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Photocatalytic thin films of TiO_2 formed by a sol–gel process using titanium tetraisopropoxide as the precursor

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Abstract

Thin TiO_2 films were prepared with the dip-coating technique by using sols deriving from titanium tetraisopropoxide. TiO_2 films were formed on glass substrates previously covered by a SiO_2 layer obtained from a tetraethylortosilicate sol. The films, after a thermal treatment at 673 K, mainly consisted of TiO_2 anatase. The samples were characterised by X-ray diffraction, UV–Vis spectroscopy, scanning electron microscopy and atomic force microscopy. The photoactivity of the various films was tested by using as probe reaction the photo-oxidation of 2-propanol in gas-solid regime. The photoreactivity results indicated that the TiO_2 films were efficient for degrading 2-propanol under UV illumination, propanone being the only compound detected as intermediate product. Films prepared by using Degussa P25 appeared to be more photoactive, but the coating was easily detached by wiping.

Keywords: Dip-coating; Titanium dioxide; Thin film; 2-Propanol photodegradation; Structural properties

1. Introduction

The volatile organic compounds (VOCs) are an important class of air pollutants usually found in the atmosphere of all urban and industrial areas [1]. Many VOCs are known to be toxic and possibly carcinogenic. In order to eliminate or to reduce the serious health risks associated with the presence of VOCs in the environment, different processes have been suggested and developed for the treatment of air containing trace amounts of these noxious chemicals [2].

Some of the traditional purification procedures are based on the pollutant removal by simple transfer to another collecting phase, but the development of methods enabling the destruction in situ of the contaminants is nowadays more promising.

Among the decontamination techniques, the photocatalytic processes have received an increasing attention in the last decades [3–5] because they are potentially able to completely oxidize many organic compounds present in gaseous wastes [6–8]. Heterogeneous photocatalysis is a process based on the excitation of a semiconductor by light of energy equal to or higher than the band gap one. This excitation generates electron-hole pairs which can give rise to redox reactions with species adsorbed on the catalyst surface. Among the various semiconductors, TiO_2 is the most suitable photocatalyst because of its high activity, photostability and availability. Anyway, serious practical problems arise from the use of TiO_2 powders in the photocatalytic processes. Indeed, fine catalysts are not easily applicable to continuous flow systems because transport resistances to the catalyst surface may occur [9]. A key technology for the practical application of photocatalysis to environmental problems is the immobilization of TiO_2 as thin film on a solid substrate (even if normally the film-type photocatalysts have low surface areas and their intrinsic photocatalytic activity is usually smaller than that of the powders).

TiO_2 films have been often prepared by expensive methods as pulsed laser deposition [10], reactive evaporation [11,12] and chemical vapour deposition [13–15]. Low cost preparation methods are the sol–gel processes [16–20] including dip or spin-coating [21] as the final step of preparation.

This work reports a study on the preparation and characterisation of photocatalytic TiO_2 films. The support was a glass

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slide pre-coated with SiO_2 by immersion in sols obtained from tetraethylortosilicate (TEOS) solutions. The films were obtained by dip-coating technique from sols derived from titanium tetraisopropoxide (TTIP). The films were characterized by X-ray diffraction (XRD), optical and scanning electron microscopy (SEM), UV–Vis spectroscopy and atomic force microscopy (AFM). The photocatalytic activity of the various samples was evaluated by using the photooxidation of 2-propanol in gas–solid regime as a probe reaction, and compared to that of a coating of commercial Degussa P25 TiO_2. The influence of the thickness of the films on the photoactivity was investigated.

2. Experimental details

2.1. Preparation of the films

TiO_2 thin films were deposited on optical transparent microscopy glass slides (75 × 25 × 1 mm) covered by SiO_2 layers. The substrates were carefully precleaned prior to coating. A dip-coating apparatus, constructed in our laboratory, was used for the deposition. The substrates were immersed into the coating solution and then withdrawn at a regulated speed of 96 mm/min.

The SiO_2 coatings were obtained by immersing the substrate in a TEOS sol prepared according to the following procedure: 77 ml of 2-propanol, mixed with 5 ml of H_2O and 4 ml of HNO_3, were added dropwise at 273 K to 22 ml of TEOS mixed with 78 ml of 2-propanol. The resultant solution was stirred for 2 h. After each SiO_2 coating, the films were rinsed with water, dried for 5 min at 423 K and then calcined at 573 K for 3 h. The coating process was repeated three times.

