

Paper-based titania/hollow silica photocatalysts for ethanol abatement

M. Pera-Titus,^{1*} S. Adjimi,² P.-X. Thivel,² F. Delpech,² J.-C. Roux,² N. Sergent,² A. Kanaev³
¹E2P2L UMI 3464 CNRS – Solvay, Shanghai, 201108 China
²CNRS, LRP, LEPMI, LGP-2, Grenoble, 38000 France
³LPMTM, CNRS, Université Paris 13, Sorbonne Paris Cité, Villetaneuse, 93430 France
 *corresponding author: marc.pera-titus-ext@solvay.com

Introduction

Industrial malodorous pollution is hazardous for human life and provides a negative public image for industrial plants. Moreover, most of odorous compounds are volatile organic compounds (VOCs) having an unpleasant smell even at trace concentrations. The development of TiO₂-photocatalytic processes offers promising perspectives for odour removal.¹ Useful TiO₂-based products have been developed for environmental cleanup such as TiO₂-containing paper or simply photocatalytic paper.² Two methods are possible for supporting a catalyst on paper sheets: (1) “coating process”, where a TiO₂ suspension is coated on the fibrous support surface, and (2) introduction of TiO₂ into a cellulosic fiber suspension, where TiO₂ is deposited onto individual fibers before sheet formation.

Here we present the preparation of a novel photocatalytic paper by wet-end addition consisting of sol-gel titania nanoparticles immobilized on porous silica as an attempt to promote both the photocatalytic activity and stability of the papers. The photocatalytic activity has been tested on the decomposition of ethanol vapor as model VOC pollutant.

Materials and Methods

The silica support was prepared using a reported method.² Briefly, calcium carbonate OMYA Hydrocarb 90 with a mean particle size of 700 nm was used as template for the synthesis of hollow silica. The template was first dispersed in 1 L of water with 1 wt. % of sodium hexametaphosphate at 80.0°C. Sodium silicate (27 wt.% SiO₂, 10 wt.% NaOH) diluted twice was added dropwise to the CaCO₃ suspension for 2 h at 1.55mL/min⁻¹. The pH was kept at 9 by adding a HCl solution (0.1 M). The final suspension was then filtered, and rinsed with distilled water. The hollow structure was obtained by removing the CaCO₃ using a HCl solution (2 M) overnight at 80.0°C, followed by filtering and drying at 200°C.

Titanium tetra-isopropoxide (TTIP 98%) and 2-propanol were used in the preparation of sol-gel derived TiO₂ colloids with mean size =5.2 nm at 4.6-13.2 wt.% loading using a protocol described elsewhere.^{3,4} The photocatalytic material was further crystallized at 800°C to obtain a pure anatase phase. The composite TiO₂-SiO₂ material was characterized using complementary techniques, including ICP-AES, XRD, TEM, SEM and Raman.

Bleached softwood kraft pulp from TEMBEC-Fiber was used for the preparation of photocatalytic paper with a basis weight ranging from 60 to 200 g/m² (ISO 5269-2). Cationic polyacrylamide (C-PAM, FENNOPOL K3400 R from KEMIRA) was used as retention agent (0.1 wt.% dry fiber) in the silica-based TiO₂ papermaking system.

The activity of the photocatalytic papers was tested on a home-made continuous gas-flow reactor (500 mL(STP)/min) at 28 °C for an inlet ethanol concentration of 50 mg/cm³ and an incident UV radiation of 14.4 mW/cm² (HPK 125 W, Philips). The UV radiation could be introduced either in co-current or counter-current mode compared to the flow direction. The steady-state ethanol concentration leaving the reactor was monitored *online* using a GC equipped with a FID detector.

Results and Discussion

Figure 1A shows a TEM micrograph of the TiO₂-SiO₂ composite material (152 m²/g) after calcination at 800°C ensuring the genesis of a pure anatase phase as inferred by Raman spectroscopy (bands centered at 143, 196, 396, 515 and 639 cm⁻¹). Figure 1B shows the top view SEM micrograph a paper sheet pointing out an excellent homogeneity of the TiO₂-SiO₂ loading within. This homogeneity is confirmed by a Ti-mapping (EDS) on the paper sheet (Figure 1C).

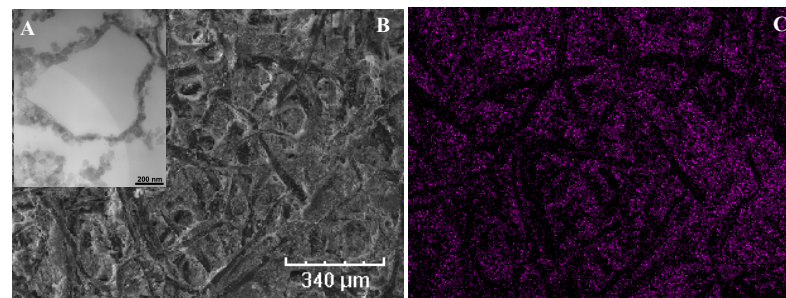


Figure 1. (A) TEM image of SiO₂-TiO₂ composite particle after crystallization at 800 °C, (B) top view SEM micrograph of a photocatalytic paper sheet with a basis weight of 200 g/m², and (C) Ti mapping in the paper sheet (EDS).

The photocatalytic performance of a series of TiO₂-SiO₂-loaded papers was inspected as a function of the basis weight and TiO₂-SiO₂ loading (Table 1). A minimum basis weight of 200 g/m² was found compulsory for enhancing the stability of the paper and ensuring enough photocatalyst. At these conditions, the activity of the paper was >5 mg.g_{TiO₂}⁻¹.min⁻¹, improving the activity of commercial TiO₂-coated paper (Ahlstrom) and offering a much better stability and recyclability even after exposure at a high UV intensity. A detailed simulation study combining the Kubelka-Munk equations and the convection-diffusion model for mass transfer revealed an active zone of ca. 30% of the paper thickness near the irradiated surface.

Table 1. Summary of ethanol conversion of different photocatalytic papers with variable basis weights and TiO₂-SiO₂ loading. Conditions: 50 mg/cm³, 14.4 mW/cm², counter-current mode.

Paper	Basis weight (g/m ²)	TiO ₂ -SiO ₂ loading (wt.%)	TiO ₂ loading (wt.%)	TiO ₂ basis weight (g/m ²)	Thickness (µm)	Ethanol conversion (%)
P1	200	40	1.7	3.3	466 ± 8	27
P2	200	40	3.4	6.9	477 ± 9	38
P3	200	40	4.8	9.6	421 ± 6	44
P4	100	10	1.3	1.3	189 ± 5	21
P5	60	12.5	0.9	1.6	139 ± 4	<5

References

1. Matsubara, H.; Takada, M.; Koyama, S.; Hashimoto, K. et al. *Chem. Lett.* **1995**, 767.
2. Amiche, F. US6221326B1, **2001**.
3. Rivallin, M.; Benmami, M.; Kanaev, A.; Gaunand, A. *Chem. Eng. Res. Des.* **2005**, 83, A1.