, but the usage of TiO_2 to improve the environment is one of the most promising ones. This is evidenced by the presence of such functional properties as the high adsorption capacity and photocatalytic activity (especially in the nanodispersed range) in relation to pollutants of aquatic systems, in particular, organic substances [1].

It is known that the controlled regulation of the functional properties of metal oxide materials based on titanium(IV) oxide can be done by changing their phase composition, which largely determines their physical and chemical properties. TiO_2 exists in three different crystalline structures: rutile, anatase, and brookite. The structural unit of the TiO_2 crystal lattice in all polymorphic modifications occurs to be the distorted TiO_6 octahedrons, which are arranged so that each of oxygen ions belongs to three octahedrons simultaneously. Only rutile and anatase are believed to have an applied value among three polymorphic titanium(IV) oxide modifications. Rutile is a more thermodynamically stable structure, but anatase is considered to be the more promising one due to its greater photochemical activity. However, there is an evidence in the literature that the greater photocatalytic activity is attributed to the TiO_2 nanomaterials consisting of mixed phases, such as anatase and rutile, anatase and brookite, or even the mixtures of all three phases [2-5].

Synthesis method, precursors and parameters of obtaining are of decisive importance in creating nanomaterials of ecological direction, especially for their usage as adsorbents and photocatalysts. Variation of these parameters allows obtaining of nanoparticles of certain shape and size. These parameters affect not only the shape and size of the particles, but also the nanostructure, crystallinity, textural characteristics, sorption and photocatalytic properties, *etc*. [6-10]. For the synthesis of titanium(IV) oxide in scientific literature such methods as a chemical precipatation, hydro(solvo)thermal synthesis, sol-gel technology, chemical vapor deposition synthesis, green synthesis and others are most often considered [11-22]. Moreover, to obtain metal oxide products with more varied properties, these synthesis methods can be easily combined with each other or different additional processings. For example, the ultrasound or high frequency radiation is used with basic synthesis methods to influence such properties of TiO_2 nanoparticles as the size, morphology, specific surface area, sorption capacity, *etc*. Ultrasonic treatment enables to avoid enlargement of the formed particles, as well as to achieve a high level of their homogeneity [23].

The sol-gel method has become quite widely used to obtain TiO_2 due to the relative ease of synthesis and the wide range of control parameters [24, 25]. By varying the parameters during synthesis, such as concentration,

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temperature, duration, reaction medium, *etc*., this method can purposefully regulate the final physicochemical and structural-adsorption properties of TiO_2 powders over a wide range [19, 26-28]. The sol-gel method also allows obtaining the homogeneous primary TiO_2 particles which are characterized by fewer structural defects than those obtained by other methods, such as chemical precipitation, because of the homogeneity of the formation and the growth of particles due to hydrolysis and polycondensation reactions occurring during sol-gel synthesis [29-35].

Despite numerous studies in the scientific literature regarding the synthesis of metal oxide nanopowders by the sol-gel method, the choice of precursors to obtain TiO_2 nanomaterials with specified physicochemical properties is still a debatable issue. A problem is also the choice of sol-gel synthesis parameters such as a precursor type, concentration, temperature, duration, etc. and their impact on the sorption-photocatalytic properties of TiO_2 materials. In the synthesis of environmental materials, the priority is given to surface-structural characteristics (specific surface area, porosity, pore distribution by radius, acidity) of TiO_2 powders and the possibility of their purposeful regulation by changing synthesis parameters. The solution of these problems is important not only for the further development of production technology of sorption-catalytic materials based on the TiO_2 sol-gel method, but also for the development of theoretical basis for the sol-gel technology of obtaining TiO_2 nanomaterials.

Thus, this article is devoted to the TiO_2 synthesis by diverse variations of the sol-gel method and to the influence of the precursor type, as well as certain conditions of synthesis on the physicochemical, surface-structural characteristics of the obtained TiO_2 powders and their sorption-photocatalytic properties in order to establish the relationship between them.

2. Experimental

The chemicals used in this study were titanium(IV) chloride ($TiCl_4$), titanium(IV) isopropoxide $Ti\{OCH(CH_3)_2\}_4$, titanium(IV) oxysulfate ($TiOSO_4$), titanium(III) chloride in hydrochloric acid ($TiCl_3$), titanium(III) sulfate in sulfuric acid $Ti_2(SO_4)_3$, isopropyl alcohol, butyl alcohol, isobutyl alcohol, isoamyl alcohol, organic dye (Methylene blue and Congo red). All the reagents were of chemical grade.

