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Photocatalytic self-cleaning materials: Principles and impact on atmosphere

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Abstract. This chapter deals with self-cleaning materials which are one of the applications of photocatalysis. The ability of TiO_2 to be activated under UV light allows one to perform oxidation reaction under sunlight. Consequently, since the middle of the ninety's, many new products for outdoor applications, especially glasses, have been developed and commercialized. However, if photocatalytic principles are still true for them, some new mechanisms intervene and could modify chemical reaction implicated. At last, if the chemical reactions occurring at the surface of such products are well studied at laboratory scale, the researches for their impact on atmosphere only begin.

1 Introduction

Heterogeneous photocatalytic reactions were studied for more than fifty years. If few publications have been published before, the mostly cited one is the one of Honda and Fujishima in 1972 [1] largely considered as the first one. Since this moment, heterogeneous photocatalysis has been worldly studied for a large variety of reactions such as mild or total oxidation, hydrogen production from water, water detoxification, gaseous pollutants removal, etc. During the last thirty years, research has been focused on oxidation reactions. Thus, the photocatalytic oxidation of the quasi totality of the organic and inorganic compounds has been studied and this has demonstrated that photocatalysis is efficient enough to be considered as one of the new "advanced oxidation technology" (AOT) for air and water treatment [2–6]. Consequently, in the middle of the ninety's, industrial interest has increased for this technology. As an environmental point of view, photocatalysis for water and air treatment seems to be very promising, its application is limited because of chemical engineering limitations such as support of photocatalysts or separation of the photocatalysts from the effluent. This is why, the most largely application of photocatalysis is the self-cleaning materials.

2 Principle of photocatalysis

Heterogeneous photocatalysis is based on the generation of activated species at the surface of an irradiated semi-conductor with photons having energy greater than the one of their band gap. Theoretically, considering only optoelectronic properties, many oxides could have photocatalytic properties even in visible light range. Unfortunately, it has been clearly demonstrated that the only semiconductor showing sufficient photocatalytic properties is TiO_2. Its band gap, as a function of its allotropic form, varies between 3 and 3.2 eV meaning that it can only be activated with UV-light.

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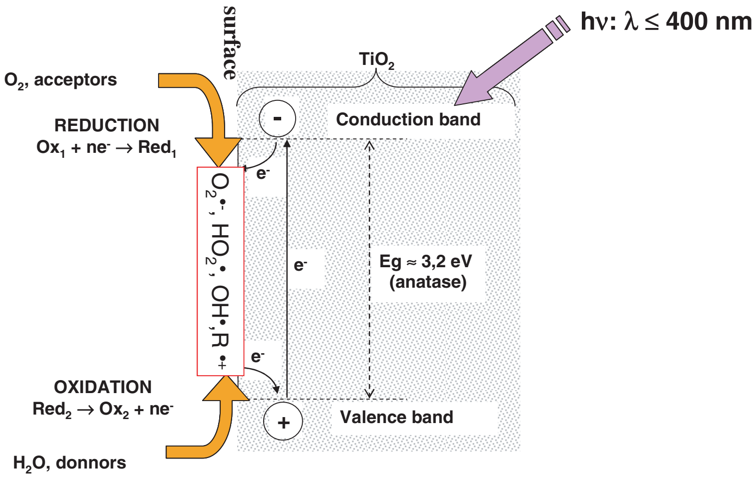

Fig. 1. Scheme of the photocatalytic process over TiO_2.

After absorption of UV photons by TiO_2, electron/hole pairs (e^-/h^+) are generated, electrons are promoted in the conduction band of the semi-conductor while holes are in valence band. Many of them recombine but some could be separated at the surface of TiO_2 and electrons and holes are able to react with electron acceptors (O_2) and donors (OH^-, H_2O) respectively, leading to the formation of adsorbed free radicals. The process implied is described by the following equations:

$$\mathrm{TiO_2} + \mathrm{h}\nu \rightarrow e^-_{\mathrm{BC}} + h^+_{\mathrm{BV}}$$
$$\mathrm{O_2} + \mathrm{e}^-_{\mathrm{BC}} \rightarrow \mathrm{O_2^{\circ -}} \rightarrow \ldots. \rightarrow \mathrm{HO_2^{\circ -}}$$
$$\mathrm{H_2O} + h^+_{\mathrm{BV}} \rightarrow \mathrm{OH^\circ} + \mathrm{H^+}.$$

These species are able to induce strongly oxidative reactions with organic molecules adsorbed on TiO_2 surface. Thus, it has been demonstrated that total photocatalytic oxidation, i.e. total mineralization, is obtained for organics such as alkanes, aliphatic alcohols, aromatics, phenolic compounds, amides, alkenes, aldehydes, carboxylic acids, surfactants, herbicides, pesticides, dyes [7]; the hetero atoms contained in molecules are also completely oxidized, nitrogen atoms in nitrate anions, sulphur atoms in sulphite anions, phosphate atoms in phosphate anions.

