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TiO₂-anatase modified by carbon as the photocatalyst under visible light

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Abstract

The photocatalytic oxidation of phenol in water under a visible light over anatase-type titanium dioxide (Tytanpol A11, Poland), modified by carbon deposited via *n*-hexane carbonisation, was investigated. The catalysts, which had small (0–0.2 mass%) and high (0.69–0.85 mass%) contents of carbon showed a little lower catalytic photoactivity than pristine TiO₂. However, the catalyst with high content of carbon (0.85 mass%) gave almost 14-times lower turbidity in the phenol solution after the photocatalyst sedimentation. These two factors depend on the carbon content and have an influence on the ‘practical efficiency’ of the catalysts. The ‘practical efficiency’ of the catalyst under visible light, calculated from these two factors, was therefore 14-times higher for the catalyst containing 0.85 mass% carbon (whereas for UV radiation, it was found to be lower – 0.2 mass% –; this is the result of a previous work). The surface modification of the catalyst with 0.85% carbon seemed to be stable under visible light. The deposition of carbon on TiO₂ by carbonisation of *n*-hexane was supposed to lead to obtain the catalyst, which could be easily used in a water-treatment system under visible light. **To cite this article:** A.W. Morawski *et al.*, *C. R. Chimie* 9 (2006). © 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Résumé

L’oxydation photocatalytique du phénol dans l’eau à la lumière visible a été étudiée sur le dioxyde de titane de type anatase (Tytanpol A11, Pologne), modifié par du carbone déposé par carbonisation du *n*-hexane. Les catalyseurs de teneur en carbone faible (0–0,2 % en masse) ou forte (0,69–0,85 % en masse) ont montré une activité photocatalytique un peu moindre que celle du TiO₂ initial. Cependant, le catalyseur de teneur en carbone la plus élevée (0,85 % en masse) a révélé une turbidité presque 14 fois plus faible dans la solution de phénol après sédimentation du photocatalyseur. Ces deux facteurs dépendent du contenu de carbone et ont une influence sur l’« efficacité pratique » du catalyseur. L’« efficacité pratique » du catalyseur sous la lumière visible, calculée à partir de ces deux facteurs, a été trouvée 14 fois plus élevée pour le catalyseur contenant 0,85 % en masse de carbone, alors que, pour le rayonnement UV, elle a été trouvée plus faible (0,2 % en masse), d’après le résultat d’un travail antérieur. Une modification de surface du catalyseur avec 0,85 % de carbone semble être stable à la lumière visible. Le dépôt du

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carbone sur TiO₂ obtenu par carbonisation du *n*-hexane a été supposé mener à l'obtention du catalyseur, lequel peut être utilisé facilement pour le traitement de l'eau à la lumière visible. **Pour citer cet article :** A.W. Morawski et al., C. R. Chimie 9 (2006). © 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

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Mots clés : TiO₂–carbone ; Photocatalyse ; Lumière visible

1. Introduction

Recently, many researches on the photocatalytic process of water treatment using titanium dioxide to eliminate different contaminants from water have been highlighted. [1–8]. At present, the researchers are searching for the possibility of using TiO₂ under visible-light irradiation (the absorption spectrum of TiO₂ is then shifted toward the solar spectrum range, over 380 nm). One approach was doping a transition metal into TiO₂, another was formation of the reduced TiO_x phase of TiO₂ photocatalyst [9].

Herrmann et al. [10], investigated the photocatalytic degradation of the pollutants under a visible light on the different kinds of titanium dioxides. They used various TiO₂ samples of industrial origins (P25, Hombikat UV 100, TiLCOM HC 120, TiONa PC 10). From their research follows the fact that Degussa P25, despite its moderate specific surface area (50 m² g⁻¹), was a very efficient photocatalyst [10]. They investigated also a new series of titania, which was comprised of industrially photocatalysts that had been elaborated by Millennium Inorganic Chemicals and were denoted Millennium-PC/10, PC/25 and PC/50, with respective surface areas equal to 11, 23 and 43 m² g⁻¹, and concluded that Millennium-PC/50 was a better catalyst than Degussa P25. A practical advantage of Millennium-PC photocatalysts is their fast rate of decantation, which is very helpful for final separation of photocatalyst from purified water [13]. They have been also interested in the synergistic effect between titania and activated carbon in an aqueous suspension. The synergy effect took place in a large solar pilot plant scale, working in the near UV-fringe of sun-light [11]. It has been demonstrated that the tedious filtration of titania in slurry can be avoided by using a new photocatalytic material, Millennium PC500 titania coated on Ahlstrom non-woven paper [14].

