ANALYSIS OF ADSORPTION/DESORPTION OF NITROGEN TiO_2 NANOPOWDERS OBTAINED BY THE METHOD PECHINI

P. C. Ribeiro Fernandes, pollyanacae@yahoo.com.br
A. C. F. M. da Costa, anacristina@dema.ufcg.edu.br
H. L. Lira, helio@dema.ufcg.edu.br
Departament of Materials Engineering, Federal University of Campina Grande, Campina Grande, PB, Brazil.

Abstract. *Titanium dioxide (TiO_2) is a semiconductor which is mainly in the form of three crystal structures, anatase, rutile and brookite. TiO_2 is an amphoteric oxide, insoluble and is dissolved only in extreme conditions with high acidity or low pH values, has no toxicity, is photostable, biologically inert and has low cost. Because of these characteristics, TiO_2 has been widely used in applications such as photocatalysis, and in recent years has aroused great interest in the scientific community, in particular, in research related to wastewater treatment as photocatalysis, being versatile and effective pollution control aqueous, modifying, degrading or mineralizing organic compounds. In laboratory scale crystalline structures, anatase and rutile are found more often in the literature and there are several chemical methods being used to obtain powders of TiO_2. Among the methods being investigated for obtaining powders of TiO_2 and has highlighted the Pechini method. Thus, this work aims at characterization by nitrogen adsorption of samples of TiO_2 synthesized by the Pechini method at a ratio of citric acid/metal ions of 1:1, 3:1 and 5:1. From the adsorption isotherms of gases on the samples of TiO_2 was possible to obtain the characteristics of their textures. The determination of surface area of TiO_2 samples were analyzed by nitrogen adsorption / helium developed by Brunauer, Emmett and Teller (BET). This technique was also used to determine the particle size. BET analysis revealed that samples of TiO_2 mesopores materials with pore diameters from 2 to 50 nm with a type IV isotherm and hysteresis loop of type II. One can also observe that the samples 1:1, 3:1 and 5:1 showed a reasonable amount of surface area of 47.49, 49.11 and 39.90 m^2/g, respectively, and hence particle size 29.6, 31.0 and 41.0 nm. The results show that the Pechini method is a promising technique for obtaining nanosized TiO_2 powders, and that with the increase in the proportion of citric acid/metal ions, a reduction in surface area and consequently an increase in particle size.*

Keywords: *TiO_2, Pechini method, adsorption and desorption analysis*

1. INTRODUCTION

Titanium dioxide (TiO_2) is a compound of great technological interesting and is one of the most studied oxide due to the chemical, electrical and optical properties (Zhao and Lian, 2007), this make possible the use of titania in several applications, such as, ink, gas sensor and catalisys process (Vieira et al., 2009). Titania presents three crystalline phases, rutile (tetragonal structure), anatase (tetragonal structure) and brookite (orthorhombic structure). Anatase phase is easier to obtain and is more used in catalysis process (Hussain et al., 2010).

Different methods are used in laboratory scale to prepare TiO_2. But, among these the Pechini method is increase in consistency in the synthesis of nanomaterials, including TiO_2. Among some researches using this method it can be cited: the synthesis of TiO_2 nanoparticles (Ochoa et al., 2009); nanostructure TiO_2 films (Stroppa et al., 2008); TiO_2 preparation to ceramic membranes (Vilar, 2004); zinc oxide films doped with cobalt to be applied as luminescent materials (Ribeiro, 2008); Ni-Zn ferrite powder preparation (Simões et al., 2009), and others.

In this way, the Pechini method permit a precise stoichiometric control, particle and agglomerate size handle, high purity, wide range of temperature synthesis to phase formation, reaction homogeneity due to better distribution of cations in a atomic level in the polymer structure and low cost once the reactants used in great quantity are relatively low price. Furthermore, the adequate thermal treatment of the resin, produce a organic material degradation that gives cations oxidation to generate monophase oxide and with nanometric particle size (Leite et al., 1995a and 1995b).

The aim of this work is to study the influence of the ratio between citric acid and metallic cations in the textural characteristics through adsorption and desorption analysis by Branauer, Emmett and Telle (BET) and by Bruanuer, Jouner and Halenda (BHJ) theory of TiO_2 sample.

2. MATERIALS AND METHODS

The TiO_2 samples were prepared with titanium isopropoxide IV, $Ti[OCH(CH_3)_2]_4$, 97% PA (supplied by Aldrich); monohydrated citric acid ($C_6H_8O_7.H_2O$), 99.5% PA (from Nuclear) and glycol ethylene, ($C_2H_6O_2$), 99.5% PA (from Vetec). The sample were obtained from citric acid and titanium isopropoxide reaction and adding of glycol ethylene in a ration of 40/60% in weight, in relation to citric acid, and follow the methodology developed by Pechini (1967). It was prepared three samples of TiO_2 according to molar ratio citric acid/metallic cations of 1:1, 3:1 and 5:1.

To sample preparation, firstly titanium citrate was produced from citric acid and titanium isopropoxide reaction. Citric acid and titanium isopropoxide were mixed under stir for 24 hours at 80°C until homogeneous mixture formation. Followed, it was added glycol ethylene slowly. After, the mixture of reactants was submitted to a heating at 100°C, to obtain a resin that was pyrolyzed at 400°C/1 h, with heating rate of 10°C/min. The resin was deagglomerate in agata mortar and passed in a sieve ABNT n° 200 (74µm). After, the powder was calcined at 500°C/1 h, with heating rate of 10°C/min to obtain TiO_2 that was submitted to a textural characterization.

