

Effect of calcination temperature on photocatalytic activity of TiO₂. Photodecomposition of mono- and polyazo dyes in water

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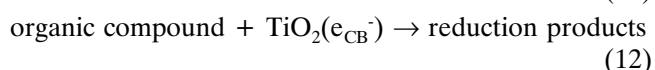
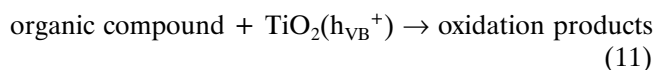
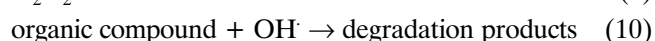
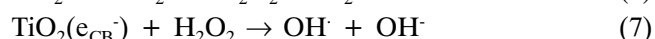
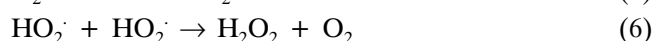
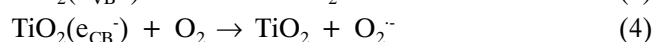
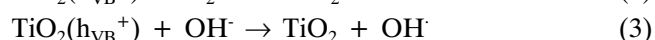
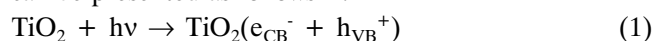
The presented studies have focused on the influence of TiO₂ properties, such as crystalline phase, crystallite size and surface area, on the effectiveness of degradation of azo dyes in water under UV irradiation. Two monoazo dyes: Acid Red 18 (AR18, C₂₀H₁₁N₂Na₃O₁₀S₃) and Acid Yellow 36 (AY36, C₁₈H₁₄N₃NaO₃S), and one polyazo dye Direct Green 99 (DG99, C₄₄H₂₈N₁₂Na₄O₁₄S₄) were applied as model compounds. The photocatalysts were prepared from a crude titanium dioxide obtained directly from the production line (sulfate technology) at the Chemical Factory „Police” (Poland). The crude TiO₂ was calcinated in air for 1 – 4h at the temperatures ranging from 600 to 800°C. The BET specific surface area of TiO₂ decreased gradually with increasing the calcination temperature. The crude TiO₂ exhibited specific surface area of 277 m²/g. In case of the catalysts heated at 600, 700 and 800°C the BET surface area amounted to 62.3 – 53.3, 33.4 – 26.8 and 8.9 – 8.3 m²/g, for the calcination time of 1 – 4h, respectively. The crystallite size of anatase increased with increasing heat treatment temperature and ranged from 19 to 53 nm, for the temperatures of 600 – 800°C, respectively. The catalysts annealed at 600 and 700°C contained primarily anatase phase (94 – 97%), whereas the photocatalysts heated at 800°C were composed mainly of rutile (97 – 99%). The highest effectiveness of azo dyes degradation was obtained in case of the photocatalyst calcinated for 1h at 700°C. The photocatalyst was composed mainly of anatase (97%) with crystallite size of 27 nm. The most effectively photodegraded was AR18, having the molecular weight of 640.4 g/mol. The most difficult to degrade was AY36 exhibiting the lowest molecular weight from all the dyes used (375.4 g/mol).

Keywords: photocatalysis, titanium dioxide, TiO₂, anatase, rutile, crystallite size, azo dye.

INTRODUCTION

Textile industries generate wastewaters that contain considerable amounts of non-fixed dyes, especially of azo dyes, and a huge amount of inorganic salts¹. The most common treatment methods, including adsorption, biological degradation, chlorination or ozonation, are not efficient enough to remove these compounds from the treated water streams. In view of these, „Advanced Oxidation Processes” (AOP) seem to be a very promising way of treatment of wastewaters from textile industry. Among these processes, heterogeneous photocatalysis was found as very attractive technology leading to the total mineralization of numerous organic pollutants. The most often used photocatalyst due to its considerable photocatalytic activity, high stability, non-environmental impact and low cost is TiO₂.

Photocatalytic degradation of azo dyes under UV irradiation in the presence of TiO₂ has been investigated by numerous researchers^{2–13}. In brief, the mechanism of this process can be presented as follows^{3, 4}:



When a semiconductor absorbs a photon of energy that is equal to or greater than its band gap width ($h\nu \geq E_G$), an electron (e^-) may be promoted from the valence band (VB) to the conduction band (CB) thus generating an electron vacancy – „hole” (h^+) (eq. 1). The electron and the hole can migrate to the catalyst surface where they participate in redox reactions (eqs 2 – 6) with different species adsorbed on catalyst surface. Holes can react with surface-bond H₂O or OH⁻ to produce the hydroxyl radical OH[·] (eqs 2 – 3), whereas electrons during reaction with oxygen can generate superoxide radical anion O₂^{-·} (eq. 4). Hydroxyl radicals can be also formed following the path represented by reactions (5) – (9). The hydroxyl radicals (OH[·]) are supposed to be the primary oxidizing species in the photocatalytic oxidation processes (eq. 10)⁵. An example of oxidation of organic compounds by holes is so-called photo – Kolbe reaction, in which holes react directly with carboxylic acids generating CO₂¹⁴. The role of reductive pathways (eq. 12) in heterogeneous photocatalysis is of a minor significance than oxidation⁴.