The different kinds of pollutants were decomposed under a visible light: 4-chlorophenol [10,11,13,14], pes-

ticides [14–16], dyes [14,17], and nitrobenzene. The presence of anions – chloride, carbonate, bicarbonate, sulphate, and nitrate –, initial pH and small amount of FeSO₄ (0.01 M) had negligible effect on the photocatalytic degradation of nitrobenzene [12,13], 2-chlorobenzoic acid, and hydrobutanedioic acid [13].

The photocatalytic process under a visible light was applied to different kinds of installations, such as a flow reactor of the pilot plant at Plataforma Solar de Almeria (PSA) in Spain [10,11,13], the parabolic concentrator (CPC) [16] and reactor with a multi-step cascade falling-film [14].

In this paper, a photocatalytic activity under visible light on new TiO₂ catalysts modified by carbon via carbonisation of *n*-hexane was presented.

2. Experimental

2.1. Materials

Tytanpol A11 (Police, Poland) was as TiO₂ particles for carbon deposition. According to the manufacturer's data, Tytanpol A11 has a specific surface area of 11.4 m² g⁻¹ and consists mainly of anatase crystalline phase (min. 98.5%) with particle size of 0.2–0.4 μm.

2.2. Preparation of modified photocatalyst samples

TiO₂/carbon catalysts were obtained by keeping of TiO₂ in an atmosphere of *n*-hexane for 3, 4.5 and 6 h at temperatures of 400, 450 and 500 °C. In Fig. 1, the scheme of the installation is presented, which is equipped with the pipe furnace type R40/250/12-C40 (Nabertherm, Germany), where the modification of the catalysts was performed. About 1 g of titanium dioxide in a porcelain boat was placed into the tube of the furnace. The vapours of *n*-hexane were introduced inside to the furnace by bubbling of pure argon gas through liquid *n*-hexane at room temperature. The samples were

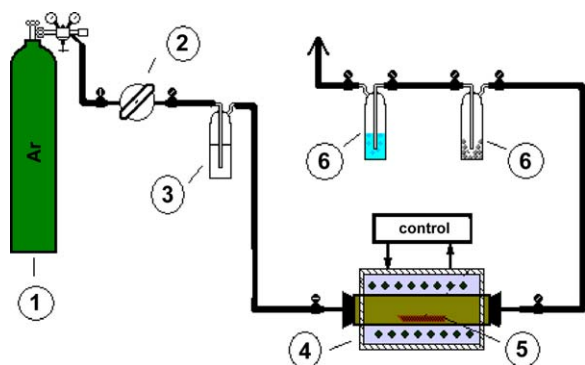


Fig. 1. The installation set-up for deposition of carbon on TiO_2 by carbonisation of *n*-hexane. 1–Gas cylinder with argon, 2–controller, 3–washer with *n*-hexane, 4–pipe furnace, 5–sample, 6–scrubber.

heated up to a programmed temperature (400, 450 or 500 °C) for 40 min and kept for 3, 4.5 and 6 h. After that time, the flow of *n*-hexane vapour was stopped, and then the pipe furnace was slowly cooled down to the room temperature (about 1.5 h). With increasing the heating time and the temperature, the samples changed from light to intensive grey colour. This colour was caused exclusively by carbon. The change of colour as result of reduction of Ti ions in TiO_2 from Ti(IV) to Ti(III) was eliminated. According to Szczepankiewicz [18], a band of ion Ti(III) around 3716 cm^{-1} should be found, whereas on the our FTIR spectra of photocatalysts modified by carbon, the presence of ion Ti(III) was not observed.

2.3. Experimental procedures and techniques

The photocatalytic decomposition of phenol was carried out in the glass beakers. The sample of 0.1 g was added to 500 ml of aqueous phenol solution with a concentration of 0.1 g l^{-1} . The solution was mixed 24 h with a magnetic stirrer during the irradiation of visible light (light Philips 100 W) with an intensity of about 354 W m^{-2} ($> 400\text{ nm}$) and UV irradiation 0.16 W m^{-2} ($< 400\text{ nm}$). The visible-light intensity was measured by the radiation intensity meter LB-901 with external sensors PD204AB (Macam Photometrics Ltd) and CM3 (Kipp and Zonen). In order to determine the concentration of phenol, a few millilitres of the solution were taken from the reaction mixture and loaded in the UV–Vis spectrometer (Jasco, Japan) after filtration by Millipore disk ($0.45\text{ }\mu\text{m}$). The concentration of phenol in the solution was calculated by a computer program, using a calibration curve.

