Chemical Engineering and Processing 74 (2013) 83–89

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Parameter studies of the synthesis of titanium dioxide nanoparticles: Effect on particle formation and size

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ARTICLE INFO

Article history:
Received 23 May 2013
Received in revised form 4 July 2013
Accepted 10 August 2013
Available online 21 August 2013

Keywords:
Process parameters
Nano particles
Anatase
Reaction mechanisms

ABSTRACT

The large scale synthesis of TiO_2 nanoparticles in the nonaqueous benzyl alcohol route was investigated with respect to the influence of process parameters, like temperature, pressure, reactor filling ratio, agitator speed and precursor concentration, on the induction time of particle formation and particle size. A coherence of the varied process parameters and the molecular reaction mechanism was found that supports the suggested mechanism of particle formation, representing an important step toward a controllable and predictable particle synthesis.

1. Introduction

Titanium dioxide is a semiconducting material with a broad range of applications, e.g. in pigments [1,2], cosmetics [3–6], solar cells [7–12], gas sensing systems [13–15] or for photocatalytics [16–21]. For several applications the availability of nanocrystalline TiO_2 is required, for example when transparent coatings are desired [22,23,21]. In the synthesis of metal oxide nanoparticles in general the control of particle size and morphology as well as the modification of the resulting product represents an essential aspect and can be achieved for instance with non aqueous methods like the benzyl alcohol route that has been established in the recent years [24–27]. In this process a metal organic precursor or a metal halide is mixed with the solvent benzyl alcohol, which acts as reactant as well, and heated in an autoclave system resulting in highly crystalline nanoparticles with well defined characteristics. Because of the relatively slow molecular reaction processes this type of synthesis is much more controllable regarding the particle characteristics like crystallinity, modification and size, compared to aqueous systems [25,27–29].

One more aspect for the industrial relevance of a synthesis process is the ability of a large scale preparation. Our group showed before that the large scale synthesis of ZrO_2 via the benzyl alcohol route can be performed without difficulty, resulting in more than 20 g solid in a 1 L reaction vessel [30], and lately we reported the scale up of the synthesis of Fe_3O_4 in benzyl alcohol as well as in triethylene glycol [26]. For a better understanding of a synthesis process, particularly in relation to a large scale implementation, the investigation of the influence of various parameters on the reaction progress and on the particle characteristics is inevitable, as demonstrated repeatedly in the literature for solvothermal and precipitation processes and the gas-phase production of nanoparticles [31–36].

Here we investigate the large scale synthesis of TiO_2 nanoparticles from the precursor titanium isopropoxide in benzyl alcohol in a sealed 1.5 L reaction vessel with a special focus on the influence of the process parameters on the reaction. The reaction type proceeds via an ether elimination including a ligand exchange of the isopropyl against the benzyl group and a condensation reaction resulting in the formation of dibenzyl ether among others [25,27]. Furthermore, we recently presented that besides the ether byproducts water is formed in large quantity, resulting in a spontaneous increase of pressure in the reaction system after an induction time of several hours. Within this time span the molecular reactions leading to nucleation take place, and nucleation occurs at the beginning of the pressure increase, whereas during the pressure surge particle growth can be observed [27].

In this study we utilize the pressure increase to determine the beginning of the nucleation and hence to define the induction time of particle formation. The used reactor was equipped with a manometer enabling the monitoring of the pressure during the whole reaction. By varying several process parameters like temperature, pressure or agitator speed we investigated their influence on the induction time and on the particle characteristics, thus getting more information concerning the reaction mechanism, with

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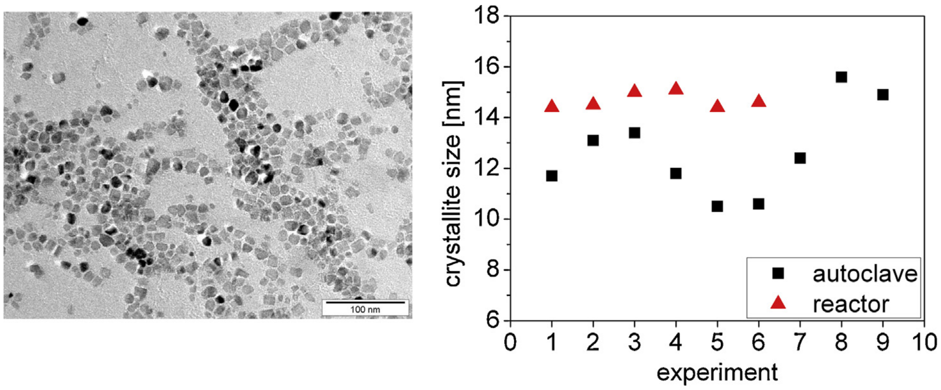
http://dx.doi.org/10.1016/j.cep.2013.08.001



(a)

(b)

Fig. 1. (a) TEM image of anatase nanoparticles from a typical synthesis and (b) reproducibility of the reaction compared for the two reaction vessels, expressed by means of the resulting primary particle sizes calculated from the (0 1 1) reflection from the PXRD patterns using Scherrer's equation.

a detailed understanding of the process leading toward a rational synthesis of nanoparticles with desired characteristics.

