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Nanoparticle synthesis in gas-phase systems
process design and scale-up for metals and metal oxides

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NANOPARTICLE SYNTHESIS IN GAS-PHASE SYSTEMS: 
PROCESS DESIGN AND SCALE-UP FOR METALS AND METAL OXIDES

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
DOCTOR OF TECHNICAL SCIENCES

presented by
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Zusammenfassung


Eine Computersimulation des Mischverhaltens der Dreifachstrahlbrenner, die hier zur Flammensynthese verwendet wurden, zeigte, dass das Misch- und Quenchverhalten der Flammenreaktoren stark von der Austrittsgeschwindigkeitsdifferenz der Brennstoff- und Oxidationsmittelströme beeinflusst wird. So wurden Primärpartikel mit gleichem mittleren Durchmesser in verschiedenen Brennern bei gleicher Austrittsgeschwindigkeitsdifferenz hergestellt, nicht aber bei gleicher Oxidationsmittelstrom. Somit konnte eine gemeinsame Operationsline für die untersuchten Flammenreaktoren entwickelt werden, die bei gleichen Produktionsraten den mittleren Primärpartikeldurchmesser mit der Austrittsgeschwindigkeitsdifferenz verbindet.

Verschiedene Produktionsraten resultierten in unterschiedlichen Operationslinien, die zu einem Prozessdiagramm zusammengefasst wurden. Anhand dieser Operationslinien wurde ein Scale-up Verfahren für Gleichstrom-Diffusions-
flammenreaktoren entwickelt. Die Partikelmorphologie wurde während des Scale-up Prozesses beibehalten, so dass bei geringer Austrittsgeschwindigkeitsdifferenz runde und wenig agglomerierte TiO₂ und SiO₂ Partikel mit mittleren Primärpartikeldurchmessern von 50 - 100 nm unabhängig von der Produktionsrate hergestellt werden konnten.


Summary

Gas phase processes for the synthesis of nanoparticles were examined for their potential to produce particles with reduced agglomeration. Though emphasis was placed on flame aerosol reactors for synthesis of silica and titania, the production of metal nanoparticles by inert gas evaporation-condensation was covered as well. The focus of the research was on process characterization and scale-up by operation diagrams and the application of different aerosol quenching procedures to suppress particle agglomeration.

A process parameter study for the production of silica nanoparticles by oxidation of hexamethyldisiloxane in co-flow diffusion flames was carried out, investigating the influence of the oxidant flow rate and composition, the flame configuration, and the burner size on the product particle size and morphology. The oxidant flow rate was found to have the strongest influence on the particle synthesis conditions in the flame. Separate operation lines for each burner reporting the specific surface area as a function of oxidant flow rate were obtained and showed that silica particles of 10 – 90 nm average primary particle diameter and high or low degree of agglomeration could be made with these flame reactor units.

The computational investigation of flow mixing in the triple concentric jet burners employed here for flame synthesis revealed that the burner outlet velocity difference of the fuel and oxidant jets rather than the reactant flow rate was a key parameter determining reactant mixing and flame quenching. Burners of different size produced particles of the same average primary particle diameter at the same outlet velocity difference but not at the same oxidant flow rate. Thus, for all the investigated co-flow diffusion flame aerosol reactors operated at the same production rate a common reactor operation line was obtained, relating the average primary product particle diameter with the velocity difference.

A flame aerosol reactor operation diagram was developed giving different operation lines corresponding to different production rates. A mass balance-based correlation related these operation lines resulting in a scale-up procedure for co-flow diffusion flame aerosol reactors. Spherical silica and titania particles with a low degree of agglomeration and average diameter down to 50 nm were made at low burner outlet
velocity difference. This particle morphology was retained when the production rate was scaled up in accordance with the operation diagram.

The length of the particle growth zone in flame reactors could be controlled by rapid quenching of the flame aerosol with a critical flow nozzle placed into the particle-laden flame at any distance from the burner. With this new quenching strategy titania nanoparticle growth could be frozen at desired levels resulting in virtually non-agglomerated and spherical titania particles of 5 – 55 nm average diameter and product powder phase composition of 85 – 5 wt-% anatase and the balance rutile. An operation diagram showed that the independent control of the primary product particle diameter and the phase composition could be achieved by varying the burner-nozzle distance and the precursor flow rate, making anatase or rutile nanoparticles with high or low specific surface area.

Application of the nozzle-quenching strategy to the flame synthesis of silica significantly reduced the degree of agglomeration in the product powder but had little effect on the particle size. Here the precursor flow rate was identified as a key parameter for the controlled production of silica nanospheres of 25 – 120 nm average diameter and limited degree of agglomeration.

A cross-flow quenching strategy was applied to the synthesis of bismuth nanoparticles by vapor condensation. Cold flow visualization, CO₂ tracer gas analysis and computational fluid dynamics showed that rapid quenching of the Bi-vapor flow in cross-flow produced particles with narrow size distribution while counterflow quenching resulted in early particle formation, broad particle residence time distributions and a wide size distribution. By rapid cross-flow quenching of the metal vapor spherical bismuth nanoparticles were formed in the gas phase but sintered at room temperature to agglomerates with 10 – 40 nm average primary particle diameter on the collection filter.
1 Flame Aerosol Reactors for Synthesis of Nanoparticles

Abstract

This chapter presents an overview of recent basic research on flame aerosol reactors for gas phase synthesis of nanoparticles. Emphasis is placed on flame reactor technology as it is widely used in industry for large-scale manufacture of oxide and carbon nanoparticles. The importance of reactant gas mixing, additives and external electric fields in flame technology is highlighted for the control of product particle properties by affecting chemistry, temperature and collision histories. Laser induced fluorescence (LIF), Fourier transform infrared spectroscopy (FTIR) and thermophoretic sampling are addressed as some of the promising diagnostics in flame aerosol research and even for on-line process control. Recent work on aerosol dynamics modeling is presented and the growing importance of computational fluid dynamics (CFD) for a better understanding of particle formation and growth mechanisms in flames is emphasized, focusing on synthesis of non-agglomerated nanoparticles.

1.1 Introduction

In the last few years the scientific community has cherished the potential of nanosize clusters or particles (Andres et al., 1989; Gleiter, 1989; Pratsinis and Mastrangelo, 1989). These entities have distinctly different properties than bulk material because the number of atoms or molecules on their surface can become comparable to that inside the particles (Ichinose, 1992). Some people even believe that nanosize particles may constitute another state of matter. Laboratory studies in various scientific fields show that especially non-agglomerated nanoparticles can be used to develop new materials with unique characteristics such as optical, mechanical, electrical, catalytic, and heat transfer properties. With nanoparticles the particle melting point decreases (Buffat and Borel, 1976), light absorption increases, and magnetic, optoelectronic (Kruis et al., 1998) and other material properties change compared with those in the bulk material.
Their large surface area to volume ratio and high density of active sites make nanoparticles attractive for applications in catalysis. By reducing the grain size to nanometer scale the sintering temperature of structural ceramics can be decreased while the plasticity is increased (Siegel et al., 1988). Nanoparticles can also be used in thin membrane films, as protective glass, metal and polymer coatings, in the production of inorganic/polymeric nanocomposites, as electronic devices and, if assembled in chains or arrays, as novel recording and storage media for digital data.

In general, nanosized powders can be synthesized via the wet chemical route and gas-phase processes. The latter are advantageous for powder manufacture since they do not involve the tedious and expensive steps of solid-liquid separation, washing and drying of wet chemistry processes and avoid the use of high liquid volumes and surfactants (Pratsinis and Mastrangelo, 1989). Today, flame processes are by far the most widely used methods for gas-phase manufacture of commercial quantities of nanoparticles, the most important of which are carbon blacks and fumed silica, produced for instance by Cabot and Degussa, as well as pigmented titania, made by DuPont, Ishihara, Kerr-McGee, Millenium, Tioxide, and others. The annual production volume of the flame industry is several million metric tons and aerosol reactors produce nanoparticles at a rate of 100 metric tons per day (Pratsinis, 1998). Other commercial aerosol processes include hot-wall reactors for industrial synthesis of filamentary (nanostructured) nickel and iron powders from decomposition of the corresponding metal carbonyls (BASF, INCO). In addition, these reactors have been used for commercial synthesis of nanostructured carbides, nitrides, borides, and other non-oxide ceramics (Dow, Bayer). More recently, the inert gas condensation technique has been scaled up for manufacture of rather costly (about $100/kg) nanostructured metals and ceramic powders (Nanophase). Spray pyrolysis technologies are used primarily by small start-up companies (for example, Particle Technology, Nanochem, SSC, and others) for manufacture of precious metal, ceramic and especially nanostructured composite ceramic powders from nitrate, organic and other solutions.

Despite the age and significance of industrial gas-phase processes, their design and operation rely heavily on experience and empiricism. As a result, it is nearly impossible for existing industrial units to address synthesis of nanosize powders without
going through the laborious and expensive cycle of Edisonian research that was followed for the development of the current units and processes (e.g. the so-called “chloride” process for TiO₂ synthesis). However, in contrast to the past state of affairs in industry, substantial work has been done on a laboratory scale toward understanding the fundamentals of nanoparticle formation and growth at high temperatures (Pratsinis, 1998; Wooldridge, 1998) and even the use of computational fluid dynamics for reactor design is actively investigated in industry today (Schild et al., 1999).

1.2 Synthesis Methods

1.2.1 Process Classification

Gas-phase synthesis methods for nanoparticles can be divided into gas-to-particle and droplet-to-particle processes. Gas-to-particle conversion refers to production of particles from individual atoms or molecules in the gas phase. Product powders generally exhibit small particle size, narrow particle size distribution, non-porous particles and high purity (Fig. 1.1).

Fig. 1.1: Spherical, dense titania nanoparticles synthesized in a diffusion flame reactor by oxidation of titanium-tetra-isopropoxide (dₚ=35 nm).
Compared to droplet-to-particle or wet chemical processes it is more difficult to produce multicomponent materials, and special care has to be taken in handling hazardous off-gases and precursors. Examples of these processes include flame (Ulrich, 1984), hot-wall (Alam and Flagan, 1986; Akhtar et al., 1991), evaporation-condensation (Yatsuya et al., 1973; Granqvist and Burman, 1976), plasma (Girshick et al., 1993; Vissokov et al., 1988), laser (Bauer et al., 1991) and sputtering (Johnson et al., 1992; Hahn and Averback, 1990).

In the droplet-to-particle route, solution droplets are suspended in gases by liquid atomization or by condensation of a superheated vapor. This is followed by evaporation of solvent from droplets and solute crystallization to form a dried particle undergoing solid state reactions and sintering upon heating. Compact nanostructured particles can be formed by spray drying of a nanoparticle slurry, as is shown in Fig. 1.2.

Fig. 1.2: Granules of nanostructured titania particles built by re-processing of flame-made TiO$_2$ ($d_p=35$ nm) through spray-drying of a slurry (courtesy O. Wilhelm and L. Mädler, ETH Zürich).

In general, the advantages of droplet-to-particle processes are: the ability to process organic and inorganic materials to form a variety of multicomponent particles, simplicity, many choices for inexpensive liquid phase precursors and a low degree of particle agglomeration. Porous or hollow particles can be formed at certain conditions.
However, the spread of the particle sizes is limited by the spread of the starting droplets. Spray drying (Lukasiewicz, 1989) and spray pyrolysis (Messing et al., 1993) are typical industrial processes employing droplet to powder conversion and can be used for manufacture of nanoparticles as well as flame spray pyrolysis (Bickmore et al., 1996), electrosprays (Borra et al., 1997; Mahoney et al., 1987), and freeze drying (McGrath and Laine, 1992). Recent books give a detailed picture of the field (Kodas and Hampden-Smith, 1999; Friedlander, 2000).

1.2.2 Gas-Phase Synthesis Route

In the gas-to-particle route nanoparticles are made by “building” them from individual molecules all way up to the desired size as is shown in Fig. 1.3. The particle formation process is driven by the generation of molecules by chemical reaction from precursor gases or by rapid cooling of a superheated vapor. High temperatures are usually required to accomplish the reaction or to bring the vapor to the superheated state. Depending on the thermodynamics of the process, the product molecules can form particles either by uninhibited collisions (collision-controlled nucleation) or by a balanced condensation and evaporation to and from molecular clusters (condensation-evaporation controlled nucleation). The newly formed particles grow further by collision with product molecules (condensation or reaction on the particle surface) and/or with particles (coagulation). In coagulation, two particles collide and stick to form an aggregate or agglomerate. The particles within this agglomerate can coalesce (fuse) by sintering into a spherical particle of the same volume and mass. However, as coagulation continues, the ratio of the sintering rate (the rate of particle coalescence) and the rate of coagulation determines the morphology of the final product particle. When the rate of coalescence is faster than that of coagulation, spherical particles are obtained. However, as particles grow the sintering rate decreases and particle coalescence usually becomes slower than coagulation. As a result, irregularly shaped agglomerate particles are formed. These are termed hard or soft agglomerates (or aggregates) depending on how easy it is to break the bonds connecting the primary particles (Pratsinis, 1998).
1.3 Flame Synthesis

In flame reactors the energy of a flame is used to drive chemical reactions of precursor compounds that result in the formation of product molecules, which then nucleate to form particles following the mechanism described earlier (Pratsinis, 1998). High flame temperatures of 1200 to 3000 K constitute a self-purifying environment for particle synthesis resulting in high-purity powders as for manufacture of optical fiber preforms (Bautista and Atkins, 1991). Even though non-oxide ceramic powders like silicon nitride (Calcote et al., 1990) and tungsten carbide (Zhao et al., 1990) have been synthesized in flame reactors, the production of carbon and metal oxide nanoparticles dominates the field. One distinguishes two types of flame reactors: diffusion and premixed. While premixed flames have the advantage of more uniform radial temperature profiles, diffusion flames are safer to operate (no flashback) and offer flexibility in product quality by controlling the reactant gas composition over broad ranges. Turbulent coflow diffusion flame reactors are used in industry for large-scale manufacture of ceramic powders. Counterflow diffusion flame reactors, on the other hand, are often used in laboratory studies (Pratsinis, 1998). The flow along the axial stagnation streamline of a counterflow diffusion flame can be approximated as one-dimensional, facilitating the use of optically-based diagnostics for non-intrusive study of nanoparticle formation (Wooldridge, 1998).
A typical laboratory set-up of an diffusion flame aerosol reactor is depicted in Fig. 1.4. The co-flow reactor is made of three concentric stainless steel tubes of about 120 mm length. The inner diameter of the center tube is 5 mm, while the o.d. of the outer tube is 18 mm and the width of the two annular ports is about 1.5 mm. Oxygen is delivered through the outer tube while methane flows through the center port. High purity argon loaded with the precursor vapor is added to the fuel stream prior to entering the burner. A small stream of nitrogen is introduced between the fuel and oxidant streams to prevent deposition of particles on the burner mouth. An evaporator or a bubbler can be used to load the inert gas stream with the precursor. When a bubbler is used, controlled amounts of precursor can be delivered into the reactor by adjusting the temperature of the liquid compound with the help of a thermostated bath. Evaporators offer the advantage of precise precursor dosing, easier handling of moisture-sensitive chemicals and the evaporation of mixtures.

**Fig. 1.4: Diffusion flame reactor set-up for nanoparticle synthesis.**

Industrial processes usually operate with halide precursors. In laboratory units organometallic compounds are preferred to circumvent HCl and chlorine removal from the off-gas and to avoid post-cleaning of the powders. In order to prevent condensation of precursor vapor, the precursor delivery tubes and the reactor are heated above the
temperature of the evaporator or bubbler. Product particles are collected on a filter with the aid of a vacuum pump. The flame is surrounded by a quartz glass cylinder in order to achieve stable burning. The outer tube of the reactor can be surrounded by a sheath of nitrogen for flame stabilization.

In diffusion flames, the maximum flame temperature usually occurs at the tip of the cone-shaped flame front, where agglomerates fuse (Zhu and Pratsinis, 1997). Upon leaving the flame, the temperature drops quickly and particles continue to coagulate while sintering takes place at much lower rates. In many systems the characteristic time for coalescence is longer or in the same order as the characteristic time for coagulation resulting in agglomerates consisting of a few up to many thousands of primary particles (Koch and Friedlander, 1990). The characteristics of the product particles such as morphology, crystallinity and size strongly depend on the precursor concentration, temperature profile and residence time distribution in the flame.

1.3.1 Current State of Research

The current state of research in this field has been recently reviewed by Pratsinis (1998) and Wooldridge (1998) so that here only the keypoints are reported. Fumed silica became industrially important in the 1940s as a substitute for carbon black (Ulrich, 1984) and was first marketed under the name “Aerosil” by Degussa AG (Kloepfer, 1949). Flame technology was soon also applied in the manufacture of titanium dioxide from TiCl₄ as precursor (chloride process) to replace the wet-chemistry-based sulfate process (Ulrich, 1984). The manufacture of uranium dioxide by oxidation of uranium hexafluoride in a flame became the third industrially important flame process with high potential to replace its wet precipitation counterpart (Ulrich, 1984). The flame generation of UO₂, as described by Federer et al. (1969), yields powders of high purity which can be pressed and sintered to form fuel pellets for nuclear reactors.

Paralleling the growing industrial importance of flame processing of chemicals in the mid-20th century, research in this field was first led by industrial laboratories. Emphasis was placed on burner design and use of additives (Pratsinis, 1998). The early
The establishment of flame technology in industry stimulated a number of research issues in academia. Especially Ulrich and co-workers (Ulrich, 1971; Ulrich et al., 1976; Ulrich and Subramanian, 1977; Ulrich and Riehl, 1982) along with Formenti et al. (1972) pioneered research on flame synthesis of ceramic powders. The group of Ulrich studied synthesis of SiO₂ by SiCl₄ oxidation in premixed laminar and turbulent jet flames. Thereby, they recognized that coagulation rather than nucleation was the dominant particle formation mechanism and that the size distributions of the product particles were self-preserving (Friedlander and Wang, 1966). These early studies revealed that the appearance of agglomerates of primary particles results from the competition between particle collision and sintering (Ulrich and Subramanian, 1977).

In the mid-80s an idea already mentioned in a 1936-patent by Corning Glass Works, New York, (Corning Glass Works, 1936; Hyde, 1942) further accelerated research in the field: the deposition of flame-generated silica to form transparent articles of high purity led to the introduction of flame reactors in large scale manufacture of optical fiber preforms (Bautista and Atkins, 1991). Today, the production of optical waveguide preforms which are used to draw hair-thin fibers is one of the most profitable processes of Corning Inc.. In academia, opposed jet (counterflow) diffusion flame reactors were introduced by Chung and Katz (1985) for synthesis of oxide powders. The flat and stable flame of the burner exhibits uniform temperature and species concentration distributions in the horizontal plane, thus allowing a precise tracing of particle formation. The importance of sintering in oxide particle formation was demonstrated by Helble and Sarofim (1989) while investigating fly ash formation during coal combustion. Hurd and Flower (1988) introduced fractal concepts to describe the structure of the resulting silica agglomerates from a laminar premixed methane flame. Koch and Friedlander (1990) presented a simple but elegant model describing the formation of non-spherical particles by coagulation and sintering.

Renewed interest in flame technology for manufacture of advanced materials intensified research in the field since the early 90s. Mixed oxide systems like SiO₂-GeO₂, Al₂O₃-TiO₂, and V₂O₅-Al₂O₃ were studied by Hung, Miquel and Katz (Hung and Katz, 1992; Hung et al., 1992; Miquel et al., 1993) while Zachariah and co-workers...
(Zachariah et al., 1995; McMillin et al., 1996) made superparamagnetic nanoparticles in a premixed methane-oxygen flame. When synthesizing submicron YBa$_2$Cu$_3$O$_7$ particles in an oxy-hydrogen diffusion flame reactor, Zachariah and Huzarewicz (1991) found that flame configuration may have a profound effect on the product powder properties. Pratsinis et al. (1996) observed that by merely altering the position of fuel and oxidant streams in diffusion flame reactors the average particle size of product titania powders can be changed by as much as a factor of ten.

As a result, great emphasis was placed on determining the role of flame process variables like flame configuration, temperature, oxidant composition, and precursor type. For example, Lindackers et al. (1994) made titania and silica particles in low pressure, premixed oxy-hydrogen flat flames. This flame configuration resulted in enlarged reaction zones compared to standard pressure flames and allowed them to observe the formation of titania particles. Probably of all variables, temperature has the most drastic effect on process and product characteristics. Bautista and Atkins (1991) found that hydrolysis is the main route for SiCl$_4$ conversion at low temperatures while oxidation is the dominating mechanism at high temperatures. Hung and Katz (1992) found that increasing flame temperatures resulted in high concentrations of fine particles during synthesis of SiO$_2$ and TiO$_2$ in a counterflow diffusion flame reactor. Large temperature gradients can generate strong thermophoretic forces on the newly formed particles drastically altering their residence time at the decisive region where nucleation, growth, coagulation and sintering occur, affecting thus the morphology of flame made particles (Gomez and Rosner, 1993). Today, oxides like SiO$_2$, TiO$_2$, Al$_2$O$_3$, ZrO$_2$, V$_2$O$_5$, and most other oxides of metal elements in the periodic table and their composites have been produced in powder form in hydrocarbon flames on a laboratory scale (Pratsinis, 1998; Kodas and Hampden-Smith, 1999).

1.3.2 Control of Particle Properties

The size and morphology of flame synthesized particles depend on the structure and properties of the flame. The most important parameters are the temperature field of the
flame, the particle residence time and, for diffusion flame reactors, the mixing of precursor and oxidant. These parameters depend on the reactor geometry and the gas flow rates into the burner.

The advantage of coflow diffusion flame reactors regarding their flexibility in reactant mixing is illustrated in Fig. 1.5 by the example of titania synthesis from TiCl$_4$ (Pratsinis et al., 1996) along with the corresponding temperature fields of the flame calculated by computational fluid dynamics (Johannessen, 1999). Different flame configurations referred to as the A, B, C, or D-flame were achieved by introducing the reactants through different ports of the burner.

Fig. 1.5: Influence of the flame configuration on the morphology of titania particles synthesized with a diffusion flame reactor (Pratsinis et al., 1996). The center tube diameter of this burner is 4 mm and the spacing between the successive tubes is 1 mm. Temperature profiles of the double diffusion flames A, B, as well as those of single diffusion flames C and D were calculated by computational fluid dynamics (CFD) and are adapted from Johannessen (1999). The reactant mixing leads to control of primary particle size up to a factor of 10.
As can be seen from Fig. 1.5, the particle size and morphology changes drastically with the mode of mixing. Double diffusion flame A produces the finest TiO$_2$ particles with an average primary particle diameter of about 10 nm. Here, the precursor stream is diluted with air prior to its oxidation in the flame and the particles experience rather low temperatures (Pratsinis, 1998; Pratsinis et al., 1996). In double diffusion flame B, the mixing of precursor and air streams takes place further downstream from the burner, resulting in particles larger than those of flame A. In the single diffusion flame C, mixing of precursor vapor and methane takes place much earlier than in flames A and B (Johannessen, 1999). The newly formed particles experience higher temperatures than in flames A and B with the temperature maximum being at the middle of the flame. As a result, sintering is rapid, creating large non-agglomerate particles ($\approx$ 80 nm in diameter) as shown by TEM and proven by small angle X-ray scattering (Hyeon-Lee et al., 1998). Titania particles synthesized in single diffusion flame D are a bit larger than those synthesized in flame C. Flowing methane through the center tube results in a narrow flame front and high flame temperatures leading to fast sintering rates and large particles with a low degree of agglomeration. By using pure oxygen instead of air as oxidant, the flame can even produce non-agglomerated, perfectly spherical particles (Zhu and Pratsinis, 1996) as is shown in Fig. 1.6a.

Fig. 1.6: Influence of oxidant composition on the morphology of flame-synthesized titania particles by TiCl$_4$ oxidation, using: a) pure oxygen, b) 50% nitrogen, c) air as oxidant. Pure oxygen accelerates combustion leading to the highest temperature and synthesis of perfectly spherical non-agglomerated particles. Adapted from Zhu and Pratsinis (1996).
For a given flame configuration, the oxygen flow rate as well as the choice of the precursor compound affects the size and morphology of flame-generated nanoparticles by altering the temperature field of the flame and the gas mixing properties (Briesen et al., 1998). Our recent work on a diffusion flame reactor operated in C-flame configuration, like in Fig. 1.5, shows that the specific surface area of silica particles increases from 40 to about 200 m$^2$/g when the oxygen flow rate is increased from 1000 to 12000 cm$^3$/min (Fig. 1.7). The average BET-equivalent particle diameters range from 63 to about 13 nm. Also the degree of agglomeration is reduced when the oxygen flow rate is decreased from 8000 to 2000 cm$^3$/min.

Fig. 1.7: Specific surface area of fumed silica determined by liquid nitrogen adsorption as a function of the oxygen flow rate. TEM micrographs show the effect of the oxygen flow on product particle morphology. Increasing oxidant flow rate lowers the particle residence time at high temperature leading to smaller nanoparticles.
Electric charges offer another tool for control of the characteristics of flame-made powders. Electric fields applied across a particle-generating flame charge the newly formed nanosized particles. As a result, the coagulation rate of these particles is reduced in the high temperature region of the flame. Furthermore, particles are removed from the flame toward the external electrodes by electrophoresis. In premixed (Vemury et al., 1995a; Vemury and Pratsinis, 1996) and diffusion flames (Vemury and Pratsinis, 1995a) making titania, tin oxide, silica, and even carbon or silica-carbon composites (Artelt et al., 1997; Spicer et al., 1998) the agglomerate and primary particle size decrease proportionally to the applied electric field strength.

**Fig. 1.8:** Influence of the electric field of plate electrodes on the average primary particle diameter and morphology of titania particles made by TiCl$_4$ oxidation. Increasing the electric field strength from 0 to 1.6 kV/cm reduces the primary particle size from 30 to 13 nm as charges slow down coagulation and particle growth. [Pictures courtesy of S. Vemury, Lucent Technologies].
Figure 1.8 shows the average primary particle diameter of titania particles as a function of the applied electric field intensity across the flame together with TEM micrographs and pictures of the premixed flame. As can be seen, the average primary particle and agglomerate size of these powders can be narrowly controlled by applying external electric fields across the flame. Recently, it was demonstrated by Kammler and Pratsinis (2000) that electric fields can also be applied for control of fumed silica particle properties when the production rate of a lab-scale burner was increased from a few grams per hour to almost 100 g/h. Kammler and Pratsinis (2000) further confirmed that the location of the electrodes with respect to the flame is a decisive factor in electrically-assisted flame aerosol synthesis (Vemury and Pratsinis, 1995a). Thus, electric fields provide the unique opportunity for making powders with closely controlled size, composition and morphology.

