SYNTHESIS OF ANATASE TiO_2 NANOPARTICLES IN SUPERCRITICAL CO_2: EFFECT OF HYDROLYSIS REACTANT AND REACTION MECHANISM

E. Alonso*, I. Montequi, M. J. Cocero

Dpto. Ingeniería Química y Tecnología del Medio Ambiente. Universidad de Valladolid
Prado de la Magdalena s/n.- Valladolid (Spain) 47011
Telf.: +34 983 42 31 75, Fax: +34 983 42 30 13
ealonso@iq.uva.es

TiO_2 anatase nanoparticles have been synthesised by chemical reaction of Diisopropoxititanium bis(acetilacetonate) (DIPBAT) in supercritical CO_2. Previous results [1] have shown that product crystallinity is strongly related with temperature, and temperatures higher than 250 ºC are necessary to obtain well-crystallized TiO_2 anatase. Synthesis pressure (in the studied range: 100-200 bar) is not a key parameter, and it affects mainly to particle pollution due to its influence onto precursor solubility and byproducts removal. In all the experiments, particle size is in the nanometric scale (< 200 nm) and they exhibit high surface area..
In the present paper, three different reactants have been tested: ethanol, isopropyl alcohol and water, and the molar ratio hydrolysis reactant/DIPBAT (r) has been varied in the range 4-21. Isopropyl alcohol appears as the best hydrolysis reactant. Molar ratios higher than 16 are needed to reach reaction efficiencies higher than 80% and product purities higher than 95%.
Experimental results have shown that DIPBAT is not hydrolysed directly with water, and it needs a direct attack of an alcohol to start the substitution of the acetylacetonate ligands. These results have allowed us to propose a chemical reaction mechanism for the decomposition of DIPBAT in supercritical CO_2.

INTRODUCTION

Titanium dioxide is an excellent photocatalyst and it has been extensively tested in environmental applications dealing with photodegradation of organic pollutants in water and air [2-4]. 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 procedure.
One of the most used preparation techniques is the sol-gel process. In this process, metal alkoxides undergo hydrolysis and condensation reactions in solution to form amorphous (or hydrated) metal oxide with large surface areas; however these surface areas are drastically decreased on calcinations at the temperatures where corresponding oxides begin to crystallize. Moreover, particle agglomeration is difficult to control during this solvent removal step, and the process is very long usually it takes several days. These process limitations can be avoided by the use of Supercritical fluids (SCFs) [5] as reaction medium, instead of a liquid solution. In this case, the absence of surface tension facilitates solvent removal and diminishes particle agglomeration, reaction is very quick and calcination step is avoided [1].
Titanium hydroxide nanoparticles have been produced by hydrolysis of Titanium (IV) isopropoxide (TTIP) in SC-CO_2 using water as hydrolysis reactant [6,7]. Pommier et al. [8] have used SC-Isopropyl alcohol as reagent, and they have proposed the subsequent reaction mechanism, where titanium-alkoxide is attacked by water molecules obtained from alcohol dehydration:

$$ROH \rightleftharpoons R' + H_2O$$
$$Ti(OR)_4 + H_2O \rightleftharpoons Ti(OR)_3(OH) + ROH$$
$$Ti(OR)_3(OH) + H_2O \rightleftharpoons Ti(OR)_2(OH)_2 + ROH$$
$$Ti(OR)_2(OH)_2 + H_2O \rightleftharpoons Ti(OR)(OH)_3 + ROH$$
$$Ti(OR)_2(OH)_2 \longrightarrow TiO_2 + 2\ ROH$$
$$Ti(OR)(OH)_3 \longrightarrow TiO_2 + H_2O + ROH$$

TTIP is easily hydrolyzed and transformation to metal oxide is very fast and difficult to control. Working with TTIP in a continuous synthesis process is difficult because of this easiness to form $Ti(OH)_4$ at ambient temperature in presence of humidity. Because of this, it is necessary to implement a drying stage in the pumping line of the reactant, and alcohol must be added inside the reactor [1].
In the sol-gel process, chemical modification of TTIP with alcohols, chlorides, acids or bases, and chelating ligands is commonly used to retard the hydrolysis and condensation rates [9,10]. Acetylacetone (acacH), acting as a bidentate monocharged acetylacetonate ligand (acac), has been used as a stabilizing reagent for TTIP by several authors to prepare TiO_2 [11,12]

