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Flame Spray Technology

Method for Production of Nanopowders

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Flame Spray Technology

Method for Production of Nanopowders

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Preface

This book contains an updated overview of flame spray process, an important method to synthesize nanostructured materials. Its effective role in tuning the properties of nanostructured powders (or even coatings) at low cost explains the growing interest of the academy and industry in this technique.

Nanomaterials produced by flame spray processes have been largely investigated in the last decade. They have great potential for applications in different fields such as engineering, physics, chemistry, biology, and medicine. Synthesis and characterization of nanostructured materials is a subject of great interest involving science, technology, market, politicians, government, and society. Based on the results obtained by our research group during the past years, this book mainly addresses the materials synthesized by flame spray and their properties such as crystallinity and crystallite size, specific surface area, particle size, and morphology. Hence, this book is aimed for students, researches, and engineers who search for methodologies to obtain and characterize nanostructures in detail.

After a brief introduction (Chap. 1), the book is split into five sections: the history of flame spray technique (Chap. 2), the principles of nanoparticle formation (Chap. 3), the apparatus used in flame spray process (Chap. 4), ceramic products by flame spray (Chap. 5), and future trends in flame spray process (Chap. 6).

We hope that the clear language and the application-oriented perspective are suitable for professionals and students who want to access major knowledge about Science and Technology involving synthesis and characterization of nanostructured materials.

Finally, we would thank the staff of Springer Verlag for their professional guidance in regards to this book.

Porto Alegre, Brazil
November 2014

Rafael M. Trommer
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Chapter 1
Introduction

The nanoscience and nanotechnology have been arising as an important field of science to change the industrial production and economics for the next decades. These sciences have been considered a powerful tool that can bring benefits to a wide range of scientific areas, attracting fast and increasing investments by the government and companies from different places around the world.

Inside the nanotechnology "world," nanoparticles or nanostructured particles are a special topic and widely produced by varied techniques and largely used in several products, in different applications. To improve its performance, many applications and products are submitted to the use of nanoparticles.

The increasing interest in nanoparticles or nanostructured particles in the last years is motived by the fact that these entities present different properties from its bulk form, because the transaction from micro- to nanoscale causes several changes in the physical properties of the material, once the particles become sufficiently small, they start to present a mechanical quantical behavior (Tok et al. 2006). This phenomenon is related to its high surface-to-volume ratio, e.g., the high fraction of atoms near or at the surface. However, the improvement of a special property of a product where nanoparticles are added requires the fundamental control of the particle size of the nanoparticles, because the properties of nanoparticles change dramatically with particle size.

A way to see the importance by which nanoparticle synthesis has been investigated in order to obtain materials with superior performance is to consult the historical of article publishing concerning to this subject. Indeed, based on Fig. 1.1, which presents a survey about the use of the term nanoparticle synthesis in the title of the article, it is possible to observe an increment year-by-year of article publishing regarding this subject.

Approximately 20 years ago, less than 25 papers have been launched in international literature about synthesis of this kind of materials using the exact expression "nanoparticle synthesis." It is important to observe that the use of this expression in the title shows an exponential behavior over the period of the survey. In 2014

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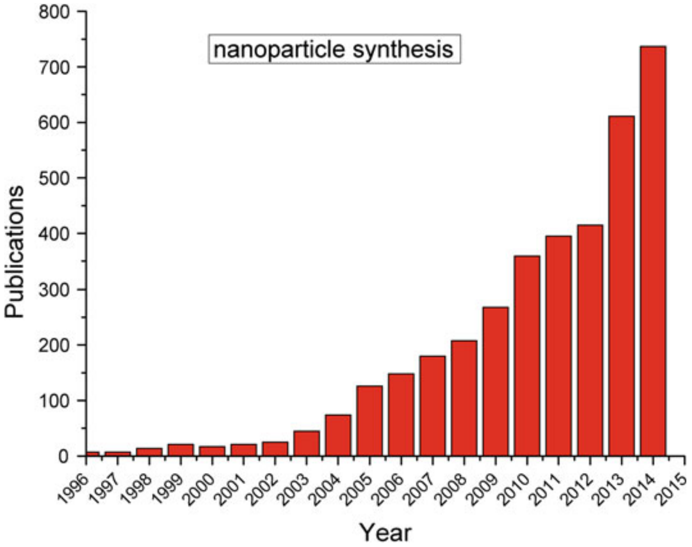

Fig. 1.1 Survey of articles publishing regarding nanoparticles synthesis in the period of 1996–2014 (from www.sciencedirect.com, accessed on December 19, 2014)

(December), the survey returned more than 700 papers using this expression. It highlights how the synthesis of nanoparticles became an important subject.

Considering this scenario of growing interest in nanotechnology and nanoparticles, more and more techniques have been developed to produce nanoparticles. Inside the several techniques reported in the literature for nanoparticles production, the actual trend is the development and use of alternative methods, mainly the ones that shows low cost, final products with high purity, and in the nanometric scale.

The flame spraying of an aerosol containing the precursor salts is a relative simple technique of synthesis that has attracted the attention of many industrial companies for the production of nanoparticles. Basically, there are two primary types of the flame aerosol process: (a) flame vapor synthesis (FVS), which is a flame-assisted vapor-to-particle conversion process, and (b) flame spray pyrolysis (FSP) that is a flame-assisted liquid droplet-to-particle conversion process. The flame aerosol technology can be used to produce a wide collection of high-purity oxide nanoparticles, ranging from single metal oxides such as alumina and titania to more complex mixed oxides, as spinels and hydroxyapatite for example. It is also possible to say that FSP is an industrial-scale method for production of single- or multi-component nanoparticles of almost all periodic table elements. Moreover, large volumes of different materials can be produced in industrial flame reactors.

The recent interest in this technique is more evident when a survey concerning the use of the strict term Flame-spray (FS) in the title of the article is proposed, as shown in Fig. 1.2. In the middle of the 1990s, approximately 75 articles reported in its title the use of FS. A slight decrease on the number of published articles occurred

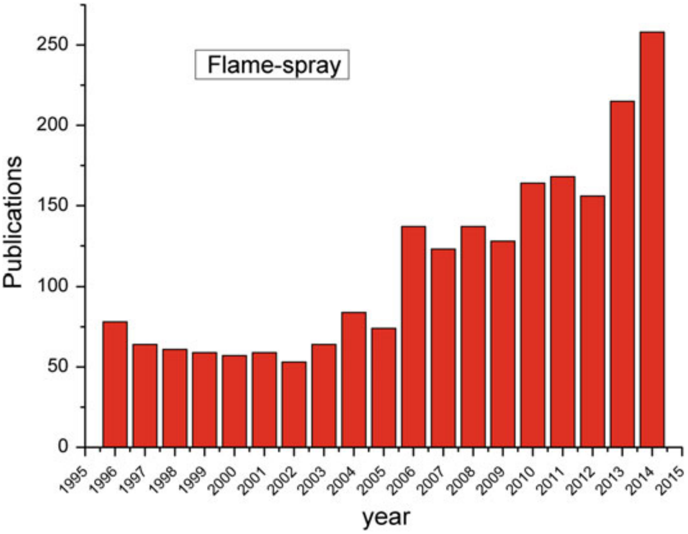

Fig. 1.2 Survey of articles publishing regarding Flame spray in the period of 1995–2014 (from www.sciencedirect.com, accessed on December 19, 2014)

until 2005, where an inversion in the trend led to an increase in the number of publications, reaching a number of more than 250 articles published in 2014 (December) considering the term FS.

Considering the production of nanoparticles or nanostructured particles at an industrial scale, the FS process has several advantages: they do not create liquid by-products requiring costly cleaning, offer easier collection of particles from gases than liquids, involve few process steps, form high-purity products and have unique filamentary morphology at high yields that is attractive for nanocomposites. Another important feature of FS is its recent use as technique for thin-film or coating production.

These advantages are confirmed when an historical analysis of the article publications in the last years using the exact expression "FS synthesis of nanoparticles" is carried out, as shown Fig. 1.3. There is a clear increase in the number of papers published between 1997 and 2014. By the half of the decade of 2000, approximately 50 papers were published. In opposite, by the end of the year 2014 more than 250 papers were published. It reinforces how the use of a spraying solution in a flame to obtain particles in nanometric dimensions has become an interesting technique.

Thus, the aim of this book is the introduction of the versatile, cost-effective, and innovative technique named FS to different people who can be use this method on their work, as scientists, students, engineers, and so far.

The importance of industrial flame spraying process is demonstrated by the production rates up to several tons per hour, in several companies, of nanostructured ceramics such as fumed silica and alumina, as well as pigmentary titania. The

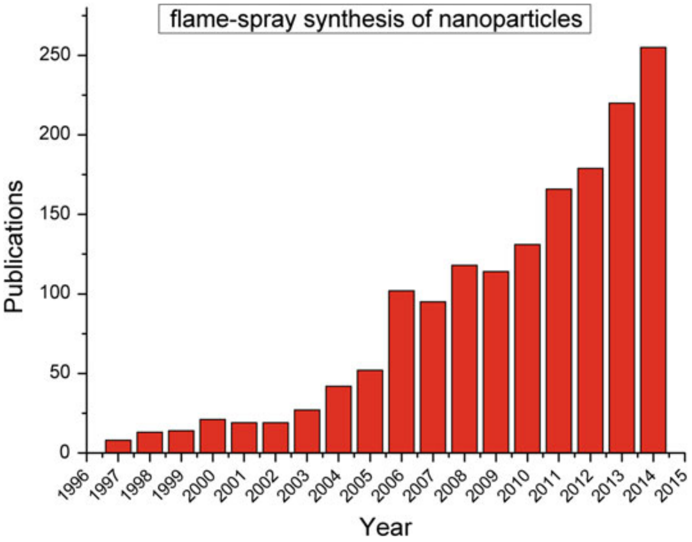

Fig. 1.3 Survey of articles publishing regarding Flame spray synthesis of nanoparticles in the period of 1997–2014 (from www.sciencedirect.com, accessed on December 19, 2014)

FS process is becoming an attractive process for nanoparticles production because it is a one step method, where the crystalline phases are obtained directly in the high-temperature conditions, and contrasting to usual techniques such as wet-chemistry routes where a further a calcination step is requested to obtain the desired crystal phases.

The history of using a flame to produce, in a not intentional way, nanoparticles is introduced in Chap 2. The first intentional apparatus, introduced in 1971 by Ulrich and his colleagues (Ulrich 1971), to prepare silica from the spraying of silicon tetrachloride ($SiCl_4$) precursor solution in a flame is also described. The main companies that nowadays use the principles of flame spraying to produce several commodities are also mentioned.

In Chap. 3, the principles of nanoparticles formation using the FS process is presented. The basic principle of FS process involves the formation of vapor or aerosol from a precursor solution, which contains the precursor salts that will supply the ions for the final product. This chapter also presents the two basic types of process used to obtain nanoparticles, which are based in the formation of an aerosol and further spraying in a flame.

The main devices that generally comprise a FS equipment are presented in Chap. 4. All fundamental principles are based in the flame configuration, atomization devices, flame temperature, powder collection system, and burner. Thus, a deep discussion about the different equipments employed to produce a wide range of nanoparticles, either industrial or academic apparatus, is presented.

The wide range of nanoparticles and particles nanostructured, produced by different flame-based apparatus, is presented in Chap. 5. The FS technique allows the production of ceramic commodities intended to be used in different applications. For example, it is possible to obtain with the aid of the FS technique since hydroxyapatite, which is a biomaterial widely used in surgical implants, until titania and black carbon, the first commercial products prepared by FS.

Finally, Chap. 6 presents the future trends in the use of FS process. The increasing interest in products with improved performance, due to the use of nanoparticles, is reported. Moreover, the recent development of flame-sprayed nanoparticles of non-ceramic materials is subject of this chapter.

References

Tok AIY, Boey FYC, Du SW, Wong BK (2006) Flame spray synthesis of ZrO_2 nano-particles using liquid precursors. Mat Sci Eng B 130:114–119. doi:10.1016/j.mseb.2006.02.069

Ulrich GD (1971) Theory of particle formation and growth in oxide synthesis flames. Combust Sci Technol 4:47–57

Chapter 2
History of Flame Spray (FS) Technique

Abstract The flame spray (FS) technique has been practiced in a non-intentional way since the prehistoric age, according to paintings observed in the walls of caves in China. At that time, its principles were not understood, but people had the knowledge to produce the pigments used in the paint by the FS process. The first contemporary reactors for nanoparticles flame synthesis started in the 1940s, by the production of fumed silica. Only in 1971, G.D. Ulrich pioneered the first principles of the FS method. Since this day, several laboratories and companies have developed different apparatus and alternative methods, aiming to obtain materials with improved properties. This is the main driving force for the evolution of the FS process during the last decades, where more materials and equipments are reported in literature.

Abbreviations

FS	Flame spray
NCPDP	Nanocerox Ceramic Powder Development Process
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy.

In the last years, scientists have been searching a way to improve the properties of several materials, aiming to develop better products for human health, environmental friendly products, electronics, oil and gas industry, steel industry, etc. Since the Richard Feynman's classic talk in December 1959 "There's Plenty of Room at the Bottom," nanomaterials have been arisen as a great opportunity to overcome this problem. According to Feynman, nanotechnology aims to create new materials and develop products and process based on the modern ability to manipulate atoms and molecules. Inside this wide field of nanotechnology and nanomaterials, particles in the nanometric size have been studied in-depth due to their unique physical and chemical properties, which are strongly different from the bulk microstructures. An extensive research activity over the past decade has led to the development of

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several methods for producing nanoscale materials with a wide range of chemical compositions: solgel, combustion solution synthesis, etc. However, a recent technique named flame spray (FS) has arrived as an alternative method to produce nanoparticles.

The technology concerning the FS method is associated to the formation of small particles from a gas or vapor phase in a flame. Consequently, each process used in the past and based in these principles can be described as a FS method. Thus, it is believed that the FS technology has been practiced in a non-intentional way since the prehistoric age, according to paintings observed in the walls of caves in China (Pratsinis 1997). Soot, which can be considered as flame-made particles, has been part of mankind's history. It is observed in drawings on cave walls in the prehistoric period and in the Egyptians, Indians, Greeks, and Chinese culture (Strobel and Pratsinis 2007).

Carbon black is the oldest aerosol that is still manufactured. In short, carbon black was first made in India and Egypt at prehistoric times and was systematically manufactured for pigments in China by pyrolysis of vegetable oils, using the "lampblack" process at about 1500 BC (Pratsinis 2011). Carbon black was also the first commodity to attain industrial significance. It is a pigment formed by 99.5 % of amorphous carbon with different levels of particle sizes with different structures, which justifies its wide range of industrial applications.

Cabot Corporation is the world largest carbon black producer. The Cabot Corporation started when Godfrey Lowell Cabot in 1882 applied for a patent for an apparatus to produce carbon black. In this apparatus to produce carbon black, Godfrey combined his knowledge of pigmentation and chemistry with an understanding of natural gas to become the earlier producer of carbon black. At that time, carbon black was found to use in newspaper and magazine printing inks as well as tires, for example.

The first contemporary reactors for nanoparticles flame synthesis started in the 1940s, by the production of fumed silica. However, only in 1971, G.D. Ulrich reported the first principles of the FS method. Basically, the work of G.D. Ulrich comprised the spraying of silicon tetrachloride ($SiCl_4$) precursor solution in a flame to produce silica as final product (Ulrich 1971).

Silica and titania were the first materials produced by FS synthesis to be patented (Keskinen 2007). TiO_2 is nowdays the largest (by volume and value) ceramic material made in flame aerosol reactors (Pratsinis 2011). For example, Degussa (Evonik Industries), one of the world largest chemical companies, produces flame-made nanoparticles named AEROXIDE® TiO_2 P25, which is a titania photocatalyst that is used widely because of its relatively high levels of activity in many photocatalytic reaction systems.

The discovery and consequently application of a new product (nanoparticles) were the main responsible for the development and research of new aerosol reactors, as for example the use of carbon black to reinforce rubber (Pratsinis 2011). Moreover, the technologies involving the FS process or aerosol manufacturing have been historically developed as a result of the specific necessity for special products. Nowadays, several companies have used the FS technique to produce a wide range of commodities, such as Evonik, DuPont, Kemira, Tioxide, Corning Glass, General Electric, and Nanocerox. For example, in 2003, Degussa started an internal program named Advanced Nanomaterials that led this company to the worldwide leading technology position in the supply of new nanomaterials via gas-phase synthesis as such as FS.

Concerning the wider range of nanomaterials nowadays produced by the FS process, in the last few years, a special attention was given to the doping of nanoparticles, as Pd/TiO_2 (Mekasuwandumrong et al. 2011), Nb/ZnO (Kruefu et al. 2011), and the mixed oxides such as CoMo/Al_2O_3 (Høj et al. 2011), Zn_2TiO_4 (Siriwong et al. 2012), CeO_2–$CeAlO_3$ (Aruna et al. 2009), $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ (Ernst et al. 2007) and SnO_2/TiO_2 (Ifeacho et al. 2005). The production of rare earth oxides was also reported, as Lu_2O_3 (Baker et al. 2012). Even biomaterials, for example, hydroxyapatite, one of the most important bioceramic used for bone regeneration purposes in medicine can be produced by the spraying of a precursor solution in a flame (Trommer et al. 2009). However, it is not the intention of this chapter to describe the different materials that can be produced by FS technique. The materials mentioned in this chapter only reinforce how the FS technique has been always in evolution. Moreover, the development of new devices, the use of new flame configurations, theoretical studies of flame synthesis process, and the use of modern tools of analysis (TEM, SEM, XPS) allowed the FS technique to grow up, since the prehistoric carbon black produced in China to novel materials and fields of application.

The use of a flame to obtain several materials has emerging as an important industrial technique and has become recognized across the scientists. The number of researchers as well laboratories that uses the FS has increased in the last years. Some start-up companies were also identified, mainly to develop new spray and flame configurations, and synthesis of novel materials with enhanced properties. One example of a start-up company that produces nanoparticles based in the FS process is the American company Nanocerox. The platform used by Nanocerox is referred to as the Nanocerox Ceramic Powder Development Process (NCPDP) and based upon an exclusive license from the University of Michigan for its patented flame spray pyrolysis process used to produce highly pure, chemically precise, and uniformly sized nanoparticles.

References

Aruna ST, Kini NS, Rajam KS (2009) Solution combustion synthesis of CeO_2–$CeAlO_3$ nanocomposites by mixture-of-fuels approach. Mater Res Bull 44:728–733. doi:10.1016/j.materresbull.2008.09.034

Baker C, Kim W, Sanghera J et al (2012) Flame spray synthesis of Lu_2O_3 nanoparticles. Mater Lett 66:132–134. doi:10.1016/j.matlet.2011.08.058

Ernst FO, Kammlera HK, Roessler A et al (2007) Electrochemically active flame-made nanosized spinels: $LiMn_2O_4$, $Li_4Ti_5O_{12}$ and $LiFe_5O_8$. Mater Chem Phys 101:372–378. doi:10.1016/j.matchemphys.2006.06.014

Høj M, Linde K, Hansen TK et al (2011) Flame spray synthesis of CoMo/Al_2O_3 hydrotreating catalysts. Appl Catal A general 397:201–208. doi:10.1016/j.apcata.2011.02.034. http://www.nanocerox.com/background.htm

Ifeacho P, Wiggers H, Roth P (2005) SnO_2/TiO_2 mixed oxide particles synthesized in doped premixed H_2/O_2/Ar flames. Proc Combust Inst 30:2577–2584. doi:10.1016/j.proci.2004.08.117

Keskinen H (2007) Synthesis of nanoparticles and preparation of deposits by liquid flame spray. Thesis. Tampere University of Technology, Tampere

Kruefu V, Liewhiran C, Wisitsoraat A, Phanichphant S (2011) Selectivity of flame-spray-made Nb/ZnO thick films towards NO_2 gas. Sens Actuators B 156:360–367. doi:10.1016/j.snb.2011.04.046

Mekasuwandumrong O, Phothakwanpracha S, Jongsomjit B, Shotipruk A, Panpranot J (2011) Influence of flame conditions on the dispersion of Pd on the flame spray-derived Pd/TiO_2 nanoparticles. Powder Technol 210:328–331. doi:10.1016/j.powtec.2011.03.017

Pratsinis SE (1997) Flame aerosol synthesis of ceramic powders. Prog Energy Combust Sci 24:197–219

Pratsinis SE (2011) History of manufacture of fine particles in high-temperature aerosol reactors. In: Ensor DS (ed) Aerosol science and technology: history and reviews, 1st edn. RTI International, Research Triangle Park

Siriwong C, Tamaekong N, Phanichphant S (2012) Characterization of single phase Pt-doped Zn_2TiO_4 nanoparticles synthesized by flame spray pyrolysis. Mater Lett 68:97–100. doi:10.1016/j.matlet.2011.10.026

Strobel R, Pratsinis SE (2007) Flame aerosol synthesis of smart nanostructured materials. J Mater Chem 17:4743–4756. doi:10.1039/b711652g

Trommer RM, Santos LA, Bergmann CP (2009) Nanostructured hydroxyapatite powders produced by a flame-based technique. Mater Sci Eng C 29:1770–1775. doi:10.1016/j.msec.2009.02.006

Ulrich GD (1971) Theory of particle formation and growth in oxide synthesis flames. Combust Sci Technol 4:47–57

Chapter 3
A Brief Overview on Flame Spray Synthesis

Abstract The technology involving the flame spraying of a precursor solution is based on the formation of small particles from the gas or vapor phase in a flame. Flame spray (FS) is regarded as a consolidated industrial technique, as discussed in the previous chapter. However, the principles and fundamentals of the particles synthesis in the flame are not completely understood. One of the main reasons for the absence of a complete description of FS synthesis is the fact that chemical reactions and particle formation occurs in a short time and high temperature during the process. The basic principle of FS technique is the formation of vapor or aerosol of the precursor compounds, which reacts in the high temperature of the flame leading to the formation of a ceramic compound. There are two basic types of process based on the formation of an aerosol and further spraying in a flame. The former is the conversion to a particle from the vapor phase, due to the presence of a flame, and named vapor synthesis in a flame. The second process comprises the conversion of a droplet to a particle, also assisted by a flame, and named FS pyrolysis.

Abbreviations

FS	Flame spray
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy

The synthesis of nanoparticles can be essentially classified into two ways: top-down or bottom-up (Teoh 2007). Briefly, the former consists in the decreasing of a bulk mass to a specific particle size, as for example, the ball-milling process. The opposite approach of bottom-up is described as the assemblage of nanoparticles at the atomic level. Thus, according to its basic principles, the flame spray (FS) process can be classified as a bottom-up approach, where nanoparticles are formed at the atomic level.

The recent interest in the development and study of the FS technique is mainly related to its enormous potential on the nanoparticle production and its low cost for the production of such materials (Pratsinis 1997; Roth 2007; Camenzind et al. 2009). The FS method is a very promising technique for synthesis of high-purity

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nanosized materials with controlled size and high surface area in one step (Siriwong and Phanichphant 2011). This method has been considered as a versatile and rapid technique for the production of homogenous nanoparticles with controlled properties (Teoh 2007).

In the last two decades, a significant advance in the understanding and advance of the FS process of particle formation allowed a new way of research. Consequently, nowadays, it is possible to produce nanoparticles by the FS process with a well-controlled morphology, which allows a deep investigation of their performance (Strobel and Pratsinis 2007).

The FS method is widely used to obtain black carbon, which is produced by the spray of aromatic hydrocarbons (oils) in a natural gas flame. A half of this oil burns to occur pyrolysis and the other half of the oil then produces black carbon. Nowadays, this process is industrially used aiming to produce in large-scale pigments such as titania and silica. Moreover, using the FS process, it is possible to produce complex oxides, by the simultaneous feed of specific compounds in the flame (Johannessen et al. 2004). For example, it is possible to obtain several ceramic materials with complex crystalline structure, as hydroxyapatite (Trommer et al. 2009).

The synthesis of nanoparticles in a flame is an industrially stabilized technique. However, its principles and fundamentals are not fully understood, mainly because the chemical reactions and particle formation occur in short times during the process (Roth 2007). Moreover, the residence time of the particle in region of the flame with the higher temperature is estimated to be about 10–100 ms (Roth 2007). The high temperatures of the process, due to the use of a flame, must be also considered, which makes difficult the collection of samples and its characterization to develop a theoretical model. Usually, the flame temperature ranges from 1000 to 2400 °C depending on the flame configurations, gases, etc. (Pratsinis 1997). To overcome this problem, and then create mathematic models, several authors have used scientific tools as phase-Doppler anemometry and thermophoretic sampling to validate the model-predicted temperature and velocity profiles as well as droplet and particle characteristics for a set of process conditions (Grohn et al. 2012). Moreover, the use of transmission electronic microscopy (TEM) strongly contributed to the development and validation of theoretical models.

One of the advantages of the FS process is the fact that the particles produced in the gas stream do not generate liquid sub-products due to the chemical process. Other advantage of this method is the simple separation of the particles produced in the flame from the gas stream. In some cases, no further treatment of the material (e.g., drying, calcination, or milling) is required, which results in a material of high purity. The FS process also provides good control of particle size and particle crystal structure (Jang et al. 2006). It also presents a low cost, simplicity, versatility to produce nanostructured powders, high efficiency to collect the powders, and flexibility to obtain complex oxides with chemical homogeneity (Karthikeyan et al. 1997). Moreover, the FS process is an adequate method for controlling the crystalline structure, primary particle size, and particle size distribution of the powders in the nanometric scale (Moiseev et al. 2011).

Flame aerosol process has been used to produce various nanoparticles such as ceramic and composite powders because it provides good control of particle size and particle crystal structure, and this method also can produce highly pure particles continuously without further subsequent process, for example, drying, calcinations, and milling in the wet chemical processes. All these advantages make the FS process a flexible synthesis method where the product properties can be tuned by changing composition of the precursor gas and the flame operating conditions (Johannessen et al. 2004).

