Synthesis of oxide nanoparticles with closely controlled characteristics

Author(s):
Kammler, Hendrik Klaus

Publication Date:
2002

Permanent Link:
https://doi.org/10.3929/ethz-a-004387091

Rights / License:
In Copyright - Non-Commercial Use Permitted
SYNTHESIS OF OXIDE NANOPARTICLES WITH CLOSELY CONTROLLED CHARACTERISTICS

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

DOCTOR OF TECHNICAL SCIENCES

presented by

HENDRIK KLAUS KAMMLER

Dipl.-Ing., Universität Karlsruhe (TH)

born on July 5\textsuperscript{th}, 1971
in Seesen, Germany

Accepted on the recommendation of

Prof. Dr. Sotiris E. Pratsinis, examiner
Prof. Dr. Philip W. Morrison, Jr., co-examiner
Prof. Dr. Konstantinos Boulouchos, co-examiner

Zurich, 2002
Acknowledgements

This work was carried out at the Institute of Process Engineering of ETH Zurich. I would like to acknowledge the financial support by the Swiss National Science Foundation (SNF 2100-055469.98), Commission of Technology and Innovation (KTI), Willi-Studer-Fonds, and Degussa. Furthermore, would like to express my thanks to the following people, who contributed significantly to the success of this work:

Prof. Dr. Sotiris E. Pratsinis for giving me the opportunity to carry out this Ph.D. thesis in his team and for his help, motivation, enthusiasm and encouragement during the whole course of research; Prof. Dr. Konstantinos Boulouchos for helpful suggestions and co-advising this work; Prof. Dr. Philip W. Morrison for co-advising this work, for the introduction to the fascinating world of FTIR spectroscopy, and for the time and ideas he spent and shared with me discussing and tackling problems; the Morrison family for hosting me during a two-month visit at the Case Western Reserve University, Cleveland (Nov./Dec. 2001); Osama I. Arabi-Katbi, for the help with the first FTIR and thermophoretic sampling experiments during a one month visit at the University of Cincinnati (Oct./Nov. 1999); Prof. Dr. Gregory Beaucage, University of Cincinnati, for the small-angle X-ray scattering (SAXS) measurements; Dr. Bernd Hemmerling and Anna Stampanoni-Panariello, Paul Scherrer Institute, for the coherent anti-Stokes Raman scattering (CARS) measurements; and Dr. Martin Müller, ETHZ, for the introduction to electron microscopy and for letting me operate the transmission electron microscopes.

Furthermore, I appreciate the work of the students doing their Semester- and Diploma theses with me: Omri Senn (WS 98/99), Beat Borer (SS 99, WS 99/00), Roger Müller (WS 98/99, WS 99/00), Thomas Schluchter (WS 99/00), David Serby (SS 00), and Rainer Jossen (SS 01) as well as the fruitful discussions and collaborations with Dr. Lutz Mädler, Dr. Georg Skillas, Dr. Karsten Wegner, Stavros Tsantilis, and Wendelin J. Stark (all ETHZ). Finally, I would like to acknowledge the work and support from the IVUK machine shop supervised by Dr. Werner Dörfler and the administrative support by the secretaries.
Table of contents

Acknowledgements..................................................................................................................III
Table of contents....................................................................................................................V
Summary..................................................................................................................................IX
Zusammenfassung.....................................................................................................................XI

1. Flame synthesis of nanoparticles ......................................................................................1
Abstract...................................................................................................................................1
1.1. Introduction ....................................................................................................................1
1.2. Nanoparticles by combustion of gases........................................................................3
  1.2.1. Control of flame aerosol reactors ........................................................................4
  1.2.1.1. Effect of reactant mixing .............................................................................6
  1.2.1.2. Effect of precursor .....................................................................................8
  1.2.1.3. Effect of additives ....................................................................................9
  1.2.1.4. Effect of external electric fields ................................................................10
  1.2.1.5. Monitoring particle growth in atmospheric flames ..................................12
  1.2.2. Multicomponent particles.................................................................................15
    1.2.2.1. Vanadia coated titania nanoparticles for selective catalytic reduction of
             NO....................................................................................................................16
    1.2.2.2. Silica-carbon composite particles............................................................18
  1.2.3. Pilot-scale production of nanoparticles.............................................................19
1.3. Nanoparticles by combustion of liquid droplets .........................................................22
  1.3.1. Flame spray reactors .......................................................................................23
  1.3.2. Effect of spray composition ...........................................................................25
    1.3.2.1. Precursor liquid composition ..................................................................25
    1.3.2.2. Liquid fuel composition ..........................................................................27
1.4. Modeling of nanoparticle formation and growth ......................................................29
1.5. Concluding remarks....................................................................................................33
1.6. References .................................................................................................................34
2. Synthesis of silica-carbon particles in a turbulent H₂-air flame aerosol reactor ..................47
   Abstract ...................................................................................................................................47
   2.1. Introduction ......................................................................................................................47
   2.2. Experimental studies ......................................................................................................49
       2.2.1. Apparatus ..............................................................................................................49
       2.2.2. Safety ..................................................................................................................52
       2.2.3. Characterization ...................................................................................................52
   2.3. Results and discussion ..................................................................................................54
       2.3.1. Influence of the air flow rate ...............................................................................55
       2.3.2. Influence of the hydrogen flow rate ....................................................................59
       2.3.3. Influence of the production rate ........................................................................61
       2.3.4. Powder composition ..........................................................................................64
   2.4. Conclusions ..................................................................................................................71
   2.5. Literature cited ..............................................................................................................72

3. Flame temperature measurements during electrically assisted aerosol synthesis of nanoparticles .......................................................... 75
   Abstract ..................................................................................................................................75
   3.1. Introduction .....................................................................................................................75
   3.2. Experimental .................................................................................................................. 77
       3.2.1. Apparatus and particle characterization ...............................................................77
       3.2.2. Temperature measurements ..................................................................................79
   3.3. Results and discussion ..................................................................................................81
       3.3.1. Comparison of FTIR and CARS (in a premixed particle-free flat flame) ..........83
       3.3.2. Electrically assisted premixed particle-laden flame .............................................90
       3.3.3. Product titania powder characteristics .................................................................99
   3.4. Concluding remarks .....................................................................................................101
   3.5. References ...................................................................................................................102

4. Nanoparticle growth inside electrically assisted flames ............................................................................. 107
   Abstract ..................................................................................................................................107
   4.1. Introduction ....................................................................................................................107
   4.2. Experimental ..................................................................................................................109
C.2. Theory.................................................................................................................. 156
C.3. Thermophoretic sampling (TS) procedure ......................................................... 158
C.4. References......................................................................................................... 161
C.5. Detailed technical drawings............................................................................... 163

Appendix D. Effect of thermophoretic sampling (TS) on the electric field ............ 169

Curriculum vitae and publications................................................................................ 173
Summary

Recent advances in synthesis of nanoparticles by vapor and spray flames are reviewed in the first chapter. In vapor flames emphasis is placed on reactant mixing and composition, additives and external electric fields for controlling the product powder characteristics. To study the growth of nanoparticles in flames, thermophoretic sampling and Fourier transform infrared (FTIR) spectroscopy are introduced for monitoring the temperature and particle growth in the flame. Furthermore, synthesis of composite nanoparticles for various applications is addressed such as in reinforcement or catalysis. The flame spray pyrolysis is reviewed in the second part of the first chapter along with a short summary about recent theoretical achievements and the use of computational fluid dynamics to rank new designs of flame aerosol reactors.

The production of fumed silica and carbon-silica nanostructured particles in a turbulent hydrogen-air flame aerosol reactor is investigated in the second chapter. For the first time, controlled synthesis and continuous production of nanoparticles at high rates (e.g. 5 h at 700 g/h) is systematically studied using a commercial baghouse filter unit for particle collection. Mass solid fractions of 2-10% by weight that are comparable to industrial units are achieved. The effect of process parameters (air, hydrogen, and hexamethyldisiloxane flow) on the product powder characteristics is investigated. The specific surface area of the product powder is controlled from 75 to 250 m²/g, and the carbon content of the product powders is controlled from 0 to 1.5 wt. %. In this study, the importance of detailed information of the flame temperature becomes apparent.

Therefore, in the third chapter, emphasis is placed on flame temperature measurements. First, flame temperatures are obtained by Fourier transform infrared (FTIR) emission/transmission spectroscopy in a particle-free premixed flat flame. The measured temperatures are then systematically compared to that obtained with coherent anti-Stokes Raman scattering (CARS), one of the most reliable gas flame temperature determination techniques. Line-of-sight FTIR measurements are tomographically reconstructed at selected heights above the burner in order to improve the spatial resolution of the FTIR technique. The advantage of FTIR is its simplicity in handling and alignment, and that it is not affected by the presence of nanometer-sized particles. After verification of the FTIR measurements, flame temperatures are measured in TiO₂.
particle-laden premixed flames. The effect of external electric DC-fields on the flame temperature profile is studied even inside the electric field. The electric field is created between two parallel plate electrodes. It is found that the external electric field does not influence the flame temperature close to the burner, however, it decreases the flame temperature significantly further downstream. This decrease is even more pronounced when increasing the field strength between the electrodes. The application of the electric field decreases the average primary particle diameter of the product particles, confirming previous works. The rutile content of the TiO₂ product powder is also increased slightly when applying the electric field.

This work is extended in the fourth chapter, studying titania nanoparticle growth inside electrically assisted flames by \textit{in situ} thermophoretic sampling followed by transmission electron microscopy (TEM) and statistical evaluation of the counted images. Up to 11 g/h TiO₂ particles are produced by titanium tetraisopropoxide (TTIP) oxidation in a CH₄/O₂ premixed flame in the presence and absence of an electric field (1.5 kV/cm). The flame temperature is measured by FTIR spectroscopy, while the product powder is analyzed with nitrogen adsorption (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). The latter is also used to estimate the degree of agglomeration of the product powder. External electric fields decrease most dramatically the flame temperature downstream of the electric field controlling particle size, crystallinity and morphology and contribute to the formation of soft agglomerates (without sintering bridges).

In the fifth chapter, a short outlook is given along with recommendations for future experimental directions.
Zusammenfassung


Im zweiten Kapitel wird die kontinuierliche Herstellung von SiO$_2$ und Ruß-SiO$_2$ Mischpulvern in einer turbulenten Wasserstoff/Luft Diffusionsflamme bei Produktionsraten von bis zu 700 g/h untersucht. Dabei liegt die Partikelbeladung (2-10 Massenprozent) nahe an den in der Industrie verwendeten Prozessbedingungen. Der Einfluss des Wasserstoff- und Luftstroms sowie der Hexamethyldisiloxan Flussrate wird systematisch untersucht, wobei die massenspezifische Oberfläche der Partikeln im Bereich von 75 bis 250 m$^2$/g und deren Rußgehalt von 0 bis 1.5 Gewichtsprozent kontrolliert wird. In dieser Studie zeigt sich, dass detailliertere Informationen über die Flammentemperatur hilfreich für die Erklärung der Resultate wären.

Deshalb wird im dritten Kapitel das Hauptaugenmerk auf die Bestimmung von Flammentemperaturen gelenkt. Zunächst werden in einer vorgemischten Methan/Sauerstoffflamme mittels FTIR Spektroskopie gemessene Temperaturen systematisch mit Coherent Anti-Stokes Raman spektroskopisch (CARS) ermittelten Temperaturen verglichen. CARS ist einer der genauesten und anerkanntesten Temperaturmessmethoden, die die Flamme nicht beeinflussen und sich außerdem durch ihre exzellente räumliche und zeitliche Auflösung auszeichnet. Mit Hilfe von tomographischen Methoden kann die räumliche Auflösung der integralen FTIR Messungen verbessert werden und somit ein direkter Vergleich der beiden Messmethoden angestellt werden.

Die Untersuchungen aus dem Kapitel 3 werden im vierten Kapitel vertieft, wobei das Partikelwachstum im elektrischen Feld (1,5 kV/cm) mit thermophoretischer Probenahme untersucht wird und gleichzeitig Flammentemperaturprofile mit FTIR Spektroskopie gemessen werden. Die Produktpartikel werden mit Stickstoffadsorption (BET), Röntgenbeugung (XRD), Transmissions-Elektronenmikroskopie (TEM), und Röntgenkleinwinkelstreuung (SAXS) charakterisiert. SAXS wurde ebenfalls zur Bestimmung des Agglomerationsgrades eingesetzt. Wie im vorangegangenen Kapitel wird die Flammentemperatur in Brennernähe nicht und in größerer Entfernung nachhaltig durch das elektrische Feld gesenkt. Mit Hilfe des elektrischen Feldes können die Morphologie und Kristallinität des Pulvers kontrolliert werden. Weiterhin werden in Anwesenheit des elektrischen Feldes während des Wachstums große (weiche) Agglomerate gebildet, was durch die SAXS Messungen bestätigt wird.

Im fünften Kapitel wird ein Ausblick gegeben und Vorschläge für zukünftige Messungen werden unterbreitet.
1. Flame synthesis of nanoparticles

Abstract

An overview of recent advances in synthesis of nanoparticles by flame aerosol processes is given. In flame processes with gaseous precursors emphasis is placed on reactant mixing and composition, additives, and external electric fields for control of product characteristics. The formation and growth of nanoparticles can be monitored by thermophoretic sampling, while the corresponding temperature history can be obtained by non-intrusive Fourier transform infrared spectroscopy. Furthermore, synthesis of composite nanoparticles for various applications is addressed such as in reinforcement or catalysis as well as for scale-up from 1 to 700 g/h of silica-carbon nanostructured particles. In flame processes with liquid precursors using the so-called flame spray pyrolysis (FSP), emphasis is placed on reactant and fuel composition. The FSP processes are quite attractive as they can employ a wide array of precursors, so a broad spectrum of new nanosized powders can be synthesized. Computational fluid dynamics (CFD) in combination with gas-phase particle formation models offer unique possibilities for improvement and possible new designs of flame reactors.

1.1. Introduction

Flame processes are by far the most widely used ones for manufacture of commercial quantities of nanoparticles. The most important products today are carbon blacks made by Cabot, Columbia, Degussa-Hüls, etc., fumed silica (Cabot, Degussa-Hüls), pigmented titania (DuPont, Ishihara, Millenium, Kerr-McGee) and optical fibers (Corning, Heraeus, Lucent, Sumitomo). The annual production volume of the flame industry is several million metric tons and typical production rates are of the order of 100 metric tons per day. The success and widespread application of this technology is based on its apparent simplicity of a one-step process and “no-moving parts”

---

machinery. At the same time, this is a complex process as all product particle characteristics are determined within a few milliseconds and can be influenced by many process variables. Consequently, it is not surprising to find a large number of early patents claiming all sorts of tricks and gadgets to control product characteristics or to facilitate the operation of flame reactors (Mezey, 1966). As a result, a scientific understanding of flame synthesis of particles remains a major challenge even though a variety of scientific communities have studied it closely.

For example, in production of carbon blacks, pigments and fumed silica the focus is on understanding either how product particle size or crystallinity can be controlled within, say, 10% of specifications, or how agglomerate formation can be suppressed to avoid expensive grinding processes. Agglomerates of large nanoparticles (300 nm) can be advantageous in the manufacture of optical fiber preforms by external processes where water or HCl has to be removed away from the preform prior to consolidation. Likewise, agglomerates of small nanoparticles (10 nm) are attractive in catalyst manufacture where the open structure allows for easy access to and from the particle surface by reactants and products. In contrast, there is a lot of interest in soot formation and suppression from an environmental science and engineering standpoint, by utilities and automotive (especially diesel) manufacturers as well as in carbon film deposition processes.

During flame synthesis of particles, halide (or alkoxide) vapors are oxidized during manufacture of ceramic oxides while fuel droplets are sprayed during production of carbon blacks. This technology was developed by valiant evolutionary research, to the current rates of production of the order of 10 t/h. Recent advances in combustion and aerosol research have brought a new understanding of this technology and will be briefly summarized here. More specifically, it will be shown how reactant mixing, additives, or electric fields are used to control primary particle size and extent of agglomeration when gaseous precursors are used (Pratsinis, 1998). The use of non-intrusive temperature measurement techniques (Morrison et al., 1997) combined with size independent thermophoretic sampling allows a unique view of the evolution of particle growth from single spherical to agglomerated nanoparticles (Arabi-Katbi et al., 2001). These data can be used to develop models describing the evolution of particle growth (Pratsinis et al., 2000) without adjustable parameters revealing, thus, the dominant physicochemical phenomena. Reactor design for flame synthesis of
nanoparticles is now facilitated by interfacing these particle models with computational fluid dynamics (CFD) and particle dynamics (Johannessen et al., 2000 and 2001). Most importantly, CFD can be used to rank reactor designs for synthesis of particles with closely controlled characteristics (Wegner and Pratsinis, 2001).

In these reactors multicomponent particles can be made from gaseous precursors (Katz and Miquel, 1994; Vemury and Pratsinis, 1995b; Zachariah et al., 1995). Using the above tools silica-carbon particles that can be used as fillers in the so-called "green tires" (Byers and McNeish, 1997) can be made with closely controlled composition by controlling reactant composition or the electric field across the flame (Briesen et al., 1998b; Spicer et al., 1998; Kammler and Pratsinis, 2000). The scaling up of these reactors, making particles with controlled composition and morphology is investigated at production rates up to 700 g/h (Kammler and Pratsinis, 1999; Kammler et al., 2001). Multicomponent particles from these flames give rise to new products such as $\text{V}_2\text{O}_5$-$\text{TiO}_2$ catalysts with high selectivity at low temperatures (Stark et al., 2001).

Spray flame technology further broadens the options for synthesis of functional nanoparticles, as there are many liquid precursors available to make particles of complex composition (Laine et al., 1999). Recently, flame spray pyrolysis (FSP) is systematically investigated so as to make particles with closely controlled characteristics (Mädler et al., 2002). In these systems there are two distinct process regimes for particle synthesis depending on the competition between reaction and mass transfer. Furthermore, utilizing the framework of fuel spray combustion, models relating product characteristics to process variables are introduced, giving FSP a firm scientific basis for the synthesis of nanoparticles. This is particularly important, as FSP has not yet been utilized as widely by major industries as flame technology from gaseous precursors.

### 1.2. Nanoparticles by combustion of gases

Nanoparticles are made from gases by the so-called gas-to-particle conversion in flame reactors, hot-wall or furnace reactors, vapor-phase evaporation-condensation processes, plasma furnace reactors, laser and sputtering reactors, to name a few (Granqvist and Buhrman, 1976; Ulrich, 1984; Gurav et al., 1993; Pratsinis, 1998; Wooldridge, 1998;
Kodas and Hampden-Smith, 1999). The advantages of the gas phase processes are the production of product particles of high purity composed of nonporous primary particles with small sizes, and relatively narrow size distribution. Disadvantages include difficulties in producing non-agglomerated particles and multicomponent materials. Flame reactors are used in industrial production of pigments (TiO$_2$) or reinforcing agents (carbon black and SiO$_2$) (Mezey, 1966). For example, the white pigment market has a world wide annual volume of about 3 Mio. t (Braun et al., 1992; Braun, 1997). Half of it is made by flame technology, the so-called "chloride" process. In the USA and other developed countries most of the TiO$_2$ is used for paints (almost 50%), in paper (25 %) and in the fabrication of plastics (20%). The last 5% is used as a pigment (inks, floor coverings, elastomers, roof granules, fibers, fabrics, sealants, foods, to name a few applications), and also has non-pigmentary uses (ceramics, welding rods, catalyst support, etc.) and other applications in specialty products (Braun, 1997). Rutile TiO$_2$ particles are preferred in coatings and paints as they contribute a unique light scattering performance. For this, particles with a narrow size distribution around 200 nm and coated with a layer of SiO$_2$ are desirable (Braun, 1997).

Silica is used to control thickening, thixotropy, and reinforcement (Hartmann et al., 1989), as well as stabilizer for suspensions, as a free flowing, or chemical mechanical polishing (CMP) agent (Sniegowski and de Boer, 2000). Carbon blacks, however, are the most important fillers in rubber industries. Special properties like UV protection, electrical conductance, range of darkness, opacity and reinforcement can be achieved by adding carbon black particles to elastomers, plastics and paints (Donnet et al., 1993).

### 1.2.1. Control of flame aerosol reactors

A typical flame aerosol reactor set-up consists of a precursor unit (bubbler or evaporator), a burner accompanied by a gas delivery system and a filter unit to collect the product particles. Various flame configurations are used for manufacture of nanoparticles, such as premixed and diffusion flames run in co-flow, or counterflow. In the diffusion flame configuration the fuel and the oxidizer diffuse into each other determining flame reaction and particle formation, while in premixed flames the
precursor and the combustible gases are mixed before they enter the reaction zone (flame). A typical oxide particle producing premixed flame is shown in Fig. 1.1. In this oxygen-rich hexamethyldisiloxane (HMDSO)/methane/oxygen flame, luminescence of the flame (Fig. 1.1a) is quite different to the trail of particle formation and growth as visualized with a laser sheet (Fig. 1.1b).

Fig. 1.1: Premixed hexamethyldisiloxane (HMDSO)/methane/oxygen flat flame: (a) in the absence and (b) in the presence of a laser sheet.

Depending on the gas flow rates and burner geometry, flames are either laminar or turbulent. In industry turbulent co-flow reactors are usually used, since large quantities of particles are desired. In academia, laminar flames are preferred as experiments are easier to describe with models in the laminar flow regime than in the turbulent one. Nevertheless, understanding of particle formation in turbulent flames is essential for optimal industrial aerosol reactor design.
1.2.1.1. Effect of reactant mixing

Flame temperature and particle residence time have been shown to be the most important parameters determining the characteristics of the product powder (Ulrich, 1984; Pratsinis, 1998). In flame aerosol reactors the flame temperature field is influenced mostly by the initial reactants and their mixing, and also by the burner geometry. Typical fuels are hydrogen, methane, or ethylene while oxidants are usually air or oxygen. Sometimes these gases are diluted with inert gases such as argon, helium, or nitrogen.

![Reactant mixing configurations for a double or inverted (Flame A and B) and single or classic (Flame C and D) diffusion flame reactor (Pratsinis, 1998).](image)

*Fig. 1.2: Reactant mixing configurations for a double or inverted (Flame A and B) and single or classic (Flame C and D) diffusion flame reactor (Pratsinis, 1998).*

Reactant mixing (Fig. 1.2) can affect the product particle size by one order of magnitude (Pratsinis et al., 1996). Titania particles produced in a double (inverted) diffusion flame (primary particle diameter ~ 10 nm) (Flame A) were up to 10 times smaller than particles produced in a single (classic) diffusion flame (Flame D), where even non-agglomerated particles of a diameter of about 100 nm were made (Pratsinis et al., 1996) as proven by small angle X-ray scattering (Hyeon-Lee et al., 1998). The inverted diffusion flame produced always finer particles (SiO₂, SnO₂, TiO₂, Al₂O₃) than the classic diffusion flame due to lower temperatures in the former flames (Pratsinis et al., 1996; Zhu and Pratsinis, 1996 and 1997).
Operating a diffusion flame reactor with oxygen instead of air, Zhu and Pratsinis (1997) increased the size of product silica particles by about 5 times in a single SiCl₄/methane diffusion flame (Flame C). In inverted diffusion flames (Flame B) this difference was less pronounced, as only 50% larger particles are formed with oxygen compared to air as oxidant. Using oxygen leads to faster fuel consumption, and therefore to higher flame temperatures and to shorter flames, thus, the precursor oxidation as well as growth and sintering is enhanced. In a similar set-up, Briesen et al. (1998a) found a similar increase of the primary product particle size investigating different silica precursors (SiCl₄, hexamethyldisiloxane (HMDSO), and octamethylcyclotetrasiloxane (OMCTS)), when they replaced air by oxygen.

For SnO₂ particles from SnCl₄ the choice of oxidant (air or oxygen) did not affect the average primary particle size, even though the primary particle size could be closely controlled by the oxidant flow rate as for SiO₂ (Zhu and Pratsinis, 1997). For the same flow rates, however, only the flame configuration and therefore reactant mixing affected the SnO₂ product particles (Zhu and Pratsinis, 1997). It could be seen that particles produced in an inverted diffusion flame (Flame B) were 1.8-2.4 times smaller than those made in a single diffusion flame (Flame C). For Al₂O₃ particles made from aluminium-tri-sec-butoxide Johannessen et al. (2000) observed particles with 1.2-1.4 times larger specific surface area in the inverted diffusion flame (Flame B) set-up compared to particles made in a single diffusion flame (Flame C).

For titania the oxidant did not affect the size of the average primary particle in inverted diffusion flames (Flame A, B), while significantly larger TiO₂ particles (2-3 times) were formed in single diffusion flames (Flame C) substituting air by oxygen (Zhu and Pratsinis, 1996). In a classic diffusion flame (Flame C) the rutile content was progressively retarded from 13.2 to <0.1 wt. % by increasing the oxygen concentration of the oxidant from 21% (air) to 100% (pure oxygen). However, in an inverted diffusion flame (Flame B), the rutile content remained constant (about 8 wt. %) for all the oxidant compositions investigated. At these conditions an increasing number of perfectly spherical non-agglomerated particles (200-300 nm) were made by increasing the oxygen concentration in the classic diffusion flame (Flame C).

Wegner and Pratsinis (2001) showed that reactor geometry could also significantly change product powder characteristics. Using the same gas and precursor flow rates as Briesen et al. (1998a), they produced primary silica particles which were 4
times smaller using HMDSO in a reactor with a diameter about a quarter of the one used by Briesen et al. (1998a). The enhanced mixing of the gases in their smaller reactor leads to a steeper temperature gradient as confirmed by CFD calculations. Furthermore, the burner outlet velocities are significantly higher compared to Briesen et al. (1998a), which reduces the residence times of the particles in the hot flame zone and consequently there is less time for growth and sintering.

1.2.1.2. Effect of precursor

Zachariah and Semerjian (1990) and Ehrman et al. (1998) investigated different silica precursors and did not observe significant effects on SiO₂ particles. However, the choice of precursor becomes important when a considerable amount of heat is provided by the combustion of the precursor itself (Briesen et al., 1998a). This becomes more pronounced for higher precursor concentrations (Kammler and Pratsinis, 1999; Kammler et al., 2001). Silica particles made from organosilicon compounds had significantly lower specific surface area than those produced from SiCl₄ (Briesen et al., 1998a) for all investigated oxidant flow rates in diffusion and premixed aerosol flame reactors. In premixed flames Briesen et al. (1998a) correlated the specific surface area of the product with the adiabatic flame temperature, which is determined by the choice of precursor.

Besides altering the flame structure, the amount of precursor introduced into the flame determines the collision frequency of the particles during the growth process. Pratsinis et al. (1996) found that the specific surface area of titania particles was halved by increasing the inlet TiCl₄ concentration by a factor of 10 for inverted diffusion flames (Flame B). Similarly, the specific surface area was decreased by 1.4-1.6 times in single diffusion flames (Flame C) consistent with Formenti et al. (1972) and Ulrich et al. (1976) making SiO₂ from SiCl₄. However, Ulrich and Riehl (1982) observed that the flame temperature is more important than SiO₂ concentration for the particle specific surface area. For silica production in pure HMDSO/oxygen double diffusion flames Kammler and Pratsinis (1999) found that the specific surface area of silica product powders decreased from 175 to 22 m²/g quadrupling the HMDSO concentration. As HMDSO was the only fuel in these experiments, increasing the HMDSO concentration
increased the energy content of the flame, thus, the flame temperature and SiO₂ concentration were increased. At higher flame temperatures the growth and sintering rates are enhanced and increasing the SiO₂ concentration increased the collision frequency of the particles. Additionally, the flame height increased as more fuel was introduced, increasing the residence time of the particles in the flame, and therefore prolonging the time for growth and sintering, resulting in the observed low product specific surface areas.

