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The effect of synthesis parameters on the production of titania nanostructured spherical aggregates

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Anatase submicrometre nanostructured spherical aggregates have been obtained with a sol-gel synthesis assisted by Tween-20 as a surfactant. A low hydrolysis rate in room conditions and calcination at low temperatures were employed. Effective photocatalytic activities of up to 73% were obtained in the photodegradation of the methylene blue reaction. The effect of the synthesis parameters on the sizes of the spherical agglomerates obtained and on the crystallite size were evaluated; these parameters were the surfactant content, the molar concentration of the precursor titanium butoxide, and their relative ratios. The crystallite size had the main effect of obtaining good photocatalytic behavior, with a linear dependence on the photocatalytic activities. The morphology and anatase structure were determined by transmission electron microscopy. Use of the proposed synthesis made it possible to obtain only the anatase phase with small crystal sizes.

Key words: A. nanostructures, B. ceramics, C. chemical synthesis, D. electron microscopy, E. catalytic properties.

Introduction

Titanium oxide anatase is well known as a semiconductor catalyst. It is a powerful oxidant for harmful organic substances such as mordant yellow [1], Escherichia coli [2], rhodamine B [3], stearic acid [4], the herbicide fluoroxypyr [5], and others. Oxidation is used to degrade these substances and diminish their toxicity. This process has been of intense research interest in recent years. Titania has been proposed for several applications such as residual water decontamination [6], air cleaning and self-cleaning [7, 2], mesoporous membranes, and wet-type solar cells. Titania also has other interesting technological applications, for instance as a gas sensor, in photovoltaic cells, photonic crystals, pigments, fillers, coatings, and photoconductors [7, 8]. The photocatalytic phenomena in aqueous media can be explained as follows: When the anatase phase of TiO2 is irradiated with ultraviolet (UV) light with a wavelength of less than 400 nm, an electron excess is generated in the conduction band, which creates a number of positive holes (h+) in the valence band (Step 1). The hydroxyl radical is oxidized when it is in contact with the h+ of the catalyst, generating the hydroxyl •HO radical (Step 2). This •HO radical promotes the complete mineralization of different organic substances (Step 3) [9].

 $TiO_2 + h\nu \to \varepsilon^- (\epsilon \lambda \epsilon \chi \tau \rho o \nu) + \pi^+ (\eta o \lambda \epsilon)$ (1)

(Excitation of TiO_2 with UV light) $p^+(hole) + OH^- \rightarrow \bullet HO$ (2) $(H_2O \rightarrow H^+ + OH^-)$

Oxidation of harmful substances by the \bullet HO formed (3)

 TiO_2 has been obtained by different methods: by oxidizing pure titanium [8], by the sol-gel method [10], by electrophoretic sol-gel deposition [11], by thermal hydrolysis [12, 13], by spray drying [14], by atomic layer deposition (ALD) in a fluidized bed reactor [15], and titania fibers have been obtained by melt-spinning [9].

Fine spherical powders are desirable for producing advanced ceramics, and preparation of spherical particles in the micrometre and submicrometre size range is beneficial because of their broad applications in chromatography, bioseparation, and nanotechnology [16]. Spherical titania particles have been prepared by chemical methods [10] using organic [17, 18] and inorganic [12, 13] precursors. The present paper describes the preparation of spherical anatase powders using the surfactant Tween-20 as a dispersant at a low hydrolysis molar rate in order to produce low hydrolysis kinetics and promote greater control of the process conditions to obtain more desirable conditions for spherical morphology aggregation. The effect of the crystallite size on the photocatalytic activity was analyzed.

Experimental Procedure

Photocatalyst synthesis

Titanium butoxide Ti $(OC_4H_9)_4$ (Sigma-Aldrich) was used as the metallic precursor, buthanol (C_4H_9OH) (Sigma-

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Aldrich) was used as a solvent, and polyoxyethylene sorbitol ester Tween-20 (Fluka) was used as a dispersant agent. $Ti(OC_4H_9)_4$ was added to a Tween-20/buthanol solution in order to reach total dispersion. This solution was vigorously stirred for 3 h at room temperature. The sol obtained was then placed in a petri dish and dried at room conditions at an ambient mean humidity of 40%. The dry powder obtained was calcined in air at 673 K for 5 h with a heating rate of 2 K minute⁻¹ in order to completely remove the surfactant [1, 18, 19]. The samples obtained are described in Table 1, where ϕ represents the mass fraction of Tween-20/Ti(OC₄H₉)₄ used multiplied by 10. For each ϕ value, three different volume ratios of Tween- $20/C_4H_9OH$ were studied. The key names of the samples obtained are shown in Table 1. These names represent the synthesis conditions of each sample. The first two letters indicate titanium oxide (Ti) and the following two numbers are the ϕ value used for the sample. The following letter, T, indicates the surfactant used, which in this case was Tween-20. The last number indicates the volume ratio of the Tween-20/C₄H₉OH used multiplied by 100.