The photoactivity of TiO₂ depends on its physico-chemical parameters, such as crystal structure, crystallite size, surface area etc.^{15, 16}. From the three different allotropic forms of TiO₂ that occur in nature (anatase, rutile and brookite) the most photoactive one is anatase. The physico-chemical properties of TiO₂ depend on the preparation method (e.g. sol-gel, chemical precipitation, microemulsion, etc.), post-treatment conditions (such as calcination tem-

Table 1. Preparation conditions and properties of photocatalysts

sample	Heat treatment temperature [°C]	Time of heat treatment [h]	BET surface area [m ² /g]	Anatase to rutile ratio (A:R)	Crystallite size of anatase [nm]
A-600-1h	600	1	62.3	9.7:0.3	19
A-600-2h	600	2	56.5	9.7:0.3	20
A-600-3h	600	3	53.3	9.7:0.3	21
A-600-4h	600	4	53.3	9.7:0.3	21
A-700-1h	700	1	33.4	9.7:0.3	27
A-700-2h	700	2	30.8	9.4:0.6	28
A-700-3h	700	3	27.9	9.4:0.6	30
A-700-4h	700	4	26.8	9.4:0.6	30
A-800-1h	800	1	8.9	0.3:9.7	46
A-800-2h	800	2	8.6	0.1:9.9	51
A-800-3h	800	3	8.3	0.1:9.9	53

perature and time), incorporation of dopants into the titania structure and many other factors. Therefore, extensive investigations concerning preparation and improvement of photocatalytic properties of TiO₂ have been conducted recently.

The aim of the presented work was the investigation on the effect of TiO₂ properties, such as crystalline phase, crystallite size and surface area, on the effectiveness of degradation of azo dyes in water. Three azo-dyes having different structures: monoazo dyes Acid Red 18 and Acid Yellow 36, and polyazo dye Direct Green 99 were applied as model compounds. TiO₂ photocatalysts were prepared by heat treatment of crude titania exhibiting very low crystallinity under different calcination conditions (temperature and time).

EXPERIMENTAL

The photocatalysts used in this study were prepared from a crude TiO₂ obtained directly from the production line (sulfate technology) at the Chemical Factory „Police” (Poland). The crude TiO₂ exhibited the BET specific surface area of 277 m²/g and showed very broad and weak diffraction lines of anatase (crystallite size: 9 nm). The crude TiO₂ was calcinated in air (50 mL/min) for 1 – 4h at different temperatures ranging from 600 to 800°C. Heating rate was 10°C/min. The preparation conditions are presented in Table 1.

The photocatalysts were characterized by N₂ adsorption measurement at 77 K (Autosorb 3, Quantachrome, USA) and XRD analysis (Rigaku RINT-2000 diffractometer with CuK α radiation ($\lambda=1.54056$ Å from an 18 kV source)). TiO₂ anatase over rutile ratio was calculated from¹⁷:

$$\text{Anatase content } A = 1/(1+1.26(I_R/I_A)) \quad (13)$$

where I_A and I_R are the diffraction intensities of the (101) anatase and (110) rutile crystalline phases at $2\theta = 25.3$ and 27.4° , respectively. The average anatase crystallite diameter D (nm) was calculated using Scherrer's equation^{17, 18}:

$$D = K\lambda/\beta\cos\theta \quad (14)$$

where $K = 0.9$ is a shape factor for spherical particles, λ is the wavelength of the incident radiation ($\lambda = 1.54056$ Å), θ is half of the diffraction angle (rad) and β is the line width at half-maximum height.

Photocatalytic decomposition of azo dyes was performed in reactors containing 0.2 L of the solution. The photocatalyst loading amounted to 0.1 g TiO₂/L. Acid Red 18 (C₂₀H₁₁N₂Na₃O₁₀S₃), Direct Green 99 (C₄₄H₂₈N₁₂Na₄O₁₄S₄) and Acid Yellow 36 (C₁₈H₁₄N₃NaO₃S) obtained from Chemical Factory Boruta

– Kolor Sp. z o.o. (Poland) were applied as model azo-dyes. The molecular weights of the dyes were equal to 375.4, 640.4 and 1169 g/mol for AY36, AR18 and DG99, respectively. Chemical structures of the model compounds are presented in Fig. 1. Initial concentration of dyes was equal to 30 mg/L.

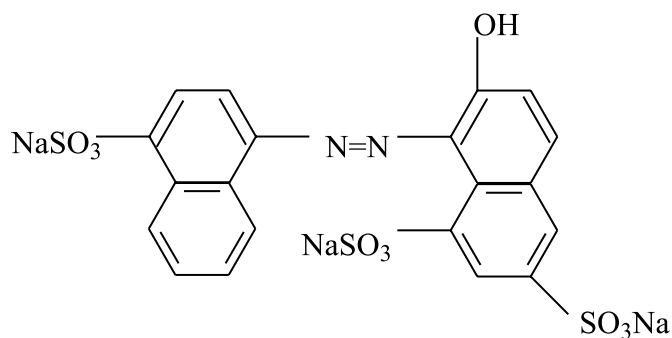
The solutions in the reactors were continuously stirred during the experiment. After 30 min in the dark, the solutions were irradiated with UV-A light (Philips Actinic BL; $\lambda_{\text{max}} = 365$ nm; light intensity at the irradiation plate: 84.5 W/m²). The UV lamp was positioned above the reactors. After a defined time of irradiation the samples of solution were filtered through a 0.45 μm membrane filter and analyzed. The photodegradation rate of model azo dyes was estimated on the basis of changes in the UV/Vis spectra (S-3100 Spectrometer, SCINCO, Korea).

