



Quantitative determination of carbon in titania photocatalysts by temperature programmed oxidation method



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ABSTRACT

This study was directed to the optimization of a reliable and innovative approach, for the qualitative and quantitative analysis of carbon-doped titania photocatalysts. In particular, we report an easy procedure, based on the Temperature Programmed Oxidation (TPO) method for the determination and prediction of the carbon amount on the final catalysts. The synthesized Ti(OH)₄ photocatalysts were doped with different amount of succinic acid and an in-depth characterization was carried out by X-ray diffraction (XRD), physisorption of gas, elemental analysis, and temperature programmed oxidation (TPO). The final amounts of C, after calcinations, were determined by TPO analysis through the setting up of a calibration curve.

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1. Introduction

Titanium dioxide is known as the most important photocatalyst because of its non-toxicity, good chemical stability and high catalytic activity in various photo-oxidation reactions [1,2]. Photocatalysis applications of wide reaching importance include water splitting for hydrogen generation [3], degradation of environmental pollutants in aqueous contamination and wastewater treatment [4], self-cleaning activity and air purification [5].

However, its large high band gap (approximately 3.2 eV) requires the use of UV light ($\lambda < 387$ nm) [6] and does not allow the much larger visible part of solar light to be utilized.

Since the solar energy includes only 5% ultraviolet radiation, environmental applications of pure TiO₂ are limited. Consequently, during the last years, many efforts have been directed toward the development of a modified titania which would be photocatalytically active also with visible light.

One approach to synthesize modified-doped titania is the substitution of Ti with transition metal ions (such as V, Cr, Mn, Fe, and Ni) [7–9]. Unfortunately these doped materials are thermally unstable, and transition metal ions can act as electron-hole recombination sites, resulting in low efficiency [10]. An alternative reliable way to expand the wavelength range response of a semiconductor toward visible light is the modification of TiO₂ with non-metal atoms, such as N [11–14], S [15,16] and C [17–19]. This kind of titania modification leads to a decrease of the band gap energy in these materials [20]. C-doped materials are most

promising since, according to the result of Janus et al. [18], photocatalytic ability of C-doped TiO₂ could be improved by the decrease of the recombination rate in photogenerated electron-hole pair. This is allowed by the existence of electron scavenger carbon doped into TiO₂ [21]. Furthermore, carbon stabilizes anatase structure and increases the adsorption of organic molecules on the photocatalyst surface. The enhancement of photocatalytic activity was attributed to either the band gap narrowing [18] or the formation of localized mid-gap state [21]. These modified materials can be synthesized using various approaches in which the doping step occurred after the preparation of pure TiO₂ or during the synthesis. One of the most used carbon doping methods is mechanical mixing [22,23] of TiO₂ with various amounts of active carbon or other carbonaceous species or alcoholic compounds [21,24]. Using this approach, it's possible to obtain doped materials with well known amount of carbon on the TiO₂ samples but unfortunately this type of technique often leads to non-homogeneous samples and then, sometimes to irreproducibility in reaction collected data. Another modification approach considers some changes during the steps of titania synthesis (for examples using sol-gel synthesis with the addition of active carbon [25] or organic templates [26] as carbon source or using TiCl₄ hydrolysis [27] with for examples tetrabutylammonium hydroxide [12]). The samples obtained by this technique are more homogeneous than the previous ones. However it's difficult to know in advance the effective amount of carbon in the final catalysts and only a post synthesis determination can be carried out.

The aim of this work is the synthesis of various reproducible C-TiO₂ samples and the development of a fast and cheap test for their carbon amount determination. The attention was centered on the temperature

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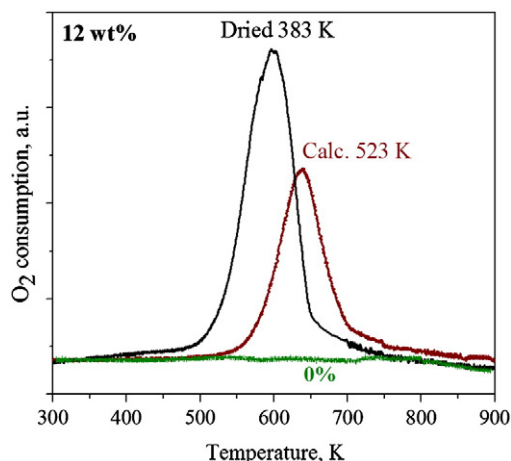


Fig. 1. TPO profiles of (a) no carbon-doped sample (green line); (b) dried carbon-doped sample (black line); (c) carbon-doped sample after calcinations to 523 K (brown line).

programmed oxidation (TPO test), that is a handy and relatively cheap analytical technique. Actually, this method is used above all for qualitative analyses and its potentiality is not fully exploited.

