Evaluation of sol-gel TiO₂ photocatalysts modified with carbon or boron compounds and crystallized in nitrogen or air atmospheres

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Abstract

Sol-gel TiO₂ photocatalysts are synthesized from titanium isopropoxide and crystallized by thermal treatment under either air atmosphere or nitrogen flow. Reference TiO₂ photocatalysts crystallized at 550 °C for 30 min in air are the most active for the degradation of diphenhydramine pharmaceutical (DPH). In addition, TiO₂ precursors are modified with carbon or boron compounds. The highest rates of conversion are obtained in the case of TiO₂ modified with boric acid and crystallized in air. The sol-gel photocatalysts with the best performances possess anatase:rutile phase ratios in excess of 95% with anatase crystallites of approximately 60 nm. The photocatalysts are characterized by different solid state and solution techniques, including powder X-ray diffraction, elemental analysis, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, diffuse reflectance ultraviolet-visible (UV-Vis), UV-Vis liquid spectroscopy, surface area analysis and ammonia thermal programmed desorption. The efficiencies of the synthesized photocatalysts are characterized by the kinetics of DPH degradation under near UV-Vis irradiation. The efficiencies of the synthesized photocatalysts are comparable or even higher than that of the reference P25, although their dispersions in water have much lower absorbance values.

Keywords: titanium dioxide; carbon; boric acid; crystallization; photocatalysis

1. Introduction

Many different strategies have been investigated for the improvement of TiO₂ photocatalytic efficiency, trying to decrease the electron/hole recombination rate and to extend the light capture ability into the visible range [1]. The possible TiO₂ modifications include, among others, noble metal loading, metal ion doping, anion doping, dye sensitization, semiconductor coupling and combination with carbon materials [1]. Doping TiO₂ implies the interstitial or substitutional insertion of other atoms, cations or anions in the TiO₂ crystalline cell [2, 3]. Doping TiO₂ with carbon has been attempted by different methods [4-8].

Apart from C-doping, carbon materials have been tested as additives, supports or coatings for improving TiO₂ photocatalytic properties [9]. Typically, the synthesis of TiO₂ composites is carried out through an intimate mixture of the component precursors followed by a high temperature treatment. In the case of C/TiO₂ composites, thermal treatments in air can produce the combustion of the carbon materials or precursors, being often substituted by hydrothermal treatments at lower temperatures. Another possibility to avoid combustion is the use of inert atmospheres for the thermal treatments [10-14]. Several studies have comparatively investigated the effect of changing the crystallization atmosphere on the final activity of the C/TiO₂ photocatalysts [15, 16]. These studies appear to indicate that there is not an established criterion regarding the preferred atmosphere for the crystallization of C/TiO₂ photocatalysts.

Sol-gel processes have been widely utilized for the synthesis of TiO₂ and TiO₂ composite photocatalysts, since amorphous TiO₂ solids can be easily prepared and subsequently crystallized at controlled conditions. A great number of C/TiO₂ composites have been synthesized by sol-gel methods, including coke-containing TiO₂ [17], multi-walled carbon nanotube/TiO₂ [10-13, 18-20], graphene oxide/TiO₂ [21], and single-walled carbon nanotube/TiO₂ [22]. Carbon materials, particularly graphite-like nanostructures and thin films, act as electron withdrawers, increasing the lifetime of the photoexcited electron/hole pairs and thus the photocatalytic efficiency [23, 24]. In addition, some of those C/TiO₂ composites demonstrate photocatalytic activity under visible light, which is attributed to a decrease in the band-gap when compared to bare TiO₂ and/or to the action of the carbon phase as a photosensitizer.

More recently, sol-gel methods have been applied to the synthesis of B/TiO₂ hybrid photocatalysts. It has been predicted that boron doping by substitution of oxygen atoms

would produce the TiO₂ band-gap narrowing [3]. However, the addition of boron compounds to TiO₂ sol-gel precursors typically leads to interstitial B-doping or the formation of B₂O₃ on the TiO₂ particles, with unclear effects in the photocatalytic activity [25-29]. In particular, a multicomponent photocatalyst of B/C/TiO₂ type showed better activity than the corresponding C/TiO₂ and pure TiO₂ materials for the degradation of acid orange dye under visible light [30]. In that report, three B/C/TiO₂ catalysts were crystallized at 300 °C in different atmospheres, showing degradation rates following the order: nitrogen flow > static air > air flow [30].

In the present article, the modification of sol-gel TiO₂ photocatalysts with various carbon compounds (glucose, citric acid and acetylacetone) or boric acid is studied. The results of TiO₂ crystallization in both air atmosphere and nitrogen flow at different temperatures are compared. It is shown that any modification in the TiO₂ precursor leads to TiO₂ crystals with different characteristics in terms of crystallite size and crystalline phase. Therefore, the heat treatment conditions were optimized for achieving the highest possible photocatalytic activities in each case. The photocatalytic activities were evaluated under near ultraviolet-visible (UV-Vis) irradiation, which can be considered as a close emulation of solar light. Our focus in this work is to find active photocatalysts for the degradation of diphenhydramine (DPH) pharmaceutical as a model pollutant in water. Results on the photocatalytic degradation of DPH have been previously reported using pure sol-gel TiO₂ catalysts and C/TiO₂ hybrids containing graphene oxide [31, 32]. Here, we propose other routes for the TiO₂ modification with carbon and boron materials and we present an extended study on the effects of thermal treatments in different atmospheres.

