Nanostructured Powders and Their Industrial Applications

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Nanostructured Powders and Their Industrial Applications

PREFACE

"Nanostructured Powders and Their Industrial Application" brings together industrial and academic researchers involved in the synthesis and use of nanostructured powders, such as fumed silica, pyrolytic titania, and precipitated silica, as well as less conventional nanostructured powders such as exfoliated clays. The proceedings book begins with a group of papers which serve as an overview of the field. The remainder of the proceedings are organized into the broad categories of physical aspects, synthesis, and applications of nanostructured powders.

The symposium was successful in bringing together workers from allied industries involved in titania, alumina, silica gel, fumed, precipitated, and colloidal silica production, as well as academic researchers involved in a variety of newer synthetic approaches and industrial users of nanostructured powders. Much common ground was found, which spurred interesting discussions during the symposium. The organizers hope to pursue this direction with future symposia aimed at these materials technologies.

Gregory Beaucage
James E. Mark
Gary T. Burns
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The organizers appreciate all of the contributions to the symposium and proceedings volume which made this event such a success.

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Part I

Overview of Nanopowder Technology

Electrically Assisted Aerosol Reactors using Ring Electrodes

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ABSTRACT

Nanostructured materials have distinctly different properties than the bulk because the number of atoms or molecules on their surface is comparable to that inside the particles creating a number of new materials and applications. Despite this potential for nanoparticles, very few practical applications have been developed because of the current high cost of these materials ($100/lb). On the other hand, flame aerosol reactors are routinely used for inexpensive production (~$1/lb) of submicron sized commodities such as carbon blacks, pigmentary titania, fumed silica and preforms for optical fibers in telecommunications. Flame technology can be used also for synthesis of nanoparticles with precisely controlled characteristics. In these reactors, gas mixing is used to *widely* control the primary particle size and crystallinity of product powders while electric fields can be used to *narrowly* control the primary, and aggregate particle size and crystallinity. Here the application of axial electrical fields on a silica producing flame using hexamethyldisiloxane (HMDS) as precursor is presented. Experiments varying the precursor delivery rate corresponding to total production rates of 10, 20 and 30 g/h are presented. Electric fields decreased the particle size by electrostatic dispersion and repulsion of charged particles and by the reduced particle residence time inside the flame.

INTRODUCTION

Flame aerosol technology has been practiced since prehistoric times as depicted with paintings in cave walls and Chinese ink artwork. Today flame aerosol reactors are routinely used in the production of commodities such as carbon blacks, pigmentary titania, fumed silica and optical fibers for telecommunications. The low cost of particles made in these reactors provides a strong incentive to better understand this process for design of new flame reactors that would allow synthesis of nanoparticles with closely controlled characteristics. A detailed review of this technology was just published (Pratsinis, 1998).

Ulrich and his co-workers (1984) pioneered the investigation of flame synthesis of ceramic powders by making SiO_2 powders by $SiCl_4$ oxidation in

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laminar and turbulent premixed flames. They first recognized that coagulation rather than nucleation was the dominant particle formation and growth mechanism. Furthermore, they explained that the appearance of agglomerates of primary particles resulted from the competition between particle collision and sintering. Though a lot of progress has been made since the early seventies in this technology emphasis is placed here on the role of specific process variables (gas mixing, electrostatics and additives) in controlling the characteristics (size, crystallinity and morphology) of flame made ceramic particles.