2.1. Synthesis of TiO_2 Samples

The synthesis of TiO_2 powders by a sol-gel method was implemented by 6 ways. All sol-gel synthesis methods were developed with the participation of the authors on the basis of literature analysis and own experimental research. By the first way (Synthesis 1) the obtaining of TiO_2 was performed from an alcoholic solution of titanium(IV) isopropoxide with the addition of a certain amount of water. The resulting solution was then placed in a Teflon reactor, which was sealed in a steel container. The reactor was heated to 453 K and maintained for 24 h. At the end of the synthesis, the reactor was cooled, and the resulting suspension of titanium(IV) oxide was centrifuged several times with simultaneous washing to pH 6. The washed powders were dried at 353 K for 24 h. Thus *TiO_2-1* sample was obtained. In the second variant (Synthesis 2), the synthesis of TiO_2 was carried out by hydrolysis of $TiCl_4$ in water at a temperature of 368 K for 40 min. The resulting precipitate was then dried at 353 K and calcined at 773 K for 2 h. In this way a *TiO_2-2* sample was obtained. The third procedure (Synthesis 3) consisted in the following. $TiCl_4$ was dissolved in the absolutized butyl alcohol and the certain amount of water was added. After that the mixture was heated to 368 K and kept for 40 min. The resulting suspension was dried at a temperature of 353 K. In this way, 3 samples were synthesized: *TiO_2-3*, *TiO_2-4*, and *TiO_2-5*. In the fourth case (Synthesis 4), the synthesis of titanium(IV) oxide was also implemented with $TiCl_4$, but in different media (aqueous, aqueous-alcohol: isopropyl, isobutyl and isoamyl alcohols). To this end, titanium(IV) chloride was added to the appropriate solution and stirred for one hour, heated and then the solvent was evaporated. The powder obtained after evaporation was calcined for 2 h at a temperature of 673 K. Fourth samples were synthesized: *TiO_2-6*, *TiO_2-7*, *TiO_2-8*, and *TiO_2-9*. The fifth version of the sol-gel method (Synthesis 5) was performed using titanium(VI) oxysulfate precursor. In this case, solutions of titanium oxysulfate with certain pH values were prepared, heated to 353 K and maintained for a certain time. The precipitate was then filtered, washed and dried in a vacuum dryer at 373 K. Sixth samples were thus obtained: *TiO_2-10*, *TiO_2-SG11*, *TiO_2-SG12*, *TiO_2-SG13*, *TiO_2-SG14*, and *TiO_2-SG15*. By the sixth way (Synthesis 6), titanium(IV) oxide was obtained by hydrolysis of Ti^{3+} salts at room temperature. Solutions of titanium(III) chloride (15 wt %) in hydrochloric acid and titanium(III) sulfate (15 wt %) in sulfuric acid were used as precursors. Using titanium(III) chloride, 7 samples were obtained: *TiO_2-16, TiO_2-17, TiO_2-18, TiO_2-19, TiO_2-20, TiO_2-21* and *TiO_2-22*; using titanium(III) sulfate – one sample *TiO_2-23*. Synthesis conditions of all TiO_2 samples are shown in Table 1.

Table 1

TiO_2 samples and conditions for their obtaining

TiO_2 sample	Synthesis parameters			Precursor
	Parameters	Solvent	Heat treatment	
TiO_2-1	1:5 ($Ti:H_2O$), 453 K, 24 h	Isopropyl alcohol	Drying 353 K	$Ti\{OCH\text{-}(CH_3)_2\}_4$
TiO_2-2	1:5 ($Ti:H_2O$), 368 K, 30 min	Isopropyl alcohol	Drying 353 K, calcination 773 K	$TiCl_4$
TiO_2-3	1:5 ($Ti:H_2O$), 368 K, 30 min	Butyl alcohol	Drying 353 K	$TiCl_4$
TiO_2-4	1:7,5 ($Ti:H_2O$), 368 K, 30 min			
TiO_2-5	1:10 ($Ti:H_2O$), 368 K, 30 min			
TiO_2-6	1:10 ($Ti:H_2O$), 293 K, 3 h	Water	Calcination 673 K	$TiCl_4$
TiO_2-7		Water-isopropyl solution		
TiO_2-8		Water-isobutyl solution		
TiO_2-9		Water-isoamyl solution		
TiO_2-10	1:50 ($Ti:H_2O$), 353 K, pH 4, 60 min	Water	Drying in a vacuum dryer 373 K	$TiOSO_4$
TiO_2-11	1:50 ($Ti:H_2O$), 353 K, pH 4, 90 min			
TiO_2-12	1:50 ($Ti:H_2O$), 353 K, pH 1, 120 min			
TiO_2-13	1:50 ($Ti:H_2O$), 353 K, pH 2, 120 min			
TiO_2-14	1:50 ($Ti:H_2O$), 353 K, pH 3, 120 min			
TiO_2-15	1:50 ($Ti:H_2O$), 353 K, pH 4, 120 min			
TiO_2-16	pH 0,8 (hydrolysis), ageing 7 h	Hydrochloric acid solution	Drying 323 K	$TiCl_3$
TiO_2-17	pH 0,8 (hydrolysis), ageing 14 days			
TiO_2-18	pH 0,8 (hydrolysis), ageing 21 days			
TiO_2-19	pH 0.8 (hydrolysis), ageing 7 h, pH 9 (precipitation by ammonia solution)			
TiO_2-20	pH 9 (precipitation by ammonia solution), ageing 1 h			
TiO_2-21	pH 0.8 (hydrolysis), 1:2 (Ti:F), ageing 7 days			
TiO_2-22	pH 0.8 (hydrolysis) 1:2 ($Ti:SO_4^{2-}$), ageing 7 days			
TiO_2-23	pH 1.2; 353 K, 30 min, ageing 7 days	Sulphuric acid solution	Drying 323 K	$Ti_2(SO_4)_3$

2.2. Characterization

Phase composition and structural analysis of the synthesized TiO_2 samples were performed using a diffractometer (Ultima IV Rigaku, Japan). The phase composition of TiO_2 samples was determined using standard cards 00-021-1276 (Rutile) and 00-021-1272 (Anatase) Crystallographic Open Database (COD). Surface structure and morphology of TiO_2 were studied using a scanning electron microscope (SEM 106I, Ukraine) and a transmission electron microscope (TEM 100-01, Ukraine). The investigation of the specific surface area and porous structure of TiO_2 samples was performed by a nitrogen adsorption-desorption (Quantachrome Autosorb Nova 2200e, USA).

2.3. Sorption and Photocatalysis Experiments

Sorption and photocatalytic activity of the synthesized TiO_2 samples were studied on dye solutions of both cationic (Methylene blue) and anionic (Congo red) nature according to the own proven methods. For this purpose, TiO_2 samples were dispersed in the initial dye solutions using an ultrasonic disperser (40 kHz, ultrasonic bath UZM-004-1, Ukraine) for 5 min. Next, to detect the sorption activity, the resulting suspensions were stirred for 10 min. After the sorption process, the spent TiO_2 photocatalysts were separated by centrifugation (5000 rpm, MPW-310 centrifuge, Poland) and the resulting aliquots were analyzed. The residual concentration of the dye was determined by a spectrophotometric method (spectrophotometer 721 UV/VIS, China) with a wavelength corresponding to the dye.

