

## Preparation of the TiO<sub>2</sub> photocatalyst using pressurized ammonia

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The industrial hydrated amorphous titanium dioxide (TiO<sub>2</sub> · xH<sub>2</sub>O) was modified by treatment inside a chemical reactor under elevated pressure at low temperatures for 4 hours in an ammonia atmosphere. On the basis of the FTIR/DRS analysis the presence of nitrogen was confirmed. The XRD patterns of all of the catalysts exhibit mainly the diffraction lines of anatase phases. The photocatalytic activity of the modified photocatalysts was determined and compared to TiO<sub>2</sub>-P25 (Degussa, Germany). The high rate of phenol and dye degradation was obtained for the catalysts modified at 180°/15atm. TiO<sub>2</sub>-P25 showed similar activity in phenol decomposition like TiO<sub>2</sub>-15bar, whereas it was more active in dye decomposition.

**Keywords:** photocatalysis, TiO<sub>2</sub>-nitrogen, dye decolorization, TiO<sub>2</sub> preparation under pressure.

### INTRODUCTION

For many years the photocatalytic process of removing contamination from air and water been of general interest. Especially in recent years researchers have placed great emphasis on the creation of the photocatalysts which could be active under visible light<sup>1-4</sup>. One approach to obtain such a photocatalyst is doping with impurities, e.g. transition metals or other substances, including C, N, F, P, S, or by reduction TiO<sub>x</sub> photocatalysts. It was found that the substitutional N-doping was a very effective method for VIS-active photocatalysts preparation<sup>5-7</sup>. Nitrogen ions substitute for oxygen in the TiO<sub>2</sub> lattice and thus the corresponding N(2p) states are located above the valence band edge. Mixing of the N(2p) states with the O(2p) states results in the reduction of the band gap of the N-doped TiO<sub>2</sub> and the photocatalyst can be active under visible light irradiation. Asahi et al.<sup>8</sup> obtained TiO<sub>2-x</sub>N<sub>x</sub> by sputtering the TiO<sub>2</sub> target in N<sub>2</sub>(40%)/Ar gas atmosphere and the following heat treatment at 550°C in N<sub>2</sub> gas for 4 hours. It was proved that the TiO<sub>2-x</sub>N<sub>x</sub> film absorbed the light at the wavelengths lower than 500 nm, whereas the TiO<sub>2</sub> film did not. The authors concluded that the visible light absorption by N-doped TiO<sub>2</sub> is due to the substitution of oxygen by nitrogen, which results in the mixing of the N(2p) and O(2p) states.

Ihara et al.<sup>9</sup> prepared the VIS-active photocatalysts by the calcination of hydrolysis products of Ti(SO<sub>4</sub>)<sub>2</sub> previously treated with the NH<sub>3(aq)</sub> solution. They concluded that oxygen-deficient sites formed in the grain-boundaries are important to emerge the VIS activity and nitrogen doped in the part of oxygen-deficient sites is important as a blocker for reoxidation.

Sawabe et al.<sup>10</sup> prepared the N-doped titanium oxides by the calcination of titanium compound in the presence of ammonia gas or by heat treatment of a titanium compound in the presence of an ammonia gas and subsequent calcination in a nitrogen or air atmosphere. The calcination was conducted at the temperatures ranging from 300°C to 600°C. The authors used titanium hydroxides, titanate acids, and other inorganic titanium compounds, organic titanium compounds, partially hydrolysed inorganic titanium compounds and partially hydrolysed organic titanium compounds. The titanium compounds included an amorphous phase. It was found that increasing the amount

of amorphous titanium compound resulted in a higher VIS-photocatalytic activity of the resulting titanium oxide. Moreover, when the titanium hydroxide contained a significant amount of nitrogen its photocatalytic activity under visible light irradiation was also higher. The titanium oxide obtained by Sawabe et al. exhibited a crystal structure of anatase. The N-doped photocatalysts can be used for the decomposition of NO<sub>x</sub> in the atmosphere, the decomposition and removal of bad-smelling substances and other environmental pollution substances.

