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Phthalocyanine-modified titania—catalyst for photooxidation of phenols by irradiation with visible light

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Abstract

The photooxidation of phenol, catalyzed by superficially modified with phthalocyanine complex (Pc) oxide supports (Al_2O_3 or TiO_2), has been studied upon irradiation with visible light. The rate of substrate photooxidation, catalyzed by Pc/TiO_2, is much higher than that over the sample obtained by anchoring the Pc complex on Al_2O_3. The degree of mineralization of phenol during photocatalysis in the presence of Pc/TiO_2 is also higher. The high photocatalytic activity of the sample is explained by the realization of an electron transfer from the conduction band of the excited phthalocyanine semiconductor particles to the conduction band of TiO_2 support. The increase of the quantum yield of the redox process comes as a result of the additional formation of superoxide radicals on the TiO_2 conduction band.

Keywords: Photocatalytic detoxification; Phthalocyanine semiconductors; TiO_2 particles; Phenol; Visible light

1. Introduction

The basic sources of natural waterways pollution and atmospheric pollution with organic compounds are the oil-processing plants, the cellulose industry, the use of oil fractions, natural gas and coal as fuels, fine chemicals and dye manufacturing industries. The phenols and the sulfur-containing compounds are among the basic soluble pollutants of communal and industrial waste waters. Oxidative decomposition and transformation of organic and inorganic substrates by oxygen using photocatalysts is one of the most frequently used methods for purification of waste waters. So far, two main techniques have been utilized for removing the sulfur and phenol containing pollutants from waste waters before discharging them into waterways. According to the first method, the pollutants are photocatalytically oxidized by oxygen with the use of semiconductors [1–3], whereas in the second one, the photocatalytic redox process occurs in the presence of molecular catalysts during irradiation with visible light [4–15].

Photocatalytic reactions on semiconductor powders are of great interest because of their applicability to the treatment of a large variety of pollutants [1–3]. During photocatalytic processes photoinduced electrons and holes can reduce and oxidize species adsorbed on the semiconductor particles [3]. One disadvantage of the particulate systems upon band gap excitation of the semiconductors is the high degree of recombination between the photogenerated charge carriers. As a results of the recombination between the photogenerated charge carriers, the photocatalyst effectivity is decreased as well as the quantum yield of the redox process. One of the semiconductors, most widely used as a photocatalyst, triggering the oxidative destruction and mineralization of organic substrates, is TiO_2. Due to the width of the band gap of TiO_2 (3.2 eV), the processes of catalytic oxidative destruction are accomplished upon irradiation with light of the UV region, where only approximately 4% of the solar radiation is effective. In order to overcome this disadvantage, semiconductors [16,17] or coupled semiconductor systems (heterotype “photochemical diodes”), in which one of them is excited upon visible light irradiation [18,19] are used. Applying photocatalysts, obtained by coupling two different semiconductor phases, an efficient charge separation can be obtained [19–21]. The anchoring of pigments, especially phthalocyanine complexes (Pcs) on wide-band gap semiconductors [17,22–24], is an alternative method in which a dye (sensitizer) adsorbed on TiO_2 surface gets excited by absorbing visible light and an intercomponent electron transfer is realized in the couple molecular semiconductor–TiO_2.

The catalytic activity of metal-free phthalocyanine complex (Pc), supported on Al_2O_3 or TiO_2, is studied in the present work upon irradiation of the sample with visible light. The oxidation of phenols and *p*-benzoquinones has

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been chosen as a model reaction. The *p*-benzoquinones are the possible intermediate products in the case of phenol catalytic oxidation in the presence of Pcs. The aim of the study is to investigate the influence of supports with semiconducting properties, such as TiO_2, upon the quantum yield of the redox process, photocatalyzed by the Pc. The photocatalytic activity of the Pc, supported on TiO_2, is compared to that displayed in the case when the pigment is supported on a support with dielectric properties (Al_2O_3).

2. Experimental

Merck phenol was used without further purification. The Merck *p*-benzoquinone was recrystallized consecutively in ethanol and tetrachloromethane before use. Fluka non-metallic 29H,31H-Pc was used without further purification. Al_2O_3 (Merck, 150, Typ T) and TiO_2 (Riedel-de Haen) were used as supports. The specific surface areas of Al_2O_3 (60 m^2/g) and TiO_2 (4 m^2/g) were measured using nitrogen adsorption method at 77 K and BET analysis. The small values of the surface area and of the porosity of the supports are suitable for supporting the large size phthalocyanine molecules. The morphological and structural differences of both carriers were observed by a scanning electron microscope (SEM) (JEOL model JSM-5300). As it can be seen from Fig. 1, the size and the porosity of the TiO_2 particles are quite smaller than those of Al_2O_3. X-ray diffraction patterns of TiO_2 powder were measured using Co Kα radiation (Fig. 2). The TiO_2 used as support is 100% anatase, which can be judged from the presence of a peak at $2\theta = 29.5°$ (Fig. 2) which is the major peak for this type of structure.

