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Disintegration process of surface stabilized sol–gel TiO_2 nanoparticles by population balances

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ABSTRACT

Titanium oxide (TiO_2) is one of the most useful oxide materials, because of its widespread applications in photocatalysis, solar energy conversion, sensors and optoelectronics. The control of particle size and monodispersity of TiO_2 nanoparticles is a challenging task in processing. The control and prediction of these dynamics are based on the process conditions and the nature of chemicals. In this work, we investigate the effect on the surface stabilization with different surfactants and temperature. The steric stabilization of the polymer and various functional groups of dispersants are also considered. Narrow distributed spherical titania particles in the size range 10–100 nm are produced in a sol–gel synthesis from titanium tetra-isopropoxide. The influence of various precursor concentrations and different surfactants on the particle size distribution is investigated. The population balance model for disintegration leads to a system of integro-partial differential equations which is numerically solved by the cell average technique. The experimental results are also compared with the simulation using two different disintegration kernels.

1. Introduction

Titanium oxide particle coating is a very important material due to its multifunctional application in solar cells, hydrophobic materials, photochromic and electrochromic devices, gas sensors, biosensors, corrosion protection, bactericides, optical devices, among others (Daoud and Xin, 2004; Toma et al., 2006). These numerous applications are due to the unique properties of titanium dioxide.

Many efforts have been made to develop appropriate processes to prepare titania nanoparticles for generating colloidal particles due to their technological importance. The most common procedures have been based on the hydrolysis of acidic solutions of titanium salts, gas-phase oxidation reactions of $TiCl_4$ and hydrolysis reactions of titanium alkoxides (Matijevic et al., 1977), also controlled hydrolysis of titanium tetraethoxide in dilute ethanolic solutions (Barringer and Bowen, 1982). Another approach for preparing micron size particles is by dispersion polymerization and it has been shown to produce particles with a very narrow size distribution (Barreit, 1975). A polymeric steric stabilizer in combination with a quaternary ammonium salt which the authors claimed acts as an electrostatic co-stabilizer (Almog et al., 1982). Production of titania particles from an alcoholic solution of titanium tetra alkoxide using an amine-containing additive and water to hydrolyze titanium alkoxide solution is another alternative method (Olson, 1989) or by chemical vapor deposition, where they can form nanoparticles by thermal decomposition (Dag et al., 1999; Jiang et al., 2003).

One of the fundamental issues that need to be addressed in modeling macroscopic mechanical behavior of nano-structured materials based on molecular structure is the large difference in length scales. On the opposite end of the length scale, the spectrum of computational chemistry and solid mechanics consists of highly developed and reliable modeling methods. Computational chemistry models predict molecular properties based on known quantum interactions, while computational solid mechanics models predict the macroscopic mechanical behavior of materials idealized as continuous media based on known bulk material properties. However, a corresponding model does not exist in the intermediate length scale range. If a hierarchical approach is used to model the macroscopic behavior of nano-structured materials, then a methodology must be developed to link the molecular structure and macroscopic properties.

Many properties of solid particles are not only a function of the material's bulk properties but also depend on the particle size distribution (PSD). These property changes arise from the increasing influence of surface properties in comparison to volumetric bulk properties as the particle size decreases. Especially nanoscaled particles show altered properties and have therefore widespread applications like pigments, pharmaceuticals, cosmetics, ceramics,

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catalysts and filling materials. Since the desired product properties might vary with particle size as well as with the degree of aggregation or the aggregate structure, controlling of the PSD and the aggregate structure is a key criterion for product quality. New and improved products can then be designed by adjusting and optimizing the PSD and the particle structure. Precipitation is a promising method for the economic production of commercial quantities of nanoparticles as it is fast and operable at an ambient temperature. However, process control due to the rapidity of the involved sub-processes and especially to prevent aggregation through stabilization represents a challenge.

To control these sub-processes, balance models are used in particle technology. Population balances for disintegration appear in a wide range of applications including nano-technology, granulation, crystallization, atmospheric science, physics and pharmaceutical industries. There are several numerical methods such as Monte Carlo, finite element, finite volume, sectional approaches to solve the disintegration population balance equations (DPBEs) (Kruis et al., 2000; Israelachvili, 1985). We now briefly outline the contents of the paper. First we give the experimental methodology for synthesizing surfactant based titanium dioxide nanoparticles. Then the population balance model for disintegration processes followed by the cell average scheme is discussed. Later the comparison between the experimental and the modeling results are shown using two well-known kernels. Finally we give some conclusions.