The introduction of additives or dopants in particle-generating flames is widely practiced in industry as they can have a profound effect on particle formation and growth mechanisms and subsequently on the product particle characteristics. Additives are used as a means to control the crystallinity (e.g. Si or Al in TiO$_2$ for anatase or rutile) or the morphology (e.g. K in carbon blacks) of the powders. Vemury and Pratsinis (1995b) added SiCl$_4$, SnCl$_4$, and AlCl$_3$ to a titaniumtetrachloride precursor stream and investigated the effect of these additives on phase composition, morphology and size of titania particles synthesized in a laminar diffusion flame. They found that the introduction of the silica-precursor inhibits the titania phase transformation from anatase to rutile, decreases the primary particle size, and, as a result, increases the specific surface area. These observations parallel those of Akhtar et al. (1992) who had shown how Si, P or B create interstitial defects in the anatase lattice of titania made in a tubular hot wall reactor. However, when SnCl$_4$ or AlCl$_3$ were used as dopants (Vemury and Pratsinis, 1995b), the phase transformation of anatase to rutile was enhanced and the specific surface area was decreased in agreement with Akhtar et al. (1994) who had shown how Al creates substitutional defects in the titania lattice. Regarding flame synthesis of silica, the role of ferrocene on product particle properties was investigated by Fotou et al. (1995). The presence of ferrocene increased the specific surface area of silica up to 150% and removed the coarse tail of the silica agglomerate size distribution.
Retardation of coagulation by charging effects was found to be a possible explanation to these results. As was briefly pointed out, the use of additives and dopants in flame synthesis of ceramic powders provides another means to control particle properties, especially when high purity of the product powders is not a concern.

1.3.3 Diagnostics

Combustion models and computational fluid dynamics (CFD) as well as state-of-the-art flame diagnostics are powerful tools for a better understanding of particle formation and growth mechanisms in the flame. Johannessen et al. (2000) developed a computational fluid dynamics model of temperature, velocity and gas composition in a diffusion flame and combined it with a simple model for coagulation and coalescence of aerosol particles. By comparing the computational results with temperature measurements throughout the flame and size analysis of alumina product particles, they gained insight into the fundamental flame synthesis mechanisms. Current efforts are toward an integration of particle dynamics models into CFD-codes as indicated in the recent works of Schild et al. (1999) and Pyykönen and Jokiniemi (2000). While Schild et al. integrated a monodisperse aerosol dynamics model (Kruis et al., 1993) into fluid mechanics for simulation of titania formation from TiCl₄ in a tubular aerosol flow reactor, Pyykönen and Jokiniemi (2000) introduced a computational fluid dynamics based sectional aerosol model to simulate aerosol formation in a laminar flow reactor.

Non-intrusive diagnostic tools for flame temperature, velocity and species concentration provide means to both verifying CFD simulations of flames and providing an accurate and detailed database characterizing the environment for particle formation and growth models. Concerning flame velocities, 3-phase Laser-Doppler Anemometry (LDA) has already been applied extensively to characterize laminar and turbulent flames. The results obtained from non-particle generating flames using micrometer-sized pigmented titania or zirconia as seeds might be directly applicable to flame reactors since their low precursor concentrations should not alter the velocity field significantly. Flame temperature measurements are usually done in the absence of
precursor (e.g. Chung and Katz, 1985) since particles either deposit on thermocouple probes or, for non-intrusive laser diagnostic methods, the interference of the response signal with particulate matter weakens the signal intensity. The oxidation especially of organometallic precursors, however, is highly exothermic and can constitute a large fraction of the overall combustion enthalpy of the flame (Briesen et al., 1998). Thus, adding the precursor to a flame is expected to alter its temperature field, making the development of fast and reliable non-intrusive temperature diagnostics for particle-generating flames a necessity in flame aerosol reactor research. In particle-laden low pressure flames spatially resolved temperature and OH species concentration could be determined by Glumac et al. (1998) using laser-induced fluorescence (LIF). One of the few applications of LIF in particle synthesis at atmospheric pressures is the work reported by Zachariah and Burgess (1994) who used LIF to measure OH and SiO concentrations and Mie scattering to measure particle distributions during flame synthesis of silica powders. Such information is of fundamental importance to a better understanding of gas-to-particle conversion processes because gas phase species determine not only the rate of particle formation, but also the chemical composition of the particles.

![Normalized radiance spectra of a premixed flame for titania nanoparticle synthesis recorded 5 mm above the burner mouth. The Planck function (blackbody) spectrum (smooth line envelopes) that matches the normalized radiance is also shown. Adapted from Arabi-Katbi (1999).](image-url)
Fourier transform infrared (FTIR) spectroscopy has been successfully applied for in-situ temperature and concentration measurements in particle-generating flames operated at atmospheric pressure. Morrison et al. (1997) and Arabi-Katbi (1999) have shown that FTIR measurements can determine particle temperature and concentrations as well as gas temperatures and concentrations in a premixed methane-oxygen flame for synthesis of titania powders (Fig. 1.9). The application of FTIR spectroscopy also enables the acquisition of in-situ temperatures during flame synthesis of particles in the presence of electric fields as reported by Morrison et al. (1997). Hitherto, process temperatures have not be measured under these conditions since conventional temperature probes such as thermocouples can not be applied.

![Diagram](image)

**Fig. 1.10: Thermophoretic sampling in a premixed flame for titania synthesis.**

- **a)** The tip of the thermophoretic sampler at a height of 3.3 cm from the burner mouth.
- **b)** TEM micrograph of particles sampled at this height on the center axis of the flame.
- **c)** Evolution of particle size in the flame and centerline temperature profile of the flame. [Pictures courtesy of H.K. Kammler, ETH Zürich].
Information on the agglomerate structure and size of particles during flame growth can be obtained by thermophoretic sampling on transmission electron microscopy (TEM) grids at different flame heights (Dobbins and Megaridis, 1987). By rapidly inserting and withdrawing a TEM grid particles can be collected on the grid by thermophoresis. The method was applied by Arabi-Katbi (1999) in a premixed flame generating titania nanoparticles. Figure 1.10a shows the tip of the sampler through which the grid was inserted into the premixed titania synthesis flame at a height of 3.3 cm above the burner. The corresponding TEM micrograph of titania particles at the flame centerline is shown in Fig. 1.10b. An average particle size of 42 nm and a standard deviation of 11 nm were obtained by image analysis. Thermophoretic sampling at different flame heights along the center axis nicely gave the particle growth evolution in this flame (Fig. 1.10c).

1.4 Modeling Particle Dynamics

There is a strong industrial interest in the development of simulators for aerosol manufacture of nanoparticles. More specifically, mathematical models relating the characteristics of the product powder (size, polydispersity, specific surface area, crystallinity and morphology) to the process variables (reactant state, composition and flow rate as well as reactor geometry) are needed that are based on sound understanding of particle formation and growth. This is best accomplished by interfacing models for computational fluid dynamics with models for particle dynamics assuming that the chemistry is fast as it is typically with high temperature processes dominated by coagulation.

The construction of such a simulator starts with the velocity and temperature profiles in the reactor that can be readily calculated even by commercial software such as CFX or Fluent. Regarding particle dynamics, moment and sectional representations of the size distribution are employed depending on the required product particle specifications. Moment models make assumptions about the shape of the particle size distribution, allowing the population balance equation to be converted to ordinary differential equations.
Lognormal models, for instance, rely on the assumption that the particle size distribution has a lognormal shape throughout the entire system. In sectional models, the particle size distribution is divided into sections in which the characteristics of the particles are described by average values (Kodas and Hampden-Smith, 1999). Typically, the specific surface area (SSA) or an average particle diameter ($d_p$) and polydispersity are key characteristics of the product powder. Assuming that particles are monodisperse further simplifies the population balance equation, making monodisperse models quite attractive for fast calculation of the specific surface area and average particle diameter. For polydispersity, however, either a sectional or lognormal moment model is required. Typically, monodisperse models offer computational simplicity while sectional provide detail. Models that distinguish between primary and agglomerate particles are attractive such as the one by Kruis et al. (1993) that has been widely used. While early models for two dimensional size (volume-area) distributions (Xiong and Pratsinis, 1993) required substantial computational time on a supercomputer, recently developed computer codes for sectional models accounting for coagulation and sintering giving both primary and agglomerate particle size distribution require far less computational effort and can be run on a personal computer without lack in accuracy (Tsantilis and Pratsinis, 2000). An introduction to particle dynamics models discussing advantages and disadvantages of different approaches and giving numerous literature references on the topic has been recently published by Kodas and Hampden-Smith (1999).

The availability of these simulators can break the Edisonian cycle for process design of aerosol reactor units and can lead to optimal reactor design and operation because it is possible to achieve better process control for existing products as the models make apparent which process variables most effectively determine powder characteristics. Second, a simulator can accelerate scale up for manufacture of new products as it provides a much better starting point for selection of process conditions. Third, a simulator assists in minimizing the down time of existing production lines as it can reveal process conditions prone to particle deposition on reactor walls. Finally, simulators can point out conditions for better process yields that translate in money and energy savings.
Running these simulators can be quite revealing as they can identify problematic regions in the reactors involving either hot spots or dead volumes. As the volume fraction of particles in the suspension is, typically, up to 0.001, the fluid and particle dynamics can be decoupled. If chemical reactions are fast, as is usually the case with high temperature processes, they can be neglected and the particle dynamics can be superimposed on the velocity and temperature profiles calculated by the commercial computational fluid dynamics simulators. This was successfully done for synthesis of titania in hot wall reactors (Schild et al., 1999), in flame synthesis of alumina (Johannessen et al., 2000) and titania (Johannessen, 1999) using a simple monodisperse model for agglomerate dynamics by coagulation and sintering (Kruis et al., 1993). Furthermore, synthesis of Pd metal nanoparticles by evaporation-condensation in jet flow condensers has been simulated by interfacing Fluent with a monodisperse model for particle dynamics (Tsantilis et al., 1999). These models (Schild et al., 1999) have been quite successful in industry as was reported by A. Gutsch (1997) since they predicted the specific surface area of the product powder within 3%.

The early success of simulators has motivated research in further development of diagnostics for verification as well as more accurate models that account for the full size distribution and the detailed chemistry. This, however, adds a load of computational demands motivating research for efficient design of algorithms for these simulators. Nevertheless, the availability of data describing the detailed evolution of particle size distribution by thermophoretic sampling and computerized image analysis coupled with accurate temperature and velocity measurements creates the foundation for rigorous testing of models and hypotheses.

1.5 Concluding Remarks

Flame aerosol synthesis is a versatile technology to manufacture nanoparticles with well defined properties. Reactant gas mixing, electric charges or dopants can be used to control size, morphology, crystallinity and phase composition of product powders. Many diagnostic tools used in combustion research can be adapted for aerosol flame
reactors, yielding important information for the understanding of particle formation and growth processes in flames. These data describing the flame environment and the stages of particle synthesis are also of high value for the validation of particle dynamics models. Recent studies show that the combination of flame diagnostics, computational fluid dynamics and particle dynamics models is an effective way to improve the understanding of flame synthesis of nanoparticles and to break the cycle of Edisonian research in this field. Gas-phase combustion technology produces some of the cheapest ceramic powders today and has high potential to provide tailor-made nanoparticles for new and commercially viable applications. Having a low cost starting material (nanoparticles) will certainly accelerate the development of nanotechnology in the future.
1.6 References


2 Aerosol-based Flame Synthesis: A Microreactor for Silica Nanoparticles

Abstract

Flame microreactors are investigated for their capacity and potential to flexibly produce nanoparticles with closely controlled characteristics. Here, the effect of the geometric dimension of a co-flow diffusion flame aerosol reactor on the properties of the product powders is studied. Fumed silica nanoparticles were synthesized by oxidation of hexamethyldisiloxane (HMDSO) in flames with two different burner configurations. The influence of the oxidant flow rate and composition on the specific surface area of the powders was determined. Nanoparticles with a specific surface area ranging from 30 to 240 m²/g and of spherical to agglomerated morphology could be made by controlling the temperature history of the process. The analysis of gas mixing in coaxial jets and flame temperature profiles revealed that properties generally attributed to chemical microreactors such as an improved mixing of flows can be applied to the diffusion flame microreactor.

2.1 Introduction

Flame aerosol reactors are routinely used for inexpensive production of submicron sized commodities such as carbon blacks, pigmentary titania and fumed silica and have high potential for manufacture of other nanoparticles (Pratsinis, 1998). The annual production volume of the flame industry is several million metric tons and aerosol reactors produce nanoparticles at rates in the order of 100 metric tons per day and higher. Compared to wet chemical production methods, these gas-phase processes are advantageous since they do not involve the tedious and expensive steps of solid-liquid separation, washing and drying and avoid the use of high liquid volumes and surfactants (Pratsinis and Mastrangelo, 1989). As a consequence, the production of pigmentary
titania by oxidation of TiCl₄ in a flame (chloride process) is replacing the wet-chemistry-based sulfate process in many areas of the titania industry (Ulrich, 1984). The manufacture of uranium dioxide by oxidation of uranium hexafluoride is another example of a flame process with high potential to substitute its wet precipitation counterpart (Ulrich, 1984).

Powders produced by gas-phase combustion synthesis are usually agglomerated and can be best described as fractal-like. These agglomerates are polydisperse and comparably large in size with dimensions that are up to two orders of magnitude higher than the primary particles (Wooldridge, 1998). Therefore, processes for the synthesis of non-agglomerated nanoparticles still operate mainly in the liquid phase, like the synthesis of monodisperse transition metal oxide colloids by sol-gel methods (Livage et al., 1988). Consequently, aerosol flame reactor research aims at the development of flexible processes which allow the synthesis of a broad variety of nanoparticles ranging from non-agglomerated spheres to fractal-like agglomerates through control of the operating conditions. The size and morphology of flame-generated particles depend on the structure and properties of the flame. The most important parameters are the flame temperature field and the particle residence time. In diffusion flame reactors, for example, these can be controlled through the mixing of precursor and oxidant, as was shown by the CFD-calculations of Johannessen et al. (2000). Recent studies have shown that by changing these parameters the properties of nanoparticles can be well controlled in laboratory-scale diffusion flame aerosol reactors at production rates from a few milligrams up to 1 kg/h.

Compared to premixed flames, diffusion flame reactors offer the advantage of high flexibility in product particle qualities by controlling the reactant gas composition over broad ranges. Zhu and Pratsinis (1996) investigated the mode of reactant gas mixing in the synthesis of titania powders with a diffusion flame reactor. They observed that the oxidant stream composition drastically changed the product morphology from highly ramified agglomerates to perfectly spherical particles. Fractal-like particles with primary particle sizes down to 11 nm as well as non-agglomerate, spherical titania nanoparticles with diameters of 100 to 200 nm could be produced. Zhu and Pratsinis
(1997) succeeded also in synthesizing spherical silica particles in the same size range which exhibited only a low degree of agglomeration. Recently, Glumac et al. (1998) reported the production of non-agglomerated silica, titania and alumina in a low pressure flame at rates up to 50 g/h. Using a double diffusion flame, Kammler and Pratsinis (1999) succeeded in producing silica nanoparticles with well defined properties at rates up to 130 g/h. Zachariah and Semerjian (1990) investigated the influence of the silica precursor material on particle growth in a counterflow diffusion flame. They found that particle formation from silane occurs earlier and at lower temperatures than from hexamethyldisiloxane (HMDSO) and tetramethylsilane (TMS). Briesen et al. (1998a) who investigated silica formation in a diffusion flame from SiCl₄, HMDSO and octamethyl-cyclotetrasiloxane (OMCTS) found that the specific surface area of the nanoparticles could be controlled in a range of 30 to 250 m²/g depending on the choice of precursor as well as the oxidant composition and flow rate. More accurately, they found a linear relationship between the specific surface area of the product powder and the adiabatic temperature of a premixed flame.

The introduction of additives or dopants into particle-generating flames is a further means to control the morphology and the crystallinity of product nanoparticles. Vemury and Pratsinis (1995a) added SiCl₄, SnCl₄, and AlCl₃ to a titaniumtetrachloride precursor stream and found that the introduction of the silica precursor inhibits the titania phase transformation from anatase to rutile, decreases the primary particle size, and, as a result, increases the specific surface area. However, when SnCl₄ or AlCl₃ were used as dopants (Vemury and Pratsinis, 1995a), the phase transformation of anatase to rutile was enhanced and the specific surface area was decreased. Fotou et al. (1995) investigated the role of ferrocene in the flame synthesis of silica and found that the presence of this additive increased the specific surface area of silica up to 150% and removed the coarse tail of the silica agglomerate size distribution. Retardation of coagulation by charging was a possible explanation for these results.

The generation of charges by external electric fields offers another tool for control of characteristics of flame-made powders. Vemury and Pratsinis (1995b) generated titania nanoparticles by oxidation of TiCl₄ in a methane/air double diffusion flame in the presence of an electric field created by two needle electrodes across the flame. They showed that the specific surface area of the product particles decreased proportionally to
the applied electric field strength and could be narrowly controlled. The influence of an
electric field on the synthesis of silica particles in a diffusion flame reactor was
investigated by Briesen et al. (1998b) and Kammler and Pratsinis (2000) for production
rates up to 30 g/h and 87 g/h, respectively. Both studies found that not only the specific
surface area of the composite silica-carbon product particles could be precisely
controlled but also the powder composition.

The above mentioned studies show that laboratory scale diffusion flame aerosol
reactors with diameters of a few centimeters are well suited to control the size and
morphology of the product particles. Little is known, however, about the influence of
the size of co-flow diffusion burners on the properties of the generated powders.
Wießmeier and Hönike (1996) showed that the performance of chemical reactors can
improve if the dimensions of the reactor are reduced to microscale. Some
microfabricated compounds that perform the same standard unit operations that are
present in large chemical processing plants have already been developed including
pumps, heat exchangers, separation units, and chemical reactors (Wegeng and Dorst,
1998). This new class of chemical process equipment has significantly different features
from classical chemical processing units because microscale phenomena like heat and
mass transport are exploited more effectively (Ehrfeld et al., 2000). Especially chemical
microreactors exhibit improved mixing of flows, extremely rapid heat and mass
transfer, and higher processing rates (Burns et al., 1997). As a result, process variables
can be controlled more precisely than in large scale units leading to higher yields and
better product quality. Another advantage of microchemical systems is the high
production flexibility for small amounts of chemicals on demand and on-site (Ehrfeld et
al., 1997). A scale-up can be done easily by operating microreactor units in parallel.
Therefore, these systems are especially suited for distributed processing applications
(Wegeng and Dorst, 1998).

Until now, the concept of microreactors has not been extended to aerosol reactors
despite the potential enhancement of reactant mixing and transport properties in
diffusion flames. The characteristics of isothermal double coaxial jets on which most
diffusion flame burners are based may illustrate this potential improvement of reactant
mixing in aerosol microreactors. A schematic of the near nozzle flow field of a double concentric jet is shown in Fig. 2.1 which refers to a typical condition with higher outer jet velocity. Due to the entrainment requirements of free jets, regions of pure nozzle fluids A and B as well as areas of mixed gases form in the initial merging zone downstream the nozzle. The conical region in front of the center tube containing fluid from the center nozzle only is called the primary or inner potential core (Ko and Kwan, 1976). The corresponding region in front of the outer tube containing just fluid from the annular jet is named the secondary or outer potential core. The initial merging zone ends roughly at the tip of the outer potential core. Between the two potential cores lies the inner mixing region containing fluids A and B. In a typical diffusion flame with fuel provided through the center and oxidant through the annular jet, the flame front would establish within this region at locations where the mixture of fuel and oxidant is stoichiometric. The secondary mixing zone starts at the outer boundary of the annular jet and contains annular jet fluid as well as gas entrained from the surrounding environment. Downstream of the initial merging zone is the intermediate zone, where mixing of the flows from the two upstream mixing regions occurs. When the two jets have combined in the fully merged zone, they behave essentially as a single jet.

**Fig. 2.1:** Schematic of the flow field in a double concentric jet. The mean exit velocity of the outer annular jet is higher than that of the central jet.
The length of the inner potential core may be taken as an indicator for the effectiveness of mixing in a double coaxial jet. Mixing between the central and annular streams, and therefore the length of the inner potential core, is influenced by the outer and inner exit velocities and diameters, the thickness of the inner duct wall and the outflow conditions of the jets (Talamelli and Petagna, 1994). Shorter distances between the two jet centerlines and thus faster mixing can be realized by reducing the tube diameters. Villermaux et al. (1994) reported a decrease of the inner potential core length proportional to the inner nozzle diameter for a given velocity ratio between the streams of a fully turbulent coaxial jet. Increasing the velocity ratio also decreased the core length proportionally. Chigier and Béer (1964) investigated the influence of the velocity ratio on gas mixing for an isothermal double concentric jet. The concentration of central nozzle fluid at the center axis of the jet decreased to 10% of its initial value after a distance of 16 nozzle diameters for a velocity ratio of 3, while it reached this value after only 4 nozzle diameters for a ratio of 9, demonstrating the importance of the velocity ratio for reactant mixing.

In this work these concepts are applied to a diffusion flame microreactor with small nozzle diameters and high outer to inner jet velocity ratios. The microreactor is performance-tested by the example of silica nanoparticle production from hexamethyldisiloxane (HMDSO) as precursor and checked for its ability to produce nanoparticles over a broad range of sizes and structures.

2.2 Experimental

A schematic of the experimental set-up is shown in Fig. 2.2. The diffusion flame microreactor (Fig. 2.3) consisted of five concentric stainless steel tubes, the outer tube having an inner diameter of 8 mm while the i.d. of the inner tube was 1.8 mm. The gap between the tubes was about 0.8 mm. An argon stream saturated with HMDSO (Fluka, purity > 99%) was introduced into the CH\(_4\) / O\(_2\) / N\(_2\) diffusion flame of the microreactor. The gases (Pan Gas, purity > 99.999 %) were delivered from cylinders with the flow rates being monitored by calibrated mass flow controllers (Bronkhorst EL-Flow).
Before entering the reactor, argon was bubbled through the precursor flask placed in a thermostated bath (Huber Unistat CC) and was saturated with the organometallic compound. By setting the bath temperature, controlled amounts of precursor could be delivered into the reactor at an Ar flow rate of 300 cm³/min. At 25°C the HMDSO delivery rate was 0.73 mmol/min if 100% saturation of the argon stream was achieved. This was confirmed by weighing the flask before and after experiments. The precursor delivery tube and the burner were heated with heating tapes 20°C above the bath temperature to avoid condensation of precursor. The precursor laden argon stream was delivered through the center tube, methane through the first annulus and the oxidant through the second annulus. This flame configuration corresponds to a C-flame (Pratsinis et al., 1996).
In another flame configuration the methane joined the precursor stream in the inner tube. The oxidant was delivered through the third tube while nitrogen flowed through the second tube in order to lift the flame a few millimeters from the burner mouth, thus preventing the deposition of particles. This flame configuration is hereafter referred to as the D-flame. In all experiments the methane flow rate was kept constant at 500 cm$^3$/min. The flow rate of the oxidant stream was varied between 1000 and 12000 cm$^3$/min. These flow rates gave a range of 1.6 to 19.2 for the velocity ratio between the outer annular and inner center jets. Either pure oxygen or an oxygen/nitrogen mixture of molar ratio 2:1 were used as oxidant. Experiments with higher nitrogen fractions were not carried out as the flame could not be stabilized and even was extinguished at oxidant flow rates larger than 6000 cm$^3$/min.

The flame was surrounded by a quartz chimney (glass cylinder, i.d. = 140 mm) in order to achieve stable burning. A stainless steel filter holder with a glass fiber filter (Whatman GF/A) was mounted on top of this cylinder. The product particles were collected on the filter by the aid of a vacuum pump (Vacuubrand RE5). Each experiment was reproduced twice.

The specific surface area (SSA) of the collected powders was analyzed by $\text{N}_2$ adsorption at 77K employing the BET isotherm (Micromeritics, Gemini 2360). The
results were cross-checked by recording a full adsorption isotherm (Micromeritics ASAP 2010 Multigas system). Samples of the synthesized powders for analysis by transmission electron microscopy (TEM, Hitachi H600, 100 kV) were taken in the gas phase with the aid of a thermophoretic sampler (Dobbins and Megaridis, 1987). Therefore, a carbon-coated copper grid was inserted for 200 ms into the aerosol stream at the location of the filter on the center axis of the burner. Thermophoretic sampling was also carried out in-situ the C-flame operated with an oxygen flow rate of 2000 cm³/min. The sampling locations were at the center axis of the flame at distances of 10, 30, and 50 mm from the burner mouth. The grid remained 50 ms in the flame.

Centerline temperatures of the flames were recorded with a 0.5 mm thin wire Pt-Rh thermocouple (Type B, Omega Engineering) in the absence of precursor and were corrected for radiation loss. The thermocouple could be positioned precisely in the rotational symmetric flame by moving the burner with a 2-stage positioning table (Föhrenbach GmbH). Heat loss by radiation was estimated using an emissivity of 0.18 for a Pt wire (Lide, 1997) and a temperature of 100°C at the walls of the combustion chamber. Heat transfer by forced convection to the 1.4 mm bead of the thermocouple was calculated with the outlet velocity of the center jet in lack of gas velocities in the flame. Those are assumed to be higher than the outlet velocity due to acceleration of the flow at the centerline by the high velocity annular jet and thermal expansion of the gas. Therefore, the reported data overpredicts the flame temperature by 50 to 100 K. The combustion of HMDSO has an enthalpy of combustion of –1409 kcal/mol (Arkles, 1995). For the investigated system, this accounts to about 20% of the methane reaction heat. Thus, temperatures of the precursor-laden flame are higher than in the methane flame.

Gas mixing in the triple coaxial jet of the microreactor was investigated by computational fluid dynamics (CFD), employing the commercial software Fluent 5.2. Therefore, an isothermal (T = 300 K) coaxial jet with the dimensions of the microreactor was simulated for atmospheric pressure, neglecting chemical reactions. The argon and methane flow rates were the same as in the powder production experiments of the C-flame. Oxygen flow rates of 2000, 4000 and 6000 cm³/min were used. Due to the rotational symmetry of the coaxial jet, the simulation was carried out
with a two-dimensional grid with a symmetry axis. A k-ε turbulence model was applied for the calculation. Coaxial jet mixing was also simulated for a larger reactor (outer diameter: 20 mm) used by Briesen et al. (1998a) for synthesis of silica nanoparticles. Conditions applied were the same as for the microreactor, with following gas flow rates: argon (center tube): 250 cm$^3$/min, methane (first annulus): 400 cm$^3$/min, oxygen (second annulus): 2500, 3800 and 5500 cm$^3$/min.

