Materials Science-Poland, 32(1), 2014, pp. 71-79
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-013-0163-z

Preparation and characterization of titania powders obtained via hydrolysis of titanium tetraisopropoxide

MAGDALENA GRZEŚKOWIAK, RAFAŁ J. WRÓBEL, JOANNA GRZECHULSKA, JACEK PRZEPIÓRSKI*

West Pomeranian University of Technology, Institute of Chemical and Environment Engineering,
ul. Pułaskiego 10, 70-322 Szczecin, Poland

TiO_2 powders were prepared through the hydrolysis of titanium isopropoxide followed by calcination at temperatures of 200 °C to 600 °C. The obtained powders were characterized by N_2 adsorption-desorption and X-ray powder diffraction. The results confirmed strong dependence between specific surface area of the TiO_2 powders and both the conditions of the hydrolysis process and the calcination temperature. While calcination temperature strongly affected crystallinity of the product, no significant influence of the hydrolysis conditions on this parameter was observed. TiO_2 powders prepared at various conditions were examined as catalysts for photodegradation of Acid Red 18 in water. Photoactivities of the prepared powders were influenced by both the amount of water used to hydrolyze the TiO_2 precursor and the temperature of calcination process. TiO_2 samples calcined at 500 °C appeared to be the most active and the photocatalytic activities of the prepared materials increased along with the amount of water used for the hydrolysis process.

Keywords: *titanium dioxide; titanium tetraisopropoxide; hydrolysis; photocatalysis; azo-dye*

1. Introduction

Titanium dioxide is a very well known, well-characterized and widely researched material [1, 2]. It occurs in several polymorphic forms and anatase is the most desirable phase for photocatalytic applications [3–6]. TiO_2 has been extensively studied in many fields related to the environmental purification as a material capable of purifying air, water, and soil from organic and inorganic pollutants, viruses, bacteria, fungi, algae and cancer cells [1, 7–13]. Besides processing titanium-bearing minerals, titania can be prepared by hydrolysis and condensation reactions of titanium alkoxides. The latter manner is suitable to generate high-purity TiO_2 or titania-containing powders. Irrespective of the preparation method, titania powders commonly vary in grain size and shape, also inhomogeneous agglomerates are typically found in the bulk [14]. For that reason, much attention has been paid to development of methods suitable for obtaining monodispersed titania powders. Among other preparation techniques, controlled hydrolysis of titanium alkoxides has been recognized as quite promising for that purpose and therefore is one of the most favored [14–17]. In the specific case, the overall hydrolysis (Eq. 1) and condensation (Eq. 2) reactions are illustrated as follows [18, 19]:

$$\begin{aligned} &\mathrm{Ti[OCH(CH_3)_2]_4 + 4H_2O \rightarrow} \\ &\mathrm{\rightarrow Ti(OH)_4 + 4(CH_3)_2CHOH} \end{aligned} \qquad (1)$$

$$\mathrm{2Ti(OH)_4 \rightarrow 2TiO_2 \cdot H_2O + 3H_2O} \qquad (2)$$

Conditions of the hydrolysis process strongly affect the properties of resultant titania. Dunuwila et al. [19] found that reduced rate of the hydrolysis process results in the synthesis of TiO_2 powders revealing favorable optical transparency, porosity, and thermal stability. Khalil et al. [16, 20] reported that titania synthesized via hydrolysis of titanium (IV) isopropoxide (TTIP) and calcined at 400 °C in air for 3 h, consists of anatase phase only and the material does not contain carbon originating from the solvent or from the additives used to stimulate pH. Considerable increase in the average size of anatase with the temperature of the calcination

---

*E-mail: jacek.przepiorski@zut.edu.pl

process up to 600 °C is a known effect [21–23]. However, no special increase in the size of rutile crystallites was noticed at temperatures ranging from 600 to 800 °C [14]. Interestingly, increasing volume of water used for hydrolysis was recognized as a factor decreasing specific surface area of titania [16, 20] and affecting porosity, i.e. mesopore and micropore areas and pore volume of the anatase powder [3, 14, 24, 25]. Mean size and morphology of TiO_2 crystallites depend on the pH of the hydrolysis process. The larger crystallites of non-spherical shape were produced at higher pH while using lower pH was reflected by formation of smaller species of spherical shape [26, 27]. In addition, titania prepared at $pH = 3$ consisted of pure anatase phase only while TiO_2 obtained at basic and neutral pH were the mixtures of both anatase and rutile phases. As suggested elsewhere [3, 16, 20], a controlled addition of a base, e.g., aqueous ammonia, during the hydrolysis process may catalyze the hydrolysis of alkoxide and thus increase the rate of the reaction. On the contrary, addition of acidic agents (e.g. acetic acid) to the process was found to be significantly inhibiting the sequence of the TTIP hydrolysis.