RESULTS AND DISCUSSION

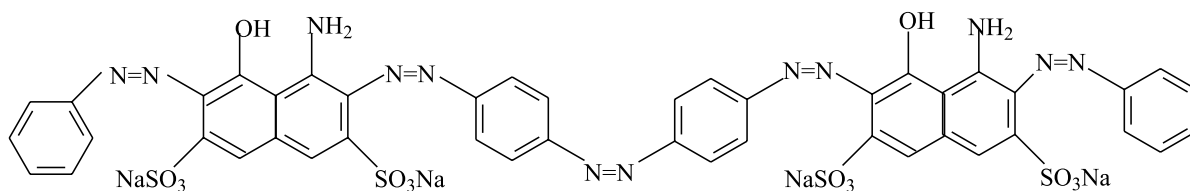
Effect of calcination conditions on TiO₂ structure

Fig. 2 presents XRD patterns of the crude TiO₂ and TiO₂ calcinated for 1h at the temperatures of 600 – 800°C. In case of the crude TiO₂, A-600-1h and A-700-1h catalysts the main crystalline phase was anatase. The diffraction lines of the crude TiO₂ were weak and broad. The increase of the heat treatment temperature up to 700°C resulted in sharpening and narrowing of the diffraction lines what corresponded to the improvement of TiO₂ crystallinity associated with anatase crystals growth. In the XRD patterns of the crude TiO₂ and the photocatalysts annealed at 600 and 700°C a weak 110 diffraction line of rutile can be also observed. The amount of rutile in these samples was constant and equal to the amount of rutile present in the as-received crude TiO₂ (c.a. 3%, Table 1). In case of the A-800-1h sample the main structure was rutile (97%, Table 1), although a small amount of anatase was also detected. The XRD patterns of TiO₂ calcinated for 2 and 3h were similar to those annealed for 1h. However, the phase composition (i.e. anatase to rutile ratio) differed to some extent what suggests that not only temperature but also time of calcination affected the crystalline phase composition of the samples. The properties of TiO₂ calcinated under different conditions are presented in Table 1. It can be observed that the samples annealed at 600°C contained 97% of anatase, regardless of the heat treatment time. However, the anatase crystallite size slightly increased with increasing the calcination time and ranged from 19 to 21 nm (Table 1). In case of the A-700 series the highest anatase content was observed for the A-700-1h catalyst (97%).

a)



b)



c)

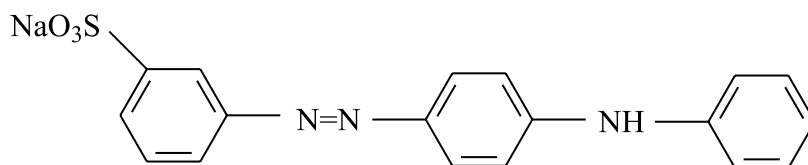


Figure 1. Chemical structures of (a) Acid Red 18, (b) Direct Green 99 and (c) Acid Yellow 36

The anatase to rutile ratio calculated for the catalysts annealed for 2 – 4h was a little lower and amounted to 94%. Similarly as in case of the A-600 series an increase of the heat treatment time resulted in an increase of anatase crystallite size (Table 1). The samples calcinated at 800°C for 1 – 3h contained a trace amount of anatase (3 – 1% for A-800-1h to A-800-3h, respectively).

From the obtained results it can be clearly seen that thermal treatment significantly affects the structure and crystallite size of TiO₂. The crystallite size of anatase increased with increasing of the calcination temperature and time, what indicates aggregation of TiO₂ nanoparticles upon annealing. Moreover, the increase of the heat treatment temperature up to 800°C time led to the phase transformation from thermodynamically metastable anatase to the most stable form of TiO₂, rutile. According to Su et al.¹⁹ during the heat treatment of TiO₂, the dehydration takes place and as a result the crystals grow to a size larger than those of the original particles. This conclusion was confirmed by the FTIR spectra (Fig. 3) of the crude and annealed TiO₂. It can be clearly seen that the intensity of the bands associated with –OH vibrations (3300 – 3500 cm⁻¹) decreased with increasing heat treatment temperature what indicates that the amount of hydroxyl groups present on TiO₂ surface was reduced upon annealing.

Table 1 presents also BET specific surface area of TiO₂ annealed under different conditions. It can be seen that the surface area of the samples decreased with increasing calcination temperature and time from 62.3 m²/g in case of A-600-1h to ca. 8 – 9 m²/g in case of the A-800 series. The BET surface area of catalysts annealed at 600 and 700°C