When establishing photocatalytic activity in TiO_2 samples, the resulting suspension in an ultrasonic bath was first stirred for 10 min and then treated with UV radiation (368 nm) with stirring for 20 min. The separation of photocatalysts from solutions and determination of residual dye concentration were performed similar to the study of sorption activity. The degree of dye removal (Re) in the model solutions was calculated by the equation:

$$\mathrm{Re} = \frac{A_0 - A_f}{A_0} \cdot 100\% \qquad (1)$$

where A_0 is the absorbance of the initial model dye solutions; A_f is the absorbance of the model solutions after adsorption or/and photocatalysis.

2.4. The Acidity

The total acidity of the surface of the synthesized TiO_2 samples was evaluated by the pH value of the isoionic point (pH_{iip}), which was determined by the pH-metric method. For this 1 wt % suspensions of these samples in bidistilled water (pH~7) were prepared and pH of their suspensions was measured for 2 h at constant stirring (Portlab 102 pH-Meter, Russia). The last measurement of pH was pH_{iip} [36].

3. Results and Discussion

The main reactions that took place during all syntheses were as follows. According to Synthesis 1, the hydrolysis of titanium(IV) isopropoxide is described by the total reaction:

$$Ti\{OCH(CH_3)_2\}_4 + 2H_2O \rightarrow$$
$$\rightarrow TiO_2\downarrow + 4(CH_3)_2CHOH \qquad (2)$$

The Syntheses 2 and 4 can be described by the reaction:

$$TiCl_4 + 3H_2O \rightarrow TiO_2{\cdot}H_2O\downarrow + 4HCl \qquad (3)$$

X-ray analysis showed that the precipitates obtained by the Syntheses 2 and 4 were characterized by 100% amorphous phase, so they were additionally treated at high temperature, and the chemical reaction occurred [37]:

$$TiO_2{\cdot}H_2O \rightarrow TiO_2 + H_2O \qquad (4)$$

According to Synthesis 3, crystalline precipitate was immediately obtained:

$$TiCl_4 + 2H_2O \rightarrow TiO_2\downarrow + 4HCl \qquad (5)$$

The chemical reaction which happened in the solution in Synthesis 5:

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \qquad (6)$$

In this case X-ray amorphous precipitate was also obtained, which was further calcined, resulting in a chemical transformation:

$$TiO(OH)_2 + H_2O \rightarrow TiO_2{\cdot}2H_2O\downarrow \qquad (7)$$

According to Synthesis 6 the hydrolysis is carried out according to the following chemical scheme. In the case of titanium(III) chloride chemism can be represented as:

$$4TiCl_3 + O_2 + 2H_2O = 4TiOCl_2 + 4HCl \qquad (8)$$

$$TiOCl_2 + H_2O = TiO_2\downarrow + 2HCl \qquad (9)$$

and in the case of titanium(III) sulfate:

$$2Ti_2(SO_4)_3 + O_2 + 2H_2O = 4TiOSO_4 + 2H_2SO_4 \qquad (10)$$

$$TiOSO_4 + H_2O = TiO_2\downarrow + H_2SO_4 \qquad (11)$$

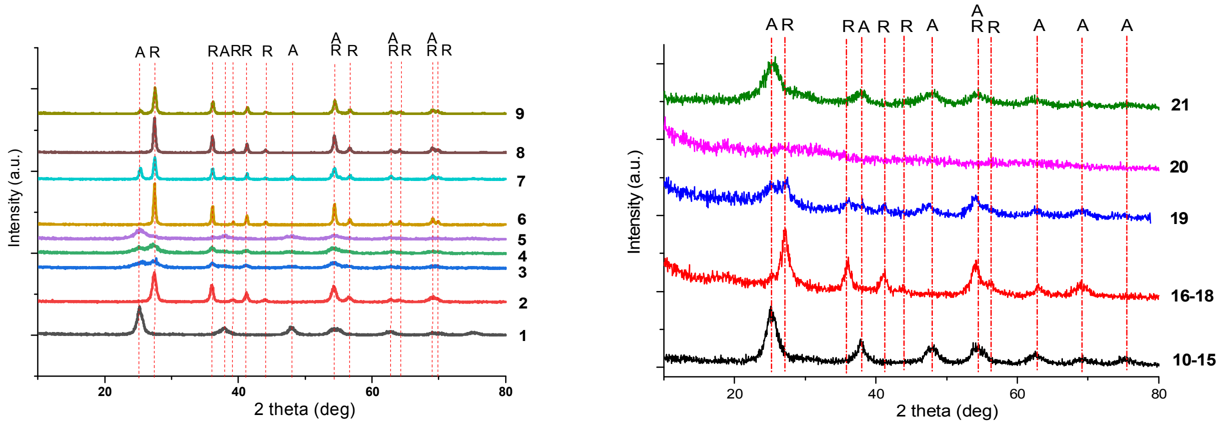
3.1. Structural Study

The respective diffraction (XRD) patterns are given in Fig. 1. The identification of TiO_2 samples showed the presence of pure rutile, pure anatase, mixed rutile-anatase and amorphous phases. The established phase composition and the calculated crystallite sizes by the Scherer formula for all obtained TiO_2 samples are shown in Table 2.

Analysis of the XRD patterns (Fig. 1a) testifies that the precursor type and parameters of sol-gel synthesis have a significant effect on the phase composition and nano-structuredness of TiO_2 samples. Thus, the use of titanium isopropoxide with a soft heat treatment results in the particles formation of anatase modification with a high crystallinity and an average crystallite size of 5 nm. The use of titanium(VI) chloride allows to obtain both the anatase and rutile modification of TiO_2, and the additional temperature treatment significantly increases the degree of crystallinity (TiO_2 samples 2, 4-9 compared with TiO_2 samples 3-5), but also reduces the content of anatase modification due to recrystallization processes during heat treatment. However, the use of some aqueous-alcoholic media (water-isopropyl and water-isoamyl) allows to get mixed anatase-rutile modifications, even when using further heat treatment. The implementation of TiO_2 synthesis by sol-gel methods at low temperatures (especially in excess of water) contributes to the anatase modification (TiO_2 sample 5), but the degree of crystallinity obtained by a low-temperature synthesis of TiO_2 samples is low. Presented in Fig. 1b XRD patterns for TiO_2 samples 10-23 only confirm the found regularities for TiO_2 samples 1-9. In this case all syntheses were carried out at low temperatures, resulting in low crystallinity for all samples. TiO_2 samples 10-15 are characterized by almost identical XRD patterns, therefore, it can be concluded that pH of the medium in the range of

1–4 during hydrolysis of titanium(IV) oxysulfate has almost no effect on the final phase composition, crystallinity and crystallite size of TiO_2 samples. In our opinion, the types of precursor and hydrolysis temperature have the biggest influence. As it is known, sulfate ions stabilize the anatase modification, which is also observed in this case, all samples obtained by this way had the anatase modification with a low degree of crystallinity.