Besides pH, the properties of TiO_2 prepared by the hydrolysis of TTIP are undoubtedly affected by a kind of solvent used for the process. For example, both n-heptane and 2-propanol, called as hydrolysis controllers, are capable of accelerating or decelerating the process [16, 20]. TiO_2 prepared in the presence of ammonia water, revealed certain content of carbon and nitrogen in its structure, dependent on a kind of organic solvent used. Contents of these elements in TiO_2 as well as specific surface area of the powders generally depend on both polarity and concentration of the solvent used [20]. In order to obtain TiO_2 of high specific surface area, a use of both polar solvent and ammonia water were recommended [16, 20].

Titanium dioxide has been considered as an attractive photocatalyst capable of degrading and mineralizing azo-dyes to carbon dioxide, water and harmless inorganic anions [5, 8, 9, 11, 28, 29]. Azo-dyes and their intermediate products were found to be toxic, carcinogenic and mutagenic to an aquatic life [30]. Significant amounts of such dyes are present in non-fixed form in effluents from the textile industry. Because common methods such as coagulation, flocculation, biological degradation, often are not enough efficient to purify wastewater containing abovementioned contaminants, heterogeneous photocatalysis using TiO_2 is proposed as an alternative for treatment [30–37]. Photocatalytic degradation of azo-dyes under TiO_2/UV system leads to the complete mineralization [35] involving holes generated during the process and hydroxyl radicals ($OH^\bullet$) [6, 16, 26, 33, 38].

In spite of large number of works dealing with photodegradation of Acid Red 18, not enough attention has been paid to the impact of the conditions of TiO_2 preparation on the photoactivity of the titania powders in this process. Therefore, we focused on studying the properties of TiO_2 prepared via hydrolysis of TTIP using various conditions in relation to photodegradation of the model contaminant. Hence, the impacts of amount of water, and calcination temperature on phase composition, specific surface area, average crystallite size of obtained titanias were elucidated. In addition, photocatalytic activity of the obtained TiO_2 powders towards Acid Red 18 was investigated and discussed.

2. Experimental

2.1. Preparation of TiO_2 powders

The TiO_2 powders were prepared through hydrolysis and condensation process at room temperature. A mixture of 10 ml of titanium (IV) isopropoxide (97 % pure liquid – Sigma-Aldrich Chemie, Germany) and 30 ml of 2-propanol (99.7 % purity – Chempur, Poland) was slowly dropped into a beaker containing either 50, 150 or 250 ml of distilled water, continuously agitated using magnetic stirrer. Addition of the alcohol to TTIP prior to dropping the water was used to slow down the hydrolysis process, which is normally abrupt and completes within few seconds [16, 28]. The white colloidal suspension obtained during the hydrolysis was vacuum filtered through the filter paper 0.45 µm, and the filter cake obtained was dried overnight at 110 °C in air. Finally, portions of the hydrated amorphous titania were subjected to 3 hours long calcinations in argon gas atmosphere at 200 °C, 300 °C, 400 °C, 500 °C, and 600 °C. Samples obtained according to the above procedure were denoted as S-x-y where x indicates the volume of water used for the hydrolysis step and y is the temperature of the calcination process.

Commercially available azo-dye Acid Red 18 (4R 100 %, supplied by The Boruta-Zachem Kolor Sp. z o.o., Poland) was used as a model chemical for photodegradation tests. The molecular structure of the dye is presented in Fig. 1.

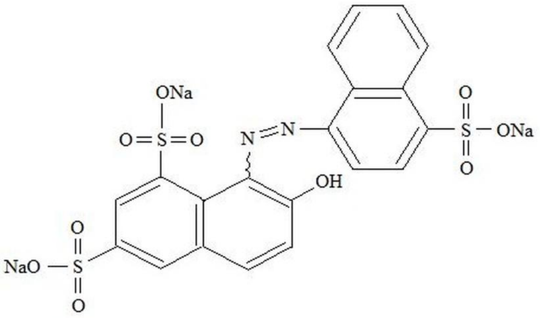


Fig. 1. The molecular structure of the Acid Red 18.

2.2. Characterization of the photocatalysts

2.2.1. X-ray diffraction measurements

X-ray diffraction (XRD) patterns were measured to determine the average sizes of titania crystallites and to estimate relative phase compositions, i.e. shares of anatase, rutile, and brookite in the prepared photocatalysts. All the XRD patterns were recorded using a diffractometer (Philips X'Pert PRO) in Bragg-Brentano configuration, operating with the Cu K_α radiation. Average crystallite sizes and phase contents were evaluated applying the Scherrer formula [39] on (101), (110) and (211) reflexes for anatase, rutile, and brookite, respectively:

$$d = K\lambda/(B-b)\cos\theta \qquad (3)$$

where: d – the average crystallite size; K – shape factor; λ – X-ray wavelength; B – full width at half maximum (FWHM) originating from both crystallite sizes and instrumental broadening; b – line width originating solely from instrumental broadening; θ – reflex position.