2. Experimental

2.1. Chemicals and materials

Titanium (IV) isopropoxide ($\geq 97.0\%$), glucose ($\geq 99\%$), ammonium hydroxide (28.0-30.0% NH₃ basis), acetylacetone ($\geq 99.5\%$) and DPH ($\geq 99\%$) were supplied by Sigma-Aldrich. Isopropanol ($\geq 99\%$) was supplied by Labkem. Citric acid, anhydrous ($\geq 99.5\%$) was supplied by Alfa Aesar. Boric acid ($\geq 99.9\%$) was supplied by Borax. Spectroscopic grade potassium bromide (KBr, $\geq 99\%$) was supplied by Scharlau. Aeroxide TiO₂ P25 (Evonik, TiO₂ $\geq 99.5\%$) was utilized as the reference photocatalyst.

The nomenclature and preparation conditions for all the studied photocatalysts are summarized in Table 1. The materials are labelled as XQ/TiO₂/YT, where X refers to the

precursor used (G – glucose, Cit – citric acid or A – acetylacetone), Q to the amount of precursor, Y to the crystallization atmosphere (A – air or N – nitrogen) and T to the crystallization temperature in °C. $\text{TiO}_2/\text{AT}(t_c)$ materials were subjected to different crystallization temperatures (T) and thermal treatment periods of isothermal stage after reaching T (t_c in minutes). TiO_2/NT was prepared under nitrogen atmosphere instead of air. The details are given in Sections 2.2, 2.3 and 2.4.

2.2. *Pure TiO_2 photocatalysts*

Titanium (IV) isopropoxide was added to isopropanol in a 1:10 v/v proportion, and 55 mL of the solution was slowly dropped into 50 mL of a water/isopropanol mixture (1:1 v/v) under constant stirring. The resulting yellowish colloid was aged for 20 h under stirring, and then vacuum filtered. The yellowish deposit was dried in an oven at 90 °C for 24 h. A white powder material of amorphous titanium oxide (a- TiO_2) was obtained, with a typical yield of 1.5 g, and finely grinded.

An appropriate amount of the a- TiO_2 material was placed in a ceramic boat and thermally treated in a Carbolite furnace provided with a custom-made cylindrical quartz reactor ($\phi \sim 30$ mm). For the optimization of pure TiO_2 catalysts, different treatment temperatures and thermal treatment periods were tested under air atmosphere (series $\text{TiO}_2/\text{AT}(t_c)$). A heating rate of 10 °C min^{-1} was used in all the experiments, and the treatment period (t_c) refers to the isothermal stage after reaching T. Mass yields of the thermal treatments were of $\sim 82\%$. For comparison with the series crystallized in air, a sample ($\text{TiO}_2/\text{N550}$) was crystallized in a nitrogen flow of $\sim 500 \text{ cm}^3 \text{ min}^{-1}$.

2.3. *C/ TiO_2 photocatalysts*

Hybrid C/ TiO_2 catalysts were prepared through two different strategies. The first one was the impregnation of the previously prepared a- TiO_2 with a solution of a carbon precursor (glucose). Aqueous glucose solutions were prepared with concentrations ranging from 5 to 40 mg mL^{-1} , and a volume of 1 mL of the glucose solution was slowly dropped onto 1 g of the a- TiO_2 solid. The impregnated solids were thermally treated in the horizontal quartz reactor at different temperatures under a nitrogen flow of $\sim 500 \text{ cm}^3 \text{ min}^{-1}$ (sample series GQ/ TiO_2/NT). The inert gas was supplied during the thermal treatment in order to avoid the combustion of the carbon precursors. In addition, a reference sample was crystallized under air atmosphere at 550 °C (GQ/ $\text{TiO}_2/\text{A550}$). The materials crystallized under an inert flow were light gray, dark gray or nearly black,

depending on their carbon content. On the contrary, the material crystallized in air was white.

A second strategy for preparing C/TiO₂ was based on the addition of carbon precursors (citric acid or acetylacetone) to water before the titanium isopropoxide hydrolysis. Citric acid/a-TiO₂ precursors were crystallized at different temperatures under a nitrogen flow (sample series CitQ/TiO₂/NT). The resulting materials were light gray or dark gray, depending on the amount of citric acid added. Also, a reference sample (Cit100/TiO₂/A550) was prepared with 100 mg of citric acid and crystallized at 550 °C in air, resulting in a white solid. The average mass yield for the crystallization process was 74.8%.

Acetylacetone has been previously utilized as a complexation agent for controlling the hydrolysis of the titanium precursor [33]. In the present work, a series of C/TiO₂ samples was prepared by the addition of acetylacetone to the water/isopropanol solution before the addition of the titanium precursor. Acetylacetone (0.5 mL) was added to 50 mL of the water/isopropanol (1:1 v/v) solution, followed by the addition of 0.25 mL of 30% ammonium hydroxide. Then, the titanium isopropoxide/isopropanol (1:10 v/v) solution was dropped onto the water solution, giving a yellowish colloid. After aging, filtering and drying, a yellow-orange solid was obtained. The acetylacetone/a-TiO₂ product was crystallized at different temperatures under a nitrogen flow, resulting in dark gray powder materials (series AQ/TiO₂/NT).

2.4. H₃BO₃/TiO₂ photocatalysts

Boric acid (~200 mg) was dissolved in 50 mL of the water/isopropanol (1:1 v/v) solution before the addition of titanium isopropoxide. The hydrolysis of the titanium precursor resulted in a white colloid, which was aged, filtered and dried as described above. A series of H₃BO₃/TiO₂ catalysts was prepared by crystallization of the H₃BO₃/a-TiO₂ material at different temperatures in a nitrogen atmosphere (series B200/TiO₂/NT). In addition, another catalyst was crystallized at 550 °C in air (B200/TiO₂/A550).

