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Photocatalytic detoxification with TiO_2 supported on glass-fibre by using artificial and natural light

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Abstract

The preparation of TiO_2 supported on glass-fibre by sol–gel method is presented. We investigated the influence of thermal treatment time on specific surface, crystallinity and photocatalytic activity of the semiconductor for the degradation of a model pollutant: the benzamide. We have evaluated the photocatalytic activity of this supported catalyst (TiO_2-FG) with the laboratory reactor and the CPC reactor. The best activity results have been achieved through a 500°C treatment lasting 20 h. These conditions have been applied to prepare TiO_2 supported on glass-fibre. We have shown that the same catalyst can be reused several times. The supported catalysts have a good photocatalytic activity towards benzamide. However, the evolution of total organic carbon (TOC) from the test with TiO_2-FG is very slow. This observation carries out that the degradation process is not the same as that with the classical TiO_2-P25. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Glass-fibre; Benzamide; TiO_2

1. Introduction

In recent years, the heterogeneous photocatalysis for total oxidation of organic and inorganic water pollutants has been studied extensively [1]. Such reactions have usually been carried out using suspensions of powdered TiO_2. However, the filtration of the slurries is very difficult for great quantities. Recently, a few studies have concerned the preparation of photocatalyst on different supports (for example, glass plate [2] or glass-fibre [3]). The most used and efficient technique to immobilise TiO_2 on the support is the sol–gel [4], providing that the experimental parameters of this technique are perfectly known.

In this paper, we present the preparation and report the use of TiO_2 supported on glass-fibre by sol–gel method. In the first step, we have improved the preparation of TiO_2 issued by sol–gel method. We investigated, with our laboratory reactor, the influence of this parameter on specific surface, crystallinity and photocatalytic activity of the semiconductor. In the second step, we have evaluated the photocatalytic activity of supported catalyst (TiO_2-FG) with the laboratory reactor and the CPC reactor (compound parabolic collectors) at the Plataforma Solar de Almería, in Spain (PSA). The aim of this work is not to compare the two reactors, but to study the efficiency and the stability of the TiO_2-FG samples.

2. Experimental

2.1. Preparation and characterisation of TiO_2 particles alone and supported [5]

The process that has been used is the sol–gel method. This method consists of synthesising a TiO_2

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gel by hydrolysis and condensation of a precursor, like titanium tetraisopropoxide (TTIP), and the thermal treatment of this gel gives the crystalline TiO_2. It is, however, necessary to control some factors in order to achieve a high quality product. Among the most important factors are the thermal treatment duration and temperature of the TiO_2 precursor gel. Different treatment times have been tested at 500°C (this temperature is necessary to obtain an anatase phase, and because the mechanical properties of glass-fibre are not preserved above 550°C). The specific surfaces of these samples were determined by N_2 adsorption analysis (BET method). The crystalline phase was determined by the X-ray diffraction method (XRD).

For the supported TiO_2, the beginning of the preparation is the same. Before the thermal treatment, the glass-fibre from Saint-Gobain Research (SGR-France) is dipped in the colloidal solution for 10 min. The fibre is withdrawn from the solution, dried for 1 h at 110°C and calcinated for 20 h at 500°C in air.

2.2. *Evaluation of the photocatalytic activity*

The photocatalytic activities of TiO_2 and TiO_2-FG were tested using benzamide solution. This aromatic amide was chosen as a model compound because it is a representative water organic pollutant [6]. In all cases, benzamide degradation follows a pseudo first-order kinetic. The evolution of benzamide concentrations related to the irradiation times has been compared for all photocatalysts, and the rate constants have been calculated. The degradation intermediates have not been determined. The TiO_2-P25 of Degussa is the reference catalyst.

2.2.1. *Reactors and light sources*

2.2.1.1. Laboratory reactor. The laboratory reactor employed has been previously described [7,8]. Experiments were carried out in a Pyrex photochemical reactor with a 450 W medium pressure mercury lamp (HANOVIA PC 451-050; arc length, 4.8 cm). Running water is passed through the timble to cool the reaction solution. Some tests are made to verify that no direct photolysis is observed in these conditions. The benzamide solution is continuously recirculated with a pump (flow rate, $8\,dm^3\,h^{-1}$); the total volume treated is 600 ml.

2.2.1.2. CPC reactor. The CPC reactor has been described by Marques et al. [9]. The CPC reactor consists of a series of tubes (diameter, 27 mm; length, 960 mm). The CPC faces south, with an elevation of 37°, to maximise the amount of radiation received by the tube (PSA is located at 37° latitude). The benzamide solution is continuously recirculated with a pump (flow rate, $4.8\,dm^3\,h^{-1}$). For the tests with the supported catalysts, we have used only one tube. The total volume of the treated solution is 1300 ml.

