



Gas phase 2-propanol degradation using titania photocatalysts: Study of the quantum efficiency



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ABSTRACT

A series of TiO₂ samples, prepared by a microwave assisted method followed by spray drying and subjected to further calcination, were tested in gas-phase photodegradation of 2-propanol under UV and Sunlight-type illumination conditions. Samples were characterized using X-ray diffraction, porosimetry, UV–vis and Photoluminescence spectroscopies. This physico-chemical characterization was completed with the in-situ analysis of the sample behavior under illumination conditions using infrared spectroscopy. The photochemical behavior of the samples was analyzed through their reaction rate and particularly efficiency parameters, the later measured as both the apparent and true quantum efficiency. To calculate the efficiency in quantitative basis we carried out a complete analysis of the light-matter interaction in the reaction system as well as the chemical response of the catalysts measuring reaction activity and selectivity. The study measures the differences observed among the most common (including the apparent and true quantum efficiency) approximations used to calculate the efficiency parameter providing evidence that they can differ in a factor of 2–4 and shows that optimum performance in our titania-based catalysts is obtained in presence of anatase-rutile interface contact. However, the analysis of the true quantum efficiency demonstrates that this is not exclusively based in the well-known effect of such interface in charge recombination but also depends critically on the variation of the optical properties of the catalytic solids through the series.

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1. Introduction

The environmental degradation as well as specific human health problems related to or encountered in the industrial era have forced to the implementation of technologies aiming at limiting the generation of pollutants and/or mitigating the noxious effects derived from their presence at the environment [1]. Advanced oxidation processes and particularly heterogeneous photocatalysis have evolved as powerful technologies to facilitate the control and elimination of pollutants [2,3]. Heterogeneous photocatalysis uses solid semiconductors to transform light into chemical energy. Titania is the semiconductor material considered as a universal photocatalyst due to its high activity in almost all degradation reactions concerning gas and liquid phase chemical pollutants. Titania

photocatalysts also found utility in other applications related to organic synthesis or microorganism elimination. Moreover, Titania is a material of relatively low cost and wide availability, further justifying the use of the semiconductor as the primary material in almost all applications within the photocatalytic field [2–5].

In this work we attempt to analyze the elimination of gas-phase 2-propanol using highly active titania based materials [6]. 2-propanol is a typical volatile organic pollutant present at urban atmospheres and particularly at indoor environments. Among the most typical sources of this pollutant, we can enumerate construction materials, household products, waxes, varnishes and many others [7–10]. The elimination of 2-propanol is thus of direct concern both to protect the environment as well as human health. Moreover, its elimination using photocatalysis has been frequently analyzed as a benchmark for titania materials [11–13]. The degradation of this alcohol produces a series of intermediates concomitantly observed with the total mineralization product, being

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typically detected acetone, formic and acetic acids, and in some cases, formaldehyde and acetaldehyde [11–16].

The widespread use of 2-propanol as a benchmark for gas-phase testing in the photocatalytic field hasn't however drive to the rigorous analysis of the corresponding photocatalytic performance in terms of the so called true quantum efficiency, as recommended by the IUPAC [17]. According to the IUPAC definition, the calculation of the efficiency concerns the ratio between the number of molecules photo-transformed and the number of photons absorbed by the catalytic material. This calculation requires the accurate measurement of the sample surface illuminated and thus catalytically active under illumination, the light handling properties of the whole (reactor + catalyst) system to calculate the net radiation flow at the catalyst surface, as well as the catalytic properties including both activity and selectivity to obtain the number of reacting molecules as well as the number of photons (through the number of charge species used to generate the reaction products) involved in the reaction [18–23]. The efficiency observable calculation thus demands for the complete elucidation of the optoelectronic properties of the catalytic materials as well as the interaction of the solid with the radiation field at reaction conditions, that is, at the reactor where the catalytic properties are measured.

To obtain an accurate measurement of the efficiency in the photo-degradation of 2-propanol we would thus measure the reaction rate and selectivity and provide information about the reaction main intermediates and mechanism using a combination of catalytic tests and in-situ infrared spectroscopy under illumination conditions. Jointly with the analysis of the interaction of the radiation field and the reaction system they will provide the framework rendering a rigorous analysis of the efficiency through a series of titania based catalysts. These catalysts concern materials obtained at different calcinations temperatures from a single precursor. The series attempts to study the evolution of the activity occurring in parallel to the increase of the calcination temperature paying attention to the evolution of the activity, particularly when the anatase-rutile interface is present at the solid material. As well known, the presence of such interface is typically found as a critical factor to provide highly active materials in photodegradation reactions [2–5,24]. Maximum photocatalytic enhancement is typically observed in presence of relatively low quantities of rutile, between 10 and 30 mol.% [25,26]. Here we will measure such enhancement on rigorous basis (using the true quantum efficiency observable) by comparing the anatase-rutile system in a system with low quantity of rutile and a closely related anatase material obtained at a lower calcination temperature. The catalytic solids were also subjected to a basic physico-chemical characterization of the materials using X-ray diffraction, porosity and UV–vis spectroscopy and their performance under reaction interpreted with the help of photoluminescence spectroscopy.

