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Comparison between the reactivity of commercial and synthetic TiO_2 photocatalysts

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Abstract

Titanium dioxide in powder form is largely used as a catalyst in the field of detoxification of aqueous effluents by photocatalysis. One of the most efficient commercial photocatalysts is TiO_2/P25 manufactured by flame hydrolysis. In this work, we compare the reactivity between this commercial TiO_2/P25 and a synthetic photocatalyst TiO_2/SG prepared in our laboratory by sol–gel method. The photocatalytic activities of TiO_2/P25 and TiO_2/FG were tested using a benzamide solution. We have noticed that the total organic carbon (TOC) evolution of the benzamide solution during the photodegradation was different between both photocatalysts (when the kinetic evolution of benzamide are similar). There is a slower decrease for TOC in the case of the TiO_2 synthetized by sol–gel method. The results of the adsorption and photodegradation experiments explain this difference between the two photocatalysts. As a matter of fact, it is known that the degradation rate depends on the capacity of the molecules to adsorb at the catalyst surface. So, we have pointed out that this adsorption capacity is lower in the case of TiO_2/SG. This explains the degradation rates found. And since the TOC variation depends on the intermediate degradation rate and not on the benzamide, it seems normal to note a lower evolution for the TOC in accordance with the irradiation times.

Keywords: Adsorption; Benzamide; Photocatalysis; Sol–gel; TiO_2

1. Introduction

In the recent years, the heterogeneous photocatalysis for total oxidation of organic and inorganic water pollutants has been studied extensively [1–6]. Such reactions have usually been carried out using suspensions of powdered TiO_2 [1]. One of the most efficient commercial photocatalysts provided by Degussa Corp. and its name is P25 [7]. This semiconductor is manufactured by flame hydrolysis (Aerosil process). Nevertheless, the classical method of preparation in laboratory is sol–gel. This process consists of an hydrolysis of the titanium tetra-*iso*-propoxide in mixture water/ethanol [8]. In this work, we compare the reactivity between the commercial catalyst P25 and a synthetic catalyst TiO_2/SG prepared in our laboratory. The photocatalytic activities of P25 and TiO_2/FG were tested using a benzamide solution. This aromatic amide was chosen as a model compound because it is a representative water organic pollutant [9].

2. Experimental

2.1. Synthesis of TiO_2/SG

The preparation of the TiO_2/SG has been described in the previous works [8,10]. A $0.1\,mol\,l^{-1}$ titanium tetra-*iso*-propoxide solution in *iso*-propyl alcohol was prepared and added with water (n (water/alcohol) $= 100$). The suspension was agitated for 2 h at room temperature, centrifugated and washed with distilled water. The isolated TiO_2 was dried for 1 h at 110°C in air. The resulting solid was calcinated for 20 h at 500°C in air.

2.2. Adsorption study

All batch equilibrium experiments were conducted in the darkness. Measurements were made on suspensions prepared by mixing 100 ml solutions of various initial concentrations of compounds (benzamide, 4-hydroxybenzamide and hydroquinone) at natural pH (5–6) and fixed amount of TiO_2/P25 and TiO_2/SG ($1\,g\,l^{-1}$). Preliminary experiments have demonstrated that equilibrium is reached after 3 h for hydroquinone in presence of TiO_2/SG and 1 h with TiO_2/P25. For the 4-hydroxybenzamide, respectively, 2 and

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1 h are necessary. No adsorption is noted for benzamide in all cases. The equilibrium concentrations were determined with using HPLC after centrifugation and filtration of the suspension through Millipore filters. The concentration of each compound in the clear filtrate was determined by HPLC analysis with a C18 column.

2.3. Evaluation of the photocatalytic activity

Experiments were carried out in a Solar box ATLAS SUNTEST CPS+ simulating a natural radiation. The light source is a vapor Xenon lamp ($300\,\mathrm{nm} < \lambda < 800\,\mathrm{nm}$). The initial concentration of each organic compound was $20\,\mathrm{mg\,l^{-1}}$ and the time zero is the beginning of irradiation. For all experiments, the photocatalyst concentration is $1\,\mathrm{g\,l^{-1}}$. The illuminated volume is 400 ml. The benzamide and intermediates concentrations at different irradiation times were followed by HPLC after filtration. The total organic carbon (TOC) was determined by a liquiTOC$^{\mathrm{TM}}$ instrument of Heraeus in presence of potassium persulfate after acidification of the non-filtered samples.