Many physical parameters govern the kinetics of the photocatalytic reactions such as [8]:

- mass of photocatalyst
- wavelength of the irradiation photons
- temperature
- radiant flux
- reactant concentration.

First of all, the direct proportionality of the initial reaction rate to the mass of catalyst (figure 1) indicates a true heterogeneous catalytic regime. However, above a certain mass value, the reaction rate levels off and becomes independent of the mass. This limit corresponds to the maximum amount of TiO_2 totally illuminated. The variations of the reaction rate as a function of the wavelength follows the absorption spectrum of the catalyst, with a threshold corresponding to its band gap energy. In the case of TiO_2, this threshold corresponds to 400 nm, i.e. near-UV wavelength. This fact is important for outdoor self-cleaning materials. Indeed, about 4% of sunlight reaching the earth surface is in this wavelength range corresponding to an irradiance of about 40 W/m^2, which is enough to activate TiO_2. Then, as a function of the temperature, the activity for photocatalytic reaction reaches a maximum level for a range of temperature. It corresponds to room temperature (between 20 °C and 80 °C). This is due

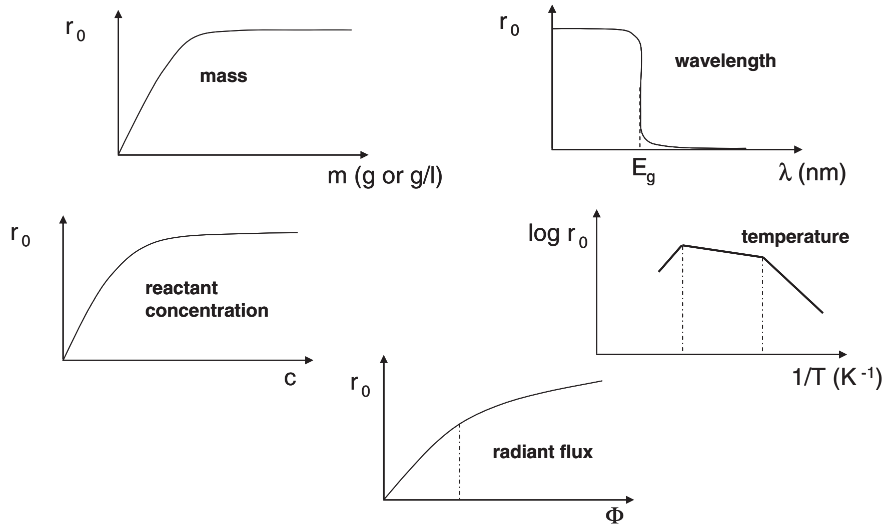

Fig. 2. Influence of the different physical parameters which govern the initial reaction rate of a photocatalytic reaction [8].

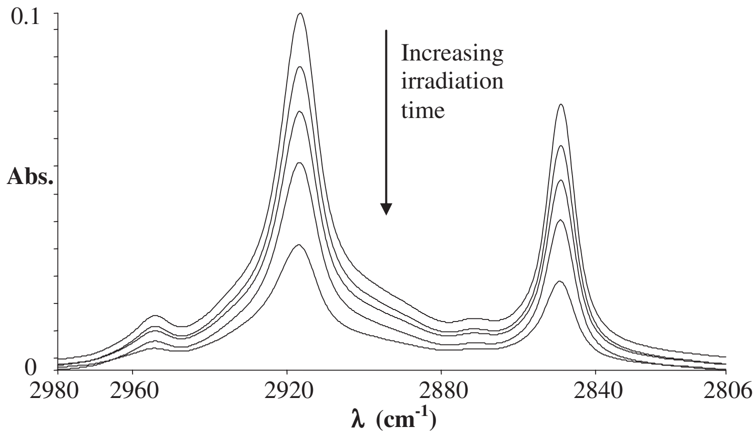

Fig. 3. Disappearance of the CH_3 and CH_2 stretching bands of a stearic acid thin layer deposited on a self-cleaning glass under UV light [18].

to the photonic activation of the photocatalytic system not requiring heating. This is also an advantage for applying photocatalysis for outdoor self-cleaning materials.

3 Self-cleaning materials

After intensive research on photocatalytic reactions, many commercial products based on these phenomena have emerged during the last years. Among them, self-cleaning materials such as glasses, tiles or concrete show some real successes.

