EFFECT OF OPERATIONAL VARIABLES ON PARTICLE SYNTHESIS BY CHEMICAL DECOMPOSITION IN SUPERCRITICAL CO_2.

E. ALONSO*, I. MONTEQUI, M.J. COCERO

DPTO. INGENIERÍA QUÍMICA.-UNIVERSIDAD DE VALLADOLID. PRADO DE LA MAGDALENA S/N 47011 VALLADOLID (SPAIN)

ealonso@iq.uva.es Telf.+34 983 42 31 74 Fax.: +34 983 42 30 13

ABSTRACT

The effect of operational variables has been studied in the synthesis of TiO_2 particles by chemical decomposition of organometallic precursors in supercritical CO_2. Variables such as pressure, temperature, additives, residence time, and concentration of precursor have been varied working in a batch and in a semicontinuous way, using a reactor of 100 mL. Two different precursors have been used in these experiments: Diisopropoxytitanium bis(acetylacetonate) and Titanium Tetraisoproxyde.

Experimental results show that it is possible to obtain anatase TiO_2 particles stabilised in the range 50-130 nm without agglomeration and well crystallized, with temperatures lower than 300 ºC, P = 20,0 MPa and residence time below 1 minute.

INTRODUCTION

At the nanometer-length scale, material dimensions lead to quantum confinement effects that give rise to unique electronic and optical properties useful for a variety of new technologies including electronic, optical, medical, coatings, catalytic, memory and sensor applications. The attractive properties of supercritical fluids (densities similar to liquids and gaslike viscosities and diffusivities) have led to increase their use as reaction media in general, and naturally also in material chemistry.

The aim of this work is to present preliminary results in the field of material synthesis by chemical reaction using supercritical fluids (SPS process). This technology is being developed within the group of High Pressure Processes at the Chemical Engineering Department (University of Valladolid). For this purpose, TiO_2 anatase has been selected as a model product in order to starting up this new research topic in the group, and to study the effect of operational variables in the process. Results are discussed in terms of product characteristics, such as chemical purity, morphology, particle size and particle size distribution (PSD). Two different organometallic precursors have been used for the chemical syntesis of TiO_2 anatase, and experiments have been performed in order to study the effect of operational variables like: reaction media composition, temperature, pressure, initial concentration and residence time.

METHODS AND MATERIALS

Precursors: Diisopropoxytitanium bis(acetylacetonate) and Titanium Tetraisoproxyde, from FLUKA

Solvent: CO_2 C- 50 quality, supplied by Carburos Metálicos S.A.

Cosolvent: Ethanol from Panreac.

In all the experiments a mixture CO_2/Ethanol (80/20) has been used as solvent:

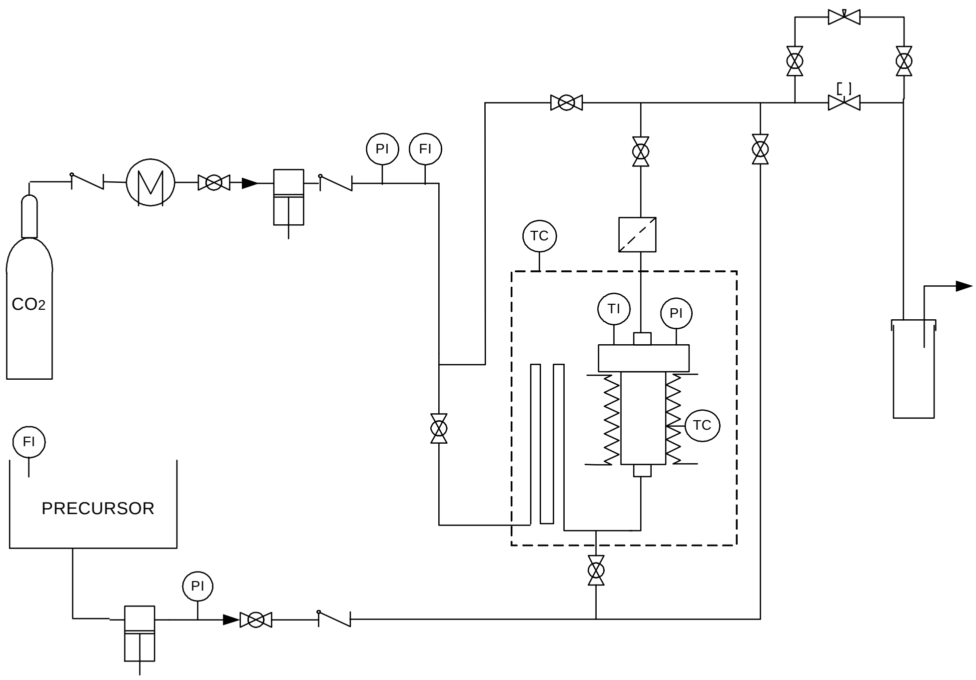

Figure 1. Flow diagram of experimental facility

Product characterisation has been performed using RX diffraction (Cu Kα radiation, Philips PW 1710), SEM (JEOL JSM -T300 Scanning Microscope), particle size distribution analysis by laser scattering (HORIBA LA900) and specific surface area (Brunauer-Emmett-Teller (BET), Omnisorp 100 CX from Coulter). Chemical purity of the product has been analysed by measuring the Carbon content in the solid product.

Experimental facility has a reactor with an internal volume of 100 mL, designed according to the AD-Merkblatt code for high pressure vessels, and the material used in the whole plant is SS 316L. The flow diagram of the plant is presented in figure 1.

At the beginning of the operation the desired amounts of precursor and cosolvent are put inside the reactor. CO_2 is pumped up to the desired pressure and all the system is heated up. Reaction takes place during two hours, and afterwards, the system is decompressed and cooled down. Solid product is recovered inside the reactor.

RESULTS AND DISCUSSION

The effect of operational parameters like pressure, temperature, and residence time has been studied in the decomposition of diisopropoxytitanium bis(acetylacetonate). In order to compare this precursor with the Titanium Tetraisoproxyde used by other authors [1], [2] [3], experiments have also carried out with this precursor.

Effect of pressure

Experiments using diisopropoxytitanium bis(acetylacetonate) as precursor have been carried out at two different pressures: 10,0 MPa y 20,0 MPa, and a temperature of 300 ºC. Product contamination is higher for the lowest pressure, with a carbon content of 7%, whereas this value diminishes to 1% for the pressure of 20,0 MPa, due to the decrease of by-product solubility. However, particles are smaller when pressure is decreased as it is shown in figure 2.

When pressure is increased, and therefore the density of the medium, the supersaturation degree is lower, reducing the nucleation rate and favouring the particle growth.

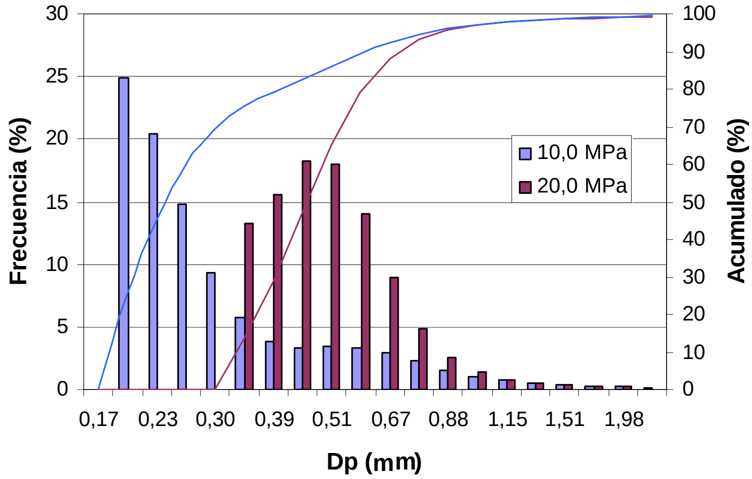

Figure 2. Effect of pressure on particle size distribution.

Effect of Temperature

Temperature has been varied in the range 200 – 300 ºC for the synthesis of TiO_2, and results have shown that in order to obtain TiO_2 anatase well crystallized, it is necessary to work above 250 ºC. The degree of product contamination decreases with temperature from 12% of carbon to 1,5%, and when temperature is increased obtained particles are smaller, although the effect of temperature is not very deep in that sense. These results show that operational temperature affects specially on chemical decomposition and product crystallinity.