2. Material and methods

2.1. TiO₂ powders preparation

Catalysts preparation was carried out in a propylene vial containing a mixture of 46.5 wt% of ethanol (Industrial grade), 8.3 wt% of titanium butoxide (Aldrich, 97.00%) and 55.3 wt% of deionized water. The mixture was transferred and heated at 200 °C under microwave irradiation by using a microwave reactor (Anton Paar, model Synthos 3000). The temperature was maintained for 2 min. The suspension obtained from de microwave reactor was atomized through a 2 mm nozzle in a YAMATO spray dryer (model DL410), at 2 bar and 200 °C. After drying, some samples received a thermal treatment (600 or 700 °C) in air during 1 h. The nomenclature used to identify the materials thermally treated was: Ti-600, Ti-700.

The Ti reference sample corresponds to the catalyst synthesized and dried by the same conditions but without subsequent thermal treatment.

2.2. Characterization

X-ray diffraction analysis was performed on a Seifert D-500 diffractometer using Ni-filtered Cu K α radiation with a 0.02 step. The average crystallite size was calculated using the Scherrer equation and the (101) anatase and (110) rutile peaks as reference. Also microstrains were measured with XRD using the Williamson–Hall formalism [27]. Specific surface area, average pore volume and size were obtained with the help of a Micromeritics equipment (model, ASAP 2010) following nitrogen adsorption at 77 K and using the Brunauer–Emmett–Teller (BET) method. Samples were degassed under flowing argon at 473 K for 2 h before nitrogen adsorption. Photoluminescence spectra were measured at room temperature on a Photoluminescence Spectrophotometer (Perkin Elmer LS50B). The optical properties of the materials (transmission or diffusive reflectance) were measured on a Shimadzu apparatus (model, UV2100) using BaSO₄ or Teflon as a reference for diffuse experiments.

Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) were taken in a Bruker Vertex 80 FTIR spectrometer using a MCT detector and running under OPUS/IR software. The set-up consists of a praying mantis DRIFTS accessory (Harrick Scientific) and a reaction cell (HVC, Harrick Scientific having a quartz window allowing UV–vis excitation). The reaction mixture was prepared by mixing 2-propanol (Aldrich, 99.00%; final concentration 600 ppmv) with 20 vol% O₂/N₂ flow, humidified at 90%, before entering the DRIFTS cell. The DRIFTS spectra were collected in the range of 4000–600 cm⁻¹ with a resolution of 2 cm⁻¹, by averaging 60 scans over a total of 50 s. In DRIFTS experiments in-situ light excitation was carried out using a Hg-Xe lamp and filtering the 365 nm (20 nm half-width filter; Andover) radiation.

2.3. Photocatalytic activity assessment

The photocatalytic activity of the different TiO₂ powders was evaluated by the photo-oxidation of 2-Propanol (Aldrich, 99.00%) in gas phase. The reaction was carried out in a continuous flow annular photo-reactor using a setup described elsewhere [22,28]. The amount of catalyst employed for determining the activity and selectivity for the gas-phase photo-oxidation was 40 mg. The powder was suspended in 1 mL of ethanol, which was deposited on a Pyrex tube (cut-off at ca. 290 nm), and dried at room temperature to form a thin film. The gaseous mixture (prepared before entering the reaction system) in the reactor (100 mL min⁻¹) was obtained by mixing 2-propanol (Aldrich, 99.00%; final concentration 600 ppmv) with 20 vol% O₂/N₂ flow, humidified at 90%. Under such conditions the reaction rate is independent of the organic pollutant concentration. After flowing the mixture for 4–6 h in the dark (control test), the photocatalytic experiments were carried out under UV-A light irradiation (Sylvania F6WBLT-65; 6W) or sunlight type irradiation (Philips TL54-765; 6W). Full detail of the illumination source(s) characteristics are presented in Ref. [22]. In both cases, four fluorescent lamps symmetrically positioned outside the photo-reactor were used (see configuration at supporting information section, Fig. S1). Reaction rates were evaluated under steady-state conditions, typically achieved after ca. 6–10 h from the irradiation starting. No change in activity was detected for all samples within the next 24 h and the C balance was higher than 99% in all cases. 2-Propanol and products formed were detected and quantified by gas chromatography using an on-line Agilent chromatograph (model, GC 6890) equipped with HP-PLOT-Q/HP-Innowax columns (0.5/0.32 mm I.D. × 30 m) and TCD/FID detectors.

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