Influence of the pH of the synthesis using sol-gel method on the structural and optical properties of TiO$_2$

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Abstract. The photocatalysis process using semiconductor materials, in particular TiO$_2$, is one of the most attractive treatment for polluted waters decontamination because of its advantages over other oxidation processes [1-6]. In this study the effect on the physical properties of TiO$_2$ due to the pH used during the manufacturing of the semiconductor is studied. Different samples were synthesized using ammonium hydroxide (NH$_4$OH) and nitric acid (HNO$_3$) as catalysts to provide basic and acid pH environments, respectively. Changes in composition, structure and morphology of the samples were studied and its dependence with the pH of the synthesis is discussed. Results indicate that the base catalysis favours the formation of anatase TiO$_2$ crystalline phase with crystallite size ~26 nm obtained by Rietveld refinement; the spherical particles formed agglomerates of ~100 nm; the average pore size is in the range of mesopores and the surface area increases with the amount of NH$_4$OH added in the process. On the other hand, with acid catalysis, a mixture of two crystalline phases, anatase and rutile, was obtained with crystallite sizes around 26 and 49 nm, respectively. The grain size is several orders of magnitude higher than those obtained by basic catalysis. The photocatalytic activity was measured using methylene blue solutions to determine their degradation with radiation. Greater efficiency was observed in the photocatalysts synthesized with NH$_4$OH.

1. Introduction

The sol-gel technique is one of the most common methods used in research laboratories to grow TiO$_2$ [7-9]. The size and the entanglement of particles are strongly dependent of the acidity or basicity of the system (pH dependent). Due to the small particle size, the Van der Waals interaction is significant; this interaction increases exponentially as the particle size decreases. These facts favor the growth of clusters. In order to conserve the sample in a powder morphology with a high surface area, it is necessary to stabilize the gel. For low pH values a positive charged transition state is generated and groups –OR from the alkoxide are able to stabilize the solution better than the –OH groups. The low-hydrolyzed species will exhibit a high condensation velocity favoring the formation of long low-branched chains and big size particles. Instead, if the catalyst is basic, the transition state charge is negative, the –OH group stabilizes the solution and the high-hydrolyzed species will condense faster, favoring the formation of highly branched chains and small sized particles [10-11]. In this work we present the influence of the synthesis-pH on the physical properties of TiO$_2$ semiconductor grown by sol-gel method. The photocatalytic behaviour of both type of samples was compared measuring the degradation of methylene blue (MB) solutions exposed to solar radiation.
2. Experimental procedures

The TiO$_2$ photocatalyst was synthesized by the sol-gel method using alkoxide tetraisopropyl orthotitanate (Ti(OC$_3$H$_7$)$_4$) 98%, and as catalyst HNO$_3$ 70% for the acid catalysis, and NH$_4$OH 28-30% for the basic catalysis. Because of the higher photocatalytic activity of basic samples in a MB solution exposed to solar radiation, in this work samples with different NH$_4$OH concentration are studied.

2.1. Sample preparation

Under N$_2$ flow, 3mL of alkoxide were added to 15mL of isopropanol. Solution was stirred for 20min. Then, a mixture of water 3mL, isopropanol 3mL and catalyst was added to the solution, and stirred for 20min. The resulting preparation was aged for 48h. After it, sample was dried at 100°C for 24h, calcinated at 500°C for 2h and finally, macerated. In this work, the chosen sample grown under acid catalysis with 0.3mL of HNO$_3$ 70% is named A-TiO$_2$. Samples grown under basic catalysis with different NH$_4$OH volumes (v) are named B-TiO$_2$ (v). The (v) values are: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5; 2; 2.5.

2.2. Photocatalyst characterization

The determination of the functional groups was achieved with a FTIR Shimadzu Prestige 21 using the middle infrared range. The presence of the TiO$_2$ crystalline phases was determined by X-ray diffraction analysis. Samples were measured in an X-ray diffractometer Bruker D8 Advance, with Cu anode, over a 20 range of 20°-80° using a 0.02° step. Crystallite size and phase percentage were calculated by Rietveld refinement using TOPAS P3. Morphological and chemical analysis were obtained by SEM and EDS using a JEOL JSM-6490LV at 25keV, and TEM images were obtained in a JEOL-1200EX with 80keV and an amplification of 200kX.

The surface area was measured in an ASAP 2020Micrometrics by the BET model measuring the adsorbed nitrogen at 77K previous degasification of samples at 180°C during 1h. Measures were made on the range from 0.01 to 0.99 for the relative pressure (P/P$_0$).

2.3. Photocatalytic activity characterization

Samples were prepared adding to the photocatalyst (50mg) 30mL of MB solution at 20ppm. All samples were exposed to solar radiation during 5h from 11 am to 4pm, for 11 cycles, under natural conditions in our geographic region. The calculated mean intensity was 27000 luxes. The evaluation of the photocatalytic activity was obtained by the measurement of MB concentration in the solution after light exposure using UV-Vis absorption technique. The absorbance value at 664nm is the standard used to measure the colorant degradation percent \[\left(\frac{(C_0-C_t)}{C_0}\right)\times100\%\].

One of the main goals in the decontamination processes is to use the same photocatalyst sample several times. In this work 11 times was repeated the discoloration process of a MB solution with the same photocatalyst. After each cycle, solutions were dried to recover the photocatalyst and a new solution of MB was added. In the eleventh cycle (last cycle), 1mL aliquot was taken each 30min during the first 2.5h. Each aliquot was diluted in 10mL of water and filtered with a 0.22µm Fisherbrand filter to avoid the absorption due to the presence of solid particles in the solution. Then, absorbance at 664nm was measured.