The shape factor used for the calculations was 0.94 and broadenings of the reflexes were assumed to originate solely from both instrumental broadenings and from the size of the crystallites. The instrumental broadening was estimated by measuring the reference silicon sample for several reflexes and interpolation for anatase (101), rutile (110) and brookite (211) positions. The percentages of each phase in the obtained titania powders were calculated using following equation 4:

$$X_R = 0.41 I_R/(0.41 I_R + 0.31 I_A + I_B) \qquad (4)$$

where: X_R – weight fraction of rutile; I_R, I_A, I_B – integral intensities of rutile (110), anatase (101), and brookite (211) peaks.

Above formula was obtained by utilization of Reference Intensity Ratio (RIR) factors collected from PDF-4+ 2012 the International Centre for Diffraction Data (ICDD) database. The cards of reference codes 01-088-1172; 01-071-1168; 01-076-1937 were used for rutile, anatase, and brookite, respectively. If no brookite was detected in a titania powder then the obtained formula was similar to that given by Inagaki [40]. Nevertheless, due to a minor difference of RIR factors used for the calculations a negligible discrepancy (0.75 vs. 0.79) can be found.

2.2.2. BET measurements

The specific surface area of the photocatalysts was calculated according to the Brunauer-Emmett-Teller (BET) model applied to nitrogen adsorption isotherms, recorded at 196 °C using Quadrasorb SI apparatus (Quantachrome Instruments, U.S.A.). Prior to the N_2 adsorption measurements all the samples were outgassed at 100 °C for 12 h applying high vacuum. The pore size distributions (PSD) were calculated from the desorption branch of N_2 adsorption/desorption isotherms applying the Barrett-Joyner-Halenda (BJH) method.

2.2.3. Photocatalytic activity

The photocatalytic decomposition tests were carried out in a quartz reactor using 0.1 g of a photocatalyst dispersed in 500 cm^3 of aqueous solution of the model compound (10 mg/dm^3). Each suspension was surrounded by three circular light bulbs (Philips'TL'-E 22W/10) stacked one on another, Fig. 2.

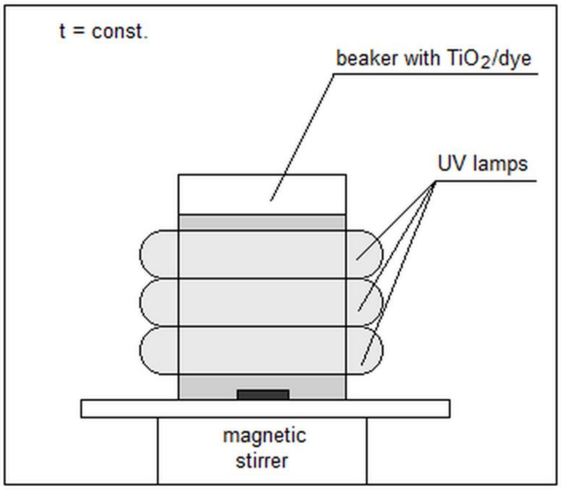


Fig. 2. Schematic drawing of the apparatus setup used for photodegradation process.

According to the supplier, the intensity of UV and VIS radiation emitted by the lamps was ca. 90 W/m^2 and 60 W/m^2, respectively. The emission spectrum of the bulbs used, measured using the LB 901 radiation meter equipped with the PD 204AB (Macam Photometrics Ltd., Scotland) and CM3 (Kipp & Zonen, Holland) external sensors, is shown in Fig. 3.

The photocatalytic processes were conducted in an incubator operating at a constant temperature of 20 °C. The suspension of TiO_2 in a solution was maintained by magnetic stirring and was irradiated for 180 min, which in most cases allowed the complete decomposition of the azo-dye. In order to achieve the adsorption equilibrium, prior to the irradiation, all the suspensions were stirred for 30 min in the dark.

The concentrations of Acid Red 18 in the tested suspensions were monitored spectrophotometrically using analytical wavelength of 507 nm.

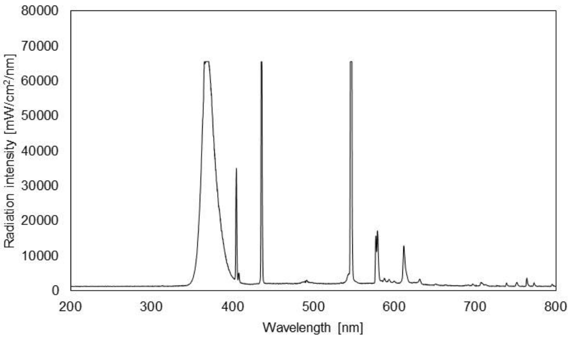


Fig. 3. The emission spectrum of the circle bulbs used in this study.

Before directing to the UV-VIS apparatus, small portions of the suspensions were filtered through a 0.45 μm membrane filter.