The usage of salts of trivalent titanium allows to obtain both rutile and anatase modifications (TiO_2 samples 16-19, 21-23). Applying of ammonia solution precipitator has traditionally led to the X-ray amorphous phase (TiO_2 sample 20). However, an interesting fact was found that the additional precipitation by ammonia solution after hydrolysis process results in the formation of a rutile-anatase modification of almost 50:50 (TiO_2 sample 19). However, as a result of hydrolysis only, a pure rutile phase is formed (TiO_2 samples 16-18 have practically identical XRD patterns). This may be due to the following: initially, as a result of hydrolysis, a rutile modification is obtained. The supplement of the precipitator after hydrolysis promoted further binding of titanium ions from the solution and crystallization of particles on the surface of rutile nucleating seed in the anatase phase.



a) b)

Fig. 1. XRD patterns of TiO_2 samples 1-9 (a) and TiO_2 samples 10-21 (b)

Table 2

Phase composition and structural-adsorption characteristics of TiO_2 samples

TiO_2 sample	Phase composition (wt%)	Crystallite size, nm	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	The average pore size (nm)
1	2	3	4	5	6
TiO_2-1 (reaction 2)	Anatase (100)	5	137	0.29	7.3
TiO_2-2 (reactions 3 and 4)	Rutile (100)	11	19	0.06	4.2
TiO_2-3 (reaction 5)	Rutile (84) / Anatase (16)	6 / 2.5	–	–	–
TiO_2-4 (reaction 5)	Rutile (82) / Anatase (18)	5.7 / 3	–	–	–
TiO_2-5 (reaction 5)	Anatase (100)	3	199	0.175	3.5
TiO_2-6 (reactions 3 and 4)	Rutile (100)	14	8	0.008	19.7
TiO_2-7 (reactions 3 and 4)	Rutile (84) / Anatase (16)	17 / 4.5	11	0.009	13.1
TiO_2-8 (reactions 3 and 4)	Rutile (100)	13	13	0.01	14.7
TiO_2-9 (reactions 3 and 4)	Rutile (92) / Anatase (8)	15 / 3.5	7	0.007	22.4
TiO_2-10 (reactions 6 and 7)	Anatase (100)	2	79	0.16	7.6

Continuation of Table 2

1	2	3	4	5	6
TiO_2-11 (reactions 6 and 7)	Anatase (100)	2.7	99	0.18	7.2
TiO_2-12 (reactions 6 and 7)	Anatase (100)	3	78	0.17	8.1
TiO_2-13 (reactions 6 and 7)	Anatase (100)	3.3	85	0.17	7.9
TiO_2-14 (reactions 6 and 7)	Anatase (100)	3.8	87	0.18	7.5
TiO_2-15 (reactions 6 and 7)	Anatase (100)	4.3	107	0.24	6.9
TiO_2-16 (reactions 8 and 9)	Rutile (100)	6	268	0.06	5.7
TiO_2-17 (reactions 8 and 9)	Rutile (100)	6.5	–	–	–
TiO_2-18 (reactions 8 and 9)	Rutile (100)	8.5	–	–	–
TiO_2-19 (reactions 8 and 9)	Rutile (50) / Anatase (50)	6.5 / 4	269	0.07	5.1
TiO_2-20 (reactions 8 and 9)	Amorphous (100)	–	430	0.16	2.5
TiO_2-21 (reactions 8 and 9)	Anatase (100)	5.2	355	0.09	3.6
TiO_2-22 (reactions 8 and 9)	Rutile (40) / Anatase (60)	6 / 4.1	15	0.01	16.7
TiO_2-23 (reactions 10 and 11)	Anatase (100)	2.5	5	0.007	24.3

It can also be seen that the presence of fluoride ions during hydrolysis gives pure anatase modification (TiO_2 sample 21), and the existence of sulfate ions in the synthesis process (TiO_2 sample 22) allows to obtaine the mixed anatase-rutile modification (XRD pattern analogous of *TiO_2-19*). That is, fluoride ions and sulfate ions contribute to the crystallization of the anatase modification (fluoride to a greater extent). The use of titanium(III) sulfate for synthesis of titanium(IV) oxide (sample *TiO_2-23*) predictably results in the formation of the anatase modification (XRD pattern the same as for TiO_2 sample 21).

Comparison of the crystallite size and phase composition data (Table 2) allows us to formulate the following regularity: the crystallite size for rutile modification is 6 nm and higher, and the crystallite size for the anatase modification varies in the range of 2–5 nm. The obtained regularity testifies to some critical size of crystallites to which the anatase modification is crystallized, upon reaching this critical size, the anatase crystallites re-crystallize in a more stable rutile modification. Analysis and comparison of the diffraction results of the study lead to the conclusion that the type of precursor, reaction medium, ions presence and heat treatment significantly affect the crystallite size, phase composition and crystallinity during the sol-gel synthesis of TiO_2.

The structural-adsorption characteristics of TiO_2 samples defined by the method of nitrogen adsorption-desorption are shown in Table 2. As can be seen from the data presented, the precursor type and synthesis parameters significantly affect the texture characteristics: the specific surface area of TiO_2 samples changes from 5 to 430 m^2/g, herewith all samples are mesoporous. Consequently, we can draw the following conclusions. TiO_2 samples, which were exposed to heat treatment after hydrolysis (*TiO_2-2*, TiO_2 samples 6-9), had predictebly smaller specific surface area (in the range of 7–19 m^2/g) compared to non-calcined ones. It was generally 5–10 times smaller than for TiO_2 samples without heat treatment.

