Synthesis of Titania Photocatalyst in Supercritical CO_2: Effect of Metallic Precursor and Hydrolysis Reactant

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TiO_2 nanoparticles have been synthesized in supercritical carbon dioxide (SC-CO_2) by thermohydrolysis of two different precursors diisopropoxititanium bis(acetylacetonate) (DIPBAT) and titanium tetraisopropoxide, (TTIP). Two different hydrolysis reactants have been tested (ethanol and isopropyl alcohol), and experimental results are presented for different molar ratios. The photocatalytic activity of the obtained powders has been determined for the oxidation of methylorange, as a prototype molecule and compared with that of commercial TiO_2. Experimental results show the influence of the acetylacetonate ligand in the precursor molecule on the structural properties of the obtained powder, and therefore on its photocatalytic activity. The photocatalytic activity of TiO_2 is influenced by the crystal structure (anatase and/or rutile), surface area, size distribution, porosity, surface hydroxyl group density, etc.

Moreover the results obtained with the different hydrolysis reactants suggest significant differences on reaction mechanism for TTIP and DIPBAT, related with the chemical stability of the acetylacetonate ligand. Isopropyl alcohol appears to be better hydrolysis reactant than ethanol for the photocatalytic activity of formed TiO_2.

Introduction

Titanium dioxide is a well known photocatalyst and it has been extensively tested in environmental applications dealing with photodegradation of organic pollutants in water and air [1-3]. A numerous of organic pollutants in water have been degraded by photocatalytic processes with TiO_2 including herbicides, aniline, oil and dyes [4]. More than water and air depollution applications, photocatalysis using TiO_2 is widely used in the self-cleaning of TiO_2 covered surfaces [1] and in photochemical solar cells [5].

Supercritical Fluids (SCF's) appear to be a suitable medium for the synthesis of titania nanoparticles, and oxides in general. In these proceses, nucleation step is very fast and particle growth can be avoided and/or controlled. TiO_2 (rutile or anatase) nanoparticles have been prepared by hydrothermal synthesis from stabilized $TiCl_4$ solutions [6]. Also, some researchers have used the combination of hydrolysis and polycondensation of titanium tetra-isopropoxide, (TTIP), in supercritical alcohol or mixtures alcohol/CO_2 [7]. The conventional hydrothermal or sol-gel methods yield larger particles and hence the SCF technology is the most viable one for producing nanoparticles with the shortest residence time. However, particle size and/or surface area are not the only parameters that have influence on the photocatalytic behaviour. It has been shown that the photocatalytic activity of TiO_2 is influenced by the crystal structure (anatase and/or rutile), surface area, size distribution, porosity, surface hydroxyl group density, etc. All these structural parameters are dependent on TiO_2 synthesis process. In principle, a photocatalytic reaction may proceed on the surface of TiO_2 powders via several steps [8], namely (a) production of electron-hole pairs, photogenerated by exciting the semiconductor with UV light energy; (b) separation of electrons and holes by traps available on the TiO_2 surface; (c) a redox process induced by the separated electrons and holes with the adsorbates present on the surface; (d) desorption of the products and reconstruction of the surface.

In this work, a second precursor is used for the synthesis of TiO_2 nanoparticles, diisopropoxititanium bis(acetylacetonate) (DIPBAT). The hydrolysis reaction is studied in terms of two reactants (ethanol and isopropyl alcohol), and product characteristics together with photocatalytic activity of the obtained powders are discussed.

Experimental

TiO_2 synthesis

TiO_2 nanoparticles have been synthesized in supercritical carbon dioxide (SC-CO_2) by thermohydrolysis of two different precursors diisopropoxititanium bis(acetylacetonate) (DIPBAT) and titanium tetraisopropoxide, (TTIP). Two different hydrolysis reactants have been tested (ethanol and isopropyl alcohol), and their initial concentration has been varied. The reaction takes place in batch at 300 ºC and 20 MPa, both values are selected from a previous work, already published [9].

Experiments have been performed in batch using a stainless steel reactor with 100 mL of internal volume, and a flowsheet of the plant is presented in fig. 1.