1.1. Experimental methodology

Titanium dioxide nanoparticles have been prepared in the laboratory by sol–gel processing in solution starting with titanium tetra isopropoxide (TTIP) ($Ti(OC_3H_7)_4$) 97% from Alfa Aesar is used as a precursor, nitric acid (HNO_3) as stabilizer and different surfactants such as polyethleneglycol 600 (PEG) ($H(OCH_2CH_2)_nOH$), ethylene glycol (EG) ($HOCH_2CH_2OH$) 100% from Merck and sodium chloride (NaCl) 10% from Sigma-Aldrich. For generating titanium dioxide nanoparticles, the procedure is as follows. A specified amount of 0.1 M HNO_3 (90 ml, p.a.) is placed into the batch reactor. Then 50 ml of surfactant (PEG, EG and NaCl with concentration of 0.1 M) in separate experiments were measured and added to the HNO_3 in the beaker. The organic precursor titanium tetra isopropoxide TTIP (9.7 ml) is added to the heated solution under stirrer operated at 500 revolutions per minute (500 rpm). Precipitation is observed to be occurring immediately due to the presence of dilute nitric acid in the reaction mixture. Temperature is maintained at 50 °C for the rest of the redispersion reaction, accordingly optimal reaction conditions for the titanium dioxide nanoparticles synthesis. Precipitation reaction started instantaneously and the solution was conditioned by stirring continuously for a period of 24 h at 50 °C.

1.2. Characterization of TiO_2 nanoparticles

Particle sizes smaller than 1 μm have been measured via dynamic light scattering (Zetasizer, Malvern Instruments) using a He–Ne laser as light source ($\lambda = 633$ nm). All size measurements have been performed at a scattering angle of 90° and 25°. For particle size distributions in the micrometer size range, a laser diffraction method is used (Mastersizer 2000, Malvern Instruments, He–Ne laser as red light source, $\lambda = 633$ nm, solid state laser as blue light source, $\lambda = 466$ nm) (Nikolov et al., 2003). Samples withdrawn are mildly stirred and dispersed at the same concentration and pH conditions of nitric acid inside a small volume sample dispersion unit HYDRO SM of Mastersizer 2000 before being measured. For evaluating particle stability, zeta-potential measurements based on electrophoretical mobility have been carried out with a Malvern Zetasizer instrument.

2. Population balance model

In a batch system, i.e., a closed system to which no particles are added or removed, the disintegration process can be defined as the reduction of bigger particles to smaller particles. The temporal change of particle number density, $f(t,x) \geq 0$ of particles of volume $x \in \mathbb{R}_{>0}$ at time $t \in \mathbb{R}_{>0}$ in a spatially homogeneous physical system undergoing disintegration process is described by the following well known population balance equation (Ziff, 1991)

$$\frac{\partial f(t,x)}{\partial t} = \int_x^\infty b(t,x,y)S(t,y)f(t,y)\,dy - S(t,x)f(t,x), \tag{1}$$

with initial data

$$f(0,x) = f_{\text{in}}(x) \geq 0, \quad x \in]0,\infty[. \tag{2}$$

The first and second terms on the right hand side of Eq. (1) are called the birth and the death terms, respectively. The disintegration function $b(t,x,y)$ for a given $y > 0$ gives the size distribution of particle sizes $x \in]0,y[$ resulting from the disintegration of a particle of size y. Conservation of mass requires that the total mass of the particles created by the disintegration is again y, i.e.,

$$\int_0^y xb(t,x,y)\,dx = y \tag{3}$$

holds. The selection function $S(t,y)$ describes the rate at which particles of size y are selected to be stressed and to break. Solutions to the DPBE must satisfy the total mass conservation, i.e.,

$$\int_0^\infty xf(t,x)\,dx = \int_0^\infty xf_{\text{in}}(x)\,dx, \quad t \geq 0. \tag{4}$$

For a particular value of $b(t,x,y) = 2/y$, the general DPBE turns into the binary DPBE, that means a particle breaks into two at a time. In the population balance equation (1) the volume variable x ranges from 0 to ∞. In order to apply a numerical scheme for the solution of the equation a first step is to fix a finite computational domain. In this work we consider the following truncated equation with truncated solution $f_{\text{truncated}} = n$

$$\frac{\partial n(t,x)}{\partial t} = \int_x^{x_{\max}} b(t,x,y)S(t,y)n(t,y)\,dy - S(t,x)n(t,x), \tag{5}$$

with initial data

$$n(0,x) = f_{\text{in}}(x), \quad x \in \Omega :=]0,x_{\max}], \ x_{\max} < \infty. \tag{6}$$

The truncated equation has been discussed in the literature by various authors. For a detailed discussion on it readers are referred to Ball and Carr (1990). There are many numerical techniques to solve the problem. However, in this work we use the well-known cell average technique. In the following section we discuss briefly the mathematical formulation of the general DPBE by using the cell average scheme.

3. The cell average technique

Recently a sectional method known as the cell average technique (CAT) has been developed for solving a general one-dimensional population balance equation (Kumar et al., 2006). It has been shown numerically that the scheme is very accurate and efficient. Moreover, reasonably good results for complete number density distribution can be obtained using a very coarse grids. The formulation relies on approximating the number density using point masses concentrated at representative points in the cell.