Characterization of TiO₂ photocatalyst

A JEOL JSM-6400 scanning electron microscope (SEM) was used to observe the morphology and size of TiO₂ aggregates. The crystalline phases of the samples were determined by X-ray diffraction (XRD) in a Philips X'Pert diffractometer, using Cu K α radiation $\lambda = 1.54$ Å, with 0.02°/s steps. Transmission electron microscopy (HRTEM) was conducted using a Philips Tecnai F-20 field emission microscope. The Brunauer-Emmett-Teller (BET) surface areas of powders were determined via N₂ adsorption using a Quantachrome Quantasorb Jr instrument. The total carbon content was measured by the colometric technique in a UIC model CM5014 instrument. Infrared spectra were recorded by a Bruker TENSOR-27 IR spectrometer.

For the catalytic tests, the photocatalysts obtained were tested for methylene blue (MB) degradation. The batch reactor consisted of a reaction cell with a compressed air supply in a tightly closed compartment equipped with an ultraviolet light, Ultravg 125 6286 model. The reaction was carried out at room temperature in an aqueous solution with 10 mg/l of MB. The ratio of TiO₂ was one gram of TiO₂ per 1 liter of MB. The solution was previously

Table 1. Synthesized samples labeled

Sample	ø	Tween-20 [®] (ml)/(C ₄ H ₉ OH(ml))
Ti2T3	2	0.029
Ti2T6	2	0.061
Ti2T9	2	0.088
Ti4T3	4	0.029
Ti4T6	4	0.061
Ti4T9	4	0.088
Ti8T3	8	0.029
Ti8T6	8	0.061
Ti8T9	8	0.088

magnetically stirred at 400 rpm for 30 minutes without the use of UV light in order to reach stable absorbance of MB on the photocatalyst surface [18]. After that, the solution was irradiated under UV light and magnetically stirred, and air was fed in simultaneously when the reaction system was started. Samples of the suspension were taken each hour during 5 h of testing. The measurement of the MB residual concentration in the solution was determined at 666 nm for absorbance using a Perkin-Elmer UV-Vis Lambda 20 spectrophotometer. The concentration of MB after each experiment was determined quantitatively through the calibration graph constructed from standard solutions of MB at various concentrations.

Results and Discussion

The morphology obtained is spherical with a narrow size distribution and monodispersed for all the studied samples. Fig. 1 shows SEM micrographs of three samples, Ti8T3 (a), Ti8T6 (b), and Ti8T9 (c), and a single Ti2T9 aggregate at 20,000× showing its spherical morphology. A lower mean size of the spherical aggregates was obtained for the higher ϕ value. This could be because with larger amounts of surfactant and alcohol, the dispersivity of the particles increases, limiting further condensation and growth.

When the amount of buthanol used as a solvent is increased, the spherical sizes of the aggregates are smaller. It has been suggested by other authors that the smallest TiO_2 colloids are obtained under slow hydrolysis conditions [20].

Histograms of the mean sizes of spherical aggregates obtained for all samples are shown in Fig. 2. In order to evaluate both parameters, alcohol and surfactant content, the mean size of aggregates has been analyzed as a function of the precursor dilution ratio and the molar concentration of the $Ti(OC_4H_9)_4$ with respect to the total volume (Tween-20 + C_4H_9OH). This is shown in Fig. 3. As this concentration increases, the mean diameter of aggregates also increases. This result indicates that at higher precursor concentrations there are more monomer and oligomer units available to condense. Gherardi and Matijevic also obtained a narrow particle size distribution of barium titanate with a low concentration of titanium precursors [21]. Control of the size, shape, and structure are important factors in determining the properties of the final material.

All samples presented a main anatase peak corresponding to the (101) plane with $d_{101} = 3.52$ Å. For the anatase phase, (Diffraction Card: ICDD 21-1272), no sample presented a rutile phase main peak (100), $d_{100} = 3.247$ Å. This is shown in Fig. 4: the samples calcined in air at 673 K showed the characteristic XRD peaks of the anatase phase (marked 'a'). The broad diffraction peaks indicate the low crystallinity and the small crystallite size obtained. Sheng *et al.* [18] obtained similar diffraction patterns for samples calcined at 673 K using dodecylamine ionic surfactant instead of the Tween-20 non-ionic



Fig. 1. SEM micrographs of the calcined samples, spherical aggregate morphologies for: (a) Ti8T3, (b) Ti8T6, (c) Ti8T9 and (d) Ti2T9 samples.