3. Results and discussion

3.1. Characteristics of A-TiO$_2$ and B-TiO$_2$ samples

FTIR measurements are presented in Figure 1 for B-TiO$_2$0.3 and A-TiO$_2$ samples synthesized in this work, and for commercial TiO$_2$. All spectra exhibit the 700 and 500cm$^{-1}$ bands associated to the Ti-O bond vibrations. Synthesized samples present bands in 3500cm$^{-1}$ and 1630cm$^{-1}$ produced by O-H bonds, attributed to the presence of H$_2$O probably adsorbed in the TiO$_2$ lattice or to residuary titanium hydroxide groups. The line shape of the B-sample is near to the commercial TiO$_2$ spectrum. In the X-
Ray diffractograms (Figure 2) it is observed the presence of crystalline phases, anatase (A) and rutile (R) in the A-TiO$_2$ sample, and just one, anatase, in the B-TiO$_2$0.3 sample.

![Figure 1. FTIR spectra in the MIR range of TiO$_2$ photocatalyst obtained by basic catalysis and acid catalysis, and commercial TiO$_2$.](image)

![Figure 2. X-ray diffractograms of B-TiO$_2$0.3 and A-TiO$_2$. The diffraction peaks of the anatase phase are labeled with A and the rutile one, with R.](image)

The images obtained by SEM (Figure 3) evidenced a great difference between the morphology of samples synthesized using basic catalyst and those obtained using acid catalyst. For the first ones the grains are well defined, spherical and, as the catalyst concentration increases the size of grains decreases. The average grain size value is ~0.55µm for B-TiO$_2$0.1 and ~0.20µm for B-TiO$_2$2.5. For samples synthesized using acid catalyst, grain size are ~2400µm and have no regular forms, nor regular sizes.

![Figure 3. SEM micrographs of (a) B-TiO$_2$0.1, (b) B-TiO$_2$2.5, and A-TiO$_2$ (c), and TEM images of B-TiO$_2$2.5 (d) and A-TiO$_2$ (e).](image)

TEM images (Figure 3) exhibit spherical particles for B-samples, homogeneous in their form, with diameters ~9nm, and they are incorporated in clusters of ~200nm diameter. A-sample also exhibit spherical particles but much bigger than B-samples, with diameters about 98nm. These morphologic characteristics are responsible for the high surface area per weight unit: less grain size, higher surface area, higher contact surface with the dye, higher degradation activity. A-TiO$_2$ sample have morphologic characteristics quite different from the B-TiO$_2$ samples; A-samples have big grains formed by two different crystalline structures. By Reitveld refinement of the diffraction patterns it was obtained a crystallite size for rutile about 49.1nm and for the anatase phase, 26.3nm.

In agreement with morphologic analysis, the porosimetry results indicated that B-samples have a higher surface area (74.79m$^2$/g) than A-sample (40.94m$^2$/g), unless the porous size is in the mesoporous range for both.

The chemical composition of samples was obtained by EDS analysis. In these spectra it was evidenced the presence of Ti, O, and C, probably as a residuary element of titanium alkoxide used in the synthesis process.
3.2. Photocatalytic activity and stability

The photocatalytic activity of samples was determined through the evolution of the degradation percent on MB solution after radiation exposure. As is shown in Figure 4, the degradation rate decreases with time. This behavior is explained considering two mechanisms in the first stages of the process: degradation due to the photocatalytic activity and adsorption of the dye by the porous microstructures.

![Figure 4](image)

**Figure 4.** Photocatalytic activity of samples synthesized with acid catalysis (A-TiO₂) and samples synthesized with basic catalysis with different NH₄OH concentration (B samples).

As the process continues, the porous could be saturated but the photocatalyst remains active. In Figure 5, for 150min it is evidenced a difference between three types of samples: sample synthesized with acid catalysis, samples synthesized with basic catalysis with NH₄OH concentration 0.3 or below, and samples synthesized with basic catalysis with NH₄OH concentration higher than 0.3. The A-TiO₂ sample exhibited a low efficiency degradation percent (67%). The B samples synthesized with low NH₄OH concentration (≤0.3) presented a higher efficiency (78±2%) than A sample. And the efficiency degradation percent for samples with higher NH₄OH concentration (B-TiO₂0.4) was 96% or higher. The degradation percent obtained for B-TiO₂0.6 sample was 99.9%.

4. Conclusions

TiO₂ photocatalyst was obtained by the Sol-Gel method. In this work we use two different catalyst in the synthesis process: HNO₃ (acid) and NH₄OH (basic). The TiO₂ synthesized with the acid catalyst exhibit two crystalline phases, rutile and anatase. The average grain size is 2400µm. The morphologic characteristics of these samples are in agreement with the low surface area obtained by BET analysis and its low photocatalytic activity. Instead, TiO₂ samples synthesized using a basic catalyst exhibit just one crystallographic phase, anatase. The grain size are not higher than 0.7µm, value that became lower as the base concentration increases. These small sizes are related to a high surface area, a high adsorption area and a high efficiency photocatalytic activity. The stability of samples as well as its high efficient photocatalytic activity is demonstrated by the results obtained after eleven cycles.

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