The concentration of carbon was determined by *in situ* burning of the samples at 1000 °C in a thermogravimetric system (STA 449 C TGA, Netzsch, Germany) under a flow of air of 25 ml min^{-1} . For carbon calculation, the amount of chemisorbed and physisorbed water was taken into consideration.

The photocatalysts were characterised by UV–Vis/DR using Specord M40 spectrometer (Carl Zeiss, Jena, Germany) equipped with an integrating sphere accessory for diffuse reflectance spectra (BaSO_4 was used as a reference). Both, spectra and band-gap energy calculation (E_G) were performed by the Jasco procedure described elsewhere [19].

The diffuse reflectance FTIR spectra by using FTIR spectrometer (Jasco, Japan) equipped with DRS accessory of Harrick (USA) were recorded.

The turbidity of TiO_2 slurry after 24 h of irradiation and 10 min of sedimentation was measured by using a turbidimeter (PCompact, Aqualytic).

3. Results and discussion

The influence of the content of carbon on phenol decomposition after 24 h of visible-light irradiation is presented in Fig. 2a. The catalysts with small carbon content (0–0.15 mass%) and with high carbon content (0.69–0.85 mass%) have almost the same rate of phenol decomposition as the pristine A11. In this case, the adsorption of phenol for the sample with the maximum carbon content (0.85 mass%) was negligible (less than 0.3%).

In Fig. 2b, the influence of the content of carbon on the turbidity of phenol solutions is presented. The turbidity parameters of these samples can be compared because the particles size after carbon deposition remains the same as before. With increasing the content of carbon in the catalyst, the turbidity of the solution also increased. But only in the case of two catalysts with the carbon contents 0.69 and 0.85 mass%, the turbidity was definitely lower. The influence of the carbon on the surface of titanium dioxide was described in our previous paper [20].

The photoactivity of the catalysts and their ability to decantation (turbidity) are two important factors that have an influence on the ‘practical efficiency’ of photocatalysts. Araña et al. [21] defined the ‘practical efficiency’ of activated carbon– TiO_2 catalysts by taking

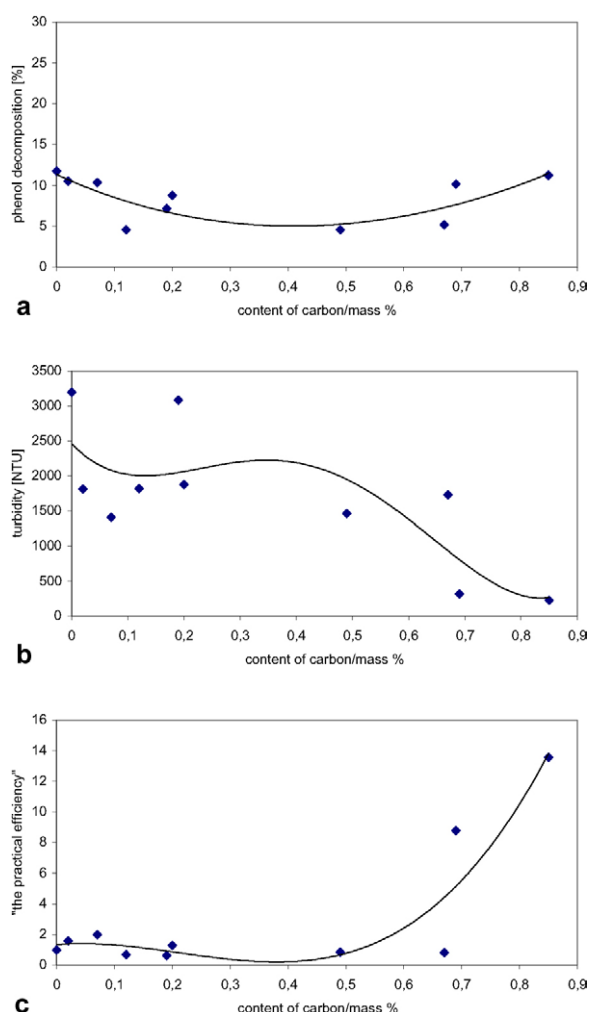


Fig. 2. The influence of the content of carbon in TiO_2 /carbon catalysts on: (a) phenol decomposition after 24 h of the visible-light irradiation; (b) turbidity of titanium slurry after 24 h of the visible-light irradiation and 10 min of sedimentation; (c) the 'practical efficiency'.