The Acid Red 18 removal degree was calculated from the following equation:

$$DR = (C_0 - C_t)/C_0 \cdot 100 \ [\%] \qquad (5)$$

where DR is the removal degree [%], C_0 [mg/l] is an initial concentration of the azo-dye (after the 30 min stirring in the dark), and C_t [mg/l] is a concentration of the azo-dye measured after irradiation for a specified time.

3. Results and discussion

The parameters of the preparation processes and the characteristics of the titania studied in this work are summarized in Table 1.

As clearly shown, the properties of the attained samples are dependent on the calcination temperature and on the amount of water used for the hydrolysis step.

3.1. Nitrogen adsorption at 77 K

Nitrogen adsorption-desorption isotherms measured at 77 K for TiO_2 samples are shown in Fig. 5. The amounts of nitrogen adsorbed on the prepared samples vary and depend on both temperature applied during the calcination (Fig. 4a) and amount of water used for the hydrolysis process (Fig. 4b). These observations are reflected by the appropriate data presented in Table 1. As a rule, nitrogen

Table 1. Preparation conditions and characteristics of TiO_2 samples used as test materials.

Name of sample	Amount of water [ml]	Calcination temperature [°C]	BET surface (S_{BET}) [m^2/g]	Amorphous phase content [%]	Anatase crystallite size d_{101} [nm]	Anatase content [%]	Rutile crystallite size d_{110} [nm]	Rutile content [%]	Brookite crystallite size d_{211} [nm]	Brookite content [%]
S-250-0	250	–	351.3	35	5.9	34	3.3	6	4.1	25
S-250-200		200	269.7	14	6.6	58	5.9	1	4.6	27
S-250-300		300	181.4	12	7.5	63	7.1	3	7.2	22
S-250-400		400	152.0	8	8.7	65	11	2	8.2	25
S-250-500		500	100.7	4	16	70	14	1	14	25
S-250-600		600	10.9	2	58	38	306	60	0	0
S-150-0	150	–	359.4	42	5.7	38	3.6	3	4.5	17
S-150-500		500	61.4	0	23.5	79	27.3	1	14.6	20
S-50-0	50	–	321.7	45	5.8	35	2.7	5	4.5	15
S-50-500		500	38.3	8	28.3	82	71.5	3	14.1	7

adsorption decreases along with the temperature used for calcination and BET specific surface area values follow the same trend. Thus, while N_2-BET area determined for uncalcined sample exceeds 350 m^2/g, this parameter calculated for titania heated at the highest temperature of 600 °C reaches only ca. 11 m^2/g. All the isotherms reveal presence of the hysteresis loop, indicating capillary condensation in mesopores [41]. The initial parts of the isotherms follow the same path as the type II isotherm, which is considered to be due to adsorption on the mesopore walls.

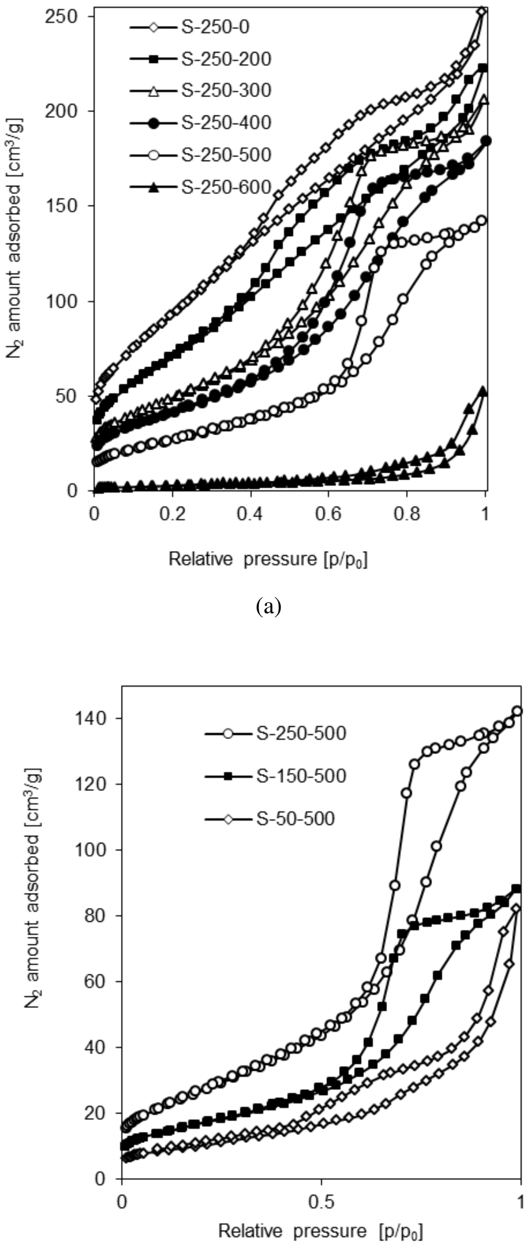
Adsorption of nitrogen is also greatly influenced by the conditions of the hydrolysis step and generally decreases with the amount of water used for preparation (Table 1, Fig. 4b). Even though the data for samples calcined at 500 °C are only shown, analogous tendencies have been observed for the samples subjected to calcination at other temperatures.