2.5. Characterization techniques

Crystal structure was assessed by powder X-ray diffraction (XRD) in a Bruker AXS D8 Advance diffractometer working with a CuK α (λ = 0.154 nm) radiation source. The software EVA and the Powder Diffraction File (PDF) database were utilized for the

semi-quantitative estimation of phase composition. The size of crystal domains was calculated by the Scherrer equation with a shape factor of 0.89. Crystallite sizes were not calculated for phase contents of less than 5 %, as the error was very high.

Elemental analysis for the determination of total carbon in the TiO₂ catalysts was performed in a Thermo Flash 1112 analyzer. In a typical experiment, the sample is treated at 950 °C in an O₂ flow and in the presence of V₂O₅. Subsequently, combustion gas products pass through a CuO oxidant bed at 950 °C and a redactor bed at 500 °C. The resulting CO₂ is separated and analyzed by gas chromatography with a thermal conductivity detector.

The B/Ti atomic ratio of the materials modified with boric acid was calculated by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed in a ESCAPlus Omicron spectrometer provided with a Mg anode working at 1253.6 eV (150W).

Fourier-transform infrared (FTIR) spectroscopy was measured in a Bruker Vertex 70 spectrometer. For the measurements, 2 mg of the samples were mixed with spectroscopic KBr (200 mg) and pressed (10 Tm, 2 min) to form pellets (ϕ = 13 mm). Optical absorbance of the powder dispersions in water was measured in a Shimadzu UV-3600 spectrometer. Dispersions were prepared by 10 min bath sonication, and the measurements were performed approximately 30 min after sonication, preceded by manual agitation. Diffuse reflectance (DR) UV-Vis spectra were also measured in the Shimadzu UV-3600 spectrometer, in this case provided with an integrating sphere accessory.

Specific surface areas (S_a) were calculated by the BET method from the nitrogen adsorption isotherms. The isotherms were measured at the liquid nitrogen temperature in a Micromeritics ASAP 2020 equipment. Surface acidity was characterized by thermal programmed desorption (TPD) of ammonia in a Micromeritics AUTOCHEM II 2920 equipment. First, samples were treated in helium at 500°C for 90 min. Subsequently, samples were saturated with ammonia passing a 50 scc min⁻¹ flow of 5% NH₃/He at 200 °C for 1 h. Physically adsorbed ammonia was removed by a 2 h treatment in helium at 200 °C. Finally, TPD of chemisorbed ammonia was carried out from 50 to 500 °C at 30 °C min⁻¹ in helium.

2.6. Photocatalysis experiments

The photocatalytic experiments were performed in a quartz cylindrical reactor (7.5 mL) at room temperature (25°C), which was loaded with the DPH aqueous solution (100 mg

L⁻¹) and the catalyst powder (1 g L⁻¹). The suspension was magnetically stirred and a dark period (30 min) was maintained before switching on the lamp, in order to achieve the adsorption-desorption equilibrium condition. For all the photocatalysts tested, the adsorption capacity was not higher than 4 % of the initial DPH concentration. Direct DPH photolysis was also evaluated, with less than 5 % of the DPH concentration decrease in 60 min.

The irradiation source consisted in a Heraeus TQ 150 medium-pressure mercury vapor lamp equipped with a UV-A/UV-B cut-off filter (main excitation lines at $\lambda = 365, 436$ and 546 nm). The irradiance reaching the photocatalytic reactor was approximately 33 mW cm⁻², as determined by using a UV-Vis spectroradiometer (USB2000+, OceanOptics, USA). The concentration of DPH was analyzed by HPLC with a Hitachi Elite LaChrom system equipped with a Hydrosphere C18 column (250 mm $\times$ 4.6 mm; 5 μ m particles), a diode array detector (L-2450) and a solvent delivery pump (L-2130). Small aliquots (a few μ L) for HPLC analysis were extracted from the reactor at three intermediate time intervals (10, 20 and 30 min) and at the end of the experiment (60 min). An isocratic method set at a flow rate of 1 mL min⁻¹ was used with the eluent consisting of an A:B (70:30) mixture of 20 mM NaH₂PO₄ acidified with H₃PO₄ at pH 2.80 (A) and acetonitrile (B). Total organic carbon (TOC) was determined for selected samples at the end of the photodegradation experiments using a Shimadzu TOC-5000A analyzer. The maximum relative standard deviation of both HPLC and TOC measurements was never larger than 2%.

The results were interpreted in terms of pseudo-first order kinetics. This procedure, which assumes a Langmuir-Hinshelwood mechanism for the degradation reactions, has been typically applied in the literature. As in previous works [31, 32], the DPH concentration (C_{DPH}) in the solution is expressed as an exponential decay (Eq.(1)).

$$C_{\text{DPH}} = C_0 \exp(-k_{\text{app}}t) \quad (1)$$

where C_0 is the concentration of DPH after stirring with the catalyst in darkness for 30 min, k_{app} is the apparent first order rate constant and t the reaction time. The fraction (%) of decomposed DPH is defined by Eq. (2).

$$X_{\text{DPH}} = 100 \cdot (1 - C_{\text{DPH}}/C_0) \quad (2)$$

3. Results and discussion

3.1. Photocatalytic activity

The photocatalytic results for a series of selected samples are summarized in Table 2. The original DPH degradation curves and the complete set of results can be seen in the Supplementary Information (SI).

3.1.1. Neat TiO₂ photocatalysts

Crystallization temperature and time needs to be optimized in order to select the synthesis standard conditions. Using neat TiO₂ as reference, samples were crystallized in air (series TiO₂/AT(*t_c*)) and their activity evaluated in DPH degradation by means of the determined first order rate constant. A maximum k_{app} was found for the sample treated at 550 °C, while k_{app} markedly decreased for higher crystallization temperatures (SI). Similar trends have been previously described, even though the optimal temperature depends on the titanium precursor, the catalyst preparation, and the photocatalytic reaction [34-36].