### 2.3 Results and Discussion

#### 2.3.1 Jet Mixing

CFD-velocity vectors of the near nozzle region of the microreactor are shown in Fig. 2.4 along with concentration profiles of argon for oxygen flow rates of 2000, 4000 and 6000 cm$^3$/min. For the lowest oxygen flow rate, the outlet velocity of the annular oxygen jet is 6 m/s and therefore about 3 times higher than the exit velocities of the methane and argon streams, which are 2.0 and 1.8 m/s, respectively. The annular jet entrains environmental air at its outer boundary and draws fluid from the two central jets at its inner boundary, radially deflecting the center jets (Fig. 2.4a). The lack of fluid in the center region results in a zone of subatmospheric pressure which deflects the annular jet toward the axis (Chigier and Béer, 1964). Increasing the oxygen flow rate by a factor of two (Fig. 2.4b) increases the entrainment requirements of the outer annular jet. Within 0.5 mm from the nozzle exit, the methane and argon streams are deflected outward and drawn into the oxygen jet. The resulting lack of fluid in the central region forces the annular jet to draw fluid from itself to satisfy its entrainment requirements at the inside boundary. A toroidal recirculating vortex is set up with its center at 1.5 mm from the nozzle exit plane. A zone of subatmospheric pressure associated with this vortex deflects the annular jet toward the axis. Increasing the oxygen flow rate to 6000 cm$^3$/min increases the length and strength of the recirculating vortex, as is indicated by steeper velocity gradients (Fig. 2.4c). The location of the vortex center has moved to 1 mm from the exit plane. All center nozzle fluid is entrained by the annular oxygen jet after only 0.25 mm.
Fig. 2.4: Velocity vectors (left) of the near nozzle region of the present microreactor calculated by computational fluid dynamics along with lines of constant argon molar fraction (right). The oxygen flow rates through the outer annular jet were a) 2000, b) 4000 and c) 6000 cm$^3$/min.
Fig. 2.5: CFD-velocity vectors and lines of constant argon molar fraction for the reactor of Briesen et al. (1998a). Oxygen flow rates through the outer annular tube were a) 2500, b) 3800 and c) 5500 cm³/min.
The influence of increasing oxygen flow rate on gas mixing is demonstrated by argon concentration profiles presented in Fig. 2.4, showing lines of constant argon molar fraction. At an oxygen flow rate of 2000 cm³/min an inner potential core of 1.5 mm length containing pure argon can develop (Fig. 2.4a). The centerline molar fraction of argon is reduced to 0.5 after about 4 mm. The inner core does not form when the oxygen flow rate is increased to 4000 cm³/min (Fig. 2.4b). The center nozzle fluid is immediately drawn toward the annular oxygen stream as is indicated by the radial deflection of the lines of constant argon concentration. A centerline Ar molar fraction of 0.5 is found at 0.8 mm from the nozzle exit, showing that the intensity of gas mixing increases with increasing outer to inner jet velocity ratio. Further increase of the O₂ flow rate to 6000 cm³/min reduces this distance to about 0.3 mm. The steep concentration gradients indicate that fast mixing of the oxygen and argon streams takes place.

Velocity vectors and argon concentration profiles of the reactor of Briesen et al. (1998a) are presented in Fig. 2.5. At an oxygen flow rate of 2500 cm³/min, giving an outlet velocity of 0.5 m/s and an outer to inner jet velocity ratio of about 0.2, the lack of entrainment fluid for the annular jet results in backstreaming of center nozzle fluid (Fig. 2.5). Still, a potential inner core of about 3 mm length can develop and the molar fraction of Ar on the centerline is decreased to 0.5 after 10 mm, compared to 4 mm in the case of the microreactor. Increasing the outer annular jet flow rate to 3800 cm³/min (Fig. 2.5b) leads to the formation of a toroidal recirculating vortex in the center region. Unlike in the case of the microreactor, where the vortex region consists mainly of premixed annular jet fluid, it mainly consumes argon in the jet configuration of Briesen et al. (1998a). Resulting, an inner potential core can develop and the centerline argon molar fraction of 0.5 is reached after 5 mm, compared to 0.8 mm for the microreactor. Thus, mixing of argon and oxygen is assumed to be less intense. For the highest oxygen flow rate of Briesen et al. (5500 cm³/min, Fig. 2.5c) a flow field similar to the one observed with the microreactor for oxygen flows of 4000 and 6000 cm³/min is established. However, due to the larger size of the reactor, Ar concentration gradients are less steep and a centerline Ar molar fraction of 0.5 is reached after about 2 mm.
2.3.2 Flame Characterization

Figure 2.6 depicts the centerline temperature profiles of the C-Flame with pure oxygen as oxidant (filled symbols) as well as oxygen/nitrogen ratios of 2:1 (open symbols). In both cases the maximum flame temperature was decreased when the oxidant flow rate was increased. For pure oxygen, the maximum temperatures were 2400, 2030, and 1850 K for oxygen flows of 4000, 6000, and 8000 cm$^3$/min, respectively. When oxidant streams of the same flow rates but different composition ($O_2:N_2 = 2:1$) were used, the maximum flame temperatures were approximately 2100 K (4000 cm$^3$/min), 1850 K (6000 cm$^3$/min) and 1800 K (8000 cm$^3$/min).

Fig. 2.6: Temperature profiles of the C-flame measured at the flame centerline in absence of precursor for pure oxygen flow rates of 4000, 6000, and 8000 cm$^3$/min (filled symbols) and for an oxidant composition of $O_2:N_2 = 2:1$ (open symbols).

Temperatures of flames with oxidant flow rates of 2000 cm$^3$/min could not be recorded as the temperature exceeded the melting point of the thermocouple alloy. The location of the maximum flame temperature with respect to the burner mouth decreased with
increasing oxidant flow rate. For pure oxygen as oxidant, that maximum was at 8, 6, and 4 mm while for \( \text{O}_2: \text{N}_2 = 2:1 \) the maximum was at 12, 10, and 8 mm for oxidant flow rates of 4000, 6000 and 8000 \( \text{cm}^3/\text{min} \), respectively. The addition of nitrogen to the oxygen stream diluted the oxygen concentration in the flame and lowered the flame temperature up to 300 \( \text{K} \), delaying the combustion of the fuel. For both oxidant compositions, lower oxidant flow rates lead to longer and colder flames. This is explained by gas cooling and mixing.

The cooling effect is reflected in the adiabatic flame temperature given in Table 2.1. With increasing excess air number \( \lambda \), defined as the ratio of oxygen present in the flame to the amount of oxygen necessary for stoichiometric combustion, the adiabatic flame temperature decreases from 3650 \( \text{K} \) (2000 \( \text{cm}^3/\text{min} \) \( \text{O}_2 \)) to 1611 \( \text{K} \) (8000 \( \text{cm}^3/\text{min} \) \( \text{O}_2 \)) since unused oxygen dissipates the generated heat. In addition to this, higher velocities of the annular oxidant stream increase the entrainment of ambient air into the flame, further lowering the flame temperature.

**Table 2.1: Adiabatic flame temperatures for different reactant compositions in the C-flame in absence of the precursor.**

\[ \lambda = \frac{\text{(Amount of oxygen provided)}}{\text{(Amount of oxygen for stoichiometric combustion)}}. \]

<table>
<thead>
<tr>
<th>Oxidant flow rate</th>
<th>cm(^3)/min</th>
<th>2000</th>
<th>4000</th>
<th>6000</th>
<th>8000</th>
<th>10000</th>
<th>12000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda ) (pure ( \text{O}_2 ))</td>
<td>--</td>
<td>1.6</td>
<td>3.3</td>
<td>4.9</td>
<td>6.6</td>
<td>8.2</td>
<td>9.9</td>
</tr>
<tr>
<td>( T_{\text{ad.}} ) (pure ( \text{O}_2 ))</td>
<td>K</td>
<td>3650</td>
<td>2495</td>
<td>1939</td>
<td>1611</td>
<td>1395</td>
<td>1241</td>
</tr>
<tr>
<td>( \lambda ) (( \text{O}_2: \text{N}_2 = 2:1 ))</td>
<td>--</td>
<td>1.1</td>
<td>2.2</td>
<td>3.3</td>
<td>4.4</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( T_{\text{ad.}} ) (( \text{O}_2: \text{N}_2 = 2:1 ))</td>
<td>K</td>
<td>3720</td>
<td>2525</td>
<td>1962</td>
<td>1631</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The mixing effect arises from the different velocities of the fuel and oxidant jets, since the exchange of mass between two parallel fluid streams increases with increasing velocity ratio of the streams (Günther, 1974). For the microreactor, the average outlet velocity of the inner argon and methane jets was 1.8 m/s (Fig. 2.4). An increase in the
annular oxidant jet velocity from 6 to 18 m/s by increasing the flow rate from 2000 to 6000 cm³/min thus resulted in an increase of the velocity ratio from 3.2 to 9.6. As was shown by computational fluid dynamics (Fig. 2.4), this results in faster mixing of the reactants for the concentric diffusion flame for higher oxidant flow rates leading to a shift of the maximum flame temperature closer to the burner mouth.

Similar, but less pronounced effects of the oxidant flow rate on the maximum flame temperature were observed by Zhu and Pratsinis (1997) and Briesen et al. (1998a). They reported, however, first an increase in the maximum flame temperature when the oxidant flow rate was increased from 2500 to 3800 cm³/min which was followed by lower maximum temperatures when the flow rate was further enlarged. The initial increase in flame temperature was attributed to the fact that flames with oxygen flow rates below 3800 cm³/min were understoichiometric.

Unlike in the microreactor, a significant influence of the oxidant flow rate on the location of the maximum flame temperature was not observed by Briesen et al. (1998a). While the temperature maximum of their flame stayed at about the same position for oxygen flow rates of 2500 and 5500 cm³/min, a noticeable shift was observed for similar flow rates in the microreactor. Different effectiveness of reactant mixing resulting from varying oxygen to fuel velocity ratios and different burner size is accounted for this observation. At O₂ flow rates of 2000 and 6000 cm³/min the oxygen to fuel velocity ratios were 3.2 and 9.6 for the microreactor and 2.5 and 5.5 for the reactor of Briesen et al. (1998a). Intense reactant mixing observed for the microreactor within the first millimeters from the nozzle exit was not achieved with the larger reactor for the employed flow rates. Thus, a significant shift of the temperature maximum to short distances from the burner mouth did not take place.

Fig. 2.7 shows centerline temperature profiles of the D-flame for different oxidant flow rates and compositions. The effect of the oxidant flow rate on the flame temperature was comparable to that of the C-flame but maximum temperatures were about 200 to 350 K lower than the ones of the corresponding C-flames. These results differ from those of Pratsinis et al. (1996), who recorded higher flame temperatures for the D-configuration than the C-configuration of their co-flow methane/air diffusion flame. The flow field of the reactor of Pratsinis et al. (1996) was different from the one
of the microreactor here as they did not introduce nitrogen between the methane and oxygen streams. The additional nitrogen stream imposes a diffusion barrier for the species taking part in the combustion leading to longer and colder flames. This effect also explains the location of the maximum D-flame temperatures at larger distances from the burner mouth compared to the C-flames, as can be seen in Figs 2.6 and 2.7.

![Graph showing temperature profiles of the D-flame](image)

**Fig. 2.7:** Temperature profiles of the D-flame measured at the flame centerline in absence of precursor for pure oxygen flow rates of 2000, 4000, 6000, and 8000 cm\(^3\)/min (filled symbols) and an oxidant composition of O\(_2\):N\(_2\)=2:1 (open symbols).

### 2.3.3 Nanoparticle Synthesis

The influence of the oxidant flow rate on the specific surface area of fumed silica nanoparticles made with the diffusion flame microreactor operated in C-flame configuration is shown in Fig. 2.8 for the two oxidant compositions. For pure oxygen, the SSA of the product particles increased from 40 to about 200 m\(^2\)/g when the oxygen flow rate was increased from 1000 to 12000 cm\(^3\)/min. The corresponding average primary particle diameters ranged from 63 to about 13 nm, when spherical particles...
were assumed. The SSA followed a rather steep increase for oxygen flow rates up to 5000 cm$^3$/min and thereafter approached an asymptotic value of 200 m$^2$/g at 8000 – 12000 cm$^3$/min. For flow rates up to 9000 cm$^3$/min the standard deviation of the measurements was smaller than 2 % of the average specific surface area, showing that the primary particle size could be precisely controlled with the microreactor.

The evolution of the SSA with increasing oxidant flow rate was similar when one third of oxygen was substituted by nitrogen. However, the maximum specific surface area of the silica powders was only 150 m$^2$/g for oxidant flow rates of 7000 and 8000 cm$^3$/min. For smaller oxidant flow rates, the average particle diameter was only a little lower with O$_2$/N$_2$ than with pure O$_2$. Flames with oxidant flow rates of less than 2000 cm$^3$/min and more than 8000 cm$^3$/min could not be stabilized. Therefore, powder production experiments were not carried out for these configurations.

![Graph showing the influence of oxidant flow rate on specific surface area](image)

**Fig. 2.8: Influence of the total oxidant flow rate on the specific surface area of silica particles synthesized in the C-flame with two different oxidant compositions.**
The temperature history and the residence time of the particles in the flame are known to be key factors influencing particle growth (Pratsinis, 1998) and thus determine the product particle size. The particle residence time in the flame depends on the gas flow rates of the reactor in two ways: First, the particle growth region is shorter at higher gas (oxidant) flow rates since the flame temperature decreases faster (Fig. 2.6). Second, the particles move faster if the velocity of the gas is increased which further decreases the residence time. Thus, smaller particles are made at higher oxidant flow rates as was observed in the particle production experiments (Fig. 2.8).

Now, the flame temperature determines the rate at which particles sinter after collisions. Ulrich and Subramanian (1977) reported that silica always formed partly sintered branchy agglomerates of small primary particles when the flame temperature was lower than about 2000 K. This was attributed to low sintering rates at these temperatures. At higher flame temperatures sintering becomes faster resulting in larger primary product particles. Here, higher flame temperatures were measured for lower oxidant flow rates (Fig. 2.6), consistent with a lower product particle SSA for both oxidant compositions (Fig. 2.8). Now, when the flame temperature maximum was shifted to larger distances from the burner by replacing some of the oxygen by nitrogen (Fig. 2.6), particles experienced high temperatures for a longer time and could sinter to larger primary particles. This explains why powders made in flames with O$_2$/N$_2$ had a lower specific surface area than those produced in undiluted methane/oxygen flames.

For temperatures above 2000 K, where sintering is fast, the primary particle size and the particle morphology also depend on the collision frequency, as was shown by Ulrich and Subramanian (1977) and Ulrich and Riehl (1982). At high number concentration, silica particles collide more frequently than they can fuse, resulting in fractal-like agglomerates. At low number concentration, particles completely coalesce after collisions and form spherical product particles. Thus the residence time of particles at temperatures above 2000 K strongly affects the morphology of the product powder.

Here, oxidant flow rates of 6000 cm$^3$/min and higher resulted in maximum flame temperatures below 2000 K (Fig 2.6). Product particles made in these flames were agglomerates of small primary particles as can be seen from TEM pictures presented in Figs 2.9c and 2.9d for pure oxygen as oxidant. Particles made in flames with oxidant
flow rates below 6000 cm$^3$/min experienced temperatures above 2000 K for considerable time (Figs 2.6). The corresponding product powder TEM pictures (Figs 2.9a and 2.9b) show that this resulted in the formation of spherical particles. When the oxygen flow rate was 4000 cm$^3$/min (Fig. 2.9b), only a few such spherical particles were formed and the degree of particle agglomeration was similar to the one at higher O$_2$ flow rates (Figs 2.9c, d). This indicates that the particle residence time at high temperatures (above 2000 K) was still too short for complete particle coalescence. When the flame temperature was increased further by decreasing the oxygen flow rate to 2000 cm$^3$/min a large number of rather big (50 – 100 nm diameter) spherical particles with a low degree of agglomeration was made (Fig. 2.9a). Agglomerates of small primary particles ($dp \approx 30$ nm) were found as well, indicating that the particles had experienced different temperature histories arising from temperature gradients perpendicular to the flame centerline.

![TEM pictures](image_url)

Fig. 2.9: TEM pictures of product silica nanoparticles synthesized in the C-flame using pure oxygen at flow rates of a) 2000, b) 4000, c) 6000 and d) 8000 cm$^3$/min.
Particle growth in the flame with 2000 cm$^3$/min O$_2$ flow is illustrated by thermophoretic sampling at 10, 30, and 50 mm from the burner mouth (Fig. 2.10). At the lowest location, particles were still agglomerated (Fig. 2.10a), indicating low temperatures close to the burner mouth. At 30 mm some agglomerates had fused into larger spherical particles (Fig. 2.10b). Smaller fractal-like agglomerates were also present, many of which were attached to the larger spheres. Only spherical particles were observed at 50 mm (Fig. 2.10c) as the small particles in Fig. 2.10b had completely fused into the large ones, consistent with theory. Even though sintering necks between the particles can not be detected in Fig. 2.10c, the large number of agglomerates in the product powder (Fig. 2.9a) indicates, however, that coagulation and fusion still continues in the upper part of the flame.

![Fig. 2.10: TEM pictures of fumed silica obtained by thermophoretic sampling in the C-flame (O$_2$ flow rate: 2000 cm$^3$/min) at a) 10, b) 30, and c) 50 mm from the burner. Particles grow from fractal-like agglomerates at 10 mm to spherical particles at 50 mm.](image)

The results of the silica nanoparticle synthesis in the D-flame are presented in Fig. 2.11, reporting the specific surface area as a function of the oxidant flow rate for the two oxidant compositions. For pure oxygen, (circles) the increase in SSA with increasing O$_2$ flow rate was similar to the one observed for the C-flame (Fig. 2.8). However, the maximum SSA of about 240 m$^2$/g (corresponding BET-equivalent particle diameter: 11 nm) obtained here with the D-flame at 10000 cm$^3$/min O$_2$ flow exceeded the one of the C-flame by 40 m$^2$/g. On the other hand, the D-flame produced smaller particles at
oxygen flow rates below 8000 cm$^3$/min. Similar findings were made for the dilution of the oxygen stream with nitrogen (squares in Figs 2.8 and 2.11).

For the D-flame the maximum flame temperature was reached at larger distances from the burner mouth than for the C-flame, especially for small oxidant flow rates (Figs 2.6 and 2.7). As a result, the time for silica particles to grow by coagulation into branchy agglomerates was longer for the D-flame configuration. When the melting point of silica ($T_{\text{melt}} \approx 1800$ K, Ulrich and Riehl, 1982) was reached at prolonged residence times, fusion continued and the collision frequency diminished resulting in particles with lower specific surface area for oxidant flow rates below 8000 cm$^3$/min (pure oxygen) or 6000 cm$^3$/min ($O_2/N_2$). This resulted in the formation of mainly non-agglomerated and spherical silica particles at 2000 cm$^3$/min oxygen flow as is shown in Fig. 2.12. At higher oxidant flow rates the melting point of silica was not reached anymore (Fig. 2.7). Sintering took place at slower rates resulting in higher specific surface area powders for the D-flame configuration.

Fig. 2.11: The effect of the oxidant flow rate on the specific surface area of silica particles synthesized in the D-flame with two oxidant compositions.
The results of nanoparticle synthesis with the diffusion flame microreactor can be best compared with Briesen et al. (1998a), as their reactor was operated with similar gas flow rates in the C-flame configuration and was also used for the production of silica nanoparticles from hexamethyldisiloxane as precursor. A comparison of the maximum specific surface area obtained with oxygen as oxidant shows that the microreactor produced much smaller particles. Briesen et al. could synthesize particles with a SSA of about 42 m²/g at their highest oxygen flow rate of 5500 cm³/min. At the same flow rate, the microreactor made particles with a specific surface area that is about four times higher, as can be seen in Fig. 2.8. The difference can be explained by shorter residence times of the particles in the flame of the microreactor and steeper temperature gradients. The small size of the reactor results in outlet velocities that are 15 times higher for similar volume flow rates. Consequently less time is available for particle growth. Furthermore, the velocity ratio between the oxidant and precursor/fuel jets is about 1.5 times higher in the case of the microreactor and with 1.8 mm the inner reactor nozzle diameter is 2.8 times smaller. Thus, reactant mixing is enhanced in the case of the
The microreactor was also more sensitive to an increase of the oxygen flow rate than the larger reactor of Briesen et al. (1998a) opening a broader operation window and giving rise to higher flexibility in product quality. An increase in oxygen flow from 2000 to 6000 cm$^3$/min resulted in a 2.8 fold increase of the specific surface area. Briesen et al. (1998a) observed only an increase by 1.2 for similar oxygen flow rates. A broader range of temperature profiles of the microreactor, expressed by the shift of the maximum temperature from the burner mouth is accounted for this observation.

2.4 Conclusions

A co-flow diffusion flame reactor with a diameter of less than 1 cm was developed and performance-tested for synthesis of silica nanoparticles. The influence of the oxidant flow rate on the nanoparticle properties was investigated for two flame configurations and oxidant compositions. The specific surface area of the produced powders could be precisely controlled from 40 to 200 m$^2$/g in the case of the C-flame configuration and between 30 and 240 m$^2$/g in the case of the D-flame configuration when oxygen was used as oxidant. The use of an oxygen/nitrogen mixture in the molar ratio of 2/1 as oxidant gave specific surface areas that were as much as 50 m$^2$/g lower. Spherical and non-agglomerated silica particles could be synthesized in the D-flame at an oxygen flow rate of 2000 cm$^3$/min. The process of coagulation and sintering was shown by thermophoretic sampling as a function of flame height. The small-scale diffusion flame
reactor exhibited improved properties generally attributed to microreactor systems. This was shown, for example, by enhanced reactant mixing in the flame as was indicated by the measured flame temperature and calculated concentration profiles. The microreactor was more sensitive to changes in oxidant flow rates than a larger scale reactor operated with similar reactant flows. This opened a broader window of operation, making it possible to produce high surface area fractal-like particles as well as spherical ones by merely changing the oxidant flow rate.
2.5 References


3 Reactor Design for Nanoparticle Synthesis in Diffusion Flames

Abstract

The scaling-up of diffusion flame aerosol reactors is investigated for synthesis of silica and titania nanoparticles from organometallic precursors. Three co-flow burners of different dimensions are studied at various precursor, oxidant and fuel flow rates. An operation line relating product particle size with reactant concentration, flow rate and burner size is developed. As a result, conditions are identified showing how the three reactors can produce same size silica and titania nanoparticles at different production rates. An operation diagram is obtained for different silica production rates and a scale-up procedure is developed.

3.1 Introduction

With the recent awareness in nanoparticles and their promising properties there is renewed interest in better understanding processes for their inexpensive and flexible manufacture. Flame reactors that are routinely used for industrial manufacture of nanostructured commodities (pigments, carbon blacks, fumed silica) for over a century may be one of the best processes for making a spectrum of oxide nanoparticles. Unfortunately, these reactors have been developed through evolutionary research to make, typically, a single product with tight specifications. As a result, there is little information regarding process design and scale-up for new products.

Diffusion flame reactors are of special interest in manufacture of oxide nanoparticles for their capacity to safely and flexibly produce particles of different sizes and compositions. While the effect of process variables on the performance of diffusion flame aerosol reactors and product powder characteristics is reasonably well understood (Pratsinis, 1998), little is known on design correlations for flame aerosol reactor scale-up. For a fully turbulent coaxial jet flow aerosol reactor producing SiC, Sadakata et al. (1996) reported that the entrance fluid conditions, the reactor temperature and pressure,
the initial reactant gas concentration and the ratio of nozzle diameter to nozzle outlet velocity must be kept constant in scale-up. Smart (1998) showed that reactant mixing is determined by the reactant velocities and burner geometry and derived correlations for constant velocity and constant residence time scaling of turbulent jet flames. He pointed out that it is impossible to scale a burner to achieve basic thermo-chemical structural features using either constant velocity or residence time scaling. Jang (1999) observed that the product particle size decreased when the burner tube diameter was increased at constant reactant flow rate. However, for fast reaction kinetics the length of the flame and the volume of the reaction zone in which particle growth takes place, is controlled by the rate at which the reactants are mixed (Chen and Driscoll, 1990; Villermaux and Rehab, 2000). Correlations describing reactant mixing in diffusion flame aerosol reactors might therefore facilitate scale-up as, typically, the oxidation reactions are very fast during nanoparticle synthesis (Pratsinis, 1998).

Here, overventilated co-flow diffusion flame aerosol reactors made of concentric jet burners are investigated (Pratsinis et al., 1996). The oxidizer (oxygen) flows through the outer annulus and typically has higher outlet velocity than the combined center jet of fuel and precursor. For given fuel and precursor flow rates through the burner, the oxygen flow rate can be varied over a broad range resulting in different reactant mixing regimes. At low oxygen flow rates, the oxidant jet velocity is similar to that of the fuel/precursor jet, resulting in laminar diffusion flames in which molecular diffusion competes effectively with flow mixing. When the annular jet (oxygen) velocity is larger than that of the center jet (fuel/precursor), eddies form on the interface (the shear layer) between the two jets introducing flame turbulence that enhances flow mixing (Abramovich, 1963). Chigier and Beér (1964) showed how flow mixing in cold-flow turbulent double concentric jets was accelerated when the annular jet velocity was increased over that of the inner jet. Villermaux et al. (1994) reported the formation of a recirculating vortex in the central, near-nozzle region of coaxial water jets when the velocity of the annular jet was more than 6 times larger than that of the center jet. This moved the jet mixing zone closer to the nozzle outlet as was shown by flow visualization (Rehab et al., 1997). Such a recirculating vortex was also observed in cold-flow CFD-simulations of co-flow aerosol reactors (Chapter 2). Chen and Driscoll (1990) and Peters (2000) reported that strong mixing of a fuel jet with co-flowing
oxidant might even result in locally premixed flames. This shows that the burner outlet velocity difference strongly influences reactant mixing and therefore the onset of particle growth in diffusion flame aerosol reactors.

Flame quenching by entrainment of cold gases in the far field of the jet determines the end of particle growth when a critical quench temperature is reached (Ulrich, 1971). For the far field gas entrainment, the mixing characteristics in the near-nozzle region of coaxial jets become unimportant and the only dynamically relevant jet property is its momentum flux (Dahm and Mayman, 1990). The momentum flux remains invariant with downstream distance and equals the source momentum flux determined with the average outlet velocity of the coaxial jet. An increase in average jet outlet velocity and therefore in momentum flux increases the entrainment of surrounding fluid into the flame. In double concentric jet flames, increasing the annular jet flow rate (velocity) decreases the relative contribution of the center jet to the total momentum flux and flame quenching is governed by the high velocity outer jet. This indicates that the annular to center jet velocity difference might be an important design parameter for reactant mixing and flame quenching in co-flow diffusion flame aerosol processes.

Here, synthesis of silica and titania nanoparticles is systematically investigated by oxidation of hexamethyldisiloxane (HMDSO) and titanium-tetra-isopropoxide (TTIP) as precursor in three diffusion flame reactors. These reactors are operated at the same precursor and fuel flow rates over a range of oxygen flow rates controlling the degree of gas mixing during particle formation. For each material, a single operation line is developed relating the average product particle diameter (measured by nitrogen adsorption) to burner outlet conditions for the three reactors covering the laminar and turbulent flame regimes. Process scale-up is investigated leading to the development of a reactor operation diagram.

3.2 Experimental

Figure 3.1 shows the experimental set-up with the co-flow diffusion flame reactor, the reactant delivery system and the particle collection unit. The flame reactor consisted of
three concentric tubes. An argon stream carrying the precursor (HMDSO or TTIP) vapor was introduced through the center tube, while methane and oxygen flowed through the second and third tubes (first and second annulus), respectively. This configuration is a classic, single diffusion flame that has been referred to as C-flame (Pratsinis et al., 1996).

Fig. 3.1: Schematic of the experimental set-up with reactant delivery system (evaporator), diffusion flame reactor and glass fiber filter for product particle recovery.
All gases were of high purity (Pan Gas, 99.999%) while their flow rates were controlled by calibrated mass flow meters (Bronkhorst EL-Flow F201). Prior to experiments, the HMDSO (Fluka, purity > 99 %) and the TTIP (Aldrich, purity > 97%) were distilled and only the high purity precursor monomer fraction was recovered for experiments. An evaporator (Bronkhorst CEM 100 W) and a liquid mass flow meter (Bronkhorst Liqui Flow) were used to deliver a constant stream of precursor vapor. The evaporator, the burner and all reactant delivery tubes were heated to 75 °C and 175 °C in experiments with HMDSO and TTIP, respectively, well above their saturation temperatures of 25 °C (HMDSO) and 125 °C (TTIP) to prevent condensation. The flame was surrounded by a stainless-steel chimney of 140 mm i.d. to assure stable burning. Product particles were collected with the aid of a vacuum pump (Vacuubrand RE 5) on a glass fiber filter (Whatman GF/A) mounted on a stainless-steel filter holder located on top of the chimney. The filter temperature was measured with a K-type thermocouple.