It can also be observed that the reaction medium slightly affects the specific surface area (for example TiO_2 samples 6-9). The use of oxysulfate-anion instead of chloride allows obtaining of mesoporous powders with smaller specific surface areas (about 80–100 m^2/g *versus* 140–200 m^2/g). The application of titanium(III) sulfate or sulfate ions in the synthesis process by a low-temperature hydrolysis results in obtaining of TiO_2 powders with very small specific surfaces areas (5–15 m^2/g). The largest surface areas are inherent in TiO_2 samples obtained by the low-temperature hydrolysis of titanium(III) chloride. At the same time usual precipitation permits to recieve a powder with the most developed surface area (up to 430 m^2/g). Therefore, based on the considered structural-adsorption characteristics of titanium(IV) oxide powders synthesized from different precursors, we can conclude that these characteristics depend significantly on the usage of post-synthesis heat treatment, slightly on the type of precursor and the least on the reaction medium.

A certain total acidity of the synthesized TiO_2 samples surface indicates the acidic nature of their surface, with the exception of TiO_2 samples 19-20, which have a weakly basic surface character, that is explained by the use of the precipitation and post-precipitation stages in the synthesis process.

3.2. Morphology Study

Electronic images of selected TiO_2 samples are shown in Figs. 2-4. As can be seen from Fig. 2, the particles of TiO_2 sample 1 are aggregates and agglomerates of irregular shape and approximately the same size.

TEM image of TiO_2 sample 2 displays the compact structure made of aggregates and agglomerates from crystalline nanoparticles. The sizes of individual TiO_2 particles which were synthesized from titanium(IV) chloride in isopropyl alcohol are close to the crystallite sizes determined by X-ray analysis.The size distribution of the nanoparticles in this case is in the range of 10–20 nm. SEM image of TiO_2 sample 2 indicates a spherical and more or less uniform shape of aggregates and agglomerates. TEM images of TiO_2 samples 3-5 which were also obtained from titanium(IV) chloride but in butyl alcohol, reveal a similar compact structure of aggregates and agglomerates. The single particles have the size range from 5 to 15 nm.

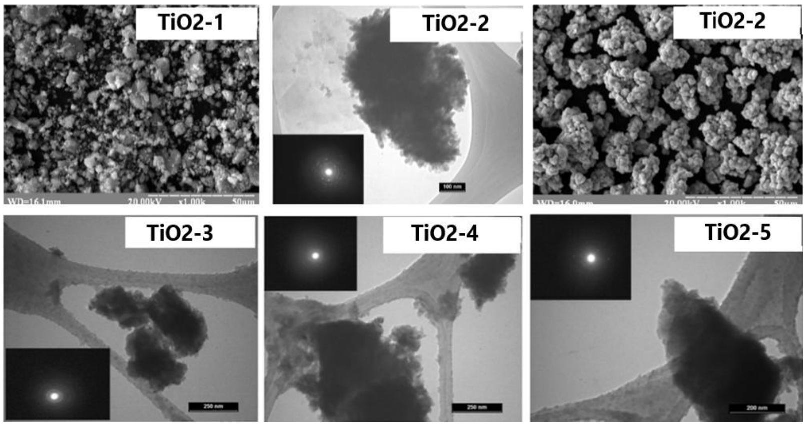


Fig. 2. SEM and TEM images:
TiO_2 sample 1 (titanium isopropoxide precursor) and TiO_2 samples 2-5 (titanium(IV) chloride precursor in different alcohol media)

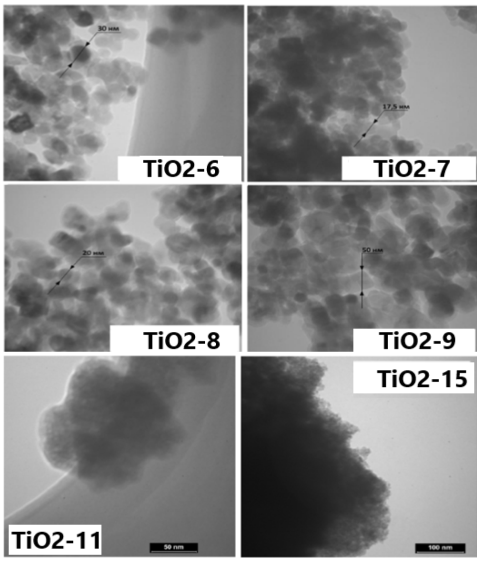


Fig. 3. TEM images: TiO_2 samples 6-9 (titanium(IV) chloride precursor) in aqueous-alcoholic media; TiO_2 samples 11 and 15 (titanium(IV) oxysulfate precursor) in aqueous medium

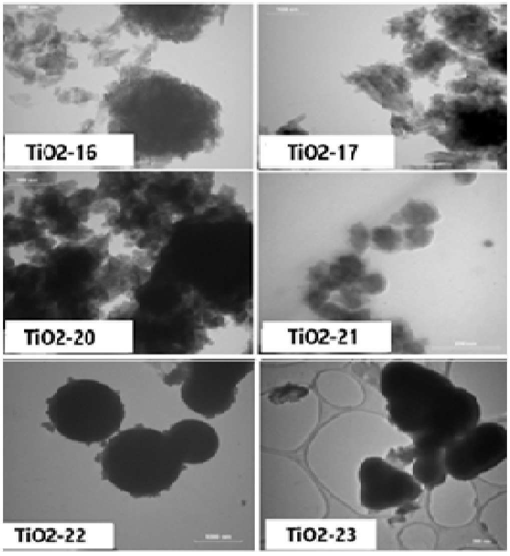


Fig. 4. TEM images: TiO_2 samples 16, 17 and 20-22 (titanium(III) chloride precursor) and TiO_2 sample 23 (titanium(III) sulfate precursor) in aqueous medium