1.2.1.3. Effect of additives

Additives can be used to control the primary particle size or crystallinity and the extent of agglomeration when the purity of the product powder is not a primary concern (Pratsinis, 1998). For example, small amounts of AlCl₃ are injected to promote the formation of rutile titania and to moderate aggregation in its manufacture from the chloride process (Braun, 1997). Vemury et al. (1995b) studied the effect of additives on phase composition, morphology and size of titania product particles in laminar diffusion flames doping the TiCl₄ stream with various amounts of SiCl₄, SnCl₄, and AlCl₃, respectively. They found that doping the titania with silica inhibits the titania phase transformation from anatase to rutile, and decreases the primary particle size, thus, increases the specific surface area. In the flame reactor significantly larger amounts of silica had to be added to completely inhibit the phase transformation from anatase to rutile compared to particles made in electrically heated hot-wall reactors (Akhtar et al., 1992) as the temperature and residence times of the particles are less homogeneous in flame aerosol reactors. Furthermore, the addition of SnCl₄, and AlCl₃ promoted the anatase to rutile phase transformation and increased the average primary particle diameter. For example, the addition of 20 mol% AlCl₃ reduced the specific surface area of the product powder from 54 to 35 m²/g. However, more dopant had to be added to the flame reactor in order to achieve identical product powder crystallinity compared with powders made in the hot wall reactor (Akhtar et al., 1994). In silica synthesis Fotou et al. (1995) observed that adding ferrocene to SiCl₄ in methane/air diffusion flames led to an increase in the specific surface area of the silica product powder of up to 150%. 
Additives are widely used in the carbon black industry to control the morphology of the product even though their exact mechanism is not well understood.

1.2.1.4. Effect of external electric fields

For precise control of product powder characteristics, external electric fields have been shown to be quite effective and are intriguing as they can be readily implemented into the reactor set-up.

![Graph showing specific surface area of TiO₂ product powder made by titanium tetraisopropoxide (TTIP) oxidation in a premixed methane/oxygen flat flame as a function of the applied electric field strength.](image)

*Fig. 1.3: Specific surface area of the TiO₂ product powder made by titanium tetraisopropoxide (TTIP) oxidation in a premixed methane/oxygen flat flame as a function of the applied electric field strength.*
The newly formed particles are charged in the electric field either by ion or electron attachment, so the coagulation rate of the particles is reduced, as unipolarly charged particles repel each other. Charged particles are also attracted toward the electrodes, thus lowering the local particle concentration and therefore the collision rate. The flame structure, height, and temperature are also altered by the electric field, which can significantly influence the particle residence time at high temperatures and therefore affect particle growth and sintering. It was shown, that external electric fields can reduce the average particle size by up to a factor of two as determined by nitrogen adsorption (Vemury and Pratsinis, 1995a and 1996; Vemury et al., 1997; Katzer, 2000). Figure 1.3 shows the narrow control of the specific surface area of product titania particles by the electric field strength between two electrodes across the flame flow. Increasing the electric field strength flattened the flame as shown by the inserts in Fig. 1.3. Recently, Kammler and Pratsinis (2000) demonstrated that external electric fields can also precisely control the specific surface area of the product powders at SiO₂ production rates up to 87 g/h. They further confirmed that positioning the electrodes near the decisive particle formation zone of the flame is necessary for successful operation of the electric fields (Vemury and Pratsinis, 1995a).

In premixed honeycomb-stabilized flat flames Vemury et al. (1997) made TiO₂ consisting of pure anatase (99.9%) and the electric field did not change the powder crystallinity. Using non-stabilized premixed flames, however, they could control the rutile fraction from 82 to 65% by increasing the electric field strength between two needle electrodes from 0 to 2.75 kV/cm (Vemury et al., 1997). In a diffusion burner set-up, they decreased the rutile content of TiO₂ powders steadily from 20 to 8 wt. % using electric field strengths between 0 and 1.75 kV/cm, respectively (Vemury and Pratsinis, 1995a). In contrast to reactant mixing, electric fields are effective for precision control over a narrow range (up to a factor of 2) and as such can find applications as a control device or for synthesis of functional nanoparticles with highly sensitive properties with respect to particle characteristics.
1.2.1.5. Monitoring particle growth in atmospheric flames

The growth of particles is mostly determined by the flame temperature and particle residence time (Ulrich, 1984). Therefore, it is of great importance to have accurate temperature profiles in flame aerosol reactors. In principle, conventional laser diagnostic methods are limited for application in particle laden flames, as interferences of the response signal with particulate matter may weaken signal intensity and increase the complexity of signal evaluation. Recently, however, laser-induced fluorescence (LIF), that has been used in gas phase combustion (Eckbreth, 1988), was successfully used in dilute particle laden low pressure flames to measure flame temperature and to detect local concentrations of SiO (Zachariah et al., 1996; Glumac et al., 1998), FeO (McMillin et al., 1996), AlO and TiO (Colibaba-Evulet et al., 2000).

Fourier transform infrared (FTIR) spectroscopy has been used to reliably determine flame temperatures in the presence of soot, silica and titania (Best et al., 1991; Solomon and Best, 1991; Morrison et al., 1997; Farquharson et al., 1998) and even inside an electrically assisted flame (Morrison et al., 1997). The FTIR relies on emission/transmission measurements to calculate the normalized radiance, which can be directly compared to a blackbody Planck function to determine the flame temperature (Best et al., 1986). Comparison of this technique with other flame diagnostics such as thermocouple injection methods or coherent anti-Stokes Raman scattering (CARS) in an ethylene-air diffusion flame demonstrates the strength of this technique (Boedecker and Dobbs, 1986; Santoro et al., 1987; Best et al., 1991).

Figure 1.4 shows an axial flame temperature profile of a premixed HMDSO/methane/oxygen flat flame, converting 20 g/h HMDSO to nanosized SiO$_2$ particles. The temperature rises quickly and decreases slowly with increasing distance, which is typical for premixed flames (Glassman, 1996). In Fig. 1.4 a typical evaluation scheme of the temperature at a flame height of 5 mm is included, in which the normalized radiance spectrum of the flame is compared to a blackbody Planck function of a certain temperature. This match is achieved by a least squares fit in the wavenumber range of hot CO$_2$ (2200-2300 cm$^{-1}$). The H$_2$O is detected at 4000-3500, 1800-1200, and 800-600 cm$^{-1}$ and the blackbody Planck function at the matched temperature fits these bands also reasonably well.
Fig. 1.4: Axial temperature profile of a premixed HMDSO/methane/oxygen flat flame. In the lower part of the figure a typical comparison of the normalized radiance spectrum with the blackbody Planck function is shown, using a least squares fit in the wavenumber range of hot CO$_2$ (2200-2300 cm$^{-1}$). Species detectable at other wavenumber ranges are named.

Arabi-Katbi et al. (2001) and Pratsinis et al. (2000) monitored particle growth in premixed titanium tetraisopropoxide (TTIP)/methane/oxygen flat flames with thermophoretic sampling (Dobbins and Megaridis, 1987; Megaridis, 1987). They measured axial flame temperature profiles for various particle concentrations by FTIR exactly at the same locations where the particle growth was monitored by a thermophoretic sampler. Figure 1.5 shows the evolution of TiO$_2$ particle growth along...
Fig. 1.5: TEM pictures of TiO$_2$ particles at increasing heights above the burner as obtained by thermophoretic sampling in a premixed TTIP/methane/oxygen flat flame making 3.1 g/h TiO$_2$. 
the height above the premixed TTIP/methane/oxygen flame as obtained by thermophoretic sampling in our laboratories making 3.1 g/h TiO₂. At low heights, small agglomerate formation was observed, while the particles are almost non-agglomerated and perfectly spherical at higher positions, before agglomeration sets in at even higher positions (close to the filter). The particles grow rapidly close to the burner and the growth levels off further downstream, when the flame temperature is reduced. These data now can be compared with particle dynamics models as will be discussed in Section 1.4. of this work.

Alternatively, in low pressure premixed flames Lindackers et al. (1994, 1997, and 1998) applied aerosol mass spectroscopy (AMS; a combination of a quadropole mass spectrometer with cross-beam ion source and a particle mass spectrometer (Roth and Hospital, 1994; Janzen et al., 1999)) to monitor the particle size evolution with increasing distance from the burner. Silica particle diameters (Lindackers et al., 1997), as well as those of alumina and tin oxide nanoparticles (Lindackers et al., 1998) increased from 3.0 to 7.6 nm, 4.7 to 8.4 nm, and 2.7 to 8.3 nm, respectively, increasing the distance between the burner and the sampling nozzle from 20 to 80 mm. The flame temperature profiles were calculated using the PREMIX code from Sandia National Laboratories (Kee et al., 1985) and are included in a particle growth model accounting for particle formation and growth by Brownian coagulation (Lindackers et al., 1997).

1.2.2. Multicomponent particles

A mixture of precursors can be used to produce multicomponent particles, which can have special properties such as superconductivity (Zachariah and Huzarewicz, 1991), superparamagnetism (Zachariah et al., 1995), or increased catalytic activity (Stark et al., 2001), for example. The formation of multicomponent particles from gaseous precursors in counterflow diffusion flame reactors has been extensively investigated by Katz and co-workers (Hung and Katz, 1992; Hung et al., 1992; Miquel et al., 1993; Katz and Miquel, 1994; Miquel and Katz, 1994) making TiO₂/SiO₂, Al₂O₃/TiO₂, SiO₂/GeO₂, V₂O₅/TiO₂, V₂O₅/Al₂O₃, and VPO.

Zachariah et al. (1995) studied the synthesis of mixed ironoxide-silica particles and found that 5-19 nm Fe₂O₃ particles embedded in much larger SiO₂ particles
exhibited superparamagnetic behavior. In premixed aerosol flame reactors Ehrman et al. (1999) investigated binary SiO₂/TiO₂ and SiO₂/Fe₂O₃ nanoparticle formation by varying the Ti or Fe to Si mole ratios. Phase segregation was observed to varying degrees in qualitative agreement with segregation expected from binary phase diagrams for the bulk systems. Differences between the SiO₂/TiO₂ and SiO₂/Fe₂O₃ systems were explained by considering the variation in the thermodynamically stable liquid-phase solubility and differences in the ability of iron and titanium ions to substitute for silicon ions in the network structure.

1.2.2.1. Vanadia coated titania nanoparticles for selective catalytic reduction of NO

In various applications segregated phases may be advantageous. For example maximum activity and selectivity of vanadia coated titania catalysts is achieved when the vanadium oxide is present as an amorphous mono-layer at the surface of the titania particles (Bond and Tahir, 1991). Vanadia coated titania is a well known catalyst e.g. for the selective oxidation of o-xylene to phthalic anhydride (Braun et al., 1992) or for selective catalytic reduction (SCR) of NO by NH₃ (Bosch and Janssen, 1988). This catalyst is typically prepared in liquid phase processes. Nevertheless, Katz and co-workers (Miquel et al., 1993; Katz and Miquel, 1994; Miquel and Katz, 1994) produced titania nanoparticles in a counterflow diffusion flame with 14, 25, and 50 wt. % vanadia from TiCl₄ and VOCl₃, however, they did not report the activity of their product. Stark et al. (2001) synthesized spherical titania particles coated homogeneously with amorphous vanadia in a co-flow diffusion flame from titanium tetraisopropoxide and vanadium oxotriisopropoxide. Flame generated titania formed small spheres with diameters of 10 to 50 nm. Using high-resolution transmission electron microscopy (HRTEM) no interstitial solution of vanadium was found inside the titania lattice. Lattice fringes were discernible up to the surface of the particles corroborating their monocristalline structure (Stark et al., 2001). X-ray photoelectron spectroscopy analysis indicated that the vanadia was dispersed on the surface of the titania particles. The vanadia content (0-10 wt. %) did not influence the specific surface area of the product powder, while the specific surface area was increased significantly from 23 to 120 m²/g,
by increasing the oxygen flow rate from 2 to 10 L/min. Adding more oxygen to the flame accelerates the oxidation process as fuel-oxidant mixing is enhanced (Wegner and Pratsinis, 2001), thus, the flame height decreases and the excess oxygen cools the flame. This leads to smaller particles as sintering rates decrease with decreasing temperatures and particle residence times reduce due the faster gas flow rate and reduced flame height. These $\text{V}_2\text{O}_5$ coated TiO$_2$ catalyst particles were tested to convert NO to N$_2$ at low temperatures in a continuous fixed flow reactor (Engweiler and Baiker, 1994; Reiche et al., 2000) at a global space velocity of 24000/h (Stark et al., 2001).

![Graph of NO conversion as a function of catalysis temperature for a flame-made (diamonds) and wet-chemistry-made (circles) vanadia coated titania catalyst (courtesy of W. J. Stark, ETHZ).](image)

In Fig. 1.6 the performance of a flame-made catalyst (diamonds) and a catalyst prepared by wet chemistry (circles) (Baiker et al., 1988) are compared at different...
catalyst temperatures. At a catalysis temperature of 480 K the NO is completely converted to N\textsubscript{2} by the flame-made catalyst, while at the same temperature only 92% NO is converted to N\textsubscript{2} by the wet-chemistry-made catalyst. One can clearly see that the flame-made catalyst can compete with state of the art catalysts, and it shows even slightly better performance even at lower process temperatures.

1.2.2.2. Silica-carbon composite particles

The combination of carbon black and silica in composite particles (Wang et al., 1998) is more effective in reinforcing rubber compared to carbon black alone, providing the potential to make the so-called "green tires". The silanol groups on the silica surface together with an organosilane coupling agent are used to form a silica network in the rubber, which enhances the tire reinforcement as it decreases the rolling resistance by up to 24% (Padula, 1995). The wet traction and tread wear are similar to that of conventional tires (Byers and McNeish, 1997), while decreasing the rolling resistance of car and truck tires significantly decreases fuel consumption (3 - 5% and 6 - 8%, respectively) (Padula, 1995). The specific surface area of silica powders in green tires should be lower than 180 m\textsuperscript{2}/g (Blume, 2000) and the carbon ensures good dispersibility and static electricity dissipation (Donnet et al., 1993; Byers and McNeish, 1997).

Various SiO\textsubscript{2}-C composite powders with a carbon content up to 30% were synthesized by Spicer et al. (1998) from SiCl\textsubscript{4} and acetylene in a premixed flame. They found a significant increase in the carbon black yield (up to three times) by the presence of silica compared with a pure acetylene flame of the same equivalence ratio. The silica particles acted as seed nuclei for carbon surface growth, while the presence of chlorine reduced the flame temperature favoring enhanced carbon (soot) formation. Kammler and Pratsinis (1999) made silica-carbon particles with carbon content up to 5 wt. % in a ring shaped HMDSO/oxygen double diffusion flame at production rates up to 130 g/h. Soot formation (up to 2 wt. %) during silica synthesis was also reported by Briesen et al. (1998b) producing 30 g/h of powder in electrically assisted flames as well as by Kammler and Pratsinis (2000). The latter could precisely control the product powder carbon content (0-1 wt. %) with the electric field intensity.
1.2.3. Pilot-scale production of nanoparticles

Scaling-up flame aerosol reactors used to involve tedious Edisonian research to make product powders with closely controlled characteristics, even though the flame aerosol process has been utilized in industry for more than 50 years (Kloepfer, 1952). However, large-scale production of new materials or special composite particles can comprise a similar evolution of steps. Therefore, fundamental research has to be conducted on pilot-scale reactors in order to establish a connection between small-scale laboratory units and their large-scale counterparts. Applying the principles of scale-up in reactor design is not as straightforward as one might wish. In many cases it is impossible to simultaneously satisfy scale-up constraints called for by different forms of similitude. Therefore, databases have to be created in order to evaluate the key parameters of these processes.

As an example, continuous production of silica and silica-carbon nanostructured particles with controlled composition and morphology is presented, at production rates up to 700 g/h and up to 10 % solid fraction by mass, which is close to that of industrial processes. These particles were made in a turbulent single diffusion flame reactor (Fig. 1.7) using hydrogen and air as fuel and oxidizer, respectively. On the left-hand side of Fig. 1.7 the baghouse filter can be seen, which allows continuous powder production as demonstrated by operating for 5 h at a production rate of 700 g/h (Kammler et al., 2001). In Fig. 1.7 the particle producing flame is shown with the collection pipe above the flame connected to the baghouse filter. On the right hand side, a typical silica particle producing flame is shown. The specific surface area of the product powders was controlled by reactant stream composition in the range of 75 to 250 m²/g, corresponding to average primary particle diameters of 36 to 11 nm, respectively.

Figure 1.8 shows the average primary particle diameter of the product powders obtained by nitrogen adsorption (BET) (Brunauer et al., 1938) as a function of the air flow rate at a production rate of 300 g/h. The average particle diameter decreases with increasing air flow rate. The increased amount of oxygen along with higher gas velocities leads to enhanced oxygen availability and reactant mixing by turbulence. This reduces the flame height and the fuel/precursor is consumed faster.
Fig. 1.7: Photograph of a pilot-scale flame aerosol reactor, which can produce nanostructured silica-carbon powders at production rates up to 700 g/h.

However, large amounts of inert gas (nitrogen) are delivered to the flame as well, which can significantly lower flame temperature. At lower flame temperatures the particle growth and sintering rates are decreased, thus smaller particles are formed.
Fig. 1.8: Average primary particle diameter obtained by nitrogen adsorption (BET) as a function of air flow rate with (circles) and without (triangles) secondary air entrainment at production rates of 300 g/h in the reactor of Fig. 1.7.

The effect of air entrainment into this flame reactor was investigated by encasing the flame with a stainless steel chimney (Kammler et al., 2001). In Fig. 1.8 the average primary particle diameter of the product silica powders in the absence (circles) and in the presence of a chimney surrounding the flame (triangles) are shown. In the absence of the chimney, air from the surroundings can be entrained into the flame leading to enhanced fuel consumption. This leads to higher flame temperatures, which increases the sintering rate and leads to the formation of larger particles for air flow rates less than 120 L/min (Fig. 1.8). At high air flow rates, however, enough air is provided to diminish the effect of entrained (secondary) air availability. The average primary particle
diameter is almost identical with or without the chimney, indicating that at high production rates that are typically encountered in industry, air entrainment is not a crucial parameter affecting product particle characteristics.

By varying the hydrogen flow rate the powder composition can be closely controlled, since the flame temperature is directly affected. At high hydrogen flow rates (36.5 L/min) pure silica powders were obtained, while decreasing the hydrogen flow rate increases the carbon weight fraction of the product powder. However, the specific surface area of these powders made at powder production rates of 300 g/h decreases slightly, when increasing the hydrogen flow rate, due to higher flame temperatures. Keeping the hydrogen and air flow rates constant and increasing the production rate from 125 to 700 g/h, the specific surface area is decreased from 222 to 75 m²/g. Increasing the production rate, however, increases the hydrocarbon fuel input to the flame by HMDSO, in contrast to the increase of hydrogen, where the hydrocarbon fuel (HMDSO) concentration was constant. This leads to enhanced carbon formation as well as increased flame heights and the carbon content of the powder increases which was determined by thermogravimetric analysis (Kammler et al., 2001). In this hydrogen/air diffusion flame reactor silica-carbon composite particles were only formed above a molar C/H ratio of 0.12, which was consistent with the onset of soot formation of acetylene-hydrogen mixtures in air diffusion flames observed by Schug et al. (1980). With C/H < 0.12, however, perfectly white silica powders were produced.

1.3. Nanoparticles by combustion of liquid droplets

In flame spray pyrolysis (FSP), sometimes called liquid flame spray (LFS), the heat is provided by the combustion of a gaseous or liquid fuel and the precursor itself. Multicomponent oxide powders such as β-SrMnO₃ and NiMn₂O₄ (Kriegel et al., 1994), and superconductors (Zachariah and Huzarewicz, 1991; Feldmann-Schlobohm et al., 1998), alumina (Tikkanen et al., 1997) as well as BaTiO₃ (Brewster and Kodas, 1997) have been made by pyrolysis of solutions containing inorganic precursors in oxy-hydrogen flames. Fully dense primary particles in the size range of 100-500 nm were produced which may have resulted from the rapid disintegration of solution droplets when they enter the high-energy flame (Law, 1982). Using organic solvents as liquid
fuel, leads to a self-sustaining spray flame. This process has the potential to produce composite mixed-metal oxide powders in the size range of 1 to 200 nm from low cost precursors (Narayanan and Laine, 1997) with production rates up to 250 g/h, as it was summarized recently by Laine et al. (1999 and 2000). Typical products synthesized are titania (Bickmore et al., 1998) and MgAl$_2$O$_4$ (Bickmore et al., 1996), $\gamma$-Fe$_2$O$_3$ (Grimm et al., 1997), alumina (Bickmore et al., 1996), manganese oxide, zirconia, and zirconia-ceria (Sokolowski et al., 1977; Karthikeyan et al., 1997; Tikkanen et al., 1997; Tani et al., 1998) particles, or very specific functional particles such as $\beta^\prime$-alumina for high temperature solid electrolytes (Sutorik et al., 1998; Treadwell et al., 1998), to name a few. These processes clearly differ from the conventional spray pyrolysis (Messing et al., 1993) as the precursor is released from the droplet environment undergoing gas phase reaction and subsequent particle growth by coagulation, surface growth and sintering. Here, direct parallels can be drawn with vapor flame synthesis.

### 1.3.1. Flame spray reactors

A typical set-up for nanoparticle synthesis by flame spray pyrolysis consists of a unit for generation and dispersion of droplets, a heat source for initial droplet evaporation and ignition (pilot flame or the spray flame itself for combustible liquids), and an oxidant to facilitate combustion. These parameters control the temperature profile and gas phase reaction of the precursor followed by subsequent particle growth and sintering, taking place within and after the spray flame. The product powder is collected by filtration or thermophoresis. The production of micron-sized liquid droplets can be achieved using various atomizers (Lefebvre, 1989), whereas ultrasonic and gas assist pressurized atomizers are most common in spray combustion. Ultrasonic atomizers show good performance with regard to droplet size and homogeneity (Rodes et al., 1990) and the droplets can be embedded in any gaseous flow for transport into the reaction zone, where the droplet velocity can be controlled independently. Gas assist pressurized atomizers, however, are easy to incorporate into the spray flame apparatus and their operation is simple and reliable. High shear rates are needed to disintegrate the liquid jet, thus, high gas velocities are inevitable leading to the high quenching ability of such reactors resulting in small product particles (Mädler et al., 2002).
Fig. 1.9: Self-sustaining spray flame, making fumed silica from a 0.1 molar HMDSO in ethanol solution.

Figure 1.9 shows a turbulent oxygen HMDSO/ethanol spray flame. The droplets are formed by a two-phase nozzle where the oxygen acts as both dispersant and oxidant gas disintegrating the liquid jet supplied by a syringe pump. A ring of six premixed methane/oxygen flamelets (shown as little bumps at the base of the spray flame, Fig. 1.9) provides enough heat for initial droplet evaporation and serves as ignition source. For a given nozzle opening the droplet size is controlled by the liquid-to-gas mass ratio
(Lefebvre, 1989; Perry, 1997). The product particles are collected on a glass fiber filter. With the current set-up a variety of metal and mixed metal oxide nanoparticles such as SiO$_2$, TiO$_2$, Bi$_2$O$_3$, Al$_2$O$_3$, BaTiO$_3$ all in the size range below 30 nm have been prepared in our laboratories.

1.3.2. Effect of spray composition

1.3.2.1. Precursor liquid composition

The precursor composition is a key parameter in flame spray pyrolysis (FSP) in order to achieve the preferred product properties. The choice of precursor depends on cost, reactivity, selectivity (e.g. suppression of carbide formation during the production of BaTiO$_3$), stability before processing, and low toxicity. In wet chemical processing of metal oxides and mixed metal oxides, nitrate precursors are often used. Spraying these precursors as aqueous solutions into hot wall reactors resulted in micrograined amorphous powders as demonstrated by Jokanovic et al. (1996). However, Karthikeyan et al. (1997) found that when a solution of nitrate precursors and organic solvents (e.g. ethanol, iso-propanol) was sprayed into a pilot flame crystalline and dense alumina nanoparticles were made. In our laboratories we produced bismuth oxide from bismuth nitrate in an ethanol solution that was stabilized with 15% nitric acid. These particles find applications in pharmaceuticals (Dresow et al., 1992) and varistors (Metz et al., 2000). Crystalline nanoparticles with an average primary particle diameter down to 13 nm were obtained as determined by nitrogen adsorption (BET) and X-ray diffraction (XRD). Figure 1.10 shows a TEM micrograph of crystalline Bi$_2$O$_3$ particles prepared by flame spray pyrolysis with a BET average primary particle diameter of 27 nm. The flame was self-sustaining, even though a nitrate precursor was used.

Vollath and Sickafus (1992), and Karthikeyan et al. (1997) reported that organometallic precursors form particles of improved homogeneity and with smaller grain size distributions when compared to aqueous solutions. This was attributed to the presence of water droplets or vapor in the reaction zone producing larger particles and was also observed for higher gas flow rates during production of Bi$_2$O$_3$ in our laboratories. Even though organometallic precursors are typically more expensive than
their halide or nitrate counterparts, the higher product powder quality (better homogeneity and smaller grain size distribution) may compensate for this. Organometallic precursors are often used in combination with an organic solvent (e.g. alkoxides, acetates, acetylacetonates, etc.), resulting in a self-sustaining spray flame.

An elegant way for manufacture of mixed metal precursors was performed by the implementation of the stoichiometric preset of the desired metals into an organic complex (Narayanan and Laine, 1997). This concept was successfully applied in production of mullite nanoparticles (Laine et al., 2000) from alkoxide complexes. In another example, BaTiO$_3$ was synthesized from organometallic precursors, where the precursor preparation from ethanol, TTIP and barium-II-ethyl-hexanoate first formed a Ba-Ti alkoxide (Thomas et al., 1997), which was then introduced into our self-

Fig. 1.10: Transmission electron micrograph of Bi$_2$O$_3$ particles made directly by flame spray pyrolysis (FSP).
sustaining spray flame reactor. BaTiO$_3$ nanoparticles with an average particle size below 50 nm were produced, which are smaller than those of Brewster and Kodas (1997) who made them by spraying nitrate solutions in oxy-hydrogen flames. The precursor release from the droplet, its decomposition and gas phase reaction are important steps in formation of the final product. The precursor composition plays an important role, but this is still not well understood. For example, it was found by Gardner and Messing (1984) that 14 nm MgO nanoparticles were formed from Mg(CH$_3$COO)$_2$, but not from Mg(NO$_3$_)$_2$. Although both salts yielded particles consisting of nanocrystallites, it was proposed that the oxidation of the carbonaceous residue from the acetate resulted in non-agglomerated nanocrystallites. In order to improve phase homogeneity, gelation of the precursor within the fuel droplet could be advantageous.

1.3.2.2. Liquid fuel composition

Besides the precursor composition, Mädler et al. (2002) found that the total energy content of the spray flame and the evaporation rate of the liquid fuel are important parameters controlling the product powder properties. Figure 1.11 shows the specific surface area of the SiO$_2$ product powder as a function of the of dispersion gas flow rate in a self-sustaining spray flame, using a 0.1 molar mixture of HMDSO and ethanol (diamonds) and iso-octane (circles) as fuel, respectively.

Increasing the dispersion gas (oxygen) flow rate, the specific surface area increases from 220 m$^2$/g (at 1.7 L/min) to a maximum value of 320 m$^2$/g (at 3 L/min) and then drops to 230 m$^2$/g (at 4.4 L/min) for higher flow rates using ethanol as solvent. At low oxidant flow rates the specific surface area increases with increasing oxidant flow rate as the height of the spray flame is reduced, leading to shorter residence times, thus, reducing the time for particle growth. At high oxidant flow rates, the fuel is consumed faster leading to shorter flames (Fig. 1.9) and higher maximum temperature. The fuel and precursor reaction is more intense for high oxygen flow rates, and takes place in a smaller unit volume initiating fast precursor release at higher temperatures, thus, leading to enhanced sintering rates and, therefore, to smaller specific surface areas. With iso-octane as fuel, only the declining branch of the specific surface area is found
(Fig. 1.11), has 1.5 times higher enthalpy content and a 1.5 times higher evaporation rate during the combustion compared to ethanol (Gutheil, 1998).

![Graph showing specific surface area of SiO₂ particles made by FSP for 0.1 molar HMDSO/organic fuel solution as a function of dispersion gas (oxygen) flow rate using ethanol (diamonds) and iso-octane (circles) as solvent.]

Since the temperature of the flame is substantially higher for iso-octane, the specific surface area is substantially lower (120 m²/g at 4.6 L/min) for higher flow rates, even though the SiO₂ production rate is 2.1 times that of the HMDSO/ethanol mixture for fixed molar ratios of HMDSO to solvent. Here, the liquid fuel composition is an important temperature profile defining parameter and therefore influences particle growth and sintering. A similar trend was found by Briesen et al. (1998a) who reported a drastic drop in the specific surface area of silica at higher adiabatic flame
temperatures, which is in accordance with the present data of the energy of the spray flames comparing ethanol and iso-octane fuels. This example clearly shows the importance of controlling the droplet evaporation and combustion in production of oxide particles by flame spray pyrolysis. Information on burning rates and droplet lifetime and thus precursor decomposition (reaction) can be gained from spray combustion models and incorporated in existing models of particle synthesis in vapor flames.

