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Evaluation of the correlations between temperature, humidity, incident UV light and the photocatalytic activity of TiO_2 films using a rationale approach

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ABSTRACT

The effect of temperature, humidity and incident UV light on the photocatalytic activity of two TiO_2 films with different microstructures (dense and mesoporous) was explored in terms of stearic acid degradation. Previous works reported in the literature suggest that the activity of TiO_2 films does not only depend on single factors but also on interactions between them. Hence, the design of experiments (DoE) approach was used in this work to plan the experiments in a systematic way, simultaneously considering several variables. This approach provided an efficient working strategy to explore both individual and interaction effects on the photocatalytic activity of the films. The statistical evidence found here revealed that single factors temperature and mesoporous microstructure have the strongest positive effect on the efficiency of the films. In the case of temperature, this was explained by easier degradation and/or desorption of reaction intermediates. On the other hand, the positive effect of the mesoporous microstructure was correlated with its large surface area. An interaction factor between temperature and incident UV light also affects the activity of the films. Results suggest that this phenomenon depends of the degree of film hydration before the deposition of SA.

1. Introduction

Since Fujishima and Honda discovered the photo-splitting of water in a TiO_2 anode photochemical cell in 1972 [1], research in the field of photocatalysis has constantly grown. The ability of TiO_2 to photo-oxidize a wide range of organic and inorganic pollutants when exposed to UV irradiation has led it to become the key component of a new generation of materials with photocatalytic self-cleaning characteristics. When a TiO_2 particle absorbs a photon with $h\nu \geq E_g$, (E_g = band gap of TiO_2 = 3.2 eV [2]) an electron is transferred from the valence band to the conduction band (e^-), leaving behind a positive hole (h^+). This electron-hole pair can recombine to generate heat or interact with adsorbed species. If they recombine, photocatalysis does not proceed. On the other hand, if holes interact with water adsorbed on the surface of TiO_2, hydroxyl radicals ($OH^\bullet$) are formed [3]. These radicals are powerful and indiscriminating oxidizing agents that are capable of degrading a wide range of organic pollutants into H_2O and CO_2 [4]. Results presented in a huge number of publications dealing with the photocatalytic activity (PCA) of TiO_2 coatings suggest that it generally depends on three groups of factors: (i) those correlated with the coating itself, i.e., microstructure, composition, doping agents, surface area, etc. [5–7]; (ii) those correlated with the kind of target pollutant such as affinity, mechanism of degradation, etc. [8,9] and (iii) those correlated with the environment including temperature, humidity, incident light, pollutant concentration and oxygen concentration [7,8,10,11]. In this work, the impact of several variables from these three groups on the PCA was evaluated. Particularly, the influence of sample temperature, relative humidity, incident UV light (expressed here as distance between the sample and the UV lamp) and microstructure was explored in terms of stearic acid (SA) degradation.

Although many efforts have been made to obtain a deeper understanding of the effect of these factors on the PCA [5,7,10,12–15], experiments were usually performed by the traditional one-factor-at-time (OFAT) approach. A major drawback of this method is that effects caused by several factors acting in combination are frequently not detected. However, there are

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evidences that the PCA is not only affected by single factors but also by combinations of them such as temperature-humidity [12,16,17], humidity-target pollutant [17,18], etc. In other words, there could be cases when the TiO_2 films are subjected to environmental conditions in which the factor A has a certain effect on the PCA for a given level of factor B, while in a different level of B, the effect of A on the PCA is changed. The identification of these interactions is not easy using the OFAT approach. To overcome this problem, the design of experiments (DoE) methodology was used here to systematically plan all the experiments. Several variables were simultaneously considered, providing an efficient working strategy to explore both individual and interaction effects. The principal aims of this work were to determine whether the interactions between factors such as *temperature*, *humidity*, *incident UV light* and *microstructure* influence the PCA of TiO_2 films and, to find a model to predict the changes in this property when varying those variables. This information is thought to be of great value for the design of specific TiO_2-coated photocatalytic materials that must exhibit the highest efficiency possible for the combination of factors that characterize the particular working environment (i.e. geographical zones, indoor environments, outdoors environments, etc.).