Three burners were used and referred to as 1, 2 and 3, having outer diameters of 5.6, 10.0, and 27.0 mm, respectively. Figure 3.2 shows the detailed dimension of the burners. In the standard set of experiments, all burners were operated with argon, methane and precursor flow rates of 0.3 L/min, 0.5 L/min, and 6.5 g/h, respectively, while the oxygen flow rate varied from 1 to 50 L/min. It should be noted that the 6.5 g/h precursor flow rate resulted in 5 g/h of SiO₂ and 2 g/h of TiO₂. In additional experiments, the standard conditions for silica production were scaled by a factor of 0.25, 0.5, 3 and 5.

![Burner Dimensions](image)

*Fig. 3.2: Geometric dimensions (in mm) of the investigated burners 1 – 3.*
Furthermore, the flame configuration in burners 1 and 2 was changed by introducing the methane stream together with the Ar - HMDSO stream (standard conditions) into the center tube while 0.3 L/min nitrogen was provided through the first annulus. This flame configuration has been referred to as D-flame (Pratsinis et al., 1996).

The specific surface area (SSA) of all product powders was measured by nitrogen adsorption at 77 K, employing the BET isotherm (Micromeritics Gemini 2360). Assuming equally sized spherical particles, the BET-equivalent average particle diameter was calculated as $d_p = 6 / (\rho_i \times SSA)$, with $\rho_{SiO_2} = 2200$ kg/m$^3$ and $\rho_{TiO_2} = 3840$ kg/m$^3$ (anatase titania, as determined by X-ray diffraction). Transmission electron microscopy (TEM, Hitachi H600, 100 kV) was used to determine the morphology of the filter powders. To measure the degree of gas mixing in the absence of combustion, cold-flow centerline argon concentrations were recorded with a mass spectrometer (Balzers Omnistar GSD 300) in the precursor-free flow field of burner 2 at heights up to 5 cm from the burner mouth. The burner was operated at standard experimental conditions and at flow rates scaled up by 5. The sampling probe (0.15 mm i.d. glass capillary supported by a 1 mm o.d. stainless steel tube) was directly connected to the mass spectrometer.

### 3.3 Results and Discussion

#### 3.3.1 Comparison of Flame Aerosol Reactors

Figure 3.3 shows the BET-equivalent particle diameter of silica produced with the three burners at standard conditions as a function of the oxygen flow rate. The BET-equivalent average particle diameter decreases with increasing oxygen flow rate in all burners, consistent with Zhu and Pratsinis (1996). At a given oxygen flow rate, bigger primary particles are produced with larger reactors. For instance, at 10 L/min oxygen flow, 13, 18 and 84 nm primary particles are made using burners 1, 2, and 3, respectively. This can be explained by examining the velocity difference between the fuel/precursor and oxidant streams that determine reactant mixing and flame quenching.
regimes of the three reactors. For example, for burner 3 at 10 L/min O₂ flow, the oxygen average outlet velocity is 0.52 m/s while the average outlet velocity of the combined argon/HMDSO and methane stream is 0.19 m/s (Table 3.1). At these conditions, a long and hot laminar diffusion flame is formed that is not disturbed by the small velocity difference between the fuel and oxidant stream resulting in rather large (84 nm) particles. In contrast, burner 1 at the same oxygen flow rate, results in an oxygen outlet velocity (30 m/s) which is about 10 times larger than that of the combined argon/HMDSO and methane stream (2.7 m/s). This results in a short turbulent flame which produces small primary product particles by fast reactant mixing and subsequent rapid quenching (Chapter 2).

Fig. 3.3: BET-equivalent silica particle diameter as a function of the oxygen flow rate for burner 1 (triangles), 2 (circles), and 3 (squares), operated with the same precursor and fuel flow rates. Three different operation lines are obtained, each giving smaller particles at higher O₂ flow rates.
Table 3.1: Outlet velocities (in m/s) of burners 1 – 3 for standard conditions at 75°C. The outlet velocity of the combined argon and methane jets (Ar + CH₄) is the sum of the two flow rates divided by the combined outlet area of the two inner tubes.

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>CH₄</th>
<th>Ar + CH₄</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burner 1</td>
<td>2.07</td>
<td>3.33</td>
<td>2.71</td>
<td>18.16</td>
</tr>
<tr>
<td>Burner 2</td>
<td>0.33</td>
<td>1.46</td>
<td>0.63</td>
<td>5.53</td>
</tr>
<tr>
<td>Burner 3</td>
<td>0.25</td>
<td>0.14</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>Ar CH₄ O₂</td>
<td>0.3 L/min 0.5 L/min 0.8 L/min</td>
<td>6 L/min 10 L/min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These different operational regimes of the burners for the same O₂ flow justify the wide use of the oxygen or oxidant flow rate for control of product particle size in the literature (Pratsinis et al., 1996; Briesen et al., 1998; Cho and Choi, 2000; Jang and Kim, 2001). For reactor scale-up, however, a common correlation of primary particle size with flow conditions for different burners is needed. A general design correlation for diffusion flame aerosol reactors should therefore be based on the similarity of flow mixing parameters such as the reactant outlet velocities accounting for reactor geometry (Smart 1998) rather than the readily measured reactant flow rates.

Figure 3.4 now shows how the data of Fig. 3.3 collapse onto a single operational line when plotted as a function of the velocity difference of the burner outlet oxygen – fuel streams. Here, the fuel velocity is the sum of the argon and methane flow rates divided by the combined outlet area of the argon and methane jets in each burner, giving velocities of 2.71, 0.63 and 0.19 m/s for burners 1, 2 and 3, respectively (Table 3.1). This operation line is related to the flow mixing parameters but is not directly dependent on burner size and oxygen flow rate (Fig. 3.3). The similarity of the product particle diameters shows that particles experienced similar temperature-collision histories in different reactors when the oxygen flow rate is adjusted to give the same reactant outlet velocity difference. Increasing the velocity difference decreases the primary particle diameter, consistent with Fig. 2.8 (Chapter 2) and Briesen et al. (1998). The largest primary particles of 84 nm are produced at 0.3 m/s velocity difference, while the smallest of 13 nm are produced at 28 m/s. This size reduction with increasing oxygen velocity is attributed to shortened particle residence times in the hot regime of the flame.
and reduced particle concentration. Reduced residence times arise from shorter flames closer to the burner by faster reactant mixing and increased flame quenching (Chen and Driscoll, 1990) as well as an increase in total gas velocity at higher oxygen flow rates. This was confirmed by temperature measurements and cold flow CFD-simulations for the burner 1 (Chapter 2). Furthermore, the increased entrainment of cold gases with higher oxygen velocity reduces the particle concentration and lowers the flame temperature, leading to reduced particle growth rates by less collisions and longer sintering times (Zhu and Pratsinis, 1996).

![Graph showing BET-equivalent silica particle diameter as a function of the oxygen – fuel outlet velocity difference for burner 1 (triangles), 2 (circles), and 3 (squares). All reactors produce same size particles at the same outlet velocity difference, giving one common operation line.](image)

**Fig. 3.4:** BET-equivalent silica particle diameter as a function of the oxygen – fuel outlet velocity difference for burner 1 (triangles), 2 (circles), and 3 (squares). All reactors produce same size particles at the same outlet velocity difference, giving one common operation line.
The three reactors cover different regions of the operation line but have significant overlap. The largest burner 3 has velocity differences of 0.3 – 2.4 m/s and operates in the laminar flame regime, giving primary particles of 84 – 52 nm (squares in Fig. 3.4). The smallest burner 1 (triangles) produces particles of 54 to 13 nm at $\Delta v = 1.8 – 28$ m/s, respectively. Similar to burner 3, the flame of burner 1 is laminar for low velocity differences, but turns turbulent for $\Delta v > 5$ m/s. The overlapping region between 1 and 18 m/s (BET-equivalent particle diameters: 62 and 16 nm) is covered by burner 2 (circles). The operation range for each reactor is defined by combustion stoichiometry and flame lift-off. The flame of burner 1, for example, is understoichiometric for $\Delta v < 1$ m/s. Particles produced at $\Delta v = 0.3$ m/s (63 nm BET-equivalent diameter, not shown in Fig. 3.4) deviate from the operation line toward smaller diameters (reactor 3 produces 84 nm primary particles at this velocity difference). When the oxygen flow rate was reduced further to give fuel-rich flames at negative velocity differences, soot-silica was formed. Velocity differences larger than 30 m/s resulted in incomplete combustion of the precursor (soot formation) and even flame lift off ($\Delta v = 35$ m/s) and extinction for burner 1. Similar observations were made for burner 2. The operation range of reactor 3 did not end at 2.4 m/s but was not extended to larger velocity differences for limitations with product particle handling and collection. Here, an oxygen flow rate of 50 L/min was necessary to obtain 52 nm primary particles at 2.4 m/s. The same particle size could be produced with reactor 2 operated at less than 1/10 of this oxygen flow rate.

Figure 3.5 shows the operation line of Fig. 3.4 (solid line) along with silica synthesis data from HMDSO oxidation in C-type CH$_4$/O$_2$ flames diffusion (hexagons) by Briesen et al. (1998) and in D-type diffusion flames for burners 1 (triangles) and 2 (circles). Figure 3.5 shows that the BET-size data of silica particles made in the D-flames of burners 1 and 2 follow the operation line of the C-flame. For the D-flame, the argon, HMDSO and methane flow rates were the same as in the C-flame experiment and the fuel outlet velocity calculation was equally based on the flow rates through the two inner tubes (center pipe and first annulus), thus adding the additional 0.3 L/min nitrogen to the fuel flow. Figures 2.8 and 2.11 (Chapter 2) showed silica particles of different specific surface area for the C- and D-flames, when the SSA was plotted as a function of the oxygen flow rate, in agreement with similar observations of Pratsinis et
al. (1996) for titania. The similarity of the BET-equivalent diameters of particles made in the C- and D-flame here by using the concept of equal outlet velocity difference indicates that the operation line is also valid for other configurations of overventilated single diffusion flames operated with the same fuel and precursor flow rates. The success of the operation line in explaining data also from another diffusion flame reactor of Briesen et al. (1998) indicates its potential for reactor scale-up.

Fig. 3.5: BET-equivalent diameter of silica particles produced in the D-flame of burners 1 (triangles) and 2 (circles) as a function of the outlet velocity difference compared to the C-flame operation line. Both single diffusion flame reactors follow the same operation line. Diffusion flame data of Briesen et al. (1998) (hexagons) also falls on this operation line, indicating its validity for other flame aerosol reactors. For high velocity differences the operation line approaches the average primary particle size obtained in premixed flames by Briesen et al., 1998 (diamonds).
Figure 3.5 shows that the operation line asymptotically approaches a minimum average primary particle diameter of 13 nm at high velocity differences ($\Delta v = 20 – 30$ m/s). This particle size is similar to the premixed flame data of Briesen et al. (1998) obtained for 1.5 – 15 g/h HMDSO flow (11 to 18 nm, diamonds).

A premixed flame represents indeed a limiting case of co-flow diffusion flames (Beér et al., 1963) and local premixing can occur at high velocity differences between the fuel jet and the surrounding oxidant (Chen and Driscoll, 1990). Peters (2000) relates the local premixing to entrainment of oxidant into his high velocity fuel jet. Here, the opposite case for entrainment of the low velocity fuel jet into the high velocity oxidant jet applies, leading to similar results. The premixed-like flame conditions at high velocity differences can be explained by fast reactant mixing in a recirculating vortex near the burner outlet (Chapter 2, Fig. 2.4; Villermaux et al., 1994). The asymptotic approach of a minimum BET-equivalent particle diameter of about 13 nm at 20 – 30 m/s, which is similar to that of silica made in premixed flames (Briesen et al., 1998), indicates the limitation of diffusion flames for synthesis of smaller particles at the employed reactant conditions and co-annular burner design. This can be explained by fast precursor conversion at high temperatures, followed by high collision rates among small particles, which almost instantaneously coalesce until they become large enough to exhibit macroscopic viscosity and surface tension (Ulrich and Subramanian, 1977; Hurd and Flower, 1988). Tsantilis et al. (2001) modeling silica particle growth in the premixed flame of Briesen et al. (1998), reported that primary particles grow to 11 nm diameter after only 3 mm from the burner. Thus, even for the shortest diffusion flames employed here at high $\Delta v$, the residence time in the flame is long enough for the primary particles to grow to a similar size (13 nm). Faster flame quenching could not be realized due to flame lift-off and blow-out at $\Delta v > 35$ m/s.

The other limiting case of co-flow diffusion flames is that having fuel and oxygen streams of the same velocity (Beér et al., 1963). Figure 3.5 shows that in the longest flames with close to zero velocity difference, the largest primary particles are obtained. In these flames, the primary particle size can reach an upper limit when fully coalesced particles have grown large enough to reduce the particle concentration sufficient for negligible further particle growth by coagulation. In high temperature gas phase
synthesis processes, coagulation is negligible when the residence time is shorter than the characteristic time for coagulation. For silica synthesis in tubular hot wall reactors of about 1500 °C, this is the case at number concentrations of $10^{13} / \text{m}^3$ or less (Seto et al., 1997). Here, the smallest particle concentration is in the order of $10^{15} / \text{m}^3$ for the largest particles of 84 nm BET-equivalent diameter made with burner 3, assuming that the total reactant flow provided into the burner is increased by a factor of 10 by jet entrainment and flame temperature. Thus, the upper primary particle size limit by negligible particle collisions is not reached for the flames investigated here, which is supported by the continuous increase in primary particle diameter when the velocity difference approaches zero (Fig. 3.4).

Figure 3.6 presents the BET-equivalent diameter of titania nanoparticles made with burners 1 – 3 as a function of the outlet velocity difference for reactant conditions similar to that of silica but half the TiO$_2$ concentration than that of SiO$_2$.

![Fig. 3.6: BET-equivalent diameters of titania nanoparticles made with burner 1 (triangles), 2 (circles), and 3 (squares) as a function of the oxygen – fuel outlet velocity difference. As for silica (Fig. 3.4), a common operation line is obtained for the three flame aerosol reactors.](image)
As for silica, a common operation line is obtained. The largest titania primary particles of 88 nm are made at 0.5 m/s velocity difference while the smallest of about 20 nm are produced at $\Delta v = 20$ m/s and higher. This shows that the concept of equal velocity differences can be applied to materials with markedly different sintering behavior, such as silica and titania (Ulrich and Subramanian, 1977; Seto et al., 1997). Silica sinters by viscous flow and due its large viscosity, silica particle growth in flames tends to be controlled by sintering (coalescence-limited particle growth, Ulrich and Subramanian, 1977), even though at high temperatures and sufficiently low concentrations the coagulation rate can become smaller than the sintering rate (collision-limited particle growth) as reported by Tsantilis et al. (2001). Titania sinters by solid state diffusion at much higher rates than silica by viscous flow (Xiong et al., 1993). As a result, titania particles fully coalesce at lower temperature than silica (Seto et al., 1997). Thus, titania nanoparticle growth in flames is more likely to be collision-limited. Also, at the same flame synthesis conditions titania grows to larger primary particles than silica (Ehrman et al., 1998). This was also observed here for all velocity differences (Figs 3.4 and 3.6), even though the amount of Ti delivered into the flame was only about half that of Si.

### 3.3.2 Process Scale-up

Figure 3.7 depicts the BET-equivalent diameter of silica particles produced with the three burners in C-flame configuration (burner 1: triangles, 2: circles, and 3: squares) as a function of the velocity difference for the standard conditions (open symbols, 5 g/h SiO$_2$) and an increase in production rate by a factor of 3 (filled symbols, 15 g/h SiO$_2$) and 5 (dot-centered symbols, 25 g/h SiO$_2$). The scale-up was carried out by increasing the fuel/precursor flow rates through the two inner tubes (Ar/HMDSO and CH$_4$) by the same factor.

Figure 3.7 shows that for each fuel flow rate an operation line is obtained. All of these operation lines are similarly shaped giving smaller average primary particle diameters at higher oxygen-fuel velocity differences. The higher the production rate, the larger the primary particles produced at each velocity difference. For instance, at a velocity difference of about 2, particles of 57, 71 and 86 nm BET-equivalent diameter
are produced at 5, 15, and 25 g/h SiO$_2$ production rate, respectively. At high velocity differences ($\Delta v > 15$ m/s), the primary particle size approaches asymptotically a minimum for each production rate. At $\Delta v = 20$ m/s these minimum average primary particle diameters are 13, 19 and 27 nm for 5, 15 and 25 g/h SiO$_2$ production rate, respectively.

![Graph](image)

**Fig. 3.7:** Burner operation lines for the standard experiment (5 g/h SiO$_2$, open symbols) and for production rate scale-up by 3 (15 g/h SiO$_2$, filled symbols) and 5 (25 g/h, dotted symbols). At each production rate, burner 1 (triangles), 2 (circles) and 3 (squares) follow similar-shaped operation lines which are shifted to larger average primary particle diameters at higher production rates.

The increase in average primary particle diameter with increasing production rate might be explained by longer particle residence times at higher temperatures and/or higher
particle concentrations in the flame. As the precursor concentration and the velocity difference determining reactant mixing were kept constant during scale-up, the effect of particle concentration can be discarded. Increasing the production rate increased the energy content of the flame and the flame temperature. As a result, particle coalescence was faster than particle coagulation for longer residence time resulting in larger particles. This explains the increase of the primary particle size at large $\Delta v$ when the diffusion flame behaves as a premixed flame.

Figure 3.8 shows centerline Ar concentrations measured in the precursor-free cold flow of burner 2 for fuel (Ar and CH$_4$) flow rates corresponding to 5 g/h (open symbols) and 25 g/h (filled symbols) SiO$_2$ production rate and velocity differences of 2 m/s (circles) and 15 m/s (triangles). The argon concentration was normalized to the one of pure argon measured directly at the burner mouth. For short distances from the burner mouth, pure argon is detected for all flow conditions. This region of pure center nozzle fluid is referred to as the potential core of the concentric jet (Fig. 2.1 (Chapter 2); Chigier and Beér, 1964; Villermaux et al., 1994). For the case of a higher velocity annular (oxygen) jet investigated here, fluid from the potential core of the lower velocity center (Ar and CH$_4$) jet is continuously entrained into the annular jet (Chigier and Beér, 1964). After the annular jet has entrained all center nozzle fluid, it is deflected toward the center line (Chigier and Beér, 1964), resulting in a rapid decay of the argon concentration to about 30% of the initial value for all flow conditions (Fig. 3.8). This fast decay is followed by a slower decrease in argon concentration to less than 5% at 5 cm from the burner. For both fuel flow rates, the length of the potential core is significantly shorter for the higher velocity difference of 15 m/s (triangles) than for $\Delta v = 2$ m/s (circles), in agreement with similar concentration measurements by Chigier and Beér (1964) and cold flow CFD-simulations for burner 1 here (Chapter 2, Fig. 2.4). This is attributed to higher entrainment rates at higher annular (oxygen) jet velocity. Specifically, for the standard fuel flow rate and $\Delta v = 2$ m/s (open circles) and 15 m/s (open triangles), the potential core length is 0.5 and 0.1 cm, respectively. Now, when the fuel flow rate is scaled up by 5, the potential core length increases to 1.7 cm (2 m/s, filled circles) and 0.7 cm (15 m/s, filled triangles), respectively. This increase in potential core length with increasing fuel flow rate can be attributed to the higher fuel jet momentum flux by higher outlet velocities but similar entrainment rates of the fuel
into the oxygen jet due to constant annular to center jet velocity differences (2 or 15 m/s).

Fig. 3.8: Cold-flow centerline argon concentration profiles for burner 2 operated at fuel flow rates corresponding to SiO$_2$ production rates of 5 g/h (open symbols) and 25 g/h (filled symbols) and $\Delta v = 2$ m/s (circles) and 15 m/s (triangles). The argon concentration decays faster at higher velocity difference and smaller fuel flow rate.

The increase in cold-flow potential core length by 3.5 (2 m/s) and 7 (15 m/s) for the fuel flow scale-up by 5 corresponds to a similar increase in visible flame length (Table 3.2) by 3 ($\Delta v = 2$ m/s) and 5 ($\Delta v = 15$ m/s) when the silica production rate (fuel flow rate) is scaled up from 5 to 25 g/h. This indicates the similarity of jet mixing in the cold flow and the flame in agreement with Béer et al. (1963) investigating the cold flow and flames of double concentric jets. Thus, the change in potential core length during scale-up can give an estimate for the length change of the flame front, which is
established at locations where fuel and oxygen mix in stoichiometric proportions and thus envelopes the potential core of pure center nozzle fluid (Ar/HMDSO and CH₄) (Turns, 2000).

**Table 3.2: Visible flame heights and oxygen outlet velocities for burner 2 at production rates of 5 – 25 g/h and velocity differences of 2, 5, and 15 m/s.**

<table>
<thead>
<tr>
<th>Production Rate</th>
<th>Flame Height, cm</th>
<th>O₂ outlet velocity, m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 m/s</td>
<td>5 m/s</td>
</tr>
<tr>
<td>5 g/h</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>15 g/h</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>25 g/h</td>
<td>27</td>
<td>18</td>
</tr>
</tbody>
</table>

After inception of particle formation and collision-limited particle growth near the flame front, the freshly formed particles follow trajectories on the oxygen-rich side upstream of the flame front (Johannessen et al., 2001). The particle residence time in this region of coalescence-limited growth thus depends also on the outlet velocity of the annular oxygen jet, which increases by 2 (Δv = 2 m/s) and 1.2 (Δv = 15 m/s) when the production rate is scaled up by 5 (Table 3.2). This increase in velocity is significantly less than the increase in flame length (potential core length, Fig. 3.8), showing that the particle residence time in the coalescence-limited growth zone is longer at higher production rates. Thus, primary particles can sinter to larger size which is reflected by larger BET-equivalent product particle diameters at higher production rates (Fig. 3.7).

Figure 3.9 shows TEM pictures of silica nanoparticles produced with burner 2 at standard conditions (5 g/h SiO₂, left) and those of particles made in flames with the production rate scaled up by 5 (25 g/h SiO₂, right) for three different velocity differences of about a) 30, b) 11, and c) 4 m/s.

At the highest velocity difference branchy agglomerates of small primary particles are made at both production rates (Fig. 3.9a). Such agglomerates are usually obtained when the residence time in the flame is insufficient for complete particle coalescence (Ulrich and Subramanian, 1977). Thus, the formation of agglomerates is in agreement
with shorter flames by faster reactant mixing (Fig. 3.8; Table 3.2) at higher velocity difference.

Fig. 3.9: TEM pictures of product silica particles made at the standard flow rates (5 g/h SiO$_2$, left) and 5 times higher production rate (25 g/h SiO$_2$, right) for outlet velocity differences of a) 30, b) 11, and c) 4 m/s. The same particle morphology is obtained for the two production rates when the outlet velocity difference is kept constant. At low velocity difference spherical nanoparticles with little agglomeration are made while fractal-like agglomerates are obtained at high velocity difference.
The TEM pictures for $\Delta v = 11$ m/s (Fig. 3.9b) show agglomerates as well as large spherical particles for both production rates. The spherical particles have apparently formed by fusion of agglomerates. Less intense reactant mixing and reduced flame quenching at this smaller velocity difference results in longer and hotter flames, giving more time for particle sintering. The presence of large spherical particles as well as fractal-like agglomerates in the product powder indicates that particles experience different temperature-collision histories.

At the lowest velocity difference of 4 m/s, spherical particles of up to 200 nm diameter with little agglomeration are obtained for both operating conditions (Figure 3.9c). The long laminar flames established at this velocity difference give enough time for particle sintering. This is in agreement with Zhu and Pratsinis (1997) who also made spherical silica particles in a laminar methane/oxygen diffusion flame.

Figures 3.9b and c show that more and larger sized spherical particles are present in the product powder sample taken from the flame with higher production rate (right pictures). This is consistent with larger BET-equivalent diameters of particles made at 25 g/h compared to 5 g/h production rate and corroborates longer particle residence times in the flames at higher fuel flow rates. These TEM pictures show that the particle morphology remains similar during scale-up, even though the BET-equivalent particle diameter increases (Figure 3.7).

### 3.3.3 Process Design Correlations

The similarly shaped aerosol reactor operation lines shown in Fig. 3.7 can be described by a set of exponential functions relating the BET-equivalent product particle diameter to the process parameter $\Delta v$:

$$d_p = d_0 + (d_m - d_0) \times \exp (-0.3 \Delta v). \quad (3.1)$$

Here, $d_0$ is the smallest primary particle diameter at high velocity differences ($\Delta v \geq 20$ m/s) and $d_m$ represents the largest primary particle diameter at zero velocity difference. Thus, the operation line for a different production rate can obtained by only determining
the constants $d_0$ and $d_m$, greatly facilitating process scale-up. However, a direct correlation between the BET-equivalent particle diameter and the production rate cannot be derived from the operation diagram (Fig. 3.7).

Figure 3.10 shows the BET-equivalent particle diameter as a function of the production rate for $\Delta v = 0, 1, 2, 5, 10,$ and $20$ m/s. For production rates of 5, 15, and 25 g/h, the primary particle diameters at these velocity differences were obtained by interpolation of the experimental data (Fig. 3.7). BET-equivalent particle diameters obtained by additional experiments with burner 1 at 1.25 and 2.5 g/h production rate for $\Delta v = 1 – 20$ m/s are depicted also. For velocity differences up to 5 m/s, Fig. 3.10 shows an initial steep increase in primary particle diameter with increasing production rate up to about 5 g/h SiO$_2$ which becomes more moderate at higher production rates. For $\Delta v = 10$ and 20 m/s the steep increase in primary particle diameter at low production rates is not observed. However, heavy particle deposition on the burner rim during these experiments can have altered the flame and therefore the particle growth conditions.

Assuming equally sized and spherical product particles, a mass balance relates the particle diameter to the production rate as:

$$d_p = \left(\frac{m}{\rho n \pi \frac{1}{6}}\right)^{1/3},$$

where, $m$ is the production rate, $n$ the production rate of primary particles of diameter $d_p$ and $\rho$ the material density. The lines in Fig. 3.10 show that for each velocity difference the dependence of the BET-equivalent particle diameter on the production rate can be well described by a similar power law:

$$d_p = k m^{1/3}.$$  

Using equation (3.2), the factor $k$, which only depends on the velocity difference but not the production rate, relates to
This indicates that for each $\Delta v$ the number of primary particles produced per time stays rather constant when the production rate is increased. This is in agreement with constant precursor concentration and similar reactant mixing (constant $\Delta v$) during scale-up, leading to similar rates of particle nucleation and primary particle growth by coagulation and subsequent sintering.

\[
k = \left( \rho \frac{\pi}{6} \right)^{-1/3}.
\]

Fig. 3.10: BET-equivalent particle diameter as a function of the production rate for velocity differences of 0 – 20 m/s. For each velocity difference, the increase of the primary particle diameter $d_p$ with increasing production rate $m$ follows a power law $d_p = k m^{1/3}$ (lines).
For any production rate, the constants \( d_0 \) and \( d_m \) of equation (3.1) can now be determined by using values of \( k \) (eq. 3.3) at the limits of premixed flames (maximum velocity difference) and equal fuel-oxidant velocity diffusion flames (zero velocity difference):

\[ \Delta v \to \infty \ (\text{here for } \Delta v \geq 20 \text{ m/s}): \quad d_{0,i} = k_{\infty} \dot{m}_i^{1/3} \quad (3.5) \]

\[ \Delta v = 0: \quad d_{m,j} = k_0 \dot{m}_i^{1/3} \quad (3.6) \]

These design correlations show that scale-up of methane–oxygen co-flow diffusion flames producing silica nanoparticles from HMDSO can be achieved with a limited number of experiments at low production rate, which must be sufficient for safe determination of \( k_0 \) and \( k_{\infty} \). The resulting operation diagram then gives the process parameter \( \Delta v \) for production of silica particles of desired BET-equivalent diameter.