The flame structure can have a profound effect on the powder characteristics. The mode of reactant gas mixing in diffusion flame reactors can be used to *broadly* control the primary particle size of product powders (Pratsinis et al. 1996). The size and crystallinity of titania or silica powders made by oxidation of $TiCl_4$ or $SiCl_4$ in diffusion flame reactors are greatly influenced by the flame structure and the employed oxidant. Gas mixing affects the temperature history and particle concentration during particle formation and growth. For example, the average primary particle size of TiO_2 was broadly controlled from 10 to 250 nm through the use of a classic (single) or an inverse (double) diffusion flame with air or pure oxygen as oxidant and methane as fuel. The former diffusion flame resulted in the highest temperatures yielding large particles having high rutile fraction. In these flame reactors, the primary particle size of silica was broadly controlled from 3 to 30 nm using oxygen as oxidant. The particle size of titania was much larger than that of silica for the higher sintering rate of titania.
Electric fields can be used to *narrowly* control the primary particle size of product TiO_2, SiO_2, SnO_2 and even mixed carbon black-fumed silica powders in diffusion (Vemury and Pratsinis, 1995a) and premixed flame reactors (Vemury et al., 1997; Spicer et al., 1998). Electric charges are used either by spraying ions (corona discharge) into the region of particle formation and growth in the flame or by attracting the flame generated ions to externally placed electrodes. In both cases, the temperature history and growth rate of particles is precisely controlled though over a limited region. For example, the average primary particle size of titania particles can be controlled within 1 nm in the range of 30 to 60 nm in by applying electric fields of 0.5 to 2 kV/cm across a methane air diffusion flame. Electric fields placed in cross flow with the particle flow, reduce the particle residence time at high temperatures and charge the particles, decreasing, thus, the primary *and* aggregate size of TiO_2, SiO_2, SnO_2 and even soot particles!

Additives or dopants can be used also to control the size but, most usually, the *phase composition* and *morphology* of the product powder. For example in flame synthesis of silica by $SiCl_4$ oxidation the presence of ferrocene increases the

specific surface area and reduces the coarse tail of the product powder (Fotou et al., 1995). The addition of $SnCl_4$ or $AlCl_3$ dopants during titania synthesis by $TiCl_4$ oxidation in diffusion flame reactors enhances the transformation of anatase to rutile and reduces the specific surface area of the product powders. On the contrary, $SiCl_4$ inhibited the transformation of anatase to rutile and increased the specific surface area (Vemury and Pratsinis, 1995b).

Though making the nanoparticles in flames is a challenge in its own merit, handling and processing them is another one equally important. For example, there is no doubt that having nanoparticles will improve catalytic performance of many processes relying on available particle surface area. However, removing and separating nanoparticles from process streams can be facilitated by immobilizing them on fibrous supports. Fotou et al. (1994) coated fibrous silica aerosols generated by the Timbrell aerosol generator with silica nanoparticles in a methane-air diffusion flame reactor. By controlling the flame temperature and residence time of the freshly coated fibers, they controlled the formation and deposition rate of nanoparticles through the precursor reaction rate and particle sintering rate. They increased the specific surface area of the nanoparticle-laden fibers by 40 times over that of bare fibers.

In the present work the scale-up of electrically -assisted flame aerosol synthesis of nanoparticles is investigated using hexamethyldisiloxane (HMDS) as precursor to silica. Also the field configuration was investigated using a nearly co-axial electrical field on the flame to facilitate understanding and model development for the ensuing particle formation and growth.

EXPERIMENTAL

A schematic of the experimental set-up is given in Figure 1. In order to create a nearly axial field, coannular ring electrodes 5 cm in diameter of 3 mm thick copper wire were used. The distance between the electrodes was 5 , 7 and 10 cm, respectively. The potential was created by a Gamma High Voltage supply source. The bottom electrode, which was even with the burner's topface was always used as a ground electrode while the potential of the top electrode was varied from -6 kV to +6 kV. The current across the flame was determined by measuring the potential difference across a resistance with a multimeter (Fluke 21 Instrumental).

The employed diffusion burner consisting of 3 concentric quartz tubes is similar to that of Vemury and Pratsinis (1995). The oxidant, pure oxygen at a flow rate of 7500 cm^3/min, is supplied in the outermost, the third tube. As fuel, methane is used in the second tube at a flow rate of 800 cm^3/min. In the center tube the