2. Materials and methods

2.1. Preparation of the TiO_2 coatings

The dense coatings were prepared using the sol-gel synthesis procedure reported by Costacurta et al. [10]. The TiO_2 precursor sol was prepared by mixing titanium isopropoxide (98+% ACROS Organics), absolute ethanol (MERCK EMSURE®) and 1 M HCl (from 32% EMSURE) in the molar ratios 1:100:0.06. Before deposition, the sol was stirred for 1 h. A Si wafer was dip-coated in the fresh sol at 85 mm min^{-1} and 15% relative humidity (RH). Four layers were deposited and each layer was subjected to two thermal treatments at 110 °C for 10 min and then 250 °C for 30 min before the subsequent layer deposition. A final treatment of 500 °C for 3 h was performed to form the anatase crystals. The mesoporous TiO_2 coating was prepared by the evaporation-induced self-assembling (EISA) method following the procedure optimized by Crepaldi et al. [19], using surfactant Pluronic F127 as pore-forming agent. In the EISA method, the preferential evaporation of the solvent from the initial diluted solution (composed of the inorganic precursor, an alcohol and the pore-forming agent) concentrates the surfactant and the inorganic species before equilibration with the atmosphere [19,20]. The formation of micelles, acting as liquid crystal templates, permits the condensation of the inorganic framework in well-defined mesostructure hybrids [19,20]. Finally, the extraction of the surfactant template by heat allows to obtain a mesoporous structure. The initial dilute solution used here was prepared as follows: $TiCl_4$ (FLUKA Analytical) was slowly poured into a mixture of absolute ethanol (Carlo Erba) and tri-block copolymer Pluronic F-127 (SIGMA). Water (18 MΩ) was added dropwise after 5 min of stirring. The resulting molar ratio was $TiCl_4$:EtOH:H_2O = 1:40:12 and the $TiCl_4$/Pluronic F-127 ratio was 0.006. Films were deposited at 28–29% RH on Si substrates at 85 mm min^{-1}. After deposition, the fresh films were exposed to 45% relative humidity for 3 days. The aged coatings were treated at 60 °C, 100 °C and 130 °C for 24 h. Finally, a treatment at 500 °C for 4 h produced the anatase phase.

2.2. Characterization

The presence of anatase in both types of films was confirmed by gracing incident X-ray diffraction (GIXRD) using a PANAlitycal X'Pert PRO diffractometer with Cu Kα1 radiation. TiO_2 phase was also observed by Fourier Transform Infrared Spectroscopy (FTIR) using a Vertex 70-BRUKER spectrometer. The microstructure (e.g. particle size, pore diameter, film thickness) was observed by Field Emission SEM (SEM-FEG) in a FEI Nova Nano SEM 450 instrument.

2.3. Photocatalytic tests

The photocatalytic tests were carried out in a closed reactor that allows to adjust both temperature and relative humidity. Depending on the temperature required for each experiment, ice, water or silicon oil baths were used. Relative humidity was set using mixtures of dry (≤5% RH) and wet (water vapour-saturated) air. The desired humidity value was obtained in an air mixer before being sent to the photocatalytic reactor. The photocatalytic activity (PCA) of the TiO_2 films was evaluated by the degradation of stearic acid (SA) under UV irradiation at 365 nm (Vilber VL-215.LC lamp). To determine whether temperature and humidity have an effect on the adsorption process of SA on TiO_2, the films were exposed to the set atmospheric conditions inside the reactor for 30 min prior to deposition of the pollutant. This step will be referred as the *conditioning* step. After conditioning, 100 μl of an 8.8×10^{-3} M SA ethanolic solution were poured on each sample to form a film of SA. The variation in SA concentration with UV exposure time was followed by FTIR. Each spectrum was acquired in transmission mode, averaging 32 scans between 4000 and 400 cm^{-1} with a spectral resolution of 4 cm^{-1}. The efficiency was measured by the integrated area of the C—H vibrational bands of stearic acid in the 3000–2700 cm^{-1} range.

2.4. Experimental design

Table 1 shows the input factors and their levels used to define the experimental design. *Temperature*, *relative humidity* (thereinafter *RH*) and *microstructure* were chosen as input factors based on the results obtained in previous works [12–14]. The *incident UV light* was included since there are many evidences of its influence on the overall photocatalytic activity of TiO_2 [5,11]. For simplicity, this was expressed in terms of the *distance between the sample and the UV lamp*, which determines the incident UV irradiation (I) that arrives to the TiO_2 sample: at 1 cm, I = 1.0 mW/cm^2 while at 3 cm, I = 0.7 mW/cm^2. The efficiency of the PCA under each environmental condition was used as the output factor, and expressed as the *percentage of SA degraded following 30 min of UV irradiation* ($[SA_d]_{30min}$).

Table 2 shows the d-optimal experimental design defined from the input factors using Design Expert 7.0 software (version 7, Stat-Ease, Inc., MN). The experiments were performed according to the randomized run order (indicated as Run in Table 2) in order to eliminate effects of unknown or uncontrolled variables. Data analysis of the output factor ($Y_1 = [SA_d]_{30min}$) was conducted using Analysis Of Variance (ANOVA) in order to evaluate the relationships between factors and the response variable and to assess the model validity [21,22]. The residuals analysis (not shown) was used to evaluate the potential deviating experiments. The regression coefficients of the model were analysed and all terms with a p-value higher than 0.05 were not considered as statically significant.

3. Results and discussion

3.1. Characterization of the coatings

Fig. 1 illustrates SEM-FEG micrographs of the mesoporous (A and C) and dense (B) coatings. The mesoporous coating is formed by spherical particles with a diameter of 13.8 ± 2.8 nm that are aggregated around small pores with a diameter of about 8.0 ± 0.6 nm (Fig. 1C). Ordered porosity is present in the whole sample. The dense coating is formed by nanoparticles with a diameter of about