Research Article

Effect of the Amount of Water in the Synthesis of B-TiO₂: Orange II Photodegradation

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A series of boron-doped TiO₂ photocatalysts (2% B-TiO₂) with different water/alkoxide molar ratio were synthesized by conventional sol-gel method. The prepared samples were characterized by BET measurement, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIRS), and diffuse-reflectance UV-vis. The phase anatasewas present, but unexpectedly a small amount of rutile phase was formed with low and excess water in the synthesis. Additionally it has been observed that the increase in the molar ratio of water significantly increases the values of band gap energy and the specific surface area. Results showed that degradation of Orange II azo dye increases with surface area, particle size, boron, and water content in photocatalysis. The boron species were introduced in the tricoordinated form.

1. Introduction

Current emission of pollutants from textile industry to different bodies of water is a serious problem, not only since this industry uses large volumes of water, but also because most of these dyes are resistant to the conventional wastewater treatment processes. Different emerging technologies have been tested to try to solve this problem; among them, the advanced oxidation processes such as heterogeneous photocatalysis employing TiO₂ have demonstrated to be the most viable alternative to eliminate several organic contaminants [1, 2]. On the other hand titanium dioxide (TiO₂) has attracted growing scientific interest due to its good chemical and photochemical stability, nontoxicity, availability, low price, or ease of synthesis. However the structural, electronic, and photocatalytic properties of TiO₂ depend on the method of synthesis, while the size, morphology, and microstructure of crystals can be controlled and modified during hydrolysis and condensation steps [2–4]; that is, the water content changes the rate of hydrolysis. In order to improve its photocatalytic activity and shift its absorption band towards the visible region, several attempts have been made to narrow the band gap energy by doping with various metals ions [5, 6], where it is suggested that the incorporation of metal to TiO₂ structure modifies both the charge carriers recombination rate and the interfacial electron-transfer rate, as well as the generation of recombination sites or the band gap energy, depending on where these ions are located in the TiO₂ structure. On the other hand, the doping of TiO₂ with non metals atoms such as carbon, nitrogen or boron atoms [7–12] have shown a higher photoactivity performance under visible light irradiation. The photoreactivity of doped TiO₂ is a complex function of the dopant concentration, the energy level, the d electronic configuration, the distribution of dopants, the electron donor concentration, and the light intensity [5]. Photocatalysis involves the absorption of photons by a molecule or the substrate to produce reactive electronically excited states and the photocatalysis process by TiO₂ is the generation of electron-hole pairs [5, 13]. Metal and nonmetal dopants influence the photoreactivity of TiO₂ by acting as electron and hole traps and by altering the e⁻/h⁺ pair recombination [13].

The boron (nonmetal) doping to the TiO₂ has been studied in the literature and the doping content as well
as the chemical state of boron element affects much the photocatalytic activity of the photocatalyst [14–17]. Likewise, it has been found that the selectivity was improved in degradation of pollutants when boron was used to dope the TiO$_2$ in photocatalytic reactions.

In this research, the effect of the amount of water on the synthesis of boron-doped TiO$_2$ photocatalyst by sol-gel method was studied. Few studies are on the water content during the synthesis of TiO$_2$ [18, 19]. Some authors have found that the higher photoactivity was shown by materials with boron content around 2-3 wt% of boron [15, 20, 21]. Moreover, the boron is a nonmetal that has been less studied doping TiO$_2$ and the corresponding literature is controversial [17]. According to this, the aim of this study is to find a relationship between the molar ratio water/alkoxide with structural, textural, and photoactivity properties of B-TiO$_2$ system and to determine the type of boron species present in this system, which can be responsible for the photoactivity.

The B-TiO$_2$ samples were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) measurement, and diffuse-reflectance UV-vis spectroscopy. The study of the degradation of Orange II was carried out by UV-visible spectrophotometer.