into account the rate constant for water mineralisation of TiO_2 and activated carbon– TiO_2 and also their ability to sedimentation. In this experiment, the formula to calculate the 'practical efficiency' of the catalysts was insignificantly modified, sedimentation was replaced with turbidity. After modification, the formula is as following:

$$\text{practical efficiency} = \frac{A_{\text{sample}}}{A_{\text{A11}}} \cdot \frac{1}{B}$$

A —% of phenol decomposition by the catalyst after 24 h of visible light irradiation;

B —normalised turbidity of the sample after 24 h of irradiation and 10 min of sedimentation.

In Fig. 2c, the 'practical efficiency', which is a relative value to the pristine catalyst A11, is presented for the present catalysts as a function of carbon content. For the catalysts that have a content of carbon under 0.69 mass%, the value of the 'practical efficiency' is around 1, but for the catalysts having the content of carbon from 0.69 to 0.85 mass%, the 'practical efficiency' is very high. The 'practical efficiency' of the catalyst containing 0.85 mass% of carbon is 14 times higher than that of pristine A11, because it has the smallest turbidity and the same photocatalytic activity as pure A11. It is worthwhile to mention that under UV radiation the present photocatalysts showed the highest value of the 'practical efficiency' at 0.2% carbon content [20].

For the catalysts containing small amounts of carbon, such as 0.2%, the character of the catalyst surface changed from hydrophobic to hydrophilic after the long time of photocatalytic reaction under visible light, as shown by the FTIR/DR spectra in Fig. 3a. From the change in spectrum before and after the photocatalytic reaction, the amount of hydroxyl groups was supposed to increase significantly after 24 h of reaction, which revealed that the modification of the surface of TiO_2 was not stable enough (the characteristic hydroxyl group bands were found at 2800–3700 and 1550–1800 cm^{-1}).

For two catalysts with high amounts of carbon, 0.69 and 0.85%, however, the character of their surfaces did not change, as shown by FTIR/DR in Fig. 3b; there is no change in the spectrums. This indicated that the modification of the surface was stable and that the reaction did not change the character of the photocatalysts surface.

For all the catalysts prepared, no difference in band-gap energy E_G measured from UV–Vis/DR spectra was detected; in other words, there is no change in E_G induced by the carbon modification, independently of the carbon content. The observed values of E_G were listed in Table 1. However, we have to point out that when we modified the surface of TiO_2 by carbon, the intensity of transmittance of visible light decreases and the catalysts adsorb the visible light, as shown in Fig. 4, e.g. for samples modified at a temperature of 400 °C. The behaviour of the intensity for the rest of the samples was the same.