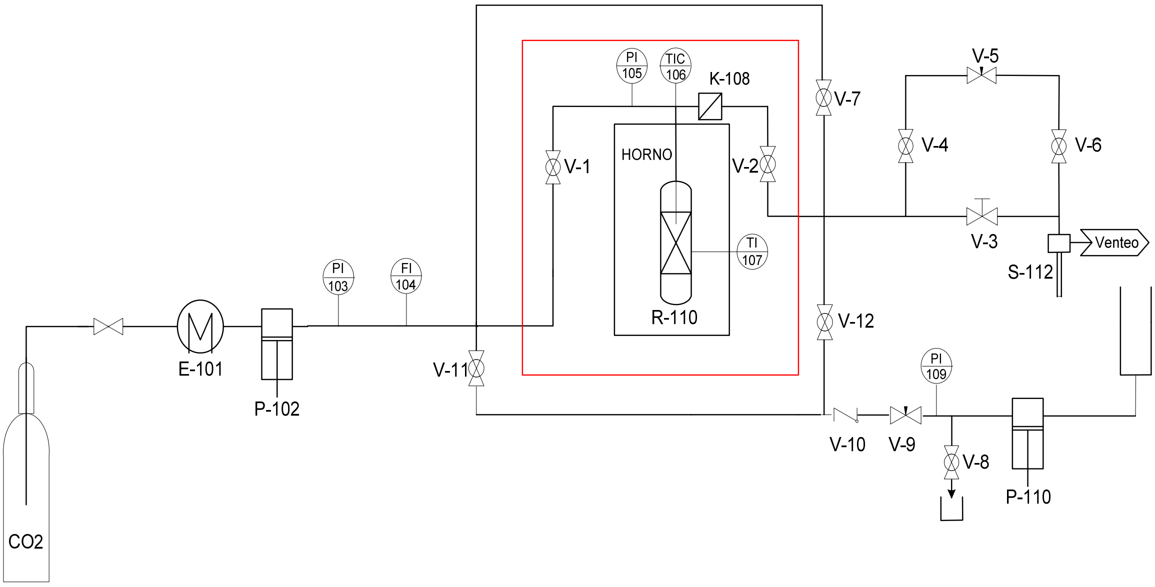

Figure 1. Experimental Facility Flowsheet

The crystal structure of the TiO_2 powders was investigated by X-ray powder diffraction (XRD) using CuKα radiation and ASTM D-476-84:1 for TiO_2 anatase crystal structure identification. The morphology and average particle size of the samples were characterized by scanning electron microscopy (SEM) using JEOL JSM-T300. The specific area of the powders was evaluated by means of nitrogen adsorption Brunauer-Emmett-Teller (BET) (Omnisorp 100 CX). The TiO_2 purity was determined by analysis of the carbon (analyzer of C and S with Leco Cs-225 deterrminator), since it is assumed that all the contamination of the samples comes from the organic part of the precursor molecule.To determine reaction efficiency, the obtained powders have been calcined up to 1000 ºC under N_2 atmosphere and the resulting product has been weighted. Reaction efficiency is defined as follow:

$$\text{Re}\textit{action Efficiency}\ (\%) = \frac{\textit{Calcined product weight}}{\textit{Theoretically } TiO_2 \textit{ weight}} \times 100$$

Evalutation of photocatalytic activity

The photocatalytic activity of the prepared TiO_2 powders was evaluated using aqueous solutions of methylorange (MO) provided by Sigma-Aldrich, with an initial concentration of approximately 35 ppm. The pH of the solution was adjusted to 2,5 using HCl (35%, Rectapur, Prolabo), and an initial concentration of TiO_2 catalyst of 1 g/l was suspended in all the tests. These conditions were optimised previously and are according to the literature [10].

The degradation of the dye was followed by using UV-Vis Spectrophotometer (Hitachi U-2000 Spectrophotometer). Samples (15 mL) were collected from the top of the reactor before and at regular intervals during the irradiation. They were centrifugated during 10 min at 10000 rpm (Multispeed Refrigerated Centrifuge PK 121R, ALC) before analysis. The concentrations of methylorange were calculated by a calibration curve obtained from the absorbance of the aqueous dye solutions (λ_{MAX} = 455 nm) at different concentrations.

The photocatalytic reactor set-up comprised the following components: air supply, air diffuser, Pyrex glass reactor, UV radiation sources and magnetic stirrer, as it is indicated in fig. 2.

