Synthesis and Characterization and Photocatalytic activity of TiO_2 Powders

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***Abstract*—Titanium (IV) isopropoxide (TTIP) was used for preparing TiO_2 nanoparticles by the precipitation technique. The precipitation was carried out following two experimental routes. In the first route titanium (IV) isopropoxide was mixing in ethanol, the solution obtained was heated at 60°C, then; glacial acetic acid and sulfuric acid were slowly added under constant magnetic stirring. In the second route titanium (IV) isopropoxide was mixed in ethanol, the solution obtained was heated at 60°C; then deionized water was added and finally hydrochloric acid was also slowly added. In both experiments a white precipitate was obtained, and then it was centrifuged, dried and calcined at different temperatures. To evaluate the photocatalytic activity, pellets were made from TiO_2 powders. The TiO_2 pellets were evaluated by the degradation of a methylene blue (MB) solution. The evolution of the MB concentration was monitored by a UV–vis spectrophotometer. The morphology and crystal structure of the powders were examined by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), respectively.**

Keywords: TiO_2; Precipitation; powders; Pellets

I. INTRODUCTION

Water is the most essential material for human survival, however only 3% of all water is fresh [1], hence the supply of drinking water is one of the most important problems facing society. This situation is compounded by the problematic of freshwater pollution. So the water treatment for human consumption takes special relevance; in that sense the advanced oxidation processes (AOPs) are growing rapidly [2], and photocatalysis represents a promising solution to the freshwater pollution. In recent years the photocatalysis has been focused on the use of semiconducting materials as photocatalysts for removing organic and inorganic species from water. The photocatalytic degradation of these species is based on reactions that are initiated when the semiconductor is illuminated with energy equal to or greater than the band gap of the semiconductor employed, exciting the electrons in the valence band to the conduction band, so an electron-hole pair is generated (eq 1) [3,4]. The reactions mechanism can be explained as follows: the holes can oxidize the pollutants directly or oxidize the absorbed water to produce $OH^\bullet$ and H^+ (eq 2), whereas the electrons can reduce the oxygen to form $O_2^{\bullet-}$ (eq 3). Moreover, the $O_2^{\bullet-}$ and H^+ can react to form $HO_2^\bullet$ (eq 4). This radical, $HO_2^\bullet$, can induce several reactions that generate more $OH^\bullet$ radicals (eqs 5-7).

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$
$$h^+ + H_2O \rightarrow OH^\bullet + H^+ \quad (2)$$
$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (3)$$
$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (4)$$
$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (5)$$
$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \quad (6)$$
$$OH^- + h^+ \rightarrow OH^\bullet \quad (7)$$

The $OH^\bullet$ radicals are strategically important, since they are highly reactive, attacking or degrading the pollutants in other molecules like carbon dioxide and water, among others [4-6]

Among the photocatalytic materials most studied, the titanium oxide (TiO_2) is the most used for photocatalysis studies due to its good photocatalytic activity, chemical stability, low cost, besides its low toxicity [7]. Titanium oxide is a polymorphic material that presents three natural structures: rutile, anatase, and brookite. The rutile phase is the most stable phase, whereas anatase and brookite are metastable [8]. Anatase is generally considered as the most photochemically active titanium oxide phase [7,9], however in some cases rutile has shown a higher photoactivity than anatase [10,11]; although brookite has exhibited considerable photoactivity as well [12,13]. According to the scientific literature, TiO_2 nanoparticles have been synthesized by using different techniques, such as spray pyrolysis [14], sol–gel [15], hydrothermal synthesis [16], and precipitation process [17], among others.

In this work, TiO_2 nanoparticles with both anatase and rutile structure have been synthesized by an easy and direct precipitation method. To evaluate the photocatalytic activity, the TiO_2 powders were pressed in pellet form, and then tested the degradation of methylene blue (MB) under UV radiation.

II. EXPERIMENTAL PROCEDURE

Two procedures were proposed in order to obtain TiO_2 powders; both were carried out via the precipitation technique using titanium (IV) isopropoxide (Sigma-Aldrich) as precursor of Ti. In the first experiment, 7 ml of titanium (IV) isopropoxide were dissolved in 25 ml of ethanol at room temperature, then the solution was heated at 60°C, followed by the slow addition of 15 ml of acetic acid, and right away 3 ml of sulfuric acid (H_2SO_4) was added drop by drop. After 20 minutes the precipitation reaction occurred, so the solution was maintained for one hour at 60°C in order to complete the precipitation reaction. Finally, the solution was cooled at 25°C. The precipitated obtained was centrifuged, dried and calcined at different temperatures (450, 500, 550, 600, 650, 700, and 750°C) for 6 h. These powders will be called powders PA.

