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Microwave-hydrothermal process for the synthesis of rutile

Sara Baldassari [b], Sridhar Komarneni [a,*], Emilia Mariani [b], Carla Villa [b]

[a] *Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Di.Sci.Far., Viale Benedetto XV, 3, University of Genoa, 16132 Genoa, Italy*

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Abstract

The synthesis of pure rutile titanium dioxide is not an easy achievement, as the crystallization process generally leads to mixtures of two or even three phases; moreover the synthetic processes normally used by industry require harsh reaction conditions. We carried out the synthesis of titanium dioxide from an aqueous titanium tetrachloride solution under microwave irradiation in the reaction time range of 5–120 min. We mostly obtained mixtures of rutile and anatase, but obtained single-phase rutile after a 2-h treatment at 160 °C; transmission electron micrographs revealed well-dispersed spherical nanoparticles. We also investigated the effects of dilution and addition of a dispersant (polyvinylpyrrolidone) on phase crystallization and particle shape.

Keywords: A. Ceramics; A. Nanostructures; A. Oxides; B. Chemical synthesis; C. X-ray diffraction

1. Introduction

Titanium dioxide has been known to exist in three main polymorphic phases: rutile, anatase and brookite. All of them have the same fundamental structural units of octahedra, but their arrangements are different [1]. Anatase and brookite are metastable phases and their exothermic and irreversible conversion to rutile at high temperatures has been widely investigated. Rutile and anatase are the most commonly synthesized phases and their thermodynamic characteristics and physical properties affect their technological applications: rutile is the main white pigment in paints and cosmetic products, being basically inert, non-toxic and possessing high light scattering and refractive index; anatase is generally

* Corresponding author. Tel.: +1 814 865 1542; fax: +1 814 865 2326.
E-mail address: komarneni@psu.edu (S. Komarneni).

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preferred as a heterogeneous catalyst, as a photocatalyst, in solar cells for the production of hydrogen and electric energy, as an oxygen sensor, as a corrosion-protective and optical coating, in ceramics, and in electronic devices such as varistors [2]. However, a recent study has shown that a mixture of both phases exhibits higher photoactivity as well as effective degradation in comparison with pure anatase or rutile catalysts [3].

Titanium dioxide is industrially produced by the sulphate or chloride processes. In the former, ilmenite ($FeTiO_3$) is hydrolyzed with sulphuric acid at >95 °C and the TiO_2 powder is obtained after calcination at >800 °C followed by pulverization. Pulverization generally leads to impure phase. In the chloride process, natural rutile treated with hydrochloric acid gas is converted into titanium tetrachloride; titania is produced by treating the aforementioned $TiCl_4$ with oxygen at >1000 °C. Compared to these two techniques, the hydrothermal method has proved to be a mild and effective alternative: the relatively lower temperatures (usually <250 °C) favor a decrease in agglomeration of particles [1], and changes in reaction conditions (temperature, pH, reactant concentration, presence of mineralizers) can lead to products with specific characteristics. Different processes have been used for the synthesis of titanium dioxide: sol–gel hydrolysis of titanium alkoxides [4,5], hydrolysis of inorganic salts (titanium sulphate [6], titanium trichloride [7] and more often titanium tetrachloride [1,6,8–12]), and hydrothermal processing of amorphous TiO_2 [13]. The hydrolysis of titanium (IV) compounds is usually carried out by conventional hydrothermal heating [8–12]. Kim et al. [9] reported the synthesis of rutile below 65 °C after treatment for 6 h. Rutile seed crystals were used [10] by Li et al., to crystallize nanocrystalline rutile below 95 °C. Concentrated HCl solutions of $TiCl_4$ were used [11] by Pottier et al., to synthesize nanometric particles of brookite and rutile. Wang et al. [12] used mixtures of hydrochloric acid and alcohol aqueous solutions to obtain rutile in the temperature range of 40–90 °C. Thus, the crystallization of rutile in acidic media involved long times [9], seed crystals [10], concentrated HCl solutions [11], alcohol [12], etc. and mineralizers such as SnO_2 [14], NH_4Cl or NaCl [1] have sometimes been added to reduce the particle size, though this could cause contamination of titania crystals. The objective of the present study is to avoid additives in the crystallization of rutile and perhaps speed up the process by microwave irradiation (see below).

The hydrothermal process is suitable for combination with microwave irradiation, i.e. microwave-hydrothermal process [15,16], which improves kinetics of crystallization. In a previous paper, an extensive study of the processing of titanium dioxide under microwave-hydrothermal conditions has been performed [17]; subsequently this technique was applied to the preparation of anatase from TiO_2 colloid [18]. We discuss here the effects of reaction time, temperature, precursor concentration and presence of dispersants on the synthesis of rutile from aqueous $TiCl_4$ under M-H conditions.

2. Materials and methods

Titanium (IV) chloride ($TiCl_4$) was supplied by Alfa Aesar Company, USA, and was used after dilution with 2 M hydrochloric acid. The as-received titanium tetrachloride was added slowly to cold 2 M hydrochloric acid to prepare a 0.5 M $TiCl_4$ solution. When $TiCl_4$ is diluted, partial hydrolysis occurs, so the solution is hereafter referred to as $TiOCl_2$ solution. Ten milliliters of the 0.5 M solution were transferred to the Teflon container of the double-walled vessel of a microwave system (MARS5) made by CEM Corporation. The double-walled vessel consists of an inner Teflon container and an outer shell of high strength polyetherimide. The system operates at a frequency of 2.45 GHz, the same frequency used