The first step for nanoparticle synthesis using the FS method is the use of specific compounds such as acetates, chlorides, or nitrates to prepare the precursor solution. These precursors, in a determined amount, are further dissolved in water or ethanol (this one is recommended, as discussed in the next chapter). In some cases, to obtain the final product in the oxide form, it is necessary to use nitrates. When the precursor solution employs nitrate, a combustible such as sucrose, urea, or glycine is usually added for the oxidation–reduction reactions. The preparation of the precursor solution will be further discussed. The combustion of the precursor solution is the responsible for the evaporation of the solvent and then provides the source of heat required for the nucleation of the first nuclei of the ceramic material. The FS method comprises the spraying and dispersion of liquid precursors into a flame (Heine et al. 2006). The contact of the dispersed (droplets) liquid precursor causes its ignition, which forms a self-sustained spray flame. After the chemical reactions, the nanoparticles with different degrees of agglomeration are produced.

Particle size distribution of product powder is the most important variable, and it depends strongly on flame dynamics inside the reactor, which in turn is a function of input process variables such as reactant flow rate and concentration, flow rates of air, fuel, and the carrier gas, and the burner geometry (Buddhiraju and Runkana 2012).

Usually in the FS process, hollow or shelllike particles with variable shell thickness are obtained, but dense particles are also obtained. The morphology of the nanoparticles produced by the FS process can be tailored by adjusting of the process parameters, further discussed in Chap. 3.

3.1 Principles of Nanoparticle Formation

Many scientists and researchers believe that particle formation in flames is an exciting research area because it is a field where science and engineering meet each other. In the last two decades, several studies have contributed to the development of models and theory about the mechanisms of particle formation using the FS process. Moreover, the use of tools such as TEM and computations allowed a systematic investigation for flame synthesis of high purity (Camenzind et al. 2009). During the synthesis of nanoparticles using the FS method, it is very important for a fundamental understanding of the flame process, from droplet evaporation to product particle formation (Heine et al. 2006).

The main principle of the FS process is the decomposition and oxidation of evaporated metal precursors in a flame. This process causes the formation of stable metal oxide monomers followed by nucleation, aggregation/agglomeration, and coalescence of aggregated nanoparticles (Johannessen et al. 2004). Aggregates are chemically sinter bonded particles of primary particles, and agglomerates are physically bonded primary particles of aggregates (Strobel and Pratsinis 2007). The FS process is often reported as the combustion aerosol process where nanoscale ceramic materials are produced using a combustible aerosol spray to deliver ceramic precursors to a reaction zone (Helble 1997).

The FS process and its different alternative methods can be also described as the process where a starting solution, usually prepared by the dissolution of the metal component of an intended product in a solvent, is atomized in droplets and then introduced in the solvent evaporator. Once in this device, evaporation of the solvent, diffusion of solute, drying, and precipitation occur to form the final product. The reaction among reactants, and sometimes with surrounding gas, is dependent on the type of the initial solution (Nandiyanto and Okuyama 2011).

Another description of the FS process is based on the evaporation of droplets, which are previously sprayed in the flame, and release of the compounds into the gas phase. The final products are formed by the rapid precursor and solvent evaporation, as shown Fig. 3.1.

During the process of particle formation in the flame, it is observed in the production of small particles in high concentration. In a first moment, the coalescence of these particles occurs by collision. Due to cooling (as the nanoparticles leave the region of high temperature in the flame), the process of coalescence of the nanoparticle is interromped. However, the individual entities are kept constant and the presence of more material produced in the flame causes the aggregation of the nanoparticles. The density of nanoparticles is reduced, and, with the decrease of the temperature, the collision still occurs, but with no deposition leads to the union of the particles. Thus, the synthesis of ceramic particles in a flame briefly involves

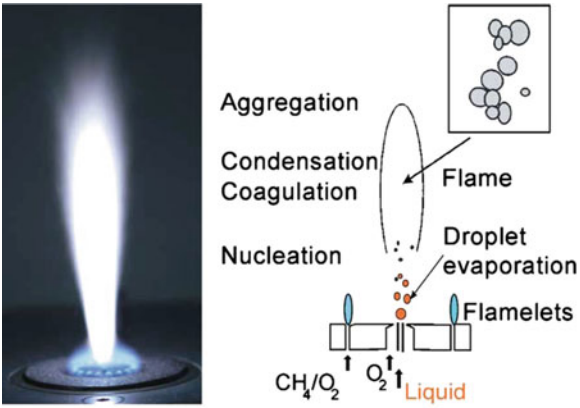

Fig. 3.1 Example of a flame reactor and the scheme of nanoparticle production using the FS process (*Aknowledge* Stark and Pratsinis 2002)

chemical–physical process of transport, chemistry, and dynamic of the particle (Pratsinis 1997).

In the FS process, the nanoparticles can be produced by two different ways (Helble 1997). The first one comprises the precursor vaporization, which is followed by nucleation and coagulation. The second way is by the nucleation within the reacting carrier aerosol droplets. In a particular way, powder synthesis from the gas phase can occur by two modes: reaction of the precursors (gas–particle conversion) or evaporation and/or reaction of the droplets in the gas stream (droplet–particle conversion). In the first process, the particles are produced from the molecules until to the desired size, throughout the control of specific parameters. In contrast, in the second mode, the particle size is determined by the reduction of the larger particles and mainly by the droplets created in the spray. The further mode is basically a simple version of the spray-drying technique, but in higher temperatures (Pratsinis and Vemury 1996).

The exothermic energy of oxidation is used to increase the temperature in the gas stream. As a result, the vaporization of the liquid precursor droplets is observed, which results in its decomposition. Clusters are formed after this step, which grows to nanoparticles by surface growing and/or coagulation and coalescence. Usually, the cluster coalescence is very fast, which results in spherical particles. As the aerosol stream leaves the high-temperature zone of the flame to a region of low temperature, where the powder is collected, the growing of the particles continues more due to coagulation than the coalescence, resulting in aggregates of primary particles. In some cases, the aggregates are kept together due to weak bondings, in structures known as agglomerates. The energy of the exothermic oxidation reactions is used to increase the temperature of the fluid flow, thus driving the chemical reactions of the precursor gas. This results in vaporization of droplets of a liquid precursor, thereby initiating its decomposition. Nuclei and clusters are formed, which further grow to nanoparticles by surface growth and/or coagulation and coalescence. This sounds quite similar to what is known about soot formation in flames.

With the FS method, the production of aggregates is possible and it is used as fillers for composites, light guide preforms, insulating materials, chemical–mechanical polishing agents, or as catalyst supports (Camenzind et al. 2009). When agglomerates are produced by the FS method, they can be easily dispersed into their constituent particles, which is interesting in the manufacture of pigments, porous electrodes, or in optics as nanophosphors or quantum dots (Camenzind et al. 2009).

Gas-phase reactions are characterized by high temperatures of up to 10,000 °C. The manufacturing process and conditions determine the size and morphology of the particles and hence their fields of application. The kinetics of the combustion reactions are only loosely coupled to the precursor's decomposition and the reactions forming particles (Roth 2007).

The growth by condensation, coagulation, and coalescence will occur within the thermal boundary region of the carbon carrier particles. As a result, the formation of ceramic oxide particles in the 1–100 nm size range will occur (Helble 1997).

After the formation of particles, coagulation and sintering occur, either by gas to particle or droplet to particle, in a similar way as other general aerosol synthesis (Teoh 2007). This process is briefly summarized by the well-established equations on particle evolution, which was earlier developed for the aerosol aggregation at high temperature. In the particle coagulation, the following equation can be applied.

$$\mathrm{d}N/\mathrm{d}t = -\tfrac{1}{2}\,\mathrm{b}N^2 \tag{3.1}$$

where N is the number concentration of particles and b is the frequency of collision.

The sintering process, which implies in the loss of surface area, can be described as follow.

$$\mathrm{d}a/\mathrm{d}t = 1/Nx.\ \mathrm{d}N/\mathrm{d}t\,x\,a - 1/\tau.(a - a_{\mathrm{s}}) \tag{3.2}$$

where the first and second terms in the right accounts for coalescence of na aggregate, which is driven by the characteristic sintering time for grain boundary diffusion (τ) and difference between actual surface area and that of a completely fused sphere (a_{s}).

Concerning the particle formation, it is important to be regarded as the process variables (flame temperature, residence time, mixing, ions, additives, precursor gas concentration, and cooling rate), which can affect the coagulation and sintering and consequently the morphology of the material produced by FS process.

3.1.1 Gas–Particle Conversion

The process of gas-to-particle conversion can be briefly described as the production of nanoparticles from individual atoms or molecules in the gas phase. The nanoparticles formed by gas-to-particle conversion, which is typically a process of oxidation, require an appropriate precursors that are delivered either as gases or as droplets that evaporate (Camenzind et al. 2009). One of the requisites of the gas-to-particle conversion, and consequently formation of particles, is the supersaturation of the gas with respect to one or more components. The supersaturation can be obtained either by cooling or by a chemical reaction that creates atoms/molecules with low vapor pressure (Johannessen 1999).

When the vapor gets in contact with the surrounding oxygen-rich gases, it will oxidize, forming relatively low vapor pressure species. The resulting supersaturation of ceramic oxide vapors is rapidly relieved by homogeneous nucleation, generating a large number of nanometer-scale condensed-phase ceramic oxide particles. These newly produced nanoparticles grow by surface reaction, coagulation, and sintering (Camenzind et al. 2009).

Growth by condensation/coagulation and coalescence will occur within the thermal boundary region of the carbon carrier particles, resulting in the formation of ceramic oxide particles in the 1–100 nm size range. Particle structure will be inherently crystalline because of the high formation temperatures, eliminating the need for post-collection calcining with this process.

The gas-to-particle conversion is basically the exothermic high-temperature oxidation of precursor compound which creates local temperature gradients for control of vapor-phase ceramic oxide particle formation and growth (Helble 1997). Due to the entrance in the high-temperature flame environment, the precursor compounds are ignited and then, it reacts exothermically. A sequence of different processes causes the vaporization and condensation of the ceramic nanoparticles within the thermal boundary region of the reacting droplets.

There are other mechanisms to explain the particle formation in the gas-to-particle conversion. In one mechanism, the gas flow containing the precursors reacts at high temperature of the flame and then forms the product molecules (Pratsinis and Vemury 1996). Due to low temperature when it leaves the zone of high temperature in the flame, these molecules are promptly transformed in particles by molecular collisions (coagulation-driven process) or by nucleation of subcritical molecular clusters (nucleation-driven process). After the transformation to particles, it can grow by condensation and/or coagulation. As the particles move away from the flame and are directed to the powder collection system, they do not fully coalesce, which results in agglomerates or aggregates of primary particles. The competition between coagulation and sintering is the responsible for the particle agglomeration (Pratsinis and Vemury 1996). However, it is also possible for the competition between particle collision and coalescence, which results in either fully coalesced, spherical particles or fractal-like aggregates (Camenzind et al. 2009).

It is expected that the powders produced by the gas-to-particle conversion in the FS process have narrow particle size distribution and morphology of dense particles. The disadvantage of this conversion route is that particles are often agglomerated.

3.1.2 Droplet–Particle Conversion

In this particular type of particle synthesis, the droplets of the liquid precursor are suspended in the gas stream, where the final product is obtained by the in situ reaction with the gas or by pyrolysis. The droplets are usually formed by the atomization of the liquid precursor. The liquid precursor can be atomized into small droplets using one of the two combustion gases, hydrogen or oxygen (Aromaa et al. 2007). Consequently, the final particle size distribution depends on the initial droplet size of the aerosol.

In the droplet-to-particle conversion, the oxidation of the reactive carrier aerosol supplies the exothermic high temperature to create a steep local temperature gradient, which controls the formation and growth of ceramic oxide particles (Helble 1997). In this environment of high temperature, the spray that contains the precursors ignites and reacts exothermically. After this step, a sequence of process causes the vaporization and condensation of the particles within the thermal

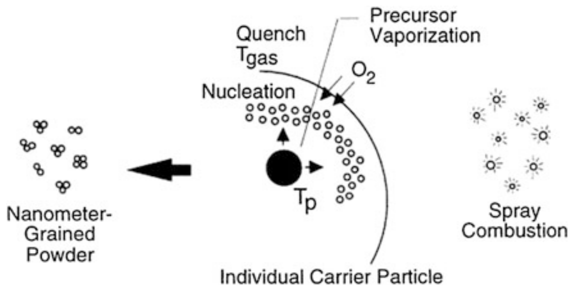

Fig. 3.2 The process of precursor vaporization and nucleation to produce a nanoparticle (*Acknowledge* Helble 1997)

boundary region of the reacting droplets. Each carrier aerosol droplet is effectively a micro-reactor. As a result, the high temperatures and short processing times required for optimal powder formation can be achieved. The exothermic droplet combustion reaction is too strong and provides the required heat for nanoscale ceramic crystalline particle production. Consequently, no additional post-treatment is needed in most of the cases (Helble 1997). A brief scheme of the principle of vaporization and nucleation of the particles is described in the Fig. 3.2.

The pyrolysis of the aerosol is a process where the precursor material is atomized and guided to a high-temperature zone, such a flame. The precursor in the spray form promptly evaporates, i.e., the solvent is removed while the required components stay in the droplets (Nandiyanto and Okuyama 2011). The precursor starts to decompose, and the precipitation of the solute inside the droplet is observed. The following step is the thermolysis and drying of the precursor particle in the high temperature to form the microporous particle, which is further sinterized to create a dense particle. The general process of particle formation by the droplet–particle conversion is summarized in Fig. 3.3. The complete description of the decomposition kinetics and oxidation reaction is rarely obtained. The decomposition kinetics is also affected by the combustion kinetics, due to the reactions via radicals (Roth 2007).

The morphology of the nanoparticles is determined by the droplet evaporation–solute precipitation and reaction history during the synthesis in the FS technique (Heine et al. 2006).

The atomized precursor to droplet formation is the introduction of the droplets in a region of high temperature (flame) by the use of a carrier gas under atmospheric pressure condition, followed by the evaporation of the solvent existing in the droplets. After this, the solutes precipitate and thermal decomposition as well as intraparticle reactions occurs, which forms the nanoparticles. Due to these reactions, sometimes the droplet is considered as a micro-reactor, producing in most of the times spherical and sub-micron-sized particles (Widiyastuti et al. 2010).

It is necessary to avoid the formation of low surface area agglomerates, which is a critical aspect of any nanoscale powder production process. This is one of the advantages of the FS process that produces powders with high surface area (Helble 1997).

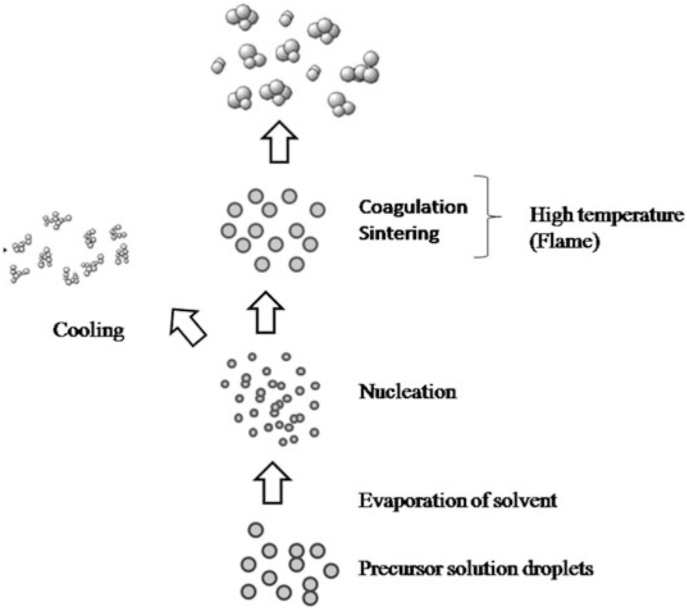

Fig. 3.3 A simplified model of the process of particle formation by the droplet–particle conversion

References

Aromaa M, Keskinen H, Mäkelä JM (2007) The effect of process parameters on the liquid flame spray generated titania nanoparticles. Biomol Eng 24:543–548. doi:10.1016/j.bioeng.2007.08.004

Buddhiraju VS, Runkana V (2012) Simulation of nanoparticle synthesis in an aerosol flame reactor using a coupled flame dynamics–monodisperse population balance model. J Aerosol Sci 43:1–13. doi:10.1016/j.jaerosci.2011.08.007

Camenzind A, Caseri WR, Pratsinis SE (2009) Flame-made nanoparticles for nanocomposites. Nano Today 5:48–65. doi:10.1016/j.nantod.2009.12.007

Grohn AJ, Pratsinis SE, Wegner K (2012) Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO_2. Chem Eng J 191:491–502. doi:10.1016/j.cej.2012.02.093

Heine MC, Mädler L, Jossen R, Pratsinis SE (2006) Direct measurement of entrainment during nanoparticle synthesis in spray flames. Combust Flame 144:809–820. doi:10.1016/j.combustflame.2005.09.012

Helble JJ (1997) Combustion aerosol synthesis of nanoscale ceramic powders. J Aerosol Sci 29:721–736

Jang HD, Chang H, Suh Y, Okuyama K (2006) Synthesis of SiO_2 nanoparticles from sprayed droplets of tetraethylorthosilicate by the flame spray pyrolysis. Curr Appl Phys 6S1:e110–e113. doi:10.1016/j.cap.2006.01.021

Johannessen T (1999) Synthesis of nanoparticles in flames. Dissertation, Technical University of Denmark

Johannessen T, Jensen JR, Mosleh M, Johansen J, Quaade U, Livbjerg H (2004) Flame synthesis of nanoparticles applications in catalysis and product/process engineering. Chem Eng Res Des 82(A11):1444–1452

Karthikeyan J, Berndt CC, Tikkanen J, Wang JY, King AH, Herman H (1997) Nanostruct Mater 8:61–74

Moiseev A, Qi F, Deubener J, Weber A (2011) Photocatalytic activity of nanostructured titanium dioxide from diffusion flame synthesis. Chem Eng J 170:308–315. doi:10.1016/j.cej.2011.03.057

Nandiyanto ABN, Okuyama K (2011) Progress in developing spray-drying methods for the production of controlled morphology particles: from the nanometer to submicrometer size ranges. Adv Powder Technol 22:1–19. doi:10.1016/j.apt.2010.09.011

Pratsinis SE (1997) Flame aerosol synthesis of ceramic powders. Prog Energy Combust Sci 24:197–219

Pratsinis SE, Vemury S (1996) Particle formation in gases: a review. Powder Technol 88:267–273

Roth P (2007) Particle synthesis in flames. Proc Combust Inst 31:1773–1788. doi:10.1016/j.proci.2006.08.118

Siriwong C, Phanichphant S (2011) Flame-made single phase Zn_2TiO_4 nanoparticles. Mater Lett 65:2007–2009. doi:10.1016/j.matlet.2011.03.058

Stark WJ, Pratsinis SE (2002) Aerosol flame reactors for manufacture of nanoparticles. Powder Technol 126:103–108

Strobel R, Pratsinis SE (2007) Flame aerosol synthesis of smart nanostructured materials. J Mater Chem 17:4743–4756. doi:10.1039/b711652g

Teoh WY (2007) Flame spray synthesis of catalyst nanoparticles for photocatalytic mineralisation of organics and Fischer—Tropsch synthesis. Doctorade thesis

Trommer RM, Santos LA, Bergmann CP (2009) Nanostructured hydroxyapatite powders produced by a flame-based technique. Mater Sci Eng C 29:1770–1775. doi:10.1016/j.msec.2009.02.006

Widiyastuti W, Balgis R, Iskandar F, Okuyama K (2010) Nanoparticle formation in spray pyrolysis under low-pressure conditions. Chem Eng Sci 65:1846–1854. doi:10.1016/j.ces.2009.11.026

Chapter 4
Apparatus

Abstract One of the most important requisites concerning the FS process is the equipment. All fundamental principles are based on the flame configuration, atomization device, flame temperature, powder collection system, and burner. The wide range of apparatus configurations contribute to the several materials that have been produced by the technique described in this book. As it has a strong influence in the final properties of the product, the description of the different equipments reported in the literature is an important feature. Most of the devices reported in this chapter were built in laboratory facilities, but several companies such as DuPont, Cabot, Degussa, Kemira, Tioxide, Corning Glass, and General Electric have been using their own equipments. The flame spray (FS) equipment can be basically divided in three sub-components: the atomization device, the group of flames, and finally the powder collection system. Each of these devices has its importance in the process of producing powders using the FS method, and all of them have different designs and different sub-components, according to the industry or institution that developed/fabricated the equipment. Thus, in this chapter, the main features of the FS apparatus are discussed, and a special attention was given to the flame device, which is the most important device of the equipment.

Abbreviations

CH	Carbohydrazide
DFH	N,N-diformylhydrazine
HMT	Hexamethylenetetramine
ODH	Oxalyldihydrazine
TFTA	Tetraformaltrisazine
FS	Flame spray
FSP	Flame spray pyrolysis
FTIIR	Fourier transform infrared spectroscopy
HA	Hydroxyapatite
HMDSO	Hexamethyldisiloxane
ITO	Indium–tin oxide
LPG	Liquefied petroleum gas

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SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TNB	Titanium (IV) tert-butoxide

The synthesis of nanomaterials using the flame spray (FS) method excludes the necessity of an additional source of energy such as lasers, heated walls, or plasma to convert the precursor into the final material. It makes the FS a rather low capital investment process with proven scalability. Therefore, in the last years, the use of FS method to produce nanoparticle has been successfully transferred from the laboratories around the world to the industries, sometimes with production rates of a few kilograms per hour (Wegner et al. 2011). The research, design, and development of new devices that comprises the FS apparatus have an enormous contribution to this fact. Moreover, recent advances have shown that the industrial process can be continuously operated, which allows the automation of the process, low cost and high efficiency in the nanoparticles production. For example, production rates of some materials can be up to 25 t/h and the corresponding reactors resemble best the rockets of the space shuttles departing from Cape Kennedy. Another important feature is the value aggregated to the final product ranging between US$ 0.5/kg for carbon black to US$ 500/kg for cermets or even US$ 20,000/kg for Pt catalysts (Stark and Pratsinis 2002).

Nowadays, the low cost of the apparatus used allows the production of single oxides in pilot and industrial plants with costs below than 100 EUR/kg, with raw materials being the largest cost factor. Consequently, a special attention must be given to all parts of the FS apparatus, aiming to produce pure materials, with high production efficiency, nanostructured, and low cost.

Despite the size, the main difference between the industrial and academic equipment is the production rate, once companies aim to produce large amounts of the commodities. Moreover, the production of new materials with improved performance is the main goal of laboratory equipments and research, while big companies aim to produce materials with low cost.

FS process is a versatile technique, where different apparatus and devices can be assembled and/or used, but the principles are quite still the same. One equipment is, in most of the situations, able to produce a wide range of nanoparticles of several materials. For example, the use of a simple and cost-effective burner developed in laboratory allowed the production of several nanoparticles as HA, alumina, and zinc oxide (Trommer et al. 2009, 2010).

The precursor solution does not belong to the equipment. However, a special attention must be given to it, which has strong influence on the final properties and morphology of the powders produced by the FS method. This is also a subject of this chapter, where the differences between the different compounds used to prepare the precursor solution are discussed.

4.1 Atomization Devices

As mentioned before, basically the FS method comprises the combustion of a specific precursor solution, the powder formation and its further collection. Thus, when the combustion of liquid fuels is an important feature, atomization is a critical stage and plays an important role in the process, once it increases the surface of the fuel and consequently makes its vaporization easier. Considering the wide industry production, burning of liquid fuels in the sprays form can provide a considerable part of our energy resources. For this reason, it is very important to understand the most favorable spray conditions for optimal performance of the appliances. The complexity of the spray combustion process does not make this task easy. Beginning with the injection to liquid breakup, dispersion, and mixing with the air, all of these processes affect spray performance and the emissions generated (Sornek et al. 2000). Atomization also allows the fuel and comburent mixture, which is expected to optimize the combustion process (Santos 2005). Thus, the use of the atomization step aims to spray fine droplets into a well-controlled hot zone, such a flame during the FS synthesis (Teoh 2007).

Atomization has several and different definitions. For example, the transition from a compact volume liquid to dispersed small droplets can be briefly described as atomization (Bremond et al. 2007). Another definition of atomization is the breaking of a liquid film to droplets, which increases its surface area and consequently increases its combustion and vaporization rates. In a simple way, atomization can be also described as the production process of an aerosol or spray (Hickey 1996). The term aerosol was created in 1920 as an analogous term to hydrosol, which comprises a liquid stable suspension of solid particles (Hinds 1982).

Most of the industrial process aims to control the nature of the spray, and then uses it in a specific application. Consequently, atomization is not a subject restricted only to engineering. Even the medicine can apply the principles of atomization for a specific medicine. An example of this is the therapeutic bioengineering, which is motivated by the development of medicines such as inhaled insulin. The use of medicine in the aerosol way comprises the development of both particles and aerosol, and the further created by the atomization of a liquid solution or suspension that contains the medicine (Edwards and Dunbar 2002).

However, atomization process requires energy to produce a large area (considering a liquid as starting situation) and the further transport of the atomized fluid. Usually, the energy available to the conversion of the jet to small droplets (in this case, the aerosol) is insufficient, which justifies the use of a gas stream with a specific velocity to pneumatically disintegrate the emerging liquid. Several are the types of forces that can be employed in the atomization process. We can easily cite the pressure, electrostatic energy, and ultrasonic energy as examples. Consequently, the main atomization devices are the ultrasonic nebulizer, rotation atomizator, and two fluids jet, as described in Fig. 4.1 (Nandiyanto and Okuyama 2011).