Crystallization time is a parameter that is not very often analysed in the literature. Previously, it has been observed that time does not have a great influence when TiO₂ precursors are hydrothermally treated in an autoclave before crystallization at high temperature [34]. However, our synthesis conditions were different as we performed the crystallization treatment just after room temperature hydrolysis, and here time results to be a very important parameter. The optimized crystallization time of 30 min was chosen for the rest of the experiments.

The photocatalytic activity parameters for TiO₂/A550(30) and TiO₂/N550 samples are listed in Table 2. Both materials were prepared under identical conditions, except for the atmosphere used during the crystallization treatment. Clearly, crystallization in air was more favourable than in a nitrogen flow, which caused a 51% decrease in the k_{app} .

The photocatalytic activity of the optimized TiO₂/A550(30) sample was compared with the standard P25 TiO₂ material at three different catalyst loads. Both materials demonstrate nearly identical k_{app} values using a 1 g L⁻¹ load. It was also observed that P25 TiO₂ reached a similar k_{app} value with only 0.5 g L⁻¹.

3.1.2. Carbon and boron modified TiO₂ photocatalysts

In a first approximation, the optimized conditions found in Section 3.1.1 for the crystallization of neat TiO₂ photocatalysts (550 °C, 30 min) under nitrogen atmosphere (TiO₂/N550) were kept for the a-TiO₂ material impregnated with glucose. It was observed that the presence of glucose caused a dramatic decrease in the photocatalytic

activity of the resulting material. Therefore, we tried to optimize the crystallization temperature for the particular case of the a-TiO₂ impregnated with glucose. An optimal crystallization temperature for DPH degradation was found at around 460 °C (SI). However, the best photocatalyst in the series (G20/TiO₂/N460) had a lower photocatalytic activity than the reference TiO₂ samples.

In order to clarify the influence of carbon content in the photocatalytic activity, a series of samples (GQ/TiO₂/N460) was prepared by impregnation with different amounts of glucose, followed by crystallization at a fixed temperature of 460 °C under N₂ atmosphere (SI). The optimal carbon content was found to be of around 1 wt.% (sample G10/TiO₂/N460). Despite the G20/TiO₂/N460 sample was prepared under previously optimized temperature and thermal treatment duration under N₂ atmosphere, its photocatalytic activity was lower than that of an analogous sample (G20/TiO₂/A550) crystallized in air at 550 °C (Table 2).

Another strategy for the preparation of C/TiO₂ composites was the addition of carbon precursors to water before the titanium isopropoxide hydrolysis. This procedure avoids the subsequent step of a-TiO₂ impregnation with glucose. However, the photocatalytic behaviour of those materials was not very different from the glucose series. For samples prepared with the citric acid precursor, optimal crystallization temperatures in a nitrogen flow were found at 460 or 500 °C (SI). The samples of the Cit5/TiO₂/NT series contained a low amount of carbon (0.24±0.03 wt.%), the best photocatalytic activity being obtained for Cit5/TiO₂/N460 sample. The k_{app} for this photocatalyst was nearly identical to the control sample TiO₂/N550. In the catalyst series Cit100/TiO₂/NT, whose samples contained a higher amount of carbon (1.54±0.03 wt.%), the best catalyst (Cit100/TiO₂/N500) showed low activity. A control sample crystallized in air (Cit100/TiO₂/A550) showed a higher photocatalytic activity than all the samples synthesized under nitrogen flow (Table 2).

The addition of acetylacetone (0.5 mL) as carbon precursor led to the presence of a higher carbon content (3.51±0.10 wt.% on the average for series A05/TiO₂/NT). The photocatalytic activity was very low, showing a $k_{app} = 0.418 \times 10^{-2} \text{ min}^{-1}$ for the best sample in the series (A05/TiO₂/N460).

The photocatalytic activity (k_{app}) for the B200/TiO₂/NT series did not noticeably change with the crystallization temperature in the range of 460-575 °C. The photocatalytic activity of the B200/TiO₂/N550 sample is higher than that of the reference material TiO₂/N550 (Table 2). When the crystallization atmosphere was changed to air, the

photocatalytic activity increased. In fact, the B200/TiO₂/A550 sample demonstrated the highest k_{app} value found in the present work. From XPS measurements, it was found that B/Ti atomic ratios for the B200/TiO₂/A550 and B200/TiO₂/N550 samples were of 0.84 and 1.66 respectively. Surprisingly, the material kept a higher amount of boron when it was crystallized under N₂ flow.

3.1.3. Mineralization vs. conversion of DPH

Apart from the apparent degradation rate constant (k_{app}), other parameters including the DPH fraction that is degraded after 1 h of irradiation (X_{DPH}) and the DPH fraction that is ultimately transformed into CO₂ (X_{TOC}), must be analyzed in order to have a complete assessment of the photocatalyst performance. Those parameters are listed in Table 2 for a series of photocatalysts.

As expected, the X_{DPH} parameter for different TiO₂ materials follows a trend nearly identical to k_{app} . The highest X_{DPH} values were found for the B200/TiO₂/A550, P25 and TiO₂/A550(30) photocatalysts. It can be observed that most of the DPH is degraded after 1 h of irradiation in the presence of those photocatalysts. The trend in the X_{TOC} values for different TiO₂ materials is also similar to k_{app} . However, conversion into CO₂ is not complete after 1 h for any of the photocatalysts. The highest X_{TOC} values were found for P25 and B200/TiO₂/A550 materials.

It is clear that TOC conversion values (X_{TOC}) are lower than those of DPH degradation (X_{DPH}) at the studied conditions. Thus, some toxic by-products could remain in water after the photocatalytic treatment. A careful control of the operation conditions, as well as the utilization of certain additives, may be recommended to maximize mineralization levels [37].