The TiO_2 precursor sol was prepared by mixing 36 ml of titanium tetraisopropoxide (TTIP), 400 ml of H_2O and 3.8 ml of HNO_3 (65% w/w). After stirring for 24 h the sol was aged for 6 h at 328 K. Bare or SiO_2 pre-coated glass substrates were immersed in this sol, withdrawn and then dried at 423 K for 5 min. Finally the films were calcined at 673 K for 3 h. This procedure was repeated several times to obtain samples with increasing thickness. Alternatively, the calcination treatment was performed at the end of the various depositions.

Films of commercial Degussa P25 TiO_2 were deposited onto glass slides covered by SiO_2. The coatings were prepared by immersing the support in an aqueous dispersion obtained after 0.5 h ultrasound treatment of P25 powder. Each layer was dried at 423 K for 5 min and the whole films were calcined at 673 K for 3 h.

2.2. Characterization

Optical microscopic observations were carried out by using a Laborlux 12 POL Leitz microscope. Scanning electron microscopy (SEM) measurements were performed with an ESEM XL30 Philips microscope operating at 25 kV on specimens upon which a thin layer of gold had been deposited.

XRD patterns of the films were obtained at room temperature by a D8 Bruker X-ray diffractometer using the Cu Kα radiation and a 2θ scan rate of 0.01°/s. To record the diffractograms, typical incident angles of 0.5° were used. The crystallite size was calculated from X-ray line broadening analysis by the Scherrer formula.

Transmittance spectra of the films were measured in the UV–visible range (300–800 nm) using a double-beam spectrophotometer Shimadzu UV-2401 PC. The film thickness was measured with a home made optical profiler and by the interference fringes of the transmittance spectra.

Surface roughness and morphology of the TiO_2 films were evaluated by atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa Multimode operating in the tapping mode.

2.3. Photoreactivity experiments

A cylindrical Teflon batch photoreactor (Φ=6.5 cm; V=40.0 cm^3) equipped with a top Pyrex window was used. The film was placed inside the photoreactor and was irradiated at room temperature from the top by a 500 W medium pressure Hg lamp (Helios Italquartz). The irradiance at the film surface was 1.3 mW/cm^2. A water filter was interposed between the lamp and the photoreactor to cut the infrared radiation. The reacting mixture, consisting of wet oxygen and 2-propanol was fluxed for ca. 0.5 h before turning off the inlet and outlet valves and switching on the lamp. 0.5 ml of the mixture was withdrawn at different irradiation times using a gas-tight syringe. 2-propanol and propanone concentrations were measured by a GC-17A Shimadzu gas chromatograph equipped with a HP-1 column and a flame ionization detector, using He as the carrier gas.

The basic experimental set-up used in this study is shown in Fig. 1.

3. Results and discussions

3.1. Characterization of the samples

The coatings of Degussa P25 and the films obtained directly from the TTIP solution badly adhered to the glass substrate and

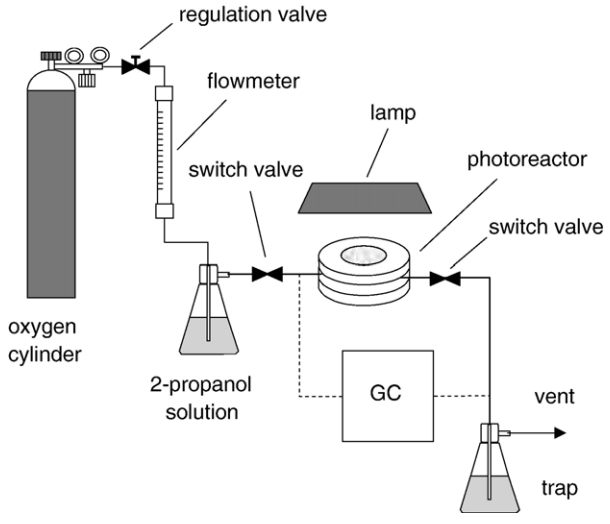

Fig. 1. Experimental set-up used in the photocatalytic degradation of 2-propanol.