FS method allows the development and use of alternative atomization devices, in laboratory, as shown Fig. 4.2. In this example, the main goal of the construction of

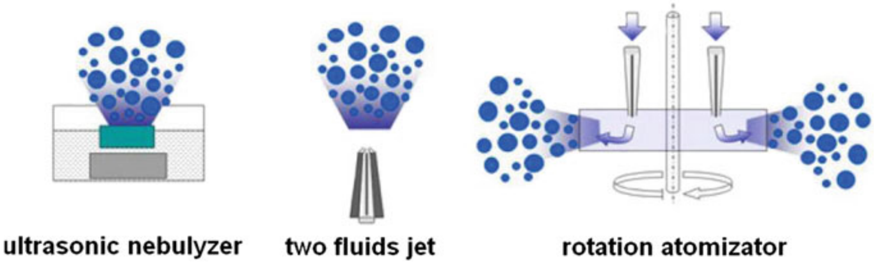


Fig. 4.1 Different atomization devices used to produce sprays

Fig. 4.2 Example of an atomization device developed in laboratory to produce a spray, which is driven to the pilot flame

this alternative atomization device was the production of a fast process with low cost to produce materials such as alumina, zinc oxide, and hydroxyapatite (HA) (Trommer et al. 2009, 2010). This alternative atomization device comprises basically two concentric needles. Through the inner needle (0.6 mm diameter) flows the precursor solution, while through the bigger one (1.5 mm diameter) flows the atomization gas (compressed air at 2 L/min). The spray produced in the atomization device is further direct to the pilot flame, and the combustion occurs.

The above discussion showed how important atomization is in the production of nanomaterials using the FS method. Thus, the parameters of the produced spray must be controlled, aiming to optimize the characteristics of the spray. The droplet size as well its uniformity depends on the solution characteristics (such as viscosity and surface tension), geometry of the nozzle, flux through the nozzle and air pressure (when two fluids are used). As discussed in the Chap. 3, the droplet size is one of the parameters that determine the final particle size of the product. Thus, it is very important to measure the droplet size of the spray produced in the atomizer. There are several techniques which can be used to measure the droplet size. These techniques may comprise the use of optical image and Fraunhofer laser diffraction (Mueller et al. 2003). However, in many situations these techniques require the use of expensive devices.

4.2 Flame Configuration and Burners

The operation parameters (temperature, flux of the gas, and precursor solution composition, etc.) strongly affect the morphology of the nanoparticles produced by FS process (Widiyastuti et al. 2010). These parameters are associated mainly with the flame, and in some times with the entire combustion process (Ozturk and Cetegen 2005). A critical outcome of the FS method is a high enthalpy flame (Teoh 2007). If the flame has not enough enthalpy, probably the final product will be formed by dense nanoparticles of homogeneous size distribution. In the same way, it is very important to have a sufficient combustion enthalpy and a hot flame, for the fast vaporization of the liquid droplets (Høj et al. 2011). When these conditions are reached, the nucleation and particle growth can occur from the gas phase. However, if these conditions are not reached, probably a micrometer sized hollow- or shell-like particles will be formed.

Several researchers that work with the FS process can mention the flame as one of the most important aspects in this technique, as the name of the method suggests. Consequently, a special attention must be given to it. Therefore, the measurement of flame temperature is an important feature in the study of precursor decomposition, and consequently the further nanoparticle formation. Since the early 1990s, a special attention was given to the measurement of the role of flame process variables, such as flame configuration, precursor type, temperature, oxidant composition (Pratsinis 1997).

It is difficult to obtain a precise definition of flame in a few words. Usually, the flame is associated with the emission of light by the overheated gases, even that certain types of flames do not present visible light emission (Gaydon 1953). The visible flame is the occurrence of light, which is produced by the radioactive decay of chemical species, and formed in an excited electronic state (Benvenutti 1999). In the case of flames formed by the combustion of hydrocarbons, the light emission from the reaction zone is observed due to the emission of the radicals OH, CH, and C_2.

The detailed knowledge of the flame phenomena is a big challenge, because several chemical and physical processes can coexist in the flame, creating the phenomenon named combustion. What is really known is that the flame involves a large sequence of reactions in that energy is produced, where a small fraction is the visible luminous energy which results in temperature gradient and atoms/molecules concentration (Junior 2006). Usually, flames are associated with the oxidant process. However, some reactions, as the fluorine and others halogens with hydrogen and hydrocarbons, do not involve oxygen and are considered flames (Gaydon 1953).

Combustion is basically defined as the fast oxidation of any substance, where this oxidation is an exothermic chemical reaction (Edwards 1974). Combustion is considered complete when the oxidation products are completely stable. The combustion of hydrocarbons (C_xH_y), where the stable products of the oxidation are CO_2 and H_2O, can be reported as example. However, this situation depends on specific conditions of combustion, as such the amount of fuel and oxidant used, and its condition in the moment of combustion. Therefore, when the complete combustion occurs, the products which are not stable will participate in the intermediary combustion, and further becoming stable products.

In summary, flames can be classified as explosive or stationary. The first one is characterized by the production of the flame in tubes or closed pipes. Stationary flames are more interesting for industrial applications, as source of heat or as reactive environment. As the FS process uses a stationary flame as source of heat and reactive environment in most of the cases, a special attention in this chapter will be given to it. The stationary flames can be further classified in two following groups: diffusive flames and premixed (Marques 1996; Benvenutti 1999; Santos 2005; Junior 2006). The main characteristic of diffusive flames is the burn of the combustible when in contact with the oxidant, which is usually the atmospheric air. The premixed flames are those in which the combustible and the comburent are mixed before the combustion.

In the specific case of oxide particle synthesis using the FS method, it is possible to use burners with premixed or diffusive flames. It is also possible to use the other two types of flames: premixed flames with a precursor jet and spray flames (Johannessen et al. 2004). The first one consists of a jet of the precursor, which contains the specific compounds for nanoparticle formation, in a gas stream and injected in a flame. The further type of flame is based on the feed of an organic solution containing the compounds in a nozzle and assisted by air, where the spray is formed and burned in the flame.

In Fig. 4.3, the classification of several types of flames (premixed and diffusion) is presented (Roth 2007).

The most famous example of a premixed flame was first described in 1855 by Bunsen, in a device that was obviously named Bunsen burner (Gaydon 1953). In this specific type of burner, the premixed gases are guided through the tube of the burner in a rate superior than the combustion rate of the mixture. In this situation, it is possible to obtain a stationary flame in the burner. However, the Bunsen burner has limitations, mainly related to the inadequate collect of air and the trend to extinguish the flame when large diameters of tubes are used. To solve this problem, another type of burner was developed and named Meker. This type of burner allows a large collection of air, which increases the flame temperature and, consequently, allows the use of burner with a large diameter (Gaydon 1953). The Meker burner has similar principles to the Bunsen burner, but the great difference is the presence of a metallic net in the top of the burner that prevents the flame extinction. Another important feature of the Meker burner is the presence of a hole above the gas orifice that aims to increase the Ar collection.

As discussed before, the flame configuration and the burner are one of the most important devices concerning the FS process. Considering the production of nanoparticles by the FS method, it is possible to identify several types of custom-

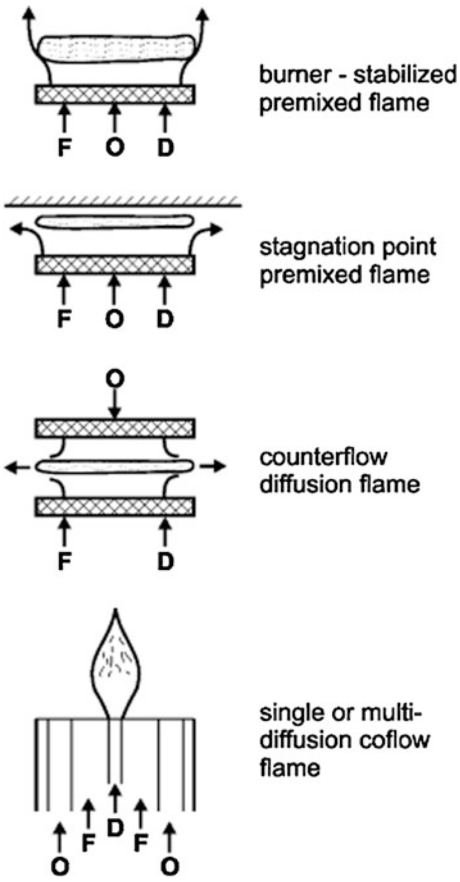


Fig. 4.3 Several types of flames (*Acknowledge* Roth 2007)

made burners in the literature. For example, to produce SiO_2, it is possible to use a diffuse burner designed in such way that the flame is created from the combustion of the mixture of argon and the precursor, argon, hydrogen, oxygen, and air, introduced by five concentric orifices, as shown Fig. 4.4 (Jang et al. 2006).

Silica nanoparticles can be also produced by the FS process, but using a different flame configuration, consisting of a stainless steel burner formed by three concentric tubes, as shown Fig. 4.5 (Mueller et al. 2004). In the case of this burner, the precursor solution and the gas (nitrogen) flow through a specific tube, by the central tube flows methane and through the third tube flows oxygen.

Two important feature in the apparatus used to produce silica nanoparticles shown in Fig. 4.5 must be highlighted: the aid of FTIR spectroscopy to measure the flame temperature and fuel, in this case, a mixture of methane (CH_4) and hexamethyldisiloxane (HMDSO).

Silica nanoparticles are one of the wide ranges of ceramic materials that can be produced by FS process. But it is possible to prepare, for example, bioceramic materials such as HA. HA nanopowders can be produced using an apparatus

Fig. 4.4 Scheme of the experimental equipment used to produce nanoparticles of SiO_2 by the FS process (*Acknowledge* Jang et al. 2006)

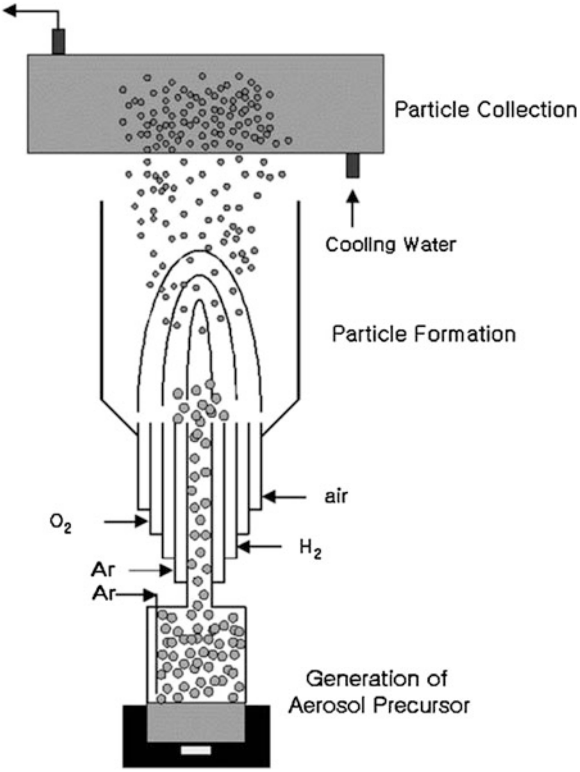
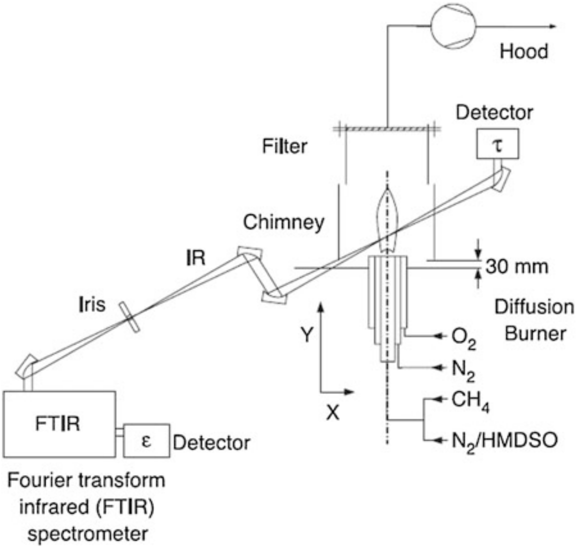


Fig. 4.5 Production of silica nanoparticles in a methane–oxygen diffusion flame (*Acknowledge* Mueller et al. 2004)



consisted basically of an ultrasonic droplet generator, a flame and a quartz tube reactor, and a powder collection system (Cho and Kang 2008). In the case of this specific equipment, to create the flame, propane and oxygen were used. Thus, the droplets produced from the precursor solution are driven to the diffusive flame through a central orifice, using oxygen as the gas.

Most of the work reported in the literature related to the FS process describes the use of special orifices to inject the precursor solution and the gas. Usually, these orifices are placed perpendicularly to the pilot flame set. However, it is also feasible the use a different configuration, which aims to develop a cost-effective device, in opposite to this special configuration observed in the usual burners (Benfer and Knözinger 1999). In this different configuration, the main flame is formed when the atomized precursor solution intercepts the pilot flame, as shown Fig. 4.6 (Trommer et al. 2010). One of the drawbacks of this burner is the requirement of a flammable precursor solution, for example, prepared with ethanol as solvent of the precursor salts. Thus, when in contact with the pilot flame, the precursor solution burns and consequently creates the main flame.

To produce Lu_2O_3 nanoparticles, a custom FS burner can be also built (Baker et al. 2012). This special apparatus is basically composed of a two phase nozzle consisting of a central capillary tube surrounded by a ring of pilot flames. Once the pilot flames are ignited, a co-flowing stream of O_2 and the liquid precursor are fed through the central capillary tube.

It is also possible to prepare strontium titanate phosphor particles using an ultrasonic droplet generator and a special burner (Kang et al. 2002). In this equipment, the flame nozzle is formed by five concentric pipes and using propane as the fuel and oxygen as an oxidizer, as shown Fig. 4.7. The droplets provided by the generator are then supplied to the diffusion flame and the reactions occurred. Finally, the ceramic material is obtained. The temperature of the diffusion flame can be controlled by changing the amounts of propane, oxygen, and carrier gas.

Fig. 4.6 Scheme of the main flame created after the contact of the atomized precursor solution with the pilot flame (Bunsen burner)

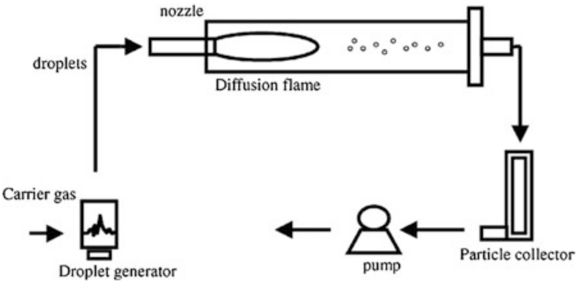


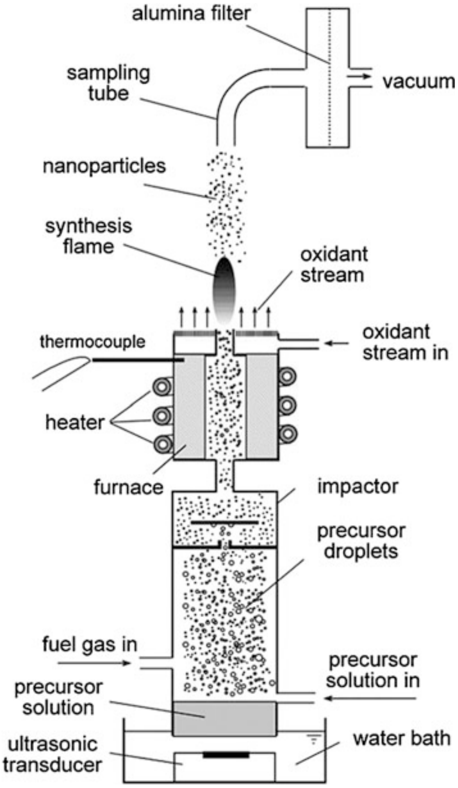
Fig. 4.7 Scheme of the FS apparatus used to produce strontium titanate phosphor particles (*Acknowledge* Kang et al. 2002)

Another important question concerning the burner is the fuel used to create the main flame. In some cases, the type of fuel used can define the crystalline phases observed in the final powder. For example, during the synthesis of alumina, the material was mainly α-$A1_2O_3$ with a hydrocarbon–oxygen flame, whereas it was mainly γ-$A1_2O_3$ with an oxyhydrogen flame (Pratsinis 1997). The most simple and cost-effective fuel is the liquefied petroleum gas (LPG), which is widely employed in industrial burners and distributed in large scale by oil companies. Briefly, this compound is formed by a mixture of paraffinic hydrocarbons (propane, n-butane, and isobutane) and olefinic (propene, *n*-butene, and isobutene), in different ratios. One important thing concerning the fuel is that the use of fuel gas to create flames, such as propane and hydrogen, can achieve high temperatures above 2000 °C (Kang et al. 2002). The variation of the amount of fuel and oxidizer gas allows the control of the flame temperature, and consequently the microstructure of the material.

One alternative way to increase the flame temperature, and consequently supply more energy to the nanoparticle formation, is the use of a jet of oxygen as oxidizer gas (Baker et al. 2012). The use of oxygen gas to increase the flame temperature is one important parameter because the process temperature has the most drastic effect on process and product characteristics (Pratsinis 1997). Even the oxygen composition can present a large effect on the nanoparticle morphology. For example, during the synthesis of titania (TiO_2), the use of pure oxygen in a diffusion flame reactor can result in spherical anatase titania particles while air caused a significant fraction of rutile (Pratsinis 1997). Moreover, the use of oxygen causes a fast consumption of fuel, higher temperatures and short flames that accelerate precursor oxidation and facilitates the particle sintering.

Because FS is a versatile technique, where its apparatus configuration can be easily tailored, some devices can be included in the design of the equipment. For example, it is possible to incorporate an impactor in the apparatus before the aerosol entered a flame to form yttria particles, as shown Fig. 4.8. A round-jet impactor is used to remove the large precursor droplets, so that the product Y_2O_3 particles were all smaller than a critical size of approximately 1.5 μm (Guo et al. 2009).

Fig. 4.8 The flame spray pyrolysis apparatus used to produce Y_2O_3 particles (*Acknowledge* Guo et al. 2009)



Another example of diffusion flame burner consists of three concentric tubes, as shown Fig. 4.9. In this device, an argon flow carrying the precursor (HMDSO) vapor is introduced through the central tube, meanwhile CH_4 and O_2 flowed through the middle and outer tubes, respectively. Another Ar flow (branch) was introduced into the central tube in order to further control the reactant flow rate.

The precursor solution, gases, and flame also have influence on the temperature of the FS process. Moreover, a good and optimized design of the burner is important because temperature plays a significant role in the particle formation process. For example, the increase of the flame temperature can enhance homogeneous nucleation, which leads to smaller particles in higher numbers (Pratsinis 1997). The concentration of the precursor solution combined with the influence of flame temperature (particle temperature) and the residence time of particles in the flame have a significant importance on the particle morphology (Roth 2007). Therefore, the flow structure and turbulence is of major importance as it determines species transport and reactant mixing, flame quenching by air entrainment, the droplet-particle residence times and effectively product particle size, polydispersity, morphology, homogeneity, and crystallinity (Heine et al. 2006).

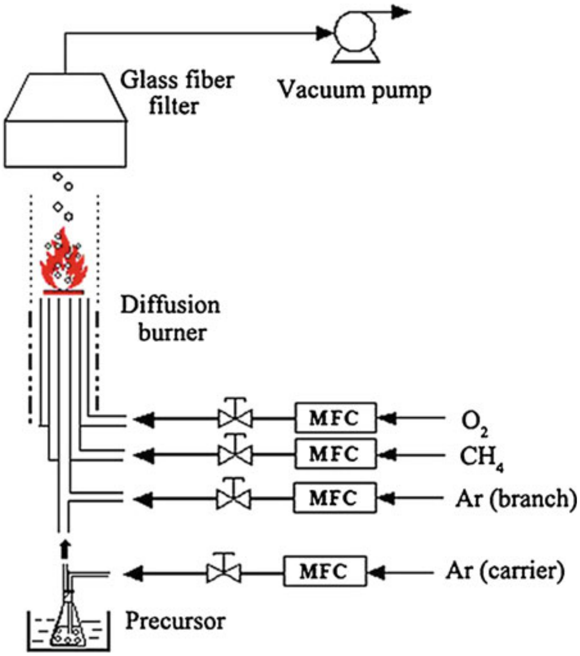


Fig. 4.9 The experimental set-up including precursor feeding system, diffusion flame burner (*Acknowledge* Chen et al. 2013)

4.3 Powder Collector Systems

After the particle formation in the flame, the solvent-free particles must be collected. Usually, it is necessary to remove the nanoparticles from the gas stream to a place where it can be collect, and further used for the final interest. Thus, to separate the final product from the gas stream, several types of powder collector systems can be used, for example, baghouse filter, electrostatic precipitator, and cyclone (Nandiyanto and Okuyama 2011). Each of these equipments has advantages and disadvantages, and usually its use is related to the apparatus employed to produce the powders. Therefore, the nanoparticles' production rate has influence on the type of powder collector system used.

In the case of industrial FS plants, the particles are often collected on filters (Johannessen et al. 2004). However, it is also possible that the hot product gas containing the particles can be applied directly in other product engineering concepts.

In some situations, the cost of the powder collector system has to be considered. The competition increases the necessity of the development of new devices to collect the nanoparticles. One example is the simple device used to collect alumina and HA powders, as shown Fig. 4.10 (Trommer et al. 2009, 2010). Basically, this powder collector system comprises a stainless steel chamber, where a metallic mesh with 25 μm opening (ASTM no. 500) is coupled perpendicular to the gas stream, retaining the powder in the own mesh. When the metallic mesh was saturated with

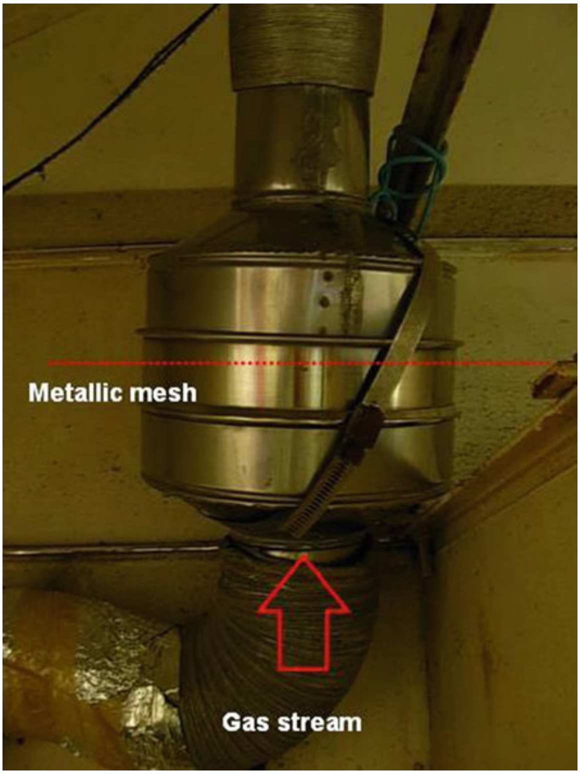


Fig. 4.10 Prototype of the powder collector system comprised of a metallic mesh coupled perpendicular to the gas stream

the particles, the equipment was turned-off (flame extinguished) to remove the powders.

Another important powder collector system widely used in the FS process is the baghouse filter. In this device, the powder is accumulated in the bottom cone of the filter, and at fixed times, it is discharged usually through a butterfly valve or shutter. In industrial plants, after the discharged from the baghouse filter, it is possible to pneumatically convey the final product to a packaging station or directly filled into containers. Several baghouse filters were used to collect different types of nanoparticles. For example, when silica powders were produced using the FS method, the baghouse filter with four PTFE-coated bags and 1.7-m^2 total filtration area to collect the product was used to collect it (Mueller et al. 2004). This powder collection system was suitable for this apparatus because the production rate of silica nanoparticles was up to 1.1 kg/h. It was possible to collect the particles using a short reverse pulse of air into each filter periodically.

After the synthesis of SiO_2 nanoparticles from sprayed droplets of tetraethylorthosilicate (TEOS) by the FS process, the nanoparticles can be easily collected on the surface of a cold glass tube by thermophoresis. This is another example of a simple device used to collect the nanoparticles (Jang et al. 2006).

Sometimes, it is necessary to use a powder collector system that allows the collection of a wide range of nanoparticles. For example, to collect a wide range of materials such as $A1_2O_3$, Mn_2O_3, ZrO_2, and Y_2O_3–ZrO_2 prepared by the FS processing, it is possible to use a parallel plate electrostatic precipitator (Karthikeyan et al. 1997). This powder collector system consists of a pair of polished (100 × 100 × 2 mm^3) stainless steel plates, which are separated by a 10-mm-thick ceramic insulator. It is necessary to use an electric field when an electrostatic precipitator is used. Thus, an electric field of 6 kV/cm in the electrostatic precipitator is used, and the particles are collected on the plates by electrophoresis (Karthikeyan et al. 1997). However, when electrostatic precipitator is used, one important thing to be regard is water vapor condensation, which can affect the removal of nanoparticles in the precipitator. A simple way to eliminate the presence of water is to warm the precipitator, for example, at 180 °C (Widiyastuti et al. 2010).

In some circumstances, with the aid of a vacuum pump, it is also possible to use a glass fiber filter to collect Pd/TiO_2 nanoparticles synthesized in a flame (Mekasuwandumrong et al. 2011). This type of filter can be used to collect flame-made nanosized spinels of $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ (Ernst et al. 2007).