3.2. XRD analysis

Figure 1 shows the XRD profiles for various neat and hybrid TiO₂ materials, including those with the best photocatalytic properties. The anatase-to-rutile phase ratio (A:R) and average crystallite sizes (d_A and d_R for the anatase and rutile phases respectively) were calculated from the diffractograms and are listed in Table 2, together with the values for the standard P25 TiO₂ material. It can be observed that the diffractograms only contain signals corresponding to anatase or rutile TiO₂ phases, except for the B200/TiO₂/A550 sample, which shows an additional band at $2\theta = 28.1^\circ$. This band clearly reveals the

presence of a separate crystal phase mixed with the TiO₂ particles, being assigned to boric oxide (B₂O₃) [25].

Another important observation from XRD profiles is that the TiO₂ modification with carbon or boron compounds did not cause any shift in the anatase and rutile peak positions. This indicates that the unit cell parameters of TiO₂ phases were not substantially modified, suggesting that carbon and boron atoms were not inserted inside the TiO₂ unit cells. Therefore, XRD analysis implies that TiO₂ doping does not take place in the bulk crystalline structure by the applied synthetic routes.

The TiO₂/A550(30) material, which was crystallized under optimized conditions in air, showed XRD parameters (A:R = 95.0%, d_A = 54.1 nm, d_R = 76.6 nm) in good agreement with a previous report [36]. When an analogous precursor material was crystallized in a nitrogen flow (TiO₂/N550 sample), the A:R phase ratio slightly decreased, and the average crystallite sizes experienced a relatively small increase. The small modifications in the crystal structure could in part explain the decrease in the photocatalytic activity observed for the TiO₂/N550 sample. In fact, it has been previously reported that small deviations from the optimal XRD parameters may be associated to great diminution in the photocatalytic activity [34].

The presence of glucose caused a decrease in the crystallite sizes after treatment in a nitrogen flow. For the optimal photocatalyst of the GQ/TiO₂/N460 series (G20/TiO₂/N460), the crystallite sizes were quite smaller than for the reference sample TiO₂/N550, which could be associated to the decrease in the photocatalytic activity. Although crystallite growth is hindered by the presence of glucose during the treatment under nitrogen atmosphere, crystallites appear to grow normally if the thermal treatment is performed under air. Actually, anatase crystallites for the G20/TiO₂/A550 sample were even larger than for the control TiO₂/A550 material. As the A:R phase ratio was nearly identical for both materials, the increase in the crystallite size for G20/TiO₂/A550 could be associated with the decrease in the photocatalytic activity, compared with the TiO₂/A550 sample, in agreement with Toyoda *et al.* [34].

The A:R ratio for samples Cit100/TiO₂/A550 and Cit100/TiO₂/N550 was much lower than the A:R measured for the blank TiO₂ samples (Table 2). Therefore, the presence of citric acid assists the phase transformation from anatase to rutile during the treatments in air or in an inert atmosphere. Crystal growth is hindered by citric acid when crystallization is carried out in an inert atmosphere, while it is not affected or it is even favoured when crystallization takes place in air (Table 2). This trend is observed for all

the carbon precursors, and the decrease in crystallite sizes after crystallization in an inert atmosphere mostly depends on the amount of carbon.

The sample B200/TiO₂/N550 showed an A:R ratio of 76%, which is substantially lower than for the reference sample TiO₂/N550. As the residual carbon content was similar in both samples, it can be deduced that the presence of boric acid causes a decrease in the A:R ratio. Thus, boric acid favours the phase transformation from A:R during the thermal treatment under N₂. However, the effect was not observed when the crystallization treatment was performed in air (B200/TiO₂/A550 sample). Crystallite sizes of samples modified with boric acid are not substantially different from those of the neat TiO₂ control materials.

The most active sol-gel photocatalysts, B200/TiO₂/A550 and TiO₂/A550(30), show A:R ratios of 97 and 95%, and anatase crystallite sizes of 61 and 52 nm respectively. In agreement with Toyoda *et al.* [34], it can be concluded that optimal TiO₂ photocatalysts show XRD parameters falling inside a quite narrow range. However, the XRD parameters for the optimal sol-gel photocatalysts are quite different from those of the standard P25 TiO₂ (A:R = 79%, d_A = 32 nm), proving that other factors not directly associated with crystallinity are also important for the resulting photocatalytic activity.

3.3. XPS analysis

XPS has been often utilized for the study of carbon doping in TiO₂ photocatalysts, although the presence of adventitious carbon makes difficult the elemental quantification and the interpretation of high-resolution C 1s spectra. Adventitious carbon removal from the surface has been attempted by ion sputtering. However, it has been shown that this technique can severely modify TiO₂ surfaces and induce carbon doping [38]. Thus, XPS analysis may not be a reliable technique for the characterization of C/TiO₂ photocatalysts. However, it can be directly applied for the study of B/TiO₂ materials.

While XRD patterns showed the presence of minute amounts of boron phases in the B200/TiO₂/A550 sample, XPS analysis detected substantial amounts of boron in both the B200/TiO₂/A550 and B200/TiO₂/N550 samples (Table 2), indicating that at least one non-crystalline boron form was settled on the TiO₂ particle surfaces. It is worthy to be mentioned that boric acid is a highly volatile solid, which could suffer alterations during the XPS measurement under high vacuum. Therefore, the thermal treatment at

550 °C most probably transformed boric acid (H_3BO_3) into boric oxide (B_2O_3) on the TiO_2 particles.