The use of the same precursor (titanium(IV) chloride) in aqueous and aqueous-alcoholic media results in larger-sized crystal-like particles (Fig. 3, TiO_2 samples 6-9). In this case, formation of agglomerates is not observed and, as can be seen from the above images, TiO_2 samples 6 and 7 have a spherical shape of particles with an average size of 20–30 nm, and TiO_2 samples 8 and 9 are characterized by an elongated shape of particles with a size of 40–50 nm. The change in a particle shape from spherical to elongated can be explained by the usage of higher molecular weight alcohols, which create an additional steric effect. TiO_2 samples 11 and 15 (TiO_2 samples 10 and 12-14 have similar images) obtained from titanium(IV) oxysulfate in the aqueous medium differ sharply from those described above. As can be seen from TEM images (Fig. 4, TiO_2 samples 11 and 15), their structure has a spongy shape consisting of very small particles. This is confirmed by X-ray diffraction analysis, which shows that TiO_2 powders obtained from titanium(IV) oxysulfate in the aqueous medium revealed the smallest crystallite sizes among all obtained TiO_2 samples.

Presented in Fig. 4 TEM images of TiO_2 samples 16, 17 and 20-22 obtained from titanium(III) chloride in the aqueous medium indicate different morphology and structure of the obtained TiO_2 particles. TiO_2 samples 16 and 17, synthesized by a low-temperature hydrolysis, are characterized by a globular structure, which is formed mainly of small crystalline particles. The globules themselves are 100–250 nm in size and are surrounded by separate rod-like TiO_2 particles, the average size of which is ~15 nm in width and 50 nm in length. TEM images for TiO_2 samples 18 and 19 are similar. TEM image of TiO_2 sample 20 indicates the formation of globules, which are combined into even larger amorphous agglomerates of size 800–1000 nm. The average size of globules for this sample is in the range of 250–500 nm. The amorphous composition of conglomerates is also confirmed by the XRD data of this sample, which is logical, since the sample has been obtained as a result of precipitation with the ammonia solution.

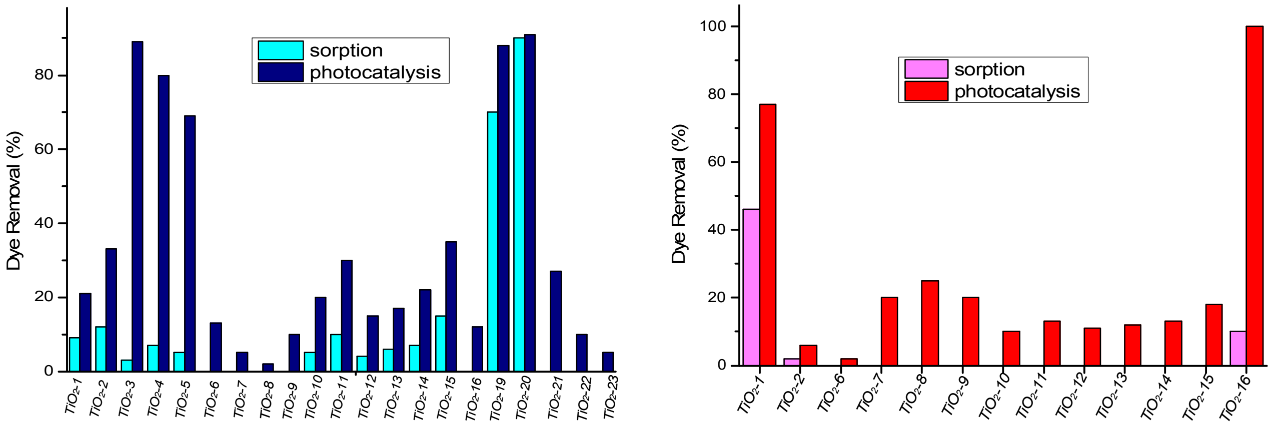
From the TEM image of TiO_2 sample 21 it is noticeable that the aggregates have a spherical shape with an average aggregate size of 30 to 70 nm. This sample was obtained by a low-temperature hydrolysis in the presence of fluorine ions. Therefore, the addition of fluoride ions promotes the formation of more spherical particles and aggregates than TiO_2 samples 16-19. As can be seen from the TEM image of TiO_2 sample 22, which was synthesized in the presence of sulfate ions, the sample has the form of spheres up to 1 μm in diameter. According to the literature [38], the formation of balls occurs through the adsorption of sulfate ions on TiO_2 aggregates. TiO_2 sample 23 was also obtained by the low-temperature hydrolysis in aqueous medium of titanium(III) sulfate precursor. In this case, large globular agglomerates were formed due to the use of the sulfate precursor.

Therefore, the type of precursor, synthesis parameters and reaction medium have a significant effect on the morphology and size of titanium(IV) oxide particles and aggregates. Additional studies of the obtained titanium(IV) oxide powders, such as surface chemistry, structural-sorption characteristics, and sorption-photocatalytic properties, are required to select TiO_2 precursor.

3.3. Sorption and Photocatalytic Activity

The sorption and photocatalytic activity of the synthesized TiO_2 samples towards dye solutions of both cationic (Methylene blue) and anionic (Congo red) nature are demonstrated in Fig. 5. As can be observed from the data on the sorption properties of TiO_2 samples to cationic dye Methylene blue, *TiO_2-19* and *TiO_2-20* samples have the highest sorption activity (70 % and 90 %, respectively). This fact is explained by absolute for *TiO_2-20* and partial for *TiO_2-19* amorphous nature of these samples (TiO_2 sample 20 was obtained by the precipitation with the ammonia solution and TiO_2 sample 19 by the post-precipitation with the ammonia solution after hydrolysis). The remaining samples show either little or no sorption activity.

