1 Introduction

The potential of nano-sized clusters or particles has been recognized in recent years since processes for the synthesis of these entities and devices for nanoparticle characterization became established and new commercial applications were clearly identified [1, 2, 3, 4, 5, 6, 7, 8, 9]. Nano-grained materials or particles have distinctly different properties compared with bulk materials, because the number of surface atoms or molecules can become comparable to the number inside the particles [10].

Nano-sized powders can be synthesized by wet-chemical routes and gas-phase processes. However, gas-phase processes are often advantageous compared to liquid-phase processes since washing, drying, and calcining process stages are redundant. Furthermore, the use of high liquid volumes and surfactants, which are necessary to produce high purity materials at high yields, can be avoided [11].

Aerosol reactors that have been developed for the manufacture of ultrafine powders include flame reactors [12], furnace reactors [13], gas-condensation methods [14, 15], plasma reactors [16], laser ablation [8] (the precursor of the previous three examples is preferentially a highly pure metal rod) and spray pyrolysis [17], to name just a few. Today, through the use of these methods, it is possible to make virtually all kinds of inorganic materials at the nano size level, giving potential for new or more cost-efficient applications in addition to existing industrial processes such as pigment generation, optical fiber fabrication, and carbon black production [7, 9]. In summary, the specific aerosol methods differ primarily in the technology of how thermal energy is transferred to the precursor species; how the precursor is delivered to the reaction site; economic aspects; and the final product characteristics.

The workhorses of the aerosol processes, flame reactors for the synthesis of nanoparticles from gaseous precursors, were first investigated in detail using diffusion and premixed flames [12, 18, 19, 20, 21]. By producing fumed silica and titania from chloride precursors, the competition between particle

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Abstract

Aerosol technology is the key process for large-scale production of nano-structured materials such as carbon black, titania and silica. The understanding of gas-phase synthesis was transferred successfully from classic vapor-fed flames to liquid-fed aerosol reactors, enabling now also the one-step production of demanding and highly functional products. Such aerosol-derived nano-structured metal oxides, mixed metal oxides, and metals on metal oxides find application in the fields of catalysis, sensors, fillers, and electronics, and have advanced the research and development of these reactors in recent years. The four main spray methods include spray pyrolysis in a tubular reactor (SP), spray pyrolysis using a vapor flame reactor (VFSP), the emulsion combustion method (ECM) and flame spray pyrolysis (FSP). These methods are discussed and key concepts are compared such as the energy source driving the solvent/fuel evaporation and precursor reaction, final particle formation. Advances in fundamental understanding, scaling and simulation are highlighted. Specific strategies for the production of homogeneous products are presented in context with existing methods and specific applications. Finally, research needs are discussed with respect to new flame-made materials, instrumental strategies for their production and process optimization, including diagnostic techniques and process simulation.

† Accepted: August 26, 2004
coagulation and sintering was studied. Research in this field accelerated, however, when industrial flame reactors were introduced in the large-scale manufacture of optical fibers. Since the early 1990s, the pace of research has been further intensified with a renewed interest in flame technology for manufacturing advanced materials, emphasizing nano-structured particles for a large variety of applications [1].

Today, flame reactors are widely used for the manufacture of commercial quantities of nanoparticles such as carbon black (made by Cabot, Columbia, Degussa., etc.), fumed silica (Cabot, Degussa., Wacker, etc.), pigmentary titania (DuPont, Ishihara, Millennium, Kerr-McGee, etc.) and optical fibers (Corning, Hereaus, Sumitomo, etc.) [2]. Industrial flame reactors are reasonably well understood for the synthesis of particles with closely controlled particle size characteristics through control of the particle concentration and residence time, temperature history, reactant mixing, external fields and additives [22, 23]. Interfacing particle dynamic models with computer fluid models [24] has led to the prediction of a product powder’s specific surface area within 3% even for industrial-scale systems [25].

Using vapor flame reactors, the variety of products is limited by the choice of metal precursors with sufficient vapor pressure to deliver the desired amount of the metal species into the reactor. Problematic examples include the low production rates for bismuth oxide [26] or Pt/TiO$_2$ catalysts [27] from vapor flame reactors. Furthermore, it is difficult to produce multi-component materials with homogeneous chemical composition because differences in the chemical reaction rate and vapor pressure of the reactants, or different nucleation and growth rates may lead to non-uniform composition within and/or between particles and often yield segregated mixed-component particles [28]. However, in spray pyrolysis, each droplet contains the precursor in the exact stoichiometry as desired in the product [17, 29]. The droplet essentially serves as a discrete microreactor [30]. This is a huge advantage over vapor-phase routes since in the latter, several reactants have to be vaporized simultaneously with special care to obtain the desired stoichiometry.