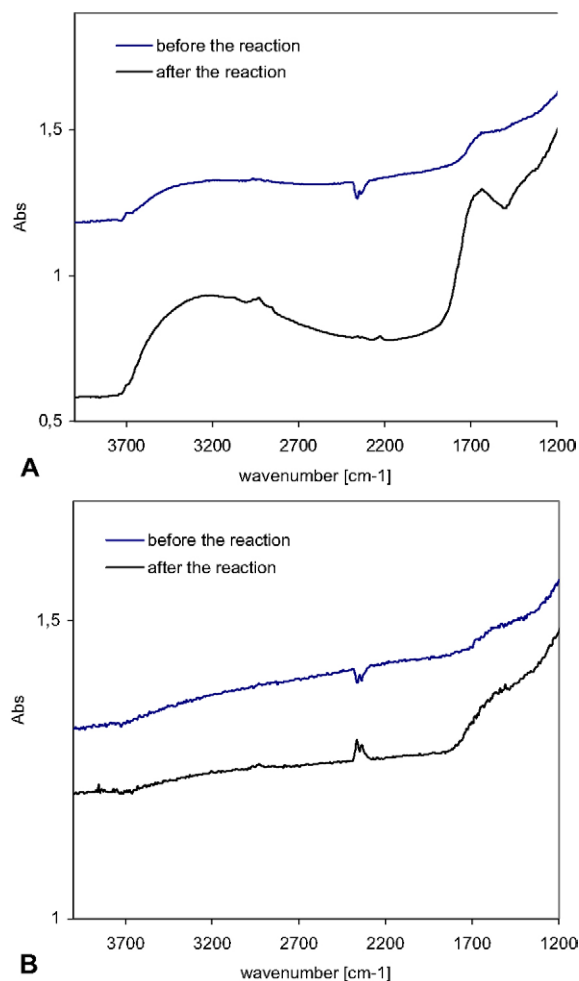


Fig. 3. FTIR spectra of TiO_2 and TiO_2 /carbon catalysts heated at: a) 450 °C for 4.5 h, before and after the photocatalytic reaction under visible light. b) 500 °C for 6 h, before and after the photocatalytic reaction under visible light.

Table 1
Calculated energy gap (E_g) for studied samples of photocatalysts

Contents of carbon in TiO_2 /carbon/mass%	E_g [eV]
0	3.31
0.07	3.36
0.12	3.36
0.19	3.38
0.20	3.38
0.49	3.39
0.67	3.34
0.69	3.42
0.85	3.42

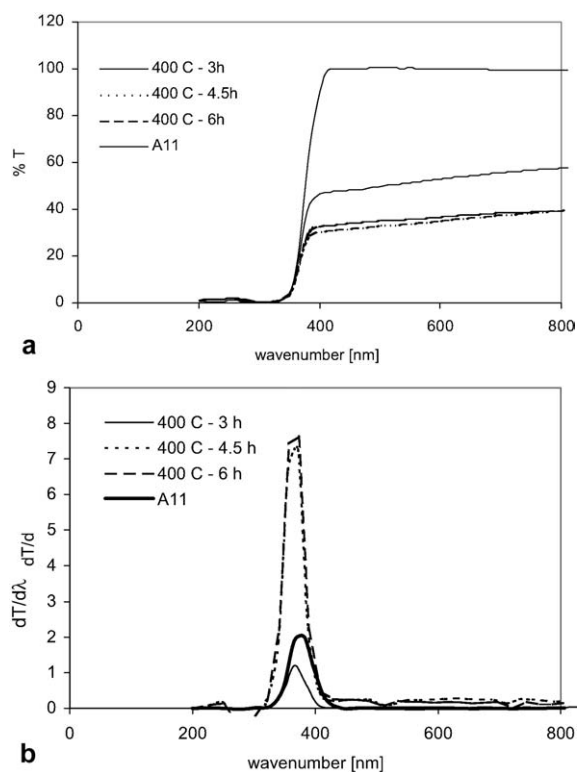


Fig. 4. The UV-Vis/DR absorption spectra (a) of a pure TiO_2 and the catalysts modified at a temperature of 400 °C and the first derivatives (b) of UV-Vis absorption.

The modification of TiO_2 by the 0.69 and more % of carbon deposition via *n*-hexane improved turbidity of solution after catalyst sedimentation, increasing in this way possibilities of practical application of TiO_2 as a photocatalyst in water-treatment systems under visible light.

4. Conclusions

The titanium dioxide of anatase form was modified by carbon deposition from carbonisation of *n*-hexane vapours at 400, 450 and 500 °C. The resultant catalysts were tested in the decomposition of phenol under visible light. The catalysts modified with 0.85 mass% carbon had only a little lower catalytic photoactivity under visible light than pure TiO_2 ; but showed almost 14-times higher turbidity in the solution than the pristine A11. The presence of carbon in TiO_2 reduces the hydroxyl groups on the surface of titanium dioxide via $-\text{CH}_3$ (alkenes) groups and in this way changes the character of

TiO₂ from hydrophilic to hydrophobic. Therefore, the photocatalyst showed a ‘practical efficiency’ 14 times higher than that of A11. Also the samples of highest carbon content (0.85%) form very stable composition with anatase under visible light.

The modification of TiO₂ by carbon deposition via *n*-hexane markedly improved turbidity of solution after catalyst sedimentation, which increases the possibilities of practical application of TiO₂ as a photocatalyst in water-treatment systems under visible light.

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