Yuan et al.<sup>11</sup> prepared the nitrogen-doped TiO<sub>2</sub> samples with high specific surface areas directly by the hydrolysis of titanium tetrachloride (TiCl<sub>4</sub>) and heating the mixture of urea and TiO<sub>2</sub>. The absorption spectrum of the N-doped TiO<sub>2</sub> shifted to the wavelength up to 600 nm with the increasing urea contents. The X-ray photoelectron spectroscopic measurements showed that the N presented in TiO<sub>2</sub> was in the state of both the molecularly chemisorbed N<sub>2</sub> and the substituted N. The photocatalytic activities of the specimens were evaluated by hydrogen evolution from water splitting.

A vis-active N-doped TiO<sub>2</sub> was also obtained by Jang et al.<sup>12</sup>. The authors synthesized amorphous precursors to a nitrogen-doped TiO<sub>2</sub> (NTP) and pure TiO<sub>2</sub> (ATP) powders by hydrolytic synthesis and the sol-gel method (SGM), respectively. The corresponding crystalline phases were obtained by the thermally induced transformation of the amorphous powders. From the FT-IR and XPS data it was concluded that a complex containing titanium and ammonia was formed in the precipitate stage while calcination drove weakly adsorbed ammonium species on the surface. The decomposed ammonia bound on the surface of the precipitated powder and led to the substitution of a nitrogen atom into the lattice of TiO<sub>2</sub> during the crystallization. The fabricated N-doped TiO<sub>2</sub> photocatalyst absorbed the visible light showing two absorption edges; one in the UV range due to titanium oxide as the main edge and the other due to nitrogen doping as a small shoulder. The TiO<sub>2-x</sub>N<sub>x</sub> photocatalyst demonstrated its photoactivity for photocurrent generation and decomposition of 2-propanol under visible light irradiation.

In this work the nitrogen doped TiO<sub>2</sub> photocatalyst is prepared by treatment inside the pressure chemical reactor under elevated pressure at low temperatures for 4

hours in an ammonia atmosphere. The photocatalyst is characterized by the FTIR/DRS spectroscopy, UV-VIS diffuse reflection spectroscopy and the X-ray powder diffraction (XRD). The photocatalytic activity of the obtained catalysts is estimated on the basis of the decomposition of phenol and Reactive Red 198, both under the UV and the artificial solar light irradiation.

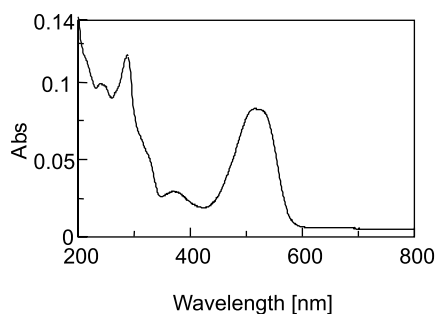
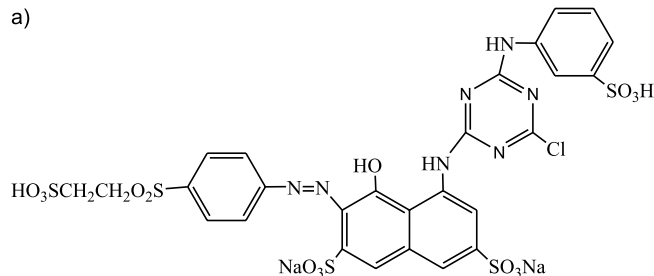
## EXPERIMENTAL AND METHODS

### Materials

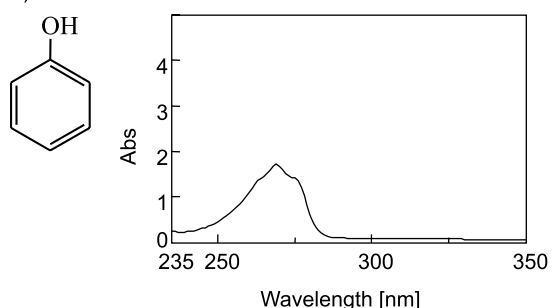
The commercially available azo dye Reactive Red 198 produced by The Chemical Factory Boruta – Color Sp. z o.o. (Poland) and phenol were used as a model compound. The chemical structure as well as the spectra of the model compounds are presented in Fig. 1 a – b.