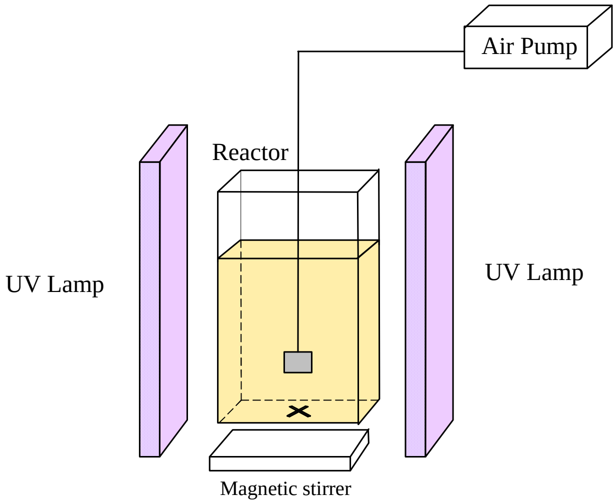

Figure 2. Schematic of the photocatalytic reactor set-up

The reaction vessel is made of Pyrex glass, it has a volume of 500 mL (49 mm inside diameter and 337 mm height). The reactor was aerated with air at 25 ºC by means of a pump M2K3 from Schego, and a diffuser 30 x 15 x 15 mm is located at the bottom of the reactor. The reactor was stirred at the bottom using a magnetic stirrer.

The UV sources were two 15 W integrally filtered low pressure mercury UV tubes (Spectronics Corp.) emitting 300-400 nm radiation with a peak of 365 at an intensity of 1100 µW/cm^2 per tube measured at a distance of 25 cm from the centre of the tube. The tubes were mounted in two silver-anodized housing positioned vertically on opposite sides of the reactor at a distance of 10 cm. The reactor was cooled by means of a fan positioned at the top of the set-up.

Results and Discussion

Organometallic precursor

Under the experimental conditions (200 bar, 300 ºC) anatase structure is the only crystalline phase that has been obtained, but crystallinity and reaction efficiency are very different from one experiment to another. The main product properties such as crystallite size and specific surface area are listed in table 1. Photocatalytic activity was evaluated for the obtained TiO_2 powders.

Sample Name	**Precursor**	**Hydrolysis Reactant**	**$r^{(a)}$**	**Reaction efficiency (%)**	**Crystallite size$^{(b)}$ d_{101} (nm)**	**S_{BET} (m^2/g)**
TTIP1	TTIP	IPA	21	85	32	81
TTIP2	TTIP	IPA	2	77	27	---
DIP1	DIPBAT	IPA	21	83	25	90
DIP2	DIPBAT	IPA	2	56	11	---

Table 1. Comparison of powders obtained from TTIP and DIPBAT precursor on final properties
P = 200 bar, T = 300 ºC
(a) r = Initial molar ratio (alcohol/ precursor)
Stoichiometric ratio (r = 4)
(b)crystallite size calculated with Scherrer´s equation, (peak 101 of XRD analysis)

TTIP is a precursor more easily hydrolisable than DIPBAT. The presence of acetylacetonate ligands in the DIPBAT molecule requires higher quantity of alcohol to complete the reaction and with a defficit of alcohol (r = 2) reaction efficiency is very low for DIPBAT (56%). When an excess of alcohol is used (TTIP1 and DIP1) reaction eficciency is quite similar for both precursors. Crystallite size, and therefore crystallinity quality, is a bit higher when TTIP is used as precursor but in any case higher than commercial TiO_2, as it is shown in figure 3. Photocatalytic activity of these two powders is similar.

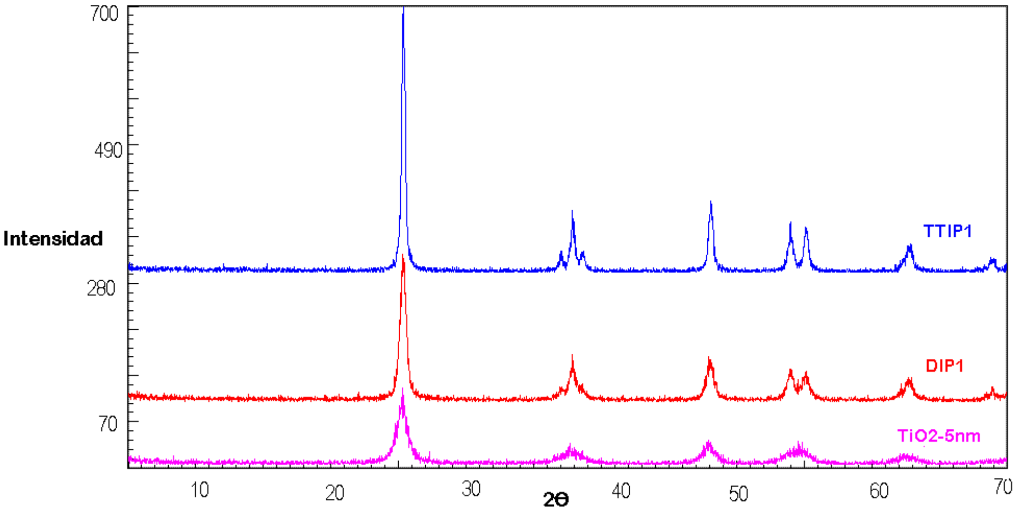

Figure 3. DRX diffractogram: TTIP1, DIP1 y TiO_2-5nm (commercial)