Photocatalytic properties of TiO_2 samples are much better than the sorption ones and they inherent to all samples. It can be seen that there is the correlation between sorption and photocatalytic properties: TiO_2 samples with higher sorption properties generally have higer photocatalytic activity, which is due first of all to the specific surface area. There are some exceptions, such as TiO_2 sample 2 that is probably related to the surface properties of this sample. It should also be noted that TiO_2 sample 20 does not have photocatalytic properties; its efficiency is due to the high sorption characteristics inherent in the hydrated precipitates of metal oxides. TiO_2 samples which were obtained by Synthesis 3 have the highest photocatalytic activity to Methylene blue. It should be noted that TiO_2-P25 commercial sample (Evonik Industries AG, Germany) has sorption and photocatalytic activities of 15 % and 40 %, respectively. Sorption and photocatalytic activities of TiO_2 samples in regard to the anionic dye Congo red are slightly worse ones. Only *TiO_2-1*, *TiO_2-16* and also slightly *TiO_2-2* have the sorption activity. The best photocatalytic activity is peculiar to *TiO_2-1* and *TiO_2-16*, which are at 77% and 100 % respectively, and they are higher than for TiO_2-P25 commercial sample, the photoactivity of which is 71 %. It should be noted that for TiO_2 samples 6-9 and 10-15, the photoactivity is in accordance with their specific surface area. TiO_2 samples which are not shown in Fig. 5b have no sorption-photocatalytic activity at all in relation to anionic dyes.



a) b)

Fig. 5. Removal of Methylene blue (a) and Congo red (b) dyes by sorption and photocatalytic processes on TiO_2 samples

The observed best sorption-photocatalytic activity for almost all TiO_2 samples with respect to the cationic dye is explained by the positive charge of their surface under conditions of sorption experiments.

A significant influence of the morphology of TiO_2 particles on their sorption-photocatalytic properties was not revealed in this work. This might be caused by the effect of more significant characteristics of TiO_2 particles in this case: phase composition, surface acidity, specific surface area and its availability. Also, according to the literature, it is known [39] that only TiO_2 particles in the form of well-formed nanotubes exhibit better photocatalytic properties compared to round-shaped nanoparticles due to the better electronic transfer. In this work, despite the different structure, particles of round shape or close to round shape were obtained, and thus morphology does not have any significant effect on their properties.

4. Conclusions

Titanium(IV) oxide was obtained using the sol-gel method, the choice of which is related to clear simplicity of the synthesis and the possibility of directional regulation of physical and chemical properties of adsorbents and photocatalysts. The synthesis of TiO_2 was carried out in different variants: in some cases the precursor type was varied; hydrolysis was performed in the presence of foreign ions and in different media; additional stages were used. Characterization by X-ray diffraction, electronic spectroscopy, of TiO_2 samples has shown that the precursor type, foreign ions, reaction medium and thermal processing after hydrolysis have the significant influence on such physicochemical characteristics as phase composition, nanostructure and morphology.

It was found that all the obtained TiO_2 powders have a crystallite size in the nanoscale, with the size of crystallites in the anatase modification varying in the range of 2–5 nm, and for rutile modification it is greater than 6 nm. Heat treatment significantly increases crystallinity of the samples, while reducing the specific surface area.

It has been found that almost all TiO_2 samples demonstrate acidic character of their surface, which explains the better sorption and photocatalysis with respect to cationic dyes than to anionic ones. A weakly basic character of surface is formed when using ammonia solution during synthesis. Also, specific surface area, porosity, and surface accessibility have a significant effect on the sorption-photocatalytic properties. Comparison of the synthesized samples with the commercial sample showed the prospects of some syntesized samples that were obtained without usage of heat treatment after hydrolysis and without foreign ions in both aqueous and alcoholic media.

References

[1] Janus M., Kusiak-Nejman E., Morawski A.: Reac. Kinet. Mech. Cat., 2011, **103**, 279. https://doi.org/10.1007/s11144-011-0326-z

[2] Dontsova T., Nahirniak S., Astrelin I.: J. Nanomater., 2019, **2019**. https://doi.org/10.1155/2019/5942194

[3] Apopei P., Catrinescu C., Teodosiu C.: Appl. Catal. B- Environ., 2014, **160–161**, 374. https://doi.org/10.1016/j.apcatb.2014.05.030

[4] Shi L., Weng D.: Int. J. Environ. Sci., 2008, **20**, 1263. https://doi.org/10.1016/S1001-0742(08)62219-6

[5] Siah W., Lintang H., Shamsuddin M.: IOP Conf. Ser.: Mater. Sci. Eng., 2016, **107**, 012005. https://doi.org/10.1088/1757-899X/107/1/012005

[6] Nyamukamba P., Okoh O., Mungondori H. *et al.*: Synthetic Methods for Titanium Dioxide Nanoparticles: A Review [in:] Yang D. (Ed.), Material for a Sustainable Environment: TiO_2, IntechOpen 2018. https://doi.org/10.5772/intechopen.75425

[7] Kulkarni M., Thakur P.: Chem. Chem. Technol., 2010, **4**, 265.

[8] Sviderskyi A., Nahirniak S., Yashchenko T. *et al.*: 2018 IEEE 8th International Conference Nanomaterials: Application &

Properties (NAP), 2018, 8914913. https://doi.org/10.1109/NAP.2018.8914913

[9] Górska P., Zaleska A., Kowalska E.: Appl. Catal. B-Environ., 2008, **84**, 440. https://doi.org/10.1016/j.apcatb.2008.04.028

[10] Randorna C., Irvine J.: J. Mater. Chem., 2010, **20**, 8700. https://doi.org/10.1039/C0JM01370F

[11] Catauro M., Tranquillo E., Dal-Poggetto G. *et al.*: Materials, 2018, **11**, 2364. https://doi.org/10.3390/ma11122364

[12] Buraso W., Lachom V., Siriya P. *et al.*: Mater. Res. Express, 2018, **5**, 115003. https://doi.org/10.1088/2053-1591/aadbf0

[13] Kutuzova A., Dontsova T.: Proceedings of the 2018 IEEE 8 the International Conference on Nanomaterials: Application & Properties (NAP), 2018, 8914747. https://doi.org/10.1109/NAP.2018.8914747