As reported before, one of the main advantages of the FS method is the flexibility. To reinforce this statement, the FS method allows the possibility of powder collector system removing and replacing it by a substrate. Thus, instead of a nanoparticle powder material, it is possible to obtain a coating. However, the coating is only produced if a suitable substrate (roughness, thickness, adequate material, etc) is placed at the correct position from the burner. In the last years, FS of nanostructured films has received much interest due to characteristically high growth rates, uniformity, and polycrystalline deposition quality. When the FS deposition process is compared to usual techniques, such as wet chemistry routes (sol–gel), it presents several advantages as the production of nanostructured films in a single step, which innately incorporates all the requisite basic mechanisms (Zhang et al. 2012). Deposition of nanostructured thin films by FS is a single continuous operating process, where the precursors are converted to monomers by oxidation, which produces a supersaturated vapor that undergoes nucleation to form primary particles. These particles grow via surface growth and agglomeration to form aggregate nanoparticles, finally depositing and sintering on a substrate to construct a porous film (Zhang et al. 2012).

Deposition can take place at several substrates in a wide range of temperatures, and the particle morphology can affect the microstructure of the coating (Strobel and Pratsinis 2007). For example, it is possible to replace the electrostatic precipitator (powder collector system) by a grit-blasted substrate, and directing the burner to the surface, a coating is produced (Karthikeyan et al. 1997). The same principles of the FS method, but removing the powder collector system, also allowed the production of HA coating on stainless steel substrate (Trommer et al. 2007). With the aid of FS principles and replacing the powder collector system by float glass substrates, transparent conducting aluminum doped zinc oxide (ZnO:Al) thin films can be produced (Muiva et al. 2011).

Another approach employed to rapidly synthesize nanostructured $LiMn_2O_4$ films by FS deposition comprises initially the preparation of a specific precursor solution of lithium acetylacetonate and manganese acetylacetonate in an organic solution. The precursor solution is then supplied through a flame spray pyrolysis (FSP) reactor. After this, the spray is ignited and stabilized by a premixed methane/oxygen flame ring surrounding the FSP nozzle, as shown Fig. 4.11. Thus, $LiMn_2O_4$ nanoparticles are formed by combustion and deposited onto a current collector. The use of two different types of current collectors, i.e., stainless steel and aluminum coated with carbon-based primer shows how the FS method is a versatile technique in the production of nanostructured materials with different morphologies.

One of the major applications of the FS method in the field of film deposition is the production of optical fibers for telecommunications, mainly by the deposition using FS of doped-silica particles (Strobel and Pratsinis 2007). With the FS process, it is possible to obtain a film by precursor droplets, precursor/product vapor, or product particles with different degrees of agglomeration, depending on the stage of particle formation upon arrival at the substrate (Strobel and Pratsinis 2007). A schematic illustration of flame deposition processes used to produce films is shown in Fig. 4.12.

Graphene is one of the recent technological materials and can be also obtained as a film using an apparatus based on the FS process. In this case, graphene films can be grown in open atmosphere on metal substrates using a multiple inverse diffusion flame burner with methane as fuel (Memon et al. 2013). Several materials can be used as substrate, such as copper, nickel, cobalt, iron, and copper–nickel alloy. The type of substrate along with its temperature (usually 750–950 °C for copper and 600–850 °C for nickel and cobalt) and hydrogen treatment has a strongly impact in the uniformity

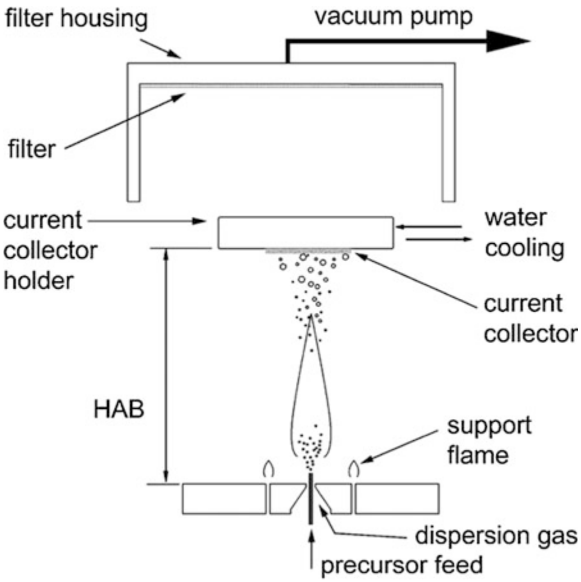


Fig. 4.11 Scheme of the deposition of $LiMn_2O_4$ thin film using the flame spray method (*Acknowledge* Chew et al. 2009)

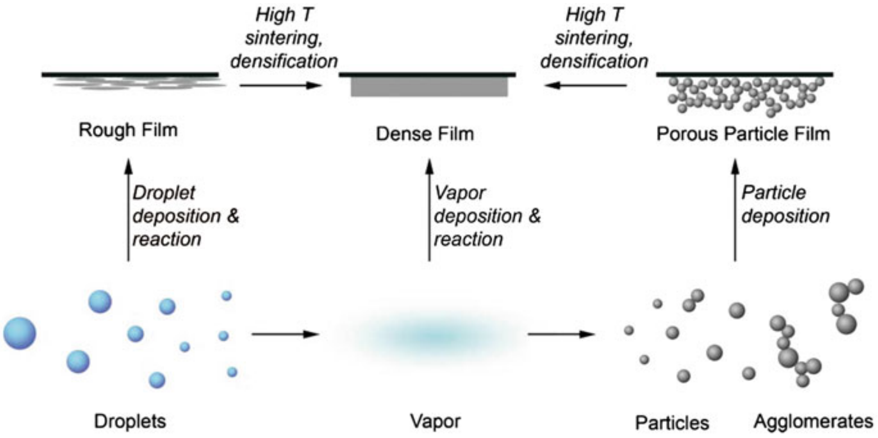


Fig. 4.12 Scheme of the film deposition using the FS process (*Acknowledge* Strobel and Pratsinis 2007)

of the graphene films. FS of graphene offers several advantages, such as the potential for continuous production at reduced costs. When utilizing combustion, the hydrocarbon gas provides both the high temperature and carbon species necessary for growth, resulting in an efficient and robust process (Memon et al. 2013).

Of all the devices that comprise the FS apparatus, the particle collector system is sometimes disregarded, because it is only a place where nanoparticles are collected. However, it needs a special attention, as given to the burners, atomization device, and precursor solution. For example, in the synthesis of alumina (Al_2O_3), the crystallization of the material was observed due to the fast quenching occurred after the particles leave the flame, as a result of the special geometry of the particle collector used (Pratsinis 1997).

4.4 Precursor Solutions

In this chapter, an extensive discussion about the apparatus used in the FS method was done. Each of the devices here described and that comprises the full equipment has its importance. However, the precursor solution used in this equipment cannot be forgotten. Thus, during the preparation of a precursor solution that will be used in FS apparatus, the following requirements are desired:

- containing the necessary ions for the nanoparticle formation;
- employ a solvent that can be atomized in the atomization device;
- burn when in contact with the main flame;
- easy to prepare and cost-effective;
- free of precipitates that can interrupt the flux in the atomization device.

These characteristics are important not only because it is desired a nanomaterial with high purity at the end of the process, but because the precursor solution used in the FS process affects the flame temperature, particle size, and crystalline structure (Qin et al. 2005).

During the development of a precursor solution, it is recommended to consider the equipment, flame, and final morphology of the product (crystalline phase, particle size, etc). For example, using a precursor solution consisted of the salts calcium acetate and ammonium phosphate, both diluted in ethanol and water, it is possible to obtain HA using the FS method (Trommer et al. 2009). In this specific case, it was necessary to adjust the Ca/P molar ratio in the precursor solution to 1.65, which is equivalent to the biological HA. It can be done by the addition of a specific amount of calcium acetate and ammonium phosphate.

In the production of Lu_2O_3 nanoparticles using the FS method, a precursor solution containing $Lu(NO_3)_3 \cdot 6H_2O$ dissolved in deionized water can be used (Baker et al. 2012). After this, the nitrate solution was purified by crystallization and subsequent washes followed by filtration. Then, batches of $Lu(NO_3)_3 \cdot 6H_2O$ were dissolved in ethanol to obtain the final FS nanoparticle precursor solution.

During the preparation of a precursor solution, it is possible to use several chemical compounds, such as salts, solvents, and fuels. Concerning the precursor salts, organometallic compounds are strongly recommended in the FS process, mainly because of its volatility. However, the high market price and the difficulty observed in its handling without moisture do not make them suitable to be used as a precursor salt. Considering a further scale-up to industrial manufacturing level, it is strongly desired the reduction of the production costs. One alternative to achieve this goal is the use of inorganic metal precursors (e.g., nitrates) dissolved in water that also has a small carbon footprint. But the use of this precursor solution has a drawback. Such precursor solutions tend to form inhomogeneous mixtures of nanoparticles by gas-to-particle conversion and much larger, spherical or irregular particles that are made by droplet-to-particle conversion (Rudin et al. 2013).

In some circumstances, when a nitrate salt is chosen as precursor salt, it is necessary to add a fuel because nitrate is an oxidant and requires the use of a fuel as reduction agent. The fuel acts in the formation of a metallic ion complex, consequently facilitating the mixture in a molecular level of the cations in the solution, as well as source of carbon and hydrogen, which in the combustion in the flame delivers heat to the chemical reactions (Sinha et al. 2011). Among the different control parameters in the combustion process, the fuel plays an important role in determining the morphology, phase, and particulate properties of the final product (Aruna et al. 2009). The most commonly used fuels for combustion synthesis are as follows: urea, glycine, oxalyldihydrazine (ODH), carbohydrazide (CH), tetraformaltrisazine (TFTA) N,N-diformylhydrazine (DFH), and hexamethylenetetramine (HMT). Urea and glycine are the most attractive and popular fuels to produce ceramic powders with controlled stoichiometry using the FS process (Aruna and Mukasyan 2008). Urea is also considered a weak complexing agent. However, urea at the same time has a low cost and is source of energy. Glycine is recognized as a strong complexing agent (Lenka et al. 2008).

The use of nitrate as precursor salt and a fuel (urea, glycine, etc) usually requires the calculation of the relative amount of these compounds, according to the total valence of the oxidant and reducing reagents. For this calculation, the knowledge of the combustion reaction is necessary, which considers nitrate and the fuel. This procedure is widely employed in a similar process of FS, named combustion synthesis and that produces nanoparticles of ceramic materials. Based on the combustion reaction, two situations are possible: stoichiometric reaction or non-stoichiometric reaction. In the first one, the ratio of fuel to oxidant is determined in such way that the total valence of reducing agents is equal to the total valence of the oxidants. When this ratio is obtained, the reaction is described as stoichiometric. An intentional deviation in the fuel to oxidant ration due to the use of one compound in excess or deficiency is named as non-stoichiometric (Lenka et al. 2008).

An example of the use of different fuels (urea, glycine, and sucrose) in the precursor solution, considering the total valence theory and the stoichiometric condition, is the production of zinc oxide by FS using zinc nitrate (Trommer 2011). Thus, to determine the amount of fuel (in weight) to be used and considering 1 mol of zinc nitrate, it is necessary to describe the combustion reactions. Equations 4.1–4.3 briefly describe the stoichiometric combustion reactions considered for the calculation of the amount of urea, glycine, and sucrose in the precursor solution. Again, zinc nitrate was used as precursor salt. The term named as *x* represents the amount of fuel, in mol, according to the total valence of the salts used.

$$\mathrm{Zn(NO_3)_2{\cdot}6H_2O} + \mathbf{x}\,\mathrm{CO(NH_2)_2} \tag{4.1}$$

$$\mathrm{Zn(NO_3)_2{\cdot}6H_2O} + \mathbf{x}\,\mathrm{C_{12}(H_2O)_{11}} \tag{4.2}$$

$$\mathrm{Zn(NO_3)_2{\cdot}6H_2O} + \mathbf{x}\,\mathrm{C_2H_5NO_2} \tag{4.3}$$

The use of stoichiometric or non-stoichiometric condition in the precursor solution has influence in the final morphology and crystalline phases of the nanoparticles, once the fluid dynamics of the flame are different for each precursor solution. In the next chapter, example of the zinc oxide nanoparticles prepared with different fuel conditions is given.

Concerning the solvent, used to dissolve the precursor salts and the fuel, ethanol (C_2H_5OH) is regarded as one of the most used solvent. The main reason for this is its flammability in the flame, which releases more energy to the chemical reactions that leads to the nanoparticle formation. Therefore, the use of ethanol allows the atomization of the precursor solution, a fundamental requirement for the production of materials using the FS method.

Water can be also used as solvent to dissolve the precursor salts, sometimes because it has low cost. However, when compared with ethanol, water produces a nanoparticle with no satisfactory properties most of times. For example, the use of ethanol as solvent in the precursor solution can lead to the formation of nanoparticles with better homogeneity, smoother surface structure and stronger photoluminescence intensity than using water as solvent (Qin et al. 2005).

Thus, care must be taken when water is used. Depending on the nanomaterial to be produced, the type of flame and burner, using water is not possible to produce a crystalline nanomaterial. It happens because water removes heat from the flame to evaporate, which usually results in an amorphous material (Trommer et al. 2010). To avoid the presence of amorphous materials, it is strongly recommended to use precursor and solvents more volatibles as possible, where smaller particles can be also produced (Aromaa et al. 2007).

Sometimes, the preparation of the precursor solution can employ both solvents, water, and ethanol. For example, it is possible to use the FS process to produce Lu_2O_3 nanoparticles using a precursor solution comprised of $Lu(NO_3)_3{\cdot}6H_2O$ dissolved in deionized water, which is the first step. Then, the nitrate solution was purified by crystallization and subsequent washes followed by filtration through 0.8-μm filter media, and batches of nitrate solution were dissolved in ethanol to obtain the final precursor solution.

It is also possible to use a mixture of alternative organic solvents, as xylene/acetonitrile mixtures in a ratio of 70/30 in volume (Mekasuwandumrong et al. 2011). The production of nanomaterials with complex structure, for example, the spinels $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$, is also possible with the preparation of a precursor solution with the correct precursor salts (Ernst et al. 2007). During the preparation of the precursor solution, it is also possible to use additives as surfactants, to produce for example Al_2O_3 hollow nanospheres with well-defined structure and shape (Hu et al. 2011).

During the preparation of the precursor solution, the addition of dopants can be done. For example, the addition of a certain amount of palladium acetylacetonate ($Pd(acac)_2$) in the precursor solution comprised of titanium (IV) tert-butoxide (TNB), xylene, and acetonitrile allowed the production of TiO_2 nanoparticles containing 5 wt% Pd as dopant (Mekasuwandumrong et al. 2011).

References

Chen Y et al (2013) One-step flame synthesis of hydrophobic silica nanoparticles. Powder Tech 235:909–913. doi.org/10.1016/j.powtec.2012.10.021

Aromaa M, Keskinen H, Mäkelä JM (2007) The effect of process parameters on the liquid flame spray generated titania nanoparticles. Biomed Eng 24:543–548. doi:10.1016/j.bioeng.2007.08.004

Aruna ST, Mukasyan AS (2008) Combustion synthesis and nanomaterials. Curr Opin Solid State Mater Sci 12:44–50

Aruna ST, Kini NS, Rajam KS (2009) Solution combustion synthesis of CeO_2–$CeAlO_3$ nanocomposites by mixture-of-fuels approach. Mater Res Bull 44:728–733. doi:10.1016/j.materresbull.2008.09.034

Baker C, Kim W, Sanghera J et al (2012) Flame spray synthesis of Lu_2O_3 nanoparticles. Mater Lett 66:132–134. doi:10.1016/j.matlet.2011.08.058

Benfer S, Knözinger E (1999) Structure, morphology and surface properties of nanostructured ZrO_2 particles. J Mater Chem 9:1203–1209

Benvenutti LH (1999) Mapeamento de radicais excitados e cinética de reação para chamas de etanol. Dissertation, Universidade Estadual de Campinas

Bremond N, Clanet C, Villermaux E (2007) Atomization of undulating liquid sheets. J Fluid Mech 585:421–456. doi:10.1017/S0022112007006775

Chew SY, Patey TJ, Waser O, Ng SH, Büchel R, Tricoli A, Krumeich F, Wang J, Liu HK, Pratsinis SE, Novák P (2009) Thin nanostructured $LiMn_2O_4$ films by flame spray deposition and in situ annealing method. J Power Sources 189:449–453. doi:10.1016/j.jpowsour.2008.12.085

Cho JS, Kang YC (2008) Nano-sized hydroxyapatite powders prepared by flame spray pyrolysis. J Alloys Compounds 464:282–287

Edwards JB (1974) Combustion: the formation and emission of trace species. Ann Arbor Science, USA

Edwards DA, Dunbar C (2002) Bioengineering of therapeutic aerosols. Ann Rev Biom Eng v:93–107

Ernst FO, Kammler HK, Roessler A et al (2007) Electrochemically active flame-made nanosized spinels: $LiMn_2O_4$, $Li_4Ti_5O_{12}$ and $LiFe_5O_8$. Mater Chem Phys 101:372–378. doi:10.1016/j.matchemphys.2006.06.014

Gaydon AG (1953) Flames: their structure, radiation and temperature. Chapman & Hall, London

Guo B, Mukundan M, Yim H (2009) Flame aerosol synthesis of phase-pure monoclinic Y_2O_3 particles via particle size control. Powder Technol 191:231–234. doi:10.1016/j.powtec.2008.11.003

Heine MC, Mädler L, Jossen R, Pratsinis SE (2006) Direct measurement of entrainment during nanoparticle synthesis in spray flames. Comb Flame 144:809–820. doi:10.1016/j.combustflame.2005.09.012

Hickey AJ (1996) Inhalation aerosols—physical and biological basis for therapy. Marcel Dekker, USA

Hinds WC (1982) Aerosol technology: properties, behavior, and measurement of airborne particles. Wiley, USA

Høj M, Linde K, Hansen TK et al (2011) Flame spray synthesis of CoMo/Al_2O_3 hydrotreating catalysts. App Catal A: General 397:201–208. doi:10.1016/j.apcata.2011.02.034

Hu Y, Ding H, Li C (2011) Preparation of hollow alumina nanospheres via surfactant-assisted flame spray pyrolysis. Particuology 9:528–532. doi:10.1016/j.partic.2011.06.003

Jang HD, Chang H, Suh Y, Okuyama K (2006) Synthesis of SiO_2 nanoparticles from sprayed droplets of tetraethylorthosilicate by the flame spray pyrolysis. Curr Appl Phys 6S1:e110–e113. doi:10.1016/j.cap.2006.01.021

Johannessen T, Jensen JR, Mosleh M, Johansen J, Quaade U, Livbjerg H (2004) Flame synthesis of nanoparticles applications in catalysis and product/process engineering. Chem Eng Res Des 82(A11):1444–1452

Junior DC (2006) Determinação de temperatura de chama por espectroscopia de emissão. Disseration, Universidade Estadual de Campinas

Kang YC, Seo DJ, Park SB, Park HD (2002) Direct synthesis of strontium titanate phosphor particles with high luminescence by flame spray pyrolysis. Mater Res Bull 37:263–269

Karthikeyan J, Berndt CC, Tikkanen J, Wang JY, King AH, Herman H (1997) Nanostruct Mater 8:61–74

Lenka RK, Mahata T, Sinha PK, Tyagi AK (2008) Combustion synthesis of gadolinia-doped ceria using glycine and urea fuels. J Alloy Compd 466:326–329

Marques CST (1996) Distribuição de espécies luminescentes em chamas explosivas de C_2H_2/O_2. Dissertation, Universidade Estadual de Campinas

Mekasuwandumrong O, Phothakwanpracha S, Jongsomjit B, Shotipruk A, Panpranot J (2011) Influence of flame conditions on the dispersion of Pd on the flame spray-derived Pd/TiO_2 nanoparticles. Powder Technol 210:328–331. doi:10.1016/j.powtec.2011.03.017

Memon NK, Tse SD, Chhowalla M, Kear BH (2013) Role of substrate, temperature, and hydrogen on the flame synthesis of graphene films. Proc Combust Inst 34:2163–2170. doi:10.1016/j.proci.2012.06.112

Mueller R, Mädler L, Pratsinis SE (2003) Nanoparticle synthesis at high production rates by flame spray pyrolysis. Chem Eng Sci 58:1969–1976

Mueller R, Kammle HK, Pratsinis SE, Vital A, Beaucage G, Burtscher P (2004) Non-agglomerated dry silica nanoparticles. Powder Tech 140:40–48

Muiva CM, Sathiaraj TS, Maabong K (2011) Effect of doping concentration on the properties of aluminium doped zinc oxide thin films prepared by spray pyrolysis for transparent electrode applications. Ceram Int 37:555–560. doi:10.1016/j.ceramint.2010.09.042

Nandiyanto ABN, Okuyama K (2011) Progress in developing spray-drying methods for the production of controlled morphology particles: from the nanometer to submicrometer size ranges. Adv Powder Technol 22:1–19. doi:10.1016/j.apt.2010.09.011

Ozturk A, Cetegen BM (2005) Experiments on ceramic formation from liquid precursor spray axially injected into an oxy-acetylene flame. Acta Mater 53:5203–5211. doi:10.1016/j.actamat.2005.08.001

Pratsinis SE (1997) Flame aerosol synthesis of ceramic powders. Prog Energy Combust Sri 24:197–219

Qin X, Ju YG, Bernhard S, Yao N (2005) Flame synthesis of Y_2O_3: Eu nanophosphors using ethanol as precursor solvents. J Mater Res v: 2960–2968

Roth P (2007) Particle synthesis in flames. Proc Combust Inst 31:1773–1788. doi:10.1016/j.proci.2006.08.118

Rudin T, Wegner K, Pratsinis SE (2013) Towards carbon-free flame spray synthesis of homogeneous oxide nanoparticles from aqueous solutions. Adv Powder Technol 24:632–642. http://dx.doi.org/10.1016/j.apt.2012.11.009

Santos LR (2005) Medições de temperatura de chamas de etanol utilizando fluorescência induzida por laser. Disseration, Universidade Estadual de Campinas

Sinha A, Nair SR, Sinha PK (2011) Single step synthesis of $GdAlO_3$ powder. J Alloy Compd v:4774–4780

Stark WJ, Pratsinis SE (2002) Aerosol flame reactors for manufacture of nanoparticles. Powder Technol 126:103–108

Sornek RJ, Dobashi R, Hirano T (2000) Effects of turbulence on dispersion and vaporization of droplets in spray combustion. Procee Comb Inst 28:1055–1062

Strobel R, Pratsinis SE (2007) Flame aerosol synthesis of smart nanostructured materials. J Mater Chem 17:4743–4756. doi:10.1039/b711652g

Teoh WY (2007) Flame spray synthesis of catalyst nanoparticles for photocatalytic mineralisation of organics and Fischer—Tropsch synthesis. Doctorade Thesis

Trommer RM (2011) Obtenção de óxido de zinco nanoestruturado por aspersão de solução em chama e caracterização de propriedades e da atividade fotocatalítica. Dissertation, Universidade Federal do Rio Grande do Sul

Trommer RM, Santos LA, Bergmann CP (2007) Alternative technique for hydroxyapatite coatings. Surf Coat Technol 201:9587–9593. doi:10.1016/j.surfcoat.2007.04.028

Trommer RM, Santos LA, Bergmann CP (2009) Nanostructured hydroxyapatite powders produced by a flame-based technique. Mater Sci Eng C 29:1770–1775. doi:10.1016/j.msec.2009.02.006

Trommer RM, Topolski DK, Takimi AS, Bergmann CP (2010) Evaluation of flame-sprayed alumina powders produced using different ethanol/water ratios in the starting solutions. Part Sci Technol 28:247–261. doi:10.1080/02726351.2010.481587

Wegner K, Schimmoeller B, Thiebaut B, Fernandez C, Rao TN (2011) Pilot plants for industrial nanoparticle production by flame spray pyrolysis. Powder Part J 29:251–265

Widiyastuti W, Balgis R, Iskandar F, Okuyama K (2010) Nanoparticle formation in spray pyrolysis under low-pressure conditions. Chem Eng Sci 65:1846–1854. doi:10.1016/j.ces.2009.11.026

Zhang Y, Li S, Deng S, Yao Q, Tse SD (2012) Direct synthesis of nanostructured TiO_2 films with controlled morphologies by stagnation swirl flames. J Aerosol Sci 44:71–82. doi:10.1016/j.jaerosci.2011.10.001

Chapter 5
Ceramic Products Produced by FS

Abstract The nanomaterials era has enormously contributed to the development of new materials, and the flame spray (FS) method has arrived as a potential technique for its development. One of the great features of the FS method is the wide range of ceramic commodities produced by this technique, as well the wide range of morphologies available for these nanomaterials. Consequently, several types of application for them are possible. In addition, more and more laboratories and companies around the world have been developed and upgraded different FS apparatus. Recent ceramic materials, which years ago were not imagined to be produced by the FS process, are nowadays obtained in a simple step process. Because the FS is a versatile technique, it allows the production of single and mixed oxides, since black carbon to more complex oxides as hydroxyapatite (HA) and spinels. Thus, this chapter presents numerous examples of ceramic nanomaterials produced in different equipments, either commercial or academic, as well their morphology and main applications. One example is black carbon, which is the first material produced by the FS technique and has a large industrial production rate, and even today, is widely used in different industries and products. Recent nanomaterials, such as $Ca_{10}(PO_4)_6(OH)_2$, ZnO, TiO_2, Al_2O_3, Y_2O_3, GeO_2, MgO-Al_2O_3, CoMo/Al_2O_3, and SnO_2, are also describe in this chapter.