The study indicates that for the successful scale-up of these diffusion flame aerosol reactors the following requirements must be fulfilled: (1) The combustion must be stoichiometric or overstoichiometric to avoid the formation of soot. (2) The center jets of argon/HMDSO and methane should have similar outlet velocities which must be equal or smaller than the outlet velocity of the annular oxygen jet. (3) All fuel flow rates (HMDSO, Ar, and CH\(_4\)) must be scaled with the same factor.

3.4 Conclusions

Silica and titania nanoparticles were synthesized with three different co-flow diffusion flame reactors operated with the same precursor and fuel flow rates over a range of oxygen flow rates. Laminar as well as turbulent flames could be realized by variation of the oxygen flow rate. The burner outlet velocity difference of the fuel and oxygen jets was identified as a key parameter determining reactant mixing and flame quenching in these particle-producing flames. When the average primary product particle size was
reported as a function of this velocity difference, all reactors followed a common operation line for each material. This shows that particles of the same BET-equivalent diameter can be made with any of the overventilated single diffusion flames operated in C or D configuration, at the same oxygen – fuel outlet velocity difference. This greatly facilitates process design and control since the commonly adopted operation diagrams reporting the particle size as a function of the reactant flow rate give separate operation lines for each reactor. Different operation lines $d_p$ vs. $\Delta v$ were obtained when the particle production rate was scaled up by increasing the fuel and precursor flow rates with the same factor. All these operation lines follow the same exponential function differing only in the smallest and largest average primary particle diameter obtained at the premixed flame and equal reactant velocity flame limits, respectively. Based on a mass balance, a correlation of these constants with the production rate was derived, giving a scaling procedure for diffusion flame aerosol reactors.
3.5 References


4 Flame-Nozzle Synthesis of Nanoparticles with Closely Controlled Size, Morphology and Crystallinity

Abstract

A process for close control of primary particle size, morphology and crystallinity of flame-made nanoparticles is presented. According to this, freshly made titania aerosol nanoparticles are rapidly quenched in a critical flow nozzle, essentially freezing particle growth at desired levels. The nanoparticles are produced in a methane/oxygen diffusion flame reactor by oxidation of titanium-tetra-isopropoxide. Precise control of the average primary particle size, reduced agglomeration and phase composition is achieved by positioning of the quenching nozzle above the burner and controlling gas and precursor flow rates.

4.1 Introduction

Many new materials using nanoparticles require non-agglomerated spherical particles. For semiconductors, the particle size and shape must be well controlled to most efficiently exploit quantum confinement effects (Salata et al., 1994). In gas sensors, small-sized particles decrease the response time and increase the gas sensitivity while a low degree of agglomeration facilitates the production of thin films (Diéguez et al., 1996). In photocatalysis, spherical titania nanoparticles show a higher activity for CO oxidation than polyhedral particles (Juillet et al., 1973).

Flame aerosol synthesis is a cost-effective and versatile process for controlled production of nanoparticles (Pratsinis, 1998). For example, flame technology produces the most inexpensive nanostructured material, carbon black, for about $0.25 / lb. In flame reactors, the energy of a flame is used to drive chemical reactions of precursors resulting in clusters which further grow to nanoparticles by surface growth and/or coagulation and coalescence at high temperatures. The characteristics of flame-made
particles are controlled by reactant mixing and composition, additives and electric fields (Pratsinis, 1998). Formenti et al. (1972) reported an increase in titania primary particle diameter made from TiCl$_4$ with increasing oxy-hydrogen flame temperature and particle residence time. Vemury and Pratsinis (1995) reported the control of the primary particle size and phase composition of flame-generated nanoparticles by addition of Si, Al, and Sn chloride to the TiCl$_4$ stream. Zhu and Pratsinis (1996) observed that diffusion flames using air as oxidant and TiCl$_4$ produced agglomerates while non-agglomerated, perfectly spherical particles of about 240 nm were made by replacing air with oxygen. Glumac et al. (1998) reported the synthesis of non-agglomerated titania nanoparticles with average size of 10 to 20 nm in a low pressure premixed methane/oxygen flat flame burner.

Here a new way to control particle properties is presented by the example of titania. This continuous flame aerosol process produces ceramic nanoparticles with a high fraction of single spherical particles having diameters down to 6 nm. This is achieved by quenching the flame in a critical flow nozzle which rapidly stops particle growth. The aerosol quenching effect relies on gas expansion and mixing with ambient air drawn into the nozzle. Quenching techniques by jet expansion have hitherto been applied for pure sampling from the product flow stream of flame aerosol reactors (Ulrich and Riehl, 1982; Lindackers et al., 1997) or in low-pressure synthesis of nanoparticles by free jet expansion of vapors (Bowles et al., 1981). Here flow quenching is directly applied on the atmospheric pressure flame.

4.2 Experimental

A coflow diffusion flame aerosol reactor consisting of three concentric tubes (outer tube diameter: 5.6 mm) was used (Fig. 4.1). An argon stream of 0.75 L/min carrying 0.11 g/min titanium-tetra-isopropoxide (TTIP) vapor from an evaporator (Bronkhorst CEM 100W) flowed through the center tube while 0.5 L/min of methane and 4 to 6 L/min of oxygen flowed through the second and third tube, respectively. The evaporator, delivery tubes and the burner were kept at 150 °C to prevent condensation of TTIP vapor. A
critical flow (quenching) nozzle was placed above the burner (Fig. 4.1) and was connected to a filter holder with glassfiber filter. The 1.5 mm nozzle bore was drilled through the convex bottom of the nozzle (Alsint 99.7). The distance between burner mouth and nozzle bore (burner – nozzle distance) was varied from 5 to 50 mm. Product titania particles were collected on the filter with the aid of a vacuum pump maintaining a pressure of 150 mbar downstream of the nozzle.

Fig. 4.1: Schematic of the experimental set-up with the reactant delivery system, the diffusion flame reactor, the quenching nozzle and the glassfiber filter.
The BET-surface area (SSA) of the powders was analyzed by nitrogen adsorption (Micromeritics, Gemini 2360). Assuming all particles to be monodisperse spheres, the BET-equivalent particle diameter was calculated as \( d_p = \frac{6}{(\rho_{\text{TiO}_2} \times \text{SSA})} \), \( \rho_{\text{TiO}_2} = 4230 \text{ kg/m}^3 \). Samples of the synthesized powders for analysis by transmission electron microscopy (TEM, Hitachi H600, 100 kV) were taken in-situ from the flame by thermophoresis. The phase composition of the product powders was determined by X-ray diffraction (XRD, Bruker D8 Advance, CuK\(\alpha\) radiation).

4.3 Results and Discussion

Figure 4.2 shows TEM pictures of particles made in flames with 6 L/min O\(_2\) flow rate. For a fixed burner – nozzle distance of 15 mm, the samples were taken 10 mm above the burner (Fig. 4.2a), 250 mm above the burner without the nozzle (Fig. 4.2b) and with the nozzle (Fig. 4.2c). It can be seen from Fig. 4.2a that early in the flame most of the particles are individual spheres (Arabi-Katbi et al., 2001) while later on agglomerates of primary particles are formed (Fig. 4.2b). Fig. 4.2c shows that after nozzle quenching the primary particle size is similar to that observed in front of the nozzle (Fig. 4.2a). This indicates that little particle growth takes place after nozzle quenching. The presence of individual spherical particles as well as some agglomerates in the samples taken upstream (Fig. 4.2a) and downstream (Fig. 4.2c) of the nozzle indicates that particle size and morphology are frozen by the quenching procedure. Similar results were obtained when using 4 L/min oxygen flow rate.

Figure 4.3 shows the BET-equivalent diameter of titania nanoparticles made using the quenching nozzle as a function of the burner – nozzle distance at oxygen flow rates of 4 (squares) and 6 L/min (circles). The BET-equivalent diameters of particles collected at the filter without the quenching nozzle (filled symbols) were 21 nm and 16 nm at 4 and 6 L/min oxygen flow rate, respectively. This is consistent with the literature, increasing the oxygen flow rate decreases the particle diameter (Formenti et al., 1972; Zhu and Pratsinis, 1996). Now when the nozzle was placed 5 mm above the burner, the BET-equivalent diameter of the product particles was 6 nm, regardless of the
oxygen flow rate (Fig. 4.3). These particles are significantly smaller than those collected without the nozzle (16 or 21 nm). For the 6 L/min O₂ flame, this was observed for burner - nozzle distances up to 30 mm, showing that quenching of the aerosol with the critical flow nozzle essentially slows down particle growth downstream of the nozzle.

Fig. 4.2: TEM pictures of titania particles sampled from the gas phase, a) 10 mm above the burner, b) 250 mm above the burner (in front of the filter) without nozzle and c) 250 mm above the burner with quenching nozzle (O₂ flow rate: 6 L/min, burner - nozzle distance: 15 mm). Flame quenching with the nozzle stops particle growth and preserves particle size and morphology.
At larger burner – nozzle distances, the product particles have approached the size of 16 nm which was also obtained without the quenching nozzle. At these large burner – nozzle distances the aerosol temperature is sufficiently low by mixing with ambient air to stop particle growth before the aerosol enters the quenching nozzle so the latter is no longer effective.

**Fig. 4.3:** BET-equivalent diameter of titania particles produced in flames with quenching nozzle at oxygen flow rates of 4 and 6 L/min as a function of the burner – nozzle distance. Particles produced with nozzle quenching early in the flame are significantly smaller than those made without nozzle (filled symbols).

Decreasing the oxygen flow rate from 6 to 4 L/min results in larger particles for burner-nozzle distances above 15 mm. Smaller oxygen flow rates increase the aerosol concentration and the flame temperature, thus increasing the total number of particle collisions as well as the effective sintering rate resulting in larger particles (Formenti et al., 1972; Zhu and Pratsinis, 1996). When using 4 L/min oxygen flow rate and burner – nozzle distances of 40 mm and larger, the product primary particle size approaches that
obtained without nozzle (21 nm). These results further confirm the effect of nozzle quenching as discussed in the previous paragraph.

All particles made with a TTIP flow rate of 0.11 g/min show the characteristic XRD-reflections of anatase titania, irrespective of the use of the quenching nozzle. Flames with an increased TTIP flow of 0.28 g/min still produce anatase titania in the absence of the quenching nozzle. However, particles made with this precursor flow rate and the quenching nozzle show increasing composition of rutile titania up to 65 % for a burner - nozzle distance of 5 mm. This indicates that not only particle size and morphology can be controlled with the flame-nozzle process but also the crystallinity.

4.4 Conclusions

A new flame aerosol process for control of product particle properties was developed and performance-tested for the synthesis of titania nanoparticles. The process relies on rapid quenching of the flame aerosol with a critical flow nozzle placed in front of the particle-laden flame. High temperature gradients across the nozzle are achieved by flow expansion and mixing with entrained ambient air. This quenching procedure rapidly slows down particle growth downstream of the nozzle, thus preserving the particle size and morphology of the upstream aerosol. Product titania powders with a large fraction of individual spherical nanoparticles were obtained. For the investigated flames with oxygen flow rates of 4 and 6 L/min, the BET-average primary particle size could be precisely controlled within 6 to 21 nm by varying the burner - nozzle distance. Furthermore, the phase composition of the product powders could be controlled also by the burner - nozzle distance. Clogging of the nozzle did not occur, even after 10 hours of operation. In the current, not flow-optimized process, 70 – 80 % of the synthesized particles were collected on the filter. The remaining particles deposited inside the nozzle after the flow expansion. The process has high potential for successful application to other flame configurations and cost-effective synthesis of carbon, silica, alumina and other oxide and non-oxide ceramics with controlled size and limited degree of agglomeration.
4.5 References


5 Control of Flame Aerosol Synthesis by Nozzle Quenching

Abstract

A detailed study of the flame-nozzle quenching process introduced in Chapter 4 is presented for synthesis of titania nanoparticles by oxidation of titanium-tetraisopropoxide (TTIP) in a methane/oxygen co-flow diffusion flame reactor. The particle growth conditions in the flame can be precisely controlled by the quenching nozzle distance and gas and precursor flow rates. Thus, weakly agglomerated titania nanoparticles of 5 – 55 nm average primary particle diameter and 5 – 97 wt-% anatase content and the balance rutile can be made. An operation diagram shows that the independent control of the product primary particle diameter and the phase composition can be achieved making anatase or rutile nanoparticles with high or low specific surface area by varying the burner – nozzle distance and the TTIP flow rate.

5.1 Introduction

Combustion synthesis has been used to produce a wide range of oxide nanoparticles (Ulrich, 1984; Wooldridge, 1998; Pratsinis, 1998), non-oxide ceramics (Dufaux and Axelbaum 1995; Glassman et al., 1992) and even pure metals (Calcote and Felder, 1992). Among these processes, flame aerosol synthesis of carbon black, titania and silica are the most important ones industrially, as is apparent from an annual production volume of several million metric tons and particle production rates up to 25 metric tons per hour.

Compared to premixed burners, co-flow diffusion flame aerosol reactors offer high flexibility by broad operation windows and safety of operation (no flash-back). Temperature fields and residence times of these reactors, both key parameters for particle growth (Formenti et al., 1972), can be controlled by changing the reactant mixing configuration or varying the reactant flow rates (Pratsinis et al., 1996). However, the range of accessible product powders is still restricted since the flame temperature
and the length of the particle growth zone, determining the particle residence time, is usually coupled in these reactors. Typically, flame-made oxide particles grow by coagulation-coalescence from perfectly spherical particles to agglomerated ones, as it has been shown by thermophoretic sampling and transmission electron microscopy (Arabi-Katbi et al., 2001). High flame temperatures necessary for complete coalescence of the refractory compounds usually go along with extended particle growth zones while short flames exhibit lower temperatures, as was shown by computational fluid dynamics for co-flow diffusion flames making titania (Johannessen et al., 2001). As a result, spherical particles with a low degree of agglomeration made in hot flames usually have primary particle diameters of 100 nm and above while colder flames typically produce highly agglomerated primary particles with diameters down to a few nanometer (Zhu and Pratsinis, 1996; Pratsinis, 1998). Control of agglomeration has been achieved with sodium flames (Dufaux and Axelbaum, 1995), and low pressure flames (Glumac et al., 1998) but is still limited in classical flame aerosol reactors, making it difficult to attain non-agglomerate particles smaller than about 100 nm with these units (Dufaux and Axelbaum, 1995; Pratsinis, 1998). Such non-agglomerated nanoparticles are, however, of key interest as starting material for ceramics as dense particle packing can be achieved (Calcote et al., 1990; Dufaux and Axelbaum, 1995).

For titania, control of the phase composition along with the particle size is of importance for its large variety of applications, e.g. in pigments, UV-light scattering, photocatalysis or solar cells (Ahonen et al., 2001). Ohno et al. (2001) showed for instance, that mixtures of anatase and rutile titania had higher activity in the photocatalytic oxidation of naphthalene than pure anatase or rutile.

Here, a flame aerosol process is presented allowing precise control of the flame length and product particle size independently of the reactant flow rates. This is achieved by quenching the flame in a critical flow nozzle which rapidly stops particle growth. The aerosol quenching effect relies on gas expansion and mixing with ambient air drawn into the nozzle. Quenching techniques by jet expansion have been applied to combustion synthesis for sampling from the product flow stream of flame aerosol reactors (Ulrich et al., 1976; Lindackers et al., 1997) or product separation and collection (Calcote and Felder, 1992). Also, quenching by cross flow air has been used
in flame synthesis of zinc oxide nanoparticles (Hansen et al., 2001). Here, critical nozzle flow quenching is directly applied on an atmospheric pressure co-flow diffusion flame producing titania nanoparticles that are characterized by transmission electron microscopy, X-ray diffraction and nitrogen adsorption. The effect of the burner – nozzle distance on product particle characteristics is investigated at various precursor and oxidant flow rates and an operation diagram relating BET-equivalent diameter and phase composition of the product titania particles is developed.

5.2 Experimental

Figure 5.1 shows a schematic of the experimental set-up. A coflow-diffusion flame aerosol reactor consisting of three concentric stainless-steel tubes was used. The inner diameters of the tubes were 1.8, 3.5 and 4.8 mm and the tube wall thickness was 0.3 mm. An argon stream of 0.75 L/min carrying TTIP (Aldrich, purity > 97%) vapor from an evaporator (Bronkhorst CEM, 100 W) was introduced through the center tube, methane flowed through the first annulus at a rate of 0.5 L/min and oxygen was provided through the outer annulus at flow rates of 2 to 6 L/min. All gas (Pan Gas, purity > 99.999%) flow rates were monitored by calibrated mass flow controllers. The TTIP liquid flow rate into the evaporator was controlled by a liquid mass flow meter (Bronkhorst Liqui-Flow). The evaporator, precursor delivery tubes and burner were heated to 150 °C to prevent TTIP condensation.

A critical flow nozzle connected with a cylinder (i.d. = 140 mm) to a filter holder with glass fiber filter (Whatman GF/A) formed a gas expansion – particle collection unit which was positioned 0.5 – 5 cm above the burner mouth. The air-cooled stainless-steel expansion nozzle had a flat bottom at the side facing the burner with a 1.5 mm nozzle bore at the center that opened conically toward the filter. A 3-stage positioning system (Föhrenbach Unipos) was used to align the burner center axis with the nozzle bore and to select the distance between burner and nozzle. Throughout the experiments, a pressure of 150 mbar was maintained in the expansion chamber by a butterfly valve in the off-gas line. Product titania particles were collected on the filter with the aid of a vacuum pump. A rotameter connected behind a condenser at the outlet of the vacuum
pump allowed the determination of the gas flow rate through the critical flow nozzle. Particles were produced at 2 to 6 L/min oxygen flow rate, 6.5 g/h TTIP flow rate and burner-nozzle distances (BND) of 0.5 – 8 cm as well as without the nozzle. In addition, experiments were performed with 3 and 5 cm BND and 2 L/min O₂ flow rate but varying the TTIP flow rate from 1.63 – 26 g/h at constant 0.75 L/min Ar, thus, changing the TTIP concentration.

![Fig. 5.1: Schematic of the experimental set-up with the reactant delivery system, the diffusion flame reactor, the quenching nozzle and the glassfiber filter.](image-url)
The specific surface area (SSA) of the collected powders was analyzed by nitrogen adsorption at 77 K employing the BET isotherm (Micromeritics TriStar 3000). Assuming all particles to be monodisperse spheres, the BET-equivalent particle diameter was calculated as $d_p = 6 / (\rho_{\text{TiO}_2} \times \text{SSA})$, where $\rho_{\text{TiO}_2}$ is the weighted density of the particles ($\rho_{\text{Rutile}} = 4.26 \text{ g/cm}^3$ and $\rho_{\text{Anatase}} = 3.84 \text{ g/cm}^3$). X-ray diffraction (XRD) patterns of all powders were obtained with a Bruker D8 advance diffractometer operating with Cu(Kα) radiation. Crystallite size and phase composition were obtained using the fundamental parameter approach (Cheary and Coelho, 1992). Particle samples for analysis by transmission electron microscopy (TEM, Hitachi H600, 100 kV) were collected by thermophoresis (Dobbins and Megaridis, 1987; Arabi-Katbi et al., 2001) at various heights in the flame and at 8 cm downstream of the nozzle.

Centerline temperature measurements in the flame were made with a 0.5 mm thin wire Pt-Rh thermocouple (Type B, Omega Engineering) in the absence of TTIP. The employed TTIP concentrations would have raised the temperature by approximately 100 – 200 °C (Arabi-Katbi et al., 2001). The spatial resolution of the flame temperature measurement was 0.2 cm and the obtained data were corrected for heat loss by radiation, using an emissivity of 0.18 for the Pt wire. The centerline temperature downstream of the nozzle was recorded with a 1 mm R-type thermocouple at a distance of 0.8 cm from the nozzle exit.

5.3 Results and Discussion

5.3.1 Flame Characterization

Figure 5.2 shows how a particle-laden flame (6.5 g/h TTIP in 0.75 L/min Ar, 0.5 L/min CH₄ and 2 L/min O₂) is drawn into the nozzle. At close distance in front of the nozzle bore, the flame is contracted and confined to the region close to the center axis. In addition to the flame aerosol, ambient air is drawn into the nozzle, forming an enveloping sheath around the particle-laden combustion gases. This sheath air prevents deposition of particles at the nozzle walls by diffusion or thermophoresis, preventing, thus, clogging of the nozzle. Determination of the off-gas flow rate at the outlet of the
vacuum pump showed that, depending on burner-nozzle distance and flame temperature, 7 – 9 L/min of ambient air are drawn into the nozzle for the flame with 2 L/min O₂ flow rate. The sheath air rapidly mixes, quenches and dilutes the hot aerosol by 2 – 3 times in the expansion chamber downstream of the nozzle.

Fig. 5.2: The titania particle-laden flame is contracted into the nozzle, enveloped by a sheath of ambient air.

Figure 5.3 shows the centerline temperatures of the co-flow methane diffusion flame with 4 and 6 L/min oxygen flow without (crossed lines) and with the nozzle at 2 cm (squares) and 3 cm (triangles) above the burner. With 4 L/min oxygen flow and without the nozzle, the maximum flame temperature is about 1650 °C at 1.2 cm above the burner and drops to 550 °C at 5 cm above the burner. This temperature decrease is attributed to mixing of the combustion gases with excess supplied oxygen and entrainment of ambient air (Chapter 2). When the nozzle is placed at 2 or 3 cm above the burner (Fig. 5.3), the centerline temperature up to 0.6 cm in front of the nozzle drops by less than 100 °C compared to that obtained without the nozzle. This indicates that the entrained air from the nozzle does not influence significantly the flame upstream of the nozzle. Temperature measurements closer to the nozzle were not made since the thermocouple notably disturbed the contracted flame directly in front of the nozzle.
Figure 5.2 indicates, however, that at short distances (< 1cm) in front of the nozzle the flame is influenced by the ambient quenching air drawn into the nozzle. For the flame with 6 L/min oxygen flow rate the maximum temperature is 1500 °C at 0.4 cm above the burner and drops to 400 °C at 5 cm. In general, increasing O₂ flow rates result in steeper temperature drop downstream of the burner due to rapid mixing with excess supplied oxygen (Chapters 2, 3). When the nozzle is placed at 2 and 3 cm in the 6 L/min O₂ flame the upstream centerline temperature is not influenced, supporting the results for the flame with 4 L/min O₂ flow rate.

Fig. 5.3: Centerline temperatures of flames with 4 and 6 L/min oxygen flow rate without the nozzle (crosses) and with the quenching nozzle placed 2 (squares) and 3 cm (triangles) above the burner. Centerline temperatures measured 0.8 cm downstream from the nozzle at 4 L/min O₂ flow rate (diamonds) for burner – nozzle distances of 0.5 to 5 cm show that nozzle quenching decreases the downstream gas temperature by 250 – 770 °C.
Figure 5.3 also shows the centerline temperature 0.8 cm downstream from the nozzle opening (diamonds) for burner-nozzle distances (BND) of 0.5 to 5 cm and the 4 L/min oxygen flame. The highest temperature of 880 °C was measured for 0.5 cm BND, the lowest (250 °C) for 5 cm BND. Thus, the nozzle decreases the temperature by 770 °C and 250 °C at 1.3 cm (0.5 cm BND) and 4.8 cm (4 cm BND) above the burner, respectively. Downstream nozzle temperatures for the less oxygen-rich flames (e.g. 2 L/min O₂) were up to 100 °C higher while those for the flame with 6 L/min O₂ flow rate were up to 50 °C lower.

5.3.2 Particle Size and Morphology

Figure 5.4 depicts the BET-equivalent diameter (circles, left axis) and phase composition (squares, right axis) of titania particles produced without the quenching nozzle as a function of the oxygen flow rate along with typical TEM pictures of product powders made at 2 and 6 L/min oxygen flow. Increasing the oxygen flow rate from 2 to 6 L/min decreased the BET-equivalent particle diameter from 55 to 17 nm, in agreement with Zhu and Pratsinis (1996) for titania from TiCl₄ and Briesen et al. (1998) for silica from hexamethyldisiloxane in similar methane/oxygen co-flow diffusion flames. This is attributed to shorter flames with increasing oxygen flow rate (Fig. 5.3). Surplus oxygen that is not taking part in combustion and increased entrainment of ambient air from higher oxygen outlet velocity (Johannessen et al., 2001) result in reduced residence times of particles at high temperature and subsequently slower sintering and reduced primary particle diameter.

Figure 5.4 shows that all powders were ≥ 90 wt-% anatase, independent of the oxygen flow rate in agreement with Zhu and Pratsinis (1996) for methane-oxygen diffusion flames and TiCl₄ oxidation in excess O₂. The TEM pictures in Figure 5.4 show that titania product particles made in the flame with 2 L/min oxygen flow were spheres with little agglomeration, indicating long particle residence times at high temperatures. In contrast, the shorter flame with 6 L/min oxygen flow rate produced agglomerate particles (Pratsinis et al., 1996; Johannessen et al., 2001).
Fig. 5.4: BET-equivalent diameter (circles, left axis) and anatase weight fraction (squares, right axis) of product titania particles as a function of the oxygen flow rate into the diffusion burner made without the quenching nozzle. Increasing the oxygen flow decreases the primary particle size and decreases the anatase content but increases the degree of agglomeration (TEM pictures for 2 and 6 L/min O₂ flow rate).

Figure 5.5 shows the BET-equivalent diameter of titania nanoparticles made with the quenching nozzle in flames with oxygen flow rates of 2 – 6 L/min as a function of the burner-nozzle distance (BND). At BND = 0.5 cm, product particles of 5 nm BET-equivalent diameter were obtained, regardless of the oxygen flow rate. These primary particles were 3 – 10 times smaller than those made without the nozzle (Fig. 5.4), showing that nozzle-quenching effectively freezes particle growth.

The independence of the average primary particle diameter from the oxygen flow rate for BNDs up to 2 cm indicates that nozzle quenching had arrested particle growth before excess oxygen flow had a chance to affect the late particle growth process. This may indicate further that flame temperatures were high enough for these particle sizes to
allow rapid coalescence after particle collisions (Wu et al., 1993). By observing titania sintering in a hot-stage electron microscope, George et al. (1973) reported a critical sintering temperature of 840 °C for rapid coalescence of titania nanoparticles similarly sized with the ones studied here. The centerline temperature profiles of the particle-free flames (Fig. 5.3) show that even the shortest flame (6 L/min oxygen flow rate) exhibited temperatures above 800 °C in this region. Temperatures in the particle-laden flame are expected to be even higher, since the combustion of TTIP is an exothermic reaction (combustion enthalpy: 8088 kJ/mol, Bradley et al., 1978) accounting for about 15 % of the total combustion enthalpy for the present flames. This supports the assumption that titania particle growth in the high temperature region (up to 2 cm above the burner) is governed by coagulation as coalescence is rapid and independent of the flame temperature for these particle sizes (Fig. 5.5).

