Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–6

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Monodispersibility and size control in the preparation of spherical titania particles by thermal hydrolysis of $TiCl_4$ in various solvents

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ARTICLE INFO

Article history:
Received 5 October 2015
Revised 6 September 2016
Accepted 9 September 2016
Available online xxx

Keywords:
Dispersant
Monodispersed titania
Photocatalyst
Titania
Thermal hydrolysis
Size control

ABSTRACT

Spherical anatase TiO_2 particles were successfully synthesized by the thermal hydrolysis of $TiCl_4$ in various solvents. In the case of n-propanol, isopropanol, and acetone with an RH ratio of 3, spherical titania particles were produced. In contrast, spherical TiO_2 particles did not form in methanol and ethanol because of their high dielectric constants. In this study, different oscillators (an oven, and isothermal and ultrasonic oscillators) were used to prepare titania prior to studying the morphology and particle size. The spherical TiO_2 particles prepared using the ultrasonic oscillator were much smaller than those obtained using the other heating methods, because of the lower temperature gradient in the solution; however, a narrower size distribution of particles was observed in the TiO_2 prepared in an oven. The presence of acetylacetone as a dispersing agent in the starting solutions significantly reduced the particle size. The optimum concentration of acetylacetone of 0.8 mg/cm^3 resulted in more uniform TiO_2 spheres with an average particle size of 1.4 µm.

1. Introduction

Research on the preparation methods and the properties of titanium dioxide has received significant attention because if it is in many practical applications. Over the past few years, low-temperature sintering of ceramic devices has gained much attention in the electronic device industry with a rapid development of technology. Sinterability can be improved by controlling the size distribution, particle size, and morphology of the materials [1–3]. TiO_2 is one of the most extensively-studied photocatalysts because of its outstanding functional properties. It is a wide band-gap material with an energy gap of 3.2 eV (anatase phase) so that it only absorbs light with wavelengths lower than 400 nm. Therefore, it is transparent to visible light and also displays excellent optical transmission when used as a thin film or coating material. Additionally, TiO_2 accounts for 70% of the total production volume of pigments worldwide [4]. TiO_2 can be used in a wide range of applications, not only in consumer products (e.g., paints, plastics, papers, medicines), but also for a large number of electronic device applications, such as gas sensors, electrochromic displays, antireflective (AR) coatings, memory devices, and so on [5–11]. In practice, there are several methods to prepare spherical un-agglomerated TiO_2 with controlled particle sizes, a narrow size distribution and nice dispersibility, such as the sol-gel process, emulsion, pyrolysis, using electrolytes, aqueous-based methods (i.e., using metal salts as a precursor material) [1,2,12–26]. Park et al. [1,2] and Jean and Ring [27,28] reported on a method to prepare monodispersed TiO_2 particles by adding hydroxypropyl cellulose (HPC) as a steric dispersant in order to reduce the size of particles to the submicrometer range and improve the dispersibility of particles suspended in the surrounding medium. They also discussed the advantages of using a dispersant to stabilize the system. Moon et al. [12,13] demonstrated that microwave treatment produced excellent spherical monodispersed ZrO_2 particles with a narrow size distribution. These are preferable for producing advanced ceramics.

One of the authors in this group reported on a preparation method for spherical TiO_2 particles through the thermal hydrolysis of $TiCl_4$ in n-propanol and acetone solutions with the presence of HPC [15,16]. In this present work, we aim to extend our previous studies for the preparation of monodispersed, spherical titania particles by thermal hydrolysis of $TiCl_4$ in various solvents with the presence of acetylacetone (AcAc) as a steric dispersant. The effects of the type of solvent, heating methods, and steric dispersant on the formation, morphology, and size distribution of TiO_2 particles were also examined.

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http://dx.doi.org/10.1016/j.jtice.2016.09.010

2. Experimental procedure

2.1. Materials

The titanium tetrachloride, ethanol, methanol were obtained from Showa Chemicals. N-propanol, iso-propanol, acetone, and NH_4OH were sourced from the Tedia Company. The hydroxypropyl cellulose (HPC, viscosity = 150–400 cps, 2% in water) came from Kasei Kogyo Co. and the Acetylacetone (AcAc, 2, 4–pentanedione 99%) was obtained from Acros Organics.

2.2. Synthesis of monodispersed TiO_2

The procedure for preparing titania powder is as follows. 1 M titanium tetrachloride was used as a starting precursor which was dissolved in distilled water. The mixture was first aged at 10 °C for 6 h under magnetic stirring. The solvent was added into the mixed solution with the solvent/aqueous medium volume ratio (RH ratio) of 3. AcAc was then added into the solution to serve as a steric hindrance for precipitation. The concentration of AcAc was varied from 0.1–1.0 mg/cm^3 in order to study the effect of the steric dispersant and study the optimal amount of dispersant to be added. The final concentration of titanium dioxide in the mixed solution was 0.10 mol/l. After aging for 6 h, the solutions were heated and aged at 70 °C in an oven or subjected to different types of oscillation (e.g., isothermal oscillator, ultrasonic oscillator) for 1 h to induce precipitation. The afore-mentioned procedure was repeated for titania powders in different solvents (e.g., n-propanol, isopropanol, acetone, methanol, ethanol). The effects of different types of oscillation on the morphology and particle size of the titania were also investigated. After precipitation occurred, the solution was neutralized with a 3 N NH_4OH solution to remove the chlorine ions, then re-checked with chloride test stripes (QUANTOFIX®). The precipitate was separated by centrifuging and washing in distilled water. The obtained precipitate was dried in an oven at 60 °C for 24 h.