Titanium dioxide Aeroxide® TiO<sub>2</sub>-P25 was supplied by the Degussa company (Germany). The industrially produced by Police S.A. (Poland) metatitanic acid (TiO(OH)<sub>2</sub>) was obtained directly from the sulphate technology installation and used as a precursor for the photocatalyst preparation. The metatitanic acid was tentatively treated by drying at 100°C for 20 hours before modification (TiO(OH)<sub>2</sub> – 100). The modification of TiO(OH)<sub>2</sub> – 100 was conducted by treatment inside the pressure chemical reactor (type BLH-800 Berghof, Germany) under elevated pressure at low temperatures (60, 120, 180°C) for 4 hours in an ammonia atmosphere. In Fig. 2 the scheme of the pressure reactor is presented. The prepara-

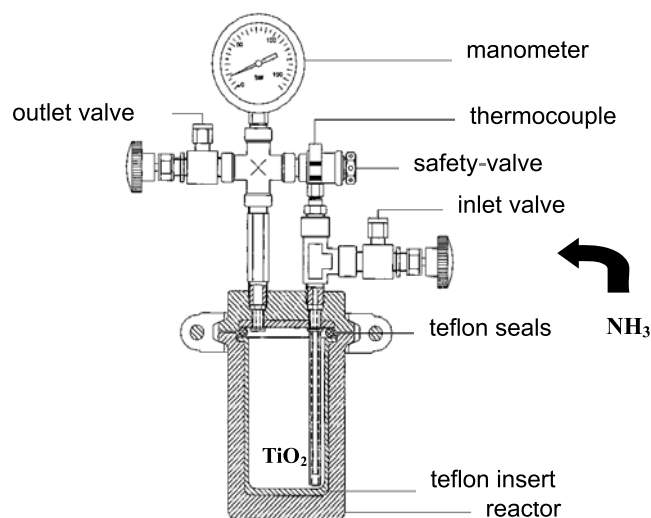
a)



b)



**Figure 1.** The chemical structure and the spectra of a) Reactive Red 198 b) phenol



**Figure 2.** A schematic diagram of the experimental setup

**Table 1.** The conditions of catalysts preparation in ammonia atmosphere

| Conditions of preparation |                        |                         |
|---------------------------|------------------------|-------------------------|
| Temperature [°C]          | Ammonia pressure [bar] | Name of the catalyst    |
| 180                       | 1                      | TiO <sub>2</sub> -1bar  |
| 60                        | 8                      | TiO <sub>2</sub> -8bar  |
| 120                       | 13                     | TiO <sub>2</sub> -13bar |
| 180                       | 15                     | TiO <sub>2</sub> -15bar |

tion conditions of the photocatalysts in Tab. 1 are shown. The atmospheric pressure modification was conducted in the pipe furnace (type R40/250/12-C40 Nabertherm, Germany) at the temperature of 180°C in a flow of ammonia gas for 4 hours (sample TiO<sub>2</sub>-1bar).

### Photocatalyst characterization

The surface properties of the photocatalysts were examined on the basis of the FTIR/DRS spectra. The measurements were performed using the Jasco FT-IR 430 (Japan) spectrometer equipped with a diffuse reflectance accessory (Harrick, USA).

The photocatalysts were characterized by the UV-VIS/DR technique using the Jasco V-530 spectrometer (Japan) equipped with the integrating sphere accessory for the diffuse reflectance spectra (BaSO<sub>4</sub> was used as a reference).

The crystalline structure of the photocatalysts was characterized by the X-ray powder diffraction (XRD) analysis (X'Pert PRO Philips diffractometer) using CuK<sub>α</sub> radiation. The mean size of the crystallite was calculated from the full-width at the half-maxima (FWHM) of the corresponding X-ray diffraction peaks using Scherrer's formula  $D = \lambda / (\beta \cdot \cos \theta)$ , where  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 1.54056$  nm CuK<sub>α</sub>),  $\beta$  is the full-width at half maximum (rad) and  $\theta$  is the reflect angle. The width of the peak at half maximum was calculated after the correction of the instrument error. The presented method was applied to estimate the change in the crystallite size of the TiO<sub>2</sub> particles.

The specific surface area was determined by the BET method (Micromeritics ASAP 2010).

