Photocatalytic decomposition of fatty stains by TiO₂ thin films

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ABSTRACT. Anatase TiO₂ nanoparticles have been prepared as aqueous colloidal solutions by a conventional sol-gel process. Thin films have been deposited onto glass substrates by dip-coating and eventually further crystallized by heat-treatment up to 300 C. The effect of the TiO₂ film thickness, porosity and particle size on the reaction kinetics has been studied as well as the starting thickness of the fatty acid layer. The photocatalytic activity of the films has been measured through the decomposition of artificial stains formed by fatty acids deposited onto the TiO₂ layer (adipic or stearic acid). The kinetics of stain photodecomposition has been studied in details by *in-situ* infrared spectroscopy absorption studies. This allows to discuss the role of UV light absorption and the interdiffusion of radicals and oxygen across the interfaces. The mechanism for stain decomposition is shown to be associated to a shrinkage of the solid film at the surface of the porous oxide film after a diffusion of the excited radicals from the oxide.

1. INTRODUCTION

The semiconducting properties of titanium oxide as well as its low price and non toxicity are making it a suitable photocatalyst for the degradation of organic or biological pollutants [1, 2] or for the photocleavage of water [3]. TiO₂ has been used as colloidal dispersions [4, 5] or as transparent thin films supported on glass [6-9].

Self cleaning windows have been investigated more recently for the decomposition of stains deposited either mechanically or by condensation of vapors or fogs in industrials areas.

The decomposition of fatty acid deposited onto the TiO₂ film is a complicated solid-solid reaction mediated by the diffusion of radicals from the interface. We discuss the effect of the TiO₂ film morphology as well as the thickness of the organic layer.

2. EXPERIMENTAL

2.1. Synthesis. Colloidal dispersions of TiO₂ were prepared by peptization of hydrous titania similar to that described by Bartlett, *et al.* [10] but using titanium tetrabutoxide. 17 ml of this precursor were dissolved in 100 ml of butanol (solution 0.5 M). They were hydrolyzed with 8 ml of a solution of nitric acid (0.2 M) slowly added. After completion of the hydrolysis (30 min) the resulting transparent gel is dispersed in 100 ml of nitric acid 0.2 M and homogeneously stirred for 24 hours at various temperatures (20 C, 40 C, 60 C and 80 C) for 24 hours. Butanol and water are not miscible. The two liquids slowly separate with the colloidal dispersion in the aqueous layer. Thermogravimetric analysis confirms that the concentration of the colloidal particles in water is 0.5 M TiO₂.

Dynamic light scattering experiments performed on these solutions indicate that the highest reflux temperatures yield particle growth and ripening (Figure 1). The average particle size ranges from 20 nm for the sample without heat-treatment up to 150 nm for the 80 C heat-treated samples.

Figure 1. Hydrodynamic diameter obtained from dynamic light scattering experiments for colloidal solutions heat-treated for 24 hours at various temperatures.

However, X-ray diffraction does not show evidence of such a large difference between all samples. The crystalline phase is predominantly anatase with small amounts of brookite. One can estimate the size of the diffraction domain from the width of the diffraction peak at 25 which is the only one in the X-ray pattern that originates from a single d-spacing (common to the anatase and brookite forms). All other peaks are composite peaks. For all colloids we obtain a constant

cristallized domain size of 4.0 nm. Heating the powders at 300 °C slightly increases the crystallite size up to a diffraction coherence length of 7.0 nm (Figure 2(c)).

Figure 2. X-ray diffraction of a powder (a) after treatment at 20 °C for 24 hours, (b) after reflux at 80 °C for 24 hours, (c) the same but heat-treated at 300 °C for 2 hours. (CuK α radiation). Arrows indicate the diffraction peaks of the Brookite phase.

2.2. Thin films. Thin films have been obtained by dip-coating soda lime microscope slides in the colloidal solution (withdrawal rate 4.6 cm/min). The film quality is improved by addition of 1% of dispersing agent (Tween[®] 80). Scratch resistant films are obtained after calcination of the films at 300 °C for 30 min. However, the films remain very porous as shown by scanning electron microscopy (Figure 3).