1.4. Modeling of nanoparticle formation and growth

The development of mathematical models for simulation of particle formation and growth is intriguing because they connect input parameters such as reactant state, composition, and volume flow as well as reactor geometry, to particle or powder characteristics such as particle size, agglomerate structure, porosity, morphology, and crystallinity. This information can contribute to process optimization and control of existing and new products, accelerate scale-up, minimizing down-time due to modifications and increase yield of the process, thus decreasing the cost of raw materials per product.

In the literature, there are numerous models (modisperse-, moment-, sectional-, and Monte-Carlo-types) describing particle growth in flames. An introduction to particle dynamics models is given e.g. by Kodas and Hampden-Smith (1999), in which they discuss advantages and disadvantageous of the certain approaches. The latest advances in the calculation of sintering rates for oxide nanoparticles was achieved by accounting for the dependence of the melting point on particle size for titania and alumina (Xing and Rosner, 1999) and for silica (Tsantilis et al., 2001). Experimental data on particle size evolution as obtained by thermophoretic sampling and information about the flame temperature from FTIR at the same location (Arabi-Katbi et al., 2001) can be used to develop models that describe the evolution of particle growth (Pratsinis et al., 2000). From this data, effective rates of reaction on the particle surface can be extracted.

One result of a better understanding of the effect of detailed flow fields and detailed temperature information on particle growth could be the design of special
burners. A first attempt was used to visualize flow patterns and gas concentration evolution of different diffusion burner geometries (Wegner and Pratsinis, 2001), putting emphasis on the mixing of the concentric jets. The mixing is controlled by the velocity gradient of co-flowing jets.

Fig. 1.12: Velocity vectors (right), iso-molar lines of argon fraction (middle), both calculated by computational fluid dynamics, and TEM micrographs of SiO$_2$ product powder (right), obtained from a micro-scale diffusion flame reactor (Wegner and Pratsinis, 2001). The flow rate of oxygen through the third (outer) tube is 1.5 L/min (a) and 8 L/min (b), while the flow rates of argon (center tube) and methane (second tube) were kept constant 0.25 and 0.4 L/min, respectively (courtesy of K. Wegner, ETHZ).

The velocity vectors of the jet and lines of constant argon molar fraction, which indicate the precursor stream, are calculated by computational fluid dynamics and are presented in Fig. 1.12. Increasing the oxygen flow from 1.5 to 8 L/min in the third (outer) tube and keeping the other flow rates constant significantly increases mixing and forms a toroidal recirculating vortex in the central region. The local precursor concentration indicated by argon diminishes almost instantaneously for the high oxygen flow rate (8
L/min), thus mixing and dilution of the reactants occurs close to the burner mouth. Silica particles formed under these conditions are highly agglomerated consisting of small primary particles (Fig. 1.12b). This particle shape typically occurs for low residence times of the particles in the hot flame zone as well as for low flame temperatures. However, for a low oxygen flow rate (1.5 L/min) the residence time of the particles is much longer and cooling by mixing with cold gases is less pronounced. During formation of these particles the time for sintering is long enough to form larger spherical silica particles (Fig. 1.12a).

Chao and Axelbaum (2000) recently introduced an analytical solution for a diffusion flame formed from three concentric tubes, similar to that calculated with CFD. They extended the Burke-Schumann methodology (Burke and Schumann, 1928) and included a third stream. The ability to have analytical solutions for special cases of a diffusion flame consisting of three reactant streams may tempt the testing of the performance and to further improve computational fluid dynamic software. Particle growth models can be implemented as demonstrated by Schild et al. (1999) and Pyykönen and Jokiniemi (2000) for TiO2 formation in a turbular flow reactor, and aerosol formation in a laminar flow reactor, respectively. These techniques provide a very effective tool for the simulation of the particle formation processes in complex reactor geometries under real production conditions. The formation of alumina from aluminium-sec-butoxide was studied experimentally by Johannessen et al. (2000), and was compared with a commercially available computational fluid dynamics (CFD-) package to simulate gas temperatures and velocity profiles of burners. After the temperature and gas composition fields were calculated, the monodisperse particle growth model by Kruis et al. (1993) was implemented, which was modified with a dilution factor (Johannessen, 1999) obtained from the CFD calculations. Following characteristic trajectory lines, the model gives a good prediction of the specific surface area of the product particles. This model was extended (Johannessen et al., 2001) to the formation of titania particles and was validated by comparison with experiments conducted in a single (classic) or double (inverted) diffusion methane/air flame reactor producing TiO2 particles (Pratsinis et al., 1996). Besides the final average product particle size, the degree of aggregation (number of primary particles per agglomerate) was predicted very well when compared to the data obtained with small angle X-ray scattering (Hyeon-Lee et al., 1998).
In flame spray pyrolysis, spray combustion models provide information on burning rates and droplet lifetime and thus precursor decomposition and reaction, which can be combined with models for aerosol growth. Droplet evaporation, ignition, and combustion have to be taken into consideration in making assumptions in order to simplify the model (Faeth, 1977). Several approximations have to be considered and validated, including: drop breakup, turbulent droplet dispersion, effects on the enveloping flame, and effects of drop dynamics and turbulence on drop transport rates (Faeth, 1983). Furthermore, the spray properties involved, have to be critically reviewed in order to implement or exclude basic phenomena in the model such as: droplet slip and internal circulation, transient heating of the droplets, multicomponent fuel vaporization and combustion and vaporization of droplet arrays, and groups (Sirignano, 1983).

Further implementation of more sophisticated models of droplet evaporation and burning (Abramzon and Sirignano, 1989), accounting for multi-component mixtures (Hallett, 2000) and combustion modes (e.g. single droplet, group, or sheath combustion) (Chiu and Liu, 1977; Labowski and Rosner, 1978; Akamatsu et al., 1997; Chen and Gomez, 1997) developed for spray combustion in turbine and automotive engineering, will add fundamental understanding to the flame spray pyrolysis processes accounting for transport and chemistry of burning sprays (Gutheil and Sirignano, 1998).

Besides the implementation of numerical codes describing centerline time dependent droplet history, accounting for multicomponent mixtures, the flow field of the spray flame, the droplet combustion, and the temperature profile can be modeled by applying computational fluid dynamics. As for aerosol reactors (Schild et al., 1999; Tsantilis et al., 1999), solvers, using a finite volume technique, can be used to describe the flow field and the droplet combustion of spray flames by solving systems of differential equations. Then, the effect of the released heat of reaction on the temperature distribution in the flame and the density of the gases can be considered in the fluid dynamics model.

After the release of the precursor from the droplet environment and its reaction, the subsequent growth of particles from molecules occurs by surface growth and/or coagulation and sintering leading to a steadily growing particle size. The description for the rate change of the number concentration of particles is based on detailed sectional models (Landgrebe and Pratsinis, 1989). Although there is a number of solutions to the
population balance equation depending on approximations on the shape of the size distribution, a simple sectional technique can be used (Tsantilis and Pratsinis, 2000):

\[
\frac{dN_i}{dt} = \left( \sum_{j=1}^{i-2} 2^{i-1} \beta_{i-1,j} N_j + \frac{1}{2} \beta_{i-1,i-1} N_{i-1}^2 - \sum_{j=1}^{i-1} 2^{i-1} \beta_{i,j} N_j - N_i \sum_{j=1}^{M} \beta_{i,j} N_j \right) \rho_g - \beta_i \rho_g N_i \tag{1.1}
\]

The first term on the right hand side (RHS) of the equation refers to the rate of birth of agglomerates in section \(i\) by collisions between agglomerates of the \(i-1\) section and \(j\) sections ranging from 1 to \(i-2\), where \(N\) is the number concentration, \(\beta\) is the collision frequency function and \(\rho_g\) the density of the gas. The second RHS term refers to birth of agglomerates in the \(i^{th}\) section by collisions of agglomerates of equal size \((i-1)\). The third RHS term accounts for the death rate of agglomerates in section \(i\) by collisions between these agglomerates and smaller ones. The fourth RHS term corresponds to the death rate of agglomerates in section \(i\) by collisions between these agglomerates and agglomerates in the same or higher size intervals. Furthermore, the effect of sintering on the agglomerate surface area \(a_i\) is (Koch and Friedlander, 1990):

\[
\frac{da_i}{dt} = -\frac{1}{\tau_{s,i}} \left( a_i - a_{s,i} \right) \tag{1.2}
\]

where \(\tau_{s,i}\) is the characteristic sintering time (the time needed to reduce the excess surface area of an agglomerate over that of an equal mass sphere by approximately 63 \%) and \(a_{s,i}\) is the surface area of a completely fused (spherical) agglomerate. The inclusion of theoretical and background knowledge of particle formation in computational tools for spray flame pyrolysis may lead to revolutionary improvements in the understanding of the formation process of these particles and optimal design of flame spray combustion, thus opening up a new area for designing particles with closely controlled characteristics.

1.5. Concluding remarks

The formation and control of particle characteristics in flame aerosol reactors from gaseous and liquid precursors was reviewed. Reactant mixing, additives, and external
electric fields are effective tools for controlling product powder characteristics. A relationship between laboratory-scale experiments and conditions close to those used in industrial pilot-scale units is developed with a systematic study on silica-carbon composite production at concentrations up to 10% solid fraction by mass. Flame spray pyrolysis further broadens the spectrum of flame made powders and their various applications, as there are more liquid than gaseous precursors for particle synthesis. Even particles with pre-defined stoichiometric composition can be easily produced. It has been shown that key parameters for the vapor flame processes are also important for flame spray pyrolysis and that the liquid fuel and precursor composition provides additional variation for special particle design and control.

Fundamental studies on particle growth, simultaneously measuring flame temperature and particle size evolution by thermophoretic sampling in the flame can be used to develop models describing the particle growth without adjustable parameters and thus revealing the dominant physicochemical phenomena. The combination of computational fluid dynamics along with further development of particle growth models helps to rank aerosol reactor designs and to guide the operation of large-scale facilities for production of particles with well-defined characteristics.

1.6. References


Briesen, H., A. Fuhrmann, and S. E. Pratsinis, Electrically assisted aerosol reactors using ring electrodes, *Nanostructured Powders and Their Industrial


Reiche, M. A., P. Hug, and A. Baiker, “Effect of grafting sequence on the behavior of titania-supported V$_2$O$_5$-WO$_3$ catalysts in the selective reduction of NO by NH$_3$,” *J. Catal.* **192** (2) 400-411 (2000).


2. Synthesis of silica-carbon particles in a turbulent H₂-air flame aerosol reactor

Abstract

Synthesis of flame-made nanostructured powders was studied, for the first time, at high production rates (up to 700 g/h) in a turbulent diffusion flame reactor, addressing also the required safety concerns. A commercial hydrogen-air burner was used for synthesis of pure silica and composite silica-carbon particles by oxidation of hexamethyldisiloxane. The product powder was collected continuously in a baghouse filter unit that was cleaned periodically by air-pressure shocks. The effect of the fuel (hydrogen) flow rate, powder production rate, and total oxidant flow rate on product particle size, morphology, and composition was also investigated. Nitrogen adsorption, transmission electron microscopy and thermogravimetric analysis coupled with a mass spectrometer, and a CO₂-analyzer were employed to characterize specific surface area and powder composition. Typically, aggregates of silica-carbon composite particles (0 to 1.4 wt. % carbon) were made with specific surface areas of 75 to 250 m²/g at production rates of 125 to 700 g/h, which correspond to particle concentrations of 17 to 93 g/m³ (2 to 10 % solid fraction by weight).

2.1. Introduction

Flame aerosol technology is used for large-scale manufacture of pigmentary titania, carbon black, fumed silica and alumina, lightguide preforms, and nuclear fuel pellets to name a few (Ulrich, 1984). Research in this field was motivated from the commercial importance of carbon black since the 19th century, and for fumed silica that was first marketed by Degussa under the name Aerosil, since the mid-20th century (Kloepfer, 1942). Properties like UV protection, electrical conductance, range of darkness, opacity

---

b This Chapter is published in *AIChE J.* 47 (7) 1533-1543 (2001).
and reinforcement can be achieved, when adding carbon black to elastomers, plastics and paints (Donnet et al., 1993). Silica is used to control thickening, thixotropy, reinforcement, and free flow of liquids and solids, and is utilized to stabilize suspensions, as well as agent for chemical mechanical polishing (CMP) during integrated circuit (IC) fabrication (Sniegowski and de Boer, 2000). Recent reviews have been written for the flame manufacture of silica particles (Pratsinis, 1998) and carbon black (Donnet et al., 1993).

Recently, carbon-silica particles to be used as dual phase fillers have been developed by Cabot Corporation treating carbon black with silica (Francis et al., 1996), opening a new generation of reinforcing agents for rubber (Wang et al., 1998). The combination of carbon black and silica is more effective in reinforcing rubber as compared to carbon black alone providing the capability for the manufacture of so-called "green tires". As the silica surface is covered with silanol groups, adding an organosilane coupling agent such as triethoxysilylpropyltetrasulfane (tradename Si-69) forms a silica network in the rubber. This filler-to-filler network enhances the tire reinforcement decreasing the rolling resistance by up to 24%, while wet traction and treadwear are similar to conventional tires (Byers and McNeish, 1997). The carbon is needed to ensure good dispersibility and static electricity dissipation (Bomal et al., 1993; Donnet et al., 1993; Byers and McNeish, 1997). Reducing the rolling resistance of car and truck tires can significantly decrease fuel consumption by 3 - 5% and 6 - 8%, respectively (Padula, 1995), and therefore reduce pollution of air and the environment. The specific surface area of silica powders for rubber reinforcement in green tires should be lower than 180 m²/g (Blume, 2000). Carbon coated silica is also used as a precursor powder in silicon carbide production (Koc and Cattamanchi, 1998) or for opaque silica aerogels (Lee et al., 1995).

Clearly, there is considerable interest in understanding flame synthesis of silica-carbon nanostructured particles in one step and at high production rates. The study of turbulent flames is of considerable importance in connection with most practical burner systems (Glassman, 1996), as almost all industrial combustion takes place in turbulent flow (Bray, 1996). Intense turbulence may effectively increase flame propagation velocities (Glassman, 1996).
Spicer et al. (1998) synthesized up to 15 g/h SiO$_2$-C powders with carbon contents up to 30 wt. % in a premixed flame using SiCl$_4$ and acetylene as precursor and fuel. A significant increase in the carbon black yield (up to three times) was detected in the presence of silica compared with a pure acetylene flame of the same equivalence ratio. The enhanced carbon formation was attributed to the presence of silica particles acting as seed nuclei for carbon surface growth, as well as to the chlorine presence reducing the flame temperature. Silica-carbon particles with carbon contents up to 5 wt. % were synthesized in a ring shaped double diffusion HMDSO-oxygen flame at production rates up to 130 g/h by Kammler and Pratsinis (1999). Briesen et al. (1998b) reported soot formation (up to 2 wt. %) when producing 30 g/h of powder in an electrically assisted flame using ring electrodes. Similarly, Kammler and Pratsinis (2000) found that soot appeared in the product powder when an external electric field was applied by needle and plate electrodes. The soot concentration increased (up to 1 wt. %) with increasing electric field intensity.

The objective of this study is to investigate continuous, high production rate (up to 700 g/h) of silica and silica-carbon particles with controlled composition in a pilot-scale, turbulent air-hydrogen diffusion flame aerosol reactor, using baghouse filters. However, producing large amounts of product powder in a hydrogen-air reactor requires a thoroughly planned safety concept, including active and passive hydrogen safety precautions and ability for a fast shut-down of the pilot plant. Employing hydrogen as fuel and HMDSO as precursor allowed simultaneous formation of silica and carbon particles, as both are introduced by HMDSO. The influence of HMDSO concentration, the oxidant (air), and fuel (hydrogen) flow rate on product powder specific surface area, morphology, and composition were studied.

2.2. Experimental studies

2.2.1. Apparatus

Figure 2.1 shows of the experimental setup. The silica precursor hexamethyldisiloxane (HMDSO, Fluka Chemie AG, 99%) is delivered by bubbling clean dry nitrogen gas
(PanGas, CH, >99.999%) through a fritted cylinder, placed into a 2 L Woulffian flask (Duran) filled up to ¾ with HMDSO. Fresh HMDSO was supplied continuously into that flask by a gear pump (Gather) from a second flask (10 L) in order to maintain a constant level of liquid HMDSO to keep the saturation of the carrier gas constant even at the highest production rates (Kammler and Pratsinis, 2000). The Woulffian flask is stored in a thermostated bath (Huber Kältemaschinenbau GmbH) to assure a stable HMDSO temperature and delivery during the experiment. The gases are metered by calibrated mass flow controllers (Hastings Inc., HFC 203) and rotameters (Vögtlin Instruments AG). Between the burner and the HMDSO flask, a 30 cm long Pyrex Allihn-condenser is installed. The cooling chamber of the condenser is filled with water, which is heated by a heating tape and the exit is filled with glass wool in order to prevent entrainment of small HMDSO droplets into the burner (Kammler and Pratsinis, 1999). The tubing between the flask and the burner is heated at least 40 K higher than the HMDSO flask.

Fig. 2.1: Experimental setup for the continuous production of silica and silica-carbon nanoparticles from HMDSO in a hydrogen-air flame.
A stainless steel hydrogen-air diffusion burner (Deutsche Forschungsanstalt für Luft- und Raumfahrt e.V.), which is typically used as a preheating unit in a downflow reactor (Geier, 1998) was modified by adding two more concentric tubes for gas delivery. The burner then consists of four concentric stainless steel tubes of 0.5 mm wall thickness each. The diameter of the center (first) tube is 6 mm, while the spacing between the following three tubes is 1, 0.5 and 3.5 mm. The outer, air (PanGas, CH, synthetic grade) delivering tube (tube 4) had to be designed larger than the other tubes not to create supersonic velocities in the burner, as it was planned to provide an excess of air for combustion. The HMDSO-laden nitrogen stream is fed through the first (center) tube while hydrogen (PanGas, CH, >99.5%) is supplied through the second and third tubes, thus preventing particle deposition on the burner. The flow rate of nitrogen was 10 L/min, for hydrogen, 12.2 to 42.5 L/min and for air, 69 to 171 L/min (at 25°C and 1.013 bar). The corresponding Reynolds numbers based on the overall nozzle diameter $D = 19$ mm (Tacke et al., 1996) $Re_D = u \cdot D/\nu$ are in the range of 3000 to 16000, where $u$ and $\nu$ are the velocity and the kinematic viscosity of the reactant stream. The flame is ignited with a spark plug, which is withdrawn after ignition. The flame is encased in a top-open 350 mm diameter steel chimney (Fig. 2.1) to shield the flame over its entire length and to prevent air entrainment from the surroundings. A Plexiglas window allows visible monitoring of the combustion process.

The particle collection unit consists of a commercial Jet filter (Friedli AG, FRR 4/1,6), with four PTFE (polytetrafluoroethylene, Teflon) coated Nomex baghouse filters (total surface area: 2.2 m²) for powder collection. The filters are set in a stainless steel filter house (2.5 m high and 0.6 m in diameter), which has an inlet 0.6 m long, and a 0.12 m diameter pipe with a cone at its open end over the burner (Fig. 2.1). The particles are collected on the outside of the baghouse filters by an air suction ventilator (Stäfa, 0.75 kW, 50 Hz) controlled by a frequency transducer (Danfoss AG, VLT 6000 HVAC). The particles are ejected every 70 s from the baghouse filters by air pressure shocks (timing pulse: 30-300 ms) using 5 bar absolute pressure. The product particles are collected in a removable container at the lower part of the filter house.
2.2.2. Safety

Between the mass flow controllers and the burner, pneumatic ball valves (Bachofen AG) are installed (Fig. 2.1). These nitrogen-pressured ball valves open when another electro-pneumatic ball valve opens the nitrogen reservoir. These valves are closed when either the energy supply or pressured nitrogen lines (operating the ball valves) are interrupted (Geier, 1998). Additional check valves are installed right before the gases enter the burner to avoid backflow of the gases. The whole piping was designed to withstand explosions (Geier, 1998). The gas-pressure reduction of air and hydrogen is made in two stages (Fig. 1): from 200 bar (gas cylinder) to 25 bar, and from 25 to 8 bar, which is close to the optimal operating pressure for the mass flow controllers (6.5 bar), as the gas pressure is crucial for maintaining constant mass flow rates. The electronic control unit permits remote valve control, ignition with the spark plug, and fast shutdown in case of operational problems. If one of the valves exceeds the pre-set range for reliable operation, the control automatically shuts down the flame reactor. The hydrogen and air supply lines delivering the gas from the cylinders to the flow controllers are fitted with mechanical safety valves that are connected to the vent. The opening pressure is adjusted to 25 bar. As the mass flow controllers can withstand up to 30 bar, they would not get damaged even in the unlikely case that both mechanical pressure controls would fail because the system pressure would never exceed 25 bar. For flame ignition, the hydrogen control was opened in a so-called slow mode, therefore without overshooting after the constant air flow was already established and the spark plug was on. As an additional passive safety feature, the laboratory is equipped with hydrogen sensors that activate ventilation, and release alarm and aeration of the laboratory, at 40% of the lower explosion limit of hydrogen in air mixtures (Geier, 1998).

2.2.3. Characterization

The HMDSO-concentration is calculated from the measured supplied volume of HMDSO to the burner at a constant carrier gas flow rate. The HMDSO-flask
temperature is measured by a calibrated K-Type thermocouple (Thermoax), as well as
the outside wall temperature of the heated manifold and the filter inlet and outlet gas
stream. They are monitored on a personal computer using LabVIEW software. The
HMDSO saturation in the nitrogen stream is calculated by a mass balance for the
precursor flask, using the HMDSO equilibrium vapor pressure (Boublik et al., 1984).
The flame location and height are determined visually. Here, the length of the flame is
defined as the distance between the burner mouth and the end of the luminous zone. The
reactant flow in the flame is characterized by the air-number, $\lambda$, which is defined as the
relative value of the stoichiometric amount of fuel (hydrogen and HMDSO) to oxidant to
the effective (actual) amount of fuel to oxidant. The air-number is most useful for
premixed flames and is the inverse of the equivalence ratio $\phi$ (Turns, 1996).

The specific surface area $A_s$ of the powder is determined from a five point
nitrogen adsorption isotherm in the relative pressure range of 0.05 to 0.25 at 77.3 K
(BET analysis) with a Gemini III 2375 (Micromeritics Instruments Corp.). Before the
adsorption, the samples are degassed (Flow prep 060, Micromeritics Instruments Corp.)
under nitrogen atmosphere at 150°C for 2 h, to remove water that is bound to the
particle surface from the air moisture. Nonporous particles are made as shown for
selected powders with full isotherm analysis with an ASAP 2010 (Micromeritics
Instruments Corp.). The BET-equivalent average primary particle diameter of the
powder can be calculated by $d_p = \frac{6}{(\rho_p \cdot A_s)}$, where $\rho_p$ is the density of SiO$_2$, 2.2 g/cm$^3$.

All experiments are reproduced at least twice on different days and the specific
surface area of the product powder from each experiment is measured, at least, twice.
Data points are averages of these results, while the error bars in all figures show two
times the corresponding standard deviation.

The carbon fraction of the collected powders is determined by thermogravimetric
analysis (TGA) in a thermobalance (TGA/SDTA851°C, LF/1100°C, Mettler Toledo AG).
The powders are heated up from 25 to 120°C using a heating rate of 10°C per min, held
at this temperature for 10 min (first step), then heated up with 20°C per min to 800°C,
and held at this temperature for 10 min under nitrogen (PanGas, CH, >99.999%) atmosphere (second step). Then, the atmosphere is switched to oxygen (PanGas, CH,
>99.95%) and the sample is heated with a heating rate of 20°C per min to 1000°C and
held at this temperature for 5 min. The carbon fraction is attributed to the loss in weight
from 800 to 1000°C (third step). The isothermal segments were inserted to assure that the examined reaction (step) is completed. Each thermogravimetric analysis was performed at least twice on each powder. During the thermogravimetric analysis, a quadrupole mass spectrometer (Quadstar 422, Balzers Instruments) is connected to the thermobalance to detect volatile compounds from the powders in the effluent gas. The gas composition was monitored continuously always scanning from 1 to 170 Daltons. Nitrogen analysis gas and surrounding atmosphere were analyzed to test the sensitivity of the mass spectrometer (detection limit 2 ppm for CO₂) before silica powders were analyzed. Additionally, the CO₂ concentration of the TGA effluent gas was directly monitored with a CO₂ analyzer (aq-5000, Metersonics, Inc.) that was calibrated with known gas mixtures of nitrogen and carbon dioxide (< 1 and 1950 ppm CO₂).

Flame temperature measurements were carried out with Pt/13%Rh-Pt thermocouples (R-type, Moser AG). Measuring the flame temperature in a particle-laden flame with a thermocouple at these HMDSO concentrations leads to considerable deposition on the tip of the thermocouples that were cleaned after each measurement. The flame temperatures are corrected for radiation loss according to Collis and Williams (1959). Nevertheless, it should be noted that these measurements are rather qualitative.

Transmission electron microscopy (TEM) pictures were prepared by dipping the carbon coated TEM grids (Ted Pella Inc., Carbon type B on 200 Mesh) into the powder, which was collected onto the baghouse filters. The TEM analysis was performed on a Hitachi H 600 electron microscope operated at 100 kV, using magnifications between 10k and 30k. Analysis of the particles on the micrographs was performed manually counting at least 100 particles. In some cases, particles were analyzed in a JEOL 2010F Scanning Transmission Electron Microscope (STEM) using Energy Dispersive X-ray (EDX) analysis to determine elemental composition.

2.3. Results and discussion

The pure hydrogen flame is about 15 cm long, light blue and almost transparent. This barely visible flame turns into a bright white-yellow flame (up to 70 cm long), when
adding HMDSO for silica particle production. The HMDSO does not only change the flame shape significantly, but also changes the temperature field as it is a fuel itself.

### 2.3.1. Influence of the air flow rate

Figure 2.2 shows particle producing flames at a molar C/H ratio of 0.09 for various air flow rates at constant HMDSO-nitrogen and hydrogen flow rates of 10 and 24.3 L/min, respectively.

![Fig. 2.2: Turbulent diffusion flames for particle production rates of 300 g/h at hydrogen flow rate of 24.3 L/min and at air flow rates of (a) 69, (b) 103, (c) 137, and (d) 171 L/min.](image)

Increasing the air flow rate from 69 to 171 L/min reduces the flame height by 15 cm. Immediately above the burner, the flame is transparent and bluish as combustion of hydrogen takes place first. Above that zone, the flame is white-yellow as combustion of the hydrocarbon component of HMDSO takes place accompanied by silica formation and simultaneous carbon formation, as well as carbon oxidation. As the air flow rate
increases, the gas velocity at the burner exit increases from 5 to 13 m/s resulting in $Re_D$ numbers from 6000 to 14000, respectively. In that way the supply of oxygen increases and the mixing of fuel and oxidant intensifies; therefore, the combustion of fuel and precursor is accelerated (Glassman, 1996) and enhanced turbulence causes a diffuse brushy flame (Fig. 2.2d). In addition, the onset of visible particle formation (lower end of the yellowish flame) moves closer to the burner.

![Graph](image)

**Fig. 2.3: Specific surface area as a function of the air flow rate at hydrogen flow rate of 12.2 L/min (triangles) and 36.5 L/min (circles) at powder production rates of 300 g/h.**

Figure 2.3 shows the specific surface area of the product powder as a function of air flow rate for hydrogen flow rates of 12.2 and 36.5 L/min at a powder production rate of 300 g/h corresponding to molar C/H ratios of 0.14 and 0.07, respectively. The specific
surface area of the product powder increases from 108 to 158 m²/g (or the average primary particle diameter is reduced from 25 to 17 nm), and the flame height decreases from 55 to 35 cm, when increasing the air flow rate from 69 to 154 L/min at a hydrogen flow rate of 12.2 L/min (triangles). At the higher hydrogen flow rate (36.5 L/min, circles in Fig. 2.3), increasing the air flow from 86 to 171 L/min increases the specific surface area from 89 to 124 m²/g (corresponding to average primary particle diameters of 31 and 22 nm, respectively) and the flame height is reduced from 50 to 40 cm. These data are in agreement with Briesen et al. (1998a) who observed a decrease of the flame from 7.5 to 5 cm and a steady increase of the specific surface area from 170 to 230 m²/g by increasing the total oxidant flow from 2.5 to 5.5 L/min of an HMDSO-methane-air diffusion flame.