Specific area is very high, around 350 m^2/g at 200 ºC, when crystallinity is not very good, decreasing to 150 m^2/g at 300 ºC.

Effect of residence time

In order to study the effect of residence time, CO_2, ethanol and precursor are continuously pumped to the reactor and particles are recovered within it at the end of the operation. In that sense, five different values have been tested (2 min, 1,5 min, 1 min, 0,5 min and 20 s), working at 20,0 MPa and 300 ºC.

In all cases, the obtained product was TiO_2 anatase, however for the shortest residence time cristallization is not very good. Product contamination is similar in all the experiments, showing that chemical decomposition is very fast, and residence time can be as short as 20 s. Particles are smaller (around 100 nm) and more homogeneous in size than those obtained in batch operation, as it is shown in figure 3.

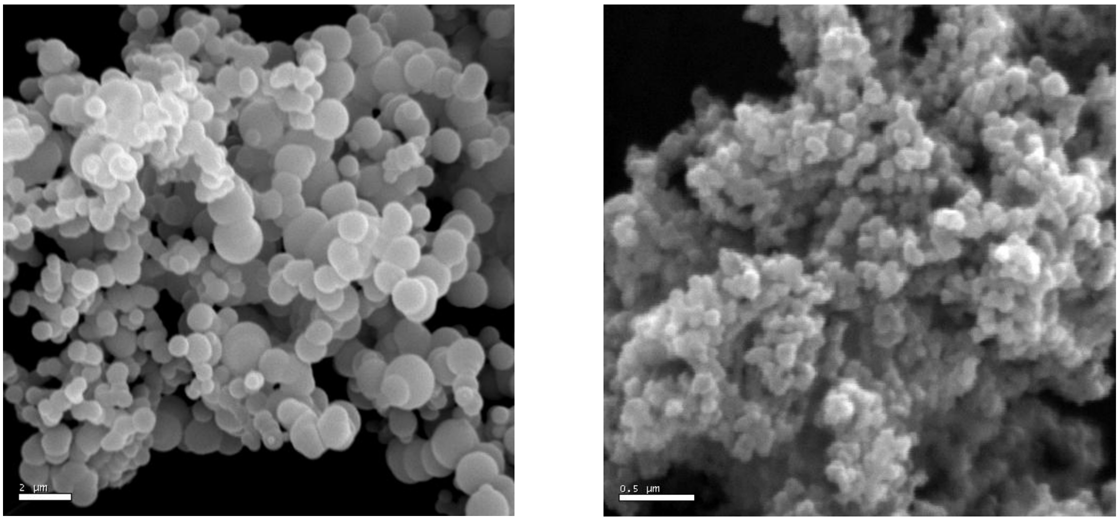

Figure 3. SEM of TiO_2 obtained in batch and in semicontinuous: residence time = 1 min. (P = 20,0 MPa, T = 300 ºC)

Effect of chemical nature of the precursor

Different works can be found in the literature related with the synthesis of TiO_2 in supercritical media [1], [2], [3]. In all of them titanium tetraisopropoxyde has been used as precursor. In this work experiments have also carried out with this organometallic precursor in order to compare the effect of operational variables. Results are similar for both compounds, but the main difference relies with particle size. Titanium tetraisopropoxyde produces bigger particle under the same operational conditions. This result can be explained form the fact that hydrolysis of this compound starts even at low temperatures, and nuclei of TiO_2 are formed during the heating up period. Subsequent decomposition of the precursor produces further material that precipitates on the surface of these nuclei leading to bigger particle formation.

CONCLUSIONS

This experimental work has allowed to start up a new research line in the group, dedicated to material synthesis in supercritical fluids by chemical decomposition of organometallic precursors. TiO_2 anatase has been obtained from diisopropoxytitanium bis(acetylacetonate) decomposition in a mixture CO_2/ethanol (80/20). The lower the pressure the smaller the particles due to the increase of supersaturation degree. Effect of temperature is related specially with cristallinity and by-product solubility, being necessary to operate above 250 ºC. Semicontinuous operation with residence time lower than 1 minute allows to obtain particles with a mean size of 100 nm.

REFERENCES

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