Abbreviations

FS	Flame spray
FSD	Flame spray deposition
FSP	Flame spray pyrolysis
HA	Hydroxyapatite
HEV	Hybrid electric vehicle
HMDSO	Hexamethyldisiloxane
MRI	Magnetic resonance imaging
NT	Nanotubes
NW	Nanowires
PEC	Photoelectrochemical
SEM	Scanning electronic microscopy

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Topics in Mining, Metallurgy and Materials Engineering,
DOI 10.1007/978-3-662-47162-3_5

SSF	Stagnation swirl flame
TCO	Transparent conducting oxide
TEM	Transmission electronic microscopy
TEOS	Tetraethylorthosilicate
TEOT	Titanium(IV) ethoxide
TTIP	Titanium(IV) isopropoxide

Ceramic materials with nanometer-scale structures have the potential to improve the mechanical, optical, electronic, etc., behavior of materials over their larger grained counterparts. The enormous potential for nanoparticles production and low cost are two of many reasons for the increased interest in the development and improvement of the flame spray (FS) process (Pratsinis 1997; Roth 2007; Camenzind et al. 2010). Consequently, a large number of academic laboratories around the world have been developed FS apparatus to study and produce several types of nanomaterials. It results in a large number of publications of nanoproducts produced by the FS process. The same behavior is observed in the industry, where several companies have its own FS reactors. The consequence is a large number of commercial products available in the market. Companies such as DuPont, Cabot, Ishihara, Degussa-Hüls, Kemira, Tioxide, Kerr-McGee, Corning Glass, and General Electric have been used the FS method to produce its commercial commodities such as carbon blacks, fumed silica, pigmentary titania, and optical fibers (Kammler 2002). Traditional flame-sprayed powders such as titania and black carbon can be directly collected on filters and packed for shipping, without any further thermal treatment (Johannessen et al. 2004).

Ceramic materials have a large use in different fields of the industry, as for example in biomaterials or photocatalysis area. It results in a large possibility of ceramic materials production and consequently in a large number of techniques available for the production of ceramics. In the recent years, FS technique has shown several advantages over the other techniques, as discussed in the other chapters, which justifies its increasing.

As the first material produced with the FS process, a special attention must be given to black carbon, which is a nanomaterial largely produced with this method. Black carbon and other important ceramic materials are discussed, as follows.

5.1 Black Carbon

Carbon black was the first flame-made product to attain industrial status (Pratsinis 2011). Black carbon is probably the most produced material using the FS process (Stark and Pratsinis 2002), which comprises the spraying of aromatic hydrocarbons (oils) in a natural gas-based flame. Half of this oil is burned to promote the pyrolysis of the other half and then obtain the black carbon.

Black carbon is a black pigment formed by 99.5 % of amorphous carbon with different levels of particle size and with different structures, which attends several industries according to a specific performance requirement. Figure 5.1 presents a TEM image of black carbon powders.

As mentioned in the previous chapter, Cabot is one of the main producers of black carbon. Degussa is another big producer of black carbon. Traditionally, black carbon is the most important fillers in rubber industries. Special properties such as UV protection, electrical conductance, and range of darkness, opacity and reinforcement can be achieved by adding black carbon particles to elastomers, plastics, and paints. Black carbon is widely used in industrial coating applications to impart jetness and to provide tinting strength. Many grades of black carbon are available for use in such applications, and each will affect coating properties differently. Today, the uses of black carbon have expanded to include acting as a pigmenting, UV stabilizing, and conductive agent in a variety of common and specialty products, including tire innerliners, carcasses, sidewalls, and treads, as well as in industrial rubber products, such as belts, hoses, and gaskets.

Black carbon is a raw material largely used as a friction modifier in brake and clutch linings. Its basic properties provide thermal conductivity that helps dissipate the heat generated in braking applications. Black carbon also reinforces friction materials, helping to keep their integrity and thus increasing their usage life.

An intensely black powder, black carbon is produced by subjecting heavy residual oil feedstock to extremely high temperatures in a carefully controlled combustion process. Black carbon is formed in the gas phase (aerosol) and is deposited by thermophoresis onto the smooth walls and ceilings of the chamber; it is then scraped from the surfaces of the chamber and is suspended in fluids for various applications (Pratsinis 2011).

Black carbon is essentially an elemental carbon in a form different from diamond, cokes, charcoal, and graphite. It consists of spherical like particles and is

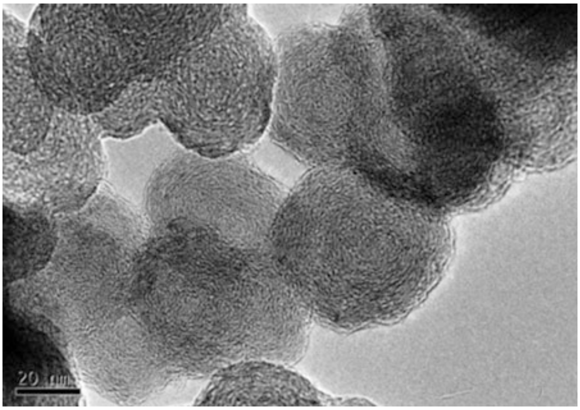

Fig. 5.1 TEM image of black carbon powder (*Acknowledge* Liu 2013)

manufactured by the incomplete combustion of a heavy aromatic feedstock in a hot flame of (preheated) air and natural gas, as described as follow.

$$C_xH_y + O_2 \rightarrow C + CH_4 + CO + H_2 + CO_2 + H_2O \qquad (5.1)$$

The primary units of black carbon are aggregates, which are formed when particles collide and fuse together in the combustion zone of the reactor. Several of those aggregates may be held together by weak forces to form agglomerates. These agglomerates will break down during mixing into rubber, so the aggregates are the smallest ultimate dispersible unit of carbon black.

Black carbon is the oldest material produced by FS. However, even today, it has been deeply investigated. For example, recently, carbon–silica particles are considered to be used as dual phase fillers and developed by Cabot Corporation.[1] This research concerns the treating of carbon black with silica, which is expected to be a new generation of reinforcing agents for rubber. The combination of black carbon and silica is more effective in reinforcing rubber as compared to black carbon alone providing the capability for the manufacture of so-called green tires (Kammler 2002).

5.2 Single Oxides

5.2.1 Titania (TiO_2)

After carbon black, TiO_2 is the second largest industrial aerosol commodity (in value and volume) produced by FS, where about 5 million tons of titanium dioxide are made annually (Pratsinis 2011). Including the nanosized condition, titania usually is consisted of two crystalline structures: anatase and rutile (Aromaa et al. 2007). The use of TiO_2 as a superior white pigment has been known since 1916, but initially the high manufacturing cost of the wet sulfate process prohibited its widespread use (Pratsinis 2011).

Inside the extensive area of FS technique, the production of photocatalytic and anti-bacterial surfaces has arrived as a key opportunity to develop nanomaterials with increased performance (Keskinen et al. 2005). Titanium dioxide (TiO_2), also known as titania, is the main material considered for photocatalytic application, but also strongly used in other practical and industrial applications such as pigments.

In the early 1960s, titania was mainly produced by wet-phase chemistry, entailing huge amounts of sulfuric acid waste. However, the development of the dry "chloride" process, which is solvent-free and produced few by-products, caused a

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[1] http://www.cabot-corp.com/Rubber-Carbon-Blacks. http://www.cabot-corp.com/Silicas-And-Aluminas.

revolution in the production of titania (Stark and Pratsinis 2002). The so-called chloride process is based in the evaporation of metal chlorides prior to their introduction into the flame reactor. This causes a limitation in the process, which is the requirement of precursors with sufficient vapor pressure and thermal stability at moderate temperatures. However, the development of flame spray pyrolysis (FSP) overcame this limitation by directly feeding a liquid precursor–solvent mixture into the flame reactor, atomizing, and igniting it (Wegner et al. 2011). Concerning the chloride process, FS has been employed to easily produce TiO_2 photocatalyst by oxidation of titanium tetrachloride ($TiCl_4$), according to Eq. 5.2 (Moiseev et al. 2011).

$$\mathrm{TiCl_4 + 4O_2 + 2CH_4 \rightarrow TiO_2 + 4HCl + 2CO_2 + 2H_2O} \tag{5.2}$$

However, the chloride process is not the only process used to produce TiO_2 using the principles of FS. The production of titania using FS can be also achieved, for example, by the use of two different precursors materials, titanium(IV) ethoxide (TEOT) and titanium(IV) isopropoxide (TTIP), both dissolved in ethanol and isopropanol (Aromaa et al. 2007). The particle size of the nanomaterial prepared using this specific configuration of the FS technique is in the range of 5–70 nm. The mechanism of titania nanoparticles formation using this process consists in thermal decomposition of the material contained in the droplet, or it hydrolyzes and creates a solid titanium dioxide particle. The chemical reactions presented below promote the formation (hydrolysis or thermal decomposition) of titania using the precursors, i.e., TTIP or TEOT (Aromaa et al. 2007).

Thermal decomposition of the precursor:

$$\mathrm{TTIP\ or\ TEOT \rightarrow TiO_2 + 4C_3H_6 + 2H_2O} \tag{5.3}$$

Hydrolysis of the precursor:

$$\mathrm{TTIP\ or\ TEOT + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH} \tag{5.4}$$

One example of the titania nanoparticles production using the FS processes is shown in the transmission electron microscopy (TEM) image of Fig. 5.2.

As mentioned before, titania has been widely used as a photocatalyst. A commercial photocatalyst named AEROXIDE® TiO_2 P25 has been subject of many studies over the years, including its use in wastewater treatment, the reduction of NO_x in exhaust gases, and the manufacture of anti-bacterial, self-cleaning or anti-fogging surfaces. Because of its high photoactivity, AEROXIDE® TiO_2 P25 is often recognized as the “gold standard” in photocatalysis. Pyrogenic (oxyhydrogen flame) TiO_2 P25, manufactured by Evonik (Germany), usually has a primary particle size of 21 nm and anatase content up to 87 wt%, and in the academic production of titania is considered as a benchmarking material due to its satisfactory activity for most organic contaminants (Moiseev et al. 2011).

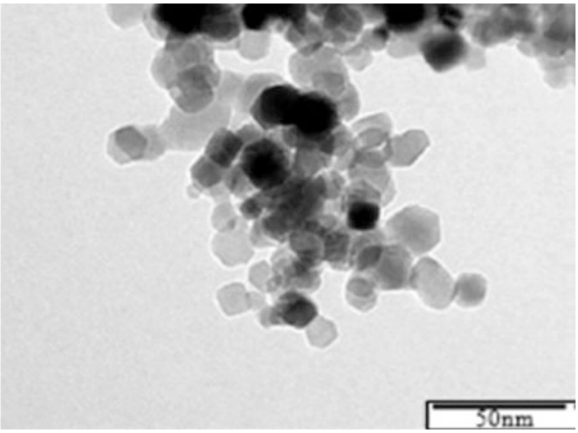

Fig. 5.2 TEM-image of TiO_2 nanoparticles synthesized using the FS process (*Acknowledge* Moiseev et al. 2011)

The earliest chapters considered that in the FSP-made catalysts, it is expected that the characteristics and structural properties of these products are often found to be different from the conventionally prepared catalysts (Mekasuwandumrong et al. 2011). In manufacture of titania pigments, the goal is to produce nearly monodisperse rutile particles lying between 150 and 250 nm to obtain the maximum hiding power per unit mass.

Recent academic publications indicate that the activity of flame-generated TiO_2 materials could be affected by doping agent added into the flame reaction (Moiseev et al. 2011). Dopants can replace Ti in the substitutional sites or be incorporated in the interstitial sites. Additives are routinely used in synthesis of particles to control the morphology and phase composition of product powders (Pratsinis and Vemury 1996). Thus, for the purpose of catalysis, titania is often doped with specific metals. As a quick example, Pd/TiO_2 nanoparticles containing 5 wt% Pd can be synthesized by one-step FS process (Mekasuwandumrong et al. 2011). Recently, copper has been increasingly investigated as a dopant for titania. Consequently, a single-step flame aerosol process can be also used to produce long-wavelength visible light absorption Cu-doped TiO_2 (Sahu and Biswas 2011). FS synthesis of Cu-doped titania has the advantage of allowing the Cu doping with a concentration that can vary from 0 to 15 wt%. The TEM and HR-TEM images of 1 wt% Cu-TiO_2 and 15 wt% Cu-TiO_2 spherical particles are shown in Fig. 5.3.

In some circumstances, other nanoparticles of different oxides are mixed with titania to improve its performance, which is possible using a one-step process as such as FS method. Because of its interesting application in the area of low thermal expansion glass and fatigue resistant optical fibers, it is possible to use flame reactors with a $H_2/O_2/Ar$ flame and feeding $Sn(CH_3)_4$ and $Ti(OC_3H_7)_4$ co-currently, to produce titania/SnO_2 mixed oxides. Usually, particle size of this material ranges between 5 and 12 nm (Ifeacho et al. 2005). One of the great features of the SnO_2/titania mixed oxide synthesis relies in the possibility of production using

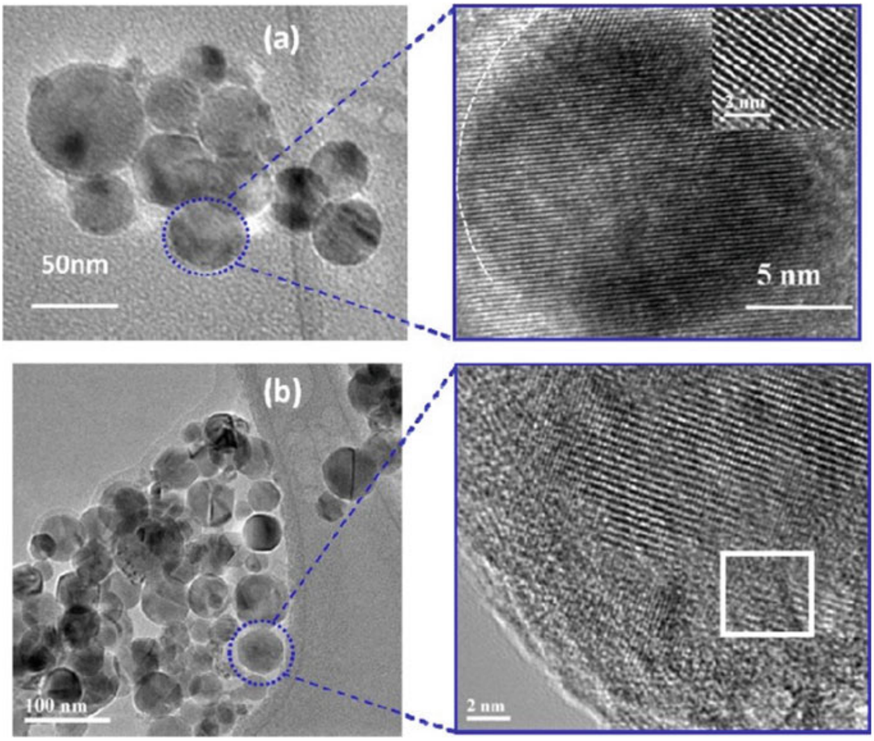

Fig. 5.3 TEM and HR-TEM images of titania doped with **a** 1 wt% and **b** 15 wt% of Cu (*Acknowledge* Sahu and Biswas 2011)

different precursors. One of the process employs the simultaneously oxidation of $TiC1_4$ and $SnCl_4$ in a diffusion flame reactor with methane as the fuel and air as the oxidant allows the production of this mixed oxide. The great advantage is that the SnO_2 addition enhances the transformation of anatase to rutile during the flame synthesis, which is beneficial when titania is used as a photocatalyst (Pratsinis and Vemury 1996).

Flame synthesis of nanostructured films has received much interest due to characteristically high growth rates, uniformity, and polycrystalline deposition quality. As titania is one of the most studied material in the FS process, it is not surprising the production of TiO_2 films. Recently, a novel premixed swirl flame in stagnation point geometry has been developed to synthesize nanostructured TiO_2 films with high quality and homogeneity (Zhang et al. 2012). The high quality of the film can be observed with the aid of scanning electron microscopy (SEM). Figure 5.4 shows the side view of nanostructured TiO_2 films synthesized by the one-step stagnation swirl flame (SSF).

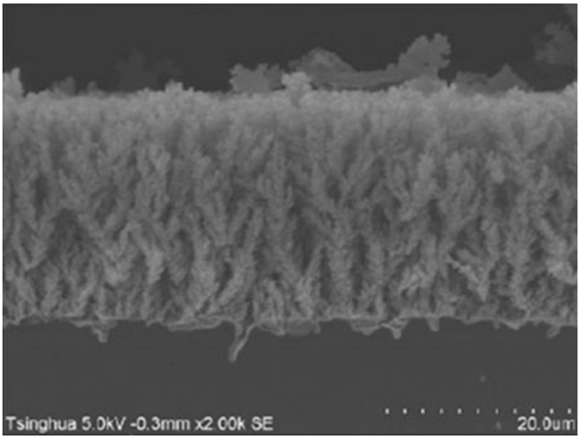

Fig. 5.4 SEM image of the cross section of nanostructured TiO_2 films produced by the stagnation swirl flame (*Acknowledge* Zhang et al. 2012)

5.2.2 Alumina (Al_2O_3)

Aluminum oxide, also known as alumina, with chemical formula given by Al_2O_3 has been used in industry mainly because of its high melting point, stability at high temperatures, high chemical inactivity, and high hardness. When used in the powder form, alumina has several applications that include cutting tools, heat- and wear-resistant materials to high temperature catalyst carriers and membranes.

As a commodity widely used in industry, alumina is a material that has attracted an enormous attention of the researchers in the FS area. Consequently, there are several equipments and precursor solutions available for the production of this oxide. For example, in the presence of a surfactant as droplet stabilizer, it is possible to produce hollow Al_2O_3 nanospheres with well-defined structure and shape via FSP, as shown Fig. 5.5 (Hu et al. 2011). It is possible to observe that the morphology of the material is comprised by hollow micro and nanospheres with well-defined structure and shape, low density, and high specific surface area. The main reason for the synthesis of alumina with this particular microstructure is the use as catalyst support, in drug delivery and controlled release, anti-reflection surface coatings, photoluminescence and optical devices, sensors, solar cells, and rechargeable batteries (Hu et al. 2011).

Using a different route, hollow alumina particles can be produced by the use of a specific flame-based equipment and precursor solution (Trommer et al. 2010a, b). In this process, the starting solution is prepared in a simple route, where only aluminum chloride ($AlCl_3 \cdot 6H_2O$), in a concentration of 1 M, is used as the precursor salt. The main reason for the use of this salt is because it can be easily dissolved in most of the solvents, as for example ethanol and water. Moreover, the easy dissolution allows the preparation of a starting solution free of precipitates, which can interrupt the flux in the atomization device. One important found out of the production of alumina using this specific apparatus is that the use of water as solvent in

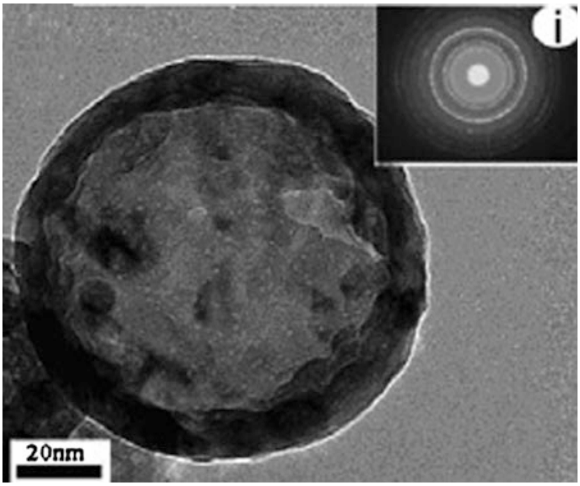

Fig. 5.5 HRTEM image of hollow Al_2O_3 nanospheres with addition of surfactants (*Acknowledge* Hu et al. 2011)

the precursor solutions leads to the production of a powder with an amorphous structure. The synthesis of amorphous alumina powders is related with the fact that water takes energy from the flame to evaporate, instead of supply more energy (as observed with ethanol) to the powder formation.

The production of hollow alumina particles using two different processes demonstrates how versatile is the FS process, allowing the development of new precursor solutions as well the assembling of alternative equipments, but based on the FS principles.

A similar process to the manufacturing of SiO_2 and P25 TiO_2, but based in the oxychloride process, has been recently used by Cabot and Evonik to produce commercial fumed alumina (Pratsinis 2011). The main application of this particular fumed alumina is in the chemical–mechanical polishing used in microelectronics. In this process, aluminum chloride ($AlCl_3$) is employed as precursor salt, but differently from the flame-based process presented earlier; in this case, the aluminum chloride vapor is supplied to the process by sublimation.

To improve the catalyst behavior of alumina, which is expected to show high activity and high selectivity toward direct desulfurization, it is possible to add metals to alumina, in a process named doping. Alumina supported and unsupported cobalt molybdenum catalysts can be prepared by the FS process through the combustion of a specific precursor solution that contains the metallic ions. The precursor solution, in this particular process doped with cobalt and molybdenum, plays an important role in the production of the final product. It is prepared by dissolving tris (acetylacetonato) aluminum, cobalt 2-ethylhexanoate, and molybdenum 2-ethylhexanoate in toluene (Høj et al. 2011). The final product obtained with the FS process is mainly formed by the crystalline phase γ-Al_2O_3, but the minor crystalline phase $CoAl_2O_4$ can be also identified.

5.2.3 Silica (SiO_2)

Silica nanoparticles are one of the main commodities produced by FS process. Because of its high specific surface area, relatively low melting points, special optical properties, high catalytic activity, and unusual mechanical properties, silica nanoparticles are important industrial materials (Yue et al. 2013). Because silica is produced in a flame, it is usually known as fumed silica or pyrogenic silica, being the last not so usual. Fumed silica (SiO_2) is the third largest industrial aerosol commodity by value and the fourth largest by volume (Pratsinis 2011). Fumed silica is one of the major chemical products of industrial importance, and it is produced by flame hydrolysis (Pratsinis 1997).

Today, the main use of silica nanoparticles or fumed silica is as additives in plastics and rubbers, aiming to improve mechanical properties of elastomers. The wide use of fumed silica for polymer reinforcing was strongly connected to the development of the flame hydrolysis process for its manufacture by Degussa, which nowadays is Evonik (Camenzind et al. 2010). Silica is also used in liquid system to improve the suspension behavior and in dental nanocomposites (Jang et al. 2006; Buddhiraju and Runkana 2012). In these applications, the particle morphology, average size, particle size distribution, and phase composition are considered the key characteristics of final product and must be controlled.

The production of fumed silica using the FS process is relatively simple and employs the combustion of $SiCl_4$ in an oxyhydrogen flame. This process was discovered in the late 1930s, where at that time Degussa scientists were looking for a replacement for carbon black (Pratsinis 2011).

It is important to report that nowadays, an important commodity is widely used in telecommunications. Thanks to the contribution of flame technology in the late 1970s, ultrapure silica fiber became the main material used in light guides in telecommunications (Stark and Pratsinis 2002).

Using the FS process, Evonik Industries has produced the extremely versatile product fumed silica and named as AEROSIL®.[2] The final application of AEROSIL® is in the cosmetics industry, where it increases the temperature stability of lipsticks. It is also used in the production of offshore yachts and in the electronics industry. Moreover, this commercial product can be used in silicone sealants which can be found in any bathtub as well as in car paints. In this case, pyrogenic oxides contribute to the optimization of low moisture absorption, mechanical stability and rheological properties as well. It is also possible to mix the silicon dioxide with approximately 1 % aluminum oxide. This product is known as AEROSIL® MOX 80 and is manufactured using the AEROSIL®-process. A different product is AEROSIL® COK 84, which is a mixture of AEROSIL® 200 and highly dispersed fumed aluminum oxide in the ratio of 5:1.

Cabot is another important producer of fumed silica. This company has produced a commercial product named CAB-O-SIL®. This material is extremely versatile and

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[2] https://www.aerosil.com/product/aerosil/en/Pages/default.aspx.

used in a variety of applications, ranging from spark plugs and printing inks to pharmaceuticals, cake mixes, and coatings. The versatility attributed to CAB-O-SIL is related to its high degree of purity and amorphous structure, both of which lead to excellent performance.

Today, several processes are reported in literature for the synthesis of fumed silica. However, the oxychloride process for oxidizing silica precursors, especially $SiCl_4$, remains as the most used process in industry and in academic studies. Briefly, the oxychloride process is described as follows:

$$SiCl_4\,(g) + 2H_2\,(g) + O_2\,(g) \rightarrow SiO_2\,(s) + 4HCl\ \ (g) \tag{5.5}$$

One alternative process for the production of silica nanoparticles involves the combustion of hexamethyldisiloxane (HMDSO) in a co-flow diffusion flame burner, using methane and oxygen as fuel and oxidant, respectively (Yue et al. 2013). The formation mechanism of the silica nanoparticles is presented in Fig. 5.6.