### Determination of the photocatalytic activity

The photocatalytic degradation of phenol and azo-dye (Reactive Red 198) were carried out in a glass batch photoreactor containing 500 cm<sup>3</sup> of a model solution and 0.1 g of the photocatalyst. The initial concentrations of phenol and Reactive Red 198 solutions were equal to 0.1g/l and 0.005g/l, respectively. The solutions were mixed with a magnetic stirrer during the reaction process. The irradiation of the solution was performed under two conditions: under the artificial solar light irradiation (light bulk, Philips 100 W) with the radiation intensity of about 385 W/m<sup>2</sup> for VIS and 0.09 W/m<sup>2</sup> for the UV range and under the UV light (six lamps with the power of 20 W, Phillips) with radiation intensity of about 100 W/m<sup>2</sup> for VIS and 154 W/m<sup>2</sup> for the UV. The irradiation intensity was measured with the LB-901 irradiation meter equipped with the PD 204AB (Macam Photometrics Ltd.) and CM3 (Kipp & Zonen) external sensors. After 15 min in the dark, the solutions of azo dye and phenol were irradiated under the artificial solar light for 5 and 24 hours, respectively, whereas under the UV light for 5 hours for phenol and until a complete decolorization of the Reactive Red 198 dye.

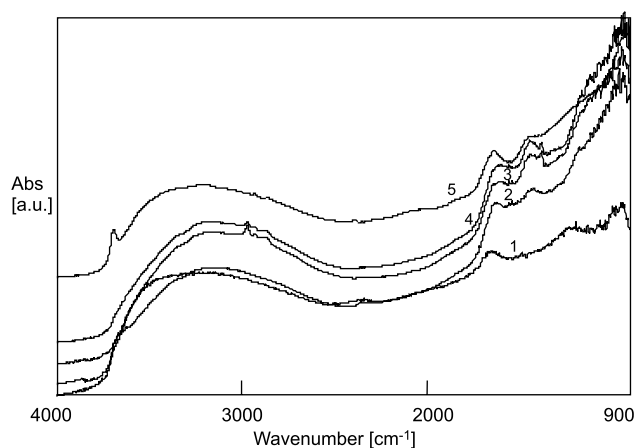
After the irradiation the solution was filtered through a 0.45 μm membrane filter. The concentrations of the model compounds were determined by the UV absorbance measurement (Jasco V-530, Japan) at the wavelength of 270 nm (phenol) or 518 nm (Reactive Red 198). The decomposition rates of phenol and dye were calculated from the equation:  $D = 100 - \left( \frac{C}{C_0} \cdot 100\% \right)$ , where D is the decom-

position rate of azo-dye or phenol, C<sub>0</sub> is the initial solution concentration and C is the solution concentration after 5 and 24 hours of irradiation, respectively.

## RESULTS AND DISCUSSION

### FTIR/DRS spectra of the modified photocatalysts

In Fig. 3 the FTIR/DRS spectra of the modified photocatalysts and TiO<sub>2</sub>-P25 are presented. In all the spectra the vibration corresponding to the hydroxyl groups can be seen: at 3695 cm<sup>-1</sup> assigned to the hydroxyl groups chemisorbed on the surface defect side of the photocatalyst, at 3300 – 3500 cm<sup>-1</sup> for both the dissociated and molecularly adsorbed water, and at 1623 cm<sup>-1</sup> for the



