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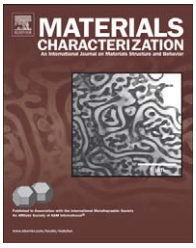

Effects of ultrasonic processing on phase transition of flame-synthesized anatase TiO_2 nanoparticles

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ABSTRACT

The effect of ultrasonic processing on the phase transformation of flame-synthesized anatase TiO_2 nanoparticles heated to the rutile phase was investigated. TiO_2 nanoparticles of various sizes were prepared using a coflow hydrogen diffusion flame and an ultrasonic processor. Smaller nanoparticles having a similar portion of anatase phase using the ultrasonic processor were produced. On the basis of scanning electron microscopy images and specific surface areas, we observed that smaller nanoparticles tended to be sintered more easily than larger nanoparticles. From X-ray diffraction analysis, we demonstrated that when heated, TiO_2 nanoparticles synthesized using the ultrasonic processor at 60% of its maximum amplitude were transformed from the anatase phase to the rutile phase more easily than those formed without or with the ultrasonic processor operated at 20% of its maximum amplitude.

1. Introduction

TiO_2 nanoparticles are a well-known photocatalyst. Photocatalytic activity depends on the nature of the reactants and on the overall process at the catalyst surface resulting from competition of various elementary phenomena. TiO_2 nanoparticles are crystallized into two main polymorphic forms: anatase and rutile. Anatase TiO_2 nanoparticles are more active as a photocatalyst than rutile nanoparticles [1]. The third crystal phase, and a less common form of titanium dioxide, is brookite. The rutile phase is the stable phase at high temperature, but anatase and brookite are common in fine-grained natural and synthetic samples [2].

In 1972, Formenti et al. [3] synthesized several metal oxide particles with diameters in the range from 10 to 200 nm by carrying the vapor of metal chloride in a hydrogen–oxygen flame. Yang et al. [4] used three different burners to obtain a wide range of flame processing conditions. Mixtures of anatase and rutile-phased titania nanoparticles were obtained at low reaction temperatures between 900 and 1430 °C. Spherical particles of 100% anatase titania were obtained at high temperatures between 1500 and 1570 °C. Yeh et al. [5] also reported that the anatase fraction of titania particles created in flames increased with an increase of oxygen concentration in the oxidizer.

Anatase TiO_2 nanoparticles can be transformed to rutile when heated. It is well known that the onset temperature of the phase transition is influenced by cation impurities, anion impurities, grain size, reaction atmosphere, synthesis condition, and other factors [6]. The onset temperatures for the transformation of prepared anatase particles into rutile particles using heat treatment range from 650 to 800 °C depending on the compact structure of the pellet [7] and the contents of the silica additive [6]. Xia et al. [8] also showed the same transformation of anatase particles into rutile particles by heat treatment of titania nanoparticles prepared by vapor-phase hydrolysis.

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Table 1 – Experimental conditions and tube inner diameters of burner.

Gas	Ar	H_2	O_2	Air	TTIP evaporation temperature	Ultrasonic processor (VCX-750)
Function	TTIP carrier gas	Fuel	Oxidizer		80 °C	To reduce particle size
Flow rates (liters per minute)	0.3	2.0	3.7	30.0		0, 20, 60% of its max. amplitude
Tube inner diameter (mm)	3.9	16.6	70.0			

In 2000, Zhang and Banfield [9] studied the kinetics of phase transformation of nanocrystalline anatase samples using X-ray diffraction at temperatures ranging from 600 to 1150 °C. They reported that the activation energy of nucleation of rutile particles were size-dependent. Also, the effects of aging on the crystalline phases, crystalline sizes, and sintering properties of TiO_2 gels were investigated by Hsiang and Lin [10]. They showed that the hydroxyl ions existing in the anatase lattice decreased with increasing aging time, and so the oxygen vacancy concentration produced after calcination decreased.

The particle size effect on the phase transformation of nanocrystalline TiO_2 was reported in [11]. The TiO_2 powders were obtained by the solvothermal method. Kim et al. [11] reported that the smaller-sized powders tended to be transformed to rutile more easily than the larger-sized powders. Zhu et al. [12] also reported the size effect on the phase transformation sequence of heat-treated TiO_2 nanocrystals prepared by the sol-gel method. The effects of grain size and phase content on the transition were studied for TiO_2 nanocrystals annealed in air for 1 h for a temperature range of 200 to 650 °C. Their results indicated that the phase transition sequence depends on the relative grain size between anatase and brookite.

We investigated the effect of ultrasonic processing on the phase transition of TiO_2 nanoparticles from anatase to rutile when heated. The TiO_2 nanoparticles were synthesized using a coflow hydrogen diffusion flame. An ultrasonic processor was used to change the diameters of the formed TiO_2 nanoparticles to those having a similar anatase fraction.

2. Experimental

The experimental setup consisted of several gases and mass flow controllers with readout units (Kofloc Co. Ltd.), a burner and a flame used as a hydrolysis reactor, a horizontal traverse with a controller for particle sampling, and a two-dimensional traverse system for moving the burner and the precursor evaporator. The burner used in this study consisted of three concentric tubes of 3.87, 16.57, and 70.0 mm inner diameters. The argon gas used as a carrier gas for the precursor was delivered through the central tube via the evaporator of the TTIP precursor ($Ti[OCH(CH_3)_2]_4$, titanium tetraisopropoxide,

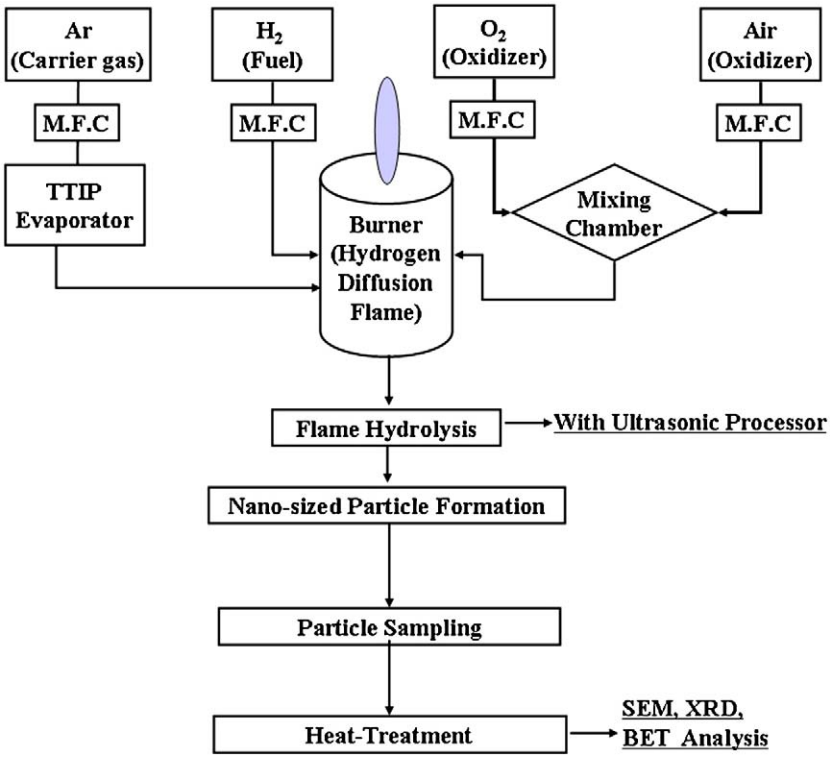

Fig. 1 – Schematic diagrams of experimental procedure.