2.2.2. *Procedure and analysis*

For both reactors, the initial concentration of benzamide was $20\,mg\,l^{-1}$ and the time zero is the beginning of irradiation. For all experiments with the suspensions, TiO_2 ($1\,g\,l^{-1}$) is introduced into the tank. The illuminated volumes were 400 and 500 ml for the laboratory reactor and the CPC, respectively.

Benzamide concentrations at different irradiation times were followed by HPLC after filtration (Whatmann, 0.45 mm) with a C18 column. The total organic carbon (TOC) was determined by a liquid TOC^{TM} instrument of Heraeus in the presence of sodium persulfate after acidification of the non-filtered samples.

3. Results and discussion

3.1. *Influence of the thermal treatment duration*

The results of thermal treatment on TiO_2 particles are presented in Table 1. The initial sol–gel layer (dried for 1 h at 110°C) presents a large specific area ($300\,m^2\,g^{-1}$). The specific surface decreases rapidly when the thermal treatment duration increases. This is in accordance with the results of Zaharescu et al. [10]. The crystallinity of the prepared TiO_2 depends much on the temperature and the duration of the initial sol–gel layer treatment. To obtain good quality TiO_2 crystals, a 500°C temperature is needed with a treatment time more than 10 h. After studying the X-ray diffraction pattern (Fig. 1), we can observe that only the crystalline form ‘anatase’ is present. This result is

Table 1
Characteristics of the TiO_2 samples

Temperature (°C)	Time (h)	Crystallinity[a] (anatase form)	Specific surface ($m^2 g^{-1}$)	k[b] (min^{-1})
100	1	am	300	0.2×10^{-2}
500	5	m	–	0.9×10^{-2}
500	10	s	67	1.8×10^{-2}
500	20	s	26	4.5×10^{-2}

[a] am, amorphe; m, medium signal; s, strong signal.

[b] Benzamide disappearance rate constant.

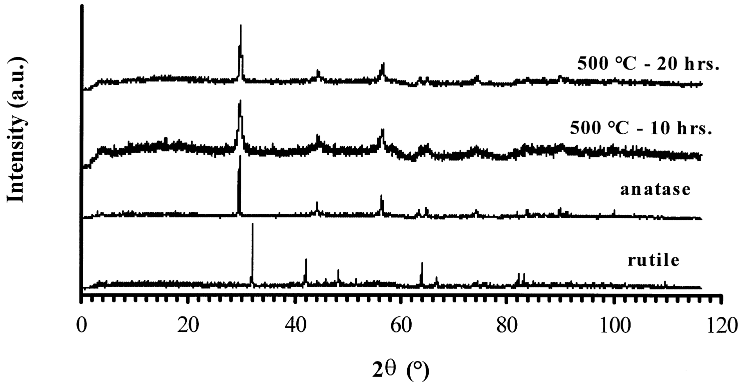

Fig. 1. X-ray diffraction pattern of the samples.

very important because anatase is the most efficient TiO_2 crystalline form for catalysis [11].

The influence of the treatment duration on the photocatalytic activity has been evaluated only with the laboratory reactor. We have noticed that the disappearance rate of the benzamide increases with the duration of thermal treatment (Fig. 2 and Table 1). In other experiments, we have noted that for pure anatase (from Prolabo), the degradation rate constant is 4.9×10^{-2} min^{-1}. In this case, the photocatalysts' specific surface has a low influence because there is a low variation between the samples treated at 500°C (see Table 1). The most important factor is the crystallinity of the catalysts. The most efficient samples are the best-crystallised ones.

3.2. Evaluation of the photocatalytic activity of TiO_2 supported on glass-fibre

According to the first results of the TiO_2 synthesis [5], all TiO_2-FG samples have been prepared for 20 h at 500°C, in order to test their reactivity and their stability after several uses.

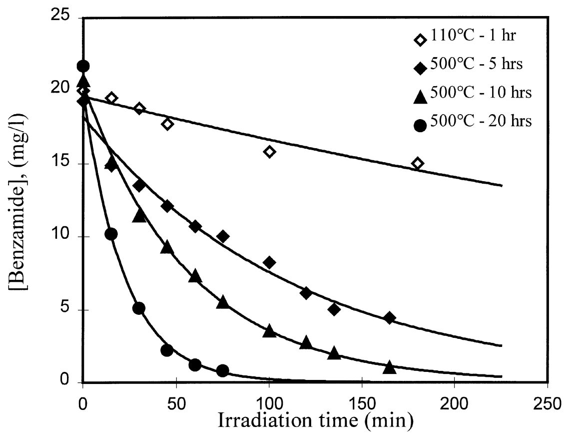

Fig. 2. Effect of thermal treatment time on the photocatalytic degradation of benzamide.