Figure 3. Electron microscopy of a film annealed at 80 °C.

On substrates without chemical barrier, the annealing temperature of 300 °C is the highest temperature that can be reached in order to avoid reaction between

some glass component and the coating. Indeed, diffusion of Na⁺ ions into the films deteriorates the photoreactivity [11].

The equivalent thickness of the film can be estimated after comparing its absorption at 312 nm with that of the parent colloidal solution diluted to 1.10⁻³ mol/l (and correction from the glass contribution). After one coating sequence the estimated mass of TiO₂ in the film is 50 μ g/cm² in good agreement with the mass uptake measured on the slide after coating. This is equivalent to 125 nm of dense TiO₂ film.

The photocatalytic activity has been measured with a method described by Y. Paz, *et al.* [8]. The films were covered by dip-coating with a solution of stearic acid in ethanol (solution concentration between 5 g/l and 60 g/l, withdrawal rate 4.6 cm/min). Films were placed in an infrared transmission spectrometer (Perkin Elmer 783) at an angle of 45° with the IR beam. They were simultaneously irradiated with a 312 nm light (measured power: 2.85 W/m²). The change of transmittance at 2910 cm⁻¹ which is the characteristic frequency of the C – H stretching vibrations of the stearic acid deposited onto TiO₂ films is recorded as a function of time. The equivalent thickness l of the film is related to the change of transmission $\Delta T = T - T_{\infty}$ between initial and infinite time (when all organics have been removed) by the relation $\Delta T = e^{-\epsilon l}$ where ϵ is the absorption coefficient of stearic vibrations. The choice of the UV radiation wavelength was based on the availability of a commercial lamp. A longer wavelength (such as 365 nm) would be more representative of the application with solar light but it is less absorbed by titanium oxide (See Figure 4) and the radicals will be generated in a larger depth of the TiO₂ layer. This effect, under study, changes quantitatively the decomposition kinetics.

Figure 4. Optical density of a film on a soda-lime glass as compared to a microscope slide and to a colloidal solution diluted to the concentration of 1 $\times 10^{-3}$ mol/l.

3. RESULTS AND DISCUSSION

3.1. Effect of colloid synthesis temperature on the photocatalytic activity. Despite of the large difference in the particle size, the photocatalytic activity of all films is similar and does not drastically depend on the synthesis temperature (Figure 5), although the particle sizes were found to range from 20 nm to 150 nm. Probably, the particle size obtained by dynamic light scattering relates to the porous assembly of smaller nanocrystallites (around 4 nm as estimated from the X-ray diffraction peak width), which form the basic element of the photocatalyst. The slightly better activity of the sample refluxed at higher temperature may then be associated to its better crystallinity as shown by X-ray diffraction.

Some films were made with additional coating sequences (two and three layers). They do not show significantly different photocatalytic activity. At 312 nm the

Figure 5. Photocatalytic activity of films obtained from colloidal suspensions refluxed at 40 °C, 60 °C and 80 °C and heat-treated at 300 °C.

optical density of the films is quite high. Therefore, all the UV light is absorbed by one single coating of TiO₂ as shown in Figure 4.

3.2. Effect of stain thickness. We have deposited various amounts of stearic acid onto a TiO₂ film. The difficulty is to measure the thickness of the stearic acid layer since part of it is found to be deposited inside the porosity of the TiO₂ film and part of it covers the film. However, thicker films can be obtained with concentrated stearic acid. They require much longer times for degradation to be completed (Figure 6) under UV. The well-known mechanism for photodegradation of organics is the following:

Under constant illumination, we may assume that the TiO₂ film generates a constant flow I_0 of radicals that have a probability μ to react with a layer dx of the stain. If this reaction probability is small and if the thickness l of the stearic acid is limited, the flow of radicals across the stearic acid will be nearly constant and equal to I_0 . The total number of reactions of type (3) in the film will be:

$$N(l) = \int_0^l \mu I_0 dx = \mu I_0 l. \quad (4)$$

Then, the decay of the stearic film thickness can be expected to follow a simple first order kinetics: $dl/dt = -\mu I_0 l$. This should lead to an exponential decay for the normalized thickness $l/L = e^{-\mu I_0 t}$, independent on the starting thickness L . Exponential fits would probably well account for the decay of the thinner films (Figure 6). Indeed, below 20 g/l all films appear to show a simpler exponential decay.