Figure 2 shows high resolution O 1s and B 1s spectra for the boron-modified catalysts, the neat $\text{TiO}_2/\text{A550}(30)$ material, and boric acid. The wide O 1s band of boric acid is symmetric and it is located at 533.9 eV. For the neat $\text{TiO}_2/\text{A550}(30)$ material, the O 1s band shows a main component at 529.9 eV, which can be assigned to Ti-O bonds, and a secondary contribution at 531.3 eV, which is associated to Ti-OH surface groups [25]. The O 1s bands of the B/ TiO_2 materials clearly show contributions related to both Ti-O and B-O bands, although their positions are shifted compared to the reference compounds. In fact, the B-O band appears at 532.8-533.2 eV, suggesting the transformation of H_3BO_3 into B_2O_3 . The Ti-O band is shifted to 530.7-530.8 eV, which may indicate a change in the chemical environment of Ti-O bonds, compared with neat TiO_2 .

B 1s signals are wide symmetric bands located at 194.2 eV for boric acid and 193.3-193.4 eV for the B/ TiO_2 materials. It can be seen that the B 1s band for the B/ TiO_2 samples shifts by 1 eV to lower binding energies, in accordance with the above referred transformation of H_3BO_3 into B_2O_3 .

3.4. FTIR spectroscopy

Figure 3 shows representative FTIR spectra of some selected TiO_2 materials. The main spectral features are a broad band at $\sim 3430\text{ cm}^{-1}$, a signal at $\sim 1630\text{ cm}^{-1}$ and the strong TiO_2 modes at wavenumbers of $<1000\text{ cm}^{-1}$. The bands at ~ 3430 and $\sim 1630\text{ cm}^{-1}$ are associated to surface hydroxyl groups and to water moisture [39]. For P25 TiO_2 (Fig. 3c), the band at wavenumbers of $<1000\text{ cm}^{-1}$ consists of three distinguishable contributions at 668, 500, and 777 cm^{-1} . The strong contributions at 668 and 500 cm^{-1} are associated to Ti-O-Ti bond vibrations, while the weak signal at 777 cm^{-1} could be related to Ti-OH functional groups [33]. For the $\text{TiO}_2/\text{A550}(30)$ sample (Fig. 3a), both the intensity and shape of the FTIR spectrum at $<1000\text{ cm}^{-1}$ are nearly identical to the P25 spectrum. The strong contributions are centred at 661 and 506 cm^{-1} , and the weak contribution appears at 779 cm^{-1} . The spectrum clearly changes if the TiO_2 precursor is crystallized in a nitrogen flow. In fact, for the $\text{TiO}_2/\text{N550}$ sample (Fig. 3b), the absorbance intensity of the band contribution at 657 cm^{-1} decreases comparatively to the contribution at 498 cm^{-1} , and the band maximum is located at 524 cm^{-1} instead of 650 cm^{-1} .

As for neat TiO₂ materials, the TiO₂ band contributions in the spectra of samples modified with carbon compounds are observed at ~660 and ~500 cm⁻¹ (Figs. 3d-g). The samples crystallized in air, G20/TiO₂/A550 and Cit100/TiO₂/A550 (Figs. 3d and 3f) have their band maxima at ~660 cm⁻¹ and clearly show a Ti-OH contribution at 785 and 765 cm⁻¹ respectively. For the samples crystallized under nitrogen atmosphere, G20/TiO₂/N460 and Cit100/TiO₂/N450 (Figs. 3e and 3g), the band maximum is shifted towards lower wavenumbers.

FTIR spectra of the TiO₂ samples modified with boric acid (Figs. 3h and 3i) can be interpreted as a mixture of features from both TiO₂ and boric oxide. The spectrum of boric acid is included in Fig. 3j, showing bands at 1463, 1195, 884, 797, 649 and 548 cm⁻¹, due to B-O bond vibrations [40]. Those boron oxide bands, together with the TiO₂ band at <1000 cm⁻¹, are clearly observed in the spectrum of the sample crystallized under nitrogen flow (B200/TiO₂/N550, Fig. 3i). In the sample crystallized in air (B200/TiO₂/A550, Fig. 3h), the boron oxide bands are relatively less intense than in the B200/TiO₂/N550 sample, while the TiO₂ band is much more intense and shows a prominent maximum at 686 cm⁻¹. Thus, the evolution of the TiO₂ band when the crystallization atmosphere is changed from nitrogen to air is quite similar to the neat TiO₂/A550(30) and TiO₂/N550 materials. Moreover, the different relative intensities of the boron oxide bands in the B200/TiO₂/A550 and B200/TiO₂/N550 samples could be associated to the different B/Ti ratios calculated from XPS spectra (Table 2).

The most active photocatalysts (P25, TiO₂/A550(30) and B200/TiO₂/A550) show very strong bands at <1000 cm⁻¹ with prominent band maxima in the range of 660-690 cm⁻¹. On the contrary, samples crystallized in a nitrogen flow, with lower photocatalytic activities, show less intense TiO₂ bands with their maximum shifted to lower wavenumbers. In addition, a low-intensity Ti-OH component in the range of 765-785 cm⁻¹ is seen in the spectra of all the catalysts crystallized in air.

3.5. UV-Vis spectroscopy

Figure 4 shows DR-UV-Vis spectra for the photocatalysts listed in Table 2. All the materials are directly compared with the reference TiO₂/A550(30). The samples crystallized under nitrogen atmosphere show increased backgrounds in the visible region, particularly the carbon modified materials. On the contrary, the materials crystallized in air show nearly zero absorbance at wavelengths longer than 450 nm, indicating the combustion and total elimination of the carbon-containing precursors.

Band edges for the P25, Cit100/TiO₂/A550 and Cit100/TiO₂/N500 materials are red-shifted due to their increased content in the rutile phase (Table 2). The spectrum of the B200/TiO₂/A550 sample is nearly identical to the reference TiO₂/A550(30) material, and a previously reported blue-shift [25] is not observed here.