![Fig. 5.5: BET-equivalent diameter of titania particles made with the quenching nozzle and an oxygen flow rate of 2 to 6 L/min as a function of the burner – nozzle distance. Flame aerosol quenching early in the flame decreases the average product particle diameter.](image-url)
At BNDs above 3 cm, product nanoparticles made with 6 L/min O₂ flow had approached the size of 17 nm which is identical to that obtained without the quenching nozzle (Fig. 5.4). At these distances, the nozzle was located well above the visible flame height and temperatures were less than 600 °C (Fig. 5.3). At these low temperatures, primary particle growth by sintering was already rather slow and the additional cooling coming from the nozzle quenching did not affect the product particle size. For oxygen flow rates of 5 and 4 L/min, this limit was reached at BNDs of 4 cm, where the same product primary particle size of 18 nm (5 L/min O₂) and 21 nm (4 L/min O₂) was obtained with and without the nozzle. At BND = 4 cm, the temperature of the flame with 4 L/min oxygen flow rate had fallen just below the characteristic temperature for rapid coalescence of these particle sizes (Fig. 5.3), which is consistent with the data of the 6 L/min O₂ flame.

In flames with 3 and 2 L/min oxygen flow rate, particle growth could still be controlled with the quenching nozzle at 5 cm BND as these flames have a longer high temperature zone than the flames using high oxygen flow rates. The BET-equivalent particle diameters were 26 nm and 28 nm while those obtained without quenching nozzle (Fig. 5.4) were 29 and 55 nm for the 3 and 2 L/min O₂ flames, respectively.

This shows that the operation window of the co-flow diffusion flame reactor (Fig. 5.4) could be extended to smaller primary particle sizes by control of the particle residence time in the flame with the quenching nozzle. A decrease or increase in pressure downstream of the nozzle to 100 or 200 mbar did not affect the particle characteristics since sonic nozzle flow was achieved at these pressures. For these critical flow conditions, the flow rate through the nozzle is only determined by the bore diameter but not the downstream pressure. The presence of critical nozzle flow for the downstream pressure range of 100 – 200 mbar was confirmed by constant flow rates measured at the outlet of the vacuum pump.

Figure 5.6 presents TEM pictures of titania particles thermophoretically sampled from the centerline of the 2 L/min O₂ flame at a) 1 and b) 5 cm above the burner in the absence of the nozzle. The titania particles are basically non-agglomerated spheres growing by rapid coalescence upon collision with increasing distance from the burner.
Figure 5.6 presents also the corresponding TEMs of particles collected at the filter but with the nozzle at BNDs of 1 cm (Fig. 5.6c) and 5 cm (Fig. 5.6d). These particles are significantly smaller than the ones collected on the filter in the absence of the nozzle (inset of Fig. 5.4) and consistent with the BET-data (Fig. 5.5). In addition, these particles have maintained their spherical shape and low degree of agglomeration after nozzle quenching for both BNDs.

Fig. 5.6: TEM pictures of titania particles sampled from the 2 L/min O₂ flame without the nozzle at a) 1 cm and b) 5 cm above the burner and those of particles sampled 8 cm downstream of the nozzle for burner-nozzle distances of c) 1 cm and d) 5 cm. The non-agglomerate state of the flame aerosol is preserved after nozzle quenching.
This indicates that the quenching rates achieved with the nozzle are high enough to suppress further particle growth and possible agglomeration at temperatures where sintering is effective (below about 800 °C for the titania particle sizes employed here (George et al., 1973)). The size of the nozzle-quenched particles (Figs 5.6c, d) is slightly smaller than that observed with particles thermophoretically sampled from the flame at the corresponding distance from the burner (Figs 5.6a, b). This is attributed to the mixing of particles of different flame streamlines in the nozzle. Thus, a sample taken downstream of the nozzle represents the whole flame aerosol population while the one taken thermophoretically from the flame centerline tends to neglect particles at the flame boundaries (Arabi-Katbi et al., 2001).

5.3.3 Particle Crystallinity

Figure 5.7 shows X-ray diffraction patterns of powders produced in the flame with 2 L/min O₂ flow rate with the nozzle at BNDs of a) 1, b) 3, and c) 5 cm and d) without the nozzle. The diffraction patterns of the powders made with the nozzle show the characteristic reflections of anatase and rutile with the anatase reflections becoming predominant at larger BND. Decreased peak broadening at increasing BND shows that the crystallites grew larger at longer residence time in the flame, in agreement with the increase in average primary particle diameter (Figs 5.5 and 5.6). An amorphous scattering hump is not observed in any of the diffraction patterns, indicating that all powders were predominantly crystalline.

Table 5.1: Anatase weight fraction of product powders made without the nozzle and with the nozzle at 0.5 to 5 cm BND in flames with 2 and 6 L/min oxygen flow rate.

<table>
<thead>
<tr>
<th>BND</th>
<th>cm</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>No nozzle</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_{Anatase}</td>
<td>2 L/min O₂</td>
<td>wt-%</td>
<td>75</td>
<td>56</td>
<td>70</td>
<td>72</td>
<td>80</td>
<td>84</td>
</tr>
<tr>
<td>X_{Anatase}</td>
<td>6 L/min O₂</td>
<td>wt-%</td>
<td>82</td>
<td>80</td>
<td>79</td>
<td>80</td>
<td>83</td>
<td>84</td>
</tr>
</tbody>
</table>
The analysis of these diffraction patterns by the fundamental parameter approach (Cheary and Coelho, 1992) gave 56, 72, and 84 wt-% anatase for 1, 3, and 5 cm BND, respectively (Table 5.1) and therefore increasing rutile content with decreasing BND.

**Fig. 5.7:** XRD patterns of product powders made in the 2 L/min oxygen flame and 6.5 g/h TTIP flow rate with the quenching nozzle at a) 5, b) 3, and c) 1 cm BND and d) without the nozzle. Early quenching in the flame increases the amount of rutile and decreases the average crystallite size. The powder made without the nozzle is predominantly anatase titania.
Rutile formation can be promoted by oxygen vacancies which are created at low oxygen partial pressures, as was reported by Iida and Ozaki (1961) and MacKenzie (1975) investigating the anatase-rutile phase transformation during calcination in atmospheres with different oxygen partial pressure. In the laminar diffusion flame here, the oxygen partial pressure in the particle growth zone should increase with increasing distance from the burner since more and more oxygen diffuses from the outer annular oxygen jet into the core region of the flame. This goes along with the formation of less rutile when particle growth is quenched with the nozzle at large BNDs. Without the nozzle, the diffraction pattern of the product powder shows the characteristic reflections of anatase titania and only a small rutile reflection at 27.45° corresponding to the rutile 110 plane (Fig. 5.7d). Here, the particle residence time in regions of high oxygen partial pressure was sufficient to produce powders of 97 wt-% anatase (Table 5.1). The average anatase crystallite size is 54 nm, which is in good agreement with the BET-equivalent particle diameter of 55 nm (Fig. 5.4), indicating that the particles are predominantly single anatase crystals. This has been observed also in HRTEM analysis of vanadia coated titania particles made with this reactor in similar flames (Stark et al., 2001).

It is interesting to note that also the product powder made at 0.5 cm BND has a rather high anatase content of 75 wt-%, compared to 56 wt-% at 1 cm BND at 2L/min O$_2$ flow (Table 5.1). This indicates that air drawn into the nozzle (Fig. 5.2) strongly changes the flame composition and increases the oxygen partial pressure at short BNDs. At 6 L/min O$_2$ flow rate the anatase fraction is about 80 wt-% independent of the burner – nozzle distance as the higher oxygen partial pressures are created early in the flame by fast turbulent reactant mixing promoting anatase formation (Chapters 2 and 3). The product powder made in the 6 L/min O$_2$ flame without the nozzle is 91 wt-% anatase compared to 97 wt-% for the 2 L/min O$_2$ flame (Table 5.1). This is attributed to shorter particle residence times in the flame with 6 L/min O$_2$ flow rate by faster flame quenching with excess oxygen (Fig. 5.3).

Figure 5.8 shows the influence of the TTIP flow rate (concentration) on the anatase weight fraction (squares), the average crystallite size of anatase (triangles) and rutile (diamonds) as well as the BET-equivalent particle diameter (circles), for powders made in flames with 2 L/min O$_2$ flow rate and a fixed burner-nozzle distance of 5 cm.
Increasing the TTIP flow rate from 1.63 to 26 g/h increases the BET-equivalent particle diameter from 14 to 40 nm. Since the nozzle keeps the flame length constant and the Ar, CH$_4$ and O$_2$ flow rates are constant also, the precursor/particle concentrations are the major parameters affecting particle growth here. The increase in primary particle diameter can thus be attributed to faster particle growth by higher particle concentrations in the flame, in agreement with George et al. (1973) in a premixed flame, Pratsinis et al. (1996) and Jang and Kim (2001) in diffusion flames using TiCl$_4$ as precursor as well as Kammler et al. (2001) for silica by oxidation of hexamethyldisiloxane.

Fig. 5.8: BET-equivalent particle diameter (circles, left axis), anatase (triangles, left axis) and rutile (diamonds, left axis) average crystallite size as well as phase composition (squares, right axis) of product powders made in flames with 2 L/min oxygen flow rate and the quenching nozzle placed at 5 cm above the burner for TTIP flow rates of 1.6 to 26 g/h. While the anatase weight fraction decreases with increasing TTIP flow rate, the BET-equivalent particle diameter increases following the 2/5 power-law dependence given by Koch and Friedlander (1991) for coagulation and rapid coalescence of spherical particles (thick solid line).
The BET data follow indeed the relationship $d_p \propto V_m^{2/5}$ (thick solid line) given by Koch and Friedlander (1991) for coagulation and rapid coalescence of spherical particles in the free molecular regime, where $d_p$ is the average particle diameter and $V_m$ the volume concentration of particles.

The increase in TTIP flow rate significantly changed the phase composition (Figure 5.8, squares) of the product powder from 85 to 18 wt-% anatase and the balance rutile. The higher rutile content at higher TTIP flow rate goes along with a decrease in the feed $O_2/Ti$ ratio from 850 to 53 at 1.63 and 26 g/h TTIP flow rate, respectively. This further supports the role of decreasing oxygen partial pressure for the increased formation of rutile (Fig. 5.7, Table 5.1). An increase in the rutile fraction of similar diffusion flame-made titania nanoparticles was also reported by Zhu and Pratsinis (1996), by replacing oxygen with air and thereby decreasing the feed $O_2/Ti$ ratio from 100 to 20. However, the obtained rutile weight fraction was always lower than 15 wt-% since the particles stayed sufficiently long in the oxygen-rich upper part of the flame. The formation of up to 82 wt-% rutile by use of the quenching nozzle at 26 g/h TTIP flow shows that a much wider range of phase compositions is accessible compared to powders made in flames without the nozzle.

Here, powders with more than 50 wt-% rutile showed a bluish coloration, typical for oxygen-deficient titania (Ehrlich, 1939), which further indicates that the $O_2/Ti$ ratio in the flame plays a key role for the control of the product powder phase composition. Wu et al. (1993) reported that high quenching rates may affect the mass transport within particles, and may result in the formation of metastable phases, in agreement with the formation of oxygen-deficient titania here. Hung and Katz (1992) similarly observed blue coloration in titania particles that were rapidly withdrawn from the flame by thermophoresis. The blue coloration of the particles here was stable in air up to 300 °C, at which the typical white color of titania pigment was restored in agreement with Haerudin et al. (1998). The phase composition of these powders did not change by the annealing procedure. Also, the formation of Magnéli phases $Ti_nO_{2n-1}$, with $n = 4$ to 10 (Andersson et al., 1957) was not observed in any of the product powder diffraction patterns, indicating that the oxygen deficiency of the titania particles was not sufficient for these phases to form or the corresponding crystal domains were too small to be
detected by XRD. The stability of the suboxide in air indicates however, that the oxygen vacancies are not only present at the particle surface but are able to migrate into the particle center at the high particle formation temperatures (Haerudin et al., 1998).

The average anatase crystallite size (Fig. 5.8, triangles) determined by the fundamental parameter approach (Cheary and Coelho, 1992) is in good agreement with the BET-equivalent particle diameter up to 10 g/h TTIP flow rate or anatase weight fractions down to 68 wt-% (average anatase crystallite size: 30 nm, BET-equivalent particle diameter: 33 nm). When the anatase weight fraction decreases further at higher TTIP flow rates, the anatase crystallite size becomes smaller than the BET-particle diameter, indicating that particles are polycrystalline. At 26 g/h TTIP flow rate (18 wt-% anatase), where 40 nm particles are obtained, the average anatase crystallite size is only 30 nm. For the whole range of TTIP flow rates, the average rutile crystallite size (Fig. 8, diamonds) is much smaller than that of anatase but increases from 8 nm to 14 nm along with the rutile weight fraction from 15 to 82 wt-% when the TTIP flow rate is increased from 1.6 to 26 g/h. There is no indication whether the product particles comprise anatase and rutile crystallites or whether polycrystalline pure anatase and pure rutile particles coexist next to each other, as was shown by Datye et al. (1995) and Ohno et al. (2001) for flame-made Degussa P-25.

Figure 5.9 is an operation diagram for the flame-nozzle process (oxygen flow rate: 2 L/min) summarizing the relationship between the BET-equivalent particle diameter with the phase composition of the product powder. Data obtained by varying the burner nozzle distance at constant 6.5 g/h (circles) and 16.3 g/h (triangles) TTIP flow rate follow the broken operation lines. Particles made at constant 3 cm and 5 cm BND (Fig. 5.8) with varying TTIP flow rate follow the solid operation lines. Increasing the BND from 1 to 8 cm at 6.5 g/h TTIP flow rate increased the BET-equivalent particle diameter from 8 to 34 nm and the anatase content from 56 to 85 wt-%, following the discussion of Figs 5.5 and 5.7. Increasing the BND further would finally result in the characteristics of particles made without the nozzle (55 nm, 97 wt% anatase) since nozzle quenching becomes less effective. At 16.3 g/h TTIP flow rate, a similar increase in the BND from 2 to 8 cm increased the BET-equivalent particle diameter from 22 to
47 nm and the anatase content from 10 to 77 wt%. The higher rutile (lower anatase) content of these powders as compared to those made with 6.5 g/h TTIP flow rate is attributed to the higher flame temperatures and lower feed O₂/Ti ratio. At 1 cm BND and 16.3 g/h TTIP, powders with 8 nm BET-equivalent particle diameter and 28 wt% anatase were made (not shown in Fig. 5.9). This relatively high anatase content is attributed to higher oxygen content of the flame by increased entrainment of air at short BNDs. For each BND, the product primary particles made in flames with 16.3 g/h TTIP flow rate were larger than those made with 6.5 g/h TTIP flow rate as higher initial particle concentrations and higher flame temperatures were employed (Fig. 5.8).

Fig. 5.9: Operation diagram for the flame – nozzle process (2 L/min oxygen flow rate) relating BET-equivalent particle diameter and phase composition to the process parameters burner-nozzle distance (BND) and TTIP flow rate. Powders are made at constant 6.5 g/h (circles) and 16.3 g/h (triangles) TTIP flow rate with BNDs of 1 – 8 cm (broken lines) and at constant 3 cm (diamonds) and 5 cm (squares) BND with 1.63 – 26 g/h TTIP flow rate (solid lines).
At constant 3 and 5 cm BND, the anatase content was about 80 wt-% for TTIP flow rates of 1.63 and 3.25 g/h. Higher anatase content was only obtained at prolonged particle residence times in unquenched flames (Fig. 5.4). Further increase in TTIP flow rate to 26 g/h significantly decreased the anatase weight fraction to 5 wt-% (3 cm BND) and 18 wt-% (5 cm BND). For each TTIP flow rate, the BET-equivalent product particle size was always bigger for the larger BND, in agreement with Figure 5.5.

The operation diagram for the 2 L/min O₂ flame (Fig. 5.8) shows that the size and crystallinity of flame-made titania can be effectively decoupled using the TTIP feed rate and the BND. The TTIP flow rate is more effective for control of the phase composition than the burner – nozzle distance. The BND, on the other hand, is more effective in control of the primary particle diameter. Thus, by selecting appropriate process parameters, control of the product primary particle diameter and the phase composition could be achieved with the nozzle over a range of 8 – 47 nm and 85 – 5 wt% anatase, respectively. The particle size range could be even extended to 5 nm (at 0.5 cm BND) and 55 nm (without nozzle) while the anatase content could be increased up to 97 wt-% by variation of the oxygen flow rate (Fig. 5.4).

5.4 Conclusions

A flame aerosol process for precise control of product particle size, morphology and phase composition was developed and performance-tested for synthesis of titania nanoparticles. The process relies on rapid quenching of the flame aerosol with a critical flow nozzle placed at desired positions in front of the particle-laden flame. While the upstream flame temperatures are not significantly influenced by the nozzle, high temperature gradients across the nozzle are achieved by flow expansion and mixing with entrained ambient air. This quenching procedure rapidly slows down particle growth downstream of the nozzle, thus “freezing” the particle size and morphology of the upstream aerosol. The BET-average primary particle size could be precisely controlled from 5 to 55 nm by selecting the burner - nozzle distance. Titania particle
growth was independent of the flame temperature as long as this exceeded a characteristic sintering temperature of about 800 °C for the employed particle sizes.

Virtually non-agglomerated and spherical titania particles were made with the flame-nozzle process. The possibility to control the BET-average diameter of these particles by the burner – nozzle distance makes this process prone to manufacture of starting powders for high-performance ceramics. An operation diagram showed that the phase composition of the product powder could be independently controlled from 85 – 5 wt-% anatase and the balance rutile by introducing and stabilizing oxygen vacancies in the titania particles with the quenching procedure. This broad operation window with respect to product particle size, morphology and crystallinity shows the high potential of the flame-nozzle process for successful application to other flame configurations and cost-effective synthesis of silica, alumina and other oxide and non-oxide ceramics and even carbon black and metals like nickel and iron with controlled size, crystallinity and limited degree of agglomeration.
5.5 References


6 Investigation of Silica Flame Synthesis by Nozzle Quenching

Abstract

The expansion of a flame aerosol through a critical flow nozzle is investigated for silica made from hexamethyldisiloxane (HMDSO) in a co-flow methane/oxygen diffusion flame. The length of the particle growth zone is controlled by placing the nozzle at desired locations into the flame and expanding the entire flame aerosol through the nozzle. Compact silica particles with a low degree of agglomeration are produced with the flame-nozzle process even when large agglomerates are present in the flame aerosol upstream of the nozzle. By variation of the HMDSO flow rate controlled synthesis of weakly agglomerated silica spheres with 25 – 120 nm average diameter can be achieved with the nozzle.

6.1 Introduction

In Chapter 4 a flame-nozzle process was introduced which allows precise control of the average primary product particle diameter over broad ranges by rapid quenching of the flame aerosol with a critical flow nozzle placed at desired locations in and above the flame. With the flame-nozzle process titania nanoparticles with a large fraction of individual spherical particles were made, showing that agglomerate formation, which usually is observed in classical flame aerosol reactors (Dufaux and Axelbaum, 1995; Pratsinis, 1998), could be reduced or even avoided. Chapter 5 showed that with the flame nozzle process also the phase composition of titania nanoparticles could be controlled over a range of 85 – 5 wt% anatase and the balance rutile, independently from the average primary particle diameter. An operation diagram relating process parameters to titania product particle phase composition and BET-equivalent diameter was developed (Chapter 5, Fig. 5.9).
Silica has a viscosity which is more than a factor of $10^5$ higher than that of titania (Ulrich and Subramanian, 1977). Thus, silica particle growth in flames is controlled primarily by sintering (Ulrich and Subramanian, 1977). Lower sintering rates for silica than for titania resulted in smaller product primary particles for silica when both oxides were made at the same conditions in premixed flat flames (Ehrman et al., 1998). Seto et al. (1997) investigating sintering of silica and titania agglomerates in a hot wall reactor reported that silica primary particles with average diameter 12 nm – 40 nm were still agglomerated at temperatures of 1500 – 1750 °C, while titania agglomerates fully coalesced into single spherical particles. Unless silica particles encounter high temperatures (above 1850 °C, Seto et al., 1997) in flame regions with high volume loading for sufficient time to coalesce into spheres, agglomerates are formed (Chapter 2).

The particle growth mechanism of titania in high temperature synthesis flames shows that due to the early formation of spherical particles in the hot flame zone titania is a favorable material for synthesis of non-agglomerate nanoparticles with the flame-nozzle process (Chapter 5). Indeed, initial experiments with silica failed as agglomerates were formed and plugged the ceramic quenching nozzle (described in Chapter 4) after only a few seconds. This is attributed to the rather long nozzle bore (8 mm length, 1.5 mm diameter) which allowed sufficient time for the large silica agglomerates to diffuse and stick to the walls of the orifice.

Here, the flame-nozzle synthesis of silica nanoparticles is systematically investigated using the improved design of the stainless-steel quenching nozzle described in Chapter 5. The particle residence time in the bore of this nozzle is much shorter since it directly opens conically on the downstream side, giving a sharp-edged orifice. Nozzle clogging was not observed in any of the experiments investigating the effect of the burner-nozzle distance on product particle characteristics at various precursor and oxidant flow rates.
6.2 Experimental

The experimental set-up was the same as the one used for flame-nozzle synthesis of titania (Chapter 5, Fig. 5.1). Instead of TTIP, hexamethyldisiloxane (HMDSO; Fluka, purity > 99%) was used as precursor, which prior to experiments was distilled in inert gas atmosphere over liquid Na to remove water and high boiling point impurities. An argon stream of 0.3 L/min carrying the HMDSO vapor was introduced through the center tube of the burner, while 0.5 L/min of methane flowed through the second tube (first annulus) and oxygen was provided through the third tube (second annulus). All gases were of high purity (Pan Gas, > 99.999 %). The evaporator, the precursor delivery tubes and the burner were heated to 75 °C to guarantee complete evaporation of HMDSO and prevent precursor condensation in the delivery line. Particles were produced at 2 – 5 L/min oxygen flow, 6.5 g/h HMDSO flow rate and burner-nozzle distances (BND) of 0.5 to 5 cm, as well as without the nozzle. In a second set of experiments the oxygen flow rate and the burner-nozzle distance were kept constant at 2 L/min and 3 or 5 cm, while 3.25 – 26 g/h of HMDSO vapor were delivered into the Ar stream of 0.3 L/min, thus changing the precursor concentration in the flame.

The specific surface area (SSA) of all product powders was measured by nitrogen adsorption at 77 K, employing the BET isotherm (Micromeritics, TriStar 3000). Assuming all particles to be monodisperse spheres, the BET-equivalent particle diameter was calculated as \( d_p = \frac{6}{\rho_{SiO_2} \times SSA} \), with \( \rho_{SiO_2} = 2200 \text{ kg/m}^3 \). Particle samples for analysis by transmission electron microscopy (TEM, Hitachi H600, 100kV) were collected by thermophoresis (Dobbins and Megaridis, 1987; Arabi-Katbi et al., 2001) at various heights in the flame and at 8 cm downstream of the nozzle.

The carbon content of powders collected on the filter powders was determined by thermogravimetric analysis (TGA) and simultaneous off-gas analysis. Therefore, the thermobalance (Mettler Toledo TGA/SDTA 851, LF/1100°C) was coupled with a mass spectrometer (MS, Balzers Omnistar GSD 300) which was calibrated for CO\(_2\) with different CO\(_2\)/N\(_2\) mixtures. Following a procedure reported by Kammler et al. (2001), the samples were first heated up in flowing N\(_2\) (70 ml/min) from 30 to 120 °C at 10 °C/min, held at this temperature for 10 min and were then heated up at 20 °C/min to 800
°C where they were kept for additional 10 min. The gas atmosphere was then switched to 70% O$_2$ and the balance N$_2$, before further heating to 1000 °C at 20°C/min. This temperature was kept for 5 min before the samples were cooled down to room temperature at a rate of about 30 °C/min. This heating procedure allows an estimation of the amount of water adsorbed physically and chemically on the sample as well as the carbon content (Kammler et al., 2001) by constantly measuring the CO$_2$ concentration in the TGA off-gas with the mass spectrometer.

6.3 Results and Discussion

6.3.1 Particle Growth in the Unquenched Flame

The growth of silica nanoparticles in the flame with 2 L/min O$_2$ and 6.5 g/h HMDSO flow rate without the nozzle was monitored by thermophoretic sampling in the flame. Figure 6.1 shows TEM pictures of particles sampled at a) 1, b) 2, c) 3, and d) 5 cm above the burner. At 1 cm (Fig. 6.1a) and 2 cm (Fig. 6.1b) above the burner the particles were fractal-like agglomerates of several hundred nanometers. It is interesting to note that the primary particles within an agglomerate at 1 cm from the burner were larger than those at 2 cm. This was also reported by Hurd and Flower (1988) investigating TEM images of similarly sampled silica particles made by oxidation of HMDSO in a premixed flame. Excluding late nucleation as a possible mechanism for the formation of smaller particles at the higher flame location by in-situ light scattering, they attributed this particle shrinkage to densification of initially porous particles by sintering or collapse. At 3 cm height above the burner (Fig. 6.1c), the agglomerates observed at lower heights had vanished. Spherical particles of up to about 50 nm diameter had formed to which smaller agglomerates were attached. This indicates that the large agglomerates observed at lower locations in the flame had fused into spherical particles at 3 cm. Also, some individual agglomerates of small primary particles were present in the sample taken at 3 cm from the burner, showing that particles had experienced different temperature-collision histories. At 5 cm above the burner, the sample shows only perfectly spherical particles and no fractal-like agglomerates (Fig. 6.1d). Compared
to the spherical particles collected at 3 cm, the size of the silica spheres had increased, showing that particle growth by sintering had continued.

Fig. 6.1: TEM pictures of silica particles withdrawn by thermophoretic sampling from the flame without the nozzle at a) 1, b) 2, c) 3, and d) 5 cm distance from the burner. At 1 and 2 cm the particles were agglomerates which coalesced into spheres at higher flame locations (3 and 5 cm).

The formation of agglomerates at 1 and 2 cm above the burner (Figs 6.1a, b) indicates that silica particle growth early in the 2 L/min O₂ flame is coalescence-limited. Here, the characteristic time for coagulation is smaller than that for sintering, meaning
that primary particles collide with each other much faster than the time needed for complete coalescence (Ulrich and Subramanian, 1977; Windeler et al., 1997; Tsantilis et al., 2001). The formation of spherical particles with low degree of agglomeration at 3 and 5 cm above the burner indicates that particles sinter faster than they collide (collision-limited particle growth). In flame synthesis of silica collision-limited particle growth is observed at high flame temperatures and low particle concentrations (Tsantilis et al., 2001).