3.2.1. With a laboratory reactor

One sample has been prepared for these tests. The quantity of TiO_2-FG is 6.1 g, with about 10% of TiO_2 in weight (0.6 g), corresponding to $[TiO_2] = 1\,g\,l^{-1}$. This sample has been tested three times with three dif-

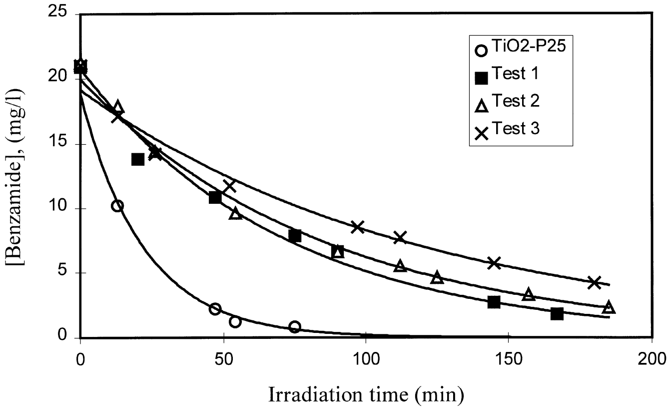

Fig. 3. Disappearance of benzamide with TiO_2 supported on glass-fibre and TiO_2-P25 in the laboratory experiments.

ferent solutions of benzamide, and TiO_2-P25 ($1\,g\,l^{-1}$) is the reference catalyst. Fig. 3 shows the disappearance of benzamide as a function of irradiation time.

The disappearance of benzamide has a pseudo first-order reaction rate. The supported catalyst presents a good photocatalytic activity (after 3 h, 90% of the benzamide is eliminated) and an acceptable stability. After three experiments, the degradation rate decreases by 30% (for tests 1, 2 and 3, the rate constants are, respectively, 1.4×10^{-2}, 1.17×10^{-2} and $0.84 \times 10^{-2}\,min^{-1}$). This decreasing activity is probably due to a small part of TiO_2 that takes off from the fibre and is eliminated after the first step. Consequently, the TiO_2 concentration is lower than $1\,g\,l^{-1}$. This quantity of TiO_2 is difficult to evaluate because a small part of fibre is also eliminated after the first experiment.

3.2.2. With a CPC reactor (PSA)

Two samples have been prepared: TiO_2-FG1 and TiO_2-FG2. TiO_2-FG1 contains 9% of TiO_2 in weight ($m_1 = 4.22\,g$). For TiO_2-FG2, the procedure is the same, but after thermal treatment, the fibre has been dipped a second time in the colloidal solution of TiO_2 and recalcinated for 20 h at 500°C. TiO_2-FG2 contains 12.5% of TiO_2 in weight ($m_2 = 4.33\,g$). The preliminary tests are made without catalyst to verify that the benzamide does not degrade by direct photolysis and with the virgin fibre (Fig. 4). All the tests have been made in the same light conditions (except for test 1 with TiO_2-FG1, conducted in cloudy weather).

In these conditions, the results show that benzamide is not degraded by direct photolysis or with virgin fibre. The results with the supported catalysts are encouraging because 60% of the benzamide is degraded after 400 min. However, the difference observed with TiO_2-P25 is significant. But it must be noticed that for the tests made with fibre, the catalyst concentrations are at most equal to $0.29\,g\,l^{-1}$ for TiO_2-FG1 and $0.4\,g\,l^{-1}$ for TiO_2-FG2 (the calculation of this concentration takes into account the fibre loss of weight after thermal treatment — about 3%). For TiO_2-P25, the concentration is $1\,g\,l^{-1}$. We have shown in other works [12] that the TiO_2 concentration (particularly between 0.1 and $1\,g\,l^{-1}$) has a significant influence on the benzamide disappearance rate. For example, the rate constant is divided per two between 0.4 and $1\,g\,l^{-1}$. There is no significant difference between both samples (TiO_2-FG1 and TiO_2-FG2) because their TiO_2 concentrations are very similar.

To verify if a TiO_2-FG sample can be reused with the CPC reactor, we have tested the sample twice with different benzamide solutions in the same conditions. The results are presented in Fig. 5.

The flux corrections have been done in order to compare all experiments. In this case, the benzamide concentration is represented versus a Q factor, calculated with the following equation: $Q = Wt(A/V)$, where Wt is direct radiation arriving at the CPCs from the beginning of the experiment to the time corresponding to the sample considered ($J\,m^{-2}$), A is the total area able to receive radiation (m^2), and V is the total volume of treated solution (l).