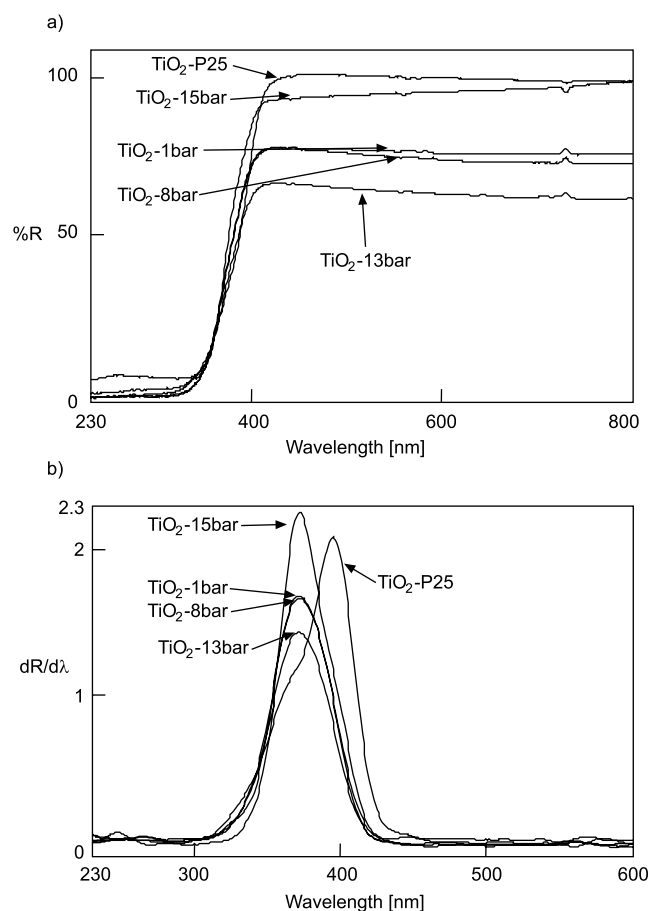
**Figure 3.** The FTIR/DRS spectra of catalysts: 1 – TiO<sub>2</sub>-P25; 2 – TiO<sub>2</sub>-1bar, 3 – TiO<sub>2</sub>-8bar, 4 – TiO<sub>2</sub>-13bar, 5 – TiO<sub>2</sub>-15bar, respectively

molecular water<sup>13</sup>. The intensity of the hydroxyl groups rather does not change after modification.

It is possible to observe for the modified catalysts that the bands at 1430 – 1440 cm<sup>-1</sup> correspond to the bending vibrations of NH<sub>4</sub><sup>+</sup><sup>9</sup>. The intensity of these bands was varied when the calcination temperature and ammonia pressure were raised, but without the reduction of the hydroxyl groups. The presented method of the preparation of the doped TiO<sub>2</sub>-N does not cause the reduction of the hydroxyl groups in contrast with the thermal method, where with the rising of the calcination temperature the intensity of these bands decreased<sup>14</sup>. From this observation it can be supposed that both the kind and the place of the built nitrogen strongly depend on the modification method.

### UV-VIS/DR spectra of the modified photocatalysts

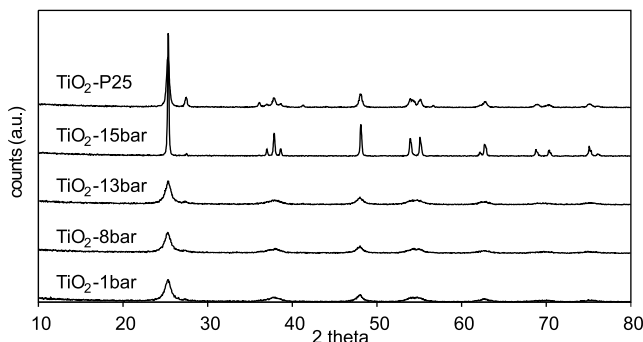
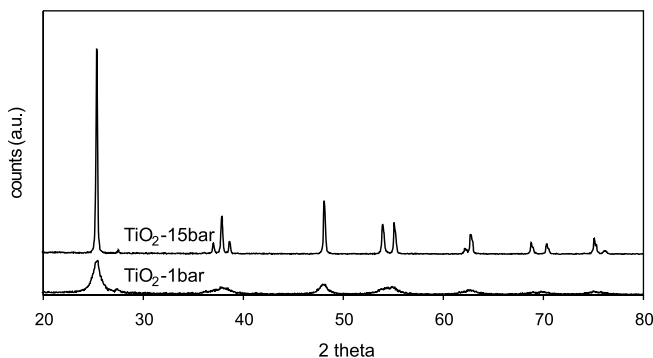
The UV-VIS/DR spectra and the first derivatives of the UV-VIS/DR absorption spectra of the photocatalysts are presented in Fig. 4a – b. It can be seen that the spectra are not shifted to the higher wavelengths. For all the catalysts prepared no difference in the band gap energy E<sub>G</sub> was detected (E<sub>G</sub> = 3.3 eV). The observed values of E<sub>G</sub> are listed in Table 2. Both for the catalyst prepared at 180°C/1bar and for the catalyst prepared under elevated pressure it can be observed that these catalysts absorbed only the UV light. On the other hand, insignificant change of the color of the prepared photocatalyst to yellowish was observed. Therefore, in Fig. 4 the decreasing of the reflectance of the catalyst at a visible region can be seen. However, we have to point out that when we modified the