However, the thicker film show much slower kinetics. This may be associated to a decay of the flow of radicals across the stearic acid layer (or a decay of their activity) due to encounters and side-reactions of the

Figure 6. Decrease of the thickness of the stearic acid layer as estimated from the transmittance at 2910 cm⁻¹.

Table 1. *Parameters involved in the kinetics of the stearic acid layer decomposition* Parameters involved in the kinetics of the stearic acid layer decomposition.

concentration	15.6 g/l	20 g/l	40 g/l	60 g/l
$\lambda \cdot L$	0.12	0.16	1.53	1.63
$\mu \cdot I_0$	27.9	22.3	38.3	52.5

radicals. Then, the radical flow at the distance x from the TiO_2 film will be $I(x) = I_0 e^{-\lambda x}$. The characteristic decay of radicals λ may be different from μ since the reaction of radicals with the stearic acid may not be their only cause of decay. The total number of reactions with the fatty acid in the layer of thickness l will then become

$$N(l) = \int_0^l \mu I_0 e^{-\lambda x} dx = \frac{\mu}{\lambda} I_0 (1 - e^{-\lambda l}). \quad (5)$$

The decay of the film becomes $dl/dt = (\mu/\lambda) I_0 (1 - e^{-\lambda l})$ that yields upon integration on time the relationship: $\lambda l(t) = \ln(1 + (e^{-\lambda L} - 1)e^{-\mu I_0 t})$ where $l(t)$ is the film thickness at time t and L the starting thickness. Thus the normalized thickness of the film can be written as

$$\begin{aligned} \text{normalized thickness} &= \frac{l(t)}{L} \\ &= \frac{1}{\lambda L} \ln(1 + (e^{-\lambda L} - 1)e^{-\mu I_0 t}). \end{aligned} \quad (6)$$

The lines in Figure 6 are the fits to the data points using this expression. The results are reported in Table 1.

The term $\lambda \cdot L$ is characteristic of the diffusion of radicals into the stain. Its low value below 20 g/l leads back to the single exponential decay. We observe that $\lambda \cdot L$ does not increase smoothly as a function of the concentration but suddenly rises between 15.6 g/l and 20 g/l. This is probably the concentration at which the stearic acid fills the pores of the TiO_2 film and starts to form a dense film above it.

The term $\mu \cdot I_0$ can be understood as the efficiency of radical production (I_0) and reaction with the organics (μ). There is no clear dependence of this term on the stearic acid film thickness. At first, $\mu \cdot I_0$ decreases. A simple explanation is that this term takes into account the fact that the fatty acid layer acts as a barrier for the diffusion of water and oxygen toward the surface of the nanoparticles. The transfer of the electron-hole pair to the radicals is therefore slower. For the thick stain layers, it drastically increases but this is probably an artefact of the model, associated to the large increase of $\lambda \cdot L$ in formula (6).

4. CONCLUSION

We have shown that at 312 nm, only one thin layer of TiO_2 is sufficient to photodecompose stearic acid. Since this wavelength is high compared to the energy gap of TiO_2 , it should be interesting to compare the photodegradation of stearic acid at longer wavelengths (around 365 nm).

We have also shown that the thickness of the organic layer of pollutant is a parameter that influences the photo-efficiency of TiO_2 layers towards self-cleaning properties. The thickness of the pollutant layer, has an effect on the kinetics of photodegradation which is probably associated to the diffusion of photo-generated species, such as radicals and possibly oxygen.

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