



## Low irradiance photocatalytic degradation of toluene in air by screen-printed titanium dioxide layers

Alberto Strini <sup>a,\*</sup>, Alessandra Sanson <sup>b</sup>, Elisa Mercadelli <sup>b</sup>, Alex Sangiorgi <sup>b</sup>, Luca Schiavi <sup>a</sup>

<sup>a</sup> Construction Technologies Institute, National Research Council of Italy (ITC-CNR), Via Lombardia 49, I-20098 San Giuliano Milanese, MI, Italy

<sup>b</sup> Institute of Science and Technology for Ceramics, National Research Council of Italy (ISTEC-CNR), Via Granarolo 64, I-48018 Faenza, RA, Italy

### ARTICLE INFO

#### Article history:

Received 13 December 2012

Received in revised form 6 August 2013

Accepted 7 August 2013

Available online 14 August 2013

#### Keywords:

Photocatalysis

Toluene

Screen-printing

Titanium dioxide

Anatase–rutile conversion

### ABSTRACT

Screen-printed titania photocatalytic layers made from Degussa P25 were studied in order to assess the potential of this deposition technology for the production of catalytic surfaces for airborne pollutant degradation. The deposited catalytic TiO<sub>2</sub> layers were characterized by a low density (about 25% of the titania bulk crystal) typical of very porous films. The study was carried out using toluene at low concentration (12 ppb) as model pollutant and with a low UV-A irradiance level on the sample surface (200 μW cm<sup>-2</sup>). The catalyst layers were deposited on alumina and quartz substrates demonstrating a good catalytic depollution activity. The relationship between the layer thickness and the catalytic activity was studied in the 1 to 6.8 μm range indicating an optimal 3–4 μm film thickness. Thicker layers do not show significant increases in the catalytic activity. The optical transmittance was studied using quartz substrate samples, showing a severely reduced photon flux for layers deeper than 5 μm. The effect of post-printing thermal treatment was studied in the 500–900 °C range, demonstrating good catalytic activity for processing temperatures ≤ 700 °C. These results indicate that the screen-printing process can be a promising technology for the realization of high efficiency photocatalytic materials for air depollution applications at low UV-A irradiance.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

The photocatalytic oxidation of ambient air pollutants [1–3], such as the volatile aromatic compounds and NO<sub>x</sub> found in urban and indoor air, is widely studied with many proposed applications for air depollution [4–6], both in passive [7] and active [8] implementations. Photocatalytic multifunctional materials can be obtained by dispersion of the photocatalyst in the material matrix itself as in the case of cement [9], paint [10] and paper [11] or by surface coating of suitable substrates. Several technologies were proposed including sol–gel [12], chemical vapor deposition [13,14], sputtering [15,16], spray-pyrolysis [17] and related techniques for the coating of substrates such as glass [16], ceramic [13], and stainless steel [18] with a photocatalytic thin layer. In these processes the photocatalyst is directly synthesized as thin film (typically <1 μm thickness) on the substrate surface during the deposition.

The screen-printing process is a well-known technique to obtain controlled layers for several different applications including solar cells [19], fuel cells [20], sensors [21] and films for electronic applications in general. The screen-printing technology has several valuable characteristics for the production of photocatalytic surfaces, including the ability to produce layers with controlled porosity up to 10 μm and more [22] and an easy process implementation and scale-up. Moreover, unlike

other coating methods based on in-situ synthesis, screen-printing also allows to create thick layers made from a previously available inorganic powder, permitting the deposition of special catalysts produced in a separated process. In the latter case an ink constituted by the inorganic component(s) dispersed into an organic matrix is printed on the substrate in tightly controlled conditions through a mesh screen. A post-printing thermal treatment is used for the inorganic fraction sintering and the concurrent elimination of the organic matrix by degradation and vaporization. Screen-printed semiconductor photocatalysts were first studied by Tsoukleris et al. [22] and Labrincha et al. [23,24] for the degradation of organic dyes in aqueous solution. However to date there is a substantial lack of studies specifically addressing the potential of screen-printed photocatalysts in the degradation of airborne micropollutants. The only exception is the work of Yüan Liu et al. who developed a special heterojunctional–electrical layered device [25].