**Figure 4.** a) The UV-VIS/DR reflection spectra of the photocatalysts b) The first derivatives of UV-VIS/DR absorption spectra of the photocatalysts

**Table 2.** The characteristics of the photocatalysts prepared under elevated pressure

| Sample name             | $\lambda_{\max}$ [nm] | $E_G$ [eV]   | BET [ $m^2/g$ ] | Phase composition [%]         |
|-------------------------|-----------------------|--------------|-----------------|-------------------------------|
| TiO <sub>2</sub> -1bar  | 372                   | 3.33         | 294.4           | 67.9 Amorph. + 28.6 A + 3.5 R |
| TiO <sub>2</sub> -8bar  | 372                   | 3.33         | –               | 60.0 Amorph. + 36.5 A + 3.5 R |
| TiO <sub>2</sub> -13bar | 372                   | 3.33         | –               | 59.8 Amorph. + 36.7 A + 3.5 R |
| TiO <sub>2</sub> -15bar | 372                   | 3.33         | 11.6            | 96.5 A + 3.5 R                |
| TiO <sub>2</sub> -P25   | 366<br>395            | 3.38<br>3.14 | 58.1            | 80 A + 20 R                   |

**Figure 5.** The XRD patterns of N-doped photocatalysts compared with TiO<sub>2</sub>-P25**Figure 6.** The transformation of the amorphous phase of TiO<sub>2</sub> to anatase on the basis the XRD patterns

surface of TiO<sub>2</sub> by nitrogen under higher temperatures, the intensity of the transmittance of visible light decreases and the catalysts adsorb the visible light<sup>15</sup>.

### XRD patterns of the modified photocatalysts

Fig. 5 presents the XRD patterns of TiO<sub>2</sub> after modification in the pressure reactor and of TiO<sub>2</sub>-P25. It can be seen that the patterns of all of the catalysts exhibit the diffraction lines of anatase and rutile phases. After the modification at low temperatures for 4 hours in an ammonia atmosphere we observed the complete transformation from the amorphous to the crystalline form of TiO<sub>2</sub> (Fig. 6). Raising the ammonia pressure results in the increasing of the amount of crystalline anatase from 28.6% at 1 bar to 96.5% at 15 bar. The rutile phase does not change during the modification (Tab. 2).

It was observed that at the ammonia pressure lower than 13 bar the TiO<sub>2</sub> applied was not completely crystallized and consisted of anatase, rutile and the amorphous form of TiO<sub>2</sub>. The XRD technique cannot be applied for the determination of an amorphous phase. Therefore, we tried to calculate the amount of amorphous titanium dioxide in the prepared samples. We assumed that at 15 bar TiO<sub>2</sub> occurs only in the crystalline form (96.5% of anatase and 3.5% of rutile phases – according to the intensity of the highest peak of anatase). Taking into account the in-

tensity of the highest diffraction peak of anatase at a given ammonia pressure (from 1 to 13 bar) and the intensity of the highest diffraction peak of anatase at 15 bar, we calculated the approximate ratio of amorphous TiO<sub>2</sub> and anatase:

$$R_{\text{am}} (\%) = 100 - \left( \frac{I_t}{I_{A_{\max}}} \cdot R_{A_c} \right) - R_{R_c}$$

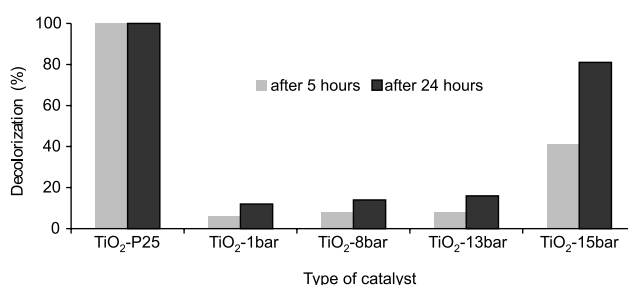
where:  $R_{\text{am}}$  – the fraction of amorphous TiO<sub>2</sub>;  $I_t$  – the intensity of a diffraction peak of anatase at a given ammonia pressure;  $I_{A_{\max}}$  – the intensity of the diffraction peak of anatase at 15 bar;  $R_{A_c}$  and  $R_{R_c}$  – the fraction of anatase and rutile, respectively (calculated according to the intensity of the highest peak of anatase).