3.1 Self-cleaning glasses

Of particular interest here is the use of titanium dioxide based films on glass for self-cleaning purposes. These films have two distinct photo-induced properties: the first one is the photocatalytic ability to oxidize organic stains deposited on windows under sunlight (figure 3), and

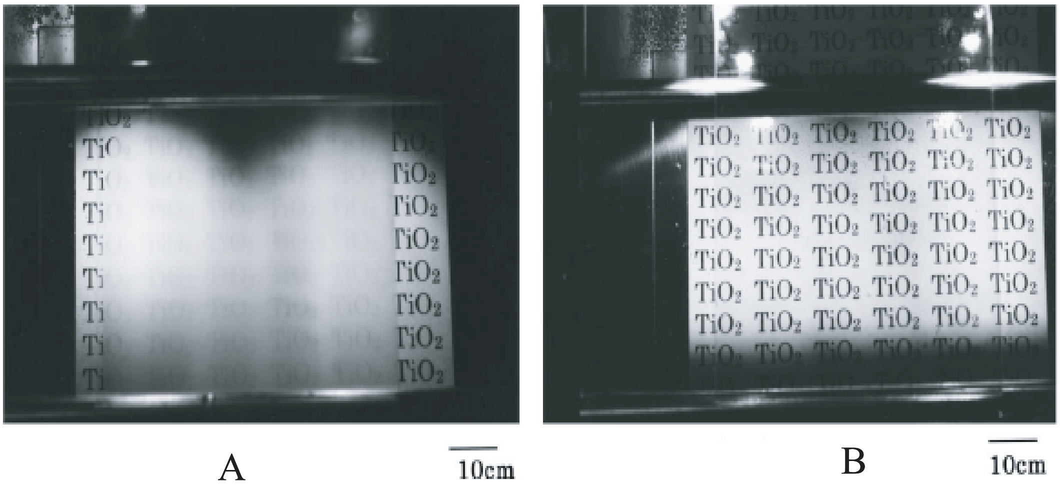

Fig. 4. Illustration of the behaviour of a water film on self-cleaning glass: (A) under visible light the film is constituted of small droplets occurring light scattering, (B) under UV light the film is homogeneous [9].

Fig. 5. Illustration for application of self-cleaning concrete; on left, Dives in Misericordia church in Rome; on right Air France company head office in Charles De Gaulle airport.

the second one is the *photoinduced superhydrophilicity* as illustrated on figure 4, which involves high wettability of the surface and allows the removal of either organic and inorganic pollutant by water films (from rain fall for instance) [9]. Thus, nowadays, TiO_2 thin films are prepared by a number of different methods, including CVD, the sol–gel process, thermal methods and sputtering [10–13]. Two physical constraints have to be respected, the optical transparency of the glasses and the mechanical resistance of the TiO_2 layer. The first one is principally guaranty by the very thin thickness of the layer (less than 100 nm and mainly around 10 nm). The second one could be reached by using binder such as SiO_2. Unfortunately, it has been demonstrated that the use of a binder reduces the photocatalytic activity of the layer [14]. Consequently, the commercial products, Activ^{TM} from Pilkington Glass [15], Bioclean^{TM} from St-Gobain [16] and Sun-Clean^{TM} from PPG [17] are only based on a very thin TiO_2 layer on glass.

A tackled question concerns the by-products formed by photocatalytic oxidation of real stains. It has been established that the composition of contaminant layers on windows contains inorganic materials such as cations (Ca^+, Na^+, $NH_4{}^+$) and anions (NO_3^-, SO_4^{2-}) which are not affected by photocatalytic oxidation and organic materials such as elemental carbon and particulate organic matter [19] which are concerned by oxidation. Many works were focused on the mechanisms of the photocatalytic degradation of thin layers of organic contaminants [20–23] such as fatty acids, aldehydes or PAH that all can be found in windows stains. These different works identify many by-products during the photocatalytic oxidation such as alkanes, aldehydes and carboxylic acid compounds, all with a shorter carbon chains than the initial pollutants and at very low concentration levels. But in all cases, because of the experimental set-up consisted in a batch reactor, the total mineralization of the pollutant is reached. However, in an open space as the atmosphere, the behaviour may be different. A photocatalytic reactor that could be the large self-cleaning glass surface of a building may be able to affect environment positively if the degradation of VOC pollutants is greater than the by-products formation or negatively if not. This question is still open and researches concerning kinetics aspects and extrapolation to city scale begin.

3.2 Self-cleaning concrete

The second family of self-cleaning materials consists in concrete for building and ceramics for tiles. In this case TiO_2 is included in the materials during the manufacture but only the part at the surface of the final product can be activated. This kind of applications is largely developed in Japan by Toto company [24] but starts to appear in European countries through the commercial products TX Active® from Italcementi [25] (figure 5).

The main claims for these products are, besides their self-cleaning properties, their ability to reduce NOx in atmosphere. As in the case of self-cleaning materials, the question of their real impact on atmosphere is still open and academic researches on their real efficiency starts only.

4 Conclusion

Photocatalysis is a promising process for environmental application. Self-cleaning applications based on this technique are now commercialized. During the last ten years, researches on this kind of materials at a lab scale have clearly shown their capacity to oxidize organic matter. But now, that the scale is up, the question of their possible impact on atmosphere is open and the answer is waited.

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