In this work, Diisopropoxititanium bis(acetilacetonate) (DIPBAT) is used to obtain TiO_2 anatase nanoparticles in supercritical CO_2. Alcohol (ethanol and isopropyl alcohol) and water has been used as reagents. DIPBAT is more stable than TTIP, sin it has two aceytlacetone ligands, and continuous operation has been performed [13]. The effect of operational variables (temperature and pressure) in the final product characteristics has been studied and published in a previous work [1]. Results have shown that product crystallinity is strongly related with temperature, and temperatures higher than 250 ºC are necessary to obtain well-crystallized TiO_2 anatase. Synthesis pressure (in the studied range: 100-200 bar) is not a key parameter, and it affects mainly to particle pollution due to its influence onto precursor solubility and byproducts removal. In all the experiments, particle size is in the nanometric scale (< 200 nm) and they exhibit high surface area..
The aim of this work is to study the influence of hydrolysis reactant nature and its concentration on nanoparticle properties, such as, crystallinity, surface area and product pollution,

MATERIALS AND METHODS

Chemicals

Diisopropoxititanium bis(acetilacetonate) 75 wt % solution in isopropanol provided by Sigma-Aldrich, without further purification. Three different additional reactants were tested: absolute ethanol (analytical reagent), isopropyl alcohol (analytical reagent) both provided by Panreac and deionized water. The CO_2 (99,9 % purity) was used as received from the commercial supplier Carburos Metálicos S.A.

Process

A laboratory-scale plant, developed in the Chemical Engineering Department at the University of Valladolid, has been used for these experiments. The flow diagram is presented in figure 1, and it is designed to operate up to 35,0 MPa and 400 ºC.

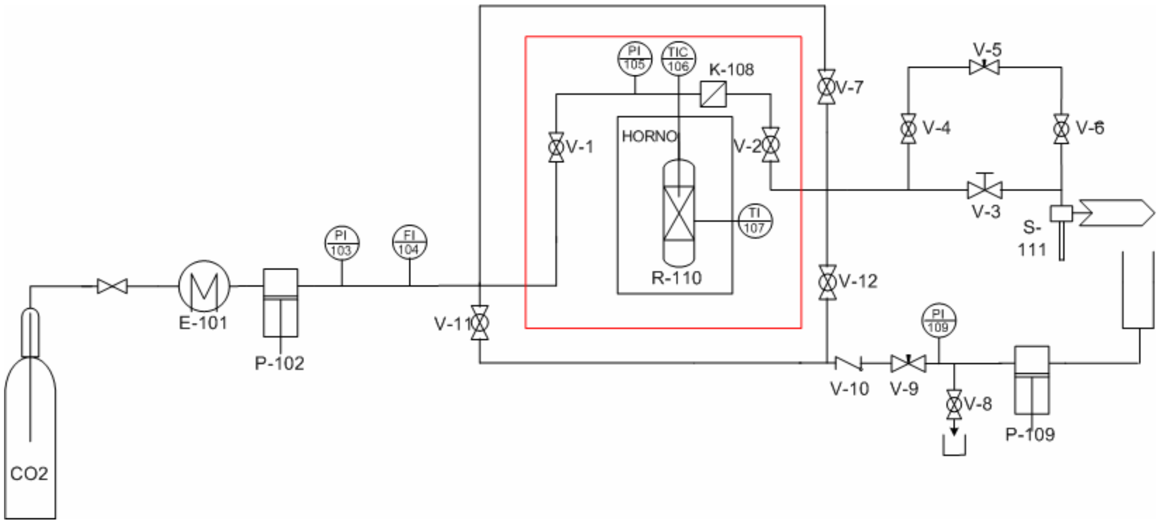

Figure 1. Flow diagram of the lab plant used for the synthesis of TiO_2 particles in sc-CO_2 (P-102: CO_2 pump; R-110: reactor; K-108: filter; V-3: back-pressure valve; V-5: decompression valve; S-111: liquid-gas separator).

Experiments are performed in batch. DIPBAT and hydrolysis reagent are charged into the reactor at the desired proportions, and CO_2 is pumped to the reactor until the work pressure is reached. At the same time the system is heated up until the desired reaction temperature. Once these values are reached time starts to count. In all the experiments operation time was 2 hours. After this time the system is decompressed and TiO_2 is recovered inside the reactor (R-110).