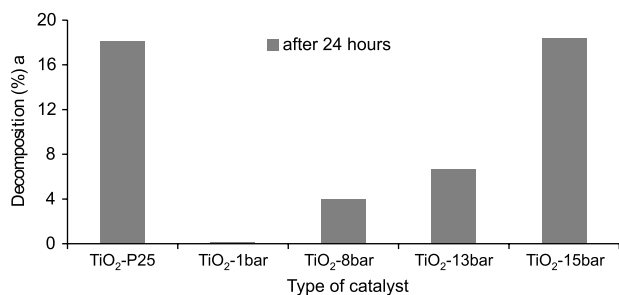
The increasing of the ammonia pressure from 1 to 15 bar resulted in a significant decrease of the BET surface area of the prepared catalysts from 294.4 for TiO<sub>2</sub>-1bar to 11.6  $m^2/g$  for TiO<sub>2</sub>-15bar, which correspond to the increasing of the anatase phases in the prepared catalysts. The BET surface area of the commercial TiO<sub>2</sub>-P25 is 58  $m^2/g$  (Tab. 2).

The XRD patterns of the modified TiO<sub>2</sub> did not exhibit any other diffraction peaks of a new crystal phase apart from anatase and rutile. No nitrogen compounds (e.g. TiO<sub>2-x</sub>N<sub>x</sub>) were found since their content was probably below the detection limit to allow the detection of their reflection peaks by the XRD. The TiO<sub>2-x</sub>N<sub>x</sub> obtained under more drastic conditions<sup>16</sup> lead to the formula with the „x” value of 0.019.

### Photocatalytic activity

Nitrogen modification conduct to the mixing of the N(2p) states with the O(2p) states results in the reduction of the band gap of the N-doped TiO<sub>2</sub> and the photocatalyst can be active under visible light irradiation. The results of the photocatalytic activity under the artificial solar light irradiation in Fig. 7 and Fig. 8 are presented. At the beginning of the investigation blank experiments were carried out, which demonstrated that Reactive Red 198 did not undergo the degradation in the aqueous TiO<sub>2</sub> suspension in the dark or when irradiated with the visible light in the absence of the TiO<sub>2</sub> particles.

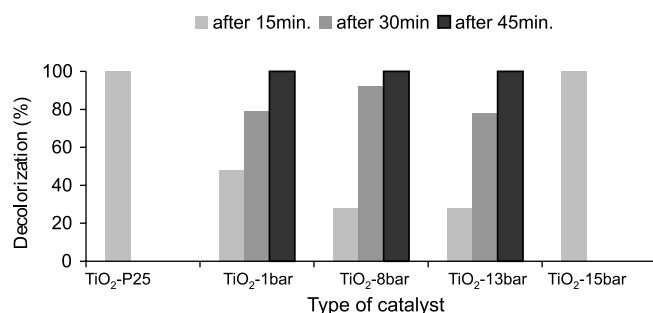
**Figure 7.** Decolorization of Reactive Red 198 (5mg/dm<sup>3</sup>) under the artificial solar light irradiation



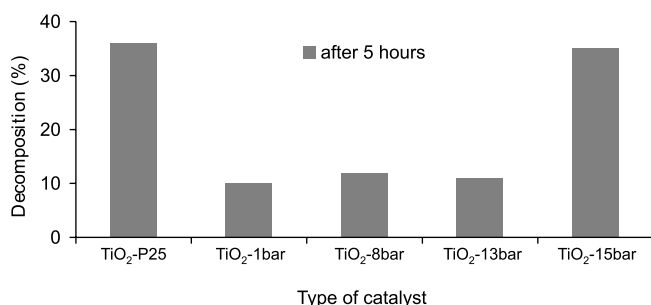
**Figure 8.** Decomposition of phenol ( $0.1\text{g}/\text{dm}^3$ ) under the artificial solar light irradiation

