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Removal kinetics of stearic acid discrete deposits on photocatalytic self-cleaning surfaces: Effect of deposit initial size distribution

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ABSTRACT

Earlier reports by Sawunyama et al. (1997, 1999) and Ghazzal et al. (2011) used atomic force microscopy (AFM) and optical microscopy to characterize the structure of stearic acid (SA) deposits on polycrystalline TiO_2 films and Ti [110] crystal surfaces. Their preparation methods and catalysts yielded island-like SA deposits, rather than continuous films, for stearic acid submonolayers and multi-layers. Ghazzal observed that individual islands showed disappearance kinetics to be zero order with respect to island area, but apparently first order with respect to total SA remaining.

We develop here kinetic models which are consistent with these “island” findings and establish the guidelines for apparent kinetic order of reaction, n:

1. Island deposits of a single size will exhibit apparent zero order kinetics., $n = 0$.
2. Island deposits with a narrow distribution of island sizes will exhibit an apparent half order behavior, $n = 0.5$.
3. Island deposits with a broad size distribution will exhibit an apparent reaction order of unity, $n = 1$.

Our conclusion is that meaningful kinetic analysis of SA island photocatalyzed disappearance, and thus that of any oxidizable, carbonaceous pollutant which deposits in island form, rather than as a continuous film, requires knowledge of the initial island size distribution. The SA deposits may also undergo significant rearrangement as the titania surface is illuminated, quickly transforming the latter from hydrophobic to hydrophilic. Thus it is the reactant film and/or island distribution after initiation of illumination which is most relevant to kinetic modeling attempts.

1. Introduction

1.1. Stearic acid: continuous thin film assumption

Stearic acid($CH_3(CH_2)_{16}COOH$) multilayer films deposited on dense, **non-porous or microporous (dp < 1–2 nm)** titania photocatalyst layers have been shown numerous times to exhibit intrinsic zero order removal kinetics as established first by Paz et al. [1] and later confirmed by Mills et al. [2], Allain et al. [3]. Peruchon et al. [4] also reported the zero order removal of stearic acid from titania-based non-porous, commercial self-cleaning glasses. (We note that FTIR measurements, used in all four studies [1–4], track the $-CH_2-$ group which serves as a convenient surrogate reactant for stearic acid oxidative removal. As these methylene groups are also found in many of the intermediates arising and disappearing in the course of stearic acid conversion to CO_2, the FTIR data widely used in photocatalysis studies, because of its convenience in measurement, does not represent mechanistically the fundamental rate of SA oxidation itself.

Similar zero order results were found with other measurement techniques and other long chain fatty acids as reactants. Thus Romeas et al. [5] showed zero order mass removal for palmitic acid ($CH_3\ (CH_2)_{14}COOH$) deposited on TiO_2, and Zaleska et al. [6] studied lauric acid ($CH_3(CH_2)_{10}COOH$) on single crystal anatase, finding zero order decrease of multi-layer lauric acid surface coverage.

However, when stearic acid was deposited on thicker, **mesoporous (dp >5 nm)** TiO_2 films, both Mills et al. [2] and Allain et al. [3] reported apparent first order kinetics of $-CH_2-$ film removal. We have shown with kinetic models that an oxidizable multi-layer reactant, distributed uniformly throughout a (meso)porous, optically thick photocatalyst, exhibits an apparent first order kinetic rate of organic film removal [7]. This kinetic order disguise is due to diminution with depth of local irradiance, and thus rate constant, because of photocatalyst absorption of bandgap or shorter wavelengths.