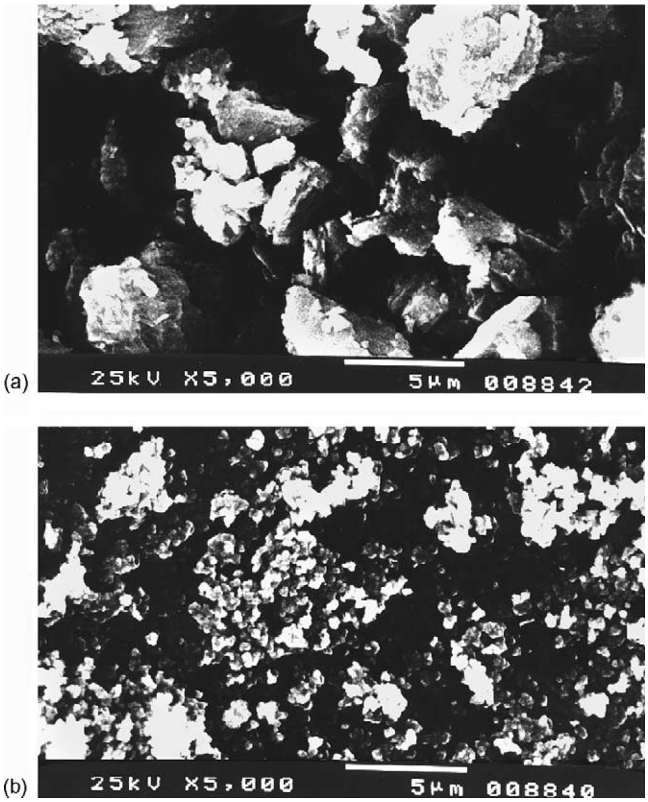


Fig. 1.

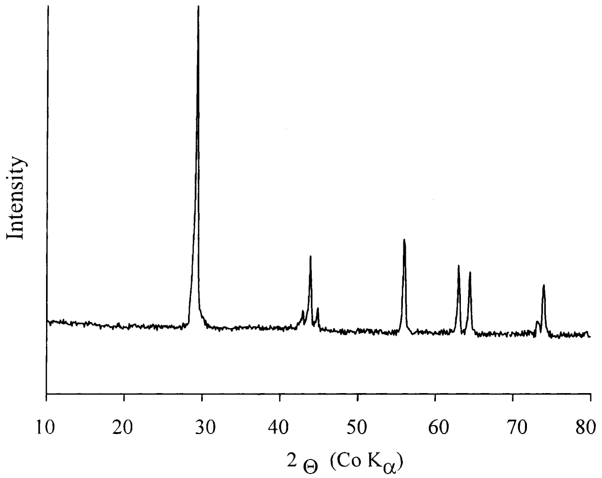


Fig. 2.

The anchoring of the Pc on Al_2O_3 and TiO_2 was carried out by their impregnation with a solution of the Pc in concentrated sulfuric acid. An amount of 1 g of the support is impregnated with 1.4 ml concentrated H_2SO_4, containing 10 mg of the Pc. The crystallization of the Pc is realized by purging the impregnated support with water vapor upon stirring and cooling down in the course of 30 min. The catalysts are washed with distilled water to pH = 7 and dried at temperature 393 K under vacuum. The supported Pc on Al_2O_3 or TiO_2 is 2.4×10^{-5} mol/g of support. The photocatalytic studies were carried out with 70 mg of the obtained catalysts, containing 1.7 μmol of the Pc. Due to the low concentration of the Pc (1.2 wt.%/g of support), it was impossible to evaluate the size of the crystallites of the pigment, supported on both supports, by means of SEM.

The rates of phenol photocatalytic oxidation were evaluated on the basis of the consumption of oxygen, which was measured using a gas burette. The oxidation process was performed at 293 K, pH = 9 and atmospheric pressure in a static reactor by exposure to a halogen lamp (12 V, 50 W), the illumination being 38 mW/cm^2. The products of the photocatalytic phenol and quinone oxidation reactions have been analyzed after the termination of the oxygen consumption. The oxidation products have been detected by elemental analysis, UV–VIS (Hewlett-Packard 89500) and IR (Bruker IRS-113V) spectroscopy.