The surface area and isothermal of adsorption/desorption of the TiO_2 samples prepared by Pechini method was done by nitrogen/helium adsorption developed by Branauer, Emmett and Telle (BET). Before, the samples were submitted to a pre-treatment under vacuum at 200°C/6h with 2 g of each sample. The isotherms were obtained in a Quantachane equipment (Nova 3200e model) with a scan of 40 points. This technique was used also to estimate the average particle size (equivalent spherical diameter) by Eq. I (Reed, 1983).

$$D_{BET} = \frac{6}{S_{BET} . \rho} \tag{1}$$

where, D_{BET} is equivalent average diameter (nm), S_{BET} is surface area estimated by BET method (m^2g^{-1}), ρ is theoretical density (gcm^{-3}) and 6 is a experimental number calculated and assumed to spherical shape particles.
Pore volume and pore diameter were calculated by theory developed by Brunauer, Joyner e Halenda (BJH).

3. RESULTS

Fig. 1 presents an isothermal of nitrogen adsorption/desorption of the TiO_2 samples prepared by Pechini method in the citric acid/metallic cations ratio of 1:1, 3:1 and 5:1.

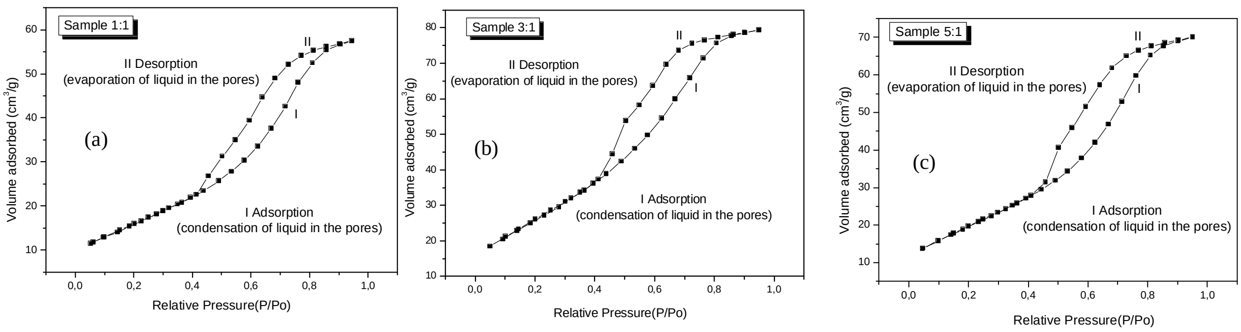

Figure 1. Isotherm adsorption/desorption of the samples calcined at 500°C/1h TiO_2 with different ratios of citric acid and metallic cations: (a) 1:1, (b) 3:1 and (c) 5:1.

From the Fig. 1 it can be observed that the isothermal of N_2 adsorption/desorption present the same behavior in the profile curves, that is, an increase in citric acid/metallic cations ratio do not change the textural characteristics of the TiO_2 samples. All samples present isothermal profile type IV that suggest a material with mesopores characteristics (pore with radius changing from 10 to 250Å), with hysteresis loop type H2 that indicate pore with open and close cylinder shape, resulting in a irregular morphology type "bottle" according to IUPAC classification (IUPAC, 1976).

This mesopores textural characteristics of TiO_2 has been reported by several researchers when prepared TiO_2 by others chemical synthesis methods. Among these researchers it can cited: Antonelli and Ying (1995) sintering mesopores TiO_2 by sol-gel process modified with surfactants; Pavasupree et al. (2008) preparing anatase phase mesopores TiO_2 by hydrothermal method at 130°C for 12 h; Li et al. (2009) preparing TiO_2 by alcohol thermal method and Hussain et al. (2010) sintering nanoparticles of TiO_2 to be applied as photocatalyst in ethylene photodegradation. All these researchers observed isotherms type IV with hysteresis loop characteristics of mesopores materials.

In Table I it was showed the surface area (S_{BET}), pore radius (R_p), pore volume (V_p) and particle size (D_{BET}) for TiO_2 samples prepared by Pechini method.

Table I. Surface area (S_{BET}), pore radius (R_p), pore volume (V_p) and particle size (D_{BET}) for TiO_2 samples with different citric acid/metallic cation ratio of 2:1, 3:1 and 5:1 and prepared by Pechini method.

Samples	Surface area (BET) (m^2/g)	Particle size (D_{BET})(1) (nm)	Pore volume (cm^3/g)	R_P (Å)
1:1	47.49	30	0.072	19.21

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3:1	49.11	31	0.065	19.39
5:1	36.90	41	0.056	19.33

(1):Calculated by surface area (BET)

From Table I it was observed that surface area change from 36.90 to 49.11 m^2/g, represents 24% of difference and indicates that the increase in citric acid/cation ratio tends to decrease the surface area and consequently contribute to an increase in the particle size of the samples. The values of surface area found in this work are similar to that related by Mendonça (2010) when prepared TiO_2 samples by OPM (Oxidant Peroxo Method) method with values change from 32.4 to 68.4 m^2/g.

Also it was verified that an increase in citric acid/ metallic cations ratio increase the distance between the metallic cations in the polymeric network and it was needed a great drive force to crystal and/or particles growth producing a reduction of the pore volume of the material. On the other hand, the radius of the pore almost do not change, presenting values close to 19 Å, that is, all prepared samples present mesopores characteristics (pore with radius changing from 10 to 250 Å).

4. CONCLUSIONS

The present work demonstrates the preparation of nanopowders of titanium dioxide by Pechini method with high surface area and nanometric particle size. This demonstrate that Pechini method is an efficient technique to produce TiO_2 samples and the increase in citric acid/metallic cations ratio gives an increase in surface area and produce samples with textural characteristics similar and with isothermal profile type IV, typical of mesopores materials and with hysteresis loop type H2.

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