The pore size distributions (PSD) calculated from the measured isotherms are shown in Fig. 6. All the presented PSD curves confirm the increased volume of mesopores ranging in diameter from 2 to ca. 10 nm. Among S-250-series samples, location and value of PSD maxima remains in relationship with calcination temperature. Thus, the uncalcined material reveals relatively high volume of the narrowest mesopores and the maxima in PSD curves tend to shift to higher values with the calcination temperature. Very low volume in mesopore range observed for S-250-600 sample confirms destructive effect of temperature on this kind of porosity.

PSDs are also affected by the amount of water used for the hydrolysis of TTIP (Fig. 5b) and evidently show that using larger amounts of water results in shifting PSD maxima to higher values and makes the obtained titania more abundant in mesopores.

3.2. XRD studies

The X-ray diffraction patterns (not shown) were measured for the materials prepared using (a) 250 ml of water for the hydrolysis step and calcined at various temperatures and (b) various quantities of water for the hydrolysis at a constant (500 °C) calcination temperature. All the recorded patterns confirm the presence of anatase in the obtained titania and intensities of characteristic reflexes typically increase and become well defined with calcination temperature. Besides that, increasing calcination temperature entails considerable growth in size of anatase crystallites, from ca. 6 nm to nearly 60 nm. Because of relatively high content and low crystallite size, calcination at 500 °C can be considered as favorable for formation of anatase ($2\theta = 25.4°$). Further increase in calcination temperature boosts formation of rutile and increase in crystallite size of both anatase and rutile. Such thermally promoted crystallite growth was also reported by others [14]. In contrast to the material subjected to calcination at 600 °C, all the other samples con-

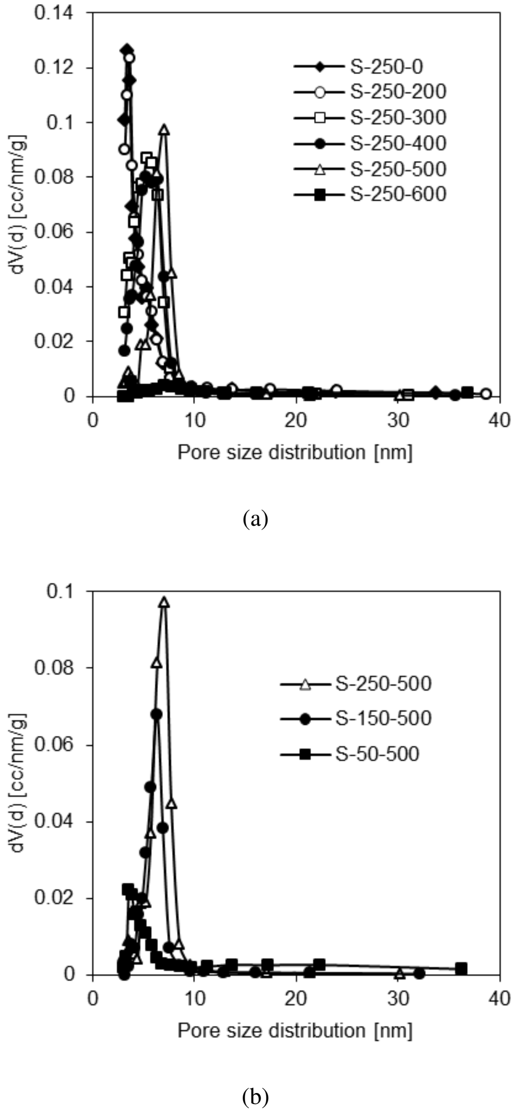


(a)

(b)

Fig. 5. The changes in concentration of Acid Red 18 during exposing to UV-VIS irradiation (a) in a presence of S-250 series samples calcined at various temperatures, (b) using test materials S-250, S-150 and S-50 and calcined at 500 °C.

tained brookite. Similar to the diffraction peaks of anatase, intensities of the reflexes corresponding to brookite tended to increase with the temperature of calcination.



(a)

(b)

Fig. 6. Pore size distribution (by BJH method) for: (a) samples from S-250 series as obtained and calcined at various temperatures, (b) calcined at 500 °C and prepared using different amounts of water.

Besides the mean crystallite size, increasing calcination temperature to 600 °C causes a distinct increase, from few to 60 %, in relative rutile phase content in the product. At the same time, the contents of two other phases evidently decrease. This finding clearly confirms transformation of both anatase and brookite to rutile. Taking into account the related results reported by others [3, 5, 8, 14, 21, 25, 42], such transition may occur within a wide range of temperatures, 400 – 1200 °C.