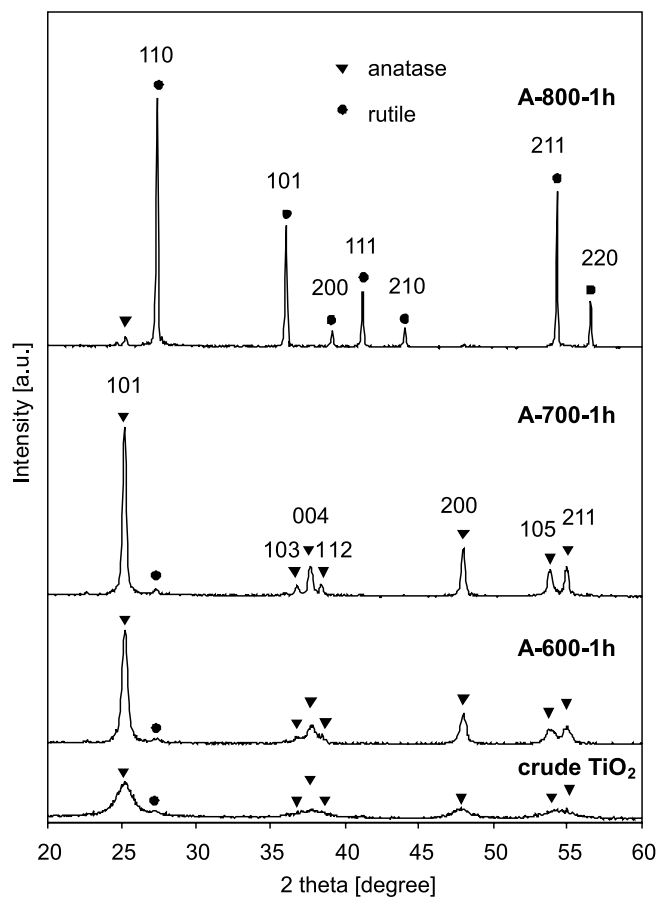


Figure 2. Effect of calcination temperature on XRD pattern of TiO₂; time of heat treatment: 1h

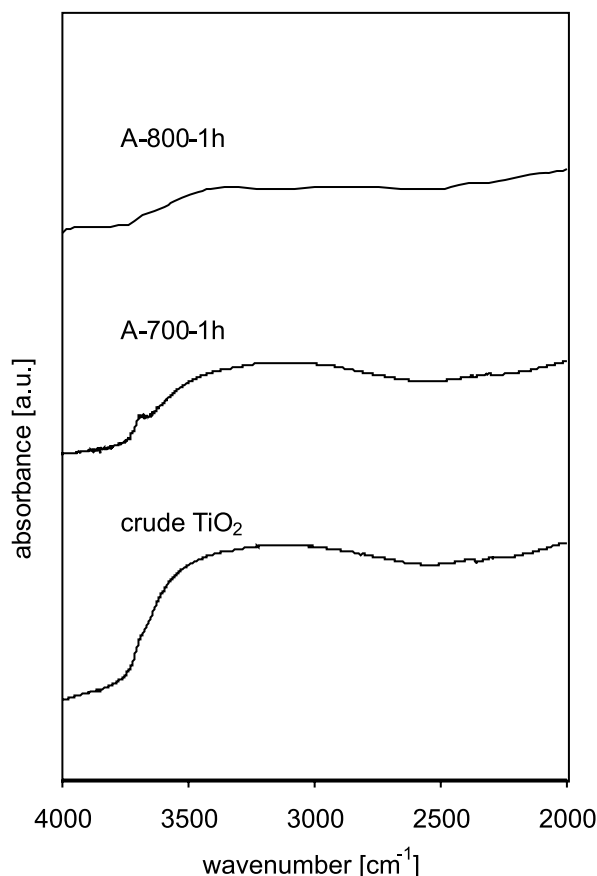


Figure 3. FTIR spectra of crude TiO_2 and TiO_2 annealed at 700 and 800°C for 1h

decreased linearly with increasing of the crystallite size of anatase (Fig. 4). Such kind of correlation was not found with reference to the A-800 series. This could be explained by the fact that the main TiO_2 phase in case of these samples was rutile. Therefore, the surface area corresponds mainly to the rutile, not anatase phase. The reason for the decrease of the BET surface area was mainly the growth of crystals upon annealing what was discussed previously.

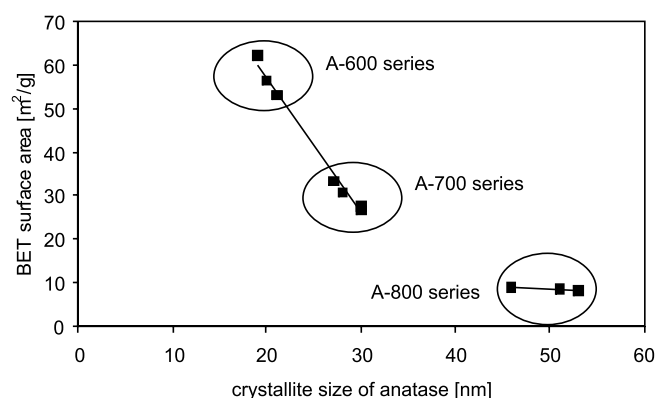


Figure 4. Correlation between BET surface area and crystallite size of anatase

Effect of TiO_2 structure on photodegradation rate of azo dyes

The photocatalytic activity of the catalysts was evaluated on the basis of decolorization of Acid Red 18, Acid Yellow 36 and Direct Green 99 solutions. At the beginning of the investigations a photolysis experiments (i.e. without addition of TiO_2) were performed in order to determine the photostability of azo dyes under the conditions applied. It was found that during 5 h of irradiation the dye concentration

was practically constant, regardless of the model compound used. Therefore, it can be stated that in the presence of TiO_2 a true heterogenous catalytic regime took place.

