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Effect of the anatase–rutile contact in gas phase toluene photodegradation quantum efficiency

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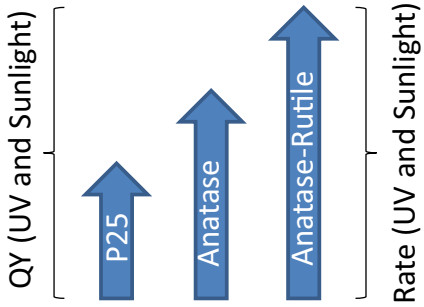
HIGHLIGHTS

- Microwave, calcined titania samples were tested under UV/Sunlight.
- Focus on the catalytic role of the anatase–rutile interface.
- Analysis of activity by means of the quantum efficiency parameter.
- Quantitative assessment of all physical variables of the efficiency parameter.
- Optimum enhancement: synergetic interplay between light-matter and chemical variables.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of TiO_2 samples prepared by a microwave assisted method followed by spray drying and calcination were tested in gas-phase photodegradation of toluene under UV and Sunlight-type illumination conditions. Samples were characterized using X-ray diffraction, porosimetry, UV–visible and photoluminescence spectroscopies as well as transmission and scanning microscopies. Their photochemical behavior was analyzed through their reaction rate and efficiency parameters, the later measured as both the apparent and true quantum efficiency. To interpret photocatalytic properties we carried out a study of the main physico-chemical variables affecting photoactivity and particularly its measurement through the efficiency parameter. In particular we focus on quantifying the catalytic effect of the anatase–rutile interface with respect to a parent anatase material prepared at different calcination temperature and in interpreting quantitatively such enhancement using the above mentioned physico-chemical analysis of the efficiency parameter. The study shows that there are some counteracting physical effects in the toluene photodegradation true quantum efficiency presented by anatase–rutile samples with respect to parent anatase counterparts.

1. Introduction

Since the early days in the photocatalytic field, it was clear that the titania semiconductor displayed the best general performance due to its versatility in photo-degradation and photo-production reactions concerning the elimination or transformation of both

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organic and inorganic molecules, its low cost and wide availability. During the subsequent studies it was however clear that the performance of many titania systems would require improvement, particularly in the wavelength region above ca. 400 nm where the oxide absorption is inherently low due to its high band gap energy. This objective appears of prime importance in order to allow the use of the sun as energy source of photocatalytic processes [1–5]. The analysis of the photocatalytic performance on quantitative basis was also discussed thoroughly in the literature and soon became evident that requires the calculation of the so-called efficiency parameter. According to the IUPAC definition, the calculation of the efficiency must take into account the number of molecules photo-transformed per photon absorbed at the catalytic material [6]. In other works it was detailed that 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 flux 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 charge species (and in turn photons) involved in the reaction [5,7–12]. Such task in turn requires 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.

Here we attempt to carry out the analysis of the efficiency in a series of titania samples prepared using a microwave procedure followed by a spray drying and calcination process at different temperatures. Microwave assisted method typically allows rather short treatments compared with other methods. Research using microwave method to obtain TiO_2 has been mostly focused in the synthesis of nanoparticulated materials, initially through the control of the primary particle size, and evaluating pH, solvents and surfactant effects. Besides, there are also examples of using such preparation method for doping titania with transition metals or nonmetal elements [13–16]. The spray drying is a suitable process extensively used in the food processing and pharmaceutical industry, and nowadays in material processing to obtain materials with a controlled morphology (primary particle size and shape, surface area, porosity, etc.) [17–19]. In this work, the sample series obtained by coupling both methods is devised to study how pure anatase, as the adequate reference, as well as the anatase–rutile contact evolving from the previous anatase polymorph perform both under UV and, more importantly, Sunlight-type illumination conditions. The anatase rutile contact is well known to provide high photocatalytic activity. However, the physical grounds of such behavior are not fully understood. It is generally accepted that the most active samples have a relatively low rutile concentration, between 10–30 mol.% [20,21]. The optimum contact is nevertheless strongly sensitive to the primary particle size of each phase (see as a summary of this issue Figure 21 in Ref. [2]) due mainly to differences in inter-phase band alignment and defect (particularly those at the interface) related influence in charge handling after light excitation, being the relative importance and significance of these two issues still under discussion [2,22,23]. Moreover, the catalytic influence through antenna and similar effects of other morphological variables (related to secondary particle size, porosity and connectivity of nanoparticles) has been described as important as the primary particle size to control charge handling after light excitation [2,24–26].

As outlined above, titania and particularly pure anatase materials are particularly poor in achieving significant activity under wavelength irradiation above the UV limit of ca. 400 nm [1–3]. To achieve significant performance under UV and visible excitation simultaneously (hence to provide high activity upon solar exposition) using titania materials without expensive modifications related to doping or surface sensitizing appears therefore as an important task in the field of photocatalysis. To test the UV, visible and Sunlight-type photocatalytic goodness of our samples, we selected the elimination of toluene as it is a typical urban contaminant and corresponds to a though still frequently used test concerning elimination of organic pollutants [27,28]. In addition, toluene photodegradation appears as an optimum tool to analyze the efficiency of the catalyst as it generates a limited number of products and thus can allow a relatively easy calculation of the observable. In fact, typically, titania materials render benzaldehyde as partial oxidation products and carbon dioxide at total, final product of the degradation. In a few cases traces of benzoic acid are also detected [29–36]. Here, a parallel structural and electronic analysis of the solids is carried out with the help of X-ray diffraction, UV–visible, photoluminescence spectroscopies and porosometry techniques. The combination of these techniques output with the efficiency analysis attempts to measure how the titania samples performs when parent anatase and anatase–rutile composite materials are tested.

2. Material and methods

2.1. TiO_2 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 different temperatures (120, 160 and 200 °C) under microwave irradiation by using a microwave reactor (Anton Paar, model Synthos 3000). The different reaction temperatures were 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 bars and 200 °C. After drying, each sample received a thermal treatment (600 or 700 °C) in air during 1 h. The nomenclature used to identify the materials thermally treated was: 1-700-SD, 1-600-SD, 2-700-SD, 2-600-SD, 3-700-SD, 3-600-SD. The first number corresponds to the reaction temperature in the microwave reactor (1 = 120 °C, 2 = 160 °C and 3 = 200 °C); the second number refers to the calcination temperature while SD refers to the spray drying process. 1-SD, 2-SD and 3-SD correspond to catalysts synthesized and dried by the same conditions without subsequent thermal treatment.

2.2. Characterization

X-ray diffraction analysis was performed on a Seifert D-500 diffractometer using Ni-filtered Cu Kα 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 Willianson–Hall formalism [37]. 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 $BaSO_4$ or Teflon as a reference for diffuse experiments.

A scanning electron microscope JEOL JSM (5300) was used to perform morphological analysis of the powders. Selected samples