It should be noticed (Table 1) that obtained TiO_2 samples reveal a certain content of an amorphous phase that steadily decreases with calcination temperature. Because calcination temperature i) does not substantially affect the content of brookite and mean size of anatase crystallites, and ii) enhances formation of anatase, the decrease in share of amorphous phase must be due to formation of smaller crystallites of anatase.

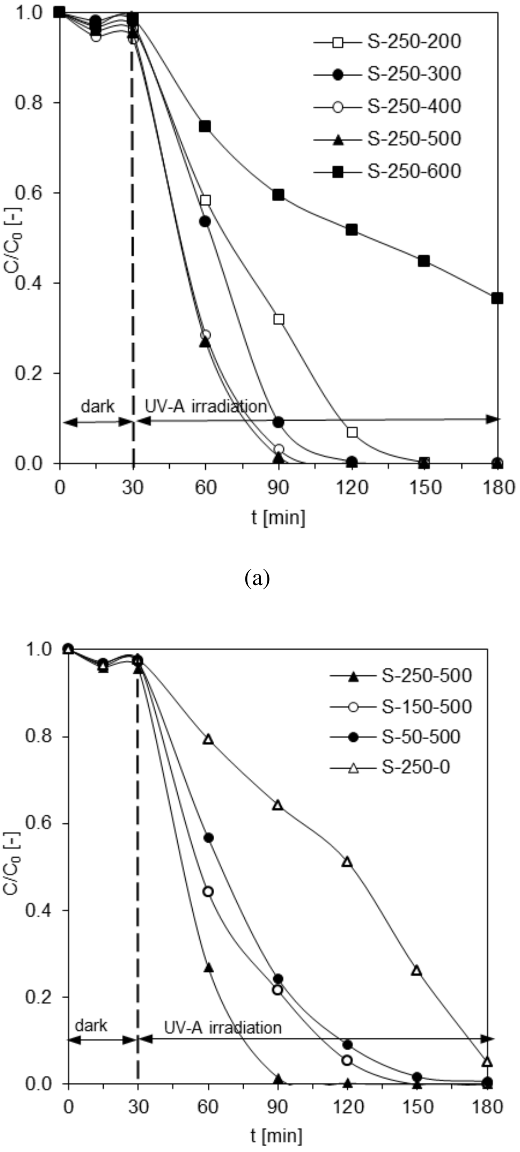
As it can be evidently seen on the XRD patterns, the phase composition of obtained titanias has also been influenced by the amount of water used for the hydrolysis of TTIP. All the samples calcined at 500 °C reveal the presence of well-formed anatase phase. As the amount of water used for the process is reduced, formation of anatase is facilitated. This is confirmed by sharper and more intense anatase peaks ($2\theta = 25.4°$) on XRD patterns measured for the samples prepared with the lower amounts of water. Opposite trend can be observed for brookite and the content of both amorphous phase and rutile remains practically unchanged with varying amount of water used for the hydrolysis.

In general, using lower quantities of water results in formation of larger TiO_2 crystallites. This concerns all phases and is particularly noticeable for rutile whereas the content of this form of titania does not depend on the amount of water used. It should be also pointed that the content of anatase phase noticeably increases with a decrease in the amount of water while the content of brookite phase considerably, by 18 %, decreases.

3.3. Photocatalytic degradation of the model contaminant

The changes in the concentration of the Acid Red 18 in water, presented in Fig. 7, reliably confirm capability of the obtained titanias to degrade the dye while irradiated with the UV-VIS light.

As clearly demonstrated in Fig. 6a, TiO_2 calcined at 400 – 500 °C performs the most efficiently during photocatalytic removal of the dye but further increase in calcination temperature results in obtaining titania of lower efficiency in this process. However, reduced, less pronounced photocatalytic action can be observed for materials calcined below 400 °C which were not subjected to any thermal treatment after the hydrolysis step, Fig. 6b.



(a)

(b)

Fig. 7. The changes in concentration of Acid Red 18 during exposing to UV-VIS irradiation (a) in a presence of S-250 series samples calcined at various temperatures, (b) using test materials S-250, S-150 and S-50 and calcined at 500 °C.