6.3.2 Particle Growth in the Nozzle-Quenched Flame

Effect of the Burner-Nozzle Distance on Particle Size and Morphology

Figure 6.2 presents photographs of the silica-laden 2 L/min O₂ flame which is quenched with the nozzle at burner-nozzle distances of a) 0.5, b) 1, c) 2, and d) 4 cm. The pictures show how the flame length can be controlled with the burner-nozzle distance (BND) by drawing the entire flame into the 1.5 mm nozzle bore.

Fig. 6.2: Photographs of the silica producing flame with 2 L/min O₂ flow rate quenched with the nozzle at BNDs of a) 0.5, b) 1, c) 2, and d) 4 cm. The flame structure is significantly altered in front of the nozzle.
At close distances in front of the nozzle, the flame structure is significantly altered by contraction and ambient air drawn into the nozzle together with the flame aerosol. The change in flame structure by the presence of the nozzle is most significant at the shortest BND of 0.5 cm (Fig. 6.2a) where only a small cone-shaped flame can develop.

Figure 6.3 shows the BET-equivalent diameter of silica product particles made in the 2 L/min O₂ flame with the quenching nozzle as a function of the burner – nozzle distance (circles) along with TEM pictures of product particles for BNDs of a) 0.5, b) 1, c) 2, d) 3, and e) 5 cm. When the quenching nozzle was placed in the 2 L/min O₂ flame, the BET-equivalent product particle diameter was 65 nm at 0.5 cm BND and decreased to 32 nm at 1.25 cm BND. This decrease was followed by an increase in BET-equivalent particle diameter to 72 nm at 2 cm BND and a second decrease to 43 nm at 3 cm BND. This primary particle diameter was also obtained at larger BNDs (e.g. 41 nm at 5 cm BND) and was equal to the BET-equivalent diameter of product particles made in this flame without the nozzle (43 nm, not shown here).

This evolution of the average silica primary particle diameter with increasing BND is also reflected in the particle morphology as shown in the TEM pictures. When the nozzle was placed at BNDs of 0.5 – 2 cm (Figs 6.3a-c), large irregularly shaped product particles were formed. A comparison with the morphology of particles taken from the flame without the nozzle at 1 cm (Fig. 6.1a) and 2 cm (Fig. 6.1b) shows that agglomerates present in the flame had apparently fused into more compact particles of up to 300 nm diameter when the nozzle was used. This indicates that up to 2 cm above the burner particles had experienced higher temperatures in the flame-nozzle process than in the undisturbed flame. Centerline temperature measurements upstream of the nozzle and in the undisturbed flame had shown that the flame was not influenced by the nozzle up to 1 cm in front of the nozzle bore (Chapter 5). However, the flame photographs (Fig. 6.2) indicate that the flame was significantly altered at short distances in front of the nozzle. This might lead to an increase in flame temperature close to the nozzle bore by enhanced reactant mixing. Such an increase in temperature by the nozzle would increase the silica sintering rate (nozzle-induced sintering), resulting in the collapse of the initially formed silica agglomerates.
Fig. 6.3: BET-equivalent particle diameter of silica made in the 2 L/min O₂ flame as a function of the burner-nozzle distance. Also, TEM pictures of the nozzle-quenched silica product powder are presented for BNDs of a) 0.5, b) 1, c) 2, d) 3, and e) 5 cm.

High magnification TEM pictures of the 2 cm BND product powder (Figure 6.4) elucidate the irregular shape of the product particles and indicate that the sintering process was frozen when the aerosol temperature rapidly dropped behind the nozzle by gas expansion and mixing with quenching air (Chapter 5, Fig. 5.3). The irregular shape of the particles further shows that the residence time at high temperatures in front of the nozzle is insufficient for most of the particles to attain the thermodynamically favorable spherical shape.

At 3 cm BND, the product powder contained large particles of approximate spherical shape as well as some agglomerates (Fig. 6.3d), similar to the sample taken from the undisturbed flame at 3 cm (Fig. 6.1c). This indicates that the nozzle expansion
had little effect on the morphology of the large primary particles in the population since these had already attained the stable spherical form in the flame upstream of the nozzle. However, nozzle-induced sintering had an effect on the small primary particles in the agglomerates (Fig. 6.1c) which had grown to larger sizes when the nozzle was used (Fig. 6.3d). At 5 cm BND (Fig. 6.3e), no significant change in product powder morphology from 3 cm BND was observed but the individual particles had become now perfect spheres with smooth surface.

![High magnification TEM pictures of silica product particles made by nozzle-quenching of the flame with 2 L/min O₂ flow rate at 2 cm BND.](image)

Fig. 6.4: High magnification TEM pictures of silica product particles made by nozzle-quenching of the flame with 2 L/min O₂ flow rate at 2 cm BND. The irregular particle morphology shows that particle sintering was rapidly frozen when the flame aerosol was quenched with the nozzle.

Compared to the particles withdrawn from the flame by thermophoretic sampling at 5 cm (Fig. 6.1d), a larger number of smaller and partly agglomerated spherical particles was observed in the product powder of the flame-nozzle process (Fig. 6.3e). This is attributed to the mixing of particles of different flame streamlines in the nozzle. Thus, a sample taken downstream of the nozzle represents the whole flame aerosol population while the one taken thermophoretically from the flame centerline tends to neglect particles at the flame boundaries (Arabi-Katbi et al., 2001).
Product powders of flames made at BNDs between 1 and 1.5 cm BND were gray, indicating that soot-silica was formed (Kammler et al., 2001). Figure 6.5 shows the results of the thermal analysis of powders made in flames with 2 L/min O₂ flow and 0.5 – 2 cm BND along with those of particles made in flames with 3 and 5 L/min O₂. Here the amount of CO₂ formed during the heat treatment of the powders per mass SiO₂ is depicted as a function of the burner-nozzle distance.

For the particles made with 2 L/min O₂ flow, the highest soot content was measured for 1.25 cm BND (34.3 µg CO₂ / mg SiO₂). Significantly less CO₂ was formed when powders were made at BNDs smaller than 1 cm (less than 6 µg CO₂ / mg SiO₂) and larger than 1.25 cm (less than less than 1.2 µg CO₂ / mg SiO₂), showing that these product powders contained little soot. For particles made in flames with 3 and 5 L/min O₂ flow rate, the evolution of the soot content with BND was similar to that observed for powders produced with 2 L/min O₂ flow but the amount of soot was significantly lower for all BNDs (e.g. only 5.6 µg CO₂ / mg SiO₂ for 5 L/min O₂ and 1.25 cm BND). This is attributed to higher oxygen concentrations by fast reactant mixing in these turbulent flames (Chapter 2).

Soot formation in diffusion flames takes place over a limited temperature range of about 1000 – 1300 °C (Turns, 2000) in fuel rich flame zones upstream of the flame front. Thus, the soot content of the product powder is an indicator for the flame temperature and the degree of reactant mixing upstream of the nozzle. The low soot content of powders made at 0.5 cm BND indicates high temperatures and the presence of sufficient oxygen for stoichiometric combustion in this flame. This further supports the enhancement of reactant mixing by the nozzle and is in agreement with the rather large BET-equivalent particle diameter of 65 nm and the compact particle morphology by rapid particle sintering (Fig. 6.3a). The high soot content of powders made in flames with 1 – 1.25 cm BND indicates that compared to the 0.5 cm BND flame the fuel-rich region close to the burner and upstream of the flame front (Chapter 3, Fig. 3.9) is less influenced by the nozzle. This is supported by the flame geometry shown in Figs 6.2a and b. Thus, soot particles can form upstream of the flame front at rather low temperatures and are apparently not fully oxidized when passing through the high temperature flame region close to the nozzle. For powders made at 1.5 cm BND and above less than 1.2 µg CO₂ / mg SiO₂ was formed. Similar amounts of CO₂ / mg SiO₂
were also detected for commercial Degussa Aerosil OX 50 powders (0.6 µg CO₂ / mg SiO₂), which are specified as carbon free. This shows that the soot that had formed earlier in the flame was almost completely oxidized at higher flame locations upstream of the nozzle.

Fig. 6.5: Amount of CO₂ per mg SiO₂ formed during the thermal analysis of nozzle-quenched soot-silica particles made in flames with 2 (circles), 3 (squares), and 5 L/min O₂ flow rate (triangles) and BNDs of 0.5 – 2 cm. The CO₂ formation shows that powders made with 1 – 1.25 cm BND have the highest soot content.

The rather small BET-equivalent diameter of particles made at 1.25 cm BND (32 nm, Fig. 6.3) compared to that of particles made at 0.5 cm (65 nm) and 2 cm BND (72 nm) goes along with the highest soot content (Fig. 6.5) and a less compact morphology of the product particles made at 1 cm BND compared to 0.5 and 2 cm BND (Figs 6.3a –
c). An influence of the soot on the surface area measurement can be excluded, since soot-silica powders which were removed from the thermobalance after the introduction of oxygen at 800 °C showed the same specific surface area as before the thermal treatment but were white, indicating that the soot was burnt off. Kammler et al. (2001) also reported no loss in specific surface area during the oxidation of similar-sized soot-silica particles at 800 °C. However, the formation of soot in flames with 1 and 1.25 cm BND (Fig. 6.5) indicates lower flame temperatures for these BNDs than for 0.5 and 2 cm BND. Lower flame temperatures result in smaller primary particles by lower sintering rates. This is supported further by the less fused product particle morphology at 1 cm BND compared to 0.5 and 2 cm BND (Figs. 6.3a–c).

An increase in the burner-nozzle distance from 2 to 3 cm decreased the BET-equivalent particle diameter from 72 nm to 43 nm (Fig. 6.3). At the same time, particles sampled at 2 and 3 cm in the unquenched flame showed a change in morphology from highly agglomerated (2 cm, Fig. 6.1b) to predominantly spherical (3 cm, Fig. 6.1c), which was attributed to coalescence at high flame temperatures. Apparently, the collapse of the agglomerate structure by nozzle-induced sintering at 2 cm results in significantly larger product particles than the sintering of the agglomerate to spherical particles at moderate rates in the flame before the nozzle is effective. A plausible explanation is the formation of several spherical particles out of an agglomerate when sintering takes place in the flame upstream from the nozzle.

Figure 6.3 shows constant BET-equivalent particle diameters for 3 – 5 cm BND, which were equal to the one of product particles made in the unquenched flame (43 nm, not shown here). Assuming that nozzle-induced sintering resulted in the coalescence of agglomerates at these BNDs, the constant BET-equivalent particle diameters indicate that particle (agglomerate) growth by coagulation had ceased after 3 cm and higher in the flame. Thus, the increase in particle size observed by TEM analysis of samples taken from the flame at 3 and 5 cm in absence of the nozzle (Figs. 6.1c and d) may be primarily due to fusion of existing agglomerates. Similar particle growth is achieved by nozzle-induced sintering, when the nozzle is placed at any BND larger than 3 cm. This is consistent with the similar morphology of particles quenched at 3 and 5 cm BND (Figs. 6.3d, e).
Coalescence-limited silica particle growth early in the 2 L/min \( \text{O}_2 \) flame (up to 2 cm) resulted in large agglomerates of small (10 nm) primary particles (Fig. 6.1a, b). Once formed, these agglomerates could not be broken into smaller spherical particles but fused into large compact particles when the flame was expanded through the flow nozzle (Figs 6.3a–c). Thus, the degree of silica agglomeration in the product powder could be reduced but large and irregular shaped particles were obtained. At BNDs above 3 cm, where spherical silica particles with a low degree of agglomeration had already formed in the flame, control of the BET-equivalent particle diameter with the nozzle was not effective since particle growth by coagulation had ceased at low number concentrations. Thus, a flame of given composition produced similar product powders of weakly agglomerated spherical silica particles with rather large average primary particle diameter (43 nm) at these BNDs.

**Effect of the Oxygen Flow Rate on Particle Size**

Figure 6.6 depicts the BET-equivalent diameter of silica nanoparticles made with the flame-nozzle process as a function of the burner – nozzle distance for oxygen flow rates of 3 L/min (squares) and 5 L/min (triangles). The BET-equivalent diameter of product particles made in the corresponding flames without the nozzle is given at the right axis.

For both flames, the evolution of the average product primary particle diameter with the burner-nozzle distance is similar to the one observed for the 2 L/min \( \text{O}_2 \) flame, indicating comparable particle growth mechanisms. The BET-equivalent diameter of product particles made without the quenching nozzle or with the quenching nozzle placed at 3 cm BND and above decreases from 43 to 16 nm when the \( \text{O}_2 \) flow rate is increased from 2 to 5 L/min. Such a decrease in the BET-equivalent particle diameter with increasing oxygen flow rate has been reported for silica (Chapter 2, Fig. 2.8; Zhu and Pratsinis, 1997; Briesen et al., 1998) as well as tin oxide (Zhu and Pratsinis, 1997) and titania (Zhu and Pratsinis, 1996) made in similar methane/oxygen co-flow diffusion flames. The decrease in BET-equivalent particle diameter is attributed to shorter and colder flames at higher oxygen flow rate by mixing of the flame gases with surplus oxygen not taking part in the combustion and increased entrainment of ambient air at higher oxygen outlet velocity (Chapter 2).
Fig. 6.6: BET-equivalent diameter of silica particles made with the flame-nozzle process and O$_2$ flow rates of 3 (squares) and 5 L/min (triangles) as a function of the burner-nozzle distance. The evolution of the average primary particle diameter with the BND is similar for both flames and is consistent with 2 L/min O$_2$ flow (Fig. 6.3). Smaller primary particles are made at higher oxygen flow rates as is also observed for particles made in flames without the nozzle (right axis).

**Effect of the Precursor Concentration on Particle Size**

Figure 6.7 shows the effect of varying precursor flow rate on the BET-equivalent diameter of silica particles made in flames with 2 L/min O$_2$ flow rate and fixed BNDs of 3 cm (circles) and 5 cm (triangles). The evolution of the BET-equivalent particle diameter of titania made at 5 cm BND (Chapter 5, Fig. 5.8) is shown also (solid line). When the nozzle was placed at 5 cm above the burner and the precursor flow was increased from 3.25 to 26 g/h, the BET-equivalent particle diameter linearly increased from 24 to 119 nm. This is in agreement with Jang (1999) who reported a similar increase in average particle diameter with increasing precursor flow rate in the flame synthesis of silica from tetraethylorthosilicate (TEOS).
Dependence of the BET-equivalent particle diameter on the precursor flow rate (concentration) for silica made in the 2 L/min O₂ flame with the nozzle placed at 3 cm (circles) and 5 cm BND (triangles) and for titania made in a similar flame with 5 cm BND. The average primary particle diameter of silica increases almost linearly with the precursor (HMDSO) flow rate. For titania, the dependence of the BET-equivalent particle diameter on TTIP flow rate (concentration) can be described by the coagulation of perfectly coalescing spheres (Koch and Friedlander, 1991).

Figure 6.7 shows that at 3 cm BND and 3.25 – 16.25 g/h HMDSO flow rate, the BET-equivalent product particle diameter is the same as for 5 cm BND. At precursor flow rates above 16.25 g/h and 3 cm BND soot-silica was formed, indicating that combustion was not complete. The BET-equivalent particle diameter of soot silica (not shown in Fig. 6.7) deviated up to 30 % from the one of product particles made at 5 cm BND. The
correspondence of the BET data for 3 and 5 cm BND corroborates that no significant particle growth by coagulation occurs in the flame region above 3 cm even when the precursor flow rate is higher or lower than 6.5 g/h (Figure 6.3).

Figure 6.8 shows TEM pictures of silica particles made with 5 cm BND and precursor flow rates of a) 3.25, b) 16.25, and c) 26 g/h. The particles are predominantly spheres which have a rather low degree of agglomeration and grow in size when the precursor flow rate is increased, in agreement with larger BET-equivalent particle diameters at higher precursor flow rates (Fig. 6.7).

Fig. 6.8: TEM pictures of silica particles made in flames with 2 L/min O_2 flow rate, 5 cm BND and HMDSO flows of a) 3.25, b) 16.25, and c) 26 g/h. Most of the product particles are spherical and show a low degree of agglomeration.

At constant BND and constant Ar, CH_4 and O_2 flow rates, an increase in precursor flow mainly affects particle coagulation by higher particle concentrations early in the flame. For titania, a similar change in early particle concentration by variation of the titanium-tetra-isopropoxide (TTIP) flow rate resulted in an increase of the BET-equivalent particle diameter following a relationship given by Koch and Friedlander (1991) for coagulation and instantaneous fusion of spheres (solid line in Fig. 6.7):

\[ d_p \propto V_m^{2/5} \]

where \( V_m \) is the particle volume loading (concentration). The linear increase of the silica BET-equivalent particle diameter with increasing HMDSO flow rate (concentration) shows that silica follows a different particle growth mechanism in the flame-nozzle process than titania.
6.4 Conclusions

The synthesis of silica nanoparticles in diffusion flames with and without nozzle quenching was investigated. Early in the flame, silica formed large agglomerates which fused into compact particles when the flame aerosol was expanded through the critical flow nozzle. Thus, the degree of agglomeration of the product particles was significantly reduced by the nozzle. When silica spheres with a low degree of agglomeration had already formed in the flame upstream of the nozzle the particle morphology and size was almost unaffected by the nozzle expansion. Silica spheres of 24 – 119 nm average diameter were made with the flame-nozzle process by controlling the HMDSO flow rate.

Nozzle expansion of silica-laden diffusion flames with 2 – 5 L/min oxygen flow and 3 – 26 g/h precursor flow rate showed that coagulation of silica particles in these flames becomes insignificant for particle growth after only 3 cm from the burner. At larger distances, particles grow predominantly by fusion of agglomerates formed early in the flame.
6.5 References


7 Design of Metal Nanoparticle Synthesis  
by Vapor Flow Condensation

Abstract

A systematic engineering study on continuous synthesis of bismuth metal nanoparticles by vapor condensation in tube flows is presented. Simulations of aerosol nucleation, condensation and coagulation are cast in a design diagram format to guide experimental studies on the effect of process parameters on product nanoparticle characteristics. Flow visualization, tracer gas analysis and computational fluid dynamics are used to unravel the effect of particle residence time distribution on product morphology during evaluation of alternate quenching designs for the metal vapor. Bismuth nanoparticles of average diameter 12 to 37 nm, as determined by nitrogen adsorption and X-ray diffraction, were made by controlling the quenching gas flow rate, carrier gas flow rate and process pressure.

7.1 Introduction

A variety of metal nanoparticles are made today for a spectrum of niche applications. Condensation of the corresponding metal vapors is widely used for manufacture of these nanoparticles (Gleiter, 1989; Siegel, 1991). Very little systematic design and operation of these processes has been performed since metal nanoparticles are still sold at rather high prices. As this technology matures and product prices become competitive, the need for optimal process design and engineering will rise. Here such an effort is made for continuous synthesis of bismuth nanoparticles that are used in dry phototools (Eickmans et al., 1996).

Pfund (1930) and Burger and van Cittert (1930) synthesized bismuth nanoparticles by evaporating bismuth from a tungsten wire at low pressure. Particles
formed in the colder region of the unit were transported by free convection to a cold surface (“cold finger”) where they were collected by thermophoresis. Since these early experiments, direct evaporation of metals from heated crucibles into a gas has been widely studied (Gleiter, 1989; Uyeda, 1991). Yatsuya, et al. (1973) synthesized aluminum particles by melt evaporation in helium and reported the formation of bigger particles for increased inert gas pressure, evaporation temperature and residence time in the reactor. Granqvist and Buhrman (1976) and Thölén (1979) made similar observations for other metal nanoparticles when they evaporated the metals from a crucible into the reduced atmosphere of an inert gas.

Sattler et al. (1980) and Mühlbach et al. (1981) generated small clusters of bismuth, antimony and lead by vapor expansion in a free jet from an oven source in a liquid-nitrogen-cooled condensation cell. They reported the formation of single bismuth atoms to 270 atom-clusters as determined by time of flight (TOF) mass spectroscopy when the cold He atmosphere of 10 Torr containing the Bi-clusters was expanded into the high vacuum TOF chamber ($\approx 10^{-7}$ Torr). However, only small quantities of clusters can be produced by this free jet expansion technique while the common inert gas condensation (IGC) method has the potential to produce gram quantities of nanoparticles in a single run (Samy El-Shall and Edelstein, 1996).

Andres et al. (1989) and Siegel (1991) proposed the utilization of forced gas flows in the IGC-process for production of larger quantities of nanoparticles. The method was applied by Haas et al. (1993) for synthesis of Cu and Pd nanoparticles. They modified the classical IGC-process by introducing a continuous inert gas jet above the heated crucible. The particle transport by forced convection resulted in a reduction of number concentration and residence time of the nuclei, so that smaller nanosize powders could be produced. Konrad et al. (1996) applied continuous gas flow also for synthesis of nanosize copper-bismuth alloys by co-evaporation. Copper crystallites with up to 10% bismuth could be synthesized by directing the gas flux over first the copper and then the bismuth melt. The jet aerosol flow condenser was investigated further by Haas et al. (1997) for synthesis of palladium nanoparticles with primary particle median diameters of 2 to 11 nm. Compared to IGC processes relying on free convection, an 80% reduction in the primary particle median diameter and a 17% reduction in the geometric standard deviation of the primary particle size distribution could be achieved with this
aerosol flow condenser. Tsantilis et al. (1999) combined computational fluid and monodisperse particle dynamics to describe the flow pattern and particle formation in this aerosol flow condenser.

Here, synthesis of metal nanoparticles by vapor condensation is systematically investigated. Aerosol process design is used, for the first time to our knowledge, to guide experimental studies on the effect of process parameters (vapor quenching rate, temperature and pressure) on product metal nanoparticle characteristics. Hence, synthesis of bismuth nanoparticles is investigated as these particles are used for dry phototools in production of printed circuit boards (Eickmans et al., 1996). The 200 nm thin bismuth imaging layer of these phototools must be uniform and requires particles to have average diameters of 50 nm or less, a low degree of agglomeration and a reasonably narrow primary particle size distribution (Eickmans et al., 1996). Here bismuth vapor is produced in an externally heated tube flow condenser containing a crucible with the Bi-melt. Transport of the vapor in an argon carrier gas jet is followed by rapid quenching with a second argon stream (in a diluter) and by particle collection on a filter. This experimental design is selected as it separates the evaporation from the particle formation zone (during quenching) allowing to systematically study the influence of cooling rate and quenching configuration on product particle characteristics using nitrogen adsorption, transmission electron microscopy and X-ray diffraction.

7.2 Experimental

7.2.1 Apparatus

Figure 7.1 shows a schematic of the jet aerosol flow condenser unit. The middle section of an Inconel pipe (length 1000 mm, inner diameter 52.5 mm) is heated to the desired process temperature by a tubular furnace (Carbolite CFM 14/1) to evaporate bismuth from an alumina crucible (Alsnit 99.7). From the pipe inlet (feed side) argon carrier gas (Pan Gas, 99.999%) is introduced above the crucible through a 2.2 mm i.d. Inconel tube.
This inlet tube is supported by a stainless steel flange which also closes the feed side of the pipe and contains connectors for pressure and temperature sensors.

![Diagram of aerosol flow condenser](image)

Fig. 7.1: Schematic of the aerosol flow condenser with its Inconel pipe (1), the crucible containing the bismuth melt (2), the furnace (3), the evaporation zone (4), and the cap-free diluter (5). An inset schematic shows the diluter configuration with gas return cap (6) used to introduce the quenching gas perpendicular to the Bi-laden carrier gas jet.

At the other side of the Inconel pipe a stainless steel lance consisting of a center and three annular tubes forms a diluter, heat exchanger and condenser outlet (Fig. 7.1). The 16.5 mm i.d. center tube of this lance (diluter tube) carries the product aerosol to a glass fiber filter (Whatman GF/A) in a stainless steel filter holder with the help of a vacuum pump (Vacuubrand RZ 16). Cooling water of 5°C flows through the first and third annulus of the lance at a flow rate of 60 l/h. An argon stream (Pan Gas 99.999%) is
introduced into the condenser through the second annulus between the cooling water shell as quenching gas. This quenching gas discharges in counterflow to the aerosol jet through 12 equally sized nozzles with an inner diameter of 2.5 mm which are uniformly arranged at the front side of the lance as is shown in the photograph in Fig. 7.1 (cap-free diluter). The schematic in Fig. 7.1 shows a stainless steel gas return cap which can be mounted on the diluter to guide the quenching gas perpendicularly to the Bi-laden carrier gas stream, thus forming a T-mixer. This cap can separate the evaporation zone from the condensation (quenching and particle formation) zone of the unit (cap-diluter). Here the performance of the two diluter (or quenching gas) configurations in gas cooling and mixing is investigated for their effect on particle formation.

An additional water-cooled heat exchanger is connected with a gate valve to the outlet of the diluter and cools the aerosol to a temperature of 30 °C at the filter. This temperature is recorded at the center of the filter with a type K thermocouple and controls the cooling water flow rate. A precision needle valve flow controller (Bronkhorst EL-Flow 201 A) connected to the gas-side inlet of the heat exchanger (10 cm after the diluter and 30 cm before the filter) allows the addition of trace amounts of oxygen (Pan Gas, 99.999%) to the aerosol stream. All tube connections are made with vacuum flanges (Balzers KF-series) to allow gas-tight operation at subatmospheric pressure. The carrier and quenching gas streams are controlled by calibrated mass flow controllers (Bronkhorst EL-Flow 201 A and AC). The pressure in the condenser is measured by a capacititative pressure sensor (MKS Baratron) and is controlled by a butterfly valve (MKS 653B) at the inlet side of the vacuum pump.

### 7.2.2 Procedure

Prior to heating the unit, the ceramic crucible was loaded with about 5 g of bismuth granules (Fluka, 99.9995%) and placed at the appropriate position in the flow condenser. The condenser was closed air-tight, purged with argon to a pressure of 1500 mbar and evacuated to 0.1 mbar afterwards. This procedure was repeated three times to remove air from the system. The condenser was then closed with the gate valve, filled with argon to atmospheric pressure and heated at a rate of 25 °C/min to the operating
temperature of 1000 °C. After the set temperature was reached, the gate valve was opened slowly and the argon flow rates and system pressure were adjusted to the desired operating conditions. The oxygen concentration in the particle collection region was set to 1000 ppm with the needle valve flow controller in order to form a passivating oxide layer at the surface of the freshly produced bismuth particles (Russel, 1967; Uchikoshi et al., 1994). Without oxygen, bismuth nanoparticles with diameters smaller than 18 nm rapidly oxidized after exposure to ambient air.

In a standard experiment the furnace temperature was 1000°C, the pressure 1000 mbar, while the oxygen, carrier and quenching gas flow rates were $11.5 \times 10^{-3}$, 1.5 and 10 l/min, respectively. Experiments were carried out from 200 to 1000 mbar, carrier gas flow rates of 0.75 to 3.0 l/min and quenching gas flow rates of 5 to 20 l/min. All volumetric flow rates are reported at 25°C and 1013 mbar. After each experimental run the gate valve was closed and the filter was changed in ambient air. If no further experiments were performed, the condenser was slowly cooled down to room temperature. Each experiment was performed twice and found to be reproducible within 5% of the product specific surface area (SSA).