[14] Abisharani J., Devikala S., Dinesh Kumar R. *et al.*: Mater. Today Proceedings, 2019, **14**, 302. https://doi.org/10.1016/j.matpr.2019.04.151

[15] Hu H., Lina Y., Hu Y.: Chem. Eng., 2019, **375**, 122029. https://doi.org/10.1016/j.cej.2019.122029

[16] Kutuzova A., Dontsova T.: Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Application & Properties (NAP), 2017, 01NNPT02. https://doi.org/10.1109/NAP.2017.8190182

[17] Awad N., Edwards S., Morsi Y.: Mater. Sci. Eng. C, 2017, **76**, 1401. https://doi.org/10.1016/j.msec.2017.02.150

[18] Wang Y., He Y., Lai Q.: J. Environ. Sci., 2014, **26**, 2139. https://doi.org/10.1016/j.jes.2014.09.023

[19] Akpan U., Hameed B.: Appl. Catal. A-Gen., 2010, **375**, 1. https://doi.org/10.1016/j.apcata.2009.12.023

[20] Lee H., Song M., Jurng J.: Powder Technol., 2011, **214**, 64. https://doi.org/10.1016/j.powtec.2011.07.036

[21] Mamaghani A., Haghighat F., Lee C.-S.: Chemosphere, 2019, **219**, 804. https://doi.org/10.1016/j.chemosphere.2018.12.029

[22] Arconada N., Durán A., Suárez S. *et al.*: Appl. Catal. B-Environ., 2009, **86**, 1. https://doi.org/10.1016/j.apcatb.2008.07.021

[23] Teng H., Xu S., Wang J.: Rare Metal Mat. Eng., 2014, **43**, 2326. https://doi.org/10.1016/S1875-5372(14)60163-6

[24] Sathiyan K., Bar-Ziv R., Mendelson O. *et al.*: Mater. Res. Bull., 2020, **126**, 110842. https://doi.org/10.1016/j.materresbull.2020.110842

[25] Rathore N., Kulshreshtha A., Shukla R.: Physica B, 2020, **582**, 411969. https://doi.org/10.1016/j.physb.2019.411969

[26] Wang Q., Kwona S.-H., Hui K. *et al.*: Vacuum, 2013, **89**, 90. https://doi.org/10.1016/j.vacuum.2011.11.020

[27] Shimizua T., Fujibayashia S., Yamaguchi S. *et al.*: Acta Biomater., 2016, **35**, 305. https://doi.org/10.1016/j.actbio.2016.02.007

[28] Cimieri I., Poelman H., Ryckaert J. *et al.*: J Photoch Photobio A, 2013, **263**, 1. https://doi.org/10.1016/j.jphotochem.2013.04.025

[29] Kutuzova A., Dontsova T.: Appl. Nanosci., 2019, **9**, 873. https://doi.org/10.1007/s13204-018-0754-4

[30] Mutuma B., Shao G., Kim W. *et al.*: J. Colloid Interf. Sci., 2015, **442**, 1. https://doi.org/10.1016/j.jcis.2014.11.060

[31] Habibi S., Jamshidi M.: Mater. Sci. Semicond. Process., 2020, **109**, 104927. https://doi.org/10.1016/j.mssp.2020.104927

[32] Henderson M.: Surf. Sci. Rep. 2011, **66**, 185. https://doi.org/10.1016/j.surfrep.2011.01.001

[33] Elsellami L., Dappozze F., Fessi N. *et al.*: Process Saf. Environ., 2018, **113**, 109. https://doi.org/10.1016/j.psep.2017.09.006

[34] Leyva-Porras C., Toxqui-Teran A., Vega-Becerra O. *et al.*: J. Alloy Compd., 2015, **647**, 627. https://doi.org/10.1016/j.jallcom.2015.06.041

[35] Pazokifard S., Farrokhpay S., Mirabedini M. *et al.*: Prog. Org. Coat., 2015, **87**, 36. https://doi.org/10.1016/j.porgcoat.2015.04.021

[36] Dontsova T., Yanushevskaya E., Nahirniak S. *et al.*: J. Nanomater., 2018, **2018**. https://doi.org/10.1155/2018/6573016

[37] Dontsova T., Ivanenko I., Astrelin I.: Springer Proc. Phys., 2015, **167**, 275. https://doi.org/10.1007/978-3-319-18543-9_19

[38] Hamal D., Klabunde K.: J. Colloid Interf. Sci., 2007, **311**, 514. https://doi.org/10.1016/j.jcis.2007.03.001

[39] Lee K., Mazare A., Schmuki P.: Chem. Rev., 2014, **114**, 9385. https://doi.org/10.1021/cr500061m

Received: April 22, 2020 / Revised: June 08, 2020 / Accepted: October 01, 2020

ХАРАКТЕРИСТИКА І ВЛАСТИВОСТІ ТИТАНУ(IV) ОКСИДУ, СИНТЕЗОВАНОГО РІЗНИМИ МЕТОДАМИ

Анотація. *Вивчено вплив типу прекурсорів та умов золь-гель синтезу* TiO_2 *на його властивості. За допомогою методів рентгенівської дифракції та електронною мікроскопіії встановлено, що всі отримані* TiO_2 *порошки мають розмір кристалітів в нанодіапазоні 2.5–17 нм. Показано, що сорбційно-фотокаталітичні властивості* TiO_2 *істотно залежать від фазового складу, кислотності поверхні, питомої поверхні та пористості. Виявлено, що аморфні* TiO_2 *мають покращені адсорбційні властивості, а кристалічні* TiO_2 *характеризуються покращеними фотокаталітичними властивостями. Визначений кислотний характер поверхні* TiO_2 *пояснює кращу в цілому сорбцію та фотокаталіз по відношенню до катіонного барвника.*

Ключові слова*: титану(IV) оксид, золь-гель метод, структурно-адсорбційні характеристики, сорбція, фотокаталіз.*