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PHOTOCATALYTIC ACTIVITY AND SURFACE PROPERTIES OF CARBON-DOPED TITANIUM DIOXIDE

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Carbon-doped TiO_2 was prepared by hydrolysis of titanium (IV) isopropoxide and calcination at 350ºC for 2h in air. Phenol (0.21 mM) was successfully degraded in the aqueous suspension of the powder, under visible light (λ>400 nm). Characteristics of obtained photocatalyst by BET method and UV-Vis diffuse reflectance spectroscopy showed about 127 m^2/g of specific surface area, absorption of light in the visible region and 3.35 eV of band gap energy. Photocatalytic activity and selected properties of five samples prepared independently were investigated.

key words: photocatalysis, carbon-doped TiO_2,visible light

INTRODUCTION

To achieve Vis light-activated TiO_2 many doping procedures using metal or non-metal heteroatoms were proposed. Single element or multi element doping with such non-metalic elements like carbon (Lettmann, 2001; Sakthivel, 2003; Tseng, 2006; Górska, 2008), nitrogen (Irie, 2003; Sakthivel, 2004; Kuroda, 2005; Zaleska 2007), sulphur (Umebayashi, 2003; Ohno, 2004), fluorine (Hattori 1998, Yamaki, 2002), iodine (Hong, 2005), chlorine (Long, 2007), phosphorus (Shi, 2006) and boron (Bettinelli, 2007; Zaleska 2008) can successfully modify TiO_2 properties and shift its photoactivity towards the visible region.

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Carbon could improve the photoactivity of TiO_2, stabilize anatase structure and increase adsorption of organic molecules on the photocatalyst surface (Tsumura, 2002; Janus, 2006; Ren, 2007; Górska, 2008). Tseng et al. studied oxidation of NO_x using their own carbon-doped catalysts, which were illuminated with UV and Vis light (Tseng, 2006). The catalysts were prepared by the sol-gel process using titanium alkoxide in ethanol solution with nitric acid as a catalyst, followed by calcination at 150 to 600ºC. Experimental results showed about 70% removal of NO_x in a continuous flow type reaction system with a modified catalyst. They stated that the presence of carbonaceous species and mixed crystalline phase in TiO_2 powder enhances absorption of visible light by the photocatalyst. A significant influence of the alkyl groups was observed by Lettmann et al. (Lettmann, 2001). TiO_2 catalysts were prepared by modified sol-gel process using different alkoxide precursors, in the absence of any dopant. Powders containing carbonaceous species revealed photocatalytic activity for 4-chlorophenol decomposition in visible light. Sakthivel and Kisch also observed 4-chlorophenol degradation in the presence of carbon-doped photocatalyst and diffused indoor daylight (Sakthivel, 2003). In this case, powders were prepared by hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide as a carbon precursor. Ren et al. reported higher rate of rhodamine B degradation for carbon-doped TiO_2 prepared by an impregnation of amorphous TiO_2 in aqueous solution of glucose in comparison to photocatalyst prepared by Sakthivel and Kisch, which was used as reference material (Ren, 2007).

Recently, TiO_2 powders were obtained by hydrolysis of TIP, in the absence of any dopant, and calcinated at temperatures ranging from 350 to 750ºC (Górska, 2008). The experimental data clearly indicated a correlation between light absorption by powders and their photocatalytic performance in phenol degradation. Absorbance over the entire VIS region and the highest phenol degradation efficiency under visible light (λ>400 nm) was observed for the sample calcinated at 350ºC. X-ray photoelectron spectroscopy confirmed presence of carbonaceous species at the TiO_2 surface. According to the literature, incorporation of carbonaceous species (C–C) occurs in highly condensed and coke-like structure, so it could play the role of a sensitizer to induce the visible light absorption and response (Lettmann, 2001; Tseng, 2006).

In this work we consider the reproducibility of carbon-doped TiO_2 effectiveness and selected properties. The photocatalyst was prepared by TIP hydrolysis and calcinations at 350°C. The photocatalytic activity in Vis light and selected properties of C–TiO_2 samples prepared in five independent runs were investigated. UV-Vis diffuse reflectance spectroscopy and BET methods were used to characterize the samples. Additionally, TiO_2 samples obtained by the same preparation procedure, but calcinated at temperatures lower than 350ºC (i.e. 250 and 300ºC), were studied.

