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The effect of process parameters on the Liquid Flame Spray generated titania nanoparticles

Mikko Aromaa *, Helmi Keskinen, Jyrki M. Mäkelä

Aerosol Physics Laboratory, Institute of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland

Abstract

Nanoparticles have become important in many applications. It is essential to be able to control the particle size because the properties of nanoparticles change dramatically with particle size.

An efficient way to generate nanoparticles is via aerosol processes. In this study we used Liquid Flame Spray consisting of liquid precursor droplets sprayed into a high-speed hydrogen/oxygen flame where they evaporate, vapours react and nucleate to form titania nanoparticles. Using flame methods, also dopants and sensitizers can easily be introduced in order to, e.g. improve the photocatalytic activity of the nanomaterial. To obtain a practical guideline in order to tailor the final nanoparticle size in the process, we have systematically studied the effects of different process parameters on the particle size of titania. Titania is used, e.g. as a photocatalyst, and then both particle size and crystal structure are important when looking at the efficiency. In this work, the generated nanoparticle size has been measured by aerosol instrumentation and the particle morphology has been verified with transmission electron microscopy. In Liquid Flame Spray method, there are several adjustable parameters such as precursor feed rate into the flame; concentration of the precursor; precursor material itself as well as solvent used in the precursor; mass flow of combustion gases and also the mechanical design of the torch used. We used metal organic based titanium precursors in alcohol solvents, predominantly ethanol and 2-propanol. Large differences in particle production between the precursors were found. Differences could also be seen for various solvents. As for precursor feed in the flame, the more mass is introduced the larger the nanoparticles are, i.e. precursor concentration and precursor feed rate have an impact on particle size. A similar phenomenon can be discovered for the combustion gas flow rates. Torch design also plays an important role in controlling the particle size.

Keywords: Liquid flame spray; Scale-up; Titania; Nanoparticles

1. Introduction

Flame based methods are widely used for nanoparticle production (e.g. Ulrich, 1984; Pratsinis, 1998; Mädler et al., 2002) and flame generated nanoparticles are even commercially available (Gutsch et al., 2005). The method applied here, liquid flame spray (LFS) (Tikkanen et al., 1997a), is used in several applications for material production for example in amplifying glass fibre production in Liekki Oy (Rajala et al., 2003) and in glass colouring (Gross et al., 1999) especially for float glass in Beneq Oy (Beneq Oy, 2006). The newest application branch of LFS is the production of photocatalytic and antibacterial surfaces (Keskinen et al., 2005). In addition to titania (Mäkelä et al., 2006; Keskinen et al., 2006a,b) also other materials have been recently studied using liquid flame spray (Mäkelä et al., 2004; Keskinen et al., 2004).

Titania (titanium dioxide) is a ceramic material used in practical applications, such as pigments and photocatalytic materials (Pratsinis, 1998). Nanosized titania most often consists of partly two crystalline structures, anatase and rutile. The photocatalytic properties of the powder are determined both by the anatase/rutile ratio and the nanoparticle size in the material (Liu et al., 2003). Therefore, it would be advantageous to be able to control both the crystalline structure and the primary particle size in the generated powder. Here we present a systematic study on flame parameters to obtain a rough guideline for controlled production of nanosized titania.

2. Experimental

In the LFS process the liquid precursor is atomized into small droplets using one of the two combustion gases, hydrogen or oxygen. The droplets are then introduced into a turbulent flame. The droplets evaporate in the flame. After and

* Corresponding author. Tel.: +358 3 31153920; fax: +358 3 31152600.
E-mail address: mikko.aromaa@tut.fi (M. Aromaa).

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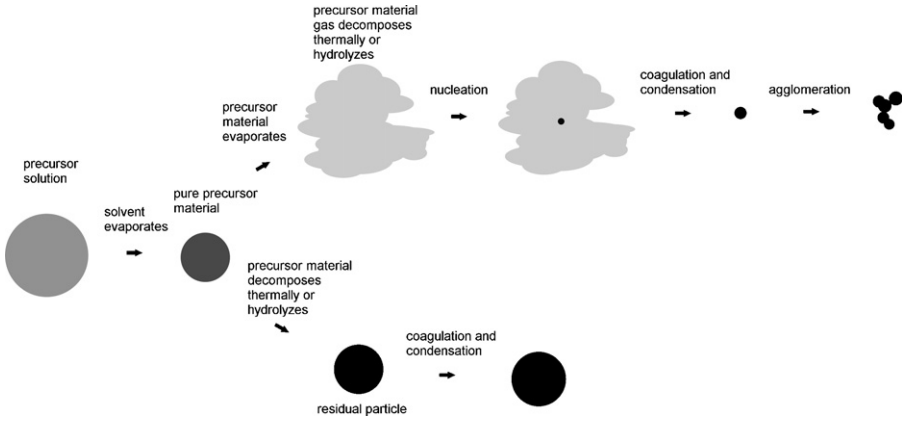

Fig. 1. A simplified model of the phenomena in the flame. Upper route is for nanoparticle formation and lower route is for residual particle formation.

during the evaporation, decomposition takes place. Finally the decomposed product re-condenses and generates material, with a relatively narrow lognormal size distribution, ready for use. This is illustrated as a simplified model in Fig. 1.