Fig. 2.4: Transmission electron micrographs of silica-carbon powders at production rates of 300 g/h, using 12.2 L/min hydrogen and 69 L/min air (a) and 154 L/min air (b), respectively. The corresponding average primary particle diameters calculated from nitrogen adsorption (BET) are 25 nm (a) and 17 nm (b), while 22 nm (a) and 14 nm (b) were obtained by TEM counting, respectively.

Increasing the air flow rate leads to two competing processes. On the one hand, higher air flow increases the oxidant supply to the reaction zone and reduces the flame height as the fuel is consumed faster. This leads to a higher flame temperature resulting in
faster growth and higher sintering rates and, therefore, to a decrease in the specific surface area. On the other hand, the increase of the air flow rate also increases the amount of inert gas (nitrogen from the air) delivered to the flame, which would otherwise increase the flame height and lower the flame temperature. At the same time, turbulence of the jet increases when the air flow rate is increased, accelerating combustion that shortens the flame. The lower flame temperature decreases the particle sintering rate, and the shorter flame and faster gas velocity lead to shorter residence times in the hot flame region. Both effects reduce product particle size; thus, larger specific surface area particles are formed. Clearly, the intensity of the turbulence here dominates with increasing air flow rate that increases the specific surface area (Fig. 2.3).

Representative TEM-pictures of powders made at production rates of 300 g/h using 12.2 L/min hydrogen are presented for 69 L/min air (Fig. 2.4a) and for 154 L/min air (Fig. 2.4b). The powders are aggregated and partly sintered, but the average primary particle sizes obtained by counting (22 and 14 nm, respectively) agree well to the calculated values by nitrogen adsorption (BET; 25 and 17 nm, respectively). The difference between the data indicate aggregation which is consistent with Fig. 2.4.

Now, increasing the supplied hydrogen flow rate from 12.2 to 36.5 L/min leads to smaller specific surface areas at the higher hydrogen flow rate. The slope of increasing specific surface area with air flow rate slightly decreases (Fig. 2.3). The cooling effect of the air flow rate is less significant at higher hydrogen flow rates as additional air accelerates oxygen-hydrogen combustion and subsequently increases the flame temperature. This is in agreement with Pratsinis et al. (1996), where an increase of the fuel flow rate decreased the specific surface area of the product TiO₂ particles as higher flame temperatures were achieved.

The effect of air entrainment in the flame was investigated by carrying out experiments in the absence and in the presence of the chimney surrounding the flame. Withdrawing the chimney, extra oxygen is drawn into the flame by entrained secondary air leading to faster fuel consumption and, therefore, to higher flame temperature. As a result, the sintering rate increases leading to larger particles and, therefore, to a decrease of the specific surface area (by 14 - 17%) for air flow rates less than 120 L/min. At high excess air flow rates (air number \( \lambda = 1.7 - 1.9 \)), no differences in the specific surface area are observed (± 3%). This may indicate that at high production rates that are typically
encountered in industry, air entrainment will not affect the characteristics of the product powder.

### 2.3.2. Influence of the hydrogen flow rate

Figure 2.5 shows axial flame temperature profiles for three hydrogen flow rates at constant C/O ratio of 0.12 (production rate 300 g/h SiO₂ and air flow rate 120 L/min).

![Axial temperature profile along the center line of the particle laden flame for production rates of 300 g/h for hydrogen flow rates of 12.2 (triangles), 24.3 (squares), and 36.5 L/min (circles). The temperatures are corrected for radiation loss according to Collis and Williams (1959).](image)

Fig.2.5: Axial temperature profile along the center line of the particle laden flame for production rates of 300 g/h for hydrogen flow rates of 12.2 (triangles), 24.3 (squares), and 36.5 L/min (circles). The temperatures are corrected for radiation loss according to Collis and Williams (1959).
The temperature increases rapidly with increasing distance from the burner, then almost reaches a plateau at maximum flame temperature, and then decreases slowly. Increasing the hydrogen flow from 12.2 (triangles) to 36.5 L/min (circles) increases the maximum flame temperature from 1350 to 1440 K. This trend is in agreement with detailed investigations in hydrogen-oxygen diffusion flames by Choi et al. (1999).

Figure 2.6 shows the influence of the hydrogen flow rate on the specific surface area of the product powder for production rates of 300 g/h and an air flow rate of 120 L/min (C/O = 0.12). Increasing the hydrogen flow rate from 12.2 to 42.5 L/min decreases the specific surface area from 129 to 96 m²/g. Increasing the hydrogen flow rate results in higher flame temperature (Fig. 2.5) that increases the sintering rate of the particles and,
therefore, results in larger particles and smaller specific surface areas. Performing full adsorption and desorption isotherms shows that particles are nonporous, while the corresponding \( t \)-plot indicates very small slit-shaped pores (Lippens and de Boer, 1965), which are attributed to the necks between the particles in the aggregates.

### 2.3.3. Influence of the production rate

The silica production rate was set by controlling the HMDSO flask temperature for carrier gas flow rate of 10 L/min. Figure 2.7 shows the specific surface area of powders made at three production rates as a function of the air flow rate at hydrogen flow rate of 12.2 L/min. The molar C/H ratios are 0.14 (triangles), 0.11 (squares), and 0.08 (diamonds), respectively. Decreasing the production rate from 300 g/h (triangles) to 200 g/h (squares) and 125 g/h \( \text{SiO}_2 \) (diamonds) increases the specific surface area of the product powder from 139 to 186 and 249 m\(^2\)/g, respectively, for an air flow rate of 137 L/min. Correspondingly, the primary particle diameter decreases from 20 to 15 and 11 nm. As the HMDSO concentration decreases with decreasing production rate, the adiabatic flame temperature decreases as less fuel (hydrogen and HMDSO) is supplied (the total thermal input decreases from 5.9 to 3.6 kW reducing the production rate from 300 to 125 g/h). As a result of the lower flame temperature, the sintering rate is decreased, which leads to higher specific surface areas. The decrease of particle concentration leads to subsequently fewer particle collisions and less growth as less precursor is delivered into the flame. Reducing the powder production rate from 300 to 125 g/h by reducing the HMDSO concentration decreases the visible flame height from 50 to 30 cm for a constant air flow rate of 103 L/min.

Lower production rates lead to significantly larger specific surface areas in agreement with Kammler and Pratsinis (1999). In that earlier study with significantly lower burner exit velocities (0.3 m/s), increasing the powder production rate from 22 to 130 g/h decreased the specific surface area from 175 to 19 m\(^2\)/g, as oxygen leads to much higher flame temperatures resulting in faster sintering and significantly smaller specific surface areas compared to the present powders (Zhu and Pratsinis, 1997). Increasing the HMDSO delivery rate increases the fuel input into the flame, resulting in
higher flame temperatures and flame heights and, therefore, longer residence times of the particles at high temperatures. Hence, particle growth takes place faster and bigger particles are formed as a result of the enhanced sintering rates.

![Graph showing specific surface area as a function of air flow rate for production rates of 125 g/h (diamonds), 200 g/h (squares), and 300 g/h (triangles). The hydrogen flow rate was 12.2 L/min.]

Fig. 2.7: Specific surface area as a function of the air flow rate for production rates of 125 g/h (diamonds), 200 g/h (squares), and 300 g/h (triangles). The hydrogen flow rate was 12.2 L/min.

Figure 2.8 shows the specific surface area of the product powder as a function of production rate at hydrogen and air flow rates of 12.2 and 103 L/min, respectively. Continuous operation of the turbulent hydrogen-air flame is demonstrated by operating the unit for 5 h at production rates of 700 g/h. As the production rate is increased from 125 to 700 g/h, corresponding to an increase of the SiO₂ mass concentration from 17 to
93 g/m$^3$, the specific surface area decreased from 222 to 75 m$^2$/g. The higher the HMDSO concentration in the reactant stream, the higher is the adiabatic flame temperature leading to enhanced sintering that results in lower specific surface areas. Increasing the production rate from 125 to 700 g/h by increasing the HMDSO delivery rate (by increasing the HMDSO flask temperature) increases the total fuel input into the flame (3.6 kW to 11.0 kW), and the flame height is increased from 30 to 70 cm.

**Fig. 2.8:** Specific surface area as a function of the production rate and SiO$_2$ mass concentration at 10 L/min nitrogen (through the HMDSO), 12.2 L/min hydrogen, and 103 L/min air.

However, this results in longer residence times of the particles at high temperatures; therefore, particle growth takes place faster and, as a result of the enhanced sintering
rates, bigger particles are formed. The increase of HMDSO concentration also increases the silica particle concentration leading to subsequently more particle collisions, and, therefore, enhanced growth which increases the particle diameter as well. These results are in agreement with studies at lower powder production rates, where an increase in the precursor concentration decreased the specific surface area of the powders (Briesen et al., 1998a and b; Kammler and Pratsinis, 1999 and 2000) but do not agree with Ulrich and Riehl (1982) and Fotou et al. (1995), who did not observe a significant influence of the particle concentration. This is attributed to the fact that the energy of combustion of HMDSO is larger than that of SiCl$_4$ oxidation (Briesen et al., 1998a; Kammler and Pratsinis, 1999).

2.3.4. Powder composition

Using hydrogen as fuel has the advantage over hydrocarbon fuels (such as methane) that it does not contain carbon; therefore, the precursor itself is the only source for carbon formation. Typically, in diffusion flames carbon inception occurs around 1400 K and depends on hydrogen atom diffusion (Glassman, 1988). As shown in Fig. 2.5, the maximum flame temperatures are close to or even above this value, as particle coating on the thermocouple tip lowers the measured temperature (Chung and Katz, 1985).

All powders are gray at production rates of 300 g/h using 12.2 L/min hydrogen (Fig. 2.3: triangles) indicating that the oxidation of HMDSO is incomplete, even at excess oxygen. In contrast, powders produced at 300 g/h with 36.5 L/min hydrogen (Fig. 2.3: circles) are white. White powders are produced as well at lower production rates (Fig. 2.7: diamonds and squares and Fig. 2.8). In Fig. 2.6 the color of the powders changes from gray to white with increasing hydrogen flow.

A typical thermogravimetric analysis plot is shown in Fig. 2.9, in which white powder (thin solid line) and carbon containing gray powder (thick solid line) of the same specific surface area (110 m$^2$/g) are compared. The sample weight is monitored with time during the temperature program, which is indicated by the broken line, consisting of isothermal and dynamic segments.
Increasing the temperature from 25 to 120°C in nitrogen atmosphere removes the physically adsorbed water from the silica powder surface (Hockey, 1965; Iler, 1979) and is not crucial for the powder characterization as it depends, for example, on the actual humidity of the surrounding air and sample preparation. The removal of physically bound water is referred here as the first step. The second step (from 120 to 800°C in nitrogen) represents the loss in weight from the reduction of silanol groups on the powder surface, the so-called chemically bound water (Iler, 1979).

**Fig. 2.9:** Sample weight normalized to the sample weight after the second step (removal of physically and chemically bound water (and volatiles)) as a function of time and temperature. It was determined by thermogravimetry for pure silica (thin line) and carbon containing (thick line) powders of specific surface area of 110 m²/g.
Of course, there is also the possibility that easily volatizable compounds are removed with the chemically bound water from the powder surface by the temperature treatment, but the TGA effluent gas analysis indicated that this amount is less than 5%. It was shown with nitrogen adsorption (BET-method) that the specific surface area of the powders remained constant up to 800°C, by analyzing powders before and directly after the heating period. This indicates that the surface area of the powders was not significantly modified, such as by evaporation of volatiles or volatile carbon, which would cause an increase of specific surface area as observed by Spicer et al. (1998) for carbon black fumed silica powders.

The weight loss from 800 to 1000°C in oxygen (third step), however, represents the carbon content (black carbon) of the powder that is verified by analyzing the CO₂ concentration of the off-gases from the thermobalance with a CO₂ detector assuming stoichiometric oxidation. For gray powder, a significant decrease in the normalized weight is detected in the third step resulting from carbon oxidation. A fraction of this loss in weight of the third step results from the residual OH-groups per nm² at 800°C (0.9 OH-groups per nm²), which is reduced to 0.4 OH-groups per nm² at 1000°C (Curthoys et al., 1974). This fraction is negligible for carbon containing powders, but explains the small weight loss of the perfectly white powders (Figs 2.9 and 2.10).

Figure 2.10 shows the normalized sample weight during TGA for powders produced at 125, 300 and 700 g/h (from Fig. 2.8) and Aerosil 380 (Degussa-Huels AG), respectively. As discussed in Fig. 2.9, physically adsorbed water (first step), chemically bound water and volatile compounds (second step), and the carbon content (third step) can be determined. Here, it can be seen clearly that both the physically (first step) and chemically (second step) bound water depend strongly on the specific surface area of the powders as the total amount of silanol groups increases for increasing specific surface area and constant OH-group density (OH-groups per nm² powder surface). This explains the larger loss in weight in the first and second step for Aerosil 380 and the powder made at production rates of 125 g/h (specific surface areas of 380 and 222 m²/g, respectively) compared to the powders produced at 300 and 700 g/h with specific surface areas of 128 and 75 m²/g, respectively. The weight loss from 800 to 1000°C in oxygen (third step) is very small for Aerosil 380 and the perfectly white powder produced at production rates of 125 g/h (further OH-removal), but is significant for gray powders and increases with
their increasing carbon content. Comparison of the TGA plot of Aerosil 380 and the white powder (thin solid line; 125 g/h) shows similar behavior in all three steps during TGA, indicating similar powder composition.

Fig. 2.10: Sample weight normalized to the sample weight after the second step (removal of physically and chemically bound water (and volatiles)) as a function of time and temperature. It was determined by thermogravimetry for powders made at production rates of 125, 300, and 700 g/h, corresponding to Figs 2.8 and 2.11, and commercial available fumed silica (Aerosil 380).

Figure 2.11 shows the carbon content (third step) as a function of the powder production rate. The powders were made at hydrogen and air flow rates of 12.2 and 103
L/min, respectively, corresponding to Figs 2.8 and 2.10. Increasing the production rate from 125 to 700 g/h increases progressively the amount of carbon in the powder from 0.15 to 1.4 wt. % (Fig. 2.11). The small loss in weight for the first two points (white powders) in this figure is attributed to OH-removal as discussed above. As the amount of supplied air was held constant, the ratio of fuel to oxidant increases with an increasing production rate; thus, understoichiometric amounts (air number $\lambda = 0.7$) are reached for production rates of 700 g/h, while there is an excess of oxygen for production rates of 125, 200, and 300 g/h (the corresponding air numbers $\lambda$ are 2.2, 1.8, and 1.2).

Fig. 2.11: Carbon content of product powders as a function of production rate. Also shown is the corresponding C/H ratio. The gas flow rates are 10 L/min nitrogen (through the HMDSO), 12.2 L/min hydrogen, and 103 L/min air.
Generally, in laminar hydrocarbon diffusion flames the soot fraction increases with temperature (Schug et al., 1980; Glassman and Yaccarino, 1981). This is in agreement with Fig. 2.11 since, as the hydrocarbon containing HMDSO concentration increases, more carbon is formed. The decrease of the specific surface area (Fig. 2.8) indicates higher temperatures, which increase particle growth and sintering. The molar C/H ratio increases with increasing HMDSO flow rate. It appears that white powders are formed below C/H ~0.12, while the carbon content increases above this ratio.

Fig. 2.12: Carbon content of product powders determined with thermogravimetric analysis (third step) as a function of the hydrogen flow rate and molar C/H ratio at C/O ratio of 0.12. These data correlate to the data of Fig. 2.6.
Figure 2.12 shows the carbon content (third step) of powders (production rate 300 g/h) made at different hydrogen flow rates (corresponding to Fig. 2.6) and at constant air flow rate of 120 L/min. At hydrogen flow rates of 12.2 L/min, the powders contain 0.43 wt. % carbon when overall excess of oxygen is provided (air number $\lambda = 1.4$). The carbon content decreases with increasing hydrogen flow rate and at hydrogen flow rates of more than 18.2 L/min; virtually no carbon remains in the product powder (they are perfectly white). Increasing the hydrogen flow even more the flame becomes fuel rich ($\lambda = 0.8$ for 42.5 L/min hydrogen), but no carbon remains in the product powder. This is attributed to the higher flame temperatures (Fig. 2.5) oxidizing carbon completely and to the increased hydrogen concentration as hydrogen radicals are known to accelerate normal pyrolysis reactions by diffusion into fuel rich zones (Glassman, 1988). Complete carbon oxidation is achieved here when increasing the total fuel input by hydrogen addition in contrast to enhanced carbon formation when the hydrocarbon (HMDSO) increases the fuel input (Fig. 2.11). The perfectly white powders produced, for example, with 36.5 L/min hydrogen, lose very little weight (up to 0.07 wt. %) due to removal of chemically bound water from the powders (in agreement with Figs 2.9 and 2.10).

Calculating the molar C/H ratio (upper x-axis in Fig. 2.12), it appears that no carbon remains in the product powder when this ratio exceeds ~0.12, the same value as observed in Fig. 2.11. Schug et al. (1980) proposed that the C/H ratio does not determine the sooting height or composition of the fuel mixture as a responsible (general) parameter for the sooting criterion. More generally, investigating different fuel mixtures in air diffusion flames, the maximum sooting height of the mixture is determined by the sooting height of the pure additive. For fuel mixtures of hydrocarbons with hydrogen, asymptotic values of the sooting height (sooting height $\rightarrow \infty$) are achieved when the C/H ratio is decreased to a critical C/H value, below which sooting cannot be observed. This may depend on the choice of the hydrocarbon and may depend also on burner geometry or other parameters, but it seems to describe the ability of a certain system to soot. Therefore, the C/H ratio may be used to describe individual burner systems and guide the production of silica powders of a certain carbon composition. As the sooting height describes the sooting tendency of a system - the smaller the sooting height the larger the
ability to soot - the C/H value for the investigated system can also give a qualitative estimate of the carbon content in the product powder. The critical C/H ratio of ~0.12 here is in agreement with the asymptotic value for the sooting height for acetylene-hydrogen mixtures by Schug et al. (1980).

According to EDX analysis, the white powders did not contain carbon. For the carbon silica powders, there was no evidence even in the darkest powders that the particles were film coated. These observations indicate that the carbon and silica particles are separate. As more fuel from HMDSO is supplied into the flame, the associated CH$_3^+$ concentration increases. Therefore, more carbon enters the system. When HMDSO is pyrolyzed first, the C-Si bonds are split resulting in separate formation of silica and hydrocarbon that will be converted to soot or carbon black, as observed in the product powder by STEM/EDX (Nicholls, 1999). This indicates that the carbon may not grow on the silica particles, but rather carbon and silica particles coagulate resulting in a spotty-coating of the silica aggregates with carbon nanoparticles.

**2.4. Conclusions**

For the first time, a systematic investigation of flame synthesis of nanoparticles at high production rates (up to 700 g/h) was carried out. The effect of process variables on the characteristics of product silica-carbon particles was investigated in a turbulent air-hydrogen diffusion flame reactor. The specific surface area of the product powder was controlled in the range of 75 to 250 m$^2$/g by reactant stream composition. Increasing the production rate from 125 to 700 g/h decreased the specific surface area from 222 to 75 m$^2$/g for constant air flow rate of 103 L/min and increased the carbon content of the powder. Increasing the air flow rate, however, increases the specific surface area and does not depend on the overall-stoichiometry of the flame in the investigated range. Decreasing the hydrogen concentration increases the specific surface area and the carbon content of the product powder, as was determined by thermogravimetric analysis (TGA) coupled with mass spectroscopy (MS). The silica aggregates are spotty-coated with carbon implying that carbon and silica particles form separately and coagulate downstream.
2.5. Literature cited


Nicholls, A. W., personal communication (1999).
3. Flame temperature measurements during electrically assisted aerosol synthesis of nanoparticles

Abstract

Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy is used to measure the temperature during TiO₂ formation by titanium tetraisopropoxide (TTIP) oxidation in a premixed flat flame. In the absence of particles, FTIR is systematically compared to coherent anti-Stokes Raman scattering (CARS) in premixed flames in the presence and absence of external electric fields including line-of-sight as well as tomographic reconstructed FTIR measurements. Time resolved CARS flame temperature measurements probe the effect of electric fields on the premixed flat flame. Furthermore, FTIR is used to measure axial and radial flame temperature profiles in TiO₂ particle-laden flames at various electric field strengths. Along with the visible reduction in flame height when applying the electric field, the external electric fields reduce the high temperature region of the flame and lead to a steeper temperature gradient further downstream. The maximum flame temperature, however, remains constant. The precision control of particle crystallinity and the specific surface area by external electric fields is confirmed as well as their effect on the anatase to rutile phase transformation is discussed.

3.1. Introduction

Flame technology is a versatile process for large-scale manufacture of carbon blacks, pigmentary titania, fumed silica and other oxides with closely controlled characteristics. The temperature history of these particles is the most important parameter affecting their size and morphology (Pratsinis, 1998). Measuring the temperature in these particle-laden flames, however, is challenging and has been hardly possible. The flame temperature, which can be controlled by reactant mixing and composition, broadly

---

* This chapter is published in a slightly reduced form in *Combust. Flame* 128 (4) 369-381 (2002).
controls particle size and morphology (Zhu and Pratsinis, 1996), while external electric fields are effective for precise (within 1 nm) particle size control (Vemury and Pratsinis, 1995 and 1996; Vemury et al., 1997; Kammler and Pratsinis, 2000).

Measuring flame temperatures is particularly challenging in electrically assisted particle-laden flames where the presence of an electric field prohibits the use of intrusive temperature measurements. The effect of external electric fields on flame temperatures of various hydrocarbon premixed flames was investigated probably first by Lewis and Kreutz (1933) with a non-intrusive sodium line reversal method. Close to the burner, no effect of the electric field was detected, while further downstream the electric field reduced the flame temperature. Katz and co-workers (Chung and Katz, 1985) measured flame temperatures by UV absorption of OH in a counterflow diffusion burner in the absence of particles. They found that the peak flame temperature was increased and its location was slightly shifted toward the oxidizer side of the flame in the presence of an electric field (Katz and Hung, 1990).

Laser-induced fluorescence (LIF) has been widely used in gas-phase combustion analysis as well (Eckbreth, 1988), but was only applied to dilute and low pressure oxide particle-laden flames to measure flame temperature (Glumac et al., 1998) and to detect local concentrations of SiO (Zachariah et al., 1996; Glumac et al., 1998; Glumac, 2001), FeO (McMillin et al., 1996), AlO and TiO (Colibaba-Evulet et al., 2000). The temperatures of these flames have been obtained also by mathematically modeling of the combustion using the PREMIX software (Lindackers et al., 1997).

Probably the most established non-intrusive technique for gas temperature determination in combustion processes (but costly (Childs et al., 2000) and quite demanding) is the coherent anti-Stokes Raman scattering (CARS) (Eckbreth, 1988). Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy (Best et al., 1986; Solomon et al., 1986), however, is less expensive, easy to transport and align, and rather simple to operate. Compared to CARS, spatial and temporal temperature information, however, are not readily available using the FTIR technique, even though improvements in the spatial resolution have been made. For a laminar ethylene/air diffusion flame Best et al. (1991) showed that there is excellent agreement between their tomographic reconstructed FTIR measurements, the CARS measurements by Boedecker and Dobbs (1986), and the thermocouple measurements by Santoro et al. (1987).
Morrison et al. (1997) measured flame temperatures with FTIR emission/transmission spectroscopy in electrically assisted TiCl₄/methane/oxygen/nitrogen flames and found an increase in temperature and a decrease in gas concentrations in the presence of electric fields. Farquharson et al. (1998) and Arabi-Katbi et al. (2001) used FTIR spectroscopy for flame temperature determination in silica and titania producing flame reactors as well. Recently, CARS has been applied to silica particle-producing diffusion flames (Hwang et al., 2001). Even though the spatial resolution was excellent, flame temperatures were obtained by averaging over 100 single shots, thus, no time resolved temperature information was obtained.

Here, flame temperatures are measured in TiO₂ particle-laden premixed flat flames with FTIR spectroscopy by comparing the best match of the blackbody Planck function and the measured spectrum, where self-absorption of the flame was taken into consideration. For a particle-free premixed flat flame, the measured temperatures by FTIR are compared with time resolved CARS measurements in the presence and absence of electric fields. Finally, measuring the flame temperature profile in electrically assisted flames enables a better understanding of the effect of the electric fields on particle formation and growth and provides data that can be implemented in computational aerosol dynamics models (Johannessen et al., 2000).

3.2. Experimental

3.2.1. Apparatus and particle characterization

Figure 3.1 shows the experimental set-up with the premixed flame aerosol reactor, the external electric field and the Fourier transform infrared (FTIR) spectrometer. The flame reactor consists of three concentric quartz glass tubes; the premixed reactants are fed through the middle (central) tube of 25 mm diameter that is filled with glass beads and on top of them a 38 mm long mullite honeycomb (64 openings/cm²) is placed (Arabi-Katbi et al., 2001). The particle-free flat flame is established with 0.4 L/min methane (Pangas, 99.5%), 1.2 L/min oxygen (Pangas, 99.5%), and 3.95 L/min nitrogen (Pangas, 99.999%), respectively. During flame synthesis of TiO₂, 0.65 L/min argon gas (Praxair, 99.99%) saturated with titanium tetraisopropoxide (TTIP, Aldrich, 97% purity)
is added to the premixed gases. The TTIP mass flow (11 g/h) is verified by measuring the weight loss of the precursor flask during the experiments. At these conditions the production rate of TiO$_2$ is 3.1 g/h. All lines and the burner are heated 20 K above the liquid TTIP temperature of 125°C to prevent condensation. The second tube of the burner is closed while 3.0 L/min shield nitrogen gas flows through the outside (third) tube (44 mm ID; 47 mm OD) to stabilize the flame. Powders are collected on glass fiber filters (Gelman, 142 mm diameter) which are kept 200 mm above the burner.

Fig. 3.1: Experimental set-up of the electrically assisted premixed TTIP/methane/oxygen/nitrogen flame reactor using Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy for flame temperature determination.

The external electric fields are created by two parallel plate electrodes of 25 mm height, 38 mm width and 4 mm thickness each (Kammler and Pratsinis, 2000). The distance between the electrodes is 50 mm, and the lower edge of the electrodes is aligned 1 mm above the burner mouth. One electrode is connected to a negative high voltage supply (Gamma High Voltage, Inc.), and the other is grounded. The current
through the flame is monitored by measuring the potential across a 624 kΩ resistance R between earth and the ground electrode using a multimeter (Fluke) (Vemury and Pratsinis, 1996) and recorded in a computer with a rate of 10/s (Fig. 3.1).

The specific surface area of the powder is measured by nitrogen adsorption (Gemini 2350, Micromeritics) at 77 K following BET-theory (Brunauer et al., 1938) using a five point isotherm in the relative pressure range of 0.05 to 0.25. Before the adsorption, the samples are degassed (Flow prep 060, Micromeritics) under nitrogen atmosphere at 150°C for two hours, to remove physically bound water. X-ray diffraction (XRD) is used to determine the phase composition of the TiO₂ (D500, Siemens; using CuKα radiation and “Diffrac At.” software version 3.1). The weight fraction of anatase and rutile phases is calculated from the relative intensities of the primary peaks corresponding to anatase and rutile (Spurr and Myers, 1957).

### 3.2.2. Temperature measurements

For the measurements in the particle-laden flame an FTIR spectrometer (Bomem Inc., Model MB157) is used that operates over the spectral range of 6500-500 cm⁻¹ (1.5-20 μm) with a resolution of 2 cm⁻¹. Two off-axis paraboloidal mirrors focus the IR beam through the flame (Arabi-Katbi et al., 2001). The diameter of the IR-beam is 4 mm, but 85% of the signal is within 3 mm (transmission measurements). For the emission measurements the measured emission spot diameter is also 4 mm and 90% of the signal is detected when a 3 mm aperture is put into the beam path at the focus. Earlier studies of FTIR in oxide particle-laden flames have used larger IR-beams of 8 mm (Morrison et al., 1997; Arabi-Katbi et al., 2001) and 32 mm (Farquharson et al., 1998) in diameter. Transmission and emission (radiance) spectra are collected with a wide-band deuterated-triglycine-sulfate (DTGS) detector and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector, respectively. For further improvement of spectral and spatial resolution, a Bomem MB155S FTIR spectrometer is used at the same configuration but with a 2 mm diameter IR-beam using a spectral resolution of 1 cm⁻¹. All measurements in the particle-free as well as selected ones with the particle-laden flame were carried out with this instrument. They were in good agreement with those obtained with the MB157 spectrometer. In the improved set-up two pairs of alike
paraboloidal mirrors are used (Fig. 3.1). In the first focal point an iris controls the beam
diameter, thus, the IR in the flame (second focal point) has exactly the same width as
the iris' orifice.