2. Experimental

2.1. 2% B-TiO$_2$ Oxide Preparation. A series of 2% B-TiO$_2$ materials and pure TiO$_2$ (as reference) were prepared by sol-gel method. The B-TiO$_2$ catalysts were prepared to obtain a content of 2% of boron. During solids synthesis the amount of water was modified (molar ratio water/alkoxide = 0.5, 1, 4, 8, and 16) and the catalysts with different water contents were called BTiO$_2$-X, in which X indicates the amount of water used in the synthesis (see Table 1). The TiO$_2$ used as reference was called TiO$_2$-4 (water/alkoxide = 4). Butanol and titanium isopropoxide were used in a molar ratio alcohol/alkoxide = 10. In a three-neck flask butanol, titanium isopropoxide, and boric acid were mixed at room temperature and an appropriate amount of deionized water was added dropwise into the solution. The X = H$_2$O/alkoxide molar ratios used were 0.5, 1, 4, 8, or 16 and the solution was kept under stirring for 2 hours. Then, the samples were dried at 100°C in oven for 2 days and finally calcined in muffle furnace at 450°C using a heating rate of 5°C/min for 3 h. Pure TiO$_2$ was synthesized in the same manner as the sample with water/alkoxide = 4 content, but boric acid was not added to this material during the synthesis.

2.2. Catalysts Characterization. The structural characterization of solids was carried out by powder XRD using a Philips X’Pert diffractometer, operating in 2θ mode; samples were analyzed in the range of 20 to 80, 2θ degrees using a Cu tube Kα radiation (35 kV, 25 mA) at 2° s$^{-1}$ scan rate, and wavelength $\lambda$ = 0.15405 nm. The surface areas were calculated by BET method and the pore volume was determined by the Barrett-Joiner-Halenda (BJH) method. The study was obtained on a BELSORP-max nitrogen adsorption apparatus at a temperature around 73 K. The sample was treated at 298°C before measurement. The optical properties of materials were determined using an UV-vis (Varian Cary 1 double-beam) spectrophotometer operating in the diffuse reflectance mode. The FT-IR spectroscopic measurements were carried out using a Nicolet Magna spectrophotometer and the spectra were recorded using a KBr wafer technique.

2.3. Degradation of Orange II

2.3.1. Adsorption Experiments. Degradation of Orange II dye was studied by catalytic reaction. The tests were carried out in a stirred batch reactor; it was placed inside an aluminum foil box at room temperature. In a reactor with 25 mL of Orange II solution 0.3 g of the catalyst was added, with an initial concentration of 10 mg/L of dye. The pH was monitored as a function of time and remained close to 7. Reaction monitoring is performed by a Varian Cary 1 UV-vis Spectrophotometer, which determined the amount of degraded dye and the study was carried out for 2 hours. In the quantification, the absorbance was analyzed with the wavelength of 485 nm. Likewise, in all cases, also studies were conducted without catalyst and the dye was not degraded.

2.3.2. Photocatalytic Degradation of Orange II. The same conditions of the catalytic reaction were used, but in this case a UV lamp was placed at the top of the reactor. The reactor was irradiated by the UV light at wavelength 365 nm (lamp power 5 W). Likewise, tests were conducted without catalyst and the dye was not degraded. The pH of solution was 7 and no significant modification of the pH was observed during the experiments. Figure 1 shows the photocatalytic reaction system, which is illustrated as the degradation is carried out.
using a UV lamp. The UV lamp is placed above the reactor and the reaction was maintained under moderate stirring.

3. Results and Discussion

3.1. Textural Analysis. Figure 2 and Table 1 present the textural properties of BTiO$_2$-X samples; these results show that the average pore diameter of BTiO$_2$-X samples was increased with increasing the water content in the synthesis, and a similar behavior occurs with the specific surface area and the pore volume, except the sample with a molar ratio of 16% (Figure 2). The surface area of the TiO$_2$ without boron (TiO$_2$-4) is larger than the sample containing boron (BTiO$_2$-4, see Table 1). The decrease in the specific areas and the pore diameters due to the presence of boron is known in the literature [22]. Stengl et al. [22] found that the specific surface area from the BET had tendency to decrease with increasing content of boron and the pore size distribution indicated conversion from micropores to mesopores with increasing amount of boron, but samples with the highest content of boron became microporous. The size of the pore diameter is different between the sample without boron (TiO$_2$-4, 30.1 nm) and the sample with boron (BTiO$_2$-4, 7.1 nm); there is a decrease, which can be attributed to the particle size (see XRD section). There is a strong dependence between the dimensions of the particles and the pore diameters [23]; smaller particles lead to small pores. Figure 2 shows the pore volume of BTiO$_2$-X samples; the pore volume increases with higher water concentrations in the synthesis.