3. Results and discussion

In the Fig. 1, we have compared the photodecomposition of the benzamide with P25 and TiO_2/SG in aqueous solution.

Quite surprisingly, we have noticed that the TOC evolution was different between both photocatalysts when degradation kinetics of the benzamide were comparable (Fig. 1). There is a slower decrease for TOC in the case of TiO_2 synthetized by sol–gel method. To understand the reasons of this phenomenon, we have first looked for the intermediate resultants of the benzamide photodecomposition. Then, we studied the adsorption of these products on both TiO_2. And finally, we have determined separately the degradation rates of these intermediates.

3.1. Study of the adsorption of organic compounds at the TiO_2 surface

The photodegradation scheme of benzamide is well known and determined by Pichat et al. [9]. The first step is the formation of 4-hydroxybenzamide. These intermediates are degraded into hydroquinone and finally into quinone. The final step is the total mineralization in water, carbon dioxide and other mineral products. The adsorption results cannot explain the different reactivities between the two catalysts. Nevertheless, it show that: (1) the different molecules are adsorbed more fastly at the TiO_2/P25 surface than at the TiO_2/SG surface; (2) the adsorption model of Langmuir is not adapted and (3) in both cases the benzamide is not adsorbed.

3.2. Study of the photodegradation of benzamide and their intermediates

The degradation of benzamide and their intermediates follows a first-order kinetic (Fig. 2a–c). With a first-order kinetic, it is easy to calculate the reaction rate k (in min^{-1}) and this is the reaction rate k which is discussed to compare the two photocatalysts.

From Fig. 2, we can see that the benzamide photodegradation rates with both photocatalysts are very similar. On the other hand, the following transformations are faster with TiO_2/P25 than with TiO_2/SG (the rate of hydroquinone formation is multiplied by 2.3 with TiO_2/P25 and by 1.6 for the quinone).

Concerning the mechanism and degradation kinetics of the benzamide and their intermediates, we can confirm the degradation mechanism found by Pichat et al. (Fig. 3):

As a matter of fact, the mechanism of the heterogeneous photocatalysis begins by the irradiation of the semiconductor with an energy superior or equal to the bandgap (3.2 eV).

$$TiO_2 + h\nu \rightarrow h^+ + e^- \qquad (1)$$

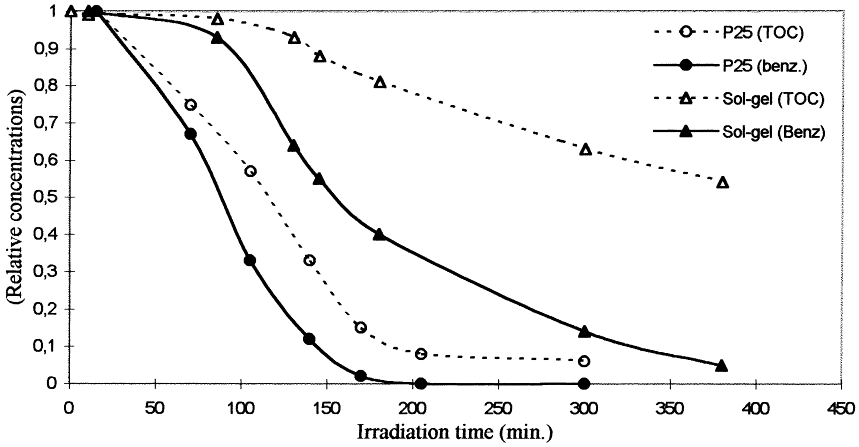

Fig. 1. Comparative evolution of the TOC and benzamide for the two types of photocatalysts.