The zero position above the burner (HAB = 0 mm) is set when half of the IR
signal is blocked by the burner. Path correction spectra for the emission measurements
are taken with a blackbody cavity in place of the burner. For data acquisition, first a
background spectrum for the transmission is taken with nitrogen, oxygen and the
outside shield gas flowing (no flame) (Morrison and Haigis, 1993). The gases are
ignited and then sixteen scans are taken for both the transmission and the emission
spectra. After the transmittance is measured, the electrodes are cleaned from possible
particle deposits, then the IR source in the spectrometer is turned off and emission
spectra are taken. Then, the electrodes are cleaned again before proceeding with another
run. As the flame is not truly optically thin, the radianc spectra are corrected for self-

For flame temperature evaluation, emission / transmission (E/T) analysis (Best et
al., 1986) is used, which compares the normalized radianc calculated from the actual
radianc of a sample to a best fit using a blackbody Planck function \(BB(\nu, T)\), which is a
function of wavenumber and temperature (Griffiths and Haseth, 1986; Morrison et al.,
1997). Thereby, the normalized radianc of a sample is defined as \(R_n(\nu) = \frac{R(\nu)}{1-\tau(\nu)}\), where \(\nu\) is the wavenumber in cm\(^{-1}\), \(R(\nu)\) is the radianc (emission) of the sample,
and \(\tau(\nu)\) is the transmittanc (Best et al., 1986). The average flame temperature is
estimated using the ET (Emission-Transmission) procedure, as well as the Normrad
(Normalized Radianc) procedure (Morrison et al., 1997). In the latter, \(R_n(\nu)\) is first
calculated and then compared to a blackbody Planck function, \(R_n(\nu) = BB(\nu, T)\),
evaled at various temperatures in the wavenumber range of hot CO\(_2\) (2300 - 2200
\(cm^{-1}\)) (Hilton et al., 1995) until a reasonable match is achieved with a least squares
regression. As the CO\(_2\) peak around 2350 cm\(^{-1}\) is the clearest in the spectrum, and the
CO\(_2\) concentration in the surrounding air is very small compared to the amount of CO\(_2\)
produced by combustion, this peak is used to match the blackbody Planck function
(Morrison et al., 1997). In contrast, the ET procedure compares the absorption spectrum
\((1 - \tau(\nu))\) with the radianc \(R(\nu)\) divided by the blackbody Planck function \(BB(\nu, T)\) at
different temperatures until both spectra are similar: \((1-\tau(\nu)) = \frac{R(\nu)}{BB(\nu,T)}\). Here,
again emphasis is placed on the clearest peak, which is the maximum absorption of CO$_2$ between 2295 and 2280 cm$^{-1}$. The average temperature used in this study is always the average of the temperatures obtained with the ET and Normrad procedures.

For validation of the FTIR technique, flame temperatures are determined with multiplex CARS probing nitrogen (Eckbreth, 1988). The complete Q-branch spectrum of nitrogen is measured with a single laser pulse. Normally, for each temperature measurement 1000 single pulse spectra are collected at 20 Hz and from each spectrum a temperature is obtained with a computer code developed at Paul Scherrer Institute, Switzerland. These one thousand temperatures are compiled in a normalized histogram and a Gaussian distribution is created by non-linear regression. The mean temperature is referred to the mode of this distribution and $\sigma(T_{\text{CARS}})$ describes the corresponding arithmetic standard deviation. Even in an isothermal environment the resulting temperature probability density function (PDF) of this system is Gaussian shaped with a standard deviation $\sigma(T_{\text{CARS}})$ of about 60 K at a mean temperature of about 2000 K (Bombach et al., 1994b) and is caused mainly by mode fluctuations of the CARS broadband dye laser. Thus, the measurement precision is about 60 K. The accuracy of CARS as evaluated at isothermal conditions is about 60 K as well (Bombach et al., 1994b). When $\sigma(T_{\text{CARS}})$ exceeds 60 K, temperature fluctuations are present. The temporal resolution, given by the duration of the laser pulse (approx. 10 ns), comfortably meets the needs of investigating laminar as well as turbulent flames (Bombach et al., 1994a). The measurement volume of 0.2 mm x 0.2 mm x 1 mm is aligned in the center of the burner. The burner is moved on a positioning system (Unipos 110, Foehrenbach AG) with an accuracy of 0.05 mm axially and can be moved laterally as well for off-centerline measurements.

3.3. Results and discussion

Figure 3.2 shows the IR spectra of the unburned absorbing species (before combustion, thin line), namely methane (3200 - 2800 and 1400 - 1250 cm$^{-1}$) and TTIP (2973, 1132, 1009, 851, 629 cm$^{-1}$) as well as those of the combustion products (after combustion, thick line), H$_2$O (4000-3200, 1800-1200, and 800-600 cm$^{-1}$), CO$_2$ (around 2350 and 667 cm$^{-1}$) and the TiO$_2$ (735 cm$^{-1}$) (Morrison et al., 1997). Additionally, the spectral features
of CO$_2$ at room temperature (referred as cold CO$_2$) are shown (small peaks at 2350 cm$^{-1}$ and 667 cm$^{-1}$; thin line).

Fig. 3.2: FTIR absorption spectra of the premixed TTIP/methane/oxygen/nitrogen gases before (thin line) and after (thick line) combustion 23 mm above the burner (HAB) as well as that of cold CO$_2$ (small peak at 2350 cm$^{-1}$; thin line).

For temperature evaluation from the transmission and emission (radiance) measurements, the normalized radiance is calculated (Fig. 3.3) and the clearest peak from the absorption and emission spectra (here the CO$_2$ peak around 2350 cm$^{-1}$) is used for temperature evaluation by comparison of the normalized radiance with a blackbody Planck function of a certain temperature, BB(ν,T) (smooth line envelope in the middle). Figure 3.3 shows the best match of BB(ν, 2595 K) and the normalized radiance spectrum at 2300 to 2200 cm$^{-1}$ as obtained by a least squares regression as well as the blackbody Planck functions of 50 and 100 K below and above the best match, 2595 K, for a titania particle-laden flame at HAB = 5 mm. As the spectral resolution is reduced to 1 and 2 cm$^{-1}$ here, 200 and 100 measured wavelengths, respectively, are considered for the least squares regression for the comparison of the normalized radiance spectrum.
to $BB(\nu, T)$. It can be seen that the blackbody of 2595 K (thick smooth enveloping line) obtained by the least squares regression only starts to deviate by more than 50 K from the normalized radiance spectrum for wavenumbers larger 2300 cm$^{-1}$ and smaller than 2200 cm$^{-1}$. Comparing the spectral features of the hot and cold CO$_2$ in Fig. 3.2, it is apparent that the features of cold CO$_2$ (found in the air surrounding the flame) are confined to the spectral region above 2300 cm$^{-1}$. Therefore, only the P-branch of the hot CO$_2$ is used for extracting the flame temperature in the 2300 to 2200 cm$^{-1}$ range.

![Normalized radiance spectrum and the best match of the blackbody Planck function](image)

*Fig. 3.3: Normalized radiance spectrum and the best match of the blackbody Planck function (thick smooth line envelope), and corresponding blackbody Planck functions 50 K and 100 K lower and higher temperatures of a premixed TiO$_2$ particle-laden at 5 mm HAB.*

### 3.3.1. Comparison of FTIR and CARS (in a premixed particle-free flat flame)

Both CARS and FTIR are applied first to a particle-free premixed flat flame to determine flame temperatures in order to compare these two non-intrusive techniques
for a well established case as CARS is not well established in particle-laden flames so far.

Fig. 3.4: Temperature evolution with time obtained with CARS at the centerline and 13 mm HAB and the corresponding probability density functions (PDFs) of temperature (inserts) in the absence (a) and in the presence (b) of an external electric field (1.5 kV/cm) in a premixed particle-free flame.
Figure 3.4a shows a time resolved plot of 1000 single-shot temperatures at the centerline and 13 mm height above the burner (HAB). The corresponding temperature PDF is depicted as an insert to the figure. It is well described by a Gaussian distribution with a mean temperature of 1969 K and a standard deviation \( \sigma(T_{\text{CARS}}) \) of 54 K. This rather small standard deviation indicates a laminar flame without temperature gradients in the measurement volume.

![Graph showing temperature measurements](image)

**Fig. 3.5:** Average flame temperature from FTIR (circles), centerline temperatures from CARS (triangles) with (full symbols) and without (open symbols) electric field of 1.5 kV/cm for a particle-free flat flame as a function of the (axial) height above the burner (HAB). Tomographic reconstructed FTIR data in the absence of electric fields (squares) are shown as well.
Figure 3.5 shows the temperature profiles along the burner axis (centerline) of this flame obtained with FTIR (circles), and CARS (triangles), without (open symbols) and with (full symbols) an external electric field of 1.5 kV/cm. With increasing HAB the flame temperature first increases, reaching a maximum (2005 K) and then slowly decreases with increasing height. As shown in the lower part of Fig. 3.5, the $\sigma(T_{\text{CARS}})$ increases only slightly with increasing HAB, while this is more pronounced in the presence than in the absence of the electric field. The $\sigma(T_{\text{CARS}})$ indicates that the flame is laminar at the flame center for the investigated HABs in the absence of electric fields and is also laminar in the presence of electric fields up to 20 mm HAB and starts then to become more turbulent further downstream. There is good agreement between CARS and FTIR, especially in the highest temperature region close to the burner mouth. In this region, both measurements overlap within the experimental error, which is shown for the FTIR measurements as bars around the data points and describe two times the standard deviation of three sets of experiments. At higher locations (HAB > 10 mm), however, the FTIR temperature is lower than that by CARS. This difference can be understood by considering that CARS has a spatial resolution of 0.2 mm x 0.2 mm x 1.0 mm, and therefore the temperature is only measured in the flame center, while the FTIR uses an integral line-of-sight through the whole flame. Thus, FTIR averages the lower CO$_2$ temperatures found at the flame edge (~ 1000 K) with higher temperatures in the flame center (~ 1800 K). However, this can be overcome by tomographic reconstruction of the line-of-sight measurements (Best et al., 1991). To demonstrate this, seventeen radial temperature measurements were conducted in the absence of the electric field and these lateral line-of-sight measurements, 2 mm in diameter each, were tomographically reconstructed to obtain the locally resolved radiance and transmittance spectra. This evaluation procedure followed Minerbo and Levy (1969) using the Abel’s Integral Equation and is described in detail in Appendix B. The tomographic reconstructed temperatures at the centerline (squares in Fig. 3.5) give essentially the same values for 5 and 12.5 mm HAB compared to the line-of-sight measurements, while at higher positions the temperature is increased significantly by the tomographic reconstruction technique (Fig. 3.5), and they are now close to the CARS data.

At the lower part of the flame (HAB < 10 mm), the temperature is so uniform (premixed flat flame) that the flame edge effects are small for the line-of-sight FTIR measurements, thus excellent agreement with CARS is obtained.
Fig. 3.6: Temperature evolution with time obtained with CARS at the 8 mm off center and 13 mm HAB in the absence (a) and in the presence (b) of an external electric field (1.5 kV/cm) in a premixed particle-free flame.
When applying electric fields (full symbols, 1.5 kV/cm) and measuring the flame temperature with CARS, the mean flame temperature is not affected in the highest temperature regions (HAB < 10 mm), but decreases significantly with increasing HAB. Close to the upper edge of the electrodes at 23 mm HAB, the mean temperature is 220 K lower in the presence than in the absence of electric fields and differs even more with increasing height (Fig. 3.5) as flame ions are attracted toward the electrodes, spreading the flame volume and entraining air from the surroundings (Lawton et al., 1968; Lawton and Weinberg, 1969), in agreement with Lewis and Kreutz (1933). Similar trends for the flame temperature are observed by FTIR. The increase of $\sigma(T_{\text{CARS}})$ in Fig. 3.5 in the presence of the electric field reflects that the temperature PDF broadens indicating the increased fluid motion with increasing height and especially the enhanced fluid motion in the presence of the electric field.

In Fig. 3.4a the time resolved 1000 single-pulse temperatures by CARS at the burner centerline and 13 mm HAB were shown in the absence of electric fields. In the presence of an external electric field the temperature PDF at the same location (Fig. 3.4b) is well described by a Gaussian distribution as well, with a mean temperature and 1948 K and a standard deviation $\sigma(T_{\text{CARS}})$ of 59 K, respectively. This temperature is only slightly lower than that obtained in the absence of an electric field (Fig. 3.4a). The $\sigma(T_{\text{CARS}})$ indicates that the flame is rather laminar at this HAB and its temperature is uniform (no temperature gradients), both in the absence as well as in the presence of electric fields. The observed temperature fluctuations (Fig. 3.4) are mainly caused by the mode fluctuations of the CARS broadband dye laser.

The mean off-axis flame temperature (13 mm HAB and 8 mm off centerline) is reduced from 1750 to 1691 K when the electric field is applied (Figs 3.6a, 3.6b, respectively), and $\sigma(T_{\text{CARS}})$ increases from 73 to 102 K, thus temperature fluctuations are present here. Close to the edge of the flame (13 mm HAB and 10 mm off centerline; Fig. 3.7), however, the mean flame temperature is significantly lower (1389 K). The flame temperature fluctuations increase significantly ($\sigma(T_{\text{CARS}}) = 130$ K) 10 mm off centerline (Fig. 3.7a) in the absence of electric fields. Cold gases (800-1000 K) are entrained into this region of the flame, which clearly is observed in the time dependent temperature plot (Fig. 3.7a), for example at measurement numbers 281, 468, 652, 811, or 973. The gas temperature is reduced by radiation to the surroundings as well. By applying the electric fields, $\sigma(T_{\text{CARS}})$ is almost doubled (Fig. 3.7b).
Fig. 3.7: Temperature evolution with time obtained with CARS at the 10 mm off center and 13 mm HAB in the absence (a) and in the presence (b) of an external electric field (1.5 kV/cm) in a premixed particle-free flame.
However, in this figure it can be observed that there are statistically higher temperatures, as well as lower temperatures, in the flame with electric fields (Fig. 3.7b) compared to the flame without electric fields (Fig. 3.7a). The increase in flame temperature (e.g. measurement numbers 65, 125, 285, 482, 638, 884, or 977 in Fig. 3.7b) is attributed to the flower-like spread of the flame (Vemury and Pratsinis, 1996; Vemury et al., 1997), entraining hot gases from the flame center into this flame region. Entrainment of cold gases (600-700 K; e.g. measurement numbers 250, 515, 695, or 825 in Fig. 3.7b) by enhanced turbulence (ionic wind) created by the electric field, however, is only observed at the flame edge (10 mm off centerline).

The time resolved measurements at 13 mm HAB showed that the flame temperature is little affected by the electric field in the center of the flame while close to the flame edge, the electric field creates intense temperature fluctuations, from entrainment of ambient air (cold entrainment) and gases from the flame center (hot entrainment).

### 3.3.2. Electrically assisted premixed particle-laden flame

The cone-shaped premixed TiO$_2$ particle-laden flame investigated in this study converts 11 g/h TTIP to nearly non-agglomerated spherical TiO$_2$ particles. Figure 3.8 shows photographs of this flame in the absence of the electric field (a) and for electric field strengths of 1.0 (b), 1.5 (c) and 2.0 kV/cm (d) along with corresponding TEMs of the product particles. The corresponding visible flame height decreases with increasing field strength from 75 to 40, 32, and 23 mm, respectively, and the flame starts to open up flower-like (Vemury et al., 1997) at field strengths larger than 1.25 kV/cm. The flame burns relatively stable under the influence of the electric field while intense turbulence by ionic wind is not detected as when needle electrodes were used (Vemury et al., 1997). This is in agreement to the time resolved radial flame temperature measurements of Figs 3.4 and 3.7. At field strengths $\geq$ 2.25 kV/cm electrical breakdown of the field is observed.
Fig. 3.8: Premixed TiO$_2$ particle-laden flames for electric field strengths of 0 kV/cm (a), 1.0 (b), 1.5 (c), and 2.0 kV/cm (d) using parallel plate electrodes, and corresponding transmission electron micrographs of the product powders.

In the absorption spectra at 5 mm HAB (Fig. 3.9), there is no detectable CO, CH$_4$ or TTIP in the flame, indicating complete combustion at this flame height. One observes a slight decrease of CO$_2$ concentration with increasing field strength at this flame location (Fig. 3.9). At a higher location (18 mm HAB, Fig. 3.10), the CO$_2$ peak around 2350 cm$^{-1}$ in both absorption and emission (radiance) spectra is significantly larger in the absence than in the presence of electric fields. As indicated by the visible flame structure (Fig. 3.8), the CO$_2$ concentration decreases as the gas spreads to a larger volume and is more diluted with ambient air by entrainment in the presence of electric fields, in agreement with Morrison et al. (1997).

From the absorption and radiance (emission), the normalized radiance is calculated in Fig. 3.11. At 5 mm HAB the normalized radiance shows a best match with the blackbody spectrum (solid straight line) for temperatures of 2580 K, 2600 K, and 2530 K (Normrad-procedure) for electric field strengths of 0, 1.0, and 1.5 kV/cm, respectively. Apparently, there is no difference in flame temperature within the experimental error for these field strengths. When comparing the absorption and the radiance divided by the blackbody Planck function (ET-procedure) at those locations, the corresponding average temperature gives a best match for blackbody temperatures
of 2530, 2600, and 2480 K, for electric field strengths of 0, 1.0, and 1.5 kV/cm, respectively (Fig. 3.12).

**Fig. 3.9:** Absorbance and radiance spectra at 5 mm height above the burner (HAB) for electric field strengths of 0.0, 1.0, and 2.0 kV/cm for a premixed TiO$_2$ particle-laden flame.

This agrees well with flame temperatures determined with the Normrad-procedure at that HAB (Fig. 3.11). However, with increasing HAB e.g. at 18, 23, 40 mm HAB, the
flame temperature in the absence of electric fields is always significantly larger compared to that in the presence of electric fields.

Fig. 3.10: Absorbance and radiance spectra at 18 mm height above the burner (HAB) for electric field strengths of 0.0, 1.0, and 2.0 kV/cm for a premixed TiO₂ particle-laden flame.

Summarizing, Fig. 3.13 shows the average flame temperatures obtained with FTIR along the centerline of the titania-laden flame for 0 kV/cm (diamonds), 1.0 kV/cm (squares), 1.5 kV/cm (triangles), and 2.0 kV/cm (circles).
Fig. 3.11: Normalized radiance spectra and the corresponding blackbody Planck functions (smooth line envelopes) at 5 mm HAB for electric field strengths of 0.0, 1.0, and 1.5 kV/cm for a premixed TiO$_2$ particle-laden flame.
Fig. 3.12: Measured absorbance spectra and the calculated absorbance spectra (measured radiance divided by a blackbody Planck function of the best matching temperature) at 5 mm HAB for electric field strengths of 0.0, 1.0, and 1.5 kV/cm for a premixed TiO$_2$ particle-laden flame, corresponding to Fig. 3.11. The 1 – transmittance spectra are shifted by 0.05 for clarity.
The error bars show two times the standard deviation of multiple measurements at the same location. Maximum average flame temperatures are observed at 3 to 5 mm HAB and then the flame temperature decreases with increasing HAB for all investigated field strengths.

Fig. 3.13: Average axial temperatures of a premixed TiO$_2$ particle-laden flame obtained with FTIR-E/T as a function of HAB without electric field (diamonds) and electric field strengths of 1.0 kV/cm (squares), 1.5 kV/cm (triangles), and 2.0 kV/cm (circles).

The average flame temperature decreases almost linearly with flame height in the absence of an electric field. There is almost no difference in flame temperature at low HAB (highest flame temperatures) at all investigated electric field strengths, but the flame temperature is significantly lower than without electric fields further downstream.
when the electric field strength increases and the flame height decreases (Fig. 3.8). The higher the electric field strength, the sharper is the drop in flame temperature above 10 mm HAB. At 18 mm HAB, the average flame temperature of the TiO$_2$ laden flame is decreased from 2410 K (without electric fields) to 2290 K (1.0 kV/cm), to 2100 K (1.5 kV/cm), and to 1710 K (2.0 kV/cm), respectively. These results are consistent with the CARS and FTIR measurements in the particle-free flame (Fig. 3.5). External electric fields affect the ion distribution in the flame (Lawton et al., 1968; Lawton and Weinberg, 1969), and this results in a reduced flame height, thus, in a smaller residence time of the particles in the flame. As the flame is suppressed by ion and particle movement to the electrodes, the temperature at a certain HAB is reduced.

![Fig. 3.14: Average radial temperatures of a premixed TiO$_2$ particle-laden flame obtained with FTIR-E/T at 5 mm (triangles) and 18 mm (circles) HAB without (open symbols) and with (full symbols) external electric fields (1.5 kV/cm).](image)
Figure 3.14 shows radial flame temperature profiles for a premixed particle-laden flame using slightly lower TTIP flow rates (10 g/h instead of 11 g/h). Thus, the maximum flame temperature is slightly lower than that measured in Fig. 3.13. At 5 mm HAB (triangles), a rather uniform radial temperature profile is detected up to 8 mm off centerline. At larger radial positions, a significant temperature drop is measured close to the visible flame edge of the TiO₂ particle-laden flame. The external electric field does not affect the uniformity and flame temperature within the experimental error at this axial location. However, further downstream (18 mm HAB, circles), the radial flame temperature profile is significantly affected by the electric field and the flame temperature is 270 K lower in the presence than in the absence of the electric field at the flame centerline and 4 mm off centerline. However, 8 mm off centerline, significantly lower temperatures than 4 mm off centerline are measured in the absence of the electric field, while for the electrically assisted flame the temperature 4 and 8 mm off centerline is almost identical as the flame is spread (Fig. 3.8) and the hot gases are drawn toward the electrodes (Lawton and Weinberg, 1969; Vemury et al., 1997).

Contrary to Morrison et al. (1997) this study does not measure a significant increase of flame temperature (up to 275 K) by the application of external electric fields, neither in axial nor radial direction. A likely explanation is the non-uniformity present in the flame of Morrison et al. (1997). The flow conditions of Morrison et al. (1997) were similar to that by Katzer et al. (2001), and in these flames one observes an inner flame cone of unburned gases. This is further corroborated by the detection of small amounts of cold methane in the transmission spectrum collected at 3 mm HAB (Fig. 2a of Morrison et al., 1997). As the electric field shrinks the high temperature zone of the flame and creates better mixing of the gases close to the burner, the flame front is moved closer to the burner. Thus, when measuring the flame temperature at the same HAB in the presence and the absence of the electric field, the electric fields have forced the flame front closer to the burner and therefore the flame temperature is higher at this location because the combustion is more complete. However, in the present study, the operating conditions did not allow this inner flame cone to form (since it is operated as a flat flame); consequently, there is no cone to move closer to the burner mouth and therefore an increase of the flame temperature by the electric field is not observed.
3.3.3. Product titania powder characteristics

The specific surface area of powders collected on the glass fiber filter from the TiO\textsubscript{2} particle-producing flame is 36 m\textsuperscript{2}/g in the absence of electric fields. Setting the potential difference between the two plates to 1.0 kV/cm increases the specific surface area to 39 m\textsuperscript{2}/g and the specific surface area increases steadily to 50 m\textsuperscript{2}/g at 2.0 kV/cm (Kammler et al., 2001). Representative TEM pictures of the product powders are shown in Fig. 3.8. Even though the particles produced in this flame are larger than the ones made by Vemury et al. (1997), since TTIP is an additional fuel and therefore increases the flame temperature, the normalized increase of the specific surface area is in the same order as that observed by Vemury et al. (1997) for plate electrodes of the same height. Increasing the electric field strength increases the specific surface area of the product powder in agreement to earlier studies (Hardesty and Weinberg, 1973; Vemury and Pratsinis, 1995 and 1996; Vemury et al., 1997; Kammler and Pratsinis, 2000). Besides the change in the temperature profile when applying the electric fields (Fig. 3.13), which leads to reduced residence times of the particles at high temperatures and therefore to less particle growth, unipolarly charged aerosol particles have the tendency to expand because of mutual electrostatic repulsion, thereby undergoing a concentration decrease with time (Kasper, 1981). A decrease of gas concentration was also observed with FTIR by Morrison et al. (1997) and in Figs 3.9, and 3.10. Hence, the reduced particle concentration leads to subsequently less particle collisions and growth, and as the particles move faster out of the hot flame temperature zone, the residence time of the particles in this region of the flame decreases and, as a result, the particle diameter decreases. However, since the particles are rather small, they are charged by diffusion charging. Because of the movement of the flame ions toward the plate electrodes, the particle residence time in the decisive region for particle growth is reduced. The present results are in agreement with Xiong et al. (1992) who showed theoretically that charges can effectively slow down the particle growth process by coagulation. A fraction of these particles deposit on the electrodes similar to the process in an electrostatic precipitator. The specific surface area of the particles which were collected on the plate electrodes is slightly higher (60 ± 5 m\textsuperscript{2}/g ) than that of the particles collected on the filter as they are removed faster from the flame. Therefore, the residence time of the
particles in the high temperature regions is reduced and the growth is inhibited as the temperature is reduced significantly.

The measured current between the two electrodes at a field strength of 1.5 kV/cm was 0.5 µA in the presence of TTIP, while the current obtained at the same field strength in a particle-free premixed flat flame was 5.5 µA, a similar value as that measured by Katzer et al. (2001).

The rutile content of these powders is 8 ± 2 wt. % without electric field and for low electric field strengths. The rutile content of the product powders, however, increased slightly to 10-15 wt. % for electric field strengths of 1.75 and 2.0 kV/cm. Powders collected on the electrodes contained 20-30 wt. % rutile. As the residence time in the high temperature region of the flame is reduced for particles deposited on the electrodes as well as for particles produced at higher electric field strengths because of the sharper temperature gradient (Fig. 3.13), higher amounts of rutile cannot be attributed to the reduced time in the high flame temperature region inhibiting the anatase to rutile phase transformation as observed by Akhtar et al. (1991). An explanation for higher rutile contents could be that rapid quenching favors the anatase to rutile phase transformation. This would explain higher rutile contents in the powders produced in the presence of electric fields and as well the higher rutile content of the powders collected on the electrodes. In contrast to the present study, Vemury et al. (1997) made pure anatase (99.9 wt. %) TiO₂ in premixed honeycomb-stabilized flat flames, and changing electric field strength did not show any influence on these powders. Vemury et al.’s flame was more fuel lean (fuel equivalence ratio (Turns, 1996) (EQR) = 0.7) than the present one (EQR = 0.9), which results in lower flame temperatures. The higher rutile content of the powders produced in this study is attributed to the higher flame temperatures because of the addition of an extra amount of fuel by the TTIP (Arabi-Katbi et al., 2001) and the increase in the EQR. Using non-stabilized premixed flames, however, Vemury et al. (1997) reduced the rutile content of the product powders from 82 to 65% by increasing the electric field strength from 0 to 2.75 kV/cm (Vemury et al., 1997). This flame was fuel rich (EQR = 2), and ionic wind, created by the electric field (needle electrodes), entrains ambient air into the flame, thus, increases the available oxygen amount. The flame temperature, however, is reduced by the air entrainment. Ionic wind becomes significant when needle electrodes are used in contrast to plate electrodes and creates significant turbulence (Vemury et al., 1997;
Kammler and Pratsinis, 2000). However, it should be noted that rutile is formed preferentially, under oxygen lean conditions as shown by Rulison et al. (1996) who studied TiO$_2$ particle formation in counterflow diffusion flames. Mostly anatase was formed when the TiCl$_4$ was added to the oxidizer stream, while feeding the TiCl$_4$ to the fuel stream, mainly rutile was formed, in agreement to the findings discussed above. They attributed this to the change in oxygen vacancies within the TiO$_2$ crystals, which increase with increasing the ambient oxygen concentration. This is in agreement to MacKenzie (1975), who studied the anatase to rutile phase-transformation in a tube furnace with stationary powder samples. They found that the reaction rate of this transformation was greatest in reducing atmospheres (5% H$_2$/95% N$_2$), while it was progressively retarded at increasing oxygen concentrations. Simultaneously to Rulison et al., Zhu and Pratsinis (1996) systematically increased the oxygen concentration in the oxidizer stream of a single diffusion flame. Even though the maximum flame temperature increased from 1020 to 1518°C by increasing the oxygen concentration from 21% (fuel rich flame) to 100% (fuel lean flame), the rutile content of the product powder decreased from 13.2 to <0.1 wt. %. This indicates that oxygen concentration seems to be as important as flame temperature, in determining the crystalline structure of flame made titania particles. The increase of oxygen availability as well as the reduction in flame temperature may explain also the reduction of rutile phase from 20 to 8 wt. % as observed by Vemury (1995) in electrically assisted diffusion flames when the electric field strength is increased from 0 and 1.75 kV/cm.