7.2.3 Measurements

The average specific surface area (SSA) of the powders was determined by nitrogen adsorption at 77K (Micromeritics Gemini 2306) employing the BET isotherm. Assuming all particles to be monodisperse spheres, the BET-equivalent particle diameter was calculated as $d_p = 6 / (\rho_{\text{Bi}} \times \text{SSA})$, with the density of bismuth at room temperature being $\rho_{\text{Bi}} = 9790$ kg/m$^3$ (Lide, 1997). Transmission electron microscopy (Hitachi H600, operated at 100 kV) was employed to determine the morphology of the bismuth nanoparticles. Therefore, 0.2 mg of powder was suspended in 1 ml of toluene (Fluka, \(\geq 99.5\%\)) and 0.1 ml of the surfactant octyltrimethoxysilane (Fluka, \(\geq 97\%\)) before it was applied to a TEM grid. X-ray diffraction analysis (XRD, Siemens D 5000, Cu Kα radiation) was performed over an angle of $20^\circ < 2\theta < 60^\circ$ in steps of 0.02°. Care was taken that all characterization methods were carried out right after synthesis since
bismuth nanoparticles slowly oxidize in air and can completely transform into bismuth oxide after a few weeks, as was observed in the course of this work.

Centerline temperatures in the flow condenser were recorded at 1000 mbar and a furnace set temperature of 1000 °C for quenching gas flow rates of 5, 10, 15 and 20 l/min and a carrier gas flow rate of 1.5 l/min. Therefore, a 750 mm long S-type thermocouple with a 0.5 mm bead supported by an alumina tube (o.d. = 4 mm) was introduced from the unit outlet. The thermocouple was mounted on an xy-positioning table allowing precise positioning inside the condenser. Temperatures were recorded every 2 cm inside the evaporation zone and every 1 cm in the quenching zone. Measurements were performed for both the cap-free and the cap-diluter.

7.2.4 Flow Characterization

Cold flow visualization experiments were carried out in a transparent (quartz glass) unit of similar dimensions at room temperature and pressure in order to visually study the influence of the diluter cap on the flow pattern of particles inside the condenser. Therefore, the crucible was filled with ammonia solution (NH₃,aq, Aldrich 24%) while the carrier gas was saturated with hydrochloric acid (HClₐq, Aldrich 25%) in a bubbler prior to introduction into the unit, leading to the formation of ammonium chloride particles above the crucible (Dahlin et al., 1981). A vertical plane through the center axis of the condenser was illuminated with a laser sheet created by an argon laser (Lexel 95, operated at 2.5 W) and a plano-concave cylindrical lens (Newport CKV513-C). The laser light was scattered by the ammonium chloride particles (corresponding to the bismuth particles of the present experiment) and made the flow pattern in the unit visible. Photographs of flow patterns were taken with a digital camera (Minolta RD 175) for carrier and quenching gas flow rates of 1.5 and 10 l/min, respectively.

The residence time distribution of the carrier gas in the flow condenser was investigated by introducing CO₂ (Pan Gas 99.995 %) as a tracer into the carrier gas stream at the unit inlet and detecting the CO₂ concentration at the unit outlet with a mass
spectrometer (Balzers GSD 300 O). Therefore, a sampling loop was loaded with 3 ml CO₂ and instantly discharged into the argon carrier gas stream with the help of a GC valve (C. Erba S.A. 40541), thus creating a Dirac-peak. The time between the discharge of the sampling loop and the drop of the CO₂ concentration in the outlet gas to its initial value was recorded along with the CO₂ concentration.

7.3 Simulation of Temperature, Velocity and Particle Growth

Temperature and velocity profiles inside the flow condenser were simulated using the commercially available computational fluid dynamics (CFD) software FLUENT™ 5.2. The geometry of the condenser can be taken as axisymmetric if the influence of the crucible on the flow is negligible and the twelve outlet nozzles of the quenching gas are modeled as an annular slit providing the same average gas outlet velocity. The influence of these simplifications on the flow characteristics inside the unit were evaluated by carrying out a three dimensional (3-D) simulation for the actual geometry at a system temperature of 1000°C, a pressure of 1000 mbar and a carrier gas flow of 1.5 l/min and comparing it to the two dimensional (2-D) axisymmetric configuration without crucible. The time consuming 3-D simulation revealed only a minor deflection of the carrier gas jet by the crucible presence which was negligible for the study of the overall flow pattern in the condenser. Thus, all CFD-simulations here were made for the 2-D axisymmetric geometry described above. The Reynolds number of the carrier gas jet at an outlet temperature of 1000 °C is about 400 for an argon flow rate of 1.5 l/min, indicating that the flow in the condenser is in the transition regime (Bejan, 1984). Therefore, the simulations were performed using the RNG k-ε model (Yakhot and Orszag, 1986) provided by FLUENT™ for flows in the transient regime (Fluent Inc., 1998) accounting for low Reynolds number effects. The temperatures at the condenser walls were measured and set as constant boundary conditions for the simulations. At a furnace set point of 1000°C, the plate supporting the carrier gas nozzle, the nozzle itself and the carrier gas had a temperature of about 980 °C. A temperature of 680 °C was measured for the walls of the cap, while the temperature of the diluter-tube and the quenching gas was 5 °C. The outer walls of the evaporation chamber exhibited a
temperature profile which could be approximated with the parabolic function \( T \, (^\circ C) = -2.58 \, x^2 - 1.50 \, x + 980 \), where \( x \, (cm) \) is the distance from the condenser inlet. The wall temperatures did not vary for different operating conditions.

A monodisperse particle dynamics model accounting for simultaneous nucleation, condensation and coagulation (Panda and Pratsinis, 1995) was employed to derive a design diagram for synthesis of bismuth nanoparticles in a jet aerosol flow condenser (Tsantilis et al., 1999). Specifically, the effects of the evaporation temperature \( T_v \, (K) \) and the inert gas flow rate \( Q_r \, (l/min) \) on bismuth average particle diameters were investigated. The Bi properties of importance were surface tension (Frurip and Bauer, 1977):

\[
\sigma \, (J/m^2) = (418 - 0.07 \times T) / 1000 \tag{7.1}
\]

and vapor pressure (Hultgren et al., 1973):

\[
p_v \, (Pa) = 1.013 \times 10^5 \times \exp(12.398 - 22,570 / T) \tag{7.2}
\]

Furthermore, the nucleation rate was given by Girshick and Chiu (1990), while the collision frequency coefficient for Brownian coagulation was based on the Fuchs interpolation function from the free molecular to the continuum regime (Seinfeld, 1986). The design calculations were carried out for a tubular aerosol flow condenser with dimensions consistent with those of the diluter (quenching zone) of the actual experimental set-up (i.d. = 16.5 mm). In addition, it is assumed that the argon carrier gas is saturated with bismuth vapor and enters the condenser at evaporation temperature \( T_v \) (ranging from 1000 K to 1150 K) and flow rate \( Q_r \) (quenching and carrier gas, ranging from 5 to 20 l/min) at 1 atm. For every set gas flow rate, the temperature was assumed to drop linearly with a constant gradient of \( (T_v - T_L) / L = 50 \, K/cm \) over the investigated length of \( L = 10 \, cm \). Therefore, the cooling rate at the exit of the condenser was calculated as:

\[
C(K/s) = \left( \frac{T_v - T_L}{L} \right) \times \frac{4 \times Q_r}{\pi \times D^2} \times \frac{T_L}{T_r} \tag{7.3}
\]
where $T_r$ is the reference temperature (296 K) and $T_L$ the gas temperature at $x = L$. For a $T_V$ and $Q_r$, the product average particle diameter was calculated following Tsantilis et al. (1999).

7.4 Results and Discussion

7.4.1 Design Diagram

Figure 7.2 shows the product bismuth particle diameter predicted by the model as a function of the cooling rate at four evaporation temperatures, $T_V$. The largest particles of about 95 nm diameter are produced at $T_V = 1150$ K and a cooling rate of about 4000 K/s, corresponding to a gas flow rate of 5 l/min.

![Design diagram for the synthesis of bismuth nanoparticles in the jet aerosol flow condenser showing the particle size predictions of a monodisperse model for Bi-vapor nucleation, condensation and coagulation. Lowering the evaporation temperature $T_V$ and increasing the cooling rate decreases the product particle size.](image)

Fig. 7.2: Design diagram for the synthesis of bismuth nanoparticles in the jet aerosol flow condenser showing the particle size predictions of a monodisperse model for Bi-vapor nucleation, condensation and coagulation. Lowering the evaporation temperature $T_V$ and increasing the cooling rate decreases the product particle size.
Decreasing $T_V$ and increasing the cooling rate leads to the formation of smaller particles, the smallest of which have diameters of about 5 nm. Lower evaporation temperatures result in lower metal vapor pressures leading to formation of smaller particles in agreement with Yatsuya et al. (1973), Granqvist and Buhrman (1976) and Panda and Pratsinis (1995). Higher cooling rates result in a higher supersaturation of the vapor and the formation of a large number of small bismuth particles. Since high cooling rates are achieved by larger gas flow rates, the residence time in the flow condenser is also shorter, decreasing the particle size further. The design diagram indicates that bismuth nanoparticles with the envisioned size of about 50 nm (Eickmans et al., 1996) can be produced with the jet aerosol flow condenser when it is operated at $T_V = 1150$ K with cooling rates of 10,000 K/s and higher.

### 7.4.2 Synthesis of Bismuth Nanoparticles

Figure 7.3a shows a typical TEM picture of bismuth nanoparticles synthesized at standard operating conditions and 200 mbar with counterflow introduction of the quenching gas (cap-free diluter). The TEM picture shows a number of large particles of 50 to 100 nm in diameter along with small particles with diameters of less than 20 nm. The broad particle size distribution indicates that particles have different temperature and residence time histories, possibly due to inefficient mixing with quenching gas. As T-mixers are known to be most efficient in rapid fluid mixing (Chilton and Genereaux, 1930; Forney et al., 1996), the cap was placed on the diluter to form such a T-mixing configuration and experiments were repeated.

A TEM picture of product particles synthesized with this cap-diluter configuration is shown in Fig. 7.3b. The primary particle size distribution is much narrower than in the configuration with the cap-free diluter (Fig. 7.3a), specifically, no large primary particles with diameters above 50 nm are found. This strong influence of mixing (diluter or quenching design) on the product particle size distribution motivated us to systematically investigate the residence time distribution in the unit by flow visualization, CO$_2$ tracer gas analysis and computational fluid dynamics.
Fig. 7.3: TEM pictures of bismuth nanoparticles synthesized at standard experimental conditions and 200 mbar with the cap-free diluter (a) and the cap-diluter (b). The primary particles have a broader size distribution for the cap-free diluter design, indicating different temperature and residence time histories.

Flow Pattern

Visualization of the interplay between flow and particle formation can be accomplished following the formation of NH$_4$Cl particles at the standard experimental conditions but at room temperature. Figure 7.4a shows how quenching gas from one of the uppermost nozzles of the cap-free diluter discharges into the evaporation zone. The carrier gas stream is diluted directly behind the crucible, creating a zone of almost uniform particle concentration, as is indicated by the rather uniform light scattering intensity there. When the cap is placed on the diluter-tube (Fig. 7.4b) the quenching gas does not enter the evaporation zone. This allows the core fluid of the carrier gas jet to flow nearly undisturbed through the condenser and to enter the diluter through the cap opening. Gas at the outer boundary of the jet deflects at the cap and backflows.

Velocity and temperature profiles were calculated by computational fluid dynamics for a furnace set temperature of 1000°C, a pressure of 1000 mbar, 1.5 l/min carrier gas flow and 10 l/min quenching gas flow for the configurations with and without cap.
Fig. 7.4: Visualization of the flow in the condenser using ammonium chloride particles freshly formed from NH₃ (in the crucible) and HCl (flowing gas) at ambient temperature and pressure for a) the cap-free diluter and b) the cap-diluter. Carrier and quenching gas flow rates were 1.5 and 10 l/min, respectively.

Figure 7.5 shows the CFD-calculated velocity vectors of unit length. The color of the velocity vectors represents the gas temperature. In both diluter (quenching gas) configurations, the 1000 °C hot carrier gas jet discharges into the evaporation chamber from the left at a velocity of about 30 m/s and entrains fluid at its outer boundaries. Fluid from the downstream jet is recirculated to the region near the nozzle exit, setting up a recirculating vortex. The core flow of Bi-vapor laden carrier gas enters the diluter-tube. In the cap-free diluter configuration (Fig. 7.5a), quenching gas at 5 °C is introduced in counterflow and mixes with the Bi-vapor laden carrier gas jet before the diluter. A fraction of the quenching gas is entrained by the carrier gas jet and directly enters the diluter-tube at a temperature of 200 to 400 °C. The rest of the quenching gas
and part of the carrier gas backflows along the outer pipe walls toward the entry of the condenser and entrains into the fresh carrier gas jet. A small pocket of recirculating fluid is formed in front of the diluter. With the cap-diluter (Fig. 7.5b) the quenching gas enters the diluter-tube in co-flow with the Bi-vapor laden carrier gas. Thus, only Bi-vapor and carrier gas are present in the evaporation zone, as was shown in the flow visualization (Fig. 7.4b). Gas at the outer boundaries of the carrier gas jet, however, is deflected at the face of the cap and streams back toward the carrier gas inlet, setting up a toroidal recirculating vortex of about 10 cm axial extension and 2.5 cm width in front of the cap. A substantial amount of Bi-vapor laden carrier gas is thus trapped in these dead volumes.

![Velocity vectors for the configurations without cap (a) and with cap (b) on the diluter. The carrier and quenching gas flow rates were 1.5 and 10 l/min, the system pressure was 1000 mbar and the furnace temperature was 1000°C.](image)

**Fig. 7.5:** Velocity vectors for the configurations without cap (a) and with cap (b) on the diluter. The carrier and quenching gas flow rates were 1.5 and 10 l/min, the system pressure was 1000 mbar and the furnace temperature was 1000°C.
The formation of dead volumes shown in the flow simulation was verified by measuring the residence time distribution (RTD) of carrier gas, following the CO$_2$ tracer gas concentration. Figure 7.6 shows the response signal to a Dirac peak of CO$_2$ that is inserted at $t = 0$ into the carrier gas stream for each diluter configuration.

![Graph showing RTD](image)

**Fig. 7.6: Residence time distribution (RTD) of carrier gas flowing through the aerosol flow condenser at a rate of 1.5 l/min and standard experimental conditions. The exit age distribution function $E(t)$ is determined by introducing a pulse signal of CO$_2$ tracer gas. Placing the cap on the diluter (b) broadens the RTD.**

For the cap-free diluter (Fig. 7.6a) most of the tracer leaves the unit after about 3.5 seconds, creating a sharp peak with a small shoulder toward longer residence times, which indicates that only a small fraction of the gas is trapped in dead volumes, as was predicted by the flow simulation (Fig. 7.5a). After 10 seconds, all CO$_2$ has left the unit. Placing the cap on the diluter drastically alters the residence time distribution, as can be seen by comparing Fig. 7.6a with 7.6b. The maximum of the response still exits the unit
after about 3.5 seconds, the height of the peak representing a normalized CO₂ concentration, however, is only about half the value of the one detected before. The RTD exhibits a distinct shoulder for t > 4s, indicating that a considerable fraction of the tracer gas is trapped in dead volume and is slowly released over a period of about 20 seconds. This difference in RTD can be explained by the visualization and simulation of the flow patterns shown in Figs 7.4 and 7.5. In the cap-free diluter configuration, carrier gas which does not directly exit the condenser is transported back to the upstream region by the counter-flowing quenching gas and is reentrained. Most of this gas now exits the evaporation chamber, resulting in a rather narrow residence time distribution. For the cap-diluter, the strong recirculating vortex of pure carrier gas in front of the cap releases the tracer gas over a long period of time, resulting in the broad residence time distribution observed in Fig. 7.6b. The broader RTD for the cap-diluter is in contradiction with the narrower particle size distribution observed for this configuration (Fig. 7.3). Therefore, temperature measurements are necessary to evaluate the effect of gas recirculation on particle formation and growth.

**Temperature**

Figure 7.7 shows the condenser temperature along the centerline with the corresponding saturation ratio $S = \frac{p}{p_S}$ for both the cap-free and the cap-diluter, where $p$ is the partial pressure of bismuth calculated with the evaporation rate from the crucible and $p_S$ is the saturation vapor pressure of bismuth (eq. 7.2). The temperature in the unit with cap-free diluter decreases almost linearly with the distance from the carrier gas nozzle (925 °C) and reaches 570 °C at the entrance of the diluter-tube, 11 cm from the nozzle exit. This rather steep temperature decrease is due to the dilution of the Bi-laden carrier gas with cold quenching gas, as was shown in Figs 7.4 and 7.5. The temperature gradient remains unchanged inside the diluter-tube and a temperature of 380 °C is reached after 19 cm from the nozzle exit. Temperatures are much higher in the evaporation zone with the cap-diluter since quenching gas does not enter this region (Figs 7.4 and 7.5). A temperature of 780 °C is obtained at the cap face, 10 cm from the carrier gas nozzle. With the cap-diluter a steep temperature gradient results inside the diluter-tube, giving a temperature of 260 °C after 19 cm from the inlet nozzle. This is about 120 °C lower than for the cap-free diluter and shows the superior performance of this configuration in
gas quenching in agreement with literature (Chilton and Genereaux, 1930; Forney et al., 1996).

Fig. 7.7: Centerline temperatures (symbols) measured under standard experimental conditions and saturation ratio $S = p / p_S$ (lines) for the two diluter configurations. Gas cooling in the case of the cap-free diluter leads to high supersaturation and particle formation in the evaporation zone. Placing a cap on the diluter results in steeper supersaturation and particle formation later in the process.

The saturation ratio $S$ in Fig. 7.7 indicates whether particle formation can already occur in the evaporation zone extending 10 cm from the carrier gas nozzle. For the cap-free diluter $S \geq 1$ is already obtained after 3.5 cm from the nozzle exit at a temperature of 805 °C. Thus, particle formation is likely to occur before the gas enters the diluter-tube. Flow simulation (Fig. 7.5) and RTD measurement (Fig. 7.6) for the cap-free diluter configuration have shown that a fraction of the gas recirculates in the evaporation zone. Particles entrapped in these fluid parcels grow larger and may lead to the observed broad particle size distribution (Fig. 7.3a). In the cap-diluter configuration, a saturation ratio larger than unity is reached only after about 8.5 cm from the carrier
gas nozzle (1.5 cm from the cap face). Particles formed in this region are likely to directly enter the diluter-tube as is apparent from the flow visualization and simulation (Figs 7.4 and 7.5). The strong vortex in front of the cap and the large dead volume detected with the RTD measurement (Fig. 7.6) for this configuration are unlikely to influence the particle formation process since only vapor exists in this high-temperature recirculation zone. Rapid quenching with the T-mixer (Fig. 7.7), however, leads to high supersaturation of the gas in the diluter and formation of a large number of similarly-sized particles. These observations underline the importance of process design for synthesis of metal nanoparticles by condensation.

The narrow primary particle size distribution obtained with the cap-diluter (T-mixer) is also confirmed from Fig. 7.8 showing a TEM micrograph of nanoparticles collected in the gas phase by thermophoretic deposition on a liquid nitrogen cooled TEM grid. The sampling location was downstream of the diluter at the center axis of the flow, approximately 10 cm ahead of the filter. Particles directly deposited from the gas phase are similarly sized spheres.

![TEM picture of spherical bismuth particles collected by thermophoretic sampling from the gas phase, 10 cm in front of the filter. Particle synthesis was carried out in the condenser with cap at standard conditions at 200 mbar.](image)
It is worth noting that these particles are essentially non-agglomerated as Au generated by vapor expansion (Fig. 2a in Andres et al., 1996). The state of agglomeration seen in Fig. 7.3b is attributed to particle necking while on the filter.

7.4.3 Effect of Process Variables on Product Powder Characteristics

In production of thin films, small particles with a narrow size distribution are preferred (Eickmans et al. 1996). This is best obtained with the cap-diluter (T-mixer) which allows controlled particle formation and guaranties the steep cooling rates necessary for synthesis of small particles (Fig. 7.2). Therefore, the effect of operating conditions on product particle characteristics was investigated using the cap-diluter (gas quenching) design.

Figure 7.9 shows the influence of the quenching gas flow rate on the centerline temperature for the cap-diluter. Flow rates of 5, 10, 15 and 20 l/min are investigated for a carrier gas flow rate of 1.5 l/min, a furnace set temperature of 1000 °C and 1000 mbar. Increasing the quenching gas flow rate leads to steeper temperature gradients in the diluter-tube but does not affect the temperature in the evaporation zone. After 19 cm from the carrier gas nozzle exit, the lowest temperature of 195 °C is reached for a quenching gas flow rate of 20 l/min whereas a flow rate of 5 l/min results in a centerline temperature of 365 °C.

Figure 7.10 shows the BET-equivalent diameter of product bismuth nanoparticles made at a furnace set temperature of 1000 °C and a carrier gas flow rate of 1.5 l/min as a function of the quenching gas flow rate at 200, 600 and 1000 mbar. Decreasing the pressure produces smaller particles: at 10 l/min quenching gas flow rate, particles with a BET-equivalent diameter of 31 nm (specific surface area: 20 m²/g) are produced at 1000 mbar while at 200 mbar 18 nm particles (specific surface area: 35 m²/g) are made. As the gas density increases with pressure, the gas velocity in the condenser decreases. As a result, the aerosol experiences longer residence times and bigger primary particles are formed. The decrease in particle size with decreasing pressure is consistent with the predictions of Panda and Pratsinis (1995) and with the measurements of Yatsuya et al. (1973) and Granqvist and Buhrman (1976).
Fig. 7.9: Axial centerline temperatures for the cap-diluter and four quenching gas flow rates (carrier gas flow rate: 1.5 l/min, pressure: 1000 mbar, furnace set temperature: 1000 °C). Steeper temperature gradients are achieved at higher quenching gas flow rates.

Fig. 7.10: BET-equivalent diameter of product bismuth nanoparticles as a function of the quenching gas flow rate for the cap-diluter at three process pressures. The carrier gas flow rate and furnace set temperature are 1.5 l/min and 1000 °C. Smaller particles are produced at higher quenching gas flow rate and lower pressure.
Increasing the quenching gas flow rate from 5 to 20 l/min leads to an almost linear decrease in particle diameter at all pressures. At 1000 mbar, the BET-equivalent particle diameter is 37 nm at a quenching gas flow rate of 5 l/min and 19 nm at 20 l/min. The corresponding specific surface areas are 16 and 33 m²/g, respectively. The smallest particles of 12 nm diameter (specific surface area: 50 m²/g) are produced at a pressure of 200 mbar and a quenching gas flow rate of 20 l/min. This is consistent with the design diagram of Fig. 7.2. The prediction of larger particle sizes by the model may be explained by the assumption of a fully saturated vapor while only 10% saturation of the carrier gas was achieved in the experiment. This was determined by gravimetric analysis which gave production rates of 0.1 g/h (1000 mbar) to 0.8 g/h (200 mbar) and is in agreement with Panda and Pratsinis (1995) for the present unit.

Figure 7.11 shows the influence of the carrier gas flow rate on the product bismuth particle size for a furnace set temperature of 1000°C and a quenching gas flow rate of 10 l/min at 200 mbar.

Fig. 7.11: BET-equivalent particle diameter (left ordinate) and specific surface area (right ordinate) of bismuth nanoparticles as a function of the carrier gas flow rate for the cap-diluter. Furnace set temperature, pressure and quenching gas flow rate are 1000 °C, 200 mbar and 10 l/min, respectively. Higher carrier gas flow rates produce smaller particles.
Increasing the carrier gas flow rate from 0.75 l/min to 3.0 l/min decreases the average primary particle diameter from 19 to 12 nm. As the carrier gas flow rate increases, the initial monomer concentration decreases, leading to the formation of smaller particles consistent with experimental data of Haas et al. (1997) and the model of Tsantilis et al. (1999).

Figure 7.12a shows a typical XRD pattern of product bismuth particles synthesized under the standard experimental conditions and 200 mbar with introduction of trace amounts of oxygen (1000 ppm).

Fig. 7.12: XRD pattern of product bismuth particles synthesized at standard experimental conditions, 200 mbar and 1000 ppm O₂ in Ar showing the characteristic peaks of Bi (a) and XRD pattern of powder oxidized in ambient air after synthesis in oxygen-free atmosphere (b). The characteristic peaks of Bi₂O₃ are labeled with “O”.

Only the distinct peaks of bismuth are visible indicating that the passivating oxide layer at the bismuth surface is either too thin to be detected by XRD or is X-ray amorphous. Particles synthesized in an oxygen-free condenser atmosphere rapidly oxidized in ambient air as is apparent from the bismuth oxide reflections highlighted in the corresponding XRD pattern (Fig. 7.12b).

7.5 Conclusions

Synthesis of bismuth nanoparticles by condensation of metal vapor was systematically investigated following design diagrams accounting for aerosol nucleation, condensation and coagulation. Cold flow visualization, CO₂ tracer gas analysis and computational fluid dynamics showed that rapid quenching of the Bi-vapor flow in a T-mixing configuration produces particles with narrow size distribution as observed by TEM. In contrast, counterflow quenching results in early particle formation and broad particle residence time distributions producing particles with a wide size distribution. Bismuth nanoparticles of average size from 12 to 37 nm were made, as determined by N₂ adsorption, transmission electron microscopy and X-ray diffraction. Increasing the carrier or quenching gas flow rates and decreasing the pressure decreases the product particle size consistent with particle formation design diagrams.
7.6 References


8 Research Recommendations

The scale-up of nanoparticle synthesis in co-flow diffusion flame aerosol reactors was successfully demonstrated for silica production rates of 5 – 25 g/h. The developed scale-up correlation now remains to be confirmed for larger production rates in pilot-scale units which can produce up to 1 kg/h of silica.

In addition to this, the scale-up procedure needs to be extended to cover a broad spectrum of flame configurations, fuels, oxidant compositions and materials such as titania, alumina or carbon black. Today, these nanoscale commodities are routinely manufactured at rates up to 25 t/h in flame reactors which have been developed through evolutionary research to make, typically, a single product with tight specifications. Hence, there is a need for better understanding of the design and scale-up of flame synthesis processes to allow the flexible and inexpensive manufacture of established as well as new nanoscale materials like flame-made catalysts.

Here, the development and application of non-intrusive diagnostics for temperature, velocity and species in particle-laden flames along with process simulators can assist in fundamental understanding of reactant mixing and flame quenching procedures and thus can contribute to the development of dimensionless groups for flame aerosol reactor scale-up.

The successful application of the flame-nozzle process to the synthesis of non-agglomerate titania nanoparticles with controlled crystallinity and size down to 5 nm average primary particle diameter clearly shows the high potential of this process for application to other flame configurations and the cost-effective manufacture of a spectrum of oxide and non-oxide nanoparticles. The production of oxygen-deficient titania with the flame-nozzle process indicates the possibility to produce a range of new metastable materials by rapid flame quenching. Here, a close investigation of the flame quenching effect on additional product properties like the particle size distribution, the surface hydroxylation or the density of catalytically active sites remains to be conducted. The increase of the production rate while retaining the quenching efficiency constitutes another field of future research.
Increasing interest in non-agglomerate metal nanoparticles of high purity for predominantly electronic applications demands a scale-up of the vapor condensation process for a spectrum of pure metals and alloys. Here, the design of large-scale aerosol jet flow condensers is especially demanding as it has to account for the processing of these easily oxidized nanoparticles in high purity and high temperature inert gas atmosphere. Strategies for surface passivation or the application of coating techniques need to be developed to prevent sintering and rapid oxidation of the product metal powders at ambient conditions.
Curriculum Vitae

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