Fig. 2. Spherical aggregate mean size histograms obtained for all samples.



Fig. 3. Effect of the molar concentration $[Ti(OBu)_4/(tween-20^{\mbox{\tiny (B)}} + C_4H_9OH)]$ on the aggregate mean size.



Fig. 4. XRD diffraction patterns of samples calcined at 673 K.

surfactant used in this study. The rutile and anatase phases of TiO_2 are commonly used in photocatalysis with the anatase phase showing higher photocatalytic activity because it has a wider band gap than the 3.2 eV of the rutile titania phase [22], so obtaining the pure anatase phase in this study is an important result.

Sample Ti8T6 was studied by TEM. The TiO₂ spherical morphology of the aggregates was observed and is shown in the bright field image in Fig. 5a. The sizes of aggregates correspond to those evaluated by SEM for this sample. High resolution TEM (HRTEM) analysis allowed us to observe the presence of transformation twinning defects in some grains, as shown in Fig. 5b. A

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Fig. 5. (a) Bright field TEM image of Ti8T6, (b) TEM image of Ti8T6, (c) Close up TEM image showing a twin defect caused by crystallization of the primary crystallites.



Fig. 6. HRTEM images (a) showing the size of nanocrystallites, (b) of Ti8T6 showing the TiO₂ anatase phase in zone axes [$1\overline{1}1$] with a=3.7852 c=9.5139; S.G I4₁/amd (141) corresponding with Diffraction Card 21-1272.

close up of the marked square of the region is also shown in Fig. 5c. The HRTEM image of the spherical aggregates allowed us to observe the nanocrystallites immersed in an amorphous matrix in which the size of the primary crystallites could be determined to be approximately 5-14 nm (Fig. 6a). Liu *et al.* obtained similar crystallite sizes using HNO₃ as a catalyst and without a surfactant [23]. The crystallite in the HRTEM image in Fig. 6b was measured and indexed as an anatase tetragonal phase with a zone axis [l-ll], corresponding to Diffraction Card 21-1272.

The residual total carbon content (RTC) recorded includes the inorganic and organic carbon present in samples after calcination at 673 K which originates as a clear brown color in the sample powders. For all the calcined samples the RTC is in the range of 2.6-3%, which is similar to the range reported by Park *et al.* [24], who reported a synthesis route starting with TiCl₄ 0.1 mol/l in propanol. The results obtained for each sample are shown in Table 2. Yoldas [25] observed that in the titania synthesis there is always a certain concentration of OR groups that remains in the structure regardless of the amount of water present.

The surface area data of the samples calculated by the BET equation are shown in Table 2. These values

 Table 2. The surface area BET, present phases and RTC (wt%) for each sample

Sample	S.S.A. BET (m ² /g)	Carbon content (wt%)
Ti2T3	21	3
Ti2T6	28	3
Ti2T9	26	3
Ti4T3	19	2.6
Ti4T6	25	3
Ti4T9	29	3
Ti8T3	29	2.6
Ti8T6	32	2.6
Ti8T9	32	2.6

are low in comparison with the photocatalytic P25 (Degussa), which has 50 m²/g, which could be explained by the low hydrolysis molar rate used in this study. This would mean that less water was used in the synthesis route, promoting low cross-linking, which leads to the formation of dense particles [25].

In order to examine whether the surfactant was totally removed in the as-synthesized and calcined samples, IR spectra of the samples were recorded in the range of 4000-700 cm⁻¹. Fig. 7 shows the IR spectra of Ti2T3, as-synthesized and calcined, as a representative result for all samples in which the IR spectra were very similar. In the IR spectra (Fig. 7), the bandwidth at $3360-3140 \text{ cm}^{-1}$ is due to the stretching vibration of the hydroxyl groups, which can be attributed to the TiO-OH species that were formed during the gelation [26] and to the OH residual groups from alcohol (C₄H₉OH). The OH flexion vibration of H₂O present at 1651 cm⁻¹ is due to the adsorbed water. The high energy vibrations at 2883 cm⁻¹ correspond to the CH₃ and CH₂ [27] groups from the Tween-20 (C₄H₉OH) and Ti(OC₄H₉)₄ carbon chains. The bands located at 1444 cm⁻¹ result from the CH₂ and CH vibrations of these groups. The C-O bond characteristic vibration is located from 1080 to 1300 cm⁻¹ and the one corresponding to the C = O vibration from the ester is located at 1750 cm⁻¹, which is present in the as-synthesized samples due to the Tween-20, which is chemically a polyoxyethylene sorbitol ester. The IR spectrum of the calcined sample shows evidence of low intensity bands of organic groups, presenting two additional bands at 2360 and 2327 cm⁻¹ corresponding to the CO₂ which is a product of the calcination of the organic compounds adsorbed in the catalyst surface. There is one band at 1539 cm⁻¹ which correspond to hydroxides metal species [1]. There are very low signals of residual organic species, indicating that the TiO₂ samples prepared were free of impurities.