In the second experiment, 6 ml of titanium (IV) isopropoxide were mixed in 150 ml of ethanol, then 5 ml of hydrochloric acid (HCl) were added, and right away a mix of 200 ml of water and 150 ml of ethanol were slowly added, all process was carried out at 60 °C. The precipitation reaction was immediate, so the solution was maintained during one hour at 60°C in order to complete the precipitation reaction. The precipitated obtained was centrifuged, dried and calcined at different temperatures (450, 500, 550, 600, 650, 700 and 750°C) for 6 h. These powders will be called powders PB.

For measuring the photocatalytic activity, the TiO_2 powders were pressed in pellet form using a hydraulic press (ITAL Mexicana) in a 10 mm diameter die. The photocatalytic test was carried out by immersing the pellets into a quartz cell containing 3 ml of an aqueous solution at $2.5x10^5$ mol/L of methylene blue (MB), then the cell was exposed to a 15W ultraviolet lamp.

The photocatalytic performance of the pellets was evaluated by monitoring the degradation of methylene blue using the UV/Vis spectroscopy.

Structural and morphological characterization was carried out by X-ray diffraction (PANalytical model XPERT-PRO diffractometer) and Scanning Electron Microscopy (AURIGA equipment), respectively.

III. Results

The synthesis was carried out by the precipitation technique. The precipitation is achieved by hydrolysis reactions. In the first experimental arrangement, the hydrolysis took place by esterification reactions [15]. A reaction in which an ester is obtained as a product is called esterification reaction [18]. The reaction between acetic acid and ethanol form an ester and water as reaction products (equation 1) [15], so the water formed hydrolyzes the alkoxide; however this hydrolysis is well controlled, slow, and homogeneous, then, the precipitation in the experiment 1 was slow, since it took 20 minutes to start the precipitation process. Hydrolysis reactions were followed by condensation reactions, which produce the precipitate of hydrous titanium oxide [19].

$$CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} H_2O + CH_3COOCH_2H_3 \qquad [8]$$

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \qquad [9]$$

$$Ti(OH)_4 \rightarrow TiO_2(xH_2O) + (2-x)\ H_2O \qquad [10]$$

In the second experiment the hydrolysis was faster than the first; in this case the precipitation occurred immediately, this is due to hydrolysis of alkoxides is carried out quicklier, and then completed in seconds by using an excess of water, however because alkoxides are immiscible in water, an alcohol is added to achieve a more homogeneous hydrolysis [20].

Depending on the experimental parameters such as the solvent type, acid catalyst, synthesis temperature, among others, TiO_2 precipitation can lead to anatase phase or rutile phase [19]. In the experimental arrays proposed, different parameters were varied, this in order to obtain the anatase and rutile phase in a relatively simple manner.

The type of acid used has a significant effect on the composition of the crystalline phases and the morphology of the TiO_2. Several studies have reported that sulfuric acid promotes the formation of anatase phase, whereas using hydrochloric acid favors the formation of rutile [15,21-22]; however it has been reported the formation of anatase phase by using HCl at low temperatures of synthesis (room temperature) [19]. Also, rutile phase was obtained using sulfuric acid as catalyst, but at higher temperatures of synthesis (70 °C) [23], suggesting that the temperature of synthesis and speed of addition of water are very significant parameters in obtaining a particular phase. For this reason, the parameters that favored the TiO_2 synthesis with desired phases were carefully selected, namely, low speed of addition of water and the use of sulfuric acid, H_2SO_4, for obtaining anatase phase; and on the other hand, high speed of addition of water and the use of HCL for obtaining the rutile phase.

Figure 2 shows the XRD patterns of powders PA calcined during 6 h at temperatures of 450, 500, 550, 600, 650, 700 and 750°C. Powders calcined at 450 and 500°C were amorphous, whereas the anatase phase was observed at 550-700°C presenting a (101) plane orientation, and it can be observed at 750°C a small reflection of rutile phase in the (110) plane. Figure 3 shows XRD patterns of powders PB. The diffractogram shows that all peaks are consistent with rutile (110) phase.

