

Nanopowders of TiO₂ obtained by combustion reaction: effect of fuels

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ABSTRACT

The aim of this work is to evaluate the effect of the different fuels in the combustion reaction synthesis. The structural and morphological characteristics of the TiO₂ powders were investigated. The powders were prepared according to the propellants theory by using a vitreous silica container and titanium isopropoxide as precursor. The fuels oxalic dihydrazide, aniline, monohydrated citric acid and carbonylhydrazide were used in a stoichiometric ratio as reducing agent. The powders were characterized by X-ray diffraction, nitrogen adsorption by BET, particle size distribution and scanning electron microscopy. The results of the X-ray diffraction showed that all fuels studied produced rutile as majority phase with presence of anatase as second phase. Carbonylhydrazide give the large amount of rutile phase, great peaks of X-ray diffraction, indicating the formation of powders with large crystallite size when comparison with the others fuels.

Keywords: TiO₂, fuels, combustion reaction, nanopowders.

1 INTRODUÇÃO

Titanium oxide is a polymorphic material, which can be found in three different crystalline phases at atmospheric pressure: rutile, anatase and brookite. The rutile phase is formed at high temperature (>1000°C), and the anatase phase is formed at low temperatures (close to 450°C) [1]. In general the brookite phase is unstable and has low interest. From the three titania crystalline phases, anatase is the most studied due to the possibility to be used in applications such as semiconductors and photocatalyst [2]. Anatase can be used to discolor residual water or to oxidize organic components [3,4]. Rutile phase can be used to applications such as pigment in paint, environmental purification, hydrogen gas generation due to their photoactivity, in the electronic industry as capacitors and electrical circuits and temperature condenser [5,6].

The use of chemical methods to prepare nanoparticles, with desirable physical, chemical and structural properties has been of great importance, due to the molecular stability and good chemical homogeneity that can be reached with materials. The combustion reaction process can offer

advantages such as is quickly and simple, do not need calcinations step and has low energy consumption during the synthesis. Also, the combustion reaction method synthesizes products of high purity, nanometric particles with good chemical homogeneity [7,8].

The study of different fuels in the combustion reaction to prepare some ceramic systems has been published in several works [9]. To obtain specifically TiO₂ it can be cited the use of citric acid, glycine, oxalic dihydrazide and urea [10,11] and others. All these fuels contain nitrogen, but with different reducer capacity, organic chain size, valence and, so, gas quantity generated by them, which define the temperature and time of the combustion flame reached during the synthesis. High temperatures favored the crystallization and sintering of the powder and as higher the amount of gas produced higher is the energy dissipation, that is, smaller will be the amount of energy available to sintering and crystallization, which generate low combustion temperatures and in some case favored the formation of secondary phase, once, part of the heat that must go to the phase formation was lost to the surrounding area. In this way, the aim of this work is to evaluate the effect of fuels (Eac, Ean, Eox and Ecb) in the combustion temperature and in the morphology and structure of the TiO₂ powder prepared by combustion reaction.

2 MATERIALS AND METHODS

To prepare TiO₂ by combustion reaction it was used aniline (C₆H₇N) – Ean, monohydrated citric acid (C₆H₈O₇.H₂O) – Eac, carbonylhydrazide (CO(N₂H₃) – Ecb, and oxalic dihydrazide (CH₆N₄O) - Eox as fuels and reducer agents, and titanium isopropoxide [Ti(OCH(CH₃)₂)₄] as source of cations and oxidizer agent. All reagents present 98% of purity. The mixture was added to a silica vitreous crucible and submitted to a direct heating by a spiral electrical resistance (temperature close to 600°C). Following, it was added the titanium isopropoxide to the fuel, with releasing a great amount of volatile gases (product of reagents decomposition). In the moment of gas release decrease, the mixture was transferred to a pre-heated oven at 700°C (Model: EDG3P – 3000) until ignition and subsequently combustion. The measurement of maximum temperature of the combustion flame was done

by a infrared pyrometer (Raytec Model-Raynger 3i) and the time of combustion flame by a digital chronometer (Model: Technos). After powder preparation with each fuel it was de-agglomerate in a mortar and passed in a sieve 325 mesh (45 μ m) to subsequent characterization.

The X-ray diffraction data were obtained from a diffractometer Shimadzu model 6000, with K α Cu radiation. The phase identification was done from the X-ray diffraction data and using a computational software (Pmgr) from Shimadzu and JCPDF data. The crystallinity was estimated with software and using the Lorentz coefficient of correction. The surface area and the adsorption/desorption isotherms were obtained from gas adsorption and using an ASAP 2000, from Micromeritics. The particle size was calculated by Braunauer, Emmet and Teller theory (BET). The morphology of the TiO₂ powder was observed by scanning electron microscopy (SEM) model XL30 FEG, from Philips.

3 RESULTS

Fig. 1 show the intensity and the aspect of the flame reached during the combustion reaction to the TiO₂ preparation and using Ean, Eac and Eox as fuels. The color of the combustion flame is a strong indicative to evaluate the heating produced by combustion during the synthesis and can be high or low.

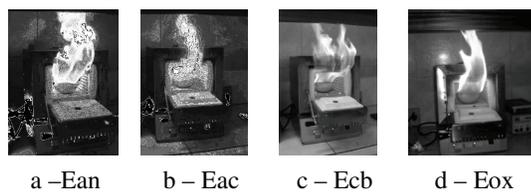


Fig. 1: Intensity and aspect of the flame burning.

From Fig. 1, it was observed that each fuel produce a characteristics combustion flame, in relation to the color, intensity or brightness color of the flame. So, it can be observed that aniline fuel (Fig. 1a) produced an intense flame, with brilliant aspect in the interior of the crucible and in the top extremity of the flame, also present dark color in the center of the flame. Eac (Fig. 1b) also produce an intense flame, but apparently less strong than Ean and with light aspect. Ecb (Fig. 1c) produced a spread and tiny flame, without brightness and clear aspect only in the extremity. The wideness of the flame give to a loss of heat to the environment and this can affect the combustion temperature reached during the synthesis. Eox (Fig. 1d) produced a clear flame with bright color close in the top extremity of the crucible, but with low intensity and dark aspect in the center and in the interior of the crucible.

Table 1 presents maximum temperature and time of the flame, also the combustion flame color observed during the combustion reaction. It can be observed that Ean fuel produce the biggest combustion temperature and an intense yellow color in the top and bottom of the flame (light grey

in the Fig. 1a), and red color close to the center of the flame (dark grey in Fig. 1a), however the time of combustion in this case was smaller when compared with others fuels. The Eox and Eac present intense yellow flame with long time of flame when compared with others fuels. The Ecb show a spread red flame and small time of combustion when compared with Eac and Eox. By analogy between the flame color, their aspect and period of time, with the measured temperature it was observed a good correlation, once the greatest temperature in the combustion was reached with Ean and the smallest temperature was reached with Ecb with a difference of 201 $^{\circ}$ C.

Table 01 – Temperature and time of combustion to the fuels use in the TiO₂ synthesis.

Fuels	Temperature ($^{\circ}$ C)	Time (seg)	Color
Ean	900	50	Intense yellow
Ecb	699	65	Red
Eac	798	172	Yellow
Eox	852	195	Intense yellow

Fig. 2 - presents the X-ray patterns of the TiO₂ powders prepared by combustion reaction with the following fuels: Ean, Eac, Ecb and Eox.

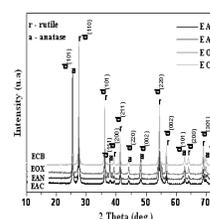


Fig. 2 - X-ray powder diffraction of TiO₂.

It can be observed that for all fuels, except for aniline, TiO₂ powder with rutile crystalline structure (JCPDF 65-0190) was obtained as major phase and traces of anatase as secondary phase (JCPDF 21-1272). Ean produces TiO₂ with anatase as major phase and rutile as secondary phase. This results is due to the Ean has bigger organic chain, greater valence and strong lateral groups or firmly bond when compared with other fuels.

Table 2 presents the results of crystallinity and crystallite size calculated from the X-ray diffraction data to TiO₂ powders prepared by combustion reaction and using Ean, Eac, Ecb and Eox.

Table 2 – Crystallinity and crystallite size of TiO₂ powders prepared by combustion reaction with Ean, Eac, Ecb and Eox.

Fuels	Cristalinity (%)	Crystallite Size - (nm)
Ean	94	43
Ecb	93	26
Eac	81	46
Eox	82	52

From Table 2 it was observed that the fuels produces powders with high crystallinity (above 80%) and crystallite size below 100nm, and characterize as nanometric powder. Ecb fuel produces powder with smallest crystallite size (26nm) when compared with other fuels. This is a consequence of small temperature reached by combustion flame during the synthesis. It was observed that the Ean give the formation of a powder with crystallite size slightly inferior to the Eac and Eox. This is due to the superior flame time produced during the synthesis with Eac and Eox, which was close to 180 s and close to 30% superior to the flame time reached with Ean.

Oliveira et al (2007) when prepared TiO₂ doped with Ni by combustion reaction and using urea as fuel, to be used as yellow pigment, show the presence of rutile phase and crystallite size between 26-38nm [12]. The researchers related only the presence of rutile as major phase and anatase as secondary phase and crystallite size of 65 and 44nm to glycine and urea fuels. By comparison these results with that one obtained in this study, it can be observed that only the Ecb produced crystallite size similar to the related by Almeida et al(2007) [13] and the others fuels produced two times crystallite size. This shows clearly, the influence of the physical-chemical character of the fuel in the structural characteristics of the TiO₂ powder prepared by combustion reaction.

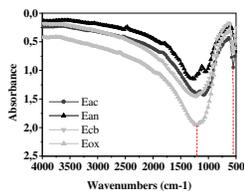


Fig. 3 – Infrared spectroscopy of the TiO₂ powder.

Fig. 3 presents results of the infrared spectroscopy of the TiO₂ powder prepared by combustion reaction and with Ean, Eac, Ecb and Eox as fuels. It can be observed similar behavior for the powders produced with different fuels, that is, for all conditions the desirable phase was the same (TiO₂). For all powders prepared it was observed a strong band in the range of 1259.95 cm⁻¹ characteristics of the O-Ti-O axial vibration. It was not possible to observe bands bellow 500cm⁻¹, due to limit of detection of the equipment, but it can be observed a tendency of absorption band formation close to 551cm⁻¹ that correspond to the O-Ti-O vibration. This absorption band between 500 and 800cm⁻¹ related with O-Ti-O also was reported by Phonthammachai et al. [14] when studied the structural and rheological aspects of TiO₂ prepared by sol-gel method.

Table 3 present the surface area, particle size and powder diameter of TiO₂ prepared by combustion reaction using Ean, Eac, Ecb and Eox as fuels. It can be observed that for all fuels do not occurred significant changing in the

values of surface area. It was observed a small reduction of 16% when compared the powder prepared with Ecb with Eac.

Table 3 – Surface area, particle size and pore diameter of the TiO₂.

Fuels	Surface área BET (m ² /g)	Particle size BET (nm)	Pore diameter Dp (nm)	D _{BET} /D _{DRX}
Eac	3.89	362	8.0	14
Ean	4.38	322	10.8	8
Ecb	4.63	304	6.8	7
Eox	4.12	342	11.8	7

* calculated from surface area (BET)
Theoretical density = 4.26 g/cm³ [15]

This is probable due to a small flame temperature and small combustion time (699°C and 65s, respectively) reached during the synthesis with Ecb in relation to the Eac (798°C and 172s, respectively). From the ratio between crystallite size calculated by DRX and particle size calculated from the values of surface area (D_{BET}/D_{DRX}) it was observed that the powder prepared with Eac more agglomerated in relation to the others fuels, and this increasing of agglomerate state (particle with pre-sintering start) give the condition to a reduction in the surface area.

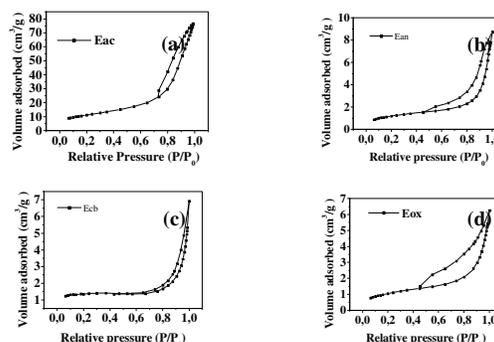


Fig. 4 – Nitrogen adsorption/desorption isothermal toTiO₂.

The results from textural characterization of TiO₂ powders prepared by combustion reaction using Ean, Eac, Ecb and Eox as fuels are represented by the N₂ adsorption/desorption isotherms in the Fig. 4. For all powders the isothermal profiles were type IV and V with a loop of hysteresis type H3, according to the IUPAC classification [16]. These isothermal profiles characterize the powders as mesopores materials (pore dimensions between 2-50 nm) and the hysteresis type H3 indicate that the pores are in shape of cone or parallel plates. Despite the powders presented similar isothermal profiles, the powder prepared with Eac presented a greatest widening curve due to the greater average diameter. Valente et al [17] when study the method to modify TiO₂ by sol-gel process with the addition of cerium oxide also showed that TiO₂ presented isothermal profile type II but hysteresis loop type H3, similar to the reported in this study.

Fig. 5 show the morphology of the powders prepared by combustion reaction using Ean, Eac, Ecb and Eox as fuels from scanning electron microscopy.

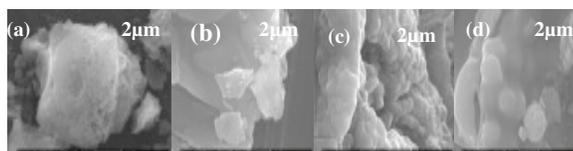


Fig. 5 – Images from SEM of the TiO₂ powders.

From the images it was observed that the TiO₂ powders prepared with all fuels presented the formation of agglomerates with pre-sintering particles, except for the powder prepared with carbonylhydrazide that presented a morphology of soft agglomerates (formed by interparticles weak forces), non-uniform and with irregular shape (Fig. 5a). Apparently these agglomerates are soft and present aspects more fragile when compared with the morphology presented by the powders prepared with Eox, Eac and Ean (Fig. 5b, 5c and 5d, respectively) that showed agglomerates with rigid aspect, that is, apparently dense.

4 CONCLUSIONS

The flame time and temperature of combustion reached with different fuels contributed to significant differences in the structural and morphological characteristics of the powders. All studied fuels used in the combustion reaction prepared TiO₂ powder with presence of rutile phase and anatase. However, Ean contributed to the formation of anatase as major phase and rutile as secondary phase. Eac produced powder with smallest crystallite size, but with greatest agglomerate size and smallest surface area. All fuels presented similar ratio between surface area and particle size. The pores presented values between 6.8 and 11.8 nm. All fuels produced powders formed by polycrystalline and agglomerates particles.

ACKNOWLEDGEMENTS

The authors would like to thank the Brazilian institutions CAPES and RENAMI-CNPq for their financial support of this research.

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