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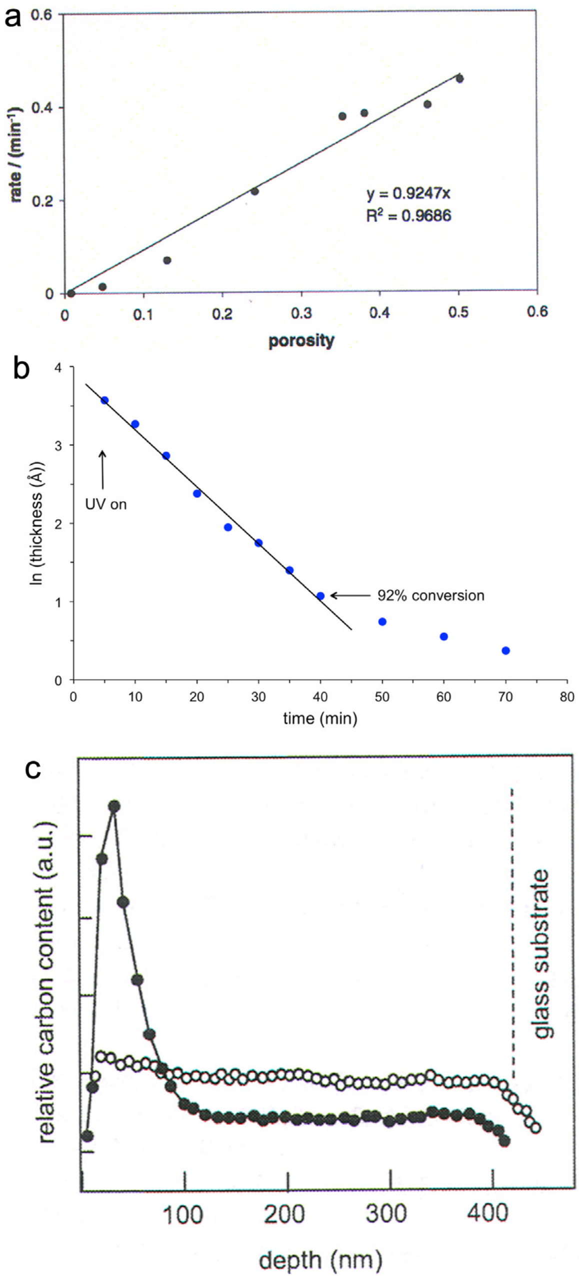

Fig. 1. (a) Rate of reaction vs. calculated porosity of titania thick film (Reprinted by permission of Springer) [8]. (b) Semilog plot of data for predicted stearic acid film thickness within a porous titania layer. Data from Fig. 11c calculated curve of Remillard et al. [9]. (c) SIMS profile of the carbon content for a microporous (filled circles) and mesoporous (open circles) films on which 1.5 μg/cm^2 stearic acid was deposited [3] (Reprinted by permission of Wiley-VCH).

Our porous photocatalyst model assumed uniform initial distribution of reactant stearic acid with a zero order local removal rate at all times, until local exhaustions of stearic acid, and demonstrated an apparent first order behavior for such non-uniformly illuminated circumstances [7]. Support for this assumption of uniform stearic acid distribution within a mesoporous photocatayst is found in reports by Mills et al. [8] and Remillard et al. [9]. The former FTIR study demonstrated a strong correlation between overall rate of reaction and photocatalyst porosity (Fig. 1a), while ellipsometry data from the latter for calculated SA film thickness within a porous catalyst show clear first order behavior for SA disappearance (Fig. 1b), a confirmation of the kinetic disguise modeled earlier for porous photocatalysts [7]. A third example is demonstrated by Allain et al. [3] in Fig. 1c showing that a microporous catalyst has stearic acid predominantly at the surface, whereas the mesoporous catalyst shows carbon initially uniformly distributed throughout the depth of the photocatalyst, as assumed in our previous analysis [7].

Thus, kinetic models corresponding to removal of uniformly deposited, continuous fatty acid layers for porous and non-porous photocatalysts appear to be validated experimentally and in suitable kinetic models.

1.2. Stearic acid: discrete island evidence

Sawunyama et al. [10,11] and Ghazzal et al. [12] have studied sub-monolayer, monolayer, and multi-layer deposits of stearic acid on non-porous surfaces, finding that, either initially or upon illumi-