In view of the data listed in Table 1, the observed trend appears to be complex, and may be considered as resulting from either favorable content of anatase phase or mean size of brookite crystallites. Because (a) the latter is photocatalytically inactive [1, 43] and (b) brookite crystallite sizes found in the photocatalysts prepared at 500 °C with the use of different amounts of water are comparable, the content of anatase in the prepared titanias was assumed to be the key factor affecting photodecomposition of AR 18. One may notice that the activity of TiO_2 calcined up to 500 °C increases along with decreasing the size of anatase crystallites and specific surface areas. However, calcination carried out at 600 °C produces material consisting of relatively large crystallites and the smallest BET surface area, exhibiting very poor photocatalytic performance. It is known [28] that smaller TiO_2 particles, revealing higher specific surface areas, are able to catalyze degradation of organics more efficiently than the bigger ones, of lower porosity. However, in some cases this tendency can be concealed by the effect of a stronger factor such as crystalline structure. Furthermore, degradation rate was reported to even decrease with increasing specific surface area of TiO_2 powders [44]. For above reasons some authors do not consider specific surface area of TiO_2 as a key factor affecting degradation rate. In addition, too small TiO_2 particles can deteriorate penetration of UV light into reacting suspension and thus certain decrease in the efficiency of photodegradation process can be observed.

In our work, decomposition of AR 18 in presence of S-250-500 proceeded more efficiently than while S-250-600 of the highest crystallinity was used. This seems to be due to the favorable combination of the high, 70 % content of anatase of relatively small crystallites size. In the case of the sample calcined at 600 °C, the content of anatase phase was only 38 %. In addition, mean size of TiO_2 (anatase and rutile) crystallites was much larger compared to these in the sample calcined at 500 °C. Because anatase surface can adsorb more radicals than rutile, photoactivity of the first one is superior. However, it is known that due to electron transfers between rutile and anatase mixed-phase TiO_2 may improve kinetics of a photooxidation process [5].

As shown in Fig. 6b, the rate of AR 18 decomposition increases with increasing the amount of water used for hydrolysis of TTIP during preparations. This seems to be related to more favorable combination of mean size of anatase crystallites and anatase content in titanias prepared with use of larger quantities of water.

4. Conclusions

Even though presented results confirmed several already known dependencies, we could find some new aspects concerning the effect of preparation conditions on the properties of titania powders obtained from titanium tetraisopropoxide. These are mainly related to the hydrolysis step that affects both the size of TiO_2 crystallites (and consequently specific surface area), and phase composition of resultant materials. The results gained during the studies allowed us to present several conclusions and indications:

1. Mean sizes of anatase and rutile crystallites decrease with the amount of water used for hydrolysis step. So, hydrolysis carried out with use of low volumes of water produces titanias of low specific surface area.
2. Phase composition of titanias calcined at 500 °C can be only slightly altered by the amount of water used for hydrolysis.
3. Increasing the amount of water for hydrolysis entails shift in maxima on PSD curves to wider pores and increases mesopore volume.
4. The photocatalytic activity of TiO_2 is a complex phenomenon affected by several factors such as phase composition and crystallite size. However, no straight relationship could be confirmed.

Above findings can be taken into consideration already during planning future experiments. By controlling the preparation conditions one can obtain the titania revealing specific and desired properties.

References

[1] MACWAN D.P., DAVE P.N., CHATURVEDI S., *J. Mater. Sci.*, 46 (2011), 3669 – 3686.