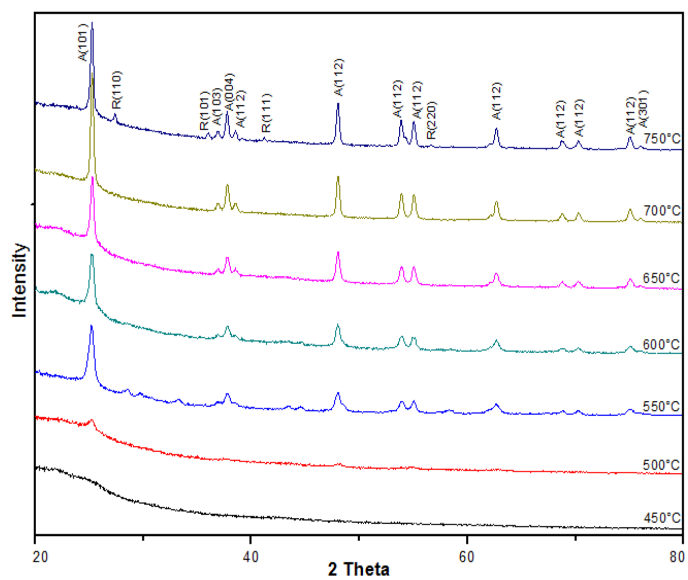

Fig. 2. X-ray diffractograms of TiO_2 powders, PA, calcined at 450, 500, 550, 650, 700, and 750°C, for 6h.

Figure 4 shows the SEM micrograph of powders PA. As it can be seen the SEM images showed well defined morphology with spherical particles with an average diameter of 20nm, likewise these structures form mesoporous agglomerates with high homogeneity.

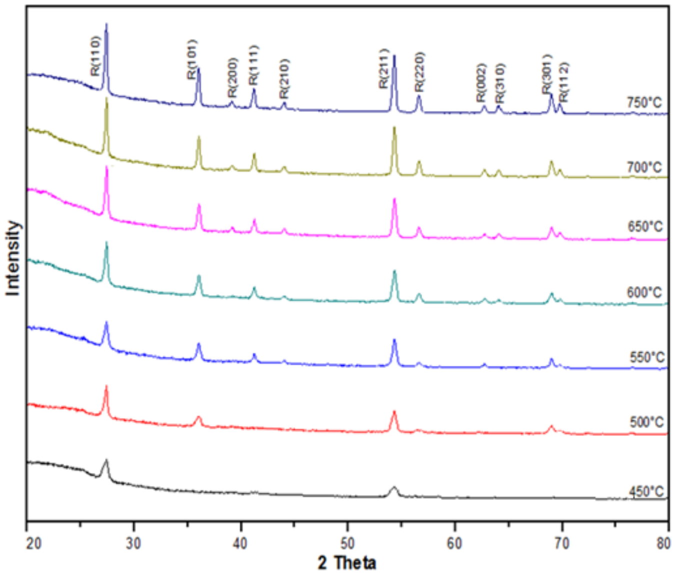

Fig. 3. X-ray diffractograms of TiO_2 powders, PB, calcined at 450, 500, 550, 650, 700, and 750°C, for 6h.

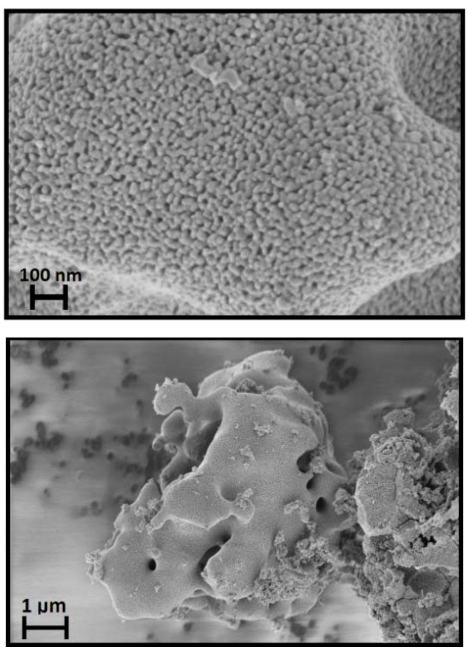

Fig. 4. SEM micrographs of TiO_2 powders synthetized from the first experimental array; sample calcined at 600°C for 6h.