METHODS

PREPARATION OF PHOTOCATALYST

Carbon-doped TiO_2 photocatalysts were obtained, according to procedures described earlier (Górska, 2006; Zaleska, 2007). Titanium (IV) isopropoxide (97%, Sigma-Aldrich Co., Germany) was hydrolyzed with distilled water only. Nitric acid was not used in the preparation procedure to avoid surface rutile, which is formed under such conditions (Tseng, 2006). After hydrolysis, the suspension was kept at 80ºC for 12h. The precipitate was filtered, rinsed with ethanol, dried at 80ºC for 12h and calcinated at 350ºC for 2h in air. The obtained carbon-doped TiO_2 was in the form of brown powder. The photocatalyst was prepared five times in separate batches, in order to investigate reproducibility of catalyst' properties.

MEASUREMENT OF PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of TiO_2 samples was estimated by measuring the decomposition rate of phenol in 0.21 mM aqueous solution under visible light. Phenol was selected as the model contaminant. Recently, phenol was proposed as one of four substrates in a multi photoactivity test (Choi, 2007). Phenol is present in wastewater from oil refining, pharmaceutical synthesis, electroplating, papermaking, coking and iron-smelting.

The experimental set-up for photocatalytic activity tests was described elsewhere (Górska, 2008). 1000 W Xenon lamp (6271H, Oriel) was used as the irradiation source. The optical path included water filter and glass filters (GG400, Schott AG) to cut off IR and UV irradiation, respectively. The temperature during the experiments was maintained at 10 ºC. 25 ml of aqueous suspension containing 125 mg of a photocatalyst and phenol were stirred magnetically and aerated (5 l/h) prior and during the irradiation. Aliquots of about 1.0 ml of the suspension were collected during irradiation and filtered through syringe filters (Ø=0.2 μm) to remove fine particles of the photocatalyst. The phenol concentration was estimated by the colorimetric method after derivatization with diazo-p-nitroaniline, using UV-Vis spectrophotometer (DU-7, Beckman).

Photocatalytic degradation runs were preceded with blind tests in the absence of a photocatalyst or illumination. Commercial TiO_2 P-25 (Degussa) was used as reference material.

CHARACTERISTICS

Gemini V Analyzer (Micromeritics Instrument Co.) was used for measurements of BET surface area, by physical adsorption and desorption of nitrogen. The UV-Vis/DR spectra were recorded using UV-Vis spectrometer (Jasco, V-530) equipped with integrating sphere accessory for diffuse reflectance. The band gap energy (E_g) was calculated from the first derivative of UV-Vis absorption, according to the Planck's equation. More details referring to these experimental procedures one can find in our previous papers (Zaleska, 2007, 2008; Górska, 2008).

RESULTS AND DISCUSSION

PHOTOCATALYTIC ACTIVITY

No degradation of phenol was observed in the absence of a photocatalyst or illumination. Phenol degradation efficiency results in Vis light for TiO_2 powders prepared by TIP hydrolysis, and for TiO_2 P-25 (Degussa) are presented in Figure 1.