Summarizing, rutile is not only formed preferentially at higher flame temperatures and longer residence times, but the rutile formation is also favored in oxygen lean environments, such as encountered in partially premixed or in counter flow diffusion flames. Additionally, there is also evidence that the cooling rate can affect the anatase to rutile phase transformation.

3.4. Concluding remarks

Non-intrusive temperature measurements are very important to understand and describe particle formation in flame aerosol reactors. Here, FTIR spectrometry was used to determine temperature profiles in typical laboratory-scale TiO$_2$ particle-laden premixed
flames and this technique was verified with CARS in a particle-free premixed flat flame. Compared to laser diagnostics, FTIR spectroscopy is relatively simple to handle and can be also applied at typical particle concentrations used in laboratory-scale experiments. Improvement in spectral (1 cm⁻¹) and spatial resolution (IR beam down to 2 mm in diameter) of the FTIR were achieved in a new set-up, giving the ability for detailed studies of temperature and species evolution. Two temperature evaluation procedures (Normrad and ET) were applied and showed good agreement in determining the gas temperatures (usually within 50 K). Detailed axial and radial flame temperature profiles were obtained in electrically assisted flames, where no effect of electric fields was found close to the burner, but much lower flame temperatures (e.g., 700 K at 18 mm HAB for 2 kV/cm) were measured further downstream. This was in agreement with CARS measurements in a premixed particle-free flat flame in the presence and absence of an electric field.

In contrast to reactant mixing, electric fields can be effectively applied to particle formation in aerosol flame reactors for precision control over a narrow range (within a factor of two in particle specific surface area) to control the synthesis of functional nanoparticles with highly sensitive properties. In this study, the effect of electric fields on the specific surface area of the titania powders as observed by Vemury et al. (1997) was confirmed. Changes in the crystallinity in the presence of electric fields were explained by the change in oxygen availability during the particle formation. Currently we are quantitatively investigating the effect of electric fields (charging and change in flame temperature history) by simulation of particle dynamics.

3.5. References

Best, P. E., R. M. Carangelo, J. R. Markham, and P. R. Solomon, “Extension of emission-transmission technique to particulate samples using FT-IR,” 


Boedecker, L. R., and G. M. Dobbs, “CARS temperature measurements in sooting laminar diffusion flames,” 

Bombach, R., B. Hemmerling, and W. Kreutner, CARS temperature measurements in a lean, turbulent, 120 kW natural gas flame, 

Bombach, R., B. Hemmerling, and W. Kreutner, Development and test of a mobile CARS system to measure temperature fluctuations in large industrial combustion systems, 


Farquharson, S., S. Charpenay, M. B. DiTaranto, P. A. Rosenthal, W. Zhu, and S. E. Pratsinis, In-situ particle size and shape analysis during flame synthesis of nanosize powders, 
*Synthesis and Characterization of advanced materials*, M. A.


4. Nanoparticle growth inside electrically assisted flames

Abstract

Titania nanoparticle growth inside electrically assisted flames is studied by in situ thermophoretic sampling followed by transmission electron microscopy (TEM) and statistical evaluation of the counted images. Up to 11 g/h TiO₂ particles are produced by titanium tetraisopropoxide (TTIP) oxidation in a CH₄/O₂ premixed flame. An electric DC-field of 1.5 kV/cm is established across the flame with two plate electrodes. At each TS location, the flame temperature is measured by Fourier transform infrared (FTIR) spectroscopy, while the product powder is analyzed with nitrogen adsorption (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). The latter is also used to estimate the degree of agglomeration of the product powder. External electric fields decrease most dramatically the flame temperature downstream of the electric field controlling particle size, crystallinity and morphology and contribute to the formation of soft agglomerates (without sintering bridges).

4.1. Introduction

Flame aerosol processing can be used for manufacture of high purity oxide particles, without the multiple steps and high liquid volumes associated with wet chemical processes (Pratsinis and Mastrangelo, 1989). Though additives, burner design and operation can be used for control of flame-made particle characteristics, external electric fields offer precision control of particle size, powder morphology and crystallinity (Vemury and Pratsinis, 1995).

Hardesty and Weinberg (1973) showed that the primary particle diameter of silica was reduced by a factor of three when applying an electric field of 6 kV between two parallel plate electrodes in direction of the flame gas flow. Katz and Hung (1990), however, found an increase of the titania, silica, and germania particle size by a factor
of 3 to 10 with light scattering techniques in a counterflow diffusion burner when electric fields were applied in co-flow also. In premixed flame aerosol reactors, Vemury and Pratsinis (1996) and Vemury et al. (1997) showed that increasing the electric field strength across needle or plate electrodes across the flame flow decreased the average primary particle diameter of product titania, silica or tin oxide powder. This was attributed to shorter particle residence times in the hot flame zone and reduced coagulation rates by electrostatic repulsion of charged particles.

Needle electrodes created highly focused electric fields that resulted in strong convection (ionic wind) across the flame, which entrained surrounding air and decreased the flame temperature (Vemury and Pratsinis, 1995). The use of plate electrodes suppressed the ionic wind, and the effect of charging of the particles by the electric field was proposed to be more distinct (Vemury and Pratsinis, 1996; Vemury et al., 1997). These studies were carried out for rather small powder production rates (1 to 4 g/h). However, Kammler and Pratsinis (2000) demonstrated that external electric fields also can be used successfully to control the specific surface area of silica at production rates of up to 87 g/h.

Katzer et al. (2001) measured local agglomerate size and number concentration with a differential mobility analyzer (DMA) and observed that the number of primary particles per agglomerate sampled at the flame centerline above the electric field was virtually unchanged when applying the electric field between plate electrodes. However, the number of primary particles per agglomerate increased significantly in the presence of the electric field created by needle electrodes. Measuring the flame temperature with thermocouples in the absence of particles further downstream of the electric field, they found that the flame temperature was decreased in the presence of the electric field even plate electrodes, while in contrast Vemury and Pratsinis (1996) and Vemury et al. (1997) did not observe a change in flame temperature there. In electrically assisted particle-laden premixed flames, Kammler et al. (2002) measured detailed flame temperature profiles with non-intrusive FTIR emission/transmission spectroscopy (Best et al., 1986) along and across the flames when an electric field between plate electrodes was created. They found that the flame temperature was not affected close to the burner mouth, but further downstream it decreased significantly with increasing the electric field strength.
Here, the latter study is extended to investigate particle growth inside these electrically assisted flames producing titania particles. This is accomplished with a thermophoretic sampler (Dobbins and Megaridis, 1987) equipped with ceramic isolators for use inside the electric field (Appendix C and D). The flame temperature is measured at the TS locations to follow precisely the temperature history of the growing particles. A flame stoichiometry close to unity is used to assure synthesis of spherical and single titania particles (Arabi-Katbi et al., 2001). Measurements are carried out at a field strength of 1.5 kV/cm, where particle size and flame temperature are influenced by the field’s presence while the flame is still rather stable (Kammler et al., 2002).

4.2. Experimental

The experimental set-up (Fig. 4.1) consists of a premixed burner with two plate electrodes, a gas and precursor delivering system as well as a filter for product particle collection. Oxygen, methane, argon (all 99.99% Pangas, CH) and nitrogen (99.9995% Pangas, CH) are mixed and then delivered through heated tubes into a heated honeycomb stabilized premixed burner made of quartz glass (Kammler et al., 2002). The burner consists of three concentric tubes, where the premixed gases flow through the central (first) tube with an inner diameter of 2.5 cm and nitrogen shield gas flows through the third tube to stabilize the flame (Kammler et al., 2002). An evaporator system (Bronkhorst CEM 100W (evaporator), EL-Flow201 (gas mass flow controller), and Liqui-Flow L1 (liquid mass flow controller) (Stark et al., 2001) set at 150°C delivers the titanium tetraisopropoxide (TTIP, Aldrich, > 97%, distilled over vacuum prior to use, thus the purity of TTIP is improved compared to that used in Chapter 3) into the burner, using nitrogen as carrier gas. Production rates of 0.5, 5.5 and 11 g/h TiO₂ are investigated. The gas flow rates are summarized in Table 4.1. The external electric field is created by two parallel plate electrodes that are 2.5 cm high, 3.8 cm wide and 0.4 cm thick (Kammler and Pratsinis, 2000). The electrodes are positioned at each side of the flame, so that the field lines are across the flame. The electrodes are 5 cm apart and their lower edge is aligned 0.05 cm above the burner mouth. One electrode is connected to a high voltage supply (negative polarity, 1.5 kV/cm, Glassmann High Voltage Inc.) and the other one is grounded (Kammler and Pratsinis, 2000).
Fig. 4.1: Experimental set-up of the premixed aerosol reactor with electric fields for precision control of the particle characteristics. Flame temperatures are measured by in situ FTIR spectroscopy at the same location where thermophoretic sampling is used to monitor the growth of particles.

Table 4.1: Gas flow rates, fuel equivalence ratio (EQR), and Ti mol-fraction of the investigated flames.

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>Ar</th>
<th>CH₄</th>
<th>N₂</th>
<th>O₂</th>
<th>EQR</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/h</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>-</td>
<td>mol fraction</td>
</tr>
<tr>
<td>0.5</td>
<td>0.65</td>
<td>0.6</td>
<td>5.0</td>
<td>1.2</td>
<td>1.03</td>
<td>0.03%</td>
</tr>
<tr>
<td>5.5</td>
<td>0.65</td>
<td>0.4</td>
<td>4.3</td>
<td>1.2</td>
<td>1.04</td>
<td>0.43%</td>
</tr>
<tr>
<td>11</td>
<td>0.65</td>
<td>0.1</td>
<td>3.9</td>
<td>1.2</td>
<td>0.92</td>
<td>0.95%</td>
</tr>
</tbody>
</table>

EQR is defined as the fuel/oxidizer ratio divided by the stoichiometric fuel/oxidizer ratio.

A precision resistor (±0.1%, 25 ppm/K) is inserted between the ground electrode and the ground to measure the current across the plates (Vemury and Pratsinis, 1995). The potential drop across this resistor is measured with a voltage module (5B31, Analog...
Devices) on a signal conditioning board (5B01, Analog Devices). The signal is recorded (10 samples/s) on a personal computer with a data acquisition board (PCI-Mio-16E-4, National Instruments) and is then converted to current using Ohm's law. The product powder is collected on 15 cm diameter glass fiber filters (Whatman GF/A), placed in a stainless steel filter holder at 20 cm height above burner (HAB), with a vacuum pump (Vacuubrand RE-8).

4.2.1. Thermophoretic particle sampling

Samples for analyzing particle morphology are collected by a thermophoretic sampler that rapidly moves a carbon type B copper TEM grid (200 mesh, Pelco) to a precisely defined position in the flame (Dobbins and Megaridis, 1987). The TEM grid is held between two stainless steel blades (0.0125 cm x 0.3 cm x 3 cm) leaving however a 0.2 cm diameter hole at one side to expose the grid to the flame. The TEM grid-holder (that will be inserted between the field of the plate electrodes) is mounted onto the end of a ceramic rod, which is connected to a double acting pneumatic cylinder (Bimba, EM-16050-UC, 1.6 cm diameter, 5 cm stroke) driven by a pneumatic 5/2 valve (SMC Pneumatic AG) using 5 bar absolute pressure. Only the grid-holder with the TEM grid travels through an isolated slotted shield (Dobbins and Megaridis, 1987) that protects the flame from any disturbances caused by the rapid movement of the ceramic rod (Appendix C). A controller varies the residence time of the TEM grid inside the flame (typically 50 ms). The residence time of the TEM grid at the flame center as well its traveling time is recorded and calibrated with a high-speed digital camera (Kodak Ektapro, Model 4540) taking 2250 frames/s.

The TEM micrographs are taken with a Zeiss electron microscope 912 Omega with ProScan and slow scan CCD camera operated at 100 kV. TEM micrographs from the filter powder are prepared from the powder as-is, dipping the TEM grid into the product powder that results in a good particle coverage of the grid. For each flame location typically 500-1000 primary particles are counted using OPTIMAS 6.51 (Media Cybernetics) software. From the counted particle size distributions the number-average primary particle size, $d_{1,0}$, Sauter mean diameter, $d_{3,2}$, standard deviation of the Sauter
mean diameter, $\sigma_{3.2}$, geometric standard deviation, $\sigma_g$, and the sixth moment of the particle size distribution, $d_{6.0}$, are calculated (Hinds, 1999).

### 4.2.2. Temperature measurements

The flame temperature is measured by an FTIR spectrometer (Bomem Inc., MB155S) operating in the range of 6500-500 cm$^{-1}$ (1.5-20 $\mu$m) with 2 cm$^{-1}$ resolution. Two pairs of identical paraboloidal mirrors guide the IR beam through the flame. At the first focal point, a 0.2 cm iris controls the beam diameter, thus, the IR in the flame center (second focal point) has the same width as the iris’ orifice (Kammler et al., 2002). Transmission and emission (radiance) spectra are collected with wide-band deuterated-triglycine-sulfate (DTGS) detectors (D36B). Path correction spectra for the emission measurements are taken with a blackbody cavity in place of the burner. For data acquisition, first a background spectrum for the transmission is taken and then, typically, sixteen scans for both transmission and emission (radiance) spectra are taken. The latter are corrected for self-absorption following Freeman and Katz (1960) as outlined by Best et al. (1991) since the flame is not truly optically thin.

For flame temperature evaluation, emission / transmission (E/T) analysis (Best et al., 1986) is used in which the normalized radiance is compared to blackbody Planck functions $BB(\nu,T)$ of different temperatures (Morrison et al., 1997). From a least squares regression, over the wavenumber region of hot CO$_2$ (2300-2200 cm$^{-1}$) the gas temperature can be obtained directly (Normrad procedure). In the ET procedure, the absorption spectrum $(1 - \tau(\nu))$ is compared with $R(\nu)$ divided by $BB(\nu,T)$ at different temperatures until both spectra match the CO$_2$ peak at its maximum absorbance (between 2295 and 2280 cm$^{-1}$). The average temperatures reported here are obtained from line-of-sight experiments, and therefore are averages of the temperature at the flame center and at the flame edge. The reported values are the average of the temperatures obtained by the ET and Normrad procedures which are typically within 50 K. The flame temperature at the flame centerline is described well by the line-of-sight measurements close to the burner (< 1 cm HAB), while further downstream the line-of-sight measurements slightly underestimate the centerline flame temperature (up to 100 K) compared to tomographic reconstructed measurements (Kammler et al., 2002).
4.2.3. Product powder characterization

The BET equivalent specific surface area (SSA) of the powder is determined with nitrogen adsorption (5 points isotherms) in the relative pressure range \((P/P_0)\) of 0.05 to 0.25 at 77 K with a Gemini III 2375 and a Tristar (both Micromeritics Instruments Corp.). The powders are degassed prior to analysis for 2 h at 150°C under nitrogen atmosphere with a Flow Prep 060 (Micromeritics Instruments Corp.) to remove air moisture. The XRD spectra are recorded with a Bruker D8 advance diffractometer, \(2\Theta = 20° - 70°\). The anatase and rutile content along with the average sizes of the respective crystals is obtained using a fundamental parameter approach (Cheary and Coelho, 1992). The mass weighted average crystal size, \(d_p(XRD)\), is calculated from these results. From the nitrogen adsorption measurements, however, \(d_p(BET) = 6/(\rho \cdot SSA)\) is calculated accounting also for the anatase and rutile mass fraction of the particles using 3.84 and 4.26 g/cm\(^3\) for their densities, \(\rho\), respectively.

Small angle X-ray scattering (SAXS) is obtained with a pinhole geometry SAXS camera (Molecular Metrology, Inc.) using focusing optics along with a 2-d wire detector (Gabriel type design). After correcting the data for detector sensitivity and background, the 2-d data is averaged, as all SAXS patterns are radially isotropic. These averaged data are then regressed with the unified equation for SAXS (Beaucage and Schaefer, 1994; Beaucage, 1995). From this regression, among other parameters, the radius of gyration of the primary particles, \(R_{g1}\), is obtained that can be directly converted to the diameter of an equivalent sphere by \(d_{ps}(SAXS) = 2 \cdot (5/3)^{1/2} \cdot R_{g1}\) (Hyeon-Lee et al., 1998).

4.3. Results and discussion

A unique feature of this study is to understand the effect of electric fields on particle characteristics by monitoring the evolution of primary particle morphology inside the electrically assisted flame. Figure 4.2 shows how the electric field (here 2.0 kV/cm) spreads or opens the flame. The flame ions are drawn toward the electrodes (Lawton
and Weinberg, 1969), and this opens and shortens the flame and significantly as shown by Vemury et al. (1997) and Kammler et al. (2002).

![Image](image_url)

Fig. 4.2: Growth of titania nanoparticles on the plate electrodes (electric field strength 2.0 kV/cm) after 15 min experimental run time.

Part of the titania particles deposits on the electrodes and grows needle-like as shown in Fig. 4.2, but particle deposition is typically less pronounced than that shown in Fig. 2. In the present experiments, however, the applied potential is lower (1.5 kV/cm) thus reducing the deposition. Furthermore the electrodes are always cleaned before a transmission and emission (radiance) measurement for flame temperature determination (Kammler et al., 2002). However, even in Fig. 4.2, the current measured between the electrodes is not affected, thus the titania deposit does not change the electric field significantly. During TS the flame current, measured between the electrodes, is reduced at most by 10% indicating that the field is not disturbed significantly by the presence of the sampling probe (Appendix D). In the absence of the electric field, the visible flame height increases from 6.5 to 8.5 and 8 cm when increasing the TiO$_2$ production rate from 0.5 to 5.5 and 11 g/h, respectively. In the presence of the electric field (1.5 kV/cm), the flame height is decreased to 3, 3.5, and 4 cm, respectively.
4.3.1. Flame temperature

Figure 4.3 shows axial flame temperature profiles of TiO$_2$ particle laden flames, obtained by *in situ* line-of-sight FTIR E/T measurements for production rates of 0.5, 5.5, and 11 g/h TiO$_2$.

![Flame temperature profiles](image)

**Fig. 4.3:** Flame temperature profiles of TiO$_2$ particle laden flames measured along the centerline by Fourier transform infrared (FTIR) spectroscopy for TiO$_2$ production rates of 0.5, 5.5, and 11 g/h in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).
For all flames, the temperature first increases, reaches a maximum at 0.5 to 1 cm HAB, and then decreases slowly with increasing HAB as air entrainment and heat loss by radiation dilute and cool the flame, respectively. In the present experiments, the methane flow rate is decreased when increasing the TiO$_2$ production rate to conserve the stoichiometry of the flame, keeping constant the fuel equivalence ratio (EQR) around unity. This resulted in relatively similar temperature profiles at all investigated TiO$_2$ production rates. The maximum temperature is around 2450 K for the 5.5 and 11 g/h TiO$_2$ flames, while it is slightly lower for the 0.5 g/h TiO$_2$ flame (2350 K). The latter can be understood, considering that the adiabatic flame temperature of the 0.5 g/h TiO$_2$ flame is 250 K lower than that of the 5.5 and 11 g/h TiO$_2$ flames. For all investigated TiO$_2$ production rates, the maximum flame temperature in the presence of electric fields does not differ from that in the absence of electric fields. Further downstream, however, the temperature decreases more rapidly in the presence of electric fields in agreement with Kammler et al. (2002). Since the EQR of the 11 g/h TiO$_2$ flame is slightly smaller compared to the 0.5 and 5.5 g/h TiO$_2$ flame (Table 4.1), this could explain the slightly lower flame temperature at larger HAB compared to the other two flames (Fig. 4.3). At lower EQR the methane and TTIP is consumed faster, shortening the actual reaction zone.

4.3.2. In situ particle sampling

Figure 4.4 shows TEM pictures from thermophoretic sampling at 0.5, 2.5, 5, 7.5, and 10 cm HAB along the flame centerline, as well as TEM micrographs of the filter powder for 0.5 g/h TiO$_2$. On the left-hand side, no electric field is applied between the electrodes, while on the right-hand side of Fig. 4.4 the electric field (1.5 kV/cm) is present. The particle size increases with increasing HAB regardless of the electric field. There is no significant change on particle size or the degree of agglomeration when applying the electric field. At all locations the particles are almost non-agglomerated and only the particles on the filter seem to be slightly agglomerated.

TEM pictures from thermophoretic sampling at 0.5, 2.5, 5, 7.5 and 10 cm HAB at the flame centerline, as well as TEMs of the filter powder for 5.5 and 11 g/h TiO$_2$ are shown in Figs 4.5 and 4.6, respectively.
Fig. 4.4: TiO$_2$ particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 0.5 g/h TiO$_2$. 
Fig. 4.5: TiO$_2$ particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 5.5 g/h TiO$_2$. 
Fig. 4.6: \( \text{TiO}_2 \) particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 11 g/h TiO\(_2\).
As in Fig. 4.4, on the left-hand side the particles made in the absence of the electric field are presented, while the ones made in the presence of electric fields are shown on the right-hand side. The particles are significantly larger at all HAB and on the filter compared to 0.5 g/h TiO$_2$ (Fig. 4.4), since the increase in particle concentration increases the particle collision frequency and thus, the coagulation and particle growth rate consistent with Pratsinis et al. (1996).

At 0.5 cm HAB small primary particles are observed that are partly agglomerated with or without electric fields. Further downstream (2.5 cm HAB), however, only larger single particles are observed that increase in size with increasing HAB in agreement with Arabi-Katbi et al. (2001). These early agglomerates enter the high temperature zone (0.5 - 1.5 cm) and rapidly sinter. For 5.5 and 11 g/h TiO$_2$ in the presence of electric fields, however, agglomerates (1-5 µm) along with widely spread single particles are observed at HAB = 5 cm (above the electrodes) and also at 7.5 and 10 cm HAB. The electric field separates the flame charges forming homopolar clouds of particles close to the electrodes (Lawton and Weinberg, 1969; Vemury and Pratsinis, 1996; Katzer et al., 2001). These charged particles, however, mix further downstream by convection (HAB > 2.55 cm, thus downstream of the electric field). The oppositely charged particles are attracted to each other, resulting in the formation of large agglomerates (1-5 µm) as the flame temperature is significantly lower.

The increase of the agglomerate diameter of aerosol particles by bipolar charging has been proposed to facilitate efficient particle collection (Gutsch and Löffler, 1994). Using non-intrusive light scattering techniques, Katz and Hung (1990) observed an increase of flame-made oxide particle diameter by a factor of 3-10 in the presence of an electric field. Considering that they measured the diameter of agglomerates and not the primary particle size by dynamic light scattering, this is in good agreement to the current observations of enhanced agglomerate formation in the presence of the electric field. However, these agglomerates (Figs 4.5 and 4.6) are most probably soft agglomerates as will be discussed in detail below.

In the TEM micrographs of the filter powders for production rates of 5.5 and 11 g/h (lowest rows of TEM pictures in Figs 4.5 and 4.6), no evidence for neck formation or sintering bridges between particles is found even at higher magnifications (100k) that is typical for hard agglomerates. In the filter powders, single particles are observed next to the agglomerates as well, and this indicates further that non-agglomerated or only
weakly agglomerated particles are produced. This observation is corroborated by small angle X-ray scattering (SAXS) analysis, in which only one characteristic scale is obtained from the unified SAXS equation (Beaucage and Schaefer, 1994; Beaucage, 1995) for the powders produced in the absence of electric fields. This strongly indicates the presence of non-agglomerated particles (Hyeon-Lee et al., 1998). Similar results are obtained for powders made in the presence of electric fields, even though a small degree of agglomeration (2.2 primary particles per agglomerate) is measured by SAXS for 11 g/h TiO₂. Katzer et al. (2001) found that the number of primary particles per agglomerate collected from the flame center above the electric field was virtually not changed, or was even slightly lower further downstream in the presence of the electric field, which is in agreement with the lowest investigated TiO₂ production rate (0.5 g/h) of the present study. The Ti mol-fraction in the flame of Katzer et al. (2001) was 1.8 times higher than that of the 0.5 g/h TiO₂ flame here. As the maximum (adiabatic) flame temperature was lower, Katzer et al. (2001) produced agglomerates, while in the present study single spherical particles are made. However, as higher precursor and, subsequently, particle concentrations were employed by Katzer et al. (2001) that increased the particle collision rate and therefore the primary particle diameter, slightly larger particles (19.5 nm by BET) were made than in the 0.5 g/h TiO₂ flame (18.8 nm by BET). Compared to the 5.5 g/h TiO₂ flame, the initial particle concentration might have been too low to form soft agglomerates in the presence of the electric field when the homopolar clouds of particles mix further downstream (above the electric field). However, even though the electric field might have resulted in enhanced agglomeration of the particles, they would have been broken apart again during the quenching/dilution step, when sampling and simultaneously freezing the aerosol before entering the DMA (Katzer et al., 2001). Therefore, an increase in the apparently soft agglomerate size with increasing electric field strength as observed by Katz and Hung (1990) or in the present results for 5.5 and 11 g/h TiO₂ might not be observed when using the DMA technique at all. Vemury and Pratsinis (1996) observed a decrease of the extent of agglomeration of silica particles collected on the filter and seen by TEM when applying a unipolar electric field between plate electrodes. The decrease of flame temperature in the presence of the electric field might have slowed down the primary particle and agglomerate growth, and therefore they observed smaller agglomerates. However, even though soft agglomerates might have been formed, they could have been easily broken
apart during the dispersion in liquids for TEM preparation. A small decrease of the silica agglomerate size with increasing electric field strength was observed by Hyeon-Lee et al. (1998) with SAXS. But again one must consider that SAXS only measures hard agglomerates, even though soft agglomerates might be present.

Figure 4.7 depicts the evolution of the TS/TEM counted Sauter mean particle diameter, \( d_{3,2} \), with HAB for 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles) TiO\(_2\) in the absence (open symbols) and presence (filled symbols) of electric fields. In the absence of electric fields, the average primary particle diameter increases steadily with increasing HAB for all TiO\(_2\) production rates. This is in agreement with earlier work (Arabi-Katbi et al., 2001; Kammler et al., 2001). However, in the presence of the electric field, the Sauter mean diameter is similar to that measured in the absence of the electric field for HAB \( \leq 2.5 \) cm inside the electric field. Further downstream at locations above the electrodes (\( \geq 5 \) cm HAB), it remains almost constant or even decreases for 11 g/h TiO\(_2\). As the electric field decreased the flame temperature (Fig. 4.3), the growth of particles was stopped as sintering was slowed down. This decrease of the particle diameter (notably at 7.5 cm HAB and 11 g/h TiO\(_2\)) is attributed to the presence of large agglomerates with significantly smaller average primary particle sizes (Figs 4.5 and 4.6) at the flame centerline. These agglomerates probably form close to the edges of the electrically assisted flame, where the flame temperature is substantially lower, and complete coalescence is not reached anymore. Enhanced mixing (fluid motion) created by the recombination of the homopolar clouds formed by the electric field brings these agglomerates then to the flame centerline. The agglomerate growth is also favored by the oppositely charged particles contained in each cloud.

The flame temperature at 5 cm HAB in the presence of the electric field is still above 1120 K, where complete coalescence of titania nanoparticles still can be observed (George et al., 1973). Thus there is the possibility that part of these agglomerates will coalesce. However, further downstream, these agglomerates cannot coalesce anymore. Considering that the flame temperature is still above 1120 K even at 10 cm HAB (Fig. 4.3), gives the answer to the question why no agglomerate formation is observed in the absence of electric fields (Figs 4.4 – 4.6) as observed by Arabi-Katbi et al. (2001) at large HABs.

The particles collected on the filter have been formed along different streamlines and therefore have experienced different temperature histories. This can explain that the
The diameter of the product powder (filter) is smaller than that of particles collected at the flame centerline at 7.5 and 10 cm HAB as observed for the experiments with 11 g/h TiO₂ (Fig. 4.7). The average primary particle diameter of the filter powder is significantly smaller (~20%) in the presence of the electric field (1.5 kV/cm) for all TiO₂ production rates, in agreement to Hardesty and Weinberg (1973), Vemury et al. (1997), and our previous work (Kammler et al., 2002).

Fig. 4.7: Evolution of the TEM counted Sauter mean primary particle diameter with height above the burner (HAB) for TiO₂ production rates of 0.5, 5.5, and 11 g/h in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).
Increasing the electric field strength would amplify the reduction of the average primary particle diameter (Vemury et al., 1997; Kammler et al., 2002). The relative reduction of product particle size (Fig. 4.7) is about the same for all investigated TiO₂ production rates and this could be attributed to the change in the flame temperature profile by the electric field (Fig. 4.3), which is relatively similar for the three investigated TiO₂ production rates.