Fig. 5 presents, as an example, changes of azo dyes concentration during their photocatalytic degradation on the crude TiO_2 and photocatalysts calcinated for 1h at different temperatures. The fading of the solutions was associated with cleavage of azo linkage in a dye molecule. Azo dyes are characterized by nitrogen to nitrogen double bonds ($-\text{N}=\text{N}-$) that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene or naphthalene rings, Fig. 1). The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band¹³. The cleavage of $-\text{N}=\text{N}-$ bonds leads to the decolorization of dyes, what was observed in the discussed experiment (Fig. 5).

The highest effectiveness of decolorization was found in case of AR18, regardless of the catalyst used. After 5h of irradiation the concentration of the dye, compared to the initial concentration of 30 mg/L, decreased for ca. 94% and 99% in case of the crude TiO_2 and A-600-1h, respectively. When A-700-1h was applied a complete decolorization of the solution was obtained (Fig. 5c). Surprisingly, even in case of the A-800-1h, containing 97% of rutile, fading of the AR18 solution was observed. After 5h of the process conducted with this photocatalyst the concentration of the dye was lowered for ca. 33% (Fig. 5d). The solutions of the other two azo dyes, AY36 and DG99, faded to a much less extent. In case of the A-600-1h (Fig. 5b) and A-700-1h (Fig. 5c) the decolorization rates of these dyes were similar one to another. After 5h of irradiation the concentration of DG99 decreased for ca. 25 and 39% (vs. $c_0=30$ mg/L) and AY36 for ca. 26 and 39% (vs. $c_0=30$ mg/L) when the A-600-1h and A-700-1h were used, respectively. However, when the crude TiO_2 (Fig. 5a) and A-800-1h (Fig. 5d) were applied, the decolorization rates of AY36 and DG99 differed significantly. At the end of the experiments with the crude TiO_2 and A-800-1h the concentration of AY36 was lowered for ca. 17 and 4%, respectively, when compared to $c_0=30$ mg/L. Fading of DG99 solution was significantly higher and amounted to ca. 34 and 27%, respectively.

The photodegradation efficiency calculated on a basis of dye concentration after 5h of irradiation and the concentration after the period of adsorption in the dark in case of AR18 was equal to 94, 99, 100 and 33%, in case of AY36: 12, 26, 38 and 3% and in case of DG99: 19, 25, 37 and 26%, for the crude TiO_2 , A-600-1h, A-700-1h and A-800-1h, respectively. The differences between the dyes removal calculated on a basis of the initial concentration and the concentration after adsorption in the dark, observed especially in case of the crude TiO_2 , resulted from adsorption ability of the dyes to the catalyst surface. The crude TiO_2 exhibited very high surface area (277 m^2/g) and therefore the adsorption of the model compounds in case of this photocatalyst was the most significant (Fig. 5).

From the obtained results it can be found that the most effectively photodegraded was AR18, having the molecular weight of 640.4 g/mol. The most difficult to degrade was AY36, what was especially observable in case of the crude TiO_2 and A-800-1h. The reason for higher degradation rate of AR18 than DG99 could be lower molecular weight

