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Kinetic study of the photocatalytic degradation of the C-polymorph of a stearic acid microcrystal grown on an amorphous titania surface scattered with anatase microdomains

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ABSTRACT

The photodegradation of a stearic acid (SA) microcrystal on an amorphous titania film surface scattered with submicrometric anatase domains is observed using a Reflected Light – Differential Interference Contrast (RL-DIC) microscopy. The SA microcrystal, grown from a saturated solution, is flat and rhombus-shaped with acute angle of 55° in agreement with the C-polymorph of SA crystal. We observe that the photodegradation initiates at the anatase microdomains under the microcrystal and creates SA holes in the shape of truncated-rhombus or elongated-hexagons having the same orientation and symmetry as the SA microcrystal. The expansion of the SA holes is ascribed to a photodegradation mechanism mediated by the photogeneration and surface diffusion of radical species across the gap between the anatase microdomain and the edges of the SA holes. A detail kinetic study of the SA holes expansion shows that the surface area of the SA holes scales almost linearly with UV exposure time in good agreement with an apparent zero-order kinetics. The morphology and the expansion kinetics of these holes are rationalized through the orientation dependence of the reactivity of the molecules with the radical species.

1. Introduction

Since the pioneer work of Paz et al. [1], the photodegradation of long-chain carboxylic acids on TiO_2 surfaces has attracted tremendous interest from both applied and fundamental points of view [1–12]. In particular, the use of stearic acid (SA) as a model pollutant quickly became a popular method to determine the activity of photocatalyst thin films for applications in the area of environmental remediation and self-cleaning surfaces. At a more fundamental level, the kinetics models and related processes involved in the photodegradation of solid organic deposits on a TiO_2 surface differ in numerous aspects from those involved in liquid- or gas phase and remain not fully understood.

The photocatalytic reaction of an oxidizable solid phase is, in numerous cases, attributed to the strong oxidation potential of active oxygen species, such as the hydroxyl radicals $OH^{\bullet}$, that are photogenerated on the UV-illuminated TiO_2 surface [13]. The bimolecular reaction between these active species and the organic co-reactant is responsible for initiating the photocatalytic degradation process. Furthermore, there is a body of evidence supporting the fact that this bimolecular reaction can even be mediated via the diffusion of $OH^{\bullet}$ radicals [14–17]. As regards the degradation kinetics, the reaction rates strongly depend on the respective structure and morphology of both photocatalyst and organic layer. D. Ollis [11] examined different photocatalyst/organic layer configurations and proposed simple kinetic models associated to each case. Recently, we highlighted the dependence of the initial morphology of the SA deposit on the degradation kinetics of SA which is largely influenced by the deposition method and conditions [10]. SA deposits are usually prepared by solution casting methods such as dip– [2,10] or spin-coating [1,3,7] but also by more sophisticated Langmuir–Blodgett film method [5,8,9]. While the latter allows the deposition of one or more monolayers of SA with very accurate thickness, the formers lead in most cases to the formation of microscopic islands with irregular shapes and presenting a distribution in sizes and heights [10,12]. The

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nucleation and crystallization of fatty acid on a surface is a complex process which is influenced by numerous parameters including solution concentration and temperature [18]. By varying the SA deposition conditions, it is possible to grow faceted islands on the photocatalyst surface and even well-defined SA microcrystals [19]. Two main polymorphic forms of SA crystal can be grown from solution: the B polymorph which crystalizes as a flat and rhombus-shaped crystal with an acute angle of 74° and the C-polymorph which is also flat and rhombus shaped but with an acute angle of 54° [19,20]. These two forms of SA crystals can be therefore easily distinguished by the measure of their acute angles. In a very recent report [21], using Reflected Light – Differential Interference Contrast (RL-DIC) microscopy, we observed the photodegradation mode of the *B-polymorph* of SA microcrystals grown on an amorphous titania film surface scattered with submicrometric anatase microdomains. Interestingly, this study revealed that the photodegradation of these microcrystals proceeded via the appearance at the anatase microdomains and widening of holes in shape of flattened hexagons within the microcrystal which exhibit the same symmetry and orientation as the microcrystal. The morphology of these holes was related to the anisotropy of the crystal structure and the related orientations of the molecules in the different crystallographic directions of the crystal. In this work, we study the photodegradation of the *C-polymorph* of SA microcrystals initially grown on an amorphous titania film surface containing submicrometric anatase microdomains. This report provides further insights into the formation of these SA holes and their relationship with the crystal morphology and structure. Emphasis is put on the holes expansion kinetics which is discussed on the basis the anisotropy of the reaction kinetics.