The particles with different size have different surface area and pore volume [2, 23]. A greater amount of water during the synthesis leads to increase of hydrolysis and condensation allowing an increase in the formation of Ti–O–B and Ti–O–Ti groups [16]. The changes in surface area and pore volume of BTiO$_2$-X samples are related to the size of the particles or the largest number of particles formed. The specific surface area and anatase phase are important in the photocatalysis of TiO$_2$ [4]. Therefore, the greater specific surface area for the B-TiO$_2$ with high water concentration in the synthesis is due to the formation of larger pore volume between aggregated particles (Figure 2).
3.2. XRD. Figure 3 shows the XRD patterns of the solids. In the case of TiO$_2$-4 only well-defined diffractions of anatase phase (JPCDS 21-1272) can be seen in the pattern at 2θ = 25.4° (101), 38.0° (004), 48.2° (200), 54.1° (105), 55.1° (211), 62.8° (204), 68.9° (116), 70.3° (220), and 75.2° (205); the number in the parenthesis indicates the hkl values [24]. The XRD powder patterns of the week rutile phase (JPCDS 21-1276) at 2θ = 27.4° (110), 36.1° (101), and 41.2° (122) appeared in BTiO$_2$-0.5 and BTiO$_2$-16 with different ratio of water/alkoxide (Figure 3). The weight fractions were calculated from the relative intensities of the strongest peaks for anatase (101) and rutile (110). The average crystal size is presented in Table 2 calculated from the strongest diffraction peak at 2θ = 25.4° in the (101) reflection using the Scherrer equation:

$$d = \frac{k\lambda}{\beta \cos \theta},$$

where $\lambda$ is the wavelength of the Cu Kα radiation used (1.542 Å), $\beta$ is the full width at half maximum of the diffraction angle considered, $k$ is the shape factor (0.89), and $\theta$ is the angle of diffraction.

The relative intensity of the peaks of BTiO$_2$-X samples is weakened and broadened compared with those of the TiO$_2$ [25] (Figure 3). No crystalline phase assigned to B$_2$O$_3$ could be found in any B-TiO$_2$ catalysts because the concentration of B$_2$O$_3$ is so low or the boron species in all samples are highly dispersed on TiO$_2$ support [26]. As it is well known, sol-gel method is an easy route to obtain high purity nanosized TiO$_2$ at mild synthesis conditions. It has been well established that the photocactivity of TiO$_2$ is correlated with its crystallinity and particle size. It can be clearly observed that the crystallinity of these BTiO$_2$-X samples is different. Table 2 shows that the BTiO$_2$-4 has the smallest particle size (11 nm) which indicated that the water in the synthesis would generate a distortion in the crystalline structure. These results indicate that the boron acted as an inhibitor for the growth of the anatase nanoparticles, because pure TiO$_2$ has larger particle size (TiO$_2$-4 = 14 nm).

The results of XRD show that water content has the greatest effect on the particle size and crystal phase of B-TiO$_2$. The obtained XRD patterns showed that with the excess amount of water (BTiO$_2$-16) used in the synthesis the particle size increased, and peaks became more evident and could result in more –OH groups on the surface of nanoparticles. Increasing the water content, the hydrolysis occurs more quickly and much more Ti–O–Ti, Ti–O–B, or Ti–O–H groups are produced. The intensity of the XRD peaks increases with increasing water content in the synthesis, and then this indicates an increase in the crystal phase (anatase).

In similar synthesis conditions regularly pure anatase phase is obtained, but unexpectedly rutile phase was formed. This study found that the rutile phase was present when the particle size is large (BTiO$_2$-0.5 and BTiO$_2$-16, see Table 2). This suggests that low and excessive water additive cause a phase transition for the synthesized BTiO$_2$-16 (Figure 3). Results are consistent with studies where rutile is obtained by thermal methods or boron doped [16, 26, 27], where the rutile has a significant increase when there is an increase in the crystal size (Table 2). The formation of rutile at low water concentration synthesis (BTiO$_2$-0.5) could be because few groups Ti–O–Ti are formed during the initial synthesis; possibly the bonds Ti–O–Ti are formed during drying or calcination. Moreover, the formation of rutile with excess water in the synthesis (BTiO$_2$-16) is explained by a structural rearrangement of the catalyst. The anatase to rutile rearrangement involves breaking of two of the six Ti–O bonds in anatase [13]. During the temperature treatment the water excess causes the Ti–O–Ti network to weaken and this facilitates the Ti–O bond breaking and a consequent structural rearrangement to more stable rutile phase. The water in excess is lost by evaporation of solid, leaving behind oxygen vacancies, which accelerates the Ti–O bond breaking and crystallite growth. In this case, boron is certainly helping in the process of rutile formation.