Figure 4.8 shows how the geometric standard deviation \( \sigma_g \) (which describes the width of the particle size distribution) varies with HAB for TiO₂ production rates of 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles). Open symbols refer to the absence and filled symbols to the presence of electric fields. In the absence of electric fields, \( \sigma_g \) increases steadily from 1.26 to 1.39 for 0.5 g/h TiO₂ as HAB increases from 0.5 to 10 cm. For 5.5 g/h TiO₂, the \( \sigma_g \) increases from 1.38 to 1.45, and for 11 g/h TiO₂, it increases from 1.46 to 1.50. The increase of \( \sigma_g \) with increasing TiO₂ production rate is attributed to larger particle concentrations (Table 4.1) which enhances particle collisions approaching faster the self-preserving limit of \( \sigma_g = 1.45 \). Upon collection on the filter the \( \sigma_g \) is above that value as particles from different streamlines and, subsequently, different sizes are collected there.

In the presence of the electric field, the \( \sigma_g \) is typically 5-10 % higher than in the absence, except at 5 cm HAB, where a much larger \( \sigma_g \) is observed for all investigated production rates. This indicates clearly the role of fluid mixing by the electric field even though this is less pronounced for plate compared to needle electrodes (where the ionic wind can be observed visually).

For the plate electrodes, the onset of the ionic wind broadens the particle size distribution by broadening the residence time distribution early on, and this has a more pronounced effect on the taller flames (5.5 and 11 g/h TiO₂). The high values for \( \sigma_g \) at 5 cm HAB can be understood by considering the presence of the large agglomerates (Figs 4.5 and 4.6) at the flame centerline that are formed at the flame edge and are drawn to the flame center by enhanced mixing by the ionic wind. However, the increase in \( \sigma_g \) is also observed for the 0.5 g/h TiO₂ flame where no agglomerates are observed, thus here the fluid mixing introduced by the electric field plays probably also an important role. At 7.5 cm HAB, \( \sigma_g \) decreases again, as the flame temperature is still high enough for particle sintering that narrows the primary particle size distribution (thus decreases \( \sigma_g \)).
as the sintering rate of titania is inversely proportional to the particle diameter (Kobata et al., 1991). Further downstream, however, the flame temperature is significantly lower, and complete coalescence is not reached anymore. Therefore, $\sigma_g$ increases again because agglomeration continues, and this explains also why the self-preserving limit is exceeded. At the filter, particles formed at different streamlines are collected and therefore the $\sigma_g$ is significantly larger compared to that of the centerline at 10 cm HAB.

![Graph showing the evolution of the geometric standard deviation, $\sigma_g$, with height above the burner (HAB) for TiO$_2$ production rates of 0.5, 5.5, and 11 g/h in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).](image)

*Fig. 4.8: Evolution of the geometric standard deviation, $\sigma_g$, with height above the burner (HAB) for TiO$_2$ production rates of 0.5, 5.5, and 11 g/h in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).*
4.3.3. Product powder characteristics

Table 4.2 summarizes the characterization of the product powder made at 0.5, 5.5, and 11 g/h TiO$_2$ production rate using nitrogen adsorption (BET), XRD, TEM analysis, and SAXS. The $d_p$(BET) is within ±6% of the $d_p$(XRD) indicating that most of the titania particles are single crystals at all conditions. The rutile content increases with increasing TiO$_2$ production rate in agreement with Zhu and Pratsinis (1996). The flame temperature history of the particles that can affect the anatase to rutile phase transformation is relatively similar for the investigated flames (Fig. 4.3, Table 4.1) even though the visible flame height increased slightly, indicating longer residence times of the particles for larger TiO$_2$ production rates. The rutile phase is typically preferred at higher temperatures. However, Zhu and Pratsinis (1996) showed that the rutile content of the product powders made in diffusion flames was decreased with increasing the oxygen/Ti ratio, even though the measured maximum flame temperature was increased. It is possible that the steep cooling of these oxygen flames did not allow for the anatase to rutile transformation of the big particles while smaller ones were able to transfer to rutile.

For all powders the count mean diameter $d_{1,0}$ is the smallest, while $d_p$(BET) is between $d_{1,0}$ and the Sauter mean diameter, $d_{3,2}$. This is typical for unimodal (self-preserving) size distributions (Hinds, 1999). The $d_{ps}$(SAXS) is always 19-30% larger than $d_p$(BET) as shown in Table 4.2. The $d_{ps}$(SAXS) is close to the $d_{6,0}$, consistent with the dependence of light scattering to particle diameter (Hinds, 1999). Applying 1.5 kV/cm decreases the primary particle diameter by about 20% for all investigated TiO$_2$ production rates which is consistent with Vemury et al. (1997) and Kammler et al. (2001). The decrease is measured with all applied techniques (TEM, BET, XRD, and SAXS, Table 4.2). Increasing the electric field strength would lead to a more pronounced decrease in the average particle diameter as shown by Vemury and Pratsinis (1995), Vemury et al. (1997), Katzer et al. (2001) or Kammler et al. (2002).

The presence of the electric field increases the rutile content of the 0.5 and 5.5 g/h TiO$_2$ powders slightly from 9 and 8 to 11 wt. %, respectively, in agreement to earlier findings in a premixed flat flame (Kammler et al., 2002). The rutile content of
the powder made at 11 g/h TiO$_2$, however, is more than doubled in the presence of the electric field. It increases from 22 to 46 wt. %.

Table 4.2: Various measurements of product powder particle size for TiO$_2$ produced at rates of 0.5, 5.5, and 11 g/h in the presence and absence of external electric fields. Comparison of the BET average primary particle diameter [$d_p$(BET)], the mass weighted average primary particle diameter obtained by XRD [$d_p$(XRD)] along with the rutile content of the powders, the crystal size for the anatase and rutile particles obtained from the XRD spectra [$d_p$(Anatase)], and [$d_p$(Rutile)], the count mean particle diameter by TEM counting [$d_{1,0}$], the geometric standard deviation [$\sigma_g$], the Sauter mean particle diameter [$d_{3,2}$], its standard deviation [$\sigma_{3,2}$], the diameter of the sixth moment [$d_{6,0}$] all by TEM, and the average primary particle diameter of an equivalent sphere obtained by SAXS [$d_{ps}$(SAXS)].

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>EF</th>
<th>BET</th>
<th>XRD</th>
<th>TEM</th>
<th>SAXS</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/h</td>
<td>kV/cm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>18.8</td>
<td>20.0</td>
<td>9</td>
<td>21</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>16.2</td>
<td>17.1</td>
<td>11</td>
<td>18</td>
</tr>
<tr>
<td>5.5</td>
<td>0</td>
<td>47.6</td>
<td>45.7</td>
<td>8</td>
<td>47</td>
</tr>
<tr>
<td>5.5</td>
<td>1.5</td>
<td>38.8</td>
<td>37.8</td>
<td>11</td>
<td>39</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>54.4</td>
<td>54.7</td>
<td>22</td>
<td>56</td>
</tr>
<tr>
<td>11</td>
<td>1.5</td>
<td>44.3</td>
<td>50.3</td>
<td>48</td>
<td>45</td>
</tr>
</tbody>
</table>

Similar to the amplified decrease of the particle diameter with increasing electric field strength, more rutile is formed at higher electric field strengths (Kammler et al., 2002). As a result, Kammler et al. (2002) proposed that quenching (by the electric field) may have a significant influence on the anatase to rutile phase transformation. The electric field withdraws particles from the hot flame zone by attraction towards the electrodes and also reduces the flame temperature further downstream. Consequently, the particle residence time at high temperatures is decreased, and the time for oxygen to react with the hot particle surface is also decreased. Similarly, Wegner (2002) found that more rutile was formed in the product powder when a quench-nozzle was used, even though the residence time of the particles in the high flame temperature zone was decreased.
However, despite of the change in flame temperature and particle residence time by the electric field it should be noted that the ionic wind created by the electric field enhances the mixing and air entrainment, thus decreasing not only the flame temperature but increasing also the oxygen concentration. From studies in counterflow and co-flow diffusion burners by Rulison et al. (1996) and Zhu and Pratsinis (1996), respectively, it is known that rutile is formed preferentially under fuel rich conditions. The rutile phase is preferred in reducing atmospheres as shown by MacKenzie (1975), and this was attributed to the oxygen vacancies in the TiO₂ crystal. Therefore, experiments de-coupling the effect of temperature and oxygen availability (oxygen/Ti ratio) might help to improve the current understanding.

4.4. Concluding Remarks

In situ thermophoretic sampling (TS) is used in combination with Fourier transform infrared (FTIR) spectroscopy to follow the particle growth in electrically assisted flame aerosol reactors and to monitor concurrent flame temperatures. While for small particle concentrations (0.5 g/h TiO₂) the electric field did not change the particle morphology, at higher TiO₂ production rates (5.5 and 11 g/h TiO₂) the formation of large (soft) agglomerates is observed consistent with light scattering results of Katz and Hung (1990). Small angle X-ray scattering (SAXS) of the product powders further indicated that the electric field leads only to the formation of soft agglomerates (without sintering bridges), which explains also why Vemury and Pratsinis (1996) did not observe an increase of the silica agglomerate size with increasing electric fields strength, since the dispersion during preparation for TEM analysis most probably broke the soft agglomerates. This further stresses the importance of in situ sampling techniques such as TS without post-processing steps before analysis, such as dilution/quenching before entering a differential mobility analyzer (Katzer et al., 2001) or preparation of TEM from the product powder.

The electric field did neither change flame temperature nor the primary particle size close to the burner, but above the height where the electric field was applied the flame temperature is significantly lower in the presence of the electric field and this slowed down particle growth. The geometric standard deviation of the particles, σ₉.
increased sharply right above the electric field, indicating that the electric field broadens the size and residence time distribution probably by enhanced fluid motion (ionic wind). Further downstream, coagulation and sintering reduced the $\sigma_g$ again, before low temperatures and the mixing of particles arising from various streamlines widened the collected particle size distribution on the filter.

4.5. References


5. Current research state and future directions

Industrial laboratories led the research in synthesis of nanoparticles in the 20th century. This research was motivated by the industrial importance of carbon black and fumed silica, which was first made in the 1940s and marketed under the name Aerosil. Parallel to this, intensive research was carried out for flame synthesis of titania. Since the mid-1980s research in this field has been accelerated when, in industry, flame reactors were introduced in large scale manufacture of optical fiber preforms. Today most oxides and metals (e.g. Fe, Ni, Cu, Pd) have been produced as nanoparticles.

Nanoparticles are either single particles of less than 100 nm or the individual members (primary particles) of large agglomerates. In the last few years the scientific community has cherished the potential of nanoparticles. Today it is well understood that nanosize particles have distinctly different properties than meso – and macro size materials. The coordination number of atoms and thereby their physical and chemical properties are often different from that of corresponding atoms in the bulk, i.e. inside the particles. As a result, the particle melting point decreases, light absorption increases, and electromagnetic and other properties change, compared with those of the bulk. Consequently, a number of new products and applications emerge including new medicine and medical devices, cosmetics, highly efficient catalysts, advanced fuel cells, and self-cleaning surfaces.

Typically, nanoparticles are made by gas-phase and wet-chemical processes. The former are advantageous for inorganic (ceramic and metal) nanoparticle manufacture, since they do not involve the tedious steps, high liquid volumes and surfactants of wet chemistry processes. Gas-phase processes are classified further into gas-to-particle and droplet-to-particle conversion processes.

In the gas-to-particle route, nanoparticles are made by "building” them from individual molecules all the way up to the desired size. Particle formation is driven by chemical reaction from precursor gases or by rapid cooling of superheated vapors. The gas-phase technology is particularly challenging since powders are produced without feedback control of the high temperatures and extremely short process residence times (less than a second). This has the advantage of producing large amounts of product very fast, but also makes difficult the representative particle sampling, model development,
and process control. The early stage of particle formation is one of the areas that is ripe for better understanding, given the recent advances in computational chemistry and the availability of non-intrusive diagnostics such as infrared spectroscopy.

Controlling the particle temperature history is an important parameter affecting product particle characteristics. Reactant mixing can be critical in controlling process temperature and chemistry and, subsequently, product particle size and composition over a wide spectrum.

There is a reasonably good understanding of the role of additives for control of powder crystallinity through creation of interstitial or substitutional defects in the lattice. However, it is not that clear how ionic additives affect particle collision and coalescence and subsequently the extent of aggregation. Aggregate characterization has not been standardized, and various instrument readings are affected by particle structure, thus further obscuring the effect of process variables on product particle characteristics. Small angle X-ray scattering appears to be a promising technique for characterization of the degree of particle aggregation. Today, direct visual observation by electron microscopy still provides the best assessment of particle structure though it is a laborious, off-line process.

Despite the limited early use of systematic aerosol engineering in process design and operation, today the major manufacturers pay close attention to scientific developments as it is evidenced by their hiring and technical presentations. Aerosol engineers staff the research and development departments of major industries (Cabot, Degussa, Dupont, Lucent, Millenium, etc.) or even establish and lead medium size corporations (Inhale, Superior Micropowders, etc.) focusing on niche markets for particles of high value (catalysts for fuel cells, phosphors, etc.). In particular, advances in sintering models and their implementation in the general dynamic equation for aerosols allow quantitative description of particle size and morphology by detailed population balances or simplified models. The former are used to evaluate rigorously sintering mechanisms of silica and titania. The latter are interfaced with modern computational fluid dynamics either for ranking of aerosol reactor designs (e.g. Degussa) or for understanding the interaction between fundamental processes determining product particle characteristics in academia.

Large-scale synthesis of non-agglomerated nanoparticles is attractive for a number of applications including nanocomposites and medical materials. As laboratory
aerosol reactors yield new products, there is a great need for design relationships guiding reactor scale-up. Particle coating is another exciting scientific area for synthesis and characterization with many applications. Furthermore, the design of functional nanoparticles can only be successful when understanding the fundamental processes the particles are involved in catalysis for example.

Real-time diagnostics are needed for particle size, composition and morphology at high temperatures and concentrations. Here the differential mobility analyzer (DMA) would be a useful tool to implement. First, however, the sampling from the flame and the appropriate dilution system has to be developed and tested for high temperatures and especially for high concentrations.

The knowledge of the velocity profile in the flame will allow much more detailed particle dynamics simulations. Non-intrusive velocity measurements should be adopted for flame characterisation. Furthermore, computational dynamics program results could then be directly compared to the experimental results.

The dynamics of agglomerate formation could be identified and measured non-intrusively by doing small-angle X-ray scattering (SAXS) directly in the flame. These diagnostics will allow tracking the particles at different streamlines in combination with thermophoretic sampling, thus, creating an experimental base for detailed multidimensional modelling of the particle growth. Implementing \textit{in situ} SAXS will be especially challenging in diffusion flames.

It would be also challenging but useful to establish coherent anti-Stokes Raman scattering (CARS) in particle-laden flames. The time resolved temperature measurements would give insight to the dynamics of flame temperature and entrainment of cold gases into the flame edges as well as in the upper part of the flame. These measurements could help to study the effect of flame temperature fluctuations on particle growth. In addition, CARS has also the appropriate spatial resolution to measure radial flame temperature profiles in diffusion flames, where very sharp temperature gradients (up to 400 K/mm) are present. These detailed temperature measurements might be necessary for successfully describing the particle formation in diffusion flames.

Rapid algorithms for simultaneous coagulation and condensation are required in computer models of fluid – particle dynamics so they can be used in aerosol reactor design, operator training, environmental compliance, and process operation. It will be particularly challenging to model the effect of external electric fields on particle
formation (including the change in the flame temperature profile as well as the charging) and also implementing the enhanced fluid motion created by the ionic wind.

Gas-phase technology produces some of the cheapest ceramic powders made today and it has high potential for synthesis of nanoparticles. Having a low cost starting material (nanoparticles) will certainly accelerate the development of nanotechnology in our market-driven society.
Appendix A:

A. Silica-carbon nanoparticles in a turbulent hydrogen-air flame reactor: Effect of air entrainment
d

Abstract

The control of particle characteristics of flame-made composite silica-carbon nanostructured powders is investigated at high production rates (300 g/h) in a turbulent hydrogen-air diffusion flame aerosol reactor. These particles are made from hexamethyl-disiloxane (HMDSO) and are collected continuously in a 2.5 m high baghouse filter unit, which is cleaned periodically by air-pressure shocks. The effect of air entrainment using a steel chimney encasing the flame is investigated experimentally, while computational fluid dynamic calculations facilitate the theoretical understanding. Nitrogen adsorption (BET) and thermogravimetric analysis (TGA) coupled with a mass spectrometer (MS) and a CO2-analyzer were employed to characterize the product powders.

A.1. Introduction

Flame aerosol technology is used for large scale manufacture of commodities such as pigmentary titania, carbon black, fumed silica and alumina, lightguide preforms, nuclear fuel pellets in diffusion or premixed flames (Ulrich, 1984). Silica-carbon nanoparticles are important here as fillers (e.g. ecoblacks) for manufacture of low rolling resistance tires that can double the life of conventional counterparts. Recent reviews have been written for flame manufacture of silica particles (Pratsinis, 1998) and carbon black (Donnet et al., 1993). Industrial laboratories led the research in this field which was motivated from the commercial importance of carbon black in the late 19th century and for fumed silica which

\[ This\ chapter\ was\ published\ in\ the\ book\ of\ abstracts\ of\ the\ 3rd\ Joint\ ESF-NSF\ Symposium\ on\ "Nano-particles:\ Applications\ in\ materials\ science\ and\ environmental\ science\ and\ engineering"\ F.Otten, H. Fissan, J. Schooman, D.H.Y. Pui, P. Biswas eds (2000) pp 3-10.\]
was first marketed under the name Aerosil (Kloepfer, 1942). Later on, academic research was focused on these materials (Ulrich, 1971; Formenti et al., 1972).

The effect of basic aerosol reactor design on particle characteristics has been studied theoretically (Pratsinis et al., 1986). After evaluation of the type of aerosol reactor, the next step is optimization of this reactor to achieve the required performance. Therefore, experimental studies along with the development of models governing the experimental geometries, process conditions, and particle formation and growth processes are needed. Also commercially available codes can be helpful to implement as shown by Schild et al. (1999), who combined commercially available fluid mechanics codes with aerosol dynamic models (Kruis et al., 1993) for premixed aerosol reactors for nanoparticle production. These models have predicted the specific surface area of industrial reactor units within 3% (Gutsch et al., 1997). Recent experimental studies focused on scale-up of production rates of flame made powders (Kammler and Pratsinis, 1999; Kammler et al., 2001). To improve flame stability and also to perform cleaner particle processing, the flame was encased with a chimney (Kammler et al., 2001) as applied in many former studies (e.g. Ulrich and Riehl, 1982). Here, basic calculations concerning a non-burning jet as well as commercially available computational fluid dynamics software is used to design an encasing for the flame and to improve the understanding of the effect of secondary air entrainment and oxidant concentration of the entrained air on product powder characteristics. The diameter of the chimney is designed to be large enough not to influence the flame velocity profile. This was verified calculating the radial velocity profile of a free air jet of the same flow rates (Bejan, 1984).

**A.2. Experimental**

The experimental set-up is described only briefly here (Kammler et al., 2001). Nitrogen gas (PanGas, CH, 99.999%) is saturated with hexamethyldisiloxane (HMDSO, Fluka Chemie AG, 99%) in a temperature controlled bubble flask is and then delivered into the aerosol reactor. The tubing and the burner are heated up to 40 K higher than the HMDSO temperature to avoid condensation. The gases are metered by calibrated mass
flow controllers (Hastings Inc., HFC 203) and rotameters (Vögtlin Instruments AG). The diffusion burner consists of four concentric stainless steel tubes of 0.5 mm wall thickness. The inner diameter of the center (first) tube is 6 mm, and the spacing between the following three tubes is 1, 0.5 and 3.5 mm, respectively. The HMDSO-laden nitrogen stream (10 L/min) is fed through the center tube, hydrogen (12.2 L/min in total) is supplied through the second and third tube, while air (69 to 154 L/min) is fed through the fourth tube. The production rate of nanoparticles in the reactor described here is 300 g/h. The constant mass flow rate of HMDSO is double-checked weighing the HMDSO flask before and after each experiment. The effect of air entrainment is studied with and without a 350 mm diameter steel chimney with a Plexiglas window encasing the flame. The required safety concerns regarding the hydrogen handling in pilot-scale reactors are carefully addressed (Kammler et al., 2001).

Product powders are collected in a commercial „Jet filter“ (Friedli AG, FRR 4/1,6), with four PTFE (polytetrafluoroethylene, Teflon) coated Nomex baghouse filters (total surface area: 2.2 m²) which are cleaned periodically by air pressure shocks.

The BET equivalent specific surface area of the powder is determined from nitrogen adsorption isotherm in the relative pressure range of 0.05 to 0.25 at 77.3 K with a Gemini III 2375 (Micromeritics Instruments Corp.). Before the adsorption, the samples are degassed (Flow prep 060, Micromeritics Inst. Corp.) under nitrogen atmosphere at 150°C for two hours, to remove water that is bound to the particle surface from the air moisture.

Thermogravimetric analysis (TGA) coupled with mass spectroscopy (MS) is used to determine the carbon fraction of the product powders. The powders are heated up to 800°C in nitrogen atmosphere, and then the atmosphere is switched to oxygen. The carbon content is attributed to the weight reduction from 800 to 1000°C in oxygen atmosphere as the carbon oxidized (Kammler et al., 2001).
A.3. Results and discussion

The effect of secondary (side) entrainment is investigated theoretically first. Therefore, the aerosol reactor was simplified to an axissymmetric air jet of 1000°C issuing the atmosphere with or without chimney. Using the geometric properties of the current set-up, a grid was created with FLUENT 5.2. The mass flow through the jet (19 mm inner diameter) was set to $2.042 \times 10^{-3}$ kg/s corresponding to 100 L/min at 25°C, and was assumed to be incompressible using the ideal gas law and neglecting gravity. The lower plate temperature was set to 50°C, while the wall-temperature of the chimney is set to 150°C. These temperatures are obtained with thermocouples during long term experiments, operating the unit continuously for up to 5 h.

![Temperature and Velocity Contours](image)

Fig. A.1: Contour plots of static temperature (a) and velocity (b) of the encased jet calculated with FLUENT 5.2.

Figure A.1 shows the contours of temperature (a) and velocity (b) of the encased jet. Recirculation zones of the off gases with very small velocities are only evident when
the flame is encased as shown in Fig. A.1b, thus, leading to a reduction in oxygen concentration of the re-entrained air in the chimney.

The recirculation of the off-gases is also indicated by the temperature contours (Fig. A.1a) as the temperature broadens with increasing height. Setting the lower plate and chimney temperature to 25°C, FLUENT calculations indicate more pronounced recirculation of the off gases within the chimney, with also higher velocities. This, however, is also observed in the experiments, when the chimney and filter system were not heated up with a pure hydrogen flame before the experiment was started. There, the turbulent diffusion flame is unsteady and much shorter and opened up flower-like, until the chimney has reached stable temperature. After that point, however, the diffusion flame burned very stable.

Experimentally, silica-carbon powders made in the absence of the chimney (Fig. A.2a) are compared to powders where the chimney is in place during particle production (Fig. A.2b). Figure A.2b shows a schematic of the burner flows and the chimney geometry as well as the effect of air entrainment (arrows).

![Schematic of the burner flows with (a) and without (b) secondary (side) air entrainment in the flame (arrows).](image-url)
Figure A.3 shows the specific surface area of SiO$_2$ particles at production rates of 300 g/h as a function of the air flow rate for hydrogen flow rates of 12.2 L/min. The specific surface area of the product powders increases with increasing air flow rate for both configurations. Without the chimney housing the flame (circles), thus, with secondary (side) air entrainment into the flame, the specific surface area of the particles increased from 93 m$^2$/g to 153 m$^2$/g for increasing the air flow rate from 69 L/min to 154 L/min. With the chimney (triangles), the specific surface area increased from 108 m$^2$/g to 158 m$^2$/g over the same air flow rate range.

Increasing the air flow rate leads to two competing processes. On the one hand, higher air flow increases the oxidant flow to the reaction zone and reduces the flame height as the fuel is consumed faster. This leads to a higher flame temperature resulting in faster growth and higher sintering rates and therefore to a decrease in the specific surface area. On the other hand, the increase of the air flow rate also increases the amount of inert gas (nitrogen) delivered to the flame which would otherwise increase the flame height and lower the flame temperature.

**Fig. A.3:** The specific surface area of SiO$_2$-C powders as a function of inlet air flow rate with (circles) and without (triangles) secondary (side) air entrainment. The production rate is 300 g/h using hydrogen flow rates of 12.2 L/min.

**Fig. A.4:** The carbon content of SiO$_2$-C powders as a function of inlet air flow rate with (circles) and without (triangles) secondary (side) air entrainment. The production rate is 300 g/h using hydrogen flow rates of 12.2 L/min.
At the same time turbulence of the jet increases when the air flow rate is increased (the overall $Re_D$ number increases from e.g. 6000 to 14000 for the current case), accelerating combustion, which makes the flame shorter and more brushy (Glassman, 1996).

The lower flame temperature decreases the particle sintering rate, and the residence time is shorter due to the decrease in flame height and faster gas velocities. Both effects lead to smaller particles, and thus, larger specific surface area particles are formed. Clearly the intensity of the turbulence dominates since increasing the air flow rate increases the specific surface area (Fig. A.3). This is in agreement with studies for fumed silica at low powder production rates (Zhu and Pratsinis, 1997; Briesen et al., 1998); these authors reported that the flame temperature first increased with increasing air flow rate and then decreased again after the delivered amount of oxidant was overstoichiometric. The specific surface area of fumed silica made from HMDSO increased continuously from 170 to 230 m²/g by increasing the air flow from 2.5 to 5.5 L/min (Briesen et al., 1998). The specific surface area is roughly 20 % larger with chimney (thus, without secondary air entrainment into the flame) for air flow rates lower than 120 L/min. Withdrawing the chimney, extra amount of oxygen is sucked into the flame by entrained secondary air leading to faster fuel consumption and therefore to higher flame temperature. As a result, the sintering rate increases which leads to larger particles and therefore to a decrease of the specific surface area. The increase in specific surface area with the chimney is attributed to the decrease of the oxygen content of the entrained gases due to recirculation. At high excess air flow rates (air number 1.7 – 1.9), no differences in the specific surface area are observed. This is expected as excess amounts of air are not consumed, thus, reduction in the oxygen content of the recirculating gases does not occur.

Figure A.4 shows the carbon content of SiO₂ powders made at 300 g/h as a function of air flow rate without (triangles) and with (circles) secondary (side) air entrainment in the flame. Without air entrainment, the carbon content of the powders ranges between 0.3 and 0.4 wt. % for all investigated air flow rates; no significant trend in the amount of the carbon in the powders is observed. Higher carbon contents, however, are measured when the chimney is withdrawn, thus, when secondary ambient air is entrained into the flame. For air flow rates less than 137 L/min the carbon content ranges between 0.48 and 0.55 wt. %, up to 40% higher than in the absence of secondary air entrainment.
(side) air entrainment. Non-inert additives such as oxygen increase the sooting tendency substantially when trace amounts are added to the fuel (Schug et al., 1980) in agreement to the present results. The extra entrained air (using no chimney) increases the oxygen concentration in the flame and, therefore, increases the flame temperature resulting in higher carbon concentration of the produced silica powders. Angrill et al. (1999) applied Rayleigh scattering and laser induced incandescence (LII)-signal in combination with extinction (RAYLIX) on a turbulent acetylene flame and observed that with a decrease in oxygen concentration the soot formation occurs later and therefore the maximum soot concentration is lower than in flames with more oxygen in agreement with the present results. Both studies, are in contradiction to Gollahalli (1997), who investigated elliptical and circular nozzle exits and observed that the dilution effect of increased air entrainment is overshadowed by enhanced soot combustion which results in higher flame temperature for flames with larger oxygen availability.

At high excess air flow rates (137 and 154 L/min), however, the effect of air entrainment vanishes both for the specific surface area (Fig. A.3) and the carbon content (Fig. A.4). This is attributed to the high excess air flow rates which limit the effect of the reduction in oxygen concentration due to recirculation of the off gases. This may indicate that at high production rates that are typically encountered in industry, air entrainment will not affect the characteristics of the product powder.