The change in the precursor salt used to produce silica nanoparticles results in a different reaction mechanism in the flame. Thus, using tetraethylorthosilicate (TEOS) instead of HMDSO, it is also possible to produce spherical silica (SiO_2) using the FS process. As consequence of the use of a different precursor solution, in this method, the particle diameter ranges from 12 to 47 nm in average (Jang et al. 2006). Silica nanoparticles obtained by using this process are shown in Fig. 5.7. The overall reaction for the oxidation of TEOS to silica is given in Eq. 5.6.

$$Si(OC_2H_5)_4\,(g) + 12O_2\,(g) \rightarrow SiO_2\,(s) + 8CO_2\,(g) + 10H_2O\,(g) \tag{5.6}$$

As discussed before, silica is widely used as reinforcement agent in rubber and polymers. However, due to the presence of hydroxyl groups in the surface, ceramic nanoparticles (included silica, because it adsorbs substantial amounts of water at their relatively large surface area) produced by FS process are usually hydrophilic (Camenzind et al. 2010). Many technically relevant polymers (e.g., polyethylene, polypropylene, and polystyrene) are non-polar and therefore incompatible with the rather polar surfaces of inorganic particles. It makes the mixing of silica nanoparticles and polymers difficult, with poor filler particle dispersions. One alternative to overcome this problem is to bind organic compounds to the surface of silica nanoparticles. This process is called functionalization and transforms the hydrophilic surface of silica to a hydrophobic one. Thus, functionalization increases the

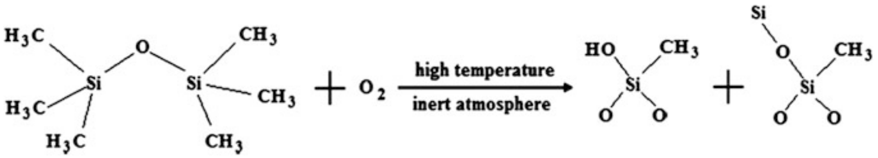

Fig. 5.6 Formation mechanism of the silica nanoparticles using the FS process (*Acknowledge* Yue et al. 2013)

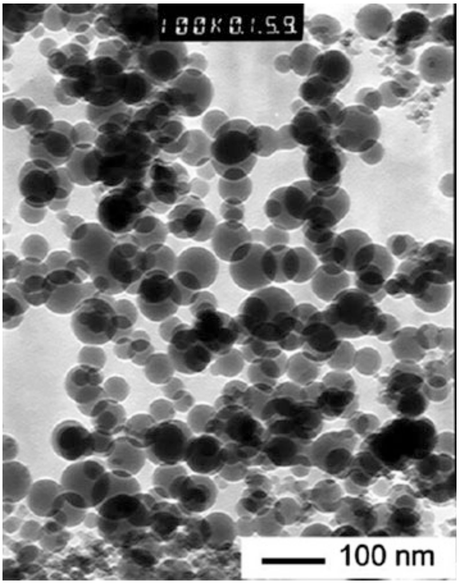

Fig. 5.7 TEM image of silica nanoparticles synthesized by the FSP process (*Acknowledge* Jang et al. 2006)

compatibility between polymer and silica nanoparticles, which reduces the surface free energy and therefore the tendency for particle agglomeration.

Typically functionalizing agents are organochlorosilanes, organoalkoxysilanes, or organosilazanes which can covalently bind to the silica particle surface by formation of Si–O–Si bonds (Camenzind et al. 2010).

5.2.4 Zinc Oxide (ZnO)

Zinc oxide, with chemical formula given by ZnO, is a compound semiconductor with a wide band gap (3.37 eV) that is suitable for short wavelength optoelectronic applications. In the last years, a special attention was given to the application of ZnO in anti-bacterial treatment and UV absorption (Trommer et al. 2010a, b).

It is well known that materials produced by FS are strong candidates for heterogeneous catalysts because they present a high surface area. In addition, the FS process is characterized by the use of precursor solutions containing several metal compounds, which allows the production of multi-metal catalyst materials in a one-step method (Høj et al. 2011).

However, it is possible to use the principles of the flame synthesis to produce highly crystalline ZnO nanorods without precursor solutions. In this case, the precursor solution is replaced by a micro-metallic Zn (Kathirvel et al. 2013). This process involves the addition of micro-metallic Zn particles into a flame, where the precursor reacts and results in the deposition of ZnO on the surface of the powder collector. An example of the material prepared with this method is presented in Fig. 5.8.

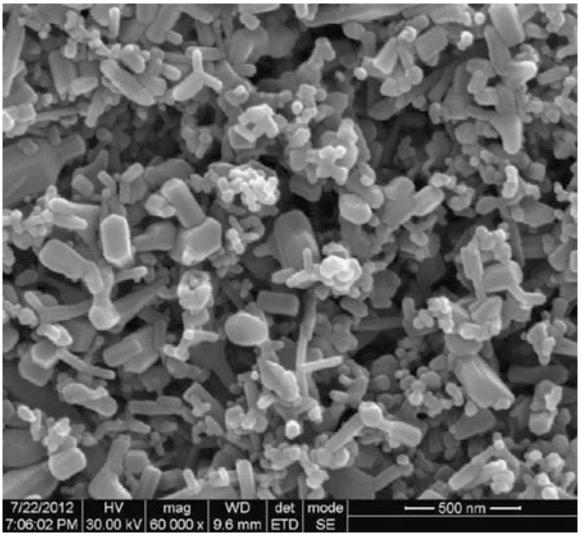

Fig. 5.8 SEM image of the zinc oxide nanorods produced by the FS process using metallic Zn as start material (*Acknowledge* Jang et al. 2006)

Due to the increasing interest in zinc oxide FS, several flame-based methods have been developed to produce this material, especially in the nanometric dimension. An alternative and simple route to produce zinc oxide comprises the use of a Bunsen burner, used as the flame and energy source, and a specific precursor solution. Sometimes, the preparation of the precursor solution, as well the assembling and use of the apparatus, aims the production of a material with low cost. Thus, in this method, the precursor solution can be easily prepared by the dissolution of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), in a concentration of 0.5 M, in ethanol (Trommer et al. 2010a, b). However, nitrate is considered as an oxidant agent. So, it is necessary to use a reduction agent, in this case, a fuel. Urea, with chemical formula given by ($CO(NH_2)_2$), is a good choice to be use as fuel, because it is a weak complexing agent, source of energy and has low cost. After the synthesis of the ZnO using the FS process, the typical morphology of the sprayed nanoparticles is shown in Fig. 5.9. It can be observed that the powder is comprised of primary particles with irregular shapes that remain aggregated. These aggregates, or secondary particles, can be classified as being hard (formed by strong bonding), or soft (weakly bonding by van der Waals forces and easily desagglomerated).

Using TEM, it is possible to observe the individual primary particles of the ZnO powder prepared with the aid of FS technology, as shown Fig. 5.10. For materials produced from precursor solutions containing fuel, the addition of urea causes a disintegration of the primary particles, leading to the formation of nanometric particles. In this specific case of FS process with the aid of a fuel (urea), the combustion of urea in the flame zone supplies an additional heat to the particles, and with the evolution of a large amount of gases, contributes to the formation of nanoparticles. Another beneficial fact for the nanoparticles formation in the FS process is the rapid decomposition of organic compounds in the flame, which

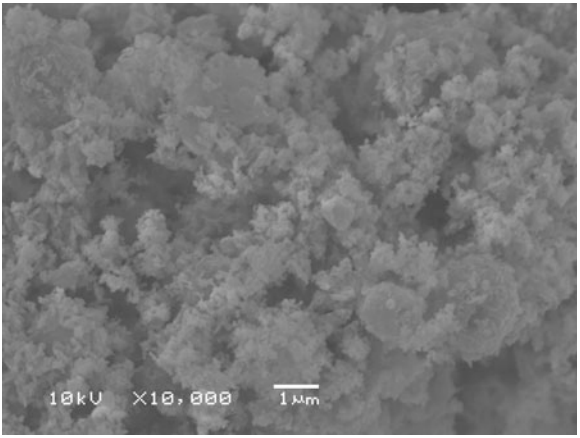

Fig. 5.9 SEM image of aggregated ZnO powder produced by FS

produces a large gradient of pressure inside the submicrometric particles, and is important for breaking the bonding in the particles' core and posterior formation of nanometric particle (Purwanto et al. 2008).

As mentioned before, the FS process allows the producer to tailor several aspects of the process, aiming the production of a material with improved properties. One parameter that can be easily changed is the amount of urea used in the precursor solution. For example, three conditions can be achieved in the precursor solution: (i) stoichiometric condition, (ii) non-stoichiometric, and (iii) without urea. The importance of the amount of urea used in the precursor solution on the morphology of the ZnO powder, in the conditions above mentioned is presented in Fig. 5.10.

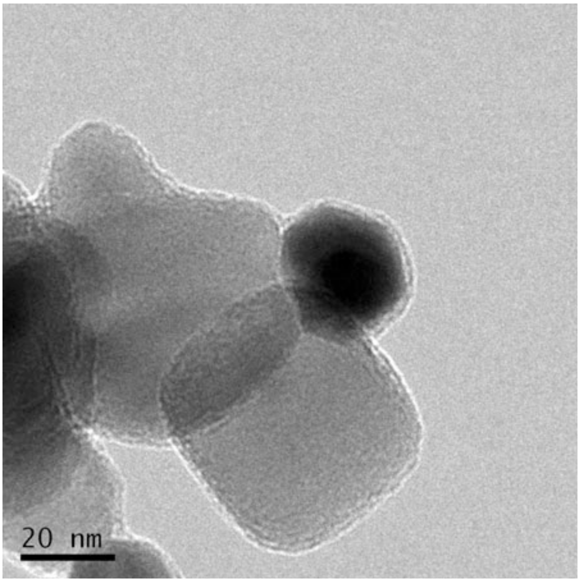

Fig. 5.10 TEM image of Zinc oxide nanoparticles synthesized by the FS process

The ZnO powder produced from the precursor solution containing zinc nitrate without urea shows a particular morphology, clearly different from the others, comprising particles with a structure similar to platelets. The mechanism of particle formation during the FS synthesis of zinc oxide is probably related to the simple evaporation of the solvent (ethanol) and further decomposition of the zinc nitrate existing in the droplets in the flame, leading to the formation of ZnO with morphology of platelets.

For the non-stoichiometric precursor solutions used to obtain ZnO powders by the FS process, two situations are possible: deficiency or excess of urea (both in relation to the zinc nitrate). Despite the different urea/zinc nitrate ratio in the precursor solution, the morphology of the powders produced from non-stoichiometric precursor solutions has no difference. The material produced in this particular condition, i.e., non-stoichiometric, is comprised of spherical particles. This morphology can be related to the droplet-to-particle conversion route that occurs in the flame. In this particle formation mechanism, the droplets of the spray produced in the atomization device are quickly converted in the final product (ZnO powder) through an in situ reaction with the gases or by pyrolysis (Kusters and Pratsinis 1995). The spherical shape is a typical morphology of flame-sprayed particles (Pratsinis 1997). Moreover, the maximum structural stability is reached with a spherical shape, because of the lower superficial energy by volume, which justifies the production of this morphology (Nandiyanto and Okuyama 2011).

Concerning the powder produced using urea and zinc nitrate in stoichiometric condition, the particle formation mechanism is different. First, in the atomization device occurs the formation of the droplets that contain the precursor salt and urea. Because the flame has a high temperature, the zinc nitrate precursor precipitates and decomposes inside the droplet, but still in the presence of urea. Until this stage, the particle formation mechanism is similar to that one observed in the non-stoichiometric precursor solutions. However, in the stoichiometric condition, the fuel (urea) remains in the droplet, and when it reaches a specific temperature due to the flame heating, it decomposes allowing the formation of nanoparticles. It has to be mentioned that, in a first moment, the solvent evaporation or the production of gases increases the pressure inside the droplet, being the primary promoter for the droplet disintegration and further dispersion of the nanoparticles. It is important to highlight that all the mechanisms proposed for ZnO formation occurs in a short time, as discussed in the previous chapters.

This book has strongly demonstrated how versatile the FS process is, mainly in the production of nanoparticles. One of the abilities that this method shows is the possibility of tailoring and modification of the precursor solution. Considering the synthesis of ZnO described above, it is possible to change the fuel used in the precursor solution, keeping zinc nitrate as the precursor salt. For example, urea can be replaced by sucrose or glycine, with chemical formula given by ($C_{12}H_{22}O_{11}$) and (NH_2CH_2COOH), respectively, while using ethanol as solvent. Therefore, as in the case of urea, it is possible to prepare precursor solutions in the stoichiometric or

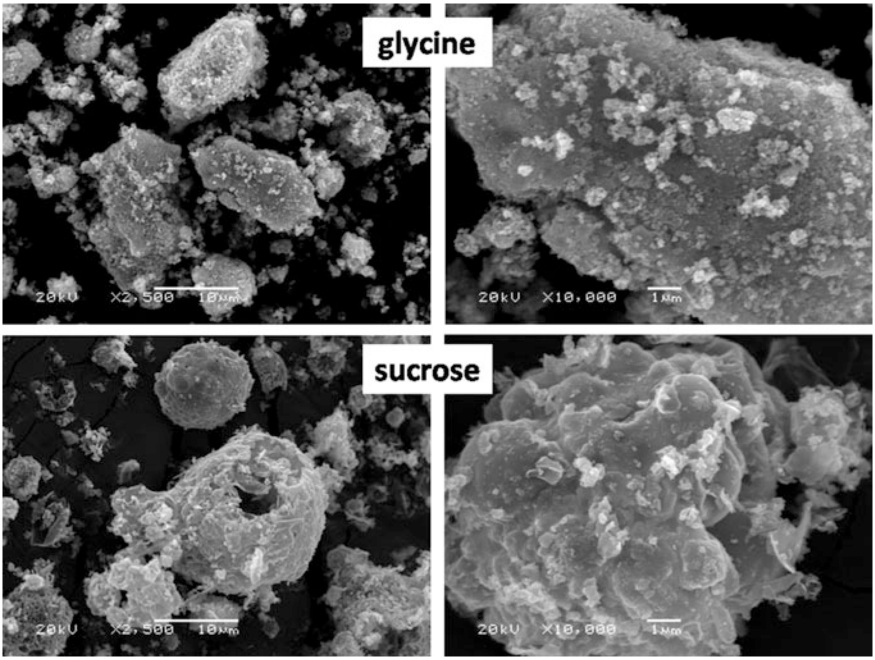

Fig. 5.11 SEM images of zinc oxide powders prepared from precursor solution with the alternative fuels sucrose and glycine

non-stoichiometric condition. The morphology of the zinc oxide powders prepared with glycine and sucrose is shown in Fig. 5.11.

The use of the alternative fuels sucrose or glycine causes a change in the morphology of the ZnO powders, when compared to the use of urea. The use of glycine in the precursor solution leads to the formation of a material comprised of irregular particles with a particle size in the micrometric scale. In opposite, the use of sucrose causes the formation of ZnO powders with a morphology closes to spherical. The particle formation mechanism in this case involves the evaporation of the solvent (ethanol), while the other compounds that will form the ZnO powder remain in the droplet. The decomposition of the precursor will occur inside the droplet. Again, because the flame has a high temperature, it is observed the drying and thermolysis of the precursor particle to create another microporous particle.

The morphology of the powders prepared by using alternative fuels is quite different from the morphology of the zinc oxide powder prepared with urea (considering the stoichiometric condition) in the precursor solution. This dissimilarity observed in the morphology is attributed to a different complexation of the fuels urea, glycine, and sucrose in the precursor solution. Moreover, the difference in the molecular structure of these compounds is another reason for the different morphology.

5.2.5 Zirconia (ZrO_2)

Zirconium dioxide, also known as zirconia and chemical formula given by ZrO_2, is a very important ceramic material, mainly because of its broad range of applications. For example, zirconia can be used as a catalyst, oxygen sensors, in fuel cells, in automobile parts and as thermal barrier coatings on metal components (Tok et al. 2006).

The use of zirconia as a catalyst, especially in the heterogeneous catalysis, is growing up because of its recognized properties. Nevertheless, the application of zirconia as a catalyst or as a catalyst support requires a high specific surface area, which is retained under process conditions (Benfer and Knözinger 1999). This requirement opens an excellent opportunity for the FS process, which is an efficient method for the production of zirconia in nanometric size and with high specific surface area.

Using the FS method, it is possible to produce zirconia nanoparticles in a relative single process (Tok et al. 2006). First of all, it is necessary to prepare the precursor solution. In this case, it comprises a precursor salt, $ZrO(NO_3)_2$, which is further dissolved in deionized water (H_2O) and ethanol. It is important to highlight that a fine spray is used to increase the rate of evaporation of the liquid in the flame, and the pilot flame used is based on oxygen and acetylene controlled by a flow controller. The morphology of zirconia nanoparticles produced by using this specific apparatus and precursor solution is presented in the Fig. 5.12.

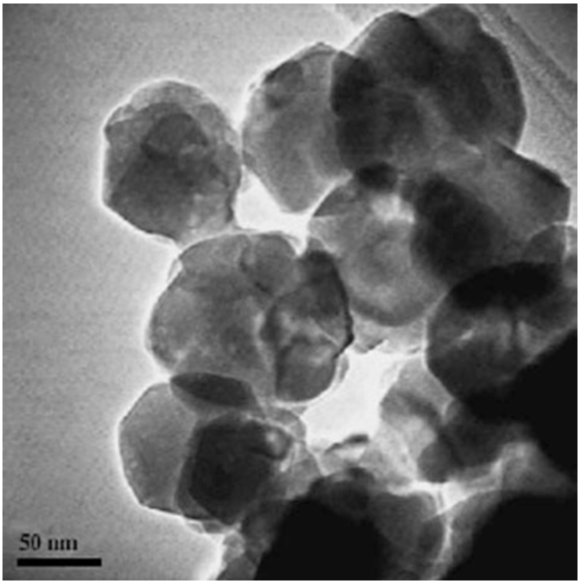

Fig. 5.12 TEM image of the zirconia nanoparticles synthesized by the FS process (*Acknowledge* Tok et al. 2006)

A different approach for zirconia production consists in the thermal decomposition of a liquid metal organic precursor in a flow reactor system (Benfer and Knözinger 1999). In this process, the decomposition of the liquid metal organic precursor, which includes zirconium tert-butoxide, occurs at temperatures in the range of 110–135 °C at a reduced pressure of 5–20 mbar in a furnace. In this place, the ZrO_2 nanoparticles are formed by the decomposition of the precursor molecules.

An alternative flame-based method for ZrO_2 nanoparticles production comprises the use of ethanol as solvent, where zirconium propoxide is added and dissolved to prepare the precursor solution. After its preparation, it is delivered to an external-mixing gas-assisted atomizer. When in contact with the flame, the precursor solution burns, resulting in the final product (Heine et al. 2006).

5.2.6 Iron Oxide (FeO, Fe_2O_3, and Fe_3O_4)

Magnetic iron oxide nanoparticles as such as maghemite (Fe_2O_3), magnetite (Fe_3O_4), and wustite (FeO) can be also prepared by FS, under controlled atmosphere. The recent and increased interest in magnetic iron oxide nanoparticles is related to particular properties of this material, which allows its use in magnetic fluids, biotechnology, magnetic resonance imaging (MRI), data storage, and environmental remediation.

Iron oxide nanoparticles can be prepared using a wide range of precursor solutions and FS apparatus. To exemplify, iron oxide nanoparticles can be produced from a precursor solution comprised of $Fe(III)(NO_3)_3 \cdot 9H_2O$ dissolved in a mixture of 2-ethylhexanoic acid:tetrahydrofuran and ethanol (Strobel and Pratsinis 2007). Independent of the crystalline phase, i.e., maghemite, magnetite, or wustite, the use of FS process produces a final product with particle size around 50 nm and with superparamagnetic behavior. However, it is important to observe that in this specific synthesis, the oxidation state of the element iron in the final products depends not only on the fuel to air ratio during combustion, but also on the valence state of the applied iron precursor during their synthesis by FS (Strobel and Pratsinis 2007).

It is also possible to produce iron oxide particles using alternative apparatus and precursor solution. The principles of the FS process remain as the base of the synthesis of this material. To obtain iron oxide nanoparticles in this alternative apparatus, it is necessary to prepare a precursor solution comprised of two precursor salts: iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$ and urea ($CO(NH_2)_2$). In this case, the amount of each precursor is determined according to the stoichiometric reaction, using a concentration of iron nitrate equals to 0.5 M. All of the devices that comprise the equipment used to produce iron oxide particles are the same as reported before for the production of HA (Trommer et al. 2010a, b). Briefly, this equipment is assembled with an atomization device, a Bunsen burner flame, and a particle collector. The use of this simple and efficient devices makes this apparatus a low cost equipment, and relatively simple to be assembled in a laboratory or company. The morphology of the particles produced with this alternative FS

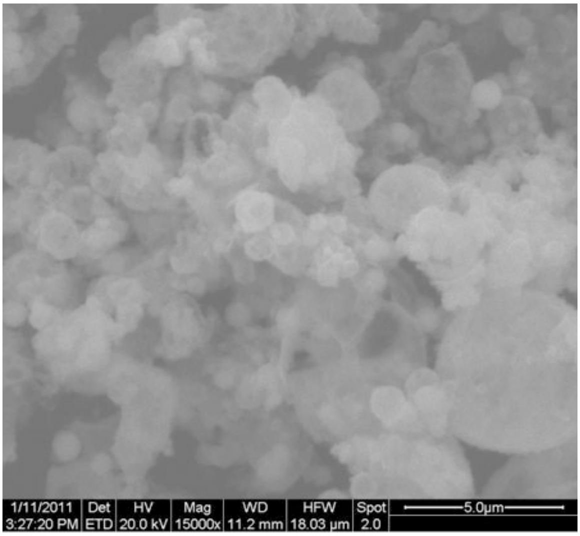

Fig. 5.13 SEM image of the iron oxide particles produced by FS

process is presented in Fig. 5.13. The remarking observation in this particular SEM image is that the iron oxide particles are formed by irregular and spherical particles, which remain in an agglomerate form.

5.3 Other Oxides

Different types of oxides and other materials have been produced using the FS technique, which has been proving to be a powerful tool for nanoparticles production. Most of the main commercial oxides are produced in industrial scale. However, non-commercial materials are usually produced in small reactors mainly that one's placed in academic sites. The literature has reported an increased number of materials prepared with the aid of FS. Each of these materials has its specific technological characteristics, which is expected to be improved when in the nanometric size.

For example, monoclinic yttrium oxide or yttria (Y_2O_3) is a not so largely produced and commercially used as titania, silica, and black carbon. However, it can be also produced using the FS process. The main applications of yttria are related to its use in phosphors, catalysts, and optical window materials. For these potential applications of monoclinic yttria (important phase for Y_2O_3 and other rare earth oxides), it is necessary to synthesize phase-pure Y_2O_3 in sufficient quantities. In this point, FS process arises as a potential solution for this requisite.

Using the principles of FS, it is possible to synthesize yttria nanoparticles using a precursor aerosol consisting of H_2 fuel gas and precursor droplets, which intercepts an impactor before enters into a flame (Guo et al. 2009). The morphology of the

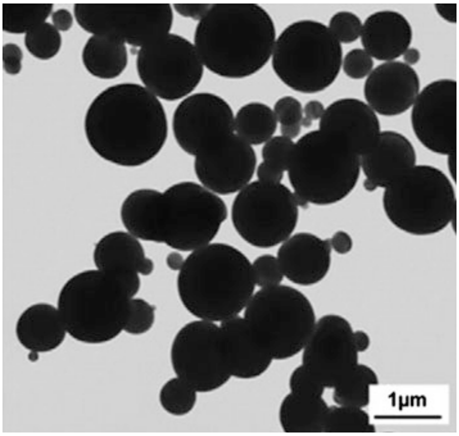

Fig. 5.14 TEM image of Y_2O_3 particles synthesized by the FS process (*Acknowledge* Guo et al. 2009)

yttria particles produced using the FS process observed shows in the micrograph obtained with the aid of TEM, as shown Fig. 5.14. It is important to note that the yttria nanoparticles are spherical, a typical morphology of flame-sprayed powders.

Another unusual oxide that has been synthesized by FS process is lutetium oxide, with chemical formula given by Lu_2O_3. Lutetium oxide is an excellent host for rare earth dopants in high energy solid-state laser applications because of its high thermal conductivity which is insensitive to the amount of rare earth ion dopant, and its low phonon scattering (Baker et al. 2012). To produce this oxide, a precursor solution must be prepared. A typical precursor salt that can be used is lutetium nitrate ($Lu(NO_3)_3 \cdot 6H_2O$), dissolved in water. However, the preparation of the precursor solution in this specific method of FS requires a further step. It comprises the purification of the nitrate solution by crystallization and subsequent washes. After this, a filtration through 0.8-μm filter media is performed, and the subsequent solution is dissolved ethanol to obtain the final precursor solution. To produce Lu_2O_3 using this particular FS method, the flame system used can be composed of a two-phase nozzle consisting of a central capillary tube surrounded by a ring of pilot flames which were supplied with CH_4 and O_2. After ignition of the pilot flames, a co-flowing stream of O_2 and the liquid precursor are fed through the central capillary tube, where the oxygen is used as a dispersion gas to atomize the liquid precursor.

A single oxide that has constantly gained attention due to its gas sensing under atmospheric conditions is tin oxide (SnO_2). Gas sensors manufactured with SnO_2 are in high demand for many applications, which includes environmental monitoring, prevention of leakage, and incomplete combustion (Liewhiran et al. 2012). Tin oxide is relatively easy to be produced using the FS process. The precursor solution can be prepared using an appropriate amount of tin(II) 2-ethylhexanoate dissolved in xylene, used as solvent (Liewhiran et al. 2012). The nanoparticles of the SnO_2 prepared using the FS process are shown in the TEM image of Fig. 5.15. The image revealed that the primary nanoparticles have morphology close to spherical, non-agglomerated, and well dispersed.