With low water molar ratios (0.5 to 4) the particle size decreases, whereas it increases with a water excess (8–16) (Table 2). The lattice parameters $a$ and $c$ are affected with possible transitions of the crystal phases (Table 2). Sample BTiO$_2$-4 prepared with a stoichiometric ratio of water (4H$_2$O:1 alkoxide) is slightly distorted as indicated by its parameter $c$ (9.42 Å) which is the closest to the data reported for the anatase ($c = 9.51$ Å) [13].

3.3. Bandgap Determination. UV-vis DRS spectra of BTiO$_2$-X photocatalysts are shown in Figure 4. The estimates band gap ($E_g$) was obtained from extrapolation of the linear region of the Kubelka-Munk transformation of the UV-vis absorption spectra ($F(R) = 0$), as shown in Figure 4.

A relevant property to the photocatalytic activity of a semiconductor is its energy band configuration, the photons with energy equal to or higher than the band gap ($E_g$) promote formation of electron-hole pairs and the redox capabilities of excited-state electrons and holes. The band gaps of the BTiO$_2$-X samples are presented in Table 2. The band
Table 2: Lattice parameters (Å), crystal size (nm), and band gap (eV) of the photocatalysts. Physical properties derived based on $d_{101}$ and the tetragonal unit cell to TiO$_2$ anatase.

| Photocatalyst | FWHM$^a$ | Lattice parameters (Å) | $E_g$ (eV) | $d$ (nm) | Composition$^b$ |
|---------------|----------|------------------------|-----------|---------|-----------------|
| TiO$_2$-4     | 0.602    | $a = 3.79; c = 9.42$    | 3.16      | 14      | (A) 100%        |
| BTiO$_2$-0.5  | 0.272    | $a = 3.78; c = 9.37$    | 2.96      | 30      | (A) 84%         |
| BTiO$_2$-1    | 0.544    | $a = 3.79; c = 9.38$    | 3.00      | 15      | (A) 100%        |
| BTiO$_2$-4    | 0.766    | $a = 3.80; c = 9.42$    | 3.14      | 11      | (A) 100%        |
| BTiO$_2$-8    | 0.608    | $a = 3.77; c = 9.37$    | 3.16      | 14      | (A) 100%        |
| BTiO$_2$-16   | 0.337    | $a = 3.78; c = 9.39$    | 3.00      | 24      | (A) 89%         |

$^a$ Full width at half maximum (FWHM).  
$^b$ Anatase (A) and rutile (R).

Figure 4: $(F(R) \times h\omega)^{1/2}$ versus photon energy ($E_g$); (a) TiO$_2$-4, (b) BTiO$_2$-0.5, (c) BTiO$_2$-1, (d) BTiO$_2$-4, (e) BTiO$_2$-8, and (f) BTiO$_2$-16.

Figure 5: FT-IR spectra of (a) TiO$_2$-4, (b) BTiO$_2$-0.5, (c) BTiO$_2$-1, (d) BTiO$_2$-4, (e) BTiO$_2$-8, and (f) BTiO$_2$-16.

gap energies ($E_g$ values) suggest a decrease in the intrinsic band gap of B doped TiO$_2$ [28]. Thus boron incorporation into TiO$_2$ lattice alters the electronic structure leading to the appearance of intermediate energy level [29, 30]. The band gap energy of BTiO$_2$-X catalysts is lower than the pure TiO$_2$ (3.16 eV, ca 380 nm) making it hardly absorbed in visible light region [31–33]. When the TiO$_2$ surface was modified with the boron ions, adsorption in the visible region increased, and therefore the number of photogenerated electrons and holes increased [34]. With the increase of water in the synthesis the band gap increases (Figure 4). However, when there is an excess of water (BTiO$_2$-16) the band gap decreases probably due to the formation of large particle size. Figure 4 (top left) shows a marked inverse relationship between particle size and $E_g$; it means that particles with larger sizes lead to lower energies, which are in good agreement with the quantum confinement effect.

3.4. FT-IR of B-TiO$_2$. Figure 5 shows FT-IR spectra of BTiO$_2$-X photocatalysts. For samples, the bands at 1398 cm$^{-1}$ can be ascribed to the vibration of tricoordinated interstitial boron (in the form of B$^{3+}$) [20, 27] and the band at 1640 cm$^{-1}$ is assigned to the stretching of hydroxyl groups and the bending vibration of H$_2$O adsorbed on the surface of the samples. In the IR spectra of the samples, another small peak appears at 1280 cm$^{-1}$ which can be ascribed to the stretching vibration of the B–O bonds of boroxol rings [27].