2. Experimental section

2.1. Preparation of the TiO_2 thin films

The TiO_2 sol was prepared according to a procedure reported by Bahtat et al. [22].Propan-2-ol (Aldrich, 99.8%) and acetic acid (ACROS Organics, 99.5%) were used as solvent and catalyst, respectively. The sol was deposited onto borosilicate glass slides (D 263 M, Schott) The glass slide was dipped 8 times in the sol with at a withdrawal speed of 100 mm/min and finally dried at 100 °C for 1 h and heat-treated for 2 h in air at 450 °C. Further details are given in ref. [21].

2.2. Photocatalytic experiment

SA microcrystals were grown onto the titania films surface according to a recently published procedure [21]. Briefly, the titania films were dipped twice in a 0.06 M methanolic solution maintained at 30 °C at a withdrawal speed of 100 mm/min and dried during 5 min between each dip and finally further dried for 2 h.

The photocatalytic degradation of the SA microcrystals was measured as a function of UV-exposure time. The films were irradiated by a 200 W mercury-xenon lamp (Lot Oriel instruments) simulating solar radiation equipped with a 0.5 m length optical fiber. The power density in the UVA was 25 W m^{-2}, as measured by a photo-radiometer (Delta Ohm DO 9021) equipped with UVA head. The photodegradation of the SA microcrystals was observed as a function of UV exposure time with a Reflection Light – Differential Interference Contrast microscope (Axio Imager A1m, Zeiss), equipped with a high-resolution camera (AxioCam MRc5). The enhanced contrast and resolution inherent to RL-DIC microscopy enables the observation of minute details on the surface and is then particularly appropriate for the simultaneous observation of the microcrystal edges and the submicrometric sumicrometric domains. The quantitative exploitation of the micro images was performed using Imagej software [23].

3. Results and discussions

3.1. RL-DIC microscopy observation of the SA microcrystal after various UV exposure times

Fig. 1 presents the RL-DIC images of the C-polymorph of a representative SA microcrystal grown on the titania film before UV-illumination (Fig. 1(a)) and after various UV exposure times (Fig. 1(b)–(h)). The TiO_2 film consists of an amorphous titania matrix with embedded anatase nanocrystals [22] and scattered with anatase microdomains [21]. On the RL-DIC image the anatase microdomains appear as dark spots uniformly dispersed on the film surface. Their diameter varies from a few hundreds of nm to about one micrometer [21]. Except for these black spots, the rest of surface appears featureless at this scale.

As previously mentioned, the SA polymorphs are known to be easily identified from the crystal morphology and their angle values. The as-grown SA microcrystal is rhombus-shaped with an acute angle of 55° in good agreement with the C-polymorph of SA crystals which is 54° [19,20]. Note the sharp contrast between the crystal (light brown) and the titania film surface (light gray) and the well-defined edges of the crystal. The high-resolution achieved by RL-DIC microscopy also enables the observation of the anatase microdomains with sub-micrometric size which appear as minute black dots on the light gray background. Anatase microdomains are also visible within the crystal surface as indicated by the arrow on the magnified images (Fig. 1(a), right panels). The light gray color around the microdomain reveals the existence of a gap between the microdomain and the microcrystal as already reported in our previous study on the photodegradation mode of the B-form of SA [21]. This gap is of the order of one micrometer or less. A possible explanation for the existence of this gap is an incidental exposure of the sample to UV light which could come from the microscope illumination. We used a Zeiss microscope equipped with a 100 W halogen lamp which has a radiation spectrum of a black body at the temperature of 3300 K. At this temperature, the lamp emits a tiny fraction of UV radiation. We also used Neofluar objectives which transmit a bit in the UVA domain. Prior to the (intentional) UV exposure, we spent some time to examine in detail the SA microcrystals grown on the TiO_2 film and depending on the selected objective the irradiance can reach 0.6 W m^{-2} in the UVA range. Therefore, it cannot be excluded that the holes observed at t = 0 were obtained during these preliminary observations. However, it should be noted that during the photodegradation experiments, the observation and image recording of the holes after UV exposures were performed in few minutes. Therefore, the contribution of the microscope light to the photodegradation of the SA microcrystal is still negligible.

At the early stage of the UV exposure Fig. 1(b), several holes appear in the SA crystal and a close inspection (see magnifications on right panels) shows that each hole initiates at the location of an anatase microdomain. As the UV exposure is further increased (Figs. 1(c)–(f)), the holes widen and become truncated rhombus or elongated hexagonal in shape with the same orientation as the microcrystal (Fig. 1(d)). The holes exhibit a preferential orientation along the major axis of the crystal. It is also worth noting that the lateral edges of the holes are parallel to those of the microcrystal. After 48 min. UV exposure, the holes merge (Fig. 1(g)) and the microcrystal totally disappears (Fig. 1(h)) after 56 min. UV exposure.

The expansion of the SA holes as a function of UV exposure time is explained by the well-documented remote photodegradation mechanism [13–16] involving active oxygen species such as $OH^{\bullet}$