3. Results and discussion

The results from phenol and *p*-benzoquinone catalytic and photocatalytic oxidation in the presence of the investigated samples are represented in Table 1. The standard calculation

Table 1
Catalytic oxidation of phenol (0.64 mmol) and *p*-benzoquinone (0.64 mmol) in an H_2O–ethanol solution (2:1)

Catalyst[a]	Substrate	ml O_2/min	μmol O_2/min	Total O_2 consumption[b] mol O_2/mol	mol CO_2/mol substrate (±10%)[b]	Degradation of Pc (±10%)[b]
No	Phenol	0.02	0.9	–	–	–
Pc/Al_2O_3[c]	Phenol	0.04	1.8	–	–	–
Pc/TiO_2[c]	Phenol	0.03	1.3	–	–	–
Pc/Al_2O_3[d]	Phenol	0.09	4.2	4.2	0.95	5
Pc/TiO_2[d]	Phenol	0.18	8.1	6.9	1.5	8
No	Benzoquinone	0.30	13.2	2.8	–	–
Pc/Al_2O_3[d]	Benzoquinone	0.31	13.9	3.9	0.8	4
Pc/TiO_2[d]	Benzoquinone	0.33	14.8	4.7	1.2	5

Temperature 298 K, pH = 9.2, O_2 partial pressure = 1 atm.

[a] 1.7 μmol phthalocyanine complex.

[b] At the end of the catalytic process.

[c] In the absence of irradiation.

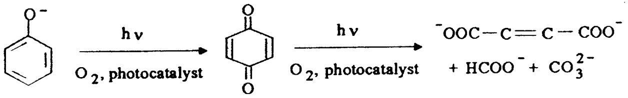
[d] Upon irradiation.

methods were applied to determine the initial rates of phenol conversion. The catalytic and photocatalytic activity of the samples in the oxidation of the substrates is expressed by the rate of oxygen consumption (mol O_2/min). The photodestruction of phenol and *p*-benzoquinone into CO_2 at the end of the catalytic process (mol CO_2/mol phenol) in the presence of Pc/Al_2O_3 and Pc/TiO_2 are also represented in Table 1. The degradation of the metal-free Pc at the end of the catalytic process, determined by a method described earlier [6,9], is represented in Table 1. The photodegradation degree of the Pc, supported on the used oxidic carriers, is considerably lower than that registered earlier [6,9] using this type of photocatalysts in homogeneous-catalytic processes. The singlet oxygen, generated by the photoexcited phthalocyanine molecules in a homogeneous phase, is the reason for the high degree of destruction of the catalysts.

The reaction products of the photocatalytic phenol oxidation have been analyzed after the termination of the oxygen consumption. The final oxygen consumption value, obtained as a result of phenol photooxidation at pH = 9, catalyzed by the Pc, anchored on supports lies within the range 3.3–4.6 mol O_2/mol phenol (Table 1). The quantity of consumed O_2 during photooxidation of phenols catalyzed by Pc anchored on supports show that the oxidation of the substrate does not occur completely to form CO_2. An amount of 5.5 mol O_2/mol phenol are needed stoichiometrically for the proceeding of the oxidative photodestruction of phenol to CO_2. This fact is confirmed by the analysis of the phenol oxidation products. After termination of the photocatalytic process, the solution was acidified down to pH = 2 and then extracted with ether. The solution is vaporized and the residual is recrystallized from ethanol–water (2:1) medium. The crystalline product is characterized by elemental analysis and IR spectroscopy and it represents a mixture of fumaric and maleic acid. The elemental analysis gives: calculated H, 3.45; C, 41.38; found H, 3.52; C, 40.95. IR (CsI): 1711, 1676 cm^{-1} (νC=O); 1430 cm^{-1} (νC–O); 1632 cm^{-1} (νC=C).

According to the method described in [8,15], it was established that CO_2 is being formed as a result of the mineralization of phenols at pH = 9. After the termination of the catalytic process the reaction mixture is treated with acidic agent and the quantity of carbon dioxide is determined as $BaCO_3$ gravimetrically. The determined amount of CO_2 in the presence of Pc/TiO_2 and Pc/Al_2O_3 (within the limits of the experimental error) is listed in Table 1.