The photocatalytic activity of all the catalysts increased with the increasing of ammonia pressure during the photocatalysts modification. The highest rate dye degradation was obtained for the catalysts modified at  $180^\circ/15\text{atm}$  – 41% after 5 hours of the photocatalytic reaction and 81% after 24 hours of irradiation. Similarly, as during the degradation of RR198, the most effective in the phenol decomposition were the catalysts modified at 15 bar. The decomposition rate amounted to 19%. TiO<sub>2</sub>-P25 showed similar activity in phenol decomposition like TiO<sub>2</sub>-15atm, whereas it was more active in dye decomposition. In the case of the catalyst modified at ammonia pressure from 1 bar to 13 bar can slight degradation of azo dye and phenol, less than 16% and 7%, respectively can be observed.

Fig. 9 presents the results obtained during the photocatalytic decolorization of Reactive Red 198 under the UV light irradiation. The photocatalytic process was conducted until the complete decolorization of the dye solution. In the case of the catalysts such as TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-15ba the complete decolorization was observed after 15 minutes. The other catalysts decomposed Reactive Red 198 after 45 minutes. The TiO<sub>2</sub> samples were also tested for phenol decomposition under the UV irradiation. In Fig. 10 the results are shown. It can be observed that the highest effectiveness was obtained in the case of



**Figure 9.** Decolorization of Reactive Red 198 ( $5\text{mg}/\text{dm}^3$ ) under the UV irradiation



**Figure 10.** Decomposition of phenol ( $0.1\text{g}/\text{dm}^3$ ) under the UV irradiation

the TiO<sub>2</sub>-P25 catalysts and the TiO<sub>2</sub>-15bar. The model phenol concentration decreased by ca. 35%. The activity of the catalysts modified at ammonia pressure from 1 bar to 13 bar was always lower than 12%.

Such activity of the catalysts prepared in different ammonia pressure could be explained by their phase composition. The phase composition of the photocatalysts is presented in Tab. 2. The catalyst prepared at  $180^\circ\text{C}/15\text{bar}$  contains mainly the anatase phase (96.5%). A very high amount of anatase results in a very low recombination of the electron/hole pairs<sup>12</sup> and its photocatalytic activity is very high. It could be explained that the amorphous phase transformed during the increase of ammonia pressure to the more photoactive anatase of suitable crystalline.

## CONCLUSIONS

A new method of the preparation of N-doped photocatalysts by the modification of titanium dioxide with ammonia was presented. The industrial hydrated amorphous titanium dioxide (TiO<sub>2</sub> · xH<sub>2</sub>O) obtained directly from the installation of the sulfate production technology of TiO<sub>2</sub> was modified by the treatment inside the pressure chemical reactor under elevated pressure at low temperatures for 4 hours in an ammonia atmosphere. The presence of nitrogen in the TiO<sub>2</sub> structure was confirmed by the FTIR spectra of the photocatalysts.

The proposed chemical method of using pure ammonia seems to be both more effective, less cost consuming than the advanced physic-chemical method (like CVD with nitrogen) used by other authors.

The complete transformation from the amorphous to the anatase form of TiO<sub>2</sub> during the process that lasted for 4 hours, at low temperatures and the pressure of ammonia equaled to 15 bar was obtained. Raising the ammonia pressure resulted in an increase of the amount of crystalline anatase from 28.6% at 1 bar to 96.5% at 15 bar, whereas the rutile phase has not changed during the modification.

The photocatalytic activity of all the catalysts increased with the ammonia pressure of the prepared catalysts. The highest rate of phenol and dye degradation was obtained for the catalysts modified at  $180^\circ/15\text{atm}$  – 19 and 41%, respectively. TiO<sub>2</sub> Aeroxide® P25 showed similar activity in phenol decomposition like TiO<sub>2</sub>/N- $180^\circ/15\text{atm}$ , whereas it was more active in dye decomposition.

The modification of TiO<sub>2</sub> by ammonia gas under elevated pressure and low temperature appeared to be beneficial in improving its photoactivity for the decomposition of RR 198 and phenol both under the UV and VIS irradiation.

## Acknowledgement

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