A.4. Conclusions

Flame technology is a versatile process for economic manufacture of a wide spectrum of oxide powders with closely controlled characteristics. Here, the synthesis of silica-carbon composite nanoparticles was investigated in a turbulent air-hydrogen flame. Computational fluid dynamic calculations showed the detailed temperature and velocity profiles in the presence and absence of secondary (side) air entrainment. Experimental investigation showed that this effect is most important at low gas flow rates decreasing the specific surface area by 20% and increasing the carbon content of the product up to 40%.
A.5. References


Appendix B:

**B. Tomographic reconstruction of line-of-sight FTIR data**

**B.1. Background**

This tomographic reconstruction method is based on the methods of Minerbo and Levy (1969), and Freeman and Katz (1960).

**B.2. Objective**

Various slices of transmittance and radiance through a cylindrical flame are measured by Fourier transform infrared (FTIR) spectroscopy at a certain height above the burner (HAB). These slices represent the transmittance $\tau(y)$ and radiance $\varepsilon(y)$, where $y$ is the lateral distance from the center of the flame. The goal of this reconstruction method, however, is to provide the radial profiles of the transmittance $\tau(r)$ and radiance $\varepsilon(r)$, from the lateral profiles using tomographic reconstruction. As the flame is cylindrical, cylindrical symmetry is assumed in the present calculations, but a full reconstruction is also possible taking enough lateral slices as it is done in CAT scan images of human bodies.

**B.3. Reconstruction technique**

**B.3.1. Transmittance reconstruction**

The reconstruction only works with linear systems, so the transmittance $\tau$ has to be converted to its Beer’s law equivalent:

$$\tau = \exp(-\alpha x) \quad (B.1)$$

$$A = -\ln \tau(x) = \alpha x \quad (B.2)$$
where \( \alpha \) is the absorption coefficient \((\text{cm}^{-1})\), and \( x \) the path length along the IR beam \((\text{cm})\), and \( A \) is the natural log absorbance. The above expression assumes that \( \alpha \) is constant across the distance \( x \), but in a flame this is not true. Therefore, the above expression has to be replaced with

\[
A = \int_{x=a}^{b} \alpha(x) \, dx \quad \text{(B.3)}
\]

Now the transmittance slices \( \tau(y) \) can be converted to \( A(y) \) slices. In the cylindrical flame, however, the challenge is to determine the radial profile of \( \alpha(r) \), especially when only \( A \) is known at various slices \( y \). Using the equation above, \( A(y) \) can be calculated by

\[
A(y) = \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} \alpha(r) \, dx \quad \text{(B.4)}
\]

where \( r \) is the radial position, \( R \) the radius of the flame, and the limits of the integration take into account the geometry of the flame. Since \( r \) is related to \( x \) and \( y \) via the equation \( r^2 = x^2 + y^2 \), determining \( A(y) \) from a known \( \alpha(r) \) is straightforward, but the reverse process is not.

The above equation is the classic statement of Abel’s problem (see Minerbo and Levy, 1969), and it is solved with tomographic reconstruction techniques. There are a large number of reconstruction methods with new methods being generated each year. One of the common features of tomographic reconstruction is that the noise in the data \( A(y) \) is amplified in the output \( \alpha(r) \). In the present calculations the orthogonal polynomial method is used because it is quite flexible, and it does not magnify the noise as much as other methods (Minerbo and Levy, 1969).

In the orthogonal polynomial method, a polynomial is fitted in \( y \) to the various values of \( A(y) \). Thereby, the number of discrete values that are used is free, and in this case \( y_1 = y_1, y_2, y_3, \ldots, y_{25} \) are chosen, where \( y_1 = -12 \text{ mm} \), \( y_{13} = 0 \text{ mm} \), and \( y_{25} = +12 \text{ mm} \). Here, twenty-five values are chosen, which are spaced equally, but that is not a requirement of the method. At each of these slices, there is a corresponding measured absorption \( A(y_i) \), twenty-five altogether. Then, a polynomial is fitted in \( y^2 \) to these \( A(y_i) \). Specifically, the polynomial has the form
The polynomial model has 6 coefficients \(a-f\), and therefore uses 6 orthogonal polynomials \(p_m(y)\) where \(m = 0\) to 5. There are no odd orders because \(A(y)\) must be an even function. Orthogonal polynomials are used as the orthogonal polynomials \(p_m(y)\) \((m = 0-5)\) are easy to generate once the values of \(y_i\) are chosen. Furthermore, generating the best fit coefficients \(a_m\) for each of these \(p_m\) involves only linear algebra (no iterating), and the quality of the fit to \(A(y_i)\) can be determined statistically. Experimentally, only 5 polynomials are significant. In the calculation, however, 6 polynomials are used and it can be shown by a \(t\)-test that the 6th coefficient \((m = 5)\) is statistically insignificant.

Since the \(p_m\) are even order polynomials and their coefficients \(a_m\) are known, it is straightforward to perform an analytical Abel reconstruction. The analytical reconstruction of each \(p_m(y)\) is \(q_m(r)\), and each \(q_m(r)\) can be calculated a priori before performing the least squares fit to \(A(y_i)\). Once the \(a_m\) coefficients are known, each \(a_m\) is used to form the reconstructed \(\alpha(r)\) from \(\alpha(r) = \frac{1}{a} \sum_{m=0}^{5} a_m \cdot q_m(r)\) where \(a = \) the flame radius = 12 mm. More details can be found in Minerbo and Levy (1969) and in the computer program \textit{tomog25.ab}.

### B.3.2. Radiance reconstruction

The reconstruction of the radiance data is a bit more complicated because for the radiance self-absorption has to be taken into account. This means that the IR-light emitted at the center of the flame is partially absorbed as it travels out from the center. Consequently, the observed radiance by the emission detector is less than it should be, and consequently reconstructing the observed data as measured is incorrect. Freeman and Katz (1960), however, have developed a way to overcome this problem.

The radiance equation for a cylindrical flame is given in Eq. B.6:
\[ J(y) = \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot \exp \left( -\int_{\eta=x}^{\eta=+\sqrt{R^2-y^2}} \alpha(\rho) d\eta \right) dx \]  

(B.6)

where \( J(y) \) is the measured radiance at the lateral slice \( y \), \( B(r) \) is the actual radiance at the radial position \( r \), \( \alpha(\rho) \) is the absorption coefficient evaluated at the radial position \( \rho \) (where \( \rho^2 = \eta^2 + y^2 \)), and \( \eta \) is a dummy variable. The exponential term takes the attenuation of the radiance \( B(r) \) into account. The outer integral, however, cannot be solved without knowing the analytical expression for the inner integral (since its lower limit depends on \( x \)). Furthermore, the equation does not have the Abel form (Eq. B.4). Consequently, solving Eq. B.6 requires knowing \( \alpha(r) \) and integrating numerically.

An analytical approximation is possible if the magnitude of \( \int \alpha(\rho) d\eta \) is small.

Please note that Eq. B.6 is written assuming that the light starts at some \( x \) and goes towards the outer edge \((R^2 - y^2)^{1/2}\). But there is another radiance going the opposite direction: from \( x \) to the other outer edge \(-(R^2 - y^2)^{1/2}\). This is called \( \tilde{J}(y) \), and has the form

\[ \tilde{J}(y) = \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot \exp \left( -\int_{\eta=-\sqrt{R^2-y^2}}^{\eta=x} \alpha(\rho) d\eta \right) dx \]  

(B.7)

As \( J(y) \) has to be equal to \( \tilde{J}(y) \) by symmetry, and therefore \( 2J(y) = [J(y) + \tilde{J}(y)] \). For small absorption values the exponential term in both Eqs B.6 and B.7 can be simplified using the Taylor series expansion for \( \exp(-x) \approx 1 - x + \frac{1}{2} x^2 + \ldots \):

\[ J(y) \approx \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot \left( 1 - \int_{\eta=x}^{\eta=+\sqrt{R^2-y^2}} \alpha(\rho) d\eta + \cdots \right) dx \]  

(B.8)

\[ \tilde{J}(y) \approx \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot \left( 1 - \int_{\eta=-\sqrt{R^2-y^2}}^{\eta=x} \alpha(\rho) d\eta + \cdots \right) dx \]
Adding these two terms together and ignoring the second order terms, this leads to

\[
2 J(y) = J(y) + \bar{J}(y) = \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \left( 2 - \int_{\eta=-\sqrt{R^2-y^2}}^{\eta=+\sqrt{R^2-y^2}} \alpha(\rho) d\eta \right) dx
\]  

(B.9)

Now the inner integral no longer contains \( x \), so the quantity in parentheses can be pulled out of the overall integral and the expression can be evaluated:

\[
2 J(y) = J(y) + \bar{J}(y) = \left( 2 - \int_{\eta=-\sqrt{R^2-y^2}}^{\eta=+\sqrt{R^2-y^2}} \alpha(r) dr \right) \cdot \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot dx
\]  

(B.10)

(Note, that there is a change in notation for the \( \alpha \) integral). Similarly, using the small argument approximation for the transmittance (see Eq. B.3), this leads to

\[
\tau(y) = \exp \left( - \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} \alpha(r) dr \right) \approx 1 - \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} \alpha(r) dr
\]  

(B.11)

As long as the quantity \( \int \alpha(\rho) d\eta \) is less than \( \sim 0.2 \), Eq. (B.11) can be written as

\[
2J(y) = J(y) + \bar{J}(y) = \left( 2 - [1 - \tau(y)] \right) \cdot \int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot dx
\]  

(B.12)

or

\[
\int_{x=-\sqrt{R^2-y^2}}^{x=+\sqrt{R^2-y^2}} B(r) \cdot dx = \frac{J(y)}{1 - \frac{1}{2} \left( 1 - \tau(y) \right)} \equiv J_{corr}(y)
\]  

(B.13)

Note, that the left hand side of the equation has the Abel form, and therefore \( J_{corr}(y) \) can be reconstructed in order to obtain the local radiance \( B(r) \) directly.
Experimentally, \( \int \alpha(\rho) d\eta > 0.2 \) is found for some flames, and therefore Eq. B.13 is not accurate at these less “high” absorption levels (transmittance less than 80%). The primary source of the error is the approximation from Eq. B.11:

\[
\int_{x=-\sqrt{y^2-z^2}}^{x=+\sqrt{y^2-z^2}} \alpha(r) dx \approx 1 - \tau(y)
\]

To overcome this, the exact value for the \( \alpha \) integral is used:

\[
\int_{x=-\sqrt{y^2-z^2}}^{x=+\sqrt{y^2-z^2}} \alpha(r) dx = -\ln[\tau(y)] = A(y).
\]

Thus, a better way to correct \( J(y) \) is:

\[
\int_{x=-\sqrt{y^2-z^2}}^{x=+\sqrt{y^2-z^2}} B(r) \cdot dx = \frac{J(y)}{1 - \frac{1}{2} \left( A(y) \right)} \equiv J_{\text{corr}}(y) \tag{B.14}
\]

which was also used in the present studies (see e.g. program \textit{tomog25.ab}).

To verify this modification, \( J(y) \) was corrected using Eq. B.14 and \( J_{\text{corr}}(y) \) and \( \tau(y) \) were tomographically reconstructed to assemble a prediction for the measured radiance along the centerline \( (J(0)) \). Then the predicted \( J(0) \) was compared to the measured \( J(0) \). The program for performing this calculation is \textit{chktomog.ab}. The calculation is as follows:

\[
J_{\text{pred}}(0) = B_{12} \cdot \tau_{11} \cdot \tau_{10} \cdots \tau_0 \cdots \tau_{11} \cdot \tau_{12} \\
+ B_{11} \cdot \tau_{10} \cdot \tau_9 \cdots \tau_0 \cdots \tau_{11} \cdot \tau_{12} \\
\cdots \\
+ B_1 \cdot \tau_0 \cdot \tau_{1} \cdots \tau_{11} \cdot \tau_{12} \\
+ B_0 \cdot \tau_{1} \cdot \tau_{2} \cdots \tau_{11} \cdot \tau_{12}
\]
\[ + B_1 \cdot \tau_2 \cdot \tau_3 \cdot \cdots \cdot \tau_{11} \cdot \tau_{12} \]
\[ + B_{11} \cdot \tau_{12} \]
\[ + B_{12} \]

where \( B \) is the reconstructed (local) radiance, \( \tau \) the reconstructed (local) transmittance, and the subscripts refer to radial positions \( r \). It was shown experimentally, that using the \( A(y) = -\ln[\tau(y)] \) in Eq. B.14 works quite well at the level of \( A(y) \) of 0.3 – 0.4 (and perhaps beyond).

**B.3.3. Experimental tomographic reconstruction procedure**

Based on the theory discussed above, the computer programs, *flame25.ab, selfab25.ab, poly25.ab, tomog25.ab, tomog25t.ab, chktom25.ab* were written by Prof. P.W. Morrison. In a first step, the radial measured line-of-sight transmittance spectra have to be loaded (-12 … 0 … +12) and the program *flame25.ab* converts them to absorbance. Then, the radial measured line-of-sight radiance spectra have to be loaded (-12 … 0 … +12), and the program *selfab25.ab* manipulates the spectra to account for the self-absorption of the flame. Then these corrected radiance spectra can be tomographically reconstructed using the program *tomog25.ab; tomog25t.ab* reconstructs the measured line-of-sight transmittance spectra. After this, the program *chktom25.ab* should be used to evaluate the level of accuracy of the performed reconstruction. Here a radiance spectrum is created from the tomographic reconstructed spectra that predicts the measured radiance spectrum at the centerline and has to be compared to the measured radiance spectrum (not the one that is corrected for self-absorption).

The tomographic reconstructed radiance and transmittance spectra can then be analysed using the programs for flame temperature determination (such as *normrad.ab* and *etanalys.ab*).
B.4. References


Appendix C:

C. Thermophoretic sampling

Abstract

In this chapter the thermophoretic sampling technique is described. Basic theoretical background is provided along with a detailed description of the experimental sampling procedure and detailed drawings of the parts of the thermophoretic sampler and the electronic control box.

C.1. Introduction

Thermophoretic deposition is driven by a temperature gradient in the vicinity of a cold surface inside a flow field of a particle-laden hot gas. This phenomenon is called thermophoresis and can be used to study particle growth in flames. The cold surface can be, for example, a TEM grid that is rapidly inserted into the flame. This technique was first employed by George et al. (1973) and further developed by Dobbins and Megaridis (1987). The exposure time has to be long enough to capture a significant sample, but short enough to maintain a cold surface and the thermophoretic gradient for particle transport. Short residence times prevent also excessive deposition that hinders particle counting by microscopy. Typical exposure times of the grid in the flame are in the order of 30-130 ms, and Dobbins and Megaridis (1987) showed experimentally that at these residence times the probe surface remains cold by inserting temperature-indicating liquids. Thus, the temperature gradient is present during the whole course of sampling. The cold surface also freezes the heterogeneous reactions of the particles and particle growth (Dobbins and Megaridis, 1987) and therefore prevents changes in particle morphology after the particles have impacted on the cold surface. Thermophoresis is not particle size selective for particles smaller than 500 nm.

This refined thermophoretic sampling technique became quite popular lately, studying especially the particle growth of soot and oxide particles in flames. Soot
formation was investigated for example in premixed flames (Cai et al., 1993; Xu et al., 1997; Xu et al., 1998) as well as in diffusion flames (Dobbins and Megaridis, 1987; Megaridis and Dobbins, 1988; Köylü et al., 1997) using various precursors. The effect of additives on soot formation (Zhang and Megaridis, 1996) or the effect of flame flickering (Zhang and Megaridis, 1998) was also studied. The growth of TiO$_2$ particles was monitored by thermophoretic sampling (Pratsinis et al., 2000; Arabi-Katbi et al., 2001; Kammler et al., 2001; Lee et al., 2001) as well as the formation of SiO$_2$ (Cho et al., 1998; Choi et al., 1999; Cho and Choi, 2000) and Al$_2$O$_3$ (Xing et al., 1999) to name a few.

C.2. Theory

The local drift velocity $u_T$ of the particles to the cold surface can be described in terms of a particle thermophoretic diffusivity $D_T$, the local gas temperature $T_g$ and the temperature gradient $\text{grad}(T_g)$ (Gomez and Rosner, 1993).

$$u_T = \frac{K_T \cdot v_g \cdot \left(-\frac{\text{grad}(T_g)}{T_g}\right)}{D_T}$$

(C.1)

where $D_T$ is the product of the thermophoretic velocity coefficient, $K_T$, and the kinematic viscosity, $v_g$, of the carrier gas at $T_g$. The $D_T$ can be derived from kinetic theory for an isolated single spherical particle in the free molecular regime (mean free path of the gas molecules, $\lambda_g >> 1$) (Waldmann and Schmitt, 1966), as

$$D_T = \frac{3 \cdot v_g}{4 \left(1 + (\pi \cdot \alpha_m / 8)\right)}$$

(C.2)

where $\alpha_m$ is the gas/surface tangential momentum accommodation coefficient ($\alpha \sim 0.9$ (Friedlander, 2000); $\alpha \sim 1$ (Gomez and Rosner, 1993)).

Talbot et al. (1980) report values for $K_T$ of 0.30, 0.51, 0.54, and 0.55 for Knudsen numbers ($\text{Kn} = 2 \cdot \lambda_g / d_p$) of 0.1, 1, 10, and 100, respectively. They can be
derived from the Brock equation for \( \lambda_g/d_p < 0.1 \) (Talbot et al., 1980; Friedlander, 2000). For calculation of the Knudsen number, it should be considered that \( \lambda_g \) is directly proportional to temperature. Taking into account that the thermophoretic velocity coefficient, \( K_T \), does not change significantly for Knudsen numbers of 10 and 100 (particle diameters of 90 and 9 nm, respectively, at \( T_g = 2000 \) K), this indicates that the error in the calculation of the drift velocity is relatively small when being close to the transition regime. For more details, describing thermophoresis in the transition and in the continuum regime, the reader is referred to the book of Hinds (1999).

There are two characteristic time scales that should be considered during the thermophoretic sampling. One is the exposure time for 10% coverage of the TEM grid surface \( \tau_e \). It can be calculated by (Dobbins and Megaridis, 1987)

\[
\tau_e = \frac{0.4}{\pi \cdot J_w \cdot d_p^2}
\]  

(C.3)

where \( J_w \) is the particle flux to the cold surface that can be expressed as

\[
J_w = \frac{6 \cdot K_T \cdot V_{g,e} \cdot f_v,e}{\pi \cdot d_p^3 \cdot \delta_t} \cdot \left( \frac{T_w}{T_g} \right)^{\kappa} \cdot \left( 1 - \frac{T_w}{T_g} \right).
\]  

(C.4)

Here, \( V_{g,e} \) is the kinematic viscosity of the hot gas mixture at the outer edge of the thermal boundary layer (2.81 cm²/s for air at \( T_g \)), \( f_v,e \) is the particle volume fraction at the outer edge of the thermal boundary layer (\( \sim 10^{-6} - 10^{-7} \) cm³/cm³ for the present flames), \( d_p \) is the particle diameter, \( T_w \) is the gas temperature at the wall (\( \sim 400 \) K), \( T_g \) is the gas carrier temperature (\( \sim 2000 \) K), \( \kappa \sim 0.84 \) is the exponent appearing in the dependence of the gas mixture thermal conductivity on temperature (Dobbins and Megaridis, 1987), and \( \delta_t \) is the thermal boundary layer thickness (\( \sim 0.06 \) cm from heat transfer analysis (Dobbins and Megaridis, 1987)).

The other characteristic time scale is the quench time, \( \tau_q \), that describes the required time for a particle to travel from the hot gas environment to the cold surface (Dobbins and Megaridis, 1987).
\[ \tau_q = \frac{T_u \cdot \delta^2}{K_r \cdot \nu_{g,a} \cdot (T_g - T_w)} \]  

(C.5)

\(\nu_{g,a}\) is the kinematic viscosity of the gas at the average temperature \(T_a\) of the thermal boundary layer (e.g. 1.26 cm\(^2\)/s for air at \(T_a = 1040\) K). Furthermore, the disturbance time, \(\tau_d\), is of interest, which is defined as the time required for the flow around the probe after its insertion to achieve velocity values equal to 90% of the values corresponding to steady flow conditions (Megaridis, 1987). Megaridis (1987) calculated a value of 3.5 ms assuming instantaneous insertion of the probe in the flame environment. He suggested that the effect of transient disturbance introduced by the motion of the probe to the flow field around it should be very low, taking into account that the residence time of the probe in the flame is in the order of 50 ms.

### C.3. Thermophoretic sampling (TS) procedure

Figure C.1 shows a schematic of the thermophoretic sampling system that withdraws representative samples of particles from the flame at different HABs. The sampler (Figs C.1 and C.2) is designed according to Megaridis (1987) and moves a TEM grid with maximum speed to a precisely defined position in the flame. A controller varies the residence time of the TEM grid inside the flame (typically 50 ms). The residence time of the TEM grid at the flame center as well its traveling time was recorded and calibrated with a high-speed digital camera (Kodak Ektapro, Model 4540) taking 2250 frames/s.

![Fig. C.1: Schematic of the thermophoretic sampler.](image-url)
Carbon type B copper TEM grids (200 mesh, Pelco) are used, and they are secured between two stainless steel sheets (0.125 mm x 3 mm x 30 mm) (1) that are perforated at one end (2 mm diameter hole) to expose the grid to the flame. This TEM grid-holder (1) is screwed onto the end of a moving rod (3), which is connected (9) to a double acting pneumatic cylinder (10, Bimba, EM-16050-UC, 16 mm diameter, 50 mm stroke) driven by a pneumatic 5/2 valve (11, SMC Pneumatic AG) using 5 bar absolute pressure. The straight movement of rod is assured with a guide plate (8).

![Fig. C.2: Photograph of the thermophoretic sampler.](image)

Only the grid-holder with the TEM grid (1) travels through a slotted shield (2) as shown in Fig. C.3 (Megaridis, 1987). The shield protects the flame from any disturbances caused by the rapid movement of the rod (3). It is fixed on the front screw (4) and can therefore be taken off easily for changing the TEM grid in the grid holder (1) without aligning the shield each time. The slot has a diameter of 0.9 mm (Fig. C.3).

![Fig. C.3: Magnification of the front part of the thermophoretic sampler with the TEM gridholder (1), the protecting shield (2), the moving rod (3), and the front screw (4).](image)
After inserting the grid into the grid holder and mounting it on the moving rod, the shield has to be aligned. Here, it has to be always assured that the grid holder \((I)\) passes through the slotted shield \((2)\) without touching. Then, the sampler which is fixed on the backplate \(B\) \((5)\) is moved on the fixed backplate \(A\) \((6)\) to the sampling position and locked there using the fast lock set screws \((7)\). The shield \((2)\) is typically positioned 4-5 mm next to the luminous flame envelope (Megaridis, 1987). Then, the actual sampling is performed, where the probe typically remains 50 ms in the flame as measured by the high speed CCD camera. The average traveling velocity over the whole stroke is 2 m/s. Specifically, the probe travels 4 ms from the flame edge to the position at the centerline, while the time needed for traveling back from the flame center to the flame edge is 12 ms. The latter can be understood considering the inertia of the system. After taking the sample, the thermophoretic sampler is withdrawn from the near flame position by moving the backplate \(B\) \((5)\) in order to avoid heating of the shield and the probe by radiation of the flame. The exposure time of the grid can be controlled with a potentiometer of the electric control box that delays the signal to the pneumatic valve \((11)\). The start signal in the electric control box can also be triggered externally, when thermophoretic sampling is combined with other flame diagnostic techniques.

The position of the sampler or the residence time in the flame can be monitored directly with a high speed CCD camera (Megaridis, 1987) like in the present work. In the design of Megaridis (Dobbins and Megaridis, 1987; Megaridis, 1987) a linear transducer was connected to the pneumatic cylinder, which was used for monitoring the TEM grid trajectory (transit times and exposure time) on an oscilloscope. Köylü et al. (Köylü et al., 1997) used a laser system to determine the residence time, and in the present design this was achieved by mounting hall sensors (Bimba) on the pneumatic cylinder.

Detailed drawings of the thermophoretic sampler and a schematic of the electric control box can be found at the end of this chapter. All distances are given in mm.

TEM analysis was performed on a Hitachi H600 and a Zeiss 930 Omega transmission electron microscope using magnifications of 10,000 to 60,000. The acceleration voltage was 100 kV. For each flame location pictures were taken from the center of the TEM grid \((±0.5 \text{ mm})\), that has a diameter of 3 mm, from which a circle of 2 mm in diameter is exposed to the flame. At each sampling location, 500-1000 particles are counted manually with Optimas software (Media cybernetics) that allows
drawing circles around the particles. Statistical analysis of the data is performed according to Hinds (1999), typically calculating the sauter mean diameter, \( d_{3,2} \), from the count mean diameter, \( d_{1,0} \), that was obtained from the TEM counting.

**C.4. References**


C.5. Detailed technical drawings
*Holes for M5 hexagonal set screws

**Long holes (5x6mm) for M5 hexagonal set screws
Guide for moving rod

Positioning clamps
Guide plate (POM or PET)

Brackets for pneumatic cylinder (two times)

Front screw

Shield
Electric control box

[Diagram of an electric control box]
Appendix D:

D. Effect of thermophoretic sampling (TS) on the electric field

To determine the effect of thermophoretic sampling (TS) on the electric field, the current was monitored as function of time while the TS probe is inserted and withdrawn from the flame.

Fig. D.1: Effect of thermophoretic sampling inside the electric field on the normalized measured flame current (data acquisition rate 10 Hz) for various residence times of the probe in the flame (30-150 ms). At each residence time, three samples were taken. The insert of the figure magnifies current data acquired during the sampling (marked with TS) with a residence time of 130 ms.

\[ I_{\text{average}} = 4.5 \times 10^{-6} \text{ A} \]
A premixed particle-free methane flat flame was used since the current in this flame is about ten times larger than in particle-laden flames (Vemury and Pratsinis, 1996; Katzer et al., 2001; Kammler et al., 2002). Figure D.1 shows the variation of the normalized flame current \( (I(t) / I_{\text{average}}) \) between plate electrodes with time. In the absence of the sampling probe, the current fluctuates roughly by \( \pm 2\% \) around its average value of \( 4.5 \times 10^{-6} \) A. *In situ* thermophoretic sampling was then performed inside the electric field at the flame center and 1.3 cm HAB using different residence times of the probe in the flame (35 – 130 ms).

The flame current indicates by how much the electric field between the electrodes has disturbed sampling and is monitored by continuous current measurements with the data acquisition system, described in Chapter 4.2. During sampling the current is reduced at most by 10%. Since the probe was inserted three times at each residence time to identify the sampling clearly, three spikes can always be observed in the current data (Fig. D.1). The reduction in flame current, however, is only clearly distinguishable from the background noise for residence times larger than 50 ms. When the disturbance of the flame and the field is too short, these changes might not be captured by the data acquisition system since it is monitoring the current only every 100 ms. It is interesting to note that the magnitude of the decrease in flame current does not change with increasing residence time of the probe at the flame center (65 to 130 ms). The reduction of the flame current was always about 10%. Magnifying the time scale (insert of Figs D.1), it appears that it takes less than 300 ms for the flame current to reach its average value after the sampling. However, this seems not to be affected significantly by the residence time of the TEM grid at the flame center comparing residence times of 65 and 130 ms (insert of Fig. D.1), respectively.

**References**


Curriculum Vitae

Hendrik Klaus Kammler

Date of birth
July 5th, 1971

Place of birth
Seesen, Germany

Research assistant at the Institute of Process Engineering,
Swiss Federal Institute of Technology (ETH) Zurich,
Switzerland

Guest researcher at the Department of Chemical Engineering,
Case Western Reserve University, Cleveland, U.S.A.

10/1999 – 11/1999
Guest researcher at the Department of Chemical Engineering,
University of Cincinnati, U.S.A.

Study of chemical engineering at the University of Karlsruhe
(TH), Germany
Graduation as Dipl.-Ing.

Diploma Thesis at the Department of Chemical Engineering,
University of Cincinnati, U.S.A.

05/1996 – 08/1996
Semester Thesis at the Department of Chemical Engineering,
Swiss Federal Institute of Technology Lausanne (EPFL),
Switzerland

06/1992 – 09/1992
Internship, basic practical training in chemical engineering,
Chemetall GmbH, Langelsheim, Germany

Military service

08/1984 – 05/1991
Ratsgymnasium Goslar, Germany

08/1982 – 06/1984
Orientierungsstufe Innenstadt Goslar, Germany

08/1978 – 06/1982
Grundschule Goetheschule Goslar, Germany
Patent


Refereed publications