2. Experimental

2.1. Synthesis of C-doped TiO₂

Titanium hydroxide was obtained by precipitation from titanyl sulfate (TiOSO₄, Aldrich) aqueous solution by the addition of 9 M ammonia solution under vigorous stirring, as previously reported [28]. The Ti(OH)₄ powder was suspended in distilled water (25 wt.% solids) [29] and stirred at 333 K. Different amounts of succinic acid (Aldrich), from 0 to 12 wt.% referred to the solid, were added and slowly stirred until the complete dissolution of the organic compound. The obtained suspension was gradually dried in vacuum to partially eliminate the solvent. The “pasty mass” was subsequently dried at 383 K and then calcined at 523 K for two hours in flowing air. The calcination temperature was selected after a TPO analysis of a dried sample. The final samples were labeled %C-TiO₂ where %C was referred to the residual amount of

carbon after calcination treatment was calculated by using elementary analysis.

2.2. Methods

The crystal structure of the doped TiO₂ samples was studied by X-ray diffraction (XRD). X-ray powder diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer equipped with a Si(Li) solid state detector (SOL-X) and a sealed tube providing Cu K α radiation. Measuring conditions were 40 kV \times 40 mA. Apertures of divergence, receiving and detector slits were 2.0 mm, 2.0 mm, and 0.2 mm respectively. Data scans were performed in the 2θ ranges 5°–75° with 0.02° stepsize and counting times of 3 s/step.

Surface area and pore size distributions were obtained from N₂ adsorption/desorption isotherm at 77 K (using a Micromeritics ASAP 2000 Analyser). The samples (300 mg) were pre-treated at 383 K for 2 h under vacuum. Surface area was calculated from the N₂ adsorption isotherm by the BET equation, and the pore size distribution was determined by the BJH method also applied on the adsorption branch [30,31].

TPO experiments were carried out in a lab-made equipment: samples (50 mg) were heated at 10 K/min from 298 K to 1073 K in a 5% O₂/He oxidative mixture (40 mL/min STP). The effluent gasses were analyzed by a Gow-Mac TCD detector using both basic trap with soda lime in order to stop CO₂ and a magnesium perchlorate trap to stop H₂O. The oxidation process was monitored by a Genesys 422 quadrupole mass analyzer (QMS).

The amount of carbon was obtained by a Carlo Erba CNS Autoanalyser, mod. NA 1500. All analyses were replicated 2–3 times and the precision was >95%.

3. Results and discussion

In order to determine the optimal calcination treatment, TPO analyses were carried out. We propose to select a suitable treatment which allows to obtain well crystallized titania, with both high surface area and pure anatase polymorph phase and to maintain a suitable amount of carbon.

Fig. 1 shows the TPO analyses of three samples. In the TPO profile of the undoped sample (0.0% C-TiO₂) no peaks were detected. This means that there is neither carbon deposits on the catalyst nor oxidable species derived from titanium precursor. On the contrary, the TPO of a C doped TiO₂ dried at 383 K (we reported the profile obtained for the sample doped with 12 wt.% of succinic acid) presents a large peak from 473 K to 723 K with a maximum (centered) at about 596 K. This peak is due

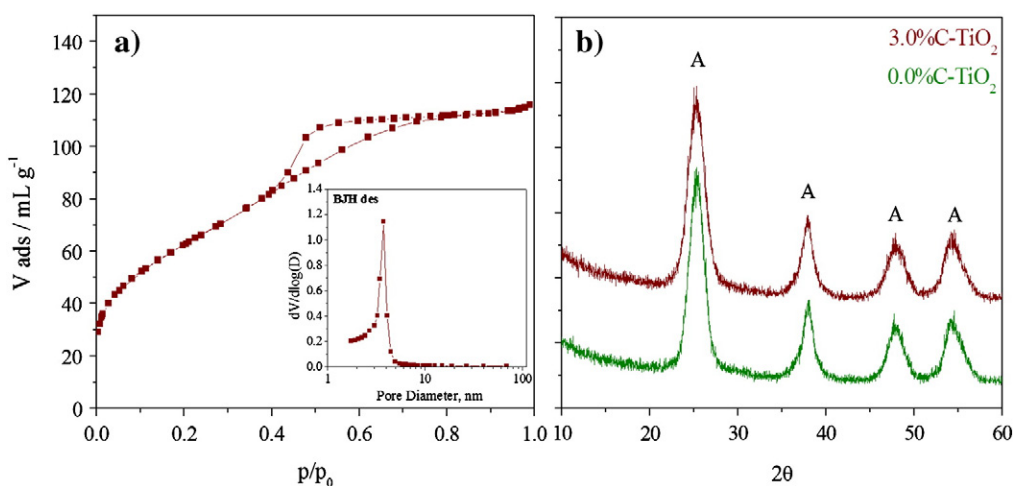


Fig. 2. (a) Isotherm and BJH desorption distribution curve (inset) for 3.0% C-TiO₂ and (b) XRD (A: anatase) for 3.0% C-TiO₂ and of the undoped TiO₂ (0% C-TiO₂).

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