2.3. Characterization

All samples were dried in air at a temperature of 80 °C for 1 h before further characterization. XRD patterns of the samples were obtained using a Siemens D500 powder diffractometer using Cu Kα radiation (1.5405 Å) at a voltage and current of 40 kV and 30 mA, respectively. The range $2\theta = 20°–80°$ at a rate of 0.05°/min was used to identify the crystalline structure.

The morphology and the particle size of samples were observed by TEM on a JEM-1200 EX II electron microscope operating at 160 kV, and SEM on a Hitachi S-800 operated at 200 kV. The images were recorded at magnifications ranging from 3000× to 20,000×.

The particle size and size distribution of the samples were measured by dynamic light scattering (DLS) on a Zetasizer 3000.

3. Results and discussion

3.1. Characteristics of TiO_2 powder prepared with different solvents

The morphologies of TiO_2 particles prepared with different solvents in an oven are shown in Fig. 1. The TiO_2 prepared by n-propanol was comprised of uniform spherical particles ranging in size from 0.8 to 1.7 µm. The TiO_2 particles prepared by isopropanol were 0.5–2.0 µm, but the size and spatial distributions of these particles were not quite uniform. The size of spherical TiO_2 particles prepared with acetone was about 1.0–3.5 µm, and had a broad size distribution. When the TiO_2 powder was prepared using methanol and ethanol, the particles were shapeless aggregate ranging between 1 and 70 µm in size. In general, the use of different solvents and the dielectric constants of the solvents (see Table 1) for the preparation of TiO_2 powder played an important role in the precipitation behavior. The greater the value of the dielectric constant of a solvent, the better it solvates and thus the smaller the interaction between those ions of opposite charge dissolved in it [30]. This is the reason why the spherical TiO_2 particles prepared using n-propanol were more uniform than those prepared with iso-propanal. It was easy to separate the TiO_2 prepared with n-propanol from the solution by heating in an oven. Additionally, the proportion of solvent to water in the aqueous medium (RH ratio) also affects the dielectric constant of the mixed solution. Based on the previous studies [15,16], an RH ratio of 3 would yield the most spherical and the most uniform TiO_2 particles. The RH ratio of all mixed aqueous solutions in this study was thus manipulated to be 3. According to Table 1, the polar protic solvents (e.g., methanol, ethanol) theoretically have greater values of dielectric constants than the others. As a result, when using methanol or ethanol as the solvent, spherical titania was found to be difficult to precipitate out and form.

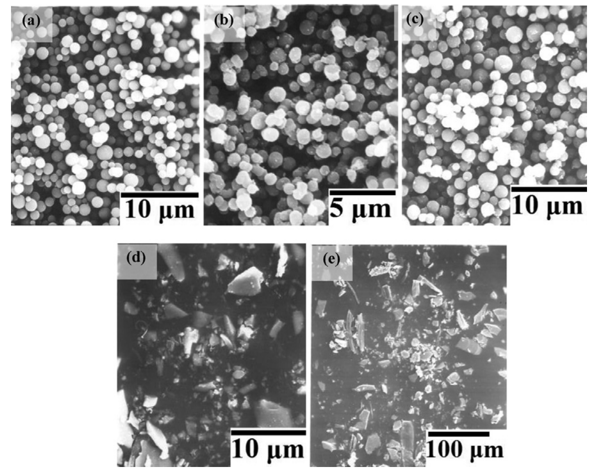

Fig. 1. SEM images of TiO_2 particles prepared using an aqueous solution without a dispersing agent: (a) n-propanol, (b) isopropanol, (c) acetone, (d) methanol and (e) ethanol in an oven.

Table 1
The dielectric constants of solvents at 20 °C [29].

Solvent	Dielectric constant
Water	80.2
Methanol	32.8
Ethanol	24.6
n-propanol	19.5
Isopropanol	20.1
Acetone	20.4

3.2. Effect of oscillators on the morphology of TiO_2

Spherical-shaped TiO_2 particles with a narrow size distribution were obtained using n-propanol as a solvent. Consequently, the other samples were thus prepared by precipitation in n-propanol but using different oscillators in order to study the effect of different heating methods on the morphology of the titania. Fig. 2a–c show SEM images of spherical TiO_2 particles prepared in an isothermal oscillator, ultrasonic oscillators and oven, respectively. The particle sizes of TiO_2 obtained by using an oven and isothermal oscillator varied in the range of 0.8–1.7 µm and 0.68–1.76 µm, respectively. In cases using an ultrasonic oscillator, the particle size of titania was about 0.26–1.73 µm. Although using both isothermal

Please cite this article as: B. Moongraksathum et al., Monodispersibility and size control in the preparation of spherical titania particles by thermal hydrolysis of $TiCl_4$ in various solvents, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.09.010