Nielsen et al. [31] performed pioneering work in the field of the spray synthesis of metal oxides, mixed metal oxides, and ferrite powders from metal chloride, sulfate, acetate, and nitrate solutions. By atomizing the liquids into oxygen or air-fuel flames, they produced flakes, hollow-shaped, as well as submicron particles. The spray pyrolysis process took place over a wide range of conditions. A further distinction is made in the present paper between processes in which the powder is formed inside the droplet (spray pyrolysis) and processes where the precursor transport into the gas-phase occurs or the droplet explodes (see also Figure 1 for reference). The latter can be

![Fig. 1](image-url)  

Fig. 1 Various mechanisms for metal oxide formation from dissolved metal precursors sprayed into a high-temperature reaction zone. Only mechanisms on the right-hand side lead to nano-grained particles (by precursor evaporation or decomposition at high temperatures), while formation of the product within the droplet environment often leads to hollow and/or larger particles (partly adapted from Kodas and Hampden-Smith [32]).
achieved by an external non-reactive heat supply (e.g. tubular reactor); in flames formed by additional reactant gases (e.g. vapor-flame-supported); or by the spray itself (droplet fuel burning, e.g. emulsion combustion method or flame spray pyrolysis).

2 Spray processes for nanoparticle production

Spray-supported methods for nanoparticle production differ mainly by how thermal energy is provided to the precursor species, influencing main particle formation parameters such as temperature profile and residence time within the high-temperature environment. Figure 2 summarizes the four main spray methods discussed in this paper, namely spray pyrolysis in a tubular reactor (SP), spray pyrolysis using a vapor flame reactor (VFSP), the emulsion combustion method (ECM) and flame spray pyrolysis (FSP).

In all four processes, the precursor is delivered under ambient pressure to the reactive environment by dispersing it into fine droplets. The main difference, however, is the energy source driving the solvent or fuel evaporation and precursor reaction (in some cases also liquid fuel reaction). As shown in Fig. 2, reactors with an external energy supply (energy which is not provided by the spray itself as in SP and VFSP) are less sensitive to the choice of precursors and solvents.

Water is often chosen as the solvent in systems with an external energy supply (SP, VFSP, ECM) due to economic aspects, ease of handling and the excellent dissolution ability for many metal-containing precursors (e.g. nitrates, chlorides, acetates). In contrast, the combustion of the entire solution (as in FSP) results in higher maximum reactor temperatures and significantly larger temperature gradients compared with other methods. In the following sections, the resulting influences on final product properties will be discussed and highlighted.

2.1 Spray pyrolysis using tubular reactors (SP)

During the spray pyrolysis (SP) process, the precursor solution is atomized into a hot-wall reactor (or series of reactors) with well defined temperature fields. The aerosol droplets undergo evaporation, concentration of the solute within the droplet, drying, thermolysis of the precipitate particle to form a microporous particle, and finally sintering to form dense spheres [17]. The final product powder is formed within the atomized droplet through precipitation.

Compared to liquid-phase precipitation, powders produced by SP are advantageous since they are more crystalline, less agglomerated (compared to calcined sol-gel-derived powders), of high purity and rarely require post-calcination [32].

Development of the spray pyrolysis process was driven largely by the need to address the lack of control of the calcination process in conventional solution-based techniques (e.g. co-precipitation, hydrolysis of organometallic compounds, sol-gel, freeze drying and spray drying) resulting in intermediate salts or hydroxide products. This led to development of the so-called “evaporative decomposition of solutions” (EDS) [33] or “spray roasting”. The EDS process has been successfully used for the production of single- and mixed-oxide powders (ferrite and chromite powders) on industrial scales [34]. A detailed investigation of the effect of the metal salt on the characteristics of EDS-derived MgO, ZnO and NiO powders, and in particular their morphology, was carried out by Gardner and Messing [35] and Gardner et al. [36]. The authors report fine-grained, high surface area, aggregate-free powders when using metal acetate precursors, whereas strongly aggregated powders were obtained from nitrate precursors. The difference was attributed to the exothermic decomposition of the acetate salt in the reaction. Similar results were obtained for $\gamma$-Fe$_2$O$_3$ by Gonzalez-Carreno et al. [37]. They report iron-oxide nanoparticles (about 5 nm) formed from acetylacetonate precursors (dissolved in methanol) due to the exothermic reaction of breaking individual crystals apart from the droplet skeletal structure. In the absence of exothermic decomposi-
post-synthesis calcination step and the dilute process for carbon-monoxide and ethanol [46]. The additional
have been demonstrated to exhibit high sensitivity