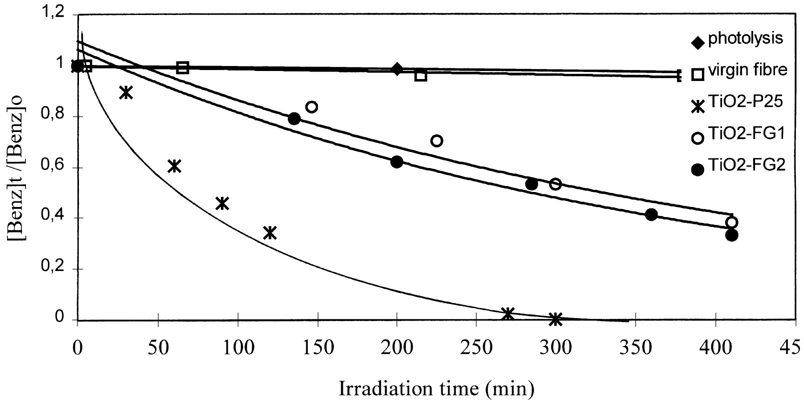

Fig. 4. Disappearance of benzamide with TiO_2 supported on glass-fibre and TiO_2-P25 in CPC experiments.

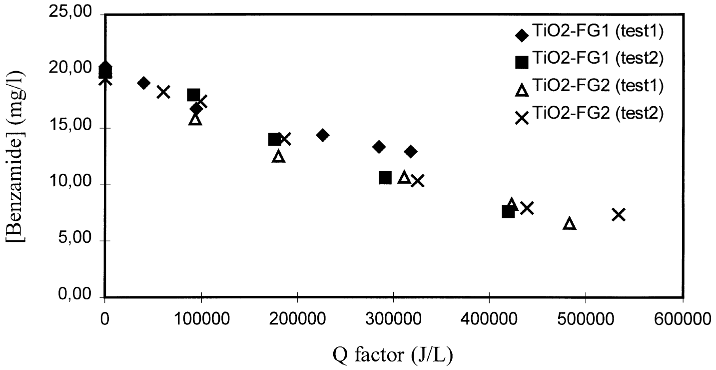

Fig. 5. Disappearance of benzamide with TiO_2 supported on glass-fibre in CPC experiments (reuse of the same sample).

We have shown from these tests that the same TiO_2-fibre sample can be reused twice. This is an important result for the industrial treatment of water by photocatalysis.

In Almería, the benzamide disappearance kinetic has been followed with the total organic carbon (Fig. 6). In the presence of TiO_2-P25, the TOC results are identical with those described by reference [6]. However, in the case of a treatment with samples prepared by sol–gel method (in slurry or immobilised on glass-fibre), the kinetic related to the TOC is different. TOC evolution is slow even after the complete disappearance of the benzamide. For example, when 90% of the benzamide is degraded, the decrease of TOC is 70% for P25 and only 45% for the sol–gel. The unlike evolution of TOC could be explained by a different degradation scheme of benzamide when used with P25 or with sol–gel, but also by a slower degradation of intermediate products with a TiO_2 prepared by sol–gel method. Experiments have been carried out to verify that TiO_2–sol–gel does not itself reject pollutants in water. In the case of sol–gel processes, the degradation intermediates are being studied to explain this difference.

4. Conclusions

The parameters of thermal treatment necessary to obtain TiO_2 (through sol–gel method) have been improved by taking into account the disappearance kinetic of benzamide. The best activity results have been achieved through a 500°C treatment lasting 20 h. These conditions have been applied to prepare TiO_2 supported on glass-fibre. The supported catalysts have a good photocatalytic activity towards benza-

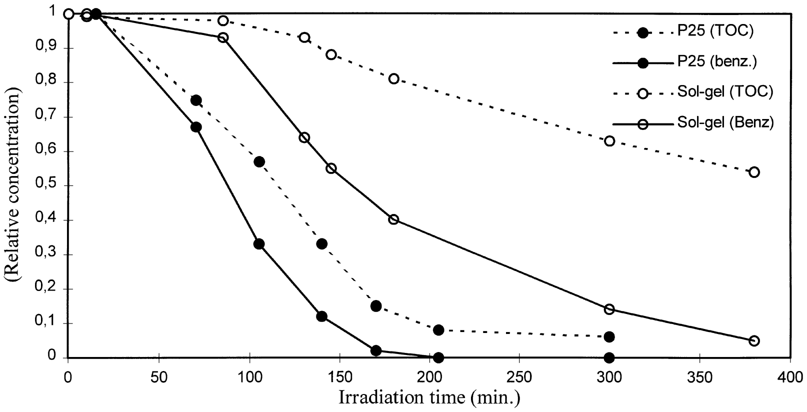

Fig. 6. Comparative evolution of the TOC and Benzamide for the two types of catalysts.

mide. But the degradation process is different when the pollutant is treated by TiO_2-P25. In addition, we have shown that the same catalyst can be reused. The direct comparison between both reactors used is not possible because the experimental conditions are very different (reactor geometry and dimension, flow light source, etc.).

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