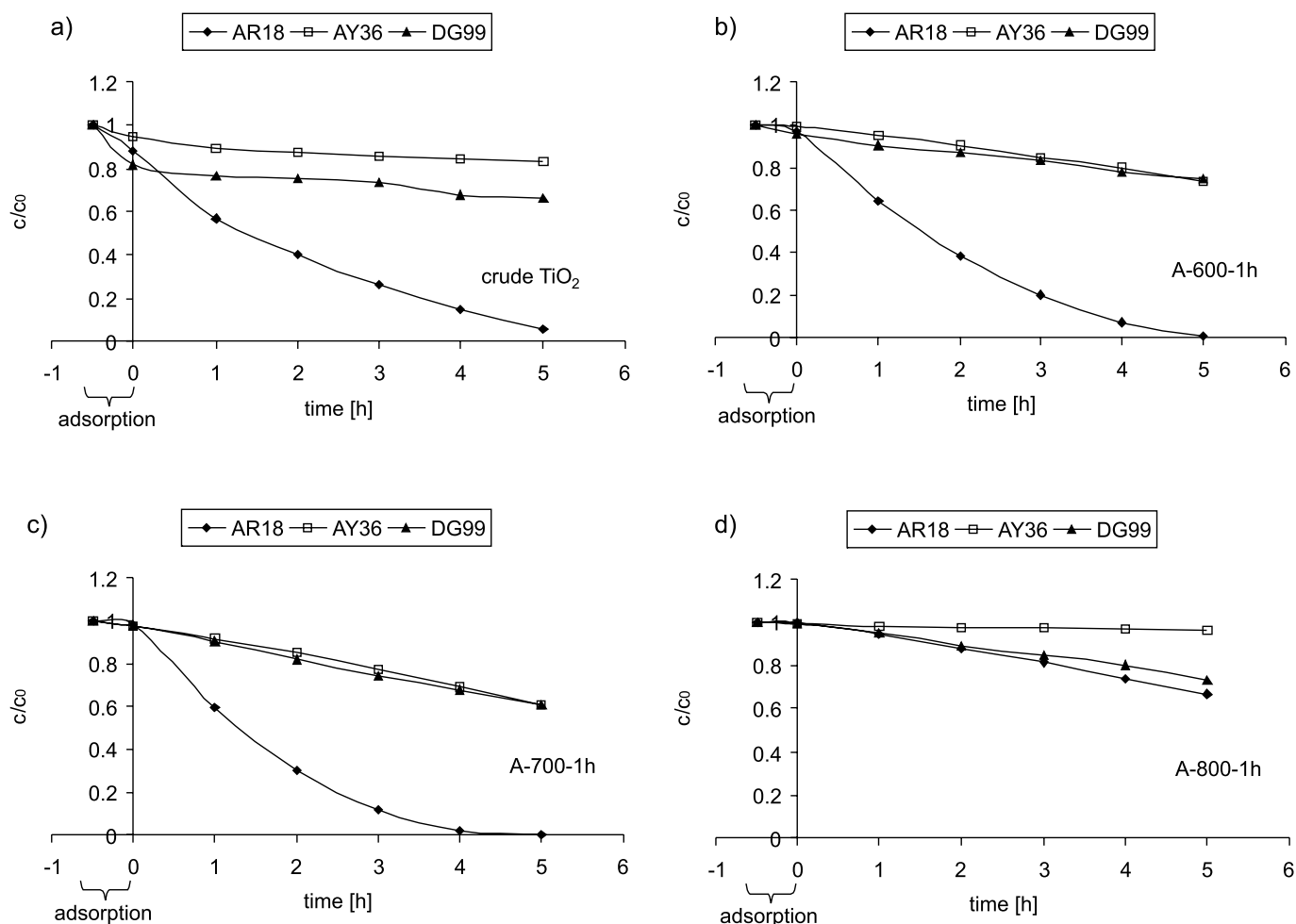


Figure 5. Changes of dyes concentration during photocatalytic degradation of Acid Red 18, Acid Yellow 36 and Direct Green 99 on different photocatalysts; TiO_2 loading: 0.1 g/L, initial dye concentration: 30 mg/L

(640.4 g/mol vs. 1169 g/mol) of this dye. The resistance of AY36 (375.4 g/mol) to UV light might be associated with the presence of electron donating $-\text{NH}-$ group in para- position to azo bond and electron withdrawing $-\text{SO}_3\text{Na}$ group in meta- position to $-\text{N}=\text{N}-$ bond, what probably stabilizes the dye molecule.

On the basis of the results obtained during photodegradation of the model azo dyes on different photocatalysts the initial degradation rates were calculated:

$$r_0 = \frac{(c_{\text{ads}} - c_t)}{t} \quad (15)$$

where: r_0 – initial degradation rate [mg/L/min], c_{ads} – dye concentration after adsorption in the dark [mg/L], c_t – dye concentration after time t [min] of irradiation.

Fig. 6 presents the effect of the crystallite size of anatase on the initial degradation rate of AR18, AY36 and DG99. It can be observed that the highest r_0 values were obtained in case of the photocatalysts from the A-700 series. The initial degradation rates were in the range of 0.18 – 0.20 mg/L/min for AR18 and 0.03 – 0.035 for AY36 and DG99. The degradation rates of the azo dyes in case of the A-600 series were lower and comparable to that obtained for the crude TiO_2 (Fig. 6). The lowest r_0 values were obtained in case of the A-800 series.

From Fig. 6 it can be clearly seen that the highest effectiveness of degradation was obtained in case of photocatalysts composed mainly of anatase with crystallite size of about 30 nm, regardless of the azo dye applied. The maximum r_0 value

was found in case of the photocatalyst calcinated at 700 °C for 1h, although the differences between the degradation rates of the azo dyes on the A-700-1h and the other samples annealed at 700°C were not very significant (Fig. 6). The reason for the highest effectiveness of the A-700-1h was probably a bit higher anatase content than in case of the catalysts heat treated for longer time (97% vs. 94%, Table 1). Initial degradation rates decreased when anatase crystallites were smaller than ca. 30 nm, although no significant differences in the r_0 values obtained for anatase crystallites of ca. 20 nm (A-600 series) and 9 nm (crude TiO_2) were observed. The lowest initial degradation rates were obtained for photocatalysts annealed at 800°C. The reason was that these catalysts were composed mainly of rutile (Table 1). The obtained results are consistent with the literature data^{15, 16}. Inagaki et al.¹⁵ investigated the effect of crystallinity of anatase on the rate constant k of Methylene Blue (MB) photodecomposition. They found that the maximum rate of MB degradation was obtained for the sample of which crystallite size was about 32 nm and the lattice strain about $0.5 \cdot 10^{-3}$. Toyoda et al.¹⁶ prepared anatase samples having different morphology by annealing hydrothermally prepared TiO_2 . The researchers found that rate constant of MB decomposition was rather low for anatase powders with small apparent crystallite size, then increased suddenly at about 35 nm size, and finally decreased with further growth of crystallites. The increase in k was explained by the depression of the recombination of electron and holes excited by UV rays in anatase phase due to the improvement in crystallinity of anatase