Characterization techniques

The crystal structure of the TiO_2 powders was investigated by X-ray powder diffraction (XRD) using CuKα radiation. The morphology and average particle size of the samples were characterized by scanning electron microscopy (SEM) using JEOL JSM-T300. The particle size distribution was determined by using a laser scattering particle size distribution analyzer (HORIBA LA900). 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.

RESULTS AND DISCUSSION

Three different reactants have been tested: ethanol, isopropyl alcohol and water, and the molar ratio hydrolysis reactant/DIPBAT (r) has been varied in the range 4-21. Table 1 presents a general comparison of obtained TiO_2 powders (surface area, crystallite size, density of surface OH groups) with these three reactants.

Hydrolysis reactant	Product	Reaction Efficiency, %	Product Purity	d_{101} (nm)	a_{BET} (m^2/g)
Water	No TiO_2	---	---	---	---
Ethanol	Anatase TiO_2	83	88	23	87
Isopropyl alcohol	Anatase TiO_2	83	95,5	25	90

Table 1. Decomposition of DIPBAT, 200 bar, 300 ºC, sc-CO_2, hydrolysis reactant/DIPBAT (r) = 21

Water as hydrolysis reactant

When water is used as reactant, a wet brown product is recovered inside the reactor, for al the tested molar ratios.

In the literature, water has been used as hydrolysis reactant in supercritical CO_2 [6, 7] when TTIP is used as precursor, however the presence of acetylacetonate ligands in DIPBAT molecule avoids direct attack of water.

Experimental results have shown that DIPBAT is not hydrolysed directly with water, and it needs a direct attack of an alcohol to start the substitution of the acetylacetonate ligands.

Alcohol as hydrolysis reactant

Two different alcohols have been tested in the reaction (isopropyl alcohol and ethanol) with molar ratios alcohol/DIPBAT varying from 4 to 21. Operational conditions have been 300 ºC and 200 bar, in all the experiments. Anatase TiO_2 has been obtained in all the experiments and crystallinity and surface area are similar for both alcohols, as it is shown in table 1. Experimental results have shown that when isopropyl alcohol is used, the TiO_2 powder obtained is less polluted, (table 1), and product purity is higher than 91% for all the tested ratios. However, with ethanol it was not possible to reduce pollution below the 10% of C, and a subsequent wash step was necessary to purify the product.

CONCLUSIONS

Diisopropoxititanium bis(acetilacetonate) (DIPBAT) appears to be a better precursor for TiO_2 anatase synthesis in sc-CO_2 than TTIP, since its stability facilitates the control of reaction and the precursor pumping. Water is not a suitable reactant for DIPBAT hydrolysis and an alcohol is needed for TiO_2 synthesis. Isopropyl alcohol appears to be as a better reactant than ethanol, since powder pollution is lower, and a subsequent wash step is avoided.

REFERENCES

[1] Alonso, E., Montequi, I., Lucas, S., Cocero, M.J., J. of Supercritical Fluids, *3*9, **2007**, p. 453
[2] Fujishima, A., Rao, T.N., Tryk, D.A., J. Photochem, Photobiol. C: Photochem. Rev. 1 (2000) 1.
[3] Malato, S., Blanco, J., Vidal, A., Richter, C., Appl. Catal. B: Environ. 37 (2002) 1.
[4] Kabra, K., Chaudhary, R., Sawhney, R.L., Ind. Eng. Chem. Res. 43 (2004) 7683.
[5] Reverchon, E., Adami, R., J. of Supercrit. Fluids, 37, **2006**, p. 1
[6] Reverchon, E., Caputo, G., Correra, S., Cesti, P., J. Supercrit. Fluids, 26, **2003**, p. 253
[7] Stallings, W.E., Lamb, H.H., Langmuir, 19, **2003** p. 2989
[8] Courtecuisse, V.G., Chhor, K., Bocquet, J.F., Pommier, C., Ind. Eng. Chem. Res. 35, **1996**, 2539
[9] Jung, M.W., Oh, H.J., Shul, Y., Bull. Korean Chem. Soc., 20, **1999**, p. 1394
[10] Burgos, M., Langlet, M., Thin Solid Films, 349, **1999**, p. 19
[11]Oja, I., Mere, A., Krunks, M., J. Mater. Sci., Mater. Electr., 15, **2004**, p. 341
[12] Djaoued, Y., Badeliscu, S., Robichaud, J., J. Sol-Gel Sci. Tech., 24, **2002**, p. 255
[13] Montequi, I., PhD Thesis, University of Vallladolid (Spain), September **2007**