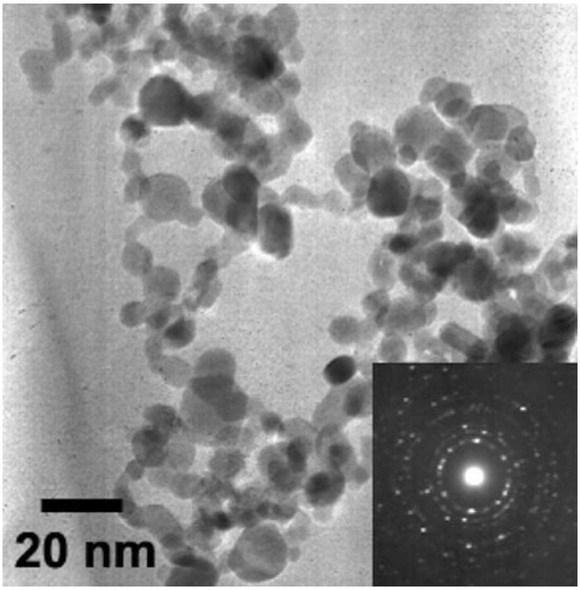

Fig. 5.15 TEM image of SnO_2 nanoparticles prepared using the FS process (*Acknowledge* Liewhiran et al. 2012)

HA is a bioceramic material widely used for clinical purposes, mainly by the fact that is the major mineral present in human hard tissues as bone and teeth. The production of HA can be done by the use of several methods, such as, precipitation, solid-state synthesis, hydrolysis, hydrothermal, and solgel. However, the FS method can be used as an alternative technique for the production of HA (Trommer et al. 2009). One characteristic of the HA powder produced with the aid of FS is that the powder is basically composed of primary particles and secondary aggregates. In addition, SEM images (Fig. 5.16) also reveal that the primary particles are spherical.

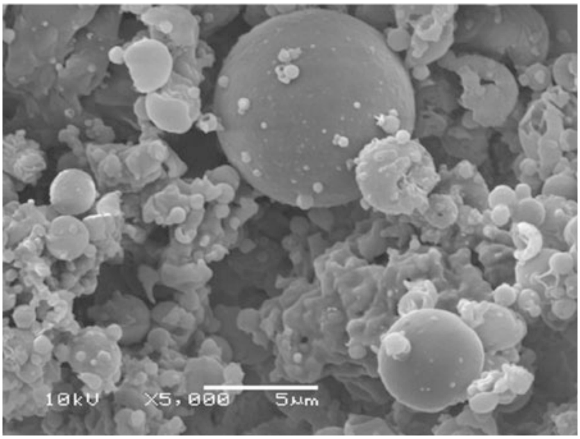

Fig. 5.16 SEM image of the HA powder prepared using the FS method (*Acknowledge* Trommer et al. 2009)

5.4 Films

As presented in the previous chapter, one of the great features of the FS process is the production of nanomaterials with a wide range of morphologies, where thin films and coatings can be included. Consequently, several types of oxides can be obtained with this morphology.

One example of oxide produced as a thin film or coating is tungsten trioxide, with chemical formula given by WO_3. This oxide is technologically important in photoelectrochemical (PEC) watersplitting for the solar production of hydrogen fuel from water (Rao et al. 2013). Moreover, tungsten trioxide has been used in commercial applications as chemical sensors and electrochromic windows, for which it is commonly used in the form of polycrystalline thin films. Because FS method is a versatile technique, the production of this oxide is also possible by the use of a flame. In this case, the flame synthesis method has been used as a promising route for the growth of high quality and functional 1-D metal oxide, as such as nanotubes (NT) and nanowires (NW), where nanomaterials are synthesized by the rapid, atmospheric, and scalable FS method (Rao et al. 2013). The cross section of WO_3 nanotubes produced with FS process, and observed with the aid of SEM, is shown in Fig. 5.17.

Another great feature of FS is the promptly providing of high temperatures and precursor carbon species, which is a good base for a scalable method for the production of 0D and 1D carbon nanostructures. Consequently, it is not a surprise that with the aid of the FS process, it is possible to produce graphene films. This type of film can be obtained by the simple use of a multiple inverse diffusion flame burner with methane as fuel (Memon et al. 2013). Due to its special properties, graphene can be used in a wide range of applications, such as flexible touch panels, thin film transistors, solar panels, and corrosion resistant coatings.

Another material that can be produced as a thin film using the FS process is the $LiMn_2O_4$ spinel. The process used to obtain this thin film oxide employs a reactor,

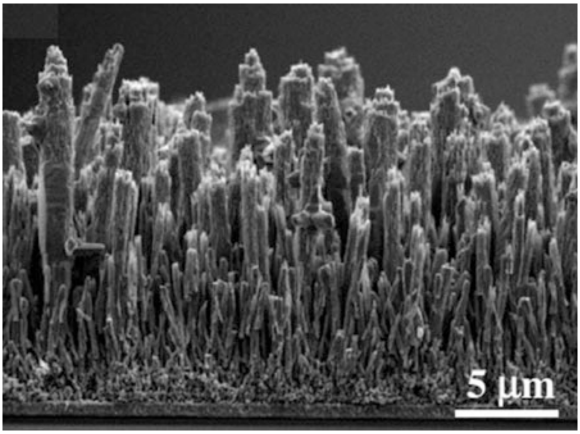

Fig. 5.17 Cross-section SEM image of WO_3 nanotubes array (*Acknowledge* Rao et al. 2013)

respecting the principles of FSP, where a precursor solution is sprayed. The precursor solution prepared to be used in this synthesis is comprised of lithium acetylacetonate and manganese acetylacetonate, both dissolved in an organic solution. This spinel oxide is of particular interest for use in hybrid electric vehicles (HEVs) as the cathode material for high-power Li-ion batteries. Moreover, when compared to other oxides that can be used in Li-ion batteries (the most recent candidates as cathode materials are the family of lithium transition metal oxides). $LiMn_2O_4$ is less toxic and cheaper due to its relative abundance (Chew et al. 2009).

As demonstrated in this book, the FS process is a novel technique that shows an enormous potential in oxide deposition. Thus, the correct assembling of a FS apparatus allows the production of the porous HA, which is a biomaterial widely used as a coating in products of medical applications. In this case, the simple substitution of the particle collection system by a substrate, placed in the correct position, leads to the production of this coating. It is possible to use 316 L stainless steel as the metallic substrates. However, it is necessary to prepare a precursor solution, which can be easily done by employing calcium acetate and ammonium, phosphate, both used as precursor salts, which are further dissolved in ethanol (Trommer et al. 2007). However, it is important to mention that in this specific type of apparatus and precursor solution, the HA coating is only obtained if the correct Ca/P molar ratio is used in the precursor solution. A different Ca/P molar ratio than 1.66 (which is equivalent to stoichiometric HA) will produce a different calcium phosphate. The top view and the cross section of the HA coating produced using an apparatus based in the flame spraying are shown in Fig. 5.18.

With the aid of FS, it is possible to produce ZnO films, and if desired, with niobium doping, as shown Fig. 5.19. To obtain a film with satisfactory properties, a special attention must be given to the preparation of the precursor solution. It can be done by using an organic paste composed of ethyl cellulose and terpineol, which acts as a vehicle binder and solvent, respectively (Kruefu et al. 2011). The doping of zinc oxide thin film can be done by the addition of niobium (V) ethoxide to the precursor solution. Usually, in this method of ZnO production, the amount of niobium dopant is 0.25–1.00 mol% Nb/ZnO. For the doped and undoped zinc oxide thin film production, the substrate used in this deposition is alumina.

5.5 Complex Oxides

Spinels of the $A(B_2)X_4$ type are used in a wide range of applications, including electrochemistry, catalysis, and electronics (Ernst et al. 2007). This is one of the reasons that modern flame aerosol synthesis of nanoparticles has been rapidly changing terrain: While producing mainly simple oxide commodities such as silica or titania in the last few decades, a deeper understanding of the process allows now the production of more sophisticated products with high functionality (Stark and Pratsinis 2002).

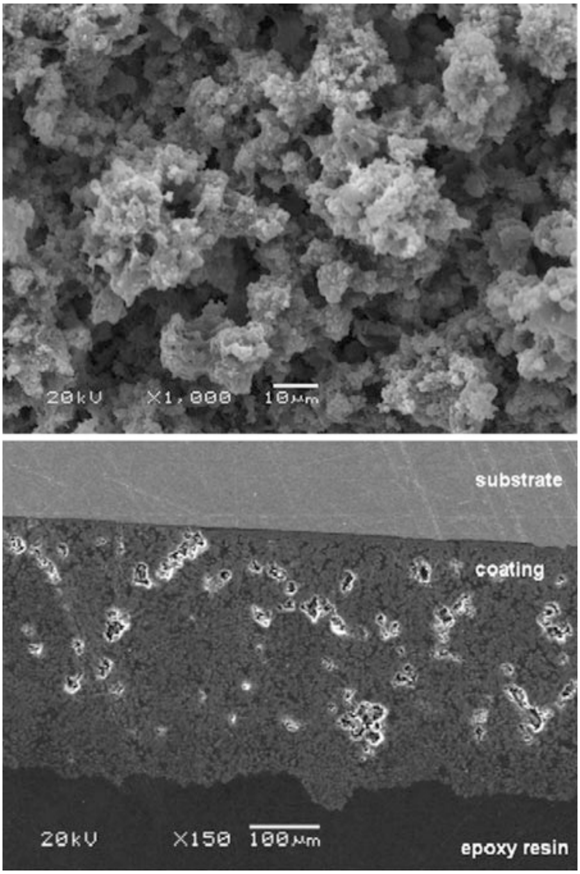

Fig. 5.18 Top view and cross section of the HA coating produced by the FS process (*Acknowledge* Trommer et al. 2007)

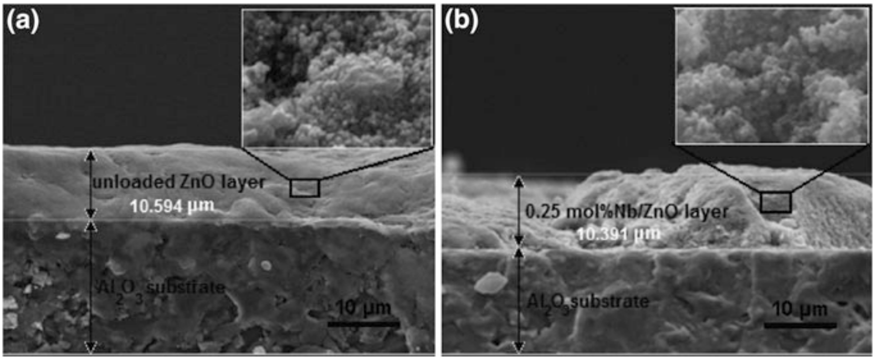

Fig. 5.19 Cross section images by SEM of: **a** pure ZnO and **b** niobium doped films produced by the FS process (*Acknowledge* Kruefu et al. 2011)

In this modern field, the use of FS allows the production of electrochemically active $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ particles with normal, mixed, and mixed inverse spinel structure, respectively (Ernst et al. 2007). The recent interest in nanoparticulate spinels in electrochemical applications is justified mainly because the small dimension of nanoparticles reduces the diffusion lengths within particles, increase the number of active sites for surface reactions and decrease the local current density (Ernst et al. 2007). Consequently, the use of the powerful technique FS allows the production of nanoparticles of these spinels.

Another complex oxide that can be produced with FS process is $SrTiO_3$:Pr. The main advantage of the use of FS process in comparison with the usual spray pyrolysis is the production of a material with better crystallinity (Kang et al. 2002). Moreover, one interesting characteristic of the $SrTiO_3$:Pr material prepared with FS is the spherical shape, which is an important feature in the flat panel displays, as shown Fig. 5.20. The production of $SrTiO_3$:Pr by FS can be achieved using a precursor solution containing tetraisopropoxide (TTIP), strontium salts, aluminum nitrate, and praseodymium nitrate dissolved in distilled water (Kang et al. 2002).

Inside the group of titanates, another nanoparticulate material that can be produced with the principles of FS is zinc titanate, with chemical formula given by Zn_2TiO_4. The main use of nanoparticles from the ZnO–TiO_2 system is as paint pigment, gas sensor, and catalytic sorbent. With the aid of an apparatus assembled with the principles of the FS process, zinc titanate can be produced by the simple preparation of a specific precursor solution. It consists in the dissolution in ethanol (used as solvent) of the precursors salts zinc naphthenate and titanium tetra isopropoxide, in a molar ratio of 1:1 (Siriwong and Phanichphant 2011).

After its preparation, the precursor solution is guided to a syringe pump while oxygen is used as dispersive gas. The spray formed then reaches the small flames, or flamelets, where methane is used as combustion gas. After the combustion of the precursor solution, the nanoparticles are collected on glass microfiber filters with

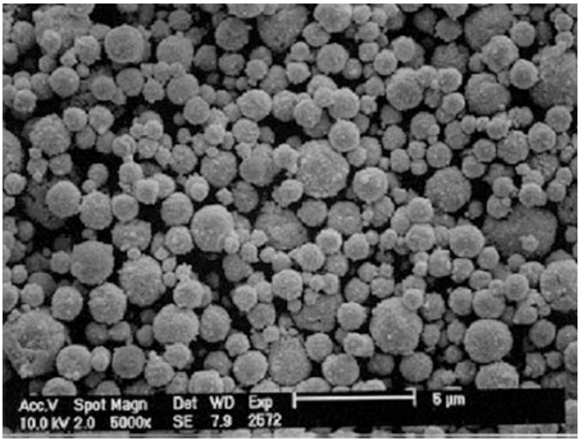

Fig. 5.20 SEM image of SrTiO3:Pr spherical particles prepared using the FS process (*Acknowledge* Kang et al. 2002)

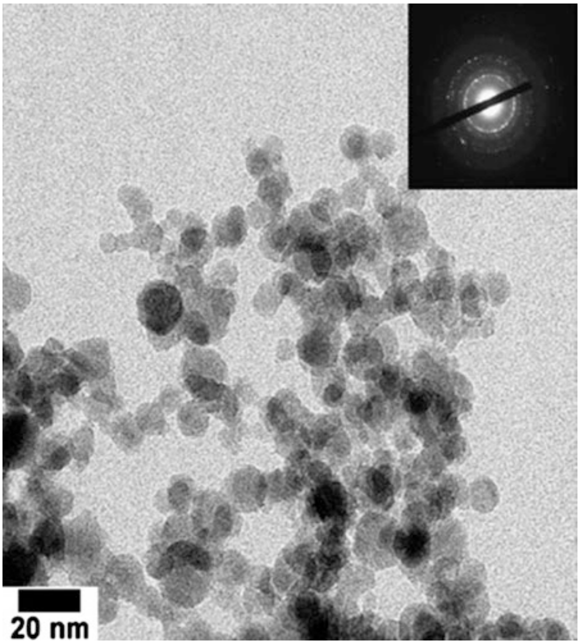

Fig. 5.21 TEM image of the zinc titanate nanoparticles produced using the FS process (*Acknowledge* Siriwong and Phanichphant 2011)

the aid of a vacuum pump. The morphology of the Zn_2TiO_4 powder produced with this particular FS apparatus can be observed in Fig. 5.21. TEM image revealed that this powder is comprised of nanoparticles, with crystallite size in a range of 5–18 nm.

As deep discussed in this book, the FS process is a versatile method widely used for nanoparticles production. At this point, the FS process allows the doping of Zn_2TiO_4 mentioned above with metals or metal oxides. It is expected that the introduction of these dopants can improve several properties of the zinc titanate, as for example photoluminescence, microwave dielectric, optical, and gas sensing. Just to give one example, zinc titanate can be doped with platinum, which can be introduced in the precursor solution in an easy way by the use of platinum(II) acetylacetonate (Siriwong et al. 2012).

Confirming its versatility, FS process can be used to produce cobalt–aluminum spinel ($CoAl_2O_4$). This oxide is widely used in the ceramic industry as coloring agent (blue). In the nanometric form, this oxide presents a high coloring potential because of its high specific surface area, which ensures a better surface coverage, high points of reflectance, and increase of scattering (Cavalcante et al. 2009). To produce this oxide, first it is necessary to prepare the precursor solution. One example of the precursor solution preparation involves the use of the respective nitrate salts and one complexing agent to reduce the nitrate. To supply the aluminum ion, it is possible to use aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$). As source of the cobalt ion, cobalt(II) nitrate ($Co(NO_3)_2 \cdot 6H_2O$) can be used. One of the advantages

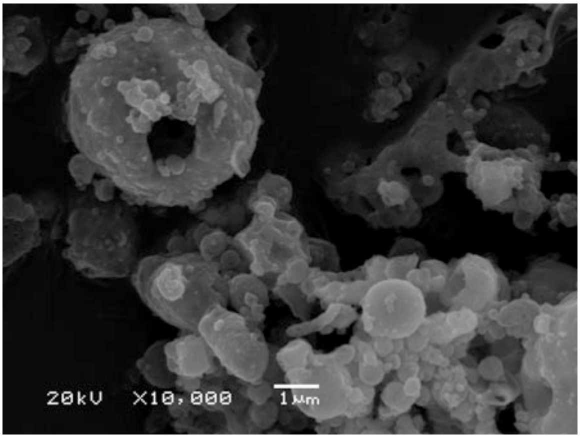

Fig. 5.22 SEM image of the cobalt–aluminum spinel particles obtained by the FS process

of these precursor salts is that both can be easily dissolved in ethanol, which can be easily employed as solvent and, additionally, is flammable in the flame. The amount of aluminum nitrate and cobalt nitrate must respect the stoichiometry of the cobalt–aluminum spinel. Once this relation is respected, the concentration of the precursor salts can be determined according the maximum solubility of the precursor salts in the solvent (ethanol). However, as mentioned before, nitrates are strong oxidizing agents. This requires the use of a reducing agent. In this case, to maintain a rapid and easy precursor solution preparation, urea can be used. Thus, the cobalt–aluminum spinel can be produced using a cost-effective FS apparatus where a precursor solution comprising the nitrates above mentioned and urea (all dissolved in ethanol) is sprayed in a Bunsen burner flame. The morphology of the final product obtained with this precursor solution, and FS apparatus can be observed in the SEM image of Fig. 5.22.

The SEM micrograph reveals that the spraying of the precursor solution in a flame (in this case, a Bunsen burner is used as pilot flame) leads to the production of powders basically comprised of particles with different morphologies, i.e., irregular and spherical particles. The different morphologies observed can be a result of the turbulent flame, once a Bunsen burner is used as pilot flame and the atomized precursor solution is sprayed into. The irregular particles formation mechanism is similar to the one reported above for zinc oxide production, where the decomposition of urea in the flame causes the disintegration of the primary particles (Trommer et al. 2010a, b). When compared to the zinc oxide mentioned earlier, the difference in the morphology of the cobalt–aluminum spinel is the existence of hollow particles, which is a result of the low flame temperatures experienced by the droplets in the turbulent flame. Other reason that contributes to the hollow morphology is the volatility of the solvent, which affects the particle formation process (Tok et al. 2006).

References

Aromaa M, Keskinen H, Mäkelä JM (2007) The effect of process parameters on the liquid flame spray generated titania nanoparticles. Biomol Eng 24:543–548. doi:10.1016/j.bioeng.2007.08.004

Baker C, Kim W, Sanghera J, Goswami R, Villalobos G, Sadowski B, Aggarwal I (2012) Flame spray synthesis of Lu_2O_3 nanoparticles. Mater Lett 66:132–134. doi:10.1016/j.matlet.2011.08.058

Benfer S, Knözinger E (1999) Structure, morphology and surface properties of nanostructured ZrO_2 particles. J Mater Chem 9:1203–1209

Buddhiraju VS, Runkana V (2012) Simulation of nanoparticle synthesis in an aerosol flame reactor using a coupled flame dynamics–monodisperse population balance model. J Aerosol Sci 43:1–13. doi:10.1016/j.jaerosci.2011.08.007

Camenzind A, Caseri WR, Pratsinis SE (2010) Flame-made nanoparticles for nanocomposites. Nano Today 5:48–65. doi:10.1016/j.nantod.2009.12.007

Cavalcante PMT, Dondi M, Guarini G, Raimondo M, Baldi G (2009) Colour performance of ceramic nano-pigments. Dyes Pigm 80:226–232

Chew SY, Patey TJ, Waser O, Ng SH, Büchel R, Tricoli A, Krumeich F, Wang J, Liu HK, Pratsinis SE, Novák P (2009) Thin nanostructured $LiMn_2O_4$ films by flame spray deposition and in situ annealing method. J Power Sources 189:449–453. doi:10.1016/j.jpowsour.2008.12.085

Ernst FO, Kammler HK, Roessler A et al (2007) Electrochemically active flame-made nanosized spinels: $LiMn_2O_4$, $Li_4Ti_5O_{12}$ and $LiFe_5O_8$. Mater Chem Phys 101:372–378. doi:10.1016/j.matchemphys.2006.06.014

Guo B, Mukundan M, Yim H (2009) Flame aerosol synthesis of phase-pure monoclinic Y_2O_3 particles via particle size control. Powder Technol 191:231–234. doi:10.1016/j.powtec.2008.11.003

Heine MC, Mädler L, Jossen R, Pratsinis SE (2006) Direct measurement of entrainment during nanoparticle synthesis in spray flames. Combust Flame 144:809–820. doi:10.1016/j.combustflame.2005.09.012

Høj M, Linde K, Hansen TK et al (2011) Flame spray synthesis of CoMo/Al_2O_3 hydrotreating catalysts. App Catal A 397:201–208. doi:10.1016/j.apcata.2011.02.034

Hu Y, Ding H, Li C (2011) Preparation of hollow alumina nanospheres via surfactant-assisted flame spray pyrolysis. Particuology 9:528–532. doi:10.1016/j.partic.2011.06.003

Ifeacho P, Wiggers H, Roth P (2005) SnO_2/TiO_2 mixed oxide particles synthesized in doped premixed H_2/O_2/Ar flames. Proc Combust Inst 30:2577–2584. doi:10.1016/j.proci.2004.08.117

Jang HD, Chang H, Suh Y, Okuyama K (2006) Synthesis of SiO_2 nanoparticles from sprayed droplets of tetraethylorthosilicate by the flame spray pyrolysis. Curr Appl Phys 6S1:e110–e113. doi:10.1016/j.cap.2006.01.021

Johannessen T, Jensen JR, Mosleh M, Johansen J, Quaade U, Livbjerg H (2004) Flame synthesis of nanoparticles applications in catalysis and product/process engineering. Chem Eng Res Design 82(A11):1444–1452

Kammler HK (2002) Synthesis of oxide nanoparticle with closely controlled characteristics. Dissertation, Swiss Federal Institute of Technology, Zurich

Kang YC, Seo DJ, Park SB, Park HD (2002) Direct synthesis of strontium titanate phosphor particles with high luminescence by flame spray pyrolysis. Mater Res Bull 37:263–269

Kathirvel P, Chandrasekaran J, Manoharan D, Kumar S (2013) Formation and characterization of flame synthesized hexagonal zinc oxide nanorods for gas sensor applications. Ceram Int 39:5321–5325. doi:10.1016/j.ceramint.2012.12.037

Keskinen H, Mäkelä JM, Hellsten S, Aromaa M, Levänen E, Mäntylä T. (2005). Generation of titania nanoparticles by liquid flame spray for photocatalytic applications. Electrochem Soc Proc 2005–09:491–498

Kruefu V, Liewhiran C, Wisitsoraat A, Phanichphant A (2011) Selectivity of flame-spray-made Nb/ZnO thick films towards NO_2 gas. Sens Actuators B 156:360–367. doi:10.1016/j.snb.2011.04.046

Kusters KA, Pratsinis SE (1995) Strategies for control of ceramic powder synthesis by gas-to-particle conversion. Powder Technol 82:79–91

Liewhiran C, Tamaekong N, Wisitsoraat A, Phanichphan S (2012) Highly selective environmental sensors based on flame-spray-made SnO_2 nanoparticles. Sens Actuators B 163:51–60. doi:10.1016/j.snb.2011.12.097

Liu M (2013) Coating technology of nuclear fuel kernels: a multiscale view, modern surface engineering treatments. In Aliofkhazraei M (ed) InTech. ISBN: 978-953-51-1149-8. doi:10.5772/55651. Available from http://www.intechopen.com/books/modern-surface-engineering-treatments/coating-technology-of-nuclear-fuel-kernels-a-multiscale-view

Mekasuwandumrong O, Phothakwanpracha S, Jongsomjit B, Shotipruk A, Panpranot J (2011) Influence of flame conditions on the dispersion of Pd on the flame spray-derived Pd/TiO2 nanoparticles. Powder Technol 210:328–331. doi:10.1016/j.powtec.2011.03.017

Memon NK, Tse SD, Chhowalla M, Kear BH (2013) Role of substrate, temperature, and hydrogen on the flame synthesis of graphene films. Proc Combust Inst 34:2163–2170. doi:10.1016/j.proci.2012.06.112

Moiseev A, Qi F, Deubener J, Weber A (2011) Photocatalytic activity of nanostructured titanium dioxide from diffusion flame synthesis. Chem Eng J 170:308–315. doi:10.1016/j.cej.2011.03.057

Nandiyanto ABD, Okuyama K (2011) Progress in developing spray-drying methods for the production of controlled morphology particles: from the nanometer to submicrometer size ranges. Adv Powder Technol 22:1–19

Pratsinis SE (1997) Flame aerosol synthesis of ceramic powders. Prog Energy Combust Sci 24:197–219

Pratsinis SE (2011) Aerosol science and technology: history and reviews. RTI International, USA. doi:10.3768/rtipress.2011.bk.0003.1109

Pratsinis SE, Vemury S (1996) Particle formation in gases: a review. Powder Technol 88:267–273

Purwanto A et al (2008) High luminance YAG: Ce nanoparticles fabricated from urea added aqueous precursor by flame process. J Alloys Compd 463:350–357

Rao PM, Cho IS, Zheng X (2013) Flame synthesis of WO_3 nanotubes and nanowires for efficient photoelectrochemical water-splitting. Proc Combust Inst 34:2187–2195. doi:10.1016/j.proci.2012.06.122

Roth P (2007) Particle synthesis in flames. Proc Combust Inst 31:1773–1788. doi:10.1016/j.proci.2006.08.118

Sahu M, Biswas P (2011) Single-step processing of copper-doped titania nanomaterials in a flame aerosol reactor. Nanoscale Res Lett 6:441. doi:10.1186/1556-276X-6-441

Siriwong C, Phanichphant S (2011) Flame-made single phase Zn_2TiO_4 nanoparticles. Mater Lett 65:2007–2009. doi:10.1016/j.matlet.2011.03.058