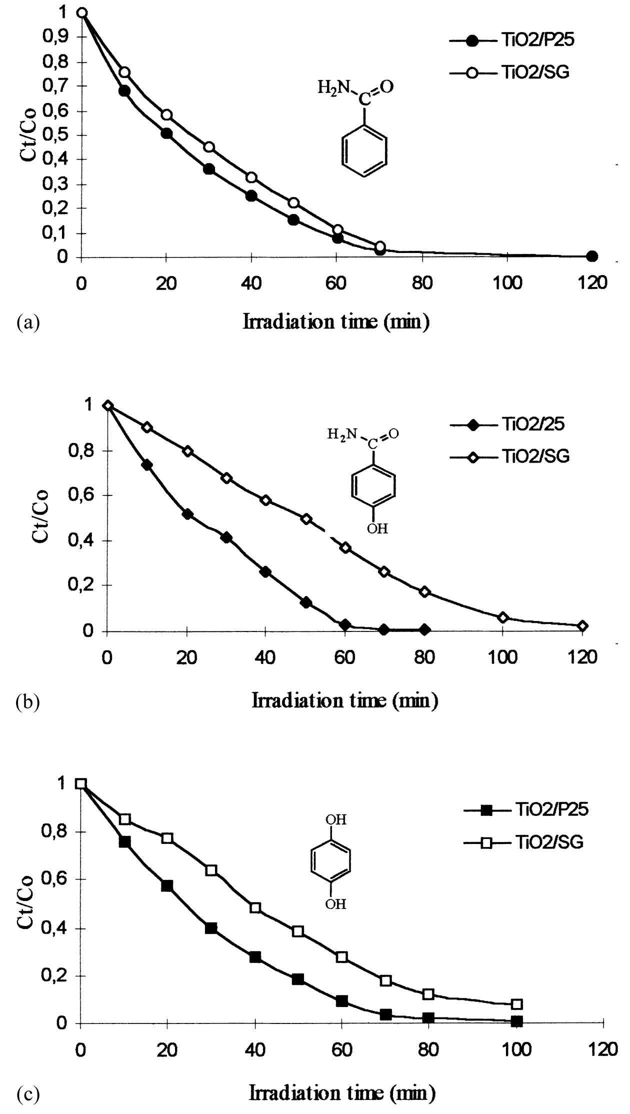

Fig. 2. Degradation kinetics of: (a) benzamide; (b) 4-hydroxybenzamide; (c) hydroquinone.

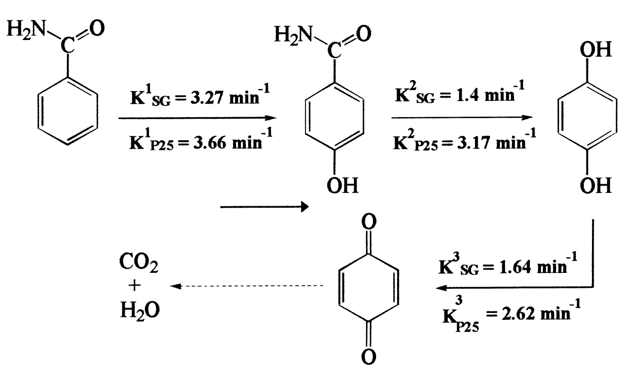

Fig. 3. Degradation mechanism of benzamide.

There is ejection of an electron from the valence band to the conduction band with formation of positive holes (h^+). These holes react with H_2O or the organic pollutants adsorbed at the TiO_2 surface following the reactions 2 and 3:

$$H_2O_{(ads)} + h^+_{(\text{valence band})} \rightarrow {}^\bullet OH + H^+ \qquad (2)$$

$$h^+_{(\text{valence band})} + \text{pollutant}_{(ads)} \rightarrow \text{polluant}^+ \qquad (3)$$

A possible second way of the organic product degradation is made at the liquid/solid interface by the attack of the hydroxyl radical formed during reaction 2:

$$^\bullet OH + \text{pollutant}_{(sol)} \rightarrow CO_2 + H_2O \qquad (4)$$

Like benzamide, there is no adsorption at both photocatalysts surface, the second way is predominant (reaction 4). The benzamide is degraded by interfacial hydroxyl radicals and the surface sites of TiO_2 have a low influence. The degradation mechanisms for 4-hydroxybenzamide and hydroquinone are different, because there is adsorption at the semiconductor surface and these compounds are probably degraded by direct action of holes and $^\bullet$OH adsorbed. Consequently, it is normal that the intermediates be slower degraded with TiO_2/SG because they are less adsorbed than at TiO_2/P25 surface.

4. Conclusion

In conclusion, the results of the adsorption and photodegradation experiments explain the difference between the benzamide degradation rate versus TOC for both catalysts. As a matter of fact, it is known that the degradation rate depends on the capacity of the molecules to adsorb at the catalyst surface. So, we have pointed out that this adsorption capacity is lower in the case of TiO_2/SG. This explains the degradation rates found. Since the TOC variation depends on the intermediate degradation rate and not on the benzamide, it seems normal to note a lower evolution for the TOC in accordance with the irradiation times.

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