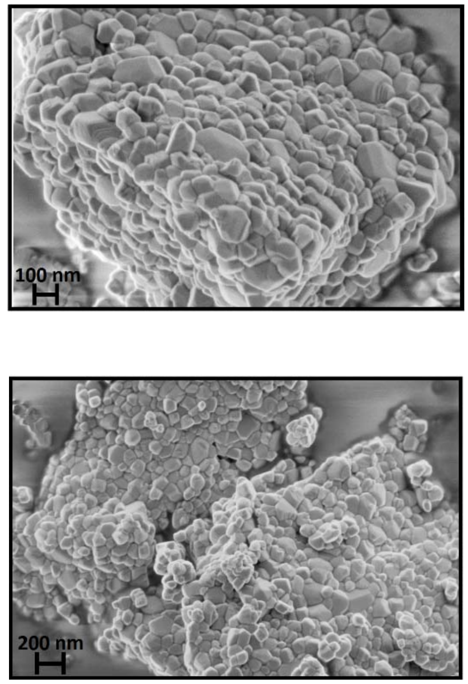

Fig. 5. SEM micrographs of TiO_2 powders synthetized from the second experimental array; sample calcined at 650°C for 6h.

Only the photocatalytic activity of the powders PA calcined at 600°C and powders PB calcined at 650°C was evaluated, because these were the lowest calcination temperatures at which the peaks fit well with the anatase and rutile phases, respectively. Figure 6 shows the photocatalytic degradation of an aqueous solution of methylene blue (at initial concentration of 2.5x105 mol/L) using pellets manufactured from powders of rutile and anatase as of photocatalysts, the figure indicates, as expected that the rutile present poor photocatalytic activity, this is because rutile is less efficient in creating electron hole pairs, however [24], however particles of pure rutile were obtained at relatively low calcination temperatures, reducing the synthesis cost, since the calcining process consumes about 60% of the total energy [25], for this reason these particles are candidates for future work of reprecipitation to modify the morphology of rutile in order to improve their photocatalytic characteristics; in this respect, it has been reported that morphology of the TiO_2 is highly significant for photocatalytic performing [11].

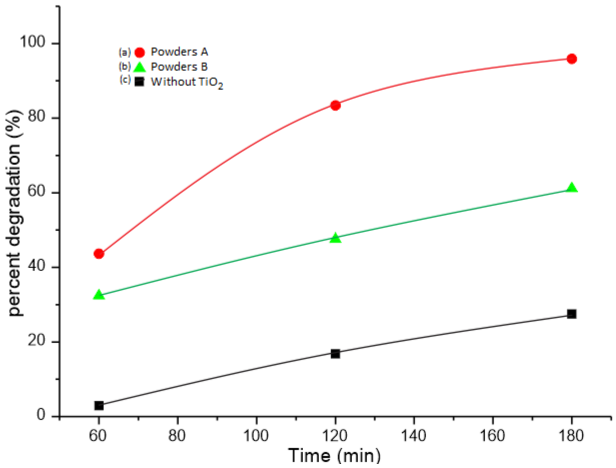

Fig. 5. Photocatalytic performance of TiO_2 pellets: (a) powders PA (anatase), (b) powders PB (rutile), and (c) reference, without TiO_2 sample.

On the other hand the anatase phase showed a good photocatalytic activity because in this phase the charge separation is more efficient because this phase has higher oxygen vacancies [26]. Also the good photocatalytic activity observed in samples of anatase may be due to its larger surface area since the anatase particles were about 7 times smaller than rutile. Additionally the particle agglomerates of anatase showed a mesoporous appearance, which could increase the active surface area and thus the photocatalytic activity.

IV. CONCLUSIONS

Anatase-TiO_2 nanoparticles, with an average particle size around 25 nm, and showing agglomerates of mesoporous characteristics were synthesized by an easy and low cost precipitation method. According to the structural and morphological characterization, the anatase powders calcined at 600°C for 6 h are good candidates for photocatalytic applications, as it can be the case of water cleaning. On the other hand, pure rutile-TiO_2 nanoparticles presented a low photocatalytic activity, nevertheless these were synthesized at relatively low temperatures of calcination.

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REFERENCES

[1] S. Ahuja, (2013). Comprehensive water quality and purification. Elsevier.

[2] C. Baird, M. Cann., (2012). Environmental Chemistry, Fifth Edition, W. H. Freeman Palgrave Macmillan.

[3] A. Omo Ibhadon, P. Fitzpatrick, “Heterogeneous Photocatalysis: Recent Advances and Applications,” Catalysts, 2013, pp. 189-218.

[4] R. Thiruvenkatachari, S. Vigneswaran y I. S. Moon, “A review on UV/TiO_2 photocatalytic oxidation process.” *Korean J. Chem. Eng.,2008, vol 25*(1), pp.64-72.

[5] E. Lichtfouse, J. Schwarzbauer, D. Robert., (2012). Environmental Chemistry for a Sustainable World: Volume 1: Nanotechnology and Healt Risk, Springer.

[6] H. de Lasa, B. Serrano, M. Salaices., (2005). Photocatalytic Reaction Engineering, Springer.