[2] WANG X., SHUI M., LI R., SONG Y., *Mater. Res. Bull.*, 43 (2008), 2476 – 2484.
[3] KATOCH A., KIM H., HWANG T., KIM S.S., *J. Sol-Gel Sci. Techn.*, 61 (2012), 77 – 82.
[4] DIEBOLD U., *Surf. Sci. Rep.*, 48 (2003), 53 – 229.
[5] HANAOR D.A.H., SORRELL C.C., *J. Mater. Sci.*, 46 (2011), 855 – 874.
[6] PAN X., MA X., *Mater. Lett.*, 58 (2004), 513 – 515.
[7] GAO B., YAP P.S., LIM T.M., LIM T.-T., *Chem. Eng. J.*, 171 (2011), 1098 – 1107.
[8] ZHEREBTSOV A.D., SYUTKIN S.A., PERVUSHIN V.Y., KUZNETSOV G.F., KLESHCHEV D.G., GERMAN V.A., VIKTOROV V.V., KOLMOGORTSEV A.M., SERIKOV A.S., *Russ. J. Inorg. Chem.*+, 55 (2010), 1197 – 1201.
[9] CARP O., HUISMAN C.L., RELLER A., *Prog. Solid State Ch.*, 32 (2004), 33 – 177.
[10] DANESHVAR N., RASOULIFARD M.H., KHATAEE A.R., HOSSEINZADEH F., *J. Hazard. Mater.*, 143 (2007), 95 – 101.
[11] FUJISHIMA A., RAO T.N., TRYK D.A., *J. Photoch. Photobio. C*, 1 (2000), 1 – 21.
[12] MAHMOODI N.M., ARAMI M., LIMAEE N.Y., GHARANJIG K., NOURMOHAMMADIAN F., *Mater. Res. Bull.*, 42 (2007), 797 – 806.
[13] YANG S., TANG W., ISHIKAWA Y., FENG Q., *Mater. Res. Bull.*, 46 (2011), 531 – 537.
[14] MAHSHID S., ASKARI M., GHAMSARI S.M., *J. Mater. Process. Tech.*, 189 (2007), 296 – 300.
[15] GABLENZ S., VÖLTZKE D., ABICHT H.-P., NEUMANN-ZDRALEK J., *J. Mater. Sci. Lett.*, 17 (1998), 537 – 539.
[16] KHALIL K.M.S., ZAKI M.I., *Powder Technol.*, 92 (1997), 233 – 239.
[17] SU C., HONG B.-Y., TSENG C.-M., *Catal. Today*, 96 (2004), 119 – 126.
[18] BISCHOFF B.L., ANDERSON M.A., *Chem. Mater.*, 7 (1995), 1772 – 1778.
[19] DUNUWILA D.D., GAGLIARDI C.D., BERGLUND K.A., *Chem. Mater.*, 6 (1994), 1556 – 1562.
[20] KHALIL K.M.S., BAIRD T., ZAKI M.I., EL-SAMAHY A.A., AWAD A.M., *Colloid Surface A*, 13 (1998), 231 – 232.
[21] KIM J.Y., JUNG H.S., NO J.H., KIM J.-R., HONG K.S., *J. Electroceram.*, 16 (2006), 447 – 451.
[22] KUBELKA P., *J. Opt. Soc. Am.*, 38 (1948), 448 – 456.
[23] LV K., YU J., DENG K., LI X., LI M., *J. Phys. Chem. Solids*, 71 (2010), 519 – 522.
[24] KARAMI A., *J. Iran. Chem. Soc.*, 7 (2010), 154 – 160.
[25] MAHSHID S., ASKARI M., GHAMSARI S.M., AFSHAR N., LAHUTI S., *J. Alloy. Compd.*, 478 (2009), 586 – 587.
[26] AGAFONOV A.V., VINOGRADOV A.V., *J. Sol-Gel Sci. Techn.*, 49 (2009), 180 – 185.
[27] HORVAT B., REČNIK A., DRAŽIĆ G., *J. Cryst. Growth*, 347 (2012), 19 – 24.
[28] HAFIZAH N., SOPYAN I., *Int. J. Photoenergy*, (2009) article ID 962783, DOI: 10.1155/2009/962783.
[29] QOURZAL S., ASSABBANE A., AIT-ICHOU Y., *J. Photoch. Photobio. A*, 163 (2004), 317 – 321.
[30] SHOKOOHI R., VATANPOOR V., ZARRABI M., VATANI A., *E-J. Chem.*, 7 (2010), 65 – 72.
[31] BUBACZ K., CHOINA J., DOLAT D., MORAWSKI A.W., *Pol. J. Environ. Stud.*, 19 (2010), 685 – 691.
[32] SURESH S., SUGUMAR R.W., MAIYALAGAN T., *Asian J. Chem.*, 23 (2011), 219 – 224.
[33] GRZECHULSKA-DAMSZEL J., TOMASZEWSKA M., MORAWSKI A.W., *Desalination*, 241 (2009), 118 – 126.
[34] WANG J.F., ZHAO J.H., LIU X.X., ZHANG S.H., WEI D.Y., HAN L., *Appl. Mech. Mater.*, 189 (2012), 52 – 57.
[35] MOZIA S., TOMASZEWSKA M., MORAWSKI A.W., *Dyes Pigments*, 75 (2007), 60 – 66.
[36] MALEKI A., ZANDSALIMI Y., SHAHMORADI B., REZAIE R., PORDEL M.A., *Sci. J. Kurdistan Univ. Med. Sci.*, 16 (2011), 101 – 108.
[37] TRYBA B., *J. Adv. Oxid. Technol.*, 10 (2007), 267 – 272.
[38] SOUTSAS K., KARAYANNIS V., POULIOS I., RIGA A., NTAMPEGLIOTIS K., SPILIOTIS X., PAPAPOLYMEROU G., *Desalination*, 250 (2010), 345 – 350.
[39] PATTERSON A.L., *Phys. Rev.*, 56 (1939), 978 – 982.
[40] INAGAKI M., NONAKA R., TRYBA B., MORAWSKI A.W., *Chemosphere*, 64 (2006), 437 – 445.
[41] GREGG S.J., *Stud. Surf. Sci. Catal.*, 10 (1982), 153 – 164.
[42] HU Y., TSAI H.-L., HUANG C.-L., *J. Eur. Ceram. Soc.*, 23 (2003), 691 – 696.
[43] ZHANG L., MENENDEZ-FLORES V.-M., MURAKAMI N., OHNO T., *Appl. Surf. Sci.*, 258 (2012), 5803 – 5809.
[44] KAPINUS E.I., KHALYAVKA T.A., SHIMANOVSKAYA V.V., VIKTOROVA T.I., STRELKO V.V., *Int. J. Photoenergy*, 5 (2003), 159 – 166.

Received 2013-09-30
Accepted 2014-01-09