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Particle production and anatase formation in amorphous particles at in-droplet hydrolysis of titanium alkoxide

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Abstract

Anatase crystallization in amorphous particles was investigated during droplet-to-particle synthesis of titania. Ethanolic solution of carboxylic acid-modified titanium tetrabutoxide precursor, including water, was dispersed and conveyed to a tube flow reactor at 350–600°C. The formed submicron-sized particles were characterized by aerosol measurements, X-ray diffraction, and electron microscopy. An aerosol number mode was observed at particle diameter of 250 nm representing the particles formed of droplet drying. Additional ultrafine particles were formed in air atmosphere at 450°C and in nitrogen at 600°C from decomposition and outgassing of precursor species and a subsequent particle formation. An anatase crystalline phase was observed in the particles produced at 500°C in nitrogen. The location of anatase formation was investigated by TEM from thinned sections of the particles. The crystals were observed near the surfaces and indicating columnar growth.

Keywords: A. Nanostructures; A. Oxides; B. Crystal growth; C. Electron microscopy; D. Crystal structure

1. Introduction

A droplet-to-particle synthesis of titanium oxide (Ti-O) powders starting from titanium alkoxide has been studied widely. The studies are based on either hydrolysis or pyrolysis of precursor droplets. In the hydrolysis studies, typically, water vapor has been used to hydrolyze the alkoxide droplets subsequent to dispersion [1–4], whereas in the in-droplet

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hydrolysis the hydrolysis water was included in the dispersed precursor solution [5,6]. The pyrolysis studies are based on thermolysis of the precursor droplets without adding water [7–9], but water is formed in the system as a product from oxidation of organic species leading to a possible hydrolysis. A thorough review of liquid-to-solid conversion processes has been published by Kodas and Hampden-Smith [10]. The produced powders typically consist of amorphous titanium oxide including residual hydroxy and alkoxy groups ($TiO_x(OH)_y(OC_nH_{n+1})_z$). Crystalline titania ($TiO_2$) is reported as a product (without thermal postannealing) only in a few studies [7,8]. However, the ability to form titania in the reactor increases the novelity of the droplet-to-particle method because postannealing is avoided.

Titania crystallization in inorganic syntheses typically follows a path: (1) amorphous solid or molecular precursor, (2) crystallization of the anatase polymorph of TiO_2 and grain growth, and (3) transformation to the thermodynamically stable rutile polymorph with consequent and subsequent grain growth. Grain growth occurs at the temperature range required for the phase changes. The amorphous-to-anatase transformation of sol-gel derived TiO_2 occurs at around 400−450°C to which, for example, dopant cations only have only a minor effect [11–13]. The formation and presence of anatase phase is standardly observed by X-ray diffraction (XRD) [14–16]. Also, spectroscopic methods as well as thermal analyses have been commonly utilized to investigate the anatase formation [17–19]. Microstructural analysis by electron microscopy has mainly included the detection of the anatase phase and crystallite size in the produced powders [11,20]. Only a few studies have concentrated on a high resolution imaging of the anatase lattice. Yin et al. [21] presented a crystallization mode based on TEM work that the contact region between neighboring particles are the likely nucleation sites for the anatase phase. Yanagisawa et al. [22] studied a formation mechanism of fine anatase crystals from amorphous titania. Commonly, the microscopy from thinned sections of material can be a powerful tool to investigate particle microstructure evolution as done by Che et al. for palladium particles [23].

The objective of this study was to further investigate the production of titania particles via the in-droplet hydrolysis method as well as the anatase phase crystallization in amorphous particles. In our earlier studies we have demonstrated that the in-droplet hydrolysis is a viable method for production of solid Ti-O particles [5]. The novelty of the method, however, could be increased with the titania crystallization in situ, in the reactor. On the other hand, we have also observed that additional ultrafine particles may be formed at higher temperatures [8]. In this work we investigated the suitable reactor conditions for particle formation. The location of the anatase crystal formation in the particles was investigated from thinned particle sections by TEM. The motivation is to develop methods for producing TiO_2 via aerosol routes with well controlled crystal phase and size.

2. Experimental

2.1. Solution preparation

Titanium (IV) n-butoxide (TTNB, Strem Chemicals Inc., 98+%) precursor was dissolved in a fraction of ethyl alcohol (50% of total ethanol amount, Alko, 99.5%) with