We draw the conclusion, based on the analysis of the reaction products and the quantity of consumed oxygen, that the photocatalytic oxidation of phenol in alkaline medium proceeds in accordance with the following general equation:



(1)

A mixture of CO_2, fumaric, maleic and formic acids is obtained finally as products from the catalytic oxidation of the phenoxide anion. During oxidation of phenols in alkaline medium, catalyzed by Pcs, *p*-benzoquinone is one of the basic intermediate products of the substrate photodestruction [8,15]. The *p*-benzoquinone is oxidized easily by oxygen in alkaline aqueous solution even in the absence of catalysts [4,25].

The metal-free Pc, deposited on the supports, does not display any catalytic activity in the dark (Table 1). Upon irradiation with visible light ($\lambda > 450$ nm), the catalytic activities of both types of catalysts grow up substantially (Fig. 3). No catalytic oxidation of phenol is registered in the presence of TiO_2 upon illumination with light of $\lambda > 450$ nm. This is explicable in view of the band gap energy E_G = 3.2 eV) of this photocatalyst of the semiconductor type. The experimental results (Fig. 3) show some differences in the photocatalytic properties of the metal-free Pc anchored on TiO_2 or Al_2O_3. The rate of phenoxide ion oxidation in the presence of Pc/TiO_2 is much higher than that of the sample, prepared by anchoring of the Pc on Al_2O_3 (Table 1). In the

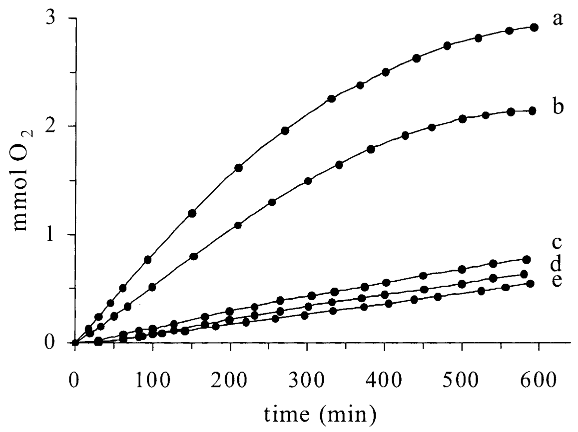


Fig. 3.

case of photocatalytic oxidation in the presence of Pc/TiO_2, the mineralization of phenol is also higher (Table 1). The catalytic properties of the deposited Pc may be explained by the different degree of involvement of the supports in the photocatalytic process.

The increase of the catalytic activity of the Pc, anchored on supports, upon irradiation with visible light is associated with the semiconductor properties in the solid state of these organic systems. One of the most important differences between these van der Waals-bonded molecular organic semiconductors and the typical covalently bonded inorganic semiconductors is the extent of orbital overlap along the conducting pathway [26]. The phthalocyanines in the solid state behave as p-type semiconductors [27–29], characterized by energy of the band gap about 2 eV [30]. This enables the excitation of the molecular semiconductor with visible light. Considering the earlier reports on the dye-sensitized photocatalytic oxidation of pollutants [17,31,32], the following mechanism is proposed for the first step of the phenoxide ion (PhO^-) oxidation upon applying non-semiconductor oxides (MeO) as supports (Eqs. (2)–(7)).

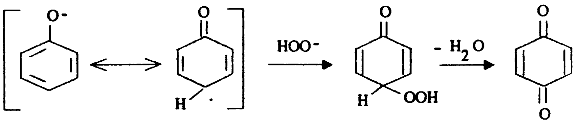
$$\mathrm{MeO–(Pc)_s} \xrightarrow{h\nu} \mathrm{MeO–(Pc^*)_s} \quad (2)$$

$$\mathrm{MeO–(Pc^*)_s} \rightarrow \mathrm{MeO–(Pc} + e^-_{\mathrm{CB}})_s \quad (3)$$

$$\mathrm{MeO–(Pc^+} + e^-_{\mathrm{CB}})_s + \mathrm{PhO^-} \rightarrow \mathrm{MeO–(Pc^+} + e^-_{\mathrm{CB}})_s + \mathrm{PhO^\bullet} \quad (4)$$

$$\mathrm{MeO–(Pc} + e^-_{\mathrm{CB}})_s + \mathrm{O_2} \rightarrow \mathrm{MeO–(Pc)_s} + \mathrm{O_2{}^{\bullet -}} \quad (5)$$

$$\mathrm{O_2{}^{\bullet -}} + \mathrm{H_2O} \rightarrow \mathrm{HOO^\bullet} + \mathrm{OH^-} \quad (6)$$



(7)