The liquid precursor was fed into the spray gun with an infusion pump so that the precursor feed rate could be adjusted manually. In this study several different feed rates from 0.25 up to 8 ml/min were used. There were also different precursors. Titanium(IV) ethoxide (TEOT) (Liu et al., 2003) and titanium(IV) isopropoxide (TTIP) (Okuyama et al., 1990) in ethanol (EtA) and isopropanol (IpA) were used. Concentrations of the solutions were varied from 3.5 to 28.0 mg/ml. In the results section a unit of production rate is used. The production rate refers to the production of pure titanium per minute.

Several modifications of a patented, specially designed spray gun were used (Tikkanen et al., 1997b). A schematic diagram of the spray gun is shown in Fig. 2, and the dimensions of the spray gun models used in this study, are presented in Table 1. The precursor was fed into the middle capillary of the tip of the gun, surrounded by a ring for the atomizing hydrogen flow used also for combustion. The next ring outwards is for the nitrogen flow and the outermost ring is used for the supply of oxygen. Only one of the spray gun models used in this study contained the nitrogen ring. The idea of the nitrogen flow in the middle of hydrogen and oxygen is to keep the flame out of the torch head. The combustion gases, hydrogen and oxygen, were supplied in a stoichiometric ratio. The O_2/H_2 flows were varied from 5/10 l/min to 40/80 l/min. The spray gun was cleaned before each run to keep the ducts open and to remove possible contaminants.

Particle size was measured using the sampling system shown in Fig. 3. The flame torch was placed head-up in a fume chamber. The sample was taken using a sample probe placed 1 m above the torch head. The sample was drawn through an ejector diluter with a dilution ratio of 1/8, although the total dilution ratio is much larger because of the open air sampling. The diluted sample was measured using a scanning mobility particle sizer, SMPS (Wang and Flagan, 1990), and an electrical low pressure impactor, ELPI (Keskinen et al., 1992). SMPS consists of a differential mobility analyzer (DMA; TSI model 3071A) and a condensation particle counter (CPC; TSI model 3025A). It classifies particles by their electrical mobility diameter in gas phase and detects them by condensation nuclei counting. The number size distribution measurement is in the range from 10 to 1000 nm. In this study the flow rate ratio of 0.6/6.0 l/min was used. ELPI measures the aerodynamic diameter of the particles in the range of 30 nm–10 μm. It was also used in real-time measurement to monitor the stability of the particle number production rate during the measurement. Using these two different diameters, electrical mobility and aerodynamic, we were able to get an estimate for the agglomerate density (Virtanen et al., 2004; Ristimäki et al., 2002).

Samples for transmission electron microscopy (TEM) were also collected in the flame using a specially designed sampling device. Samples were collected on a 200-mesh, holey carbon, copper TEM grid from different distances. Distances used were 3, 5, 10, 12, 15 and 20 cm measured from the torch head.

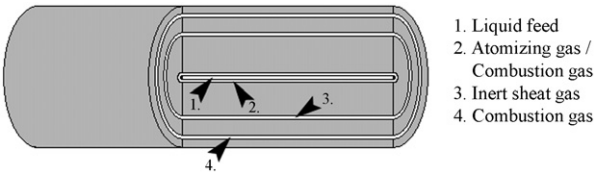

Fig. 2. A cross section of the liquid flame spray burner.

Table 1
The dimensions of the burner for the atomizing gas duct

	KP	LR	HR	L3
Liquid feed column diameter (mm)	0.5	1.3	1.3	1.3
Inner diameter of atomizing gas duct (mm)	0.9	2.0	–[a]	2.0
Outer diameter of atomizing gas duct (mm)	1.0	2.7	2.5	2.5

[a] In burner model HR the liquid feed column is square outside. Thus the inner diameter of the atomizing gas duct is not constant. The side of the square is 1.8 mm and the diagonal is 2.5 mm.

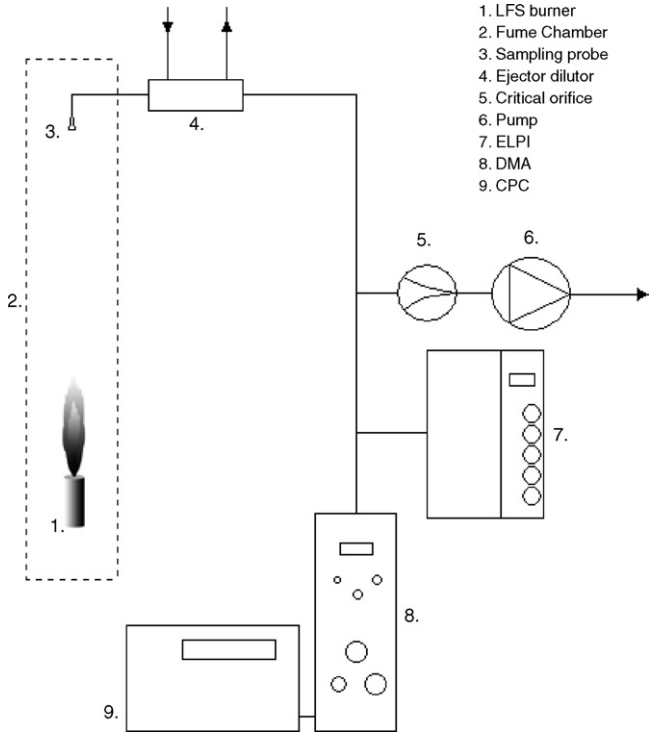

Fig. 3. Measurement setup.