[7] M. A. Behnajady, et.al. (2008). “The effect of particle size and crystal structure of titanium dioxide nanoparticles on the photocatalytic properties”, *Journal of Environmental Science and Health Part A*. Vol 43, pp. 460–467.

[8] D. A. H. Hanaor, C. C. Sorrell (2011) “Review of the anatase to rutile phase transformation” J Mater Sci, vol. 46, pp.855–874.

[9] D. C. Hurum, et.al. (2003) “Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO_2 Using EPR.” *J. Phys. Chem. B, vol. 107*, pp. 4545-4549.

[10] T. Ohno, K. Sarukawa and M. Matsumura. (2002) “Crystal faces of rutile and anatase TiO_2 particles and their roles in photocatalytic reactions” *New J. Chem*., vol. 26, pp. 1167–1170.

[11] Y. Wang, et.al, (2007) “Low Temperature Synthesis and Photocatalytic Activity of Rutile TiO_2 Nanorod Superstructures” *J. Phys. Chem. C*, vol. 111, pp. 2709-2714.

[12] B. Zhao, F. Chen, Q. Huang and J. Zhang, (2009) “Brookite TiO_2 nanoflowers” Chem. Commun., pp. 5115–5117.

[13] K. Katsumata, et.al. (2012) “Synthesis of Amphiphilic Brookite Nanoparticles with High Photocatalytic Performance for Wide Range of Application” ACS Appl. Mater. Interfaces, vol. 4, pp. 4846−4852.

[14] D. Li, et.al. (2005) “Fluorine-doped TiO_2 powders prepared by spray pyrolysis and their improved photocatalytic activity for decomposition of gas-phase acetaldehyde”, Journal of Fluorine Chemistry, vol. 126, pp.69–77

[15] J. Zhu, et.al (2005) “High activity TiO_2 photocatalysts prepared by a modified sol–gel method: characterization and their photocatalytic activity for the degradation of XRG and X-GL”, Topics in Catalysis Vol. 35, Nos. 3–4, pp.261-268.

[16] H. Cheng, J. Ma, Z. Zhao, and L. Qi, (1995) “Hydrothermal Preparation of Uniform Nanosize Rutile and Anatase Particles,” Chem. Mater., vol. **7**, pp. 663–71.

[17] S. Kim, S. Park, and Y. H. Jeong, (1999) “Homogeneous Precipitation of TiO_2 Ultrafine Powders from Aqueous $TiOCl_2$ Solution,” J. Am. Ceram. Soc, vol. 82, Nº 4, pp. 927-32.

[18] M. Clugston, R. Flemming (2000) Advanced Chemistry, Oxford.

[19] C. Sung Lim, J. H. Ryu, D. H. Kim, S. Y. Cho and W. C. Oh. (2010) “Reaction morphology and the effect of pH on the preparation of TiO_2 nanoparticles by a sol-gel method” Journal of Ceramic Processing Research. Vol. 11, No. 6, pp. 736-741.

[20] B. Viswanathan,S. Sivasanker,A. V. Ramaswamy, (2002), Catalysis: Principles and Applications, Narosa

[21] S. Nadzirah, K.L. Foo and, U. Hashim, (2015) “Morphological Reaction on the Different Stabilizers of Titanium Dioxide Nanoparticles” Int. J. Electrochem. Sci., vol. 10, pp. 5498 - 5512

[22] S. L. Jie, Y. Ru and L. Mi, “Nanocrystalline TiO_2: Crystal Structure Controlled Synthesis via Low Temperature Hydrolisis Method and Surface Texture” Chinese Journal of Inorganic Chemestry, Vol. 22, No. 7, pp. 1196-1202.

[23] R. S. Hernandez (2011) “Síntesis de TiO_2 Mediante Procesos Sol-Gel para su Aplicación en Procesos Fotocatalíticos (tesis de licenciatura)” Universidad Rey Juan Carlos, España

[24] A. Sclafani, J. M. Herrmann (1996) “Comparison of the Photoelectronic and Photocatalytic Activities of Various Anatase and Rutile Forms of Titania in Pure Liquid Organic Phases and in Aqueous Solutions” J. Phys. Chem., vol. 100, pp. 13655-13661

[25] J. G. Santos, T. Ogasawara, R. A. Correa (2009) "Synthesis of nanocrystalline rutile-phase titania at low temperatures" Materials Science-Poland, Vol. 27, No. 4, pp. 1067-1076

[26] J. C. Colmenares, Y.J. Xu (2016) Heterogeneous Photocatalysis: From Fundamentals to Green Applications, Springer

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