2. Experimental

2.1. Synthesis

Titanium isopropoxide (TIP, 97%, Sigma–Aldrich) and benzyl alcohol (BnOH, 99%, Sigma–Aldrich) were mixed in molar ratios from 1:50 to 1:15 and the solutions were transferred either into a 45 mL steel autoclave containing a Teflon inset (Parr Instruments) or into a stainless steel double walled reactor of 1.5 L capacity (Polyclave type 3/1, Büchi Glas Uster). The autoclave was filled with 20 mL of the mixture, closed and then put into a preheated oven (Memmert UNE 200). The reactor, equipped with a blade agitator, a temperature probe, a manometer and a sampling system, was charged with 1 L of the reaction mixture and heated via an external thermostat (Huber Tango HT). The temperature was varied from 175 to 225 °C. Further process parameters like pressure, filling ratio and agitator speed were also investigated. The resulting precipitates of TiO_2 were retrieved by centrifuging at 6500 × g for 10 min, washed twice with ethanol and dried under reduced pressure at room temperature for at least 24 h.

2.2. Characterization

Powder X-ray diffraction (PXRD) was performed to obtain the crystallite size (Cu Kα radiation; Empyrean Cu LEF HR goniometer; Empyrean series 2, PANalytical, PIXcel-3D detector; Si wafer; 20–90°, step size 0.05°). Transmission electron microscopy (TEM) images were received from a JEOL FEM-2100 instrument at 100 kV, therefore the washed particles were redispersed in a solution of 0.6 M oleic acid in chloroform and a drop of solution was applied on a Formvar-coated copper grid (Plano).

3. Results and discussion

3.1. General aspects

We managed to enlarge the reaction volume in the nonaqueous synthesis of titanium dioxide from 20 to 1000 mL, thereby receiving several grams of product instead of a few hundred milligrams from the initial small scale synthesis in lab autoclaves. In all experiments highly crystalline titanium dioxide in the modification of anatase in very high yields (of nearly 100% [27]) and comparable size was obtained. A representative transmission electron microscopy image is shown in Fig. 1(a). The primary particles in the sample show a relatively narrow distribution and agree in size with the calculated crystallite sizes from the XRD patterns by using Scherrer's equation for the (0 1 1) reflection[1].

Furthermore, the material of the vessel was Teflon for the small scale autoclaves and stainless steel for the large scale reactor. We found that there is no difference in the particle characteristics by varying the vessel size but in altering the vessel material because of differences in aging of the material as will be shown below. The walls of the Teflon cups get tainted with TiO_2 particles quickly and after several syntheses performed in the same cup there are visible encrustations which are not removable, rendering the particle growth hard to control for this system. In contrast, the synthesis in the stainless steel reactor results in well reproducible reactions with respect to reaction time and particle characteristics after a certain run-in period. Fig. 1(b) shows the variation in particle size in the Teflon lined autoclaves compared to the relatively good reproducibility in the reactor for a number of experiments performed under identical conditions. While the sizes of products obtained in the autoclave fluctuate from 10 to 16 nm, in the reactor the variation is substantially lower; the particle sizes stay constant at about 14.5 nm. For this reason and the possibility of sampling and monitoring the process at every point of the reaction, we utilized the stainless steel reactor for our investigations.

A scheme of the reactor is displayed in Fig. 2(a). The sampling system is composed of two outlet valves, one allowing the withdrawal of samples directly from the reaction mixture and one for samples from the gaseous phase above the reaction mixture. The development of temperature and pressure inside the system is recorded by temperature and pressure probes. Furthermore the reaction mixture is stirred with a blade agitator ensuring homogeneity in concentration and temperature throughout the entire reaction. Heating via an external thermostat leads to fast heat-up of the charge within 20 min; thereby there is no substantial difference in the heating rate for different filling ratios of the reactor as illustrated in Fig. 2(b). By contrast, the Teflon lined autoclaves offer no possibility of sampling, monitoring or homogenization and furthermore the mixture reaches the target temperature just after 4 h. For recording the development of the temperature we prepared an autoclave with a thermocouple sensor which was inserted through a hole in the lid.

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[1] The (0 1 1) reflection was used to calculate the particle size by Scherrer's equation because it is the first separated reflection at a relatively small angle, so the influence of microstrains on the signal broadening can be reduced.