In this work the photocatalytic oxidation of toluene in air by screen-printed titania layers was studied in order to assess the potential of this deposition technology for the production of catalytic surfaces for airborne pollutant degradation. The study was carried out in typical ambient conditions with respect to the temperature, relative humidity (R.H.) and pollutant concentration [2] using a relatively low UV irradiance level on the sample surface (200 μW cm<sup>-2</sup>). The titania layer samples were made from a commercially available photocatalyst screen-printed onto alumina substrate. A series of auxiliary samples was also prepared onto quartz and soda–lime glass for optical measurement and method optimization purposes. A key parameter for layered

\* Corresponding author. Tel.: +39 02 9806 434; fax: +39 02 9828 0088.

E-mail address: [alberto.strini@itc.cnr.it](mailto:alberto.strini@itc.cnr.it) (A. Strini).

photocatalysts is the optimal thickness that is strictly dependent on the physical properties of the catalytic layer and, ultimately, on the deposition process. The relationship between the layer thickness and the catalytic activity was studied using a series of screen printed titania layers prepared in the 1 to 6.8  $\mu\text{m}$  range with thickness-optimized ink formulations. The effect of the post-printing thermal treatment on the catalytic activity was studied using a series of samples processed at temperatures in the 500–900 °C range.

## 2. Experimental details

All air concentrations, volumetric flows and R.H. values in this work are given at 25 °C, and 101.3 kPa reference conditions.

### 2.1. Sample preparation

All photocatalytic samples were prepared at ISTE-CNR laboratories by screen-printing of  $\text{TiO}_2$  (P25, Degussa) photocatalytic layer onto alumina, quartz (fused silica) and glass substrates. The titania P25 catalyst was drawn from a single batch with 80/20 anatase/rutile phase ratio (Section 3.4) and, according to the manufacturer,  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$  specific surface area (Brunauer-Emmett-Teller) and 21 nm average particle size. It is well known that the quality of screen printing deposition strongly depends on the properties and consequently on the formulation of the ink used [20,26]. Particularly, the area-specific mass of the obtained final sample layer (layer loading) is related to the inorganic solid amount in the printing ink (ink solid loading). In order to modulate the titania layer loading (and therefore the thickness) of the sample films a selection of printing ink formulations was considered with solid loadings in the 7–28 wt.% range.

All screen printing inks used in this work were based on terpineol (isomer mixture, Aldrich) as solvent. The inks were prepared adding to the solvent the  $\text{TiO}_2$  powder and the proper amount of lauric acid ( $\geq 99.5\%$ , Aldrich), ethyl cellulose (45.0–46.5% w/w ethoxyl content, Fluka) and glycerol (85% reagent grade, Merk) used as deflocculant, binder and plasticizer respectively. A first ink (Ink 1) with the highest  $\text{TiO}_2$  loading (27.8 wt.%) was prepared adjusting a formulation previously reported in literature [26] to the specific morphologic characteristics of the titania powder used (Table 1). Ink 1 was used both as is and diluted with terpineol for the preparation of a first series of samples as described hereafter. The other  $\text{TiO}_2$  inks (Ink 2–5) were prepared by gradually decreasing the solid loading and keeping the solvent and the other organic components (binder and plasticizer) amounts constant. Only the deflocculant concentration was decreased according to the lowering of the  $\text{TiO}_2$  amount, in order to satisfy the deflocculant/solid powder ratio of 0.017 (w/w) previously optimized for Ink 1. It was found that the reformulation of each ink was preferable rather than a direct dilution of the first ink because the latter approach, while leading to viable samples, demonstrates to cause severe rheological alterations in the resulting inks with consequent sub-optimal film generation. All the formulations reported in Table 1 were found to be suitable for printing. The decrease in solid loading was compensated by an increase of

the organic components leading to small viscosity changes of the inks and, thus, good quality films.

After a preliminary manual mixing, each prepared ink suspension was ball-milled for 24 h and then a four-step fine milling was done with a three roll grinding mill equipped with zirconia rollers of nanometric finishing (Exakt 80E, Exakt, Nordstedt, Germany) to improve homogeneity as previously reported [26].