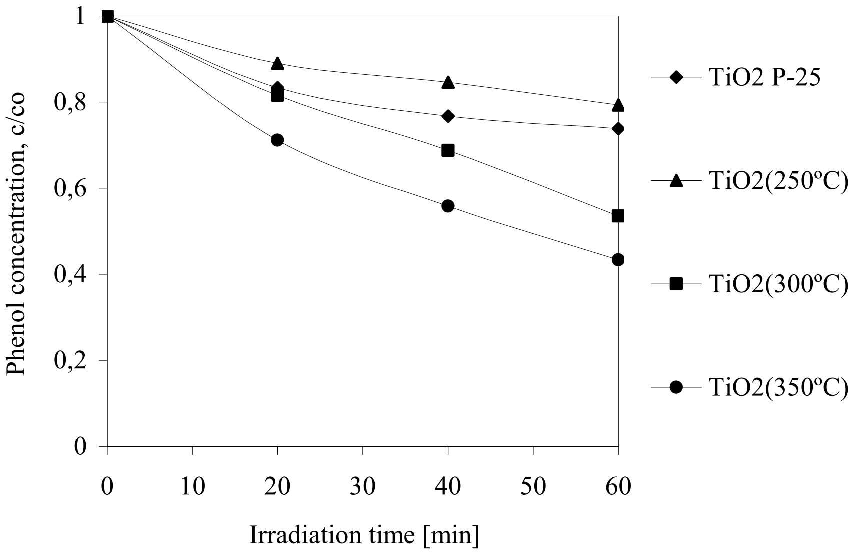

Fig. 1. Kinetics of photocatalytic degradation of phenol
in the irradiated suspension of prepared TiO_2 samples and TiO_2 P25
Experimental conditions: C_o=0.21 mM, m (TiO_2)=125 mg, T=10°C, Q_{air}=5 dm^3/h, λ>400 nm

The most efficient phenol degradation took place in irradiated suspension of sample calcinated at 350ºC i.e. TiO_2 (350ºC). After 60 min of irradiation, almost 60% of phenol was degraded. Sakthivel et al. observed 70% of TOC reduction (4-chlorophenol, c_o=0.25 mM) in carbon-doped TiO_2 suspension, irradiated with light having a wavelength equal to 455 nm (Sakthivel, 2003). The photocatalyst was prepared by $TiCl_4$ hydrolysis with tetrabutylammonium hydroxide and calcinated at 400ºC for 1 h. The authors reported that increasing the calcination temperature leads to a loss of photoactivity in the presence of visible light, which is in good agreement with our results published previously (Górska, 2008). At the same time of irradiation, Lettmann et al. reported 30% of 4-chlorophenol (c_o=0.25 mM) degradation after 100 min of irradiation (λ>400), in the presence of a catalyst obtained by TIP hydrolysis, followed by calcination at 250ºC for 3 h (Lettmann, 2001). In our case, irradiation of TiO_2 calcinated at 250ºC, resulted in the lowest contaminant degradation efficiency (20%), see Figure 1. Similarly, irradiation of reference suspension (TiO_2 P-25) resulted in 25% contaminant decomposition. Low degradation efficiency in this case was due to a poor photocatalytic activity of pure TiO_2 in the visible light (Fujishima and Zhang, 2006). TiO_2 powder calcinated at 300ºC also revealed lower photoactivity than TiO_2 (350ºC).

Phenol degradation efficiency results for five independently prepared TiO_2 (350ºC) catalyst samples are shown in Figure 2.

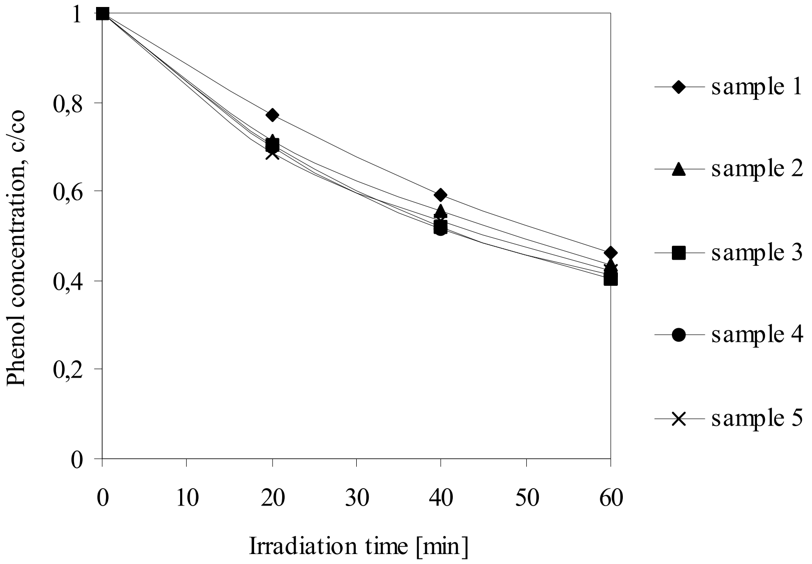

Fig. 2. Kinetics of photocatalytic degradation of phenol
in irradiated suspensions of TiO_2 calcinated at 350ºC
Experimental conditions: C_o=0.21 mM, m (TiO_2)=125 mg, T=10°C, Q_{air}=5 dm^3/h, λ>400 nm

Data in Figure 2 indicates that all TiO_2 (350°C) samples behaved similarly. Basing on these data, we calculated average values of phenol degradation efficiency after 20, 40 and 60 min of irradiation, including confidence limit, see Table 1.