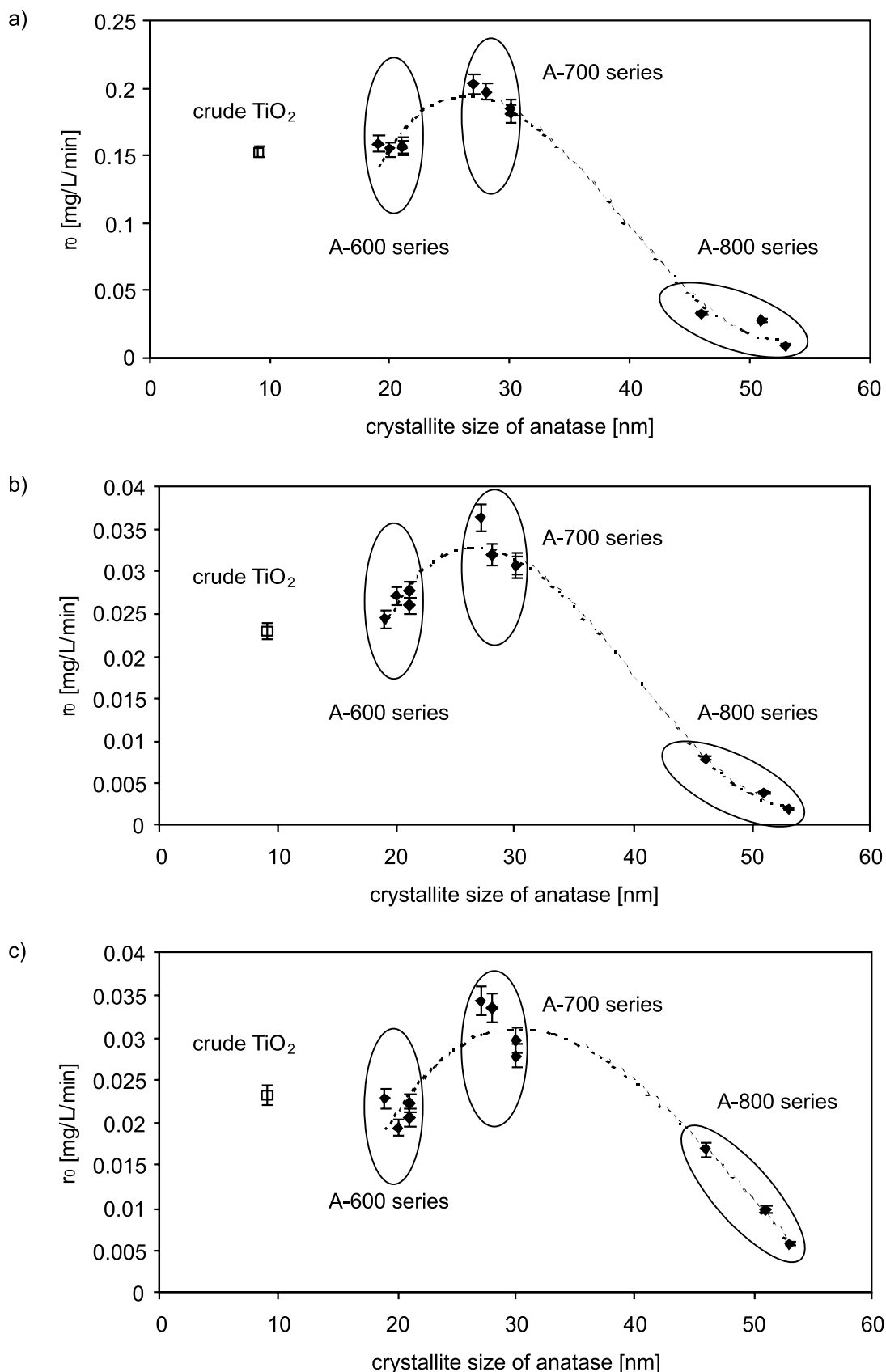


Figure 6. Influence of crystallite size of anatase on initial rate (r_0) of photodegradation of a) AR18, b) AY36 and c) DG99; TiO_2 loading: 0.1 g/L, initial dye concentration: 30 mg/L. The dashed line was added to show a possible trend

phase (increase in crystallite size). The decrease in k with further increase in crystallite size of anatase was supposed to be due to the partial transformation of anatase to rutile phase¹⁵.

Fig. 7 presents the effect of BET specific surface area on the initial rates of photodegradation of the model azo dyes.

It can be observed that an increase of the surface area did not improve the effectiveness of degradation of the dyes. The highest r_0 values were obtained in case of the A-700 series having BET surface areas lower than that in case of the A-600 series. Moreover, the crude TiO_2 , exhibiting the surface area about 10 times higher than the catalysts from the A-700