demonstrated a one-step synthesis for Zn$_2$SiO$_4$: Mn ing nitrate precursors [41, 42]. Lenggoro et al. [43]
produced from organometallic silica and correspond-
at low operating voltage (e.g. Y$_2$SiO$_5$: Tb, non-aggre-
gation of flat panel displays with high efficiency
stoichiometry is well conserved during the spray
particles. However, the previous examples show that
formation of barium carbonate and/or irregularly shaped
Examples include the preparation of small particles of
yttrium-stabilized zirconia from nitrates, where parti-
cles in the size range of 400 nm with an average crystal
size of about 100 nm were formed [38]. Further
examples include barium and strontium titanate syn-
thesized from the organometallic titanita tetraisoprox-
oide (TTIP) and the acetates and nitrates of barium
and strontium [39, 40]. The formation of pervoskites
is a challenging task and often results in the forma-
tion of barium carbonate and/or irregularly shaped particles. However, the previous examples show that stoichiometry is well conserved during the spray pyrolysis process. Luminescent materials for the next generation of flat panel displays with high efficiency at low operating voltage (e.g. Y$_2$SiO$_5$: Tb, non-aggregated Y$_2$O$_3$: Eu phosphor particles) have also been produced from organometallic silica and corresponding nitrate precursors [41, 42]. Lenggoro et al. [43] demonstrated a one-step synthesis for Zn$_2$SiO$_4$: Mn particles (0.3-1.3 µm) with spherical, non-aggregated morphology and homogeneous phase. They applied long residence times (around 4 seconds) at high temperatures (1300°C) for final product formation. The authors highlighted the advantages of the aerosol route and the possibility of extending the production for multicomponent phosphor particles.

Another promising area for particles made by aerosol processes is catalysis. Spray pyrolysis was used to produce metal-supported catalysts resulting in well-dispersed metals (silver, platinum) on ceramic materials (e.g. alumina). The surface area of the catal-
yst was rather low (about 10 m$^2$/g), but direct cat-
alytic studies showed that the metal components were available on the surface and that they were quite active for catalysis. The performance of aerosol-made catalyst was clearly identified by Moser et al. [44] (e.g. for conversion of methylyclohexane). With this leading contribution to aerosol-derived metal/ceramic systems, it still took another 8 years to demonstrate that these systems are promising alternatives to con-
ventional wet-phase-made ones using vapor flame and spray flame technology, respectively [27, 45].

Gas sensor materials can also be synthesized by spray pyrolysis. Spray-pyrolyzed Pt/SnO$_2$ particles have been demonstrated to exhibit high sensitivity for carbon-monoxide and ethanol [46]. The additional post-synthesis calcination step and the dilute process conditions or low mass loading (low production rate) are still disadvantages of this specific SP process, but further developments in this area are expected [47]. One of the limitations of the spray pyrolysis process is evident during the synthesis of ceria particles [48]. In this instance, the process is not capable of producing nanometer-sized CeO$_2$ particles unless the solution concentration is extremely low [49]. To overcome this problem, Xia et al. [49] developed the salt-assisted ultrasonic aerosol decomposition where an inert salt can be used to control crystallite size and product aggregation. The disadvantages encountered with this technique are the required washing to remove the salt from the final product and purity issues similar to those experienced in wet-phase processes. Other examples of the salt-assisted method include the production of NiO, ZnS and (Ba$_{1-x}$Sr$_x$)TiO$_3$ [50]. Spray pyrolysis has also been used for the synthesis of well-ordered spherical silica particles with stable pore mesostructure of hexagonal or cubic topology [51]. Applications of this method include catalysis, chromatography, and controlled drug release. It should be mentioned that by using a hot-wall reactor and an inert carrier gas for the precursor delivery, non-oxide ceramic nanopowders such as the Si(N,C) systems [52] can be synthesized as well.

A deeper understanding of the droplet-to-particle formation mechanisms was achieved by modeling the solid particle formation during solution aerosol ther-
mosysis combined with evaporation. Models accounting for the evaporation of such aerosol thermolysis have been successfully applied to study the effect of various parameters on the final product morphology as demonstrated by Jayanthi et al. [53], Yu [54] and Lenggoro et al. [55]. However, more detailed knowl-
edge is needed on multicomponent evaporation and precursor reaction/decomposition and particle formation to enable ab initio product design.

2.2 Vapor-flame-supported spray pyrolysis (VFSP)

The success of producing functional metal oxides, mixed-metal oxides and metals on metal oxides from cheap precursors (e.g. nitrates) in an economical aerosol process has triggered the evolution of the reactor design. Tubular reactors used in SP provide a well-controlled temperature zone over long residence times for conversion of the precursor to the final product. It was realized, however, that the synthesis of a variety of products requires higher maximum temperatures (above 