Results reveal that boron is introduced into the titania framework in the form of B–O–Ti bond, corresponding to tricoordinated interstitial boron. The results indicate that the boron species are introduced in the tricoordinated form mainly with high amounts of water used in the synthesis. This indicates that boron is more easily trapped into the titania framework when hydrolysis is favored. The peak at 1640 cm$^{-1}$ which is related to vibration of water also increases, because larger amount of water in the synthesis results in the formation of higher content of hydroxyl groups in the samples.
3.5. Adsorption Study. The catalytic activity of the BTiO$_2$-X catalysts for the degradation of Orange II was evaluated without UV irradiation. In all catalysts, the Orange II concentration decreases slightly, indicating that the degradation of Orange II is very limited. The presence of the catalyst without light does not allow an efficient degradation of the dye. In the catalysts, the concentration of water during the synthesis of BTiO$_2$-X was not a critical factor in the degradation of the dye. The low activity is present in all of the catalysts with or without boron. Figure 6(d*) displays the Orange II concentration as a function of the reaction time of the BTiO$_2$-4 catalytic degradation without visible light. The activity of other catalysts (BTiO$_2$-X and TiO$_2$-4) was very similar.

3.6. Photocatalytic Test. The photocatalytic activity of the B-TiO$_2$ catalyst for the degradation of Orange II was evaluated with a reactor irradiated by UV light at wavelength 365 nm. Figure 6 displays the Orange II concentration as a function of the reaction time. It can be seen that increasing the amount of water in the synthesis promotes an increase in the Orange dye degradation. An exception is the catalyst BTiO$_2$-16, where this catalyst with more water shows different behavior (Figure 6(f)). The BTiO$_2$-8 (e) after 2 hours of reaction showed a slightly higher activity than BTiO$_2$-16. Also, Figure 6 shows a comparison between the BTiO$_2$-4 (d) and TiO$_2$ (TiO$_2$-4 (a)) photocatalysts, which were synthesized with the same amount of water. BTiO$_2$-4 photocatalyst containing boron has greater activity than TiO$_2$-4, which is the catalyst without boron. The above results confirm that the photocatalysis is favored with the boron content and the increase of water in the synthesis. The tricoordinated interstitial boron could also play an important role in the catalytic degradation (see Figure 5). Heterogeneous photocatalysis followed the first order kinetics for Orange II degradation (Figure 7). Kinetics of Orange II photodegradation shows that the photocatalytic activity increases when the molar ratio of water increases from 0.5 to 16. According to the overall results of our investigation, we have found that a high specific surface area and the presence of the anatase phase of TiO$_2$ are indispensable in the photodegradation of Orange II but are not the only determinant factors; on the contrary, it is important to note that the photocatalytic behavior of B-TiO$_2$ system can be explained more appropriately, not only considering the values of $E_p$, but also taking into consideration the type of electronic states induced by the addition of boron. Additionally, it is important to consider that the incorporation of nonmetallic dopants, such as boron, occupying interstitial sites in the anatase TiO$_2$ structure, can generate reduced Ti$^{3+}$ species, which can act as traps for electrons or holes. As expected, several parameters are related to the photocactivity of the B-TiO$_2$ nanoparticles, so additional characterization studies are in progress in our laboratory.

4. Conclusions

BET results indicated that specific surface area increased with increasing water content in the synthesis of BTiO$_2$-X and the powders calcined at 450°C had anatase phase. However, the samples with low and high ratio of water have some content of rutile. The results showed that large amounts of water increase the crystal size and excessive water in the preparation causes a phase transition from anatase to rutile. Increasing water content in the synthesis increases the crystal phase (anatase) and the band gap energies. With the increase of water in the synthesis the band gap increases and the band gap decreases due to the presence of large particle size. The photocatalytic activity of BTiO$_2$-X powders for the degradation of Orange II increased with increasing water in the synthesis. It is noteworthy that the specific surface area and particle size of BTiO$_2$-X nanoparticles were dominant factors controlling the photocatalytic activity. As reported in recent times, the results indicate that the boron
content improves photocatalytic activity. It is also necessary to mention that boron is more easily trapped inside the TiO₂ when there is more water in the synthesis (in the form of B³⁻).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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