Siriwong C, Tamaekong N, Phanichphant S (2012) Characterization of single phase Pt-doped Zn_2TiO_4 nanoparticles synthesized by flame spray pyrolysis. Mater Lett 68:97–100. doi:10.1016/j.matlet.2011.10.026

Stark WJ, Pratsinis SE (2002) Aerosol flame reactors for manufacture of nanoparticles. Powder Technol 126:103–108

Strobel R, Pratsinis SE (2007) Flame aerosol synthesis of smart nanostructured materials. J Mater Chem 17:4743–4756. doi:10.1039/b711652g

Tok AIY, Boey FYC, Du SW, Wong BK (2006) Flame spray synthesis of ZrO_2 nano-particles using liquid precursors. Mater Sci Eng B 130:114–119. doi:10.1016/j.mseb.2006.02.069

Trommer RM, Santos LA, Bergmann CP (2007) Alternative technique for hydroxyapatite coatings. Surf Coatings Technol 201:9587–9593. doi:10.1016/j.surfcoat.2007.04.028

Trommer RM, Santos LA, Bergmann CP (2009) Nanostructured hydroxyapatite powders produced by a flame-based technique. Mater Sci Eng C 29:1770–1775. doi:10.1016/j.msec.2009.02.006

Trommer RM, Alves AK, Bergmann CP (2010a) Synthesis, characterization and photocatalytic property of flame sprayed zinc oxide nanoparticles. J Alloys Compd 491:296–300. doi:10.1016/j.jallcom.2009.10.147

Trommer RM, Topolski DK, Takimi AS, Bergmann CP (2010b) Evaluation of flame-sprayed alumina powders produced using different ethanol/water ratios in the starting solutions. Part Sci Technol 28:247–261. doi:10.1080/02726351.2010.481587

Wegner K, Schimmoeller B, Thiebaut B, Fernandez C, Rao TN (2011) Pilot plants for industrial nanoparticle production by flame spray pyrolysis. Powder Part J 29:251–265

Yue R, Meng D, Ni Y, Jia Y, Liu G, Yang J, LiuH WuX, Chen Y (2013) One-step flame synthesis of hydrophobic silica nanoparticles. Powder Tech 235:909–913. doi:10.1016/j.powtec.2012.10.021

Zhang Y, Li S, Deng S, Yao Q, Tse SD (2012) Direct synthesis of nanostructured TiO_2 films with controlled morphologies by stagnation swirl flames. J Aerosol Sci 44:71–82. doi:10.1016/j.jaerosci.2011.10.001

Chapter 6
Future Trends in Flame Spray Process

Abstract This chapter introduces the main future trends associated with the use and development of the flame spray (FS) technology. The FS process has been considered by many researchers as a novel and powerful method for the production of nanoparticles and nanostructured particles. However, if we consider that its principles and fundamentals are not fully understood, and considering that only few commodities (black carbon, titania, and silica for example) are commercially available up to now, there is a great demand for the development of the FS process. Today, there are several areas where FS process can be developed, which justify the strong efforts made by many scientists. In addition, we must consider that the increasing use and interest in the FS process makes it a promising technique for the production of a wide range of commodities, especially if we take in mind that most of the products obtained with FS are in the nanosize scale. Another important point concerning the future of the FS comprises the synthesis of unconventional oxides and can be also considered as a great development done for the improvement of this method. It is clear to many scientists that a deep understanding of the particle formation mechanisms in the flame is an important step in the development of the FS process. The better understanding of what happens in the flame basically comprises the acquisition of experimental data, leading to a further modeling and simulation of particle formation mechanisms and their kinetics in flames. The use of the principles of this technology but aiming the production of thin films and coatings is another point and has emerged as an important area inside this technology. These are just two short examples of the potential areas inside the FS technology. This chapter intends to present to reader the main future trends concerning the use of a flame to obtain ceramic products, as well as the development and improvement of new devices to be used as flame, powder collector, and atomization are discussed. Another important point of this chapter is the perspective of the production of nanoparticles aiming its application in several industrial concerns as biomaterials, electronics, catalysis, etc.

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Abbreviations

CARS	Coherent anti-Stokes Raman scattering
CFD	Computational fluid dynamics
E/T	Emission/transmission spectroscopy
FTIR	Fourier transform infrared
FS	Flame spray
LIF	Laser-induced fluorescence
MNP	Magnetic nanoparticles
MRI	Magnetic resonance imaging
NCPDP	Nanocerox ceramic powder development process
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TS	Thermophoretic sampling
XPS	X-ray photoelectron spectroscopy

This book does not intend to demonstrate how fast the progress and development of the nanotechnology is. One of the consequences of this widespread advance is the fact that nanoparticles have started to be used in commercial products sooner than times ago. However, this fast growth requires a production-level quantity of nanopowders with enhanced properties, such as multi-component or coated oxides. Moreover, nanotechnology is a dynamic area, demanding quick answers by the scientists to overcome industrial problems in special. Today, the scientific literature has demonstrated that such problems regarding advanced nanoparticles can be effectively overcome with the aid of the flame spray (FS) process.

As observed in the nanotechnology area, modern flame aerosol synthesis of nanoparticles can be also considered a quickly changing terrain. While producing mainly simple oxide commodities such as silica or titania in the last few decades, a better understanding of the process allows now the production of more sophisticated products with superior behavior. However, there is a long way until the fully understanding of the mechanisms involved in the particle's formation, which will be discussed latter. In addition, advances in process simulation and diagnostics of early particle formation and growth have a strong contribution to this quick development (Stark and Pratsinis 2002).

The last advances in aerosol (spray), combustion science, and engineering have now allowed the scientists to scale FS products up to mixed oxides, metal salts, and pure metals in the form of nanoparticles and films with closely controlled characteristics instead of single oxides that have been used to obtain in the past (Strobel and Pratsinis 2007). As a consequence, this wide range of more sophisticated materials can be only produced if an appropriate liquid solution is sprayed in a suitable flame device and then effectively collected in powder collector system. As a first example, the recent development of new flame apparatus and/or different precursor solutions leads to the production of unique materials as homogeneous

CeO_2/ZrO_2 catalysts, silica-doped ZnO quantum dots, Pt/Al_2O_3 catalysts, spinels and lasing materials, and even metal alloys (Heine et al. 2006).

In an initial moment, we can clearly conclude that three areas of development in the FS apparatus are possible: precursor solution chemistry, flame and combustion engineering, and the devices intended to be use to collect the nanoparticles.

The development of new precursor solutions is strongly associated with the final nanoparticle intended to be produced with FS. However, the advances observed in the development of the precursor solution are not so impacting in the development of the FS technology. Usually, the study of the precursor solutions concerns the use of different salts as source of the ions to the final product or as source of energy in the flame.

The powder collector system is possibly the device less studied in the last year, probably because it has no directly influence on the improvement of the nanoparticles properties and FS process. However, the main objective in the development of the powder collector system is not merely scientific, but involves economic questions. A device with a high efficiency in the collection of nanoparticles obviously allows the production of material. Thus, the main efforts concerning the devices intend to collect the nanomaterials are related to the improvement of the already existent equipments and not in the development of new ones.

One of the big challenges concerning the FS process is the scaling up of the process to a cost-efficient industrial production line. The flame can be considered as the key parameter to reach this objective. Actually, the attention of many scientists is given to phenomena in the flame that promote the formation of nanoparticles. As deeply discussed in this book, the understanding of the nanoparticles formation mechanisms in the flame plays an important role in the improvement of the FS process. Aiming to overcome this problem in a short time, robust and simple computational models accounting for the governing mechanisms in FSP synthesis of nanoparticles have been arisen as an alternative and efficient tool. Recently, the synthesis of TiO_2 nanoparticles in a diffusion flame reactor was deeply studied using a computational model, which combines the fluid dynamics with the particle kinetics (Yu et al. 2008). In a similar work, which comprised the aerosol synthesis of zirconia nanoparticles using a flame-based apparatus, the use of computational fluid dynamics (CFD) code coupled to a user-defined subroutine revealed a monodisperse population balance model accounting for coagulation and sintering (Gröhn et al. 2012).

When the flame is particularly studied, particle formation mechanisms and kinetics are not fully understood up to now. Consequently, there is a lack of knowledge on the spatially resolved localization of these formation processes in the flame, opening a great opportunity for the acquisition of experimental data and further modeling, as well as the simulation of particle formation mechanisms and kinetics in flames. This large area of study inside the FS process is usually known as diagnostics (Kilian et al. 2014). Diagnostics is a growing area inside the FS processes and comprises the clearly understanding of the phenomena involved in the nanoparticles formation in the flame. It is expected that the full understanding of these phenomena can contribute to the production of a better product with high quality at even higher production rates. In addition, if nanomaterials are to be made available at low cost, so their promising applications can be commercialized.

One example of the setup assembled for the assessment of the flame characteristics is shown in Fig. 6.1.

This interesting area of the FS processes, also known as optical diagnostic tools, is often used in the combustion research aiming to investigate transient phenomena without disturbing the sensitive combustion process. Diagnostics is considered by many researchers of the FS area as a powerful tool, allowing the monitoring and control particle growth in flame reactors. Basically, diagnostics involves the non-intrusive and in situ measurements of the liquid precursor, droplet formation, evaporation, particle nucleation, condensation, coagulation, and sintering (Camenzind et al. 2010). Diagnostic has the advantage of allowing the flame temperature measurement by the use of non-intrusively techniques such as laser-induced fluorescence (LIF), coherent anti-Stokes Raman scattering (CARS), or Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy. Thermophoretic sampling (TS) and transmission electron microscopy (TEM) are also the techniques that widely employed for the monitoring and diagnostic of the particle growth. In Fig. 6.2, the special setup designed to measure droplet size distributions and velocities in the FS is exampled.

It is possible to obtain local information on spatial droplet distribution, combustion zone, nucleation zone, and temperature in the flame by means of laser-sheet-based Mie scattering imaging, 2D-chemiluminescence imaging, and CARS (Kilian et al. 2014). One of the possible schematics used to obtain information from the flame is shown in Fig. 6.3.

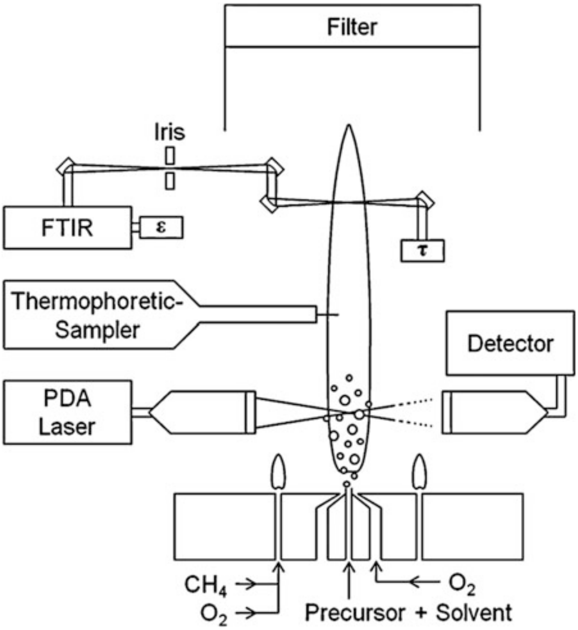

Fig. 6.1 Scheme of the diagnostic tool assembled for the assessment of the flame reactions and kinetics (*Acknowledge* Gröhn et al. 2012)

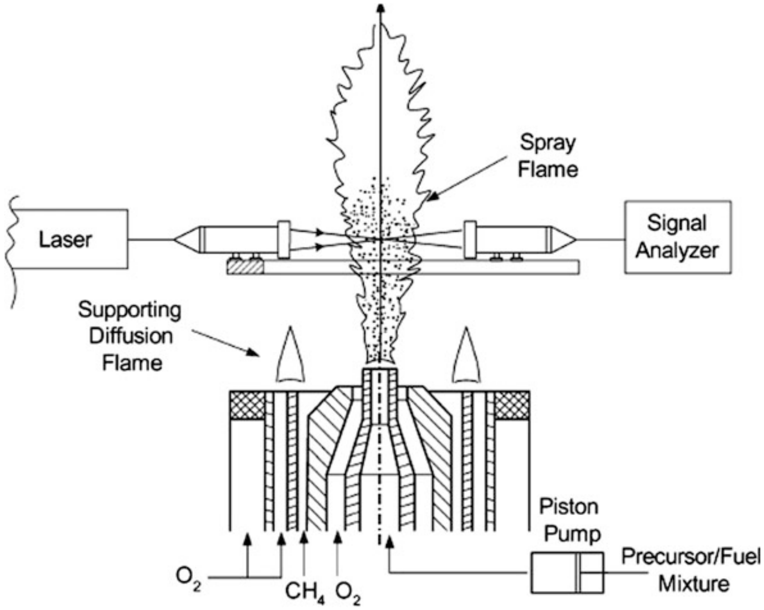

Fig. 6.2 Experimental FSP setup used for measuring droplet size distributions and velocities in the flame spray (*Acknowledge* Heine et al. 2006)

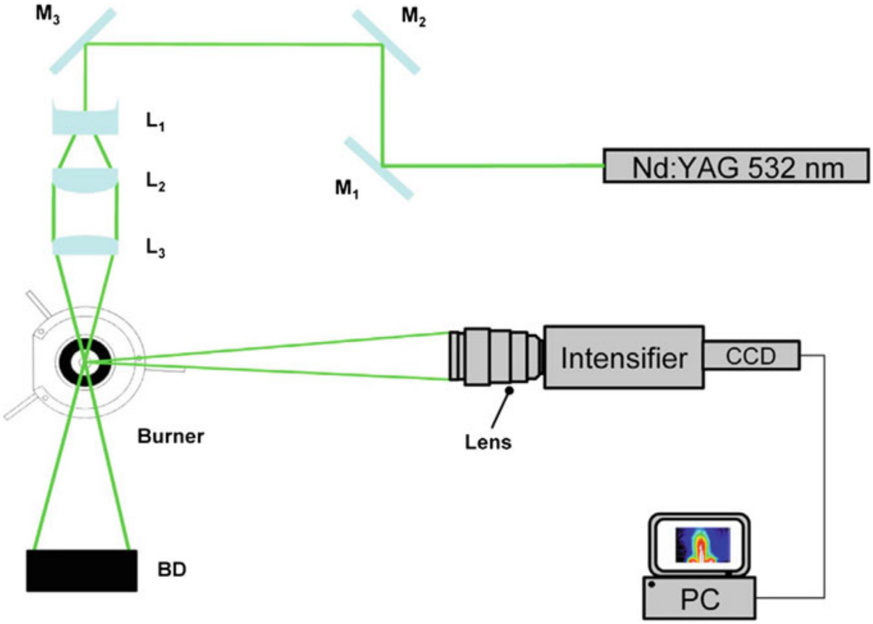

Fig. 6.3 Schematic of the Mie scattering system designed to measure the distribution of the liquid phase by laser-sheet based (*Acknowledge* Kilian et al. 2014)

These are just short examples of the deep investigation performed in the flame, which aims to obtain a better understanding of the mechanisms and phenomena involved in the particle formation in the flame.

Another important contribution for the development of FS technique is the use of computational models, which also contributes for a better understanding of the process used in laboratory. For example, when the FS method is used during the synthesis of zirconia nanoparticles (ZrO_2) employing a twin-fluid atomizer and coaxial diffusion burner, a complete description of the spray flame behavior can be obtained using the CFD combined with droplet and nanoparticle dynamics (Gröhn et al. 2012). Another example is the use of a coupled flame dynamics—monodisperse population balance model for nanoparticle synthesis in an aerosol flame (Buddhiraju and Runkana 2012). In this specific case, the particle number, concentration, particle volume, and surface area can be predicted by the simulation of the flame dynamics by means of commercial software. It is important to highlight that one of the main contributions of this model is the simple way of designing and optimization of large scale flame reactors by the use of an accurate and computationally efficient modeling. Moreover, it has an enormous potential in the contribution of the scale-up of laboratory reactors up to industrial process.

Concerning the production of materials with enhanced properties, an attractive group of materials with interesting properties and large use in medicine is the magnetic nanoparticles (MNP). Such materials have been used recently in applications such as magnetic fluids, biotechnology, biomedicine, magnetic resonance imaging (MRI), data storage, and environmental remediation. Regarding the magnetic nanoparticles, one important thing to be highlighted is that below a critical size, these nanoparticles behave like a single magnetic domain exhibiting superparamagnetic behavior. To date, in the specific case of iron oxide particles, this critical size is around 100 nm (Strobel and Pratsinis 2009). This important feature of MNPs related to a special behavior due to its nanodimension opens an enormous opportunity for the employment of FS process as a powerful tool for the production of these nanoparticles. Recently, metallic iron (Fe) nanoparticles have been produced by a simple and continuous FS pyrolysis method (Li et al. 2013). One important characteristic of these nanoparticles comprises its typical core–shell structure morphology, which consists in a corresponding Fe_3O_4 shell and a metallic Fe core, with a thickness of 4–6 nm and about 30–80 nm, respectively.

The improvement of materials' properties can be reached in an alternative way through the combination of widely used oxides such as SiO_2, TiO_2, and Al_2O_3 with not usual materials. The aim of this combination is the formation of multi-component particles, where the properties of the final product are highly improved. For example, the apparent reinforcing ability of SiO_2 when mixed into polymers for instance can be combined with other properties of Fe_2O_3 (superparamagnetic behavior) for actuators, or Ta_2O_5 (radiopacity) for dental applications, or TiO_2 for UV absorption (Camenzind et al. 2010). More importantly, all of these material combinations can be done with the aid of specifically designed flame, precursor solutions, and powder collector systems. In this particular case, the production of multi-component particles using FS has the major influence of the use of a suitable precursor solution, in which specific precursor ions are added in such way that the final product is a multi-component particle.

Nanoparticulate spinels have been showing an increasing interest in modern electrochemical applications, once its small dimensions can significantly reduce diffusion lengths within particles, increase the number of active sites for surface reactions and decrease the local current density. Due to its versatility, as demonstrated in the previous chapter, FS process has been widely used in several academic laboratories as a technique for the production of nanoparticulate spinels. For example, electrochemically active $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ nanoparticles with spinel structure (normal, mixed, and mixed inverse) can be made at production rates in a range of 10–20 gh^{-1} by flame spray pyrolysis (FSP), in a scalable one-step dry process (Ernst et al. 2007). To express how versatile and powerful the FS process is, the spinel $LiMn_2O_4$ material can be prepared not only in the particulate morphology, but also in thin films. This specific morphology can be obtained by the FS deposition and in situ annealing of a precursor solution comprised of lithium acetylacetonate and manganese (III) acetylacetonate dissolved in a mixture of acetonitrile and 2-ethylhexanoic acid. This simple, fast, and efficient method has been applied for the preparation of cathode materials (Chew et al. 2009). Again, the preparation of a suitable precursor solution plays an important role in the production of the film, in addition to the development and assembling of an adequate apparatus for the thin film deposition.

An interesting area of materials science that has been showing a remarkable interest is catalysis, in which the FS method can be a powerful tool for the production of these materials. For example, PtRu/C catalyst can be prepared with the aid of the FS process using platinum(II) acetylacetonate ($Pt(acac)_2$) powder and ruthenium(III) acetylacetonate ($Ru(acac)_3$) powder as catalyst precursors, both dissolved in xylene (Lee et al. 2014). In particular, one of the main reasons for the production of this catalyst is the circumvention of CO poisoning. Inside the catalysis area, FS has been showing a fast growing application in the production of photocatalytic and antibacterial surfaces (Aromaa et al. 2007). The main reason and advantage of using FS for photocatalytic materials production is the easy introduction of dopants and sensitizers, which is expected to increase the photocatalytic activity of the nanomaterial.

Gas-sensing materials are another group of materials with current remarkable interest and that have been produced using the FS process. Gas-sensing materials are becoming attractive because they are a prominent and most effective process that offers many advantages with excellent control over stoichiometry with inexpensive equipment. As expected, with the aid of the FS process, it is possible to obtain gas-sensing materials, such as zinc oxide (ZnO). Using a FS-based apparatus, it is possible to grow high crystalline and hexagonal closely packed ZnO nanorods, which exhibit enhanced gas sensitivity (Kathirvel et al. 2013). It is essential to note that the diameter of the nanorods can be controlled by employing suitable optimization/synthesis parameters.

As the FS method is a versatile and powerful tool for the production of nanomaterials, it is not a surprise that it can be used to produce several and not usual oxides. One example comprises the use of a solution containing Bi-nitrate (precursor salt) and pure water (solvent) and having C_2H_2 and H_2 as fuel gases, to obtain homogeneous bismuth oxide nanopowders, which are mainly used in electroceramic applications (Rudin et al. 2013).

Another great advantage of FS process is that even the properties of commercial and usual oxides such as silica can be improved. Up to now, the most of flame-made silica nanopowders produced is hydrophilic. Consequently, one of the future trends concerning silica is the development of hydrophobic silica nanoparticles. The change in the surface property of silica is motivated by the improvement in their compatibility and enhances their dispersity in polymer or organic solvents (Yue et al. 2013). This relies as a challenge inside the FS area, and the production of hydrophobic silica nanoparticles will contribute significantly for the improvement of silica-based materials.

One important future trend inside the FS area is the synthesis of films, as mentioned in Chap. 5. In addition, graphene is one of the interesting materials widely investigated in the last years. By combining these two important features, the production of graphene films represents one of the main research areas in FS process. Today, graphene films can be grown on metal substrates such as copper, nickel, cobalt, and iron by the use of a multiple inverse-diffusion flame burner in open atmosphere and using methane as fuel (Memon et al. 2013).

References

Aromaa M, Keskinen H, Mäkelä JM (2007) The effect of process parameters on the liquid flame spray generated titania nanoparticles. Biomol Eng 24:543–548. doi:10.1016/j.bioeng.2007.08.004

Buddhiraju VS, Runkana V (2012) Simulation of nanoparticle synthesis in an aerosol flame reactor using a coupled flame dynamics–monodisperse population balance model. J Aerosol Sci 43:1–13. doi:10.1016/j.jaerosci.2011.08.007

Camenzind A, Caseri WR, Pratsinis SE (2010) Flame-made nanoparticles for nanocomposites. Nano Today 5:48–65. doi:10.1016/j.nantod.2009.12.007

Chew SY, Patey TJ, Waser O, Ng SH, Büchel R, Tricoli A, Krumeich F, Wang J, Liu HK, Pratsinis SE, Novák P (2009) Thin nanostructured $LiMn_2O_4$ films by flame spray deposition and in situ annealing method. J Power Sources 189:449–453. doi:10.1016/j.jpowsour.2008.12.085

Ernst FO, Kammler HK, Roessler A et al (2007) Electrochemically active flame-made nanosized spinels: $LiMn_2O_4$, $Li_4Ti_5O_{12}$ and $LiFe_5O_8$. Mater Chem Phys 101:372–378. doi:10.1016/j.matchemphys.2006.06.014

Gröhn AJ, Pratsinis SE, Wegner K (2012) Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO_2. Chem Eng J 191:491–502. doi:10.1016/j.cej.2012.02.093

Heine MC, Mädler L, Jossen R, Pratsinis SE (2006) Direct measurement of entrainment during nanoparticle synthesis in spray flames. Combust Flame 144:809–820. doi:10.1016/j.combustflame.2005.09.012

Kathirvel P et al (2013) Formation and characterization of flame synthesized hexagonal zinc oxide nanorods for gas sensor applications. Ceram Int. doi:10.1016/j.ceramint.2012.12.037

Kilian D, Engel S, Borsdorf B, Gao Y, Kögler AF, Kobler S, Seeger T, Will S, Leipertz A, Peukert W (2014) Spatially resolved flame zone classification of a flame spray nanoparticle synthesis process by combining different optical techniques. J Aerosol Sci 69:82–97. doi:10.1016/j.jaerosci.2013.12.002

Lee H et al (2014) Flame aerosol synthesis of carbon-supported PteRu catalysts for a fuel cell electrode. Int J Hydrogen Energy. doi:10.1016/j.ijhydene.2014.02.080

Li Y, Hu Y, Huang G, Li C (2013) Metallic iron nanoparticles: flame synthesis, characterization and magnetic properties. Particuology 11:460–467. doi:10.1016/j.partic.2012.10.008

Memon NK, Tse SD, Chhowalla M, Kear BH (2013) Role of substrate, temperature, and hydrogen on the flame synthesis of graphene films. Proc Combust Inst 34:2163–2170. doi:10.1016/j.proci.2012.06.112

Rudin T, Wegner K, Pratsinis SE (2013) Towards carbon-free flame spray synthesis of homogeneous oxide nanoparticles from aqueous solutions. Adv Powder Technol 24: 632–642. doi:10.1016/j.apt.2012.11.009

Stark WJ, Pratsinis SE (2002) Aerosol flame reactors for manufacture of nanoparticles. Powder Technol 126:103–108

Strobel R, Pratsinis SE (2007) Flame aerosol synthesis of smart nanostructured materials. J Mater Chem 17:4743–4756. doi:10.1039/b711652g

Strobel R, Pratsinis SE (2009) Direct synthesis of maghemite, magnetite and wustite nanoparticles by flame spray pyrolysis. Adv Powder Technol 20:190–194. doi:10.1016/j.apt.2008.08.002

Yu M, Lin J, Chan T (2008) Numerical simulation of nanoparticle synthesis in diffusion flame reactor. Powder Technol 181:9–20. doi:10.1016/j.powtec.2007.03.037

Yue R, Meng D, Ni Y, Jia Y, Liu G, Yang J, LiuH WuX, Chen Y (2013) One-step flame synthesis of hydrophobic silica nanoparticles. Powder Technol 235:909–913. doi:10.1016/j.powtec.2012.10.021