Hydrolysis reactant

Two different alcohols, ethanol and isopropyl alcohol, were tested in the synthesis process, and the main product characteristics are pressented in table 2. The TiO_2 obtained in these experiments, DIP1 and DIP5, is 100% anatase, and they are very similar in crystallinity and specific surface area. However their behaviour as catalysts in the photoxidation of mehtylorange is significantly different as it is shown in fig. 4.

Sample Name	**Precursor**	**Hydrolysis Reactant**	**$r^{(a)}$**	**Reaction efficiency (%)**	**Crystallite size$^{(b)}$ d_{101} (nm)**	**S_{BET} (m^2/g)**
DIP1	DIPBAT	IPA	21	83	25	90
DIP5	DIPBAT	Ethanol	21	83	23	87

Table 2. Effect of chemical nature of the alcohol in the final product properties
P = 200 bar, T = 300 ºC
$^{(a)}$ r = Initial molar ratio (alcohol/ precursor)
Stoichiometric ratio (r = 4)
$^{(b)}$crystallite size calculated with Scherrer´s equation, (peak 101 of XRD analysis)

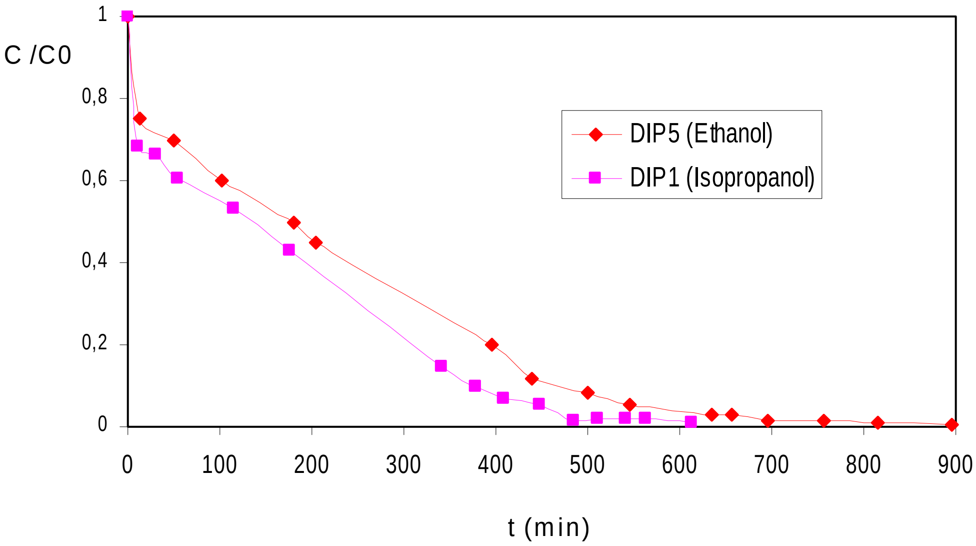

Figure 4. Photocatalytic activity of TiO_2 powders obtained at 300 ºC and 200 bar using isopropanol (DIP1) and ethanol (DIP5) as hydrolysis reactants: kinetics of methylorange photoxidation.

The photocatalytic activity of TiO_2 formed by using isopropyl alcohol as reactant (DIP1) is higher. 95% of methylorange is degraded in 456 min, whereas this time should increase to 635 min for the same elimination degree, for powders formed with ethanol (DIP5). This fact can be related with two different aspects: TiO_2 pollution and superficial concentration of OH groups. Pollution of formed TiO_2 is higher when ethanol is used as reactant hydrolysis (11,9 % of C, against 4,5 % of C). These rests of organic matter compete with TiO_2 particles for photon absorption during the photoxidation of methylorange, and therefore, the number of charge-carriers created by the TiO_2 catalyst decreases when pollution is higher. Another important difference between these two products (DIP1 and DIP5) is related with the quantity of OH groups on TiO_2 surface. Due to the difference in volatility of the alcohols, isopropyl alcohol generates a higher concentration of superficial OH groups, leading to a better photocatalytic activity of powder DIP5.

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