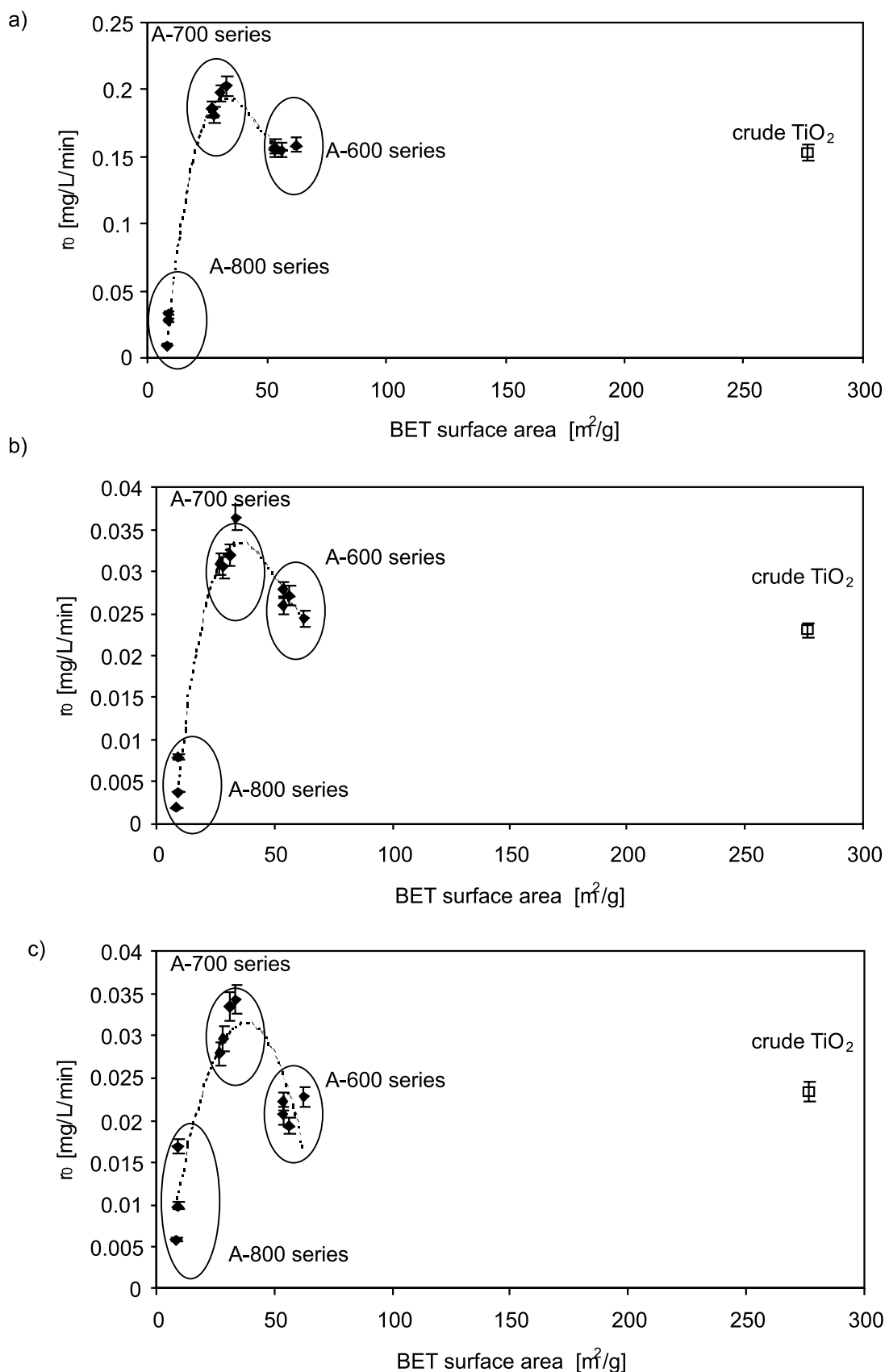


Figure 7. Influence of BET surface area of TiO₂ on initial rate (r_0) of photodegradation of a) AR18, b) AY36 and c) DG99; TiO₂ loading: 0.1 g/L, initial dye concentration: 30 mg/L. The dashed line was added to show a possible trend

series, was less effective in decomposition of the dyes than the samples annealed at 700°C. However, when the influence of the BET surface area on the initial degradation rates of azo dyes using the A-700 series catalysts was considered, a slight increase of r_0 with increasing surface area was observed (Fig. 7). The obtained results might suggest that the main

factors affecting the degradation rate of the model azo dyes were crystallite size and content of anatase. The effect of surface area was of less importance, although, for photocatalysts exhibiting similar anatase content and crystallite size an improvement of dye degradation with increasing BET surface area was observed.

CONCLUSIONS

It was shown that the calcination parameters such as temperature and time affected the structure and photocatalytic properties of TiO₂. An increase of the calcination temperature up to 700°C led to an increase of the crystallite size of anatase and a decrease of BET surface area. Further increase of the temperature up to 800°C resulted in phase transformation from metastable anatase to most stable rutile followed by a significant decrease of the BET specific surface area. The crystallite size of anatase ranged from 19 nm for A-600-1h to 53 nm for A-800-3h. The BET surface area was in the range of 62.3 m²/g to ca. 8 m²/g for the catalysts heated at 600 – 800 °C, respectively.

The initial rates of photodegradation of model azo dyes depended on the content and crystallite size of anatase. The highest effectiveness of degradation was obtained in case of the A-700-1h photocatalyst composed mainly of anatase (97%) with crystallite size of 27 nm, regardless of the azo dye applied. A bit lower degradation rates were obtained for samples annealed at 700°C for 2 – 4h, containing ca. 94% of anatase with crystallites of 28 – 30 nm. A decrease of the initial degradation rates was observed in case of samples exhibiting anatase crystallites smaller than ca. 30 nm. The lowest r_0 values were obtained for photocatalysts annealed at 800°C that were composed mainly of rutile.

The most effectively photodegraded was AR18, having the molecular weight of 640.4 g/mol. The most difficult to degrade was AY36, exhibiting the lowest molecular weight from all the dyes used (375.4 g/mol). The resistance of AY36 to UV light might be associated with the presence of electron donating –NH– group in para- position to azo bond and electron withdrawing –SO₃Na group in meta- position to –N=N– bond, what probably stabilizes the dye molecule.

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