Table 1. Phenol degradation efficiency for TiO_2(350°C) catalyst

Irradiation time [min]	Phenol degradation efficiency for TiO_2 (350°C), E [%]					$\overline{X} \pm \Delta X$
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	
20	28.9	23.0	29.7	30.1	31.2	28±4.0
40	44.2	40.8	47.8	48.6	46.8	46±3.9
60	56.6	54.0	59.8	58.7	57.8	57±2.8

The confidence level for these calculations was 95% and the statistical factor "t" (Student's t-distribusion) was 2.78 for four degrees of freedom.

CHARACTERISTICS

Values of specific surface area of five separately prepared TiO_2 (350°C) catalysts and an average S_{BET} with the confidence limit are presented in Table 2.

Table 2. Specific surface area of TiO_2 (350°C) catalyst

Specific surface area of TiO_2 (350°C), S_{BET} [m^2/g]					$\overline{X} \pm \Delta X$
Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	
127.4	127.3	127.0	127.1	126.8	127±0.3

The confidence level for these calculations was 95% and the statistical factor "t" (Student's t-distribusion) was 2.78 for four degrees of freedom.

All TiO_2 samples prepared by TIP hydrolysis and calcinated at 350°C had high specific surface area of about 127 m^2/g. An average S_{BET} value was more than two times greater than BET specific surface area of commercial TiO_2 P-25 (50 m^2/g). Large surface area may contribute to enhanced activity of TiO_2, but cannot be responsible for the highest phenol degradation efficiency in visible light, since samples with larger specific surface area, i.e. TiO_2(250°C) (136 m^2/g) and TiO_2(300°C) (131 m^2/g) revealed lower photoactivity, see Figure 1. On the other hand, large surface area is usually associated with numerous crystalline defects, which promote recombination of electrons and positively charged holes, leading to lower activity under UV irradiation (Carp, 2004).

UV-Vis absorption spectra of TiO_2 (350°C) samples and TiO_2 P-25 (Degussa) are presented in Figure 3. Pure TiO_2 P-25 showed clear absorption edge at around 350 nm and insignificant absorption in visible region above 400 nm. Visible light was absorbed by all TiO_2 (350°C) powders. In this case, absorption edge was not as sharp as the edge of reference material.

The band-gap energy values (E_g) were determined using the first derivative of UV-Vis absorption spectra. Usually, E_g values reported in the literature for anatase are around 3.2 eV, whilst 3.0 eV for pure rutile phase (Hoffmann, 1995; Ohno, 2004). The band-gap energy of pure TiO_2 P-25 was 3.15 eV, since this reference material is composed of two different TiO_2 crystalline phases, i.e. anatase (70%) and rutile (30%) (Macyk, 2003). Each investigated TiO_2 (350°C) sample had the band gap energy equal to 3.35 eV.