Figure 5 shows absorbance measurements for water dispersions of the same photocatalysts analysed by the DR mode. The spectra are shown at a concentration of 0.1 mg mL⁻¹, except for P25 TiO₂, which is presented at a concentration of 0.025 mg mL⁻¹ (Fig. 5a) in order to facilitate a profile shape comparison with the others. The P25 spectrum shows a very intensive light absorption, particularly at wavelengths in the near UV region ($\lambda < 400$ nm), while the absorbance values for dispersions of sol-gel TiO₂ photocatalysts are considerably lower.

The materials with the highest photoactivities (TiO₂/A550(30) and B200/TiO₂/A550, Figs. 5e and 5d), resulted to have higher absorbance values in the visible region ($\lambda > 400$ nm) than their counterparts crystallized under nitrogen (TiO₂/N550 and B200/TiO₂/N550, Figs. 5b and 5c). On the contrary, the dispersions of sol-gel materials that were modified with carbon compounds and crystallized under inert atmosphere (Fig. 5h and 5i) showed greater absorbance values than those of the materials crystallized in air (Figs. 5f and 5g); however, their increased absorbance is caused by residual black carbon on the TiO₂ surfaces, which is not beneficial for the photocatalytic activity. The most active sol-gel photocatalysts in this work (TiO₂/A550(30) and B200/TiO₂/A550) demonstrated higher activities than P25 TiO₂, even though the absorbance values of their dispersions are maintained at lower levels.

3.6. Surface area and surface acidity

Specific surface area (S_a) and total pore volume (V_t) are important parameters for the general characterization of heterogeneous catalysts, as they quantify the exposed solid that is available for the interaction with reactive molecules. Previously, S_a has been directly associated to the capacity of TiO₂ solids for DPH adsorption from solution [31, 32]. Among crystalline TiO₂ solids, the reference P25 material demonstrates a relatively high surface area of $> 50 \text{ m}^2 \text{ g}^{-1}$. The sol-gel TiO₂ photocatalysts show lower S_a and V_t values, ranging from 15-35 $\text{m}^2 \text{ g}^{-1}$ and 0.015-0.050 $\text{cm}^3 \text{ g}^{-1}$ (Table 3). The most active sol-gel photocatalysts, TiO₂/A550(30) and B200TiO₂/A550, show S_a values around 30 $\text{m}^2 \text{ g}^{-1}$, while photocatalysts with lower activities present lower or higher surface areas

(Table 3). Clearly, other photocatalyst features dominate over S_a and V_t in determining the degradation activity.

Surface acidity, expressed as the ammonia chemisorption capacity (V_{NH_3}), is also included in Table 3. Ammonia capacity has been often utilized as an indicative of the total surface acidity, including both strong Brönsted sites and weak Lewis sites [41]. Surface acidity is of great importance in some catalytic reactions that can be effected on TiO_2 substrates [42]. P25 presents higher V_{NH_3} than the other pure TiO_2 catalysts, $TiO_2/A550(30)$ and $TiO_2/N550$, which have nearly identical acidities. Among the carbon and boron-modified TiO_2 materials, surface acidity for the photocatalysts crystallized under nitrogen atmosphere appears to be higher than for those crystallized under air. Comparing surface acidity with the photocatalytic activity for DPH degradation, no clear trend can be outlined.

4. Conclusions

Efficient photocatalysts for DPH degradation under UV-Vis irradiation can be synthesized by crystallization of sol-gel TiO_2 under air atmosphere. Lower efficiencies are obtained if TiO_2 crystallization is carried out in a nitrogen flow or the sol-gel precursors are modified with carbon compounds. The modification of TiO_2 precursors with boric acid results in photocatalysts with a slightly improved efficiency for DPH degradation.

Crystalline structure primarily determines the photocatalytic efficiency. The sol-gel photocatalysts with the highest activities demonstrate typical crystallographic features of $A:R > 90\%$ and $d_A > 50$ nm. However, bulk crystalline structure by itself cannot explain the systematic decrease in the photoactivity for TiO_2 crystallized under nitrogen atmosphere. The presence of oxygen during crystallization is necessary to saturate the TiO_2 surfaces with Ti-O-Ti and Ti-OH bonds, as detected by FTIR spectroscopy. This fact could be also associated to an improved hydrophilic character, ultimately leading to high absorbance values for the water dispersions in the UV-Vis wavelengths. Particularly, P25 dispersions demonstrate very high absorbance values, which could be related to its excellent photocatalytic properties. The presence of carbon on TiO_2 causes an increased absorbance background in the visible region of DR spectra, which seems to be detrimental for the photocatalytic activity. Surface area and surface acidity play minor roles in determining activity differences in the studied photocatalysts.

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Appendix A. Supplementary information

Photocatalytic DPH degradation curves; optimization of reference TiO₂ photocatalysts; optimization of GQ/TiO₂/NT photocatalysts; optimization of TiO₂ photocatalysts modified with carbon and boron compounds and crystallized under nitrogen atmosphere; ammonia TPD profiles of selected photocatalysts.

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Table 1. Summary of nomenclature and preparation conditions for all the photocatalyst powder materials: Q = precursor amount, Atm = crystallization atmosphere, T = crystallization temperature, t_c = crystallization time.