Three substrate materials were selected for this work, namely commercial 96% alumina substrates (0.62 mm thickness, Aurel Automation S.p.A., Italy), quartz (1 mm thickness) for optical measurements and standard soda-lime glass microscope slides (Menzel, Germany) for method optimization. All the substrates were prepared in  $26 \times 76 \text{ mm}$  pieces, washed with a NaOH saturated ethanol solution, HCl 1 M aqueous solution and finally sonicated in ethanol for 15 min (Transsonic T460H Bath, Elma) to remove organic and inorganic impurities [27]. A suitable mask (165 mesh polyester printing screen) was used to print a rectangular  $\text{TiO}_2$  area onto the substrates. Thick films were screen printed (squeegee speed  $90 \text{ mm s}^{-1}$ , squeegee load 64 N, snap-off distance 0.7 mm) onto the pre-cleaned substrate by a single print step using a precision screen printing machine (Aurel 900, Aurel Automation S.p.A., Italy).

Unless otherwise stated the as-deposited films were dried in ambient conditions and thermally treated at 500 °C for 30 min with a heating rate of  $100 \text{ °C h}^{-1}$ . The total amount of  $\text{TiO}_2$  deposited on each sample was determined by weighting the sample substrate before the printing process and after the thermal treatment, allowing the calculation of the actual catalyst layer loading. The weighting repeatability was estimated by replicated weight measurements of selected samples, with resulting  $\pm 0.01 \text{ mg cm}^{-2}$  layer loading error (1  $\sigma$ ). The surface microstructure and the thickness of the titania films were evaluated using scanning electron microscopy (Leica Cambridge Stereoscan 360, Leica) operating at 15 and 25 kV. All the microscopy samples were metallized with gold.

A specific series of samples was prepared in order to study the post-printing process temperature, using 30 min thermal treatment at 500 °C, 700 °C and 900 °C respectively. A corresponding series of unsupported catalytic powders was processed in the same way and characterized by X-ray diffraction (D8 Advance with Linxeye detector, Bruker AXS, Germany) using  $\text{Cu K}\alpha$  radiation in the 10–80° ( $2\theta$ ) range, scan by 0.02° steps (92.5 s integration time per step). The quantitative phase analysis was performed following the reference intensity ratio technique.

The complete list of all samples used in this work is reported in Table 2.

### 2.2. Photocatalytic activity measurement

The photocatalytic activity measurements were carried out at ITC-CNR laboratories using toluene in air at ambient concentration as model pollutant. The photocatalytic activity was measured using a previously described dedicated experimental system [9] based on a continuous-flow stirred photoreactor. Briefly, the experimental apparatus comprises an artificial air generator, a 2 L photochemical reactor placed into an irradiation chamber and a gas chromatograph with photoionization detector for the measurement of the toluene concentration in the reactor effluent. Because of the reactor stirring, the toluene concentration in the effluent air stream is representative of the whole reactor internal atmosphere allowing the direct computation of the reaction rate (Section 3.3).

The photoreactor supply air was obtained by mixing and humidifying gas-chromatographic grade nitrogen and oxygen (Alphagaz 1, Air Liquide, Italy) with a 500 ppb toluene standard diluted cylinder (Sapio, Italy) using a computer controlled artificial air generator [9]. A  $100 \text{ mL min}^{-1}$  total air supply flow (20.9%  $\text{O}_2$  v/v) at  $25 \pm 0.2 \text{ °C}$ ,  $50 \pm 2\%$  R.H. ambient conditions was used for all the measurements. The nominal operating toluene concentration was selected at

**Table 1**  
Screen-printing ink formulations (weight percent). Formulation components are identified also by CAS Number.

Component	Ink 1 (wt.%)	Ink 2 (wt.%)	Ink 3 (wt.%)	Ink 4 (wt.%)	Ink 5 (wt.%)
Titania powder (P25)	27.82	19.99	11.75	8.72	6.97
Terpineol [8000-41-7]	68.63	76.26	84.28	87.24	88.94
Lauric acid [143-07-7]	0.48	0.35	0.20	0.15	0.12
Ethyl cellulose [9004-57-3]	1.21	1.34	1.48	1.53	1.56
Glycerol [56-81-5]	1.86	2.06	2.28	2.36	2.40

Download English Version:

<https://daneshyari.com/en/article/8036336>

Download Persian Version:

<https://daneshyari.com/article/8036336>

[Daneshyari.com](https://daneshyari.com)