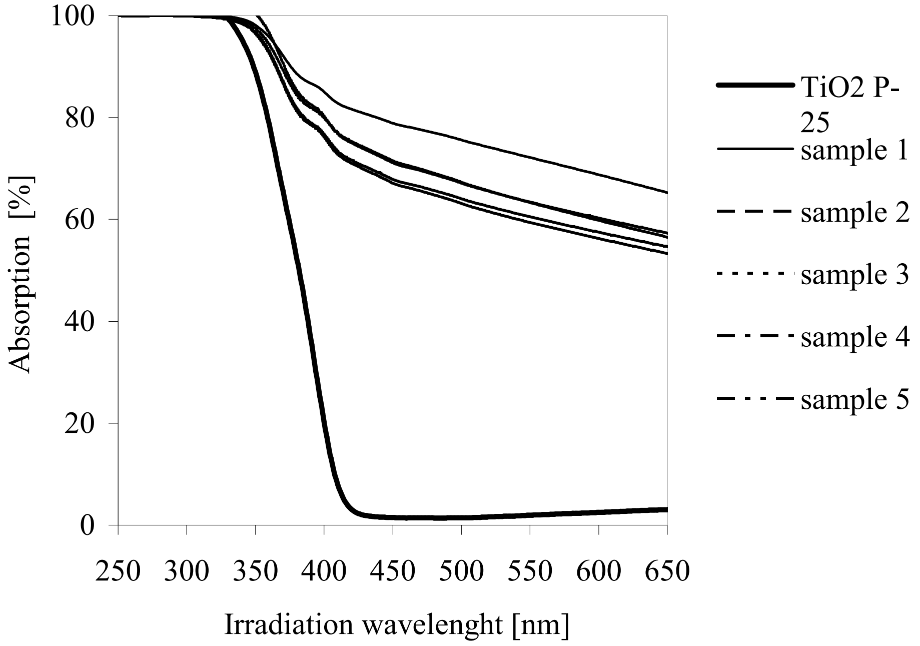

Fig. 3. UV-Vis absorption spectra of TiO_2 (350°C) samples and TiO_2 P25

The experimental results showed lack of band-gap narrowing, which was postulated by many researchers as main consequence of TiO_2 doping (Asahi, 2001; Sakthivel, 2003). The E_g value of our photocatalyst was wider than for pure bulk anatase. According to Saupe et al., this phenomenon is due to a combination of quantum size effects, caused by the crystallite size, and the dopant atoms in the structure (Saupe, 2005).

CONCLUSIONS

The experimental data confirm that the proposed preparation procedure provided reproducible effectiveness and studied properties of the photocatalyst. Five separately prepared TiO_2 (350°C) samples revealed comparable photoactivity under visible light, absorption properties and specific surface area.

According to a comparison between phenol degradation efficiencies of our carbon-doped TiO_2 and commercial TiO_2 P-25 (Degussa), see Table 3, we stated that our photocatalyst is more suitable for water purification under visible light. The experimental data confirm our earlier observations (Zaleska, 2007; 2008; Górska, 2008), that lack of band gap narrowing with increase of the absorption intensity still can lead to effective degradation of organic compounds. Enhanced visible light-activity of TiO_2 (350°C) catalyst resulted rather from the presence of carbon, mainly in the form of C–C species, as well as from high surface area, see Table 3. Content of C–C species in TiO_2 calcinated at 350ºC exceeds content in others samples, see our previous publication (Górska, 2008).

Table 3. Comparison of experimental results of TiO_2 (350°C) sample and TiO_2 P-25

Sample name	Phenol degradation efficiency after 60 min [%]	Specific surface area BET [m^2/g]	Band gap energy [eV]	Content of C–C species [at.%]
TiO_2 P_25	26.2	50	3.15	-
TiO_2 (350°C)	57.4[*]	127[*]	3.3[*]	10.3[**]

[*] an average value, calculated from data obtained for five separately prepared samples

[**] previously published result

Carbon-doped TiO_2 exhibited similar visible light activity with respect to some photocatalysts prepared in our previous investigations (Zaleska, 2007; 2008) using dopant precursors (boric acid triethyl ester, thiourea, thioacetamide). Moreover, the proposed procedure is simple, reproducible, obtained photocatalyst does not contain intentionally introduced elements, therefore, is more acceptable for industrial applications and subsequent disposal/reuse.

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GÓRSKA P., ZALESKA A., SUSKA A., HUPKA J., *Aktywność fotokatalityczna i właściwości powierzchniowe tlenku tytanu(iv) domieszkowanego węglem*

Górska P., Zaleska A., Suska A., Hupka J., *Aktywność fotokatalityczna i właściwości powierzchniowe tlenku tytanu (IV) domieszkowanego węglem,* Physicochemical Problems of Mineral Processing, 43 (2009), *21–30* (w jęz. ang)

TiO_2 domieszkowany węglem otrzymano poprzez hydrolizę izopropanolanu tytanu(IV) i kalcynację w 350 ºC w atmosferze powietrza przez 2h. Przeprowadzone badania wykazały, że fenol (0.21 mM) jest efektywnie degradowany w fazie wodnej, w obecności otrzymanego fotokatalizatora oraz światła z zakresu widzialnego (λ>400 nm). Pole powierzchni właściwej otrzymanego C–TiO_2 wynosiło około 127 m^2/g, fotokatalizator absorbuje światło z zakresu widzialnego a przerwa energetyczna E_g wynosi 3,35 eV. W pracy przebadano aktywność oraz wybrane właściwości dla pięciu niezależnie otrzymanych próbek.

słowa kluczowe: fotokataliza, TiO_2-domieszkowany węglem, światło widzialne