Sample series	Precursor	Q	Atm	T [°C]	t_c [min]
TiO ₂ /AT(t_c)	-	-	Air	0-690	0-180
TiO ₂ /NT	-	-	Nitrogen	550	30
GQ/TiO ₂ /AT	Glucose	20 mg g ⁻¹	Air	550	30
GQ/TiO ₂ /NT	Glucose	5-40 mg g ⁻¹	Nitrogen	430-550	30
CitQ/TiO ₂ /AT	Citric acid	100 mg	Air	550	30
CitQ/TiO ₂ /NT	Citric acid	5, 100 mg	Nitrogen	450-550	30
AQ/TiO ₂ /NT	Acetylacetone	0.5 mL	Nitrogen	460-550	30
BQ/TiO ₂ /AT	Boric acid	200 mg	Air	550	30
BQ/TiO ₂ /NT	Boric acid	200 mg	Nitrogen	460-575	30

Table 2. Carbon and boron content, crystallization parameters, and photocatalytic activity for P25 and other selected TiO₂ samples: B/Ti = boron to titanium atomic ratio, A:R = anatase to rutile ratio, d_A = anatase crystallite size, d_R = rutile crystallite size, X_{TOC} = fraction of total organic carbon converted after 1 h, X_{DPH} = DPH fraction removed after 1 h, and k_{app} = apparent kinetic constant for DPH degradation.

Sample	C [wt.%]	B/Ti	A:R [%]	d_A [nm]	d_R [nm]	X_{TOC} [%]	X_{DPH} [%]	k_{app} [10 ² min ⁻¹]
P25	-	-	78.8	31.8	52.1	44.5	96.7	6.03
TiO ₂ /A550(30)	0.05	-	95.0	54.1	76.6	24.1	94.8	6.81
TiO ₂ /N550	0.06	-	89.9	62.2	92.3	5.65	72.6	2.99
G20/TiO ₂ /A550	0.04	-	95.2	72.1	n.d.	3.95	83.1	3.32
G20/TiO ₂ /N460	1.35	-	93.3	20.7	16.3	5.28	69.4	2.16
Cit100/TiO ₂ /A550	0.02	-	52.4	82.8	203	10.8	90.1	4.37
Cit100/TiO ₂ /N500	1.56	-	75.8	19.0	47.6	1.32	55.1	1.33
B200/TiO ₂ /A550	0.07	0.84	97.2	61.2	n.d.	35.0	98.1	7.71
B200/TiO ₂ /N550	0.10	1.66	76.4	53.3	77.0	17.0	86.8	3.85

Table 3. Specific surface area, total pore volume, and surface acidity for P25 and other selected TiO₂ samples:

Sample	S _a [m ² g ⁻¹]	V _t [cm ³ g ⁻¹]	V NH ₃ [cm ³ g ⁻¹ STP]
P25	53	0.064	3.27
TiO ₂ /A550(30)	34	0.043	1.89
TiO ₂ /N550	24	0.030	1.87
G20/TiO ₂ /A550	33	0.051	1.62
G20/TiO ₂ /N460	32	0.041	2.11
Cit100/TiO ₂ /A550	19	0.023	1.32
Cit100/TiO ₂ /N500	33	0.046	2.71
B200/TiO ₂ /A550	28	0.034	1.75
B200/TiO ₂ /N550	15	0.016	5.01

Figure 1. XRD profiles for the TiO_2 samples in Table 2: a) $\text{TiO}_2/\text{A550}(30)$, b) $\text{TiO}_2/\text{N550}$, c) $\text{B200}/\text{TiO}_2/\text{A550}$, d) $\text{B200}/\text{TiO}_2/\text{N550}$, e) $\text{G20}/\text{TiO}_2/\text{A550}$, f) $\text{G20}/\text{TiO}_2/\text{N460}$, g) $\text{Cit100}/\text{TiO}_2/\text{A550}$, and h) $\text{Cit100}/\text{TiO}_2/\text{N450}$.

Figure 2. High resolution XPS spectra for: a) H_3BO_3 , b) $\text{TiO}_2/\text{A550}(30)$, c) $\text{B200}/\text{TiO}_2/\text{A550}$, and d) $\text{B200}/\text{TiO}_2/\text{N550}$.

Figure 3. FTIR spectra for P25 TiO₂, pure H₃BO₃ and the TiO₂ samples in Table 2: a) TiO₂/A550(30), b) TiO₂/N550, c) P25, d) G20/TiO₂/A550, e) G20/TiO₂/N460, f) Cit100/TiO₂/A550, g) Cit100/TiO₂/N450, h) B200/TiO₂/A550, i) B200/TiO₂/N550, and j) H₃BO₃.

Figure 4. DR-UV-Vis spectra for a) P25 TiO_2 , and the TiO_2 samples in Table 2: b) $\text{TiO}_2/\text{A550}(30)$, c) $\text{TiO}_2/\text{N550}$, d) $\text{G20}/\text{TiO}_2/\text{A550}$, e) $\text{G10}/\text{TiO}_2/\text{N460}$, f) $\text{Cit100}/\text{TiO}_2/\text{A550}$, g) $\text{Cit100}/\text{TiO}_2/\text{N450}$, h) $\text{B200}/\text{TiO}_2/\text{A550}$, and i) $\text{B200}/\text{TiO}_2/\text{N550}$.

Figure 5. UV-Vis spectra for aqueous dispersions of P25 TiO_2 and the TiO_2 samples in Table 2: a) P25, b) $\text{TiO}_2/\text{N550}$, c) $\text{B200}/\text{TiO}_2/\text{N550}$, d) $\text{B200}/\text{TiO}_2/\text{A550}$, e) $\text{TiO}_2/\text{A550}(30)$, f) $\text{G20}/\text{TiO}_2/\text{A550}$, g) $\text{Cit100}/\text{TiO}_2/\text{A550}$, h) $\text{G20}/\text{TiO}_2/\text{N460}$, and i) $\text{Cit100}/\text{TiO}_2/\text{N450}$. All the samples were measured at concentrations of 0.1 mg mL^{-1} , except P25, which was measured at 0.025 mg mL^{-1} .