In the case of Pc/Al_2O_3 catalyst, illumination with visible light ($h\nu$) results in the excitation of the surface adsorbed phthalocyanine particles (Eq. (2)) which effects charge transition into the conduction band in the excited state (Eq. (3)). The phenoxide anions serve to reduce the oxidized superficially adsorbed dye (Eq. (4)), while the electron in the conduction band (e^-_{CB}) is transferred to molecular oxygen (O_2) leading to the formation of superoxide/hydroperoxide radicals ($O_2{}^{\bullet -}/HO_2{}^{\bullet}$) in the system (Eqs. (5) and (6)). The hydroperoxide radicals interact with the phenoxide anions (Eq. (7)) to produce *p*-benzoquinone in the first step of the photocatalytic redox process, catalyzed by the molecular semiconductor (Pc). The next steps of the photocatalytic redox process occur through a series of consecutive reactions (Eq. (1)), studied earlier [8,12,14,15,33].

The photocatalytic behavior of the Pc supported on TiO_2 can be explained considering the position of the energy levels of the two semiconductors. At pH = 7, the conduction band of Pc ($E_G = 2.0$ eV) is estimated to be at least 600 mV more cathodic than the conduction band of TiO_2 ($E_G = 3.2$ eV), while the valence band of TiO_2 is significantly more positive than the corresponding band of Pc [22,24,34]. Upon irradiation with light $\lambda > 460$ nm, it is possible to excite only the phthalocyanine particles, supported on TiO_2, which effects a charge transition into the conduction band in the excited state inside them. The photoinduced redox process, in accordance with Eqs. (4) and (5), involving the participation of adsorbed PhO^- and O_2 on the surface of the phthalocyanine particles, can proceed. The quantum yield of the redox process, catalyzed by the molecular semiconductor is not high [22], which is a prerequisite for accomplishing the electron transfer over to the conduction band of TiO_2. The probability of realizing an electron transfer from the conduction band of the excited phthalocyanine particle, to the conduction band of TiO_2 is higher, taking into account the investigation on this process [18,22–24]. The intercomponent electron transfer in the couple, molecular semiconductor–TiO_2, and the occurring of the catalytic redox process is represented schematically in Fig. 4. As it can be seen, the oxygen molecule O_2, may interact with the conduction bands of both semiconductors (Fig. 4), as a result of which the quantum yield of the photoprocess and the

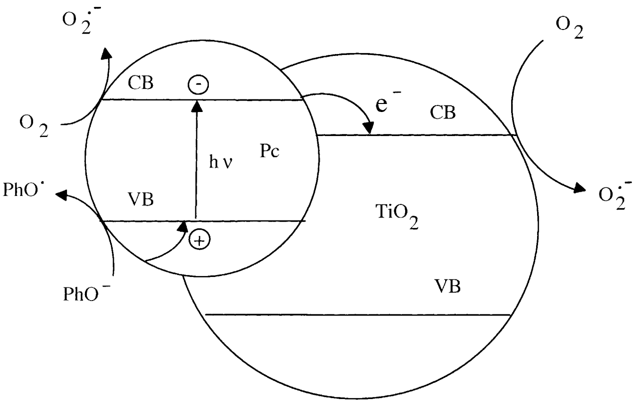


Fig. 4.

respective formation of superoxide radical ($O_2^{\bullet -}$), are increased. Therefore, the promotion of the photocatalytic activity in the system Pc-oxide semiconductor (Table 1) could be explained by the formation of superoxide radical ($O_2^{\bullet -}$) on the TiO_2 conduction band (Fig. 4) and by the additionally occurring redox process in accordance with Eqs. (6) and (7).

The size of the phthalocyanine crystallites, supported on both carriers, may also influence the photocatalytic activity of the studied samples. The effect of this factor on the photocatalytic activity could not been estimated in this study due to the low concentration of the supported Pc. Having in mind the adsorption properties of the oxidic supports with respect to dyes with strongly conjugated π-aromatic systems [35], it may be expected that the crystalline size of the Pc would not differ substantially.

4. Conclusions

The non-metallic 29H,31H-Pc anchored on TiO_2 is much more effective catalyst for the oxidation of phenols upon irradiation with visible light compared to the sample obtained by anchoring the Pc complex on Al_2O_3. The high photocatalytic activity of the Pc/TiO_2 is explained by the realization of an electron transfer from the conduction band of the excited phthalocyanine semiconductor particles to the conduction band of the TiO_2 support. The increase of the quantum yield of the redox process and the much higher degree of mineralization of the substrate comes as a result of the additional formation of superoxide radicals on the TiO_2 conduction band.

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