The photocatalytic activities of the samples were investigated by detecting the decomposition of a MB aqueous solution under UV light irradiation. The results are shown



Fig. 7. IR spectra of sample Ti2T3 as-synthesized (dry at 353 K), and calcined at 673 K.

in Fig. 8. All samples were calcined at 673 K. It was found that samples synthesized with higher values of ϕ (indicating higher amounts of surfactant and alcohol) showed the best percentage degradation. This could be attributed to the higher primary crystallite size reached at higher ϕ values. The Ti8T9 sample bleached 73% of MB in 5 h. Samples Ti8T6 and Ti2T9 bleached 67 and 69% of MB in 5 h, respectively. Random et al. obtained a 77% degradation of MB in 5 h [28]. However, they synthesized TiO₂ with 5% in the anatase phase combined with an amorphous phase using an inorganic salt. Hirano and Ota [29] obtained a 75% degradation of MB in 5 h with TiO₂/Silica; 25% Silica-TiO₂ was in the anatase phase with a BET surface area of 1123 m²/g, using 0.01 g of catalyst. The large surface area could be attributed to the silica synergy effect. Wang et al. [17] obtained a 70% degradation of MB in 1.5 h for a sample prepared with tetradecylamine, with the anatase phase and a BET area of 18 m²/g. However, they also reported another sample synthesized by the hydrothermal route using a microwave treatment, obtaining a weak anatase phase which was nearly amorphous, with a BET area of 600 m^2/g . From these, they reported a 80% degradation of MB in 1.5 h. This result indicates that good photocatalytic properties can be obtained in titania materials with low surface areas, which is supported by various authors who suggest that the difference in crystallinity of the anatase is the main reason for good photocatalytic behavior.

The effect of the volume ratio of Tween-20/C₄H₉OH and ϕ (the mass fraction of Tween-20/Ti(OC₄H₉)₄, multiplied by 10) on the percentage degradation of the MB is shown in Fig. 8. The higher percentage degradation were obtained with $\phi = 8$ and increased as the ϕ value increased. The surface areas and the crystallite size also increased with the ϕ value. For a constant ϕ value, when the Tween-20/C₄H₉OH increases, the percentage degradation of MB also increases.

Based on the Scherrer formula, the mean dimension of the crystallites was calculated from the diffraction peak width at half the intensity of the main anatase diffraction peak (101). The percentage photocatalytic degradation was



Fig. 8. Degradation of MB % with the photocatalysts: Ti2T3, Ti2T6, Ti2T9, Ti4T3, Ti4T6, Ti4T9, Ti8T3, Ti8T6, Ti8T9.



Fig. 9. Crystallite size effect on MB Degradation %.

replotted as a function of the crystallite size of primary nanocrystallites, one of the most important parameters in TiO_2 photocatalysis (Fig. 9). It was found that larger primary nanocrystallites showed the highest level of photocatalytic activity. Choo *et al.* also obtained greater chloroform degradations at larger crystallite sizes [30].

Conclusions

The synthesis route used in this study was found to be adequate to obtain microspherical nanostructured aggregates with only the anatase phase, with a narrow particle size distribution and high purity. This is proposed for effective methylene blue photodegradation. It was found that at low molar hydrolysis ratios there is less cross-linked structure, and the resultant porosity after calcination is low. Therefore, under these conditions the spherical aggregates obtained are denser, as are those shown in Fig. 5a, with low surface areas. This is because the OR groups of the organic compounds used remained in a low porosity structure, leaving a low residual carbon content after calcination. The XRD patterns and HRTEM results showed that spherical aggregates were formed by nanocrystallites with sizes ranging from 5 to 14 nm immersed in a nearly amorphous matrix. The analysis of the crystallite size showed a nearly linear dependence on the photocatalytic activity.

The results lead to the conclusion that the photocatalytic activity is clearly affected by the crystallite size and crystallization conditions as determined from the synthesis route used here. The surface areas obtained were sufficient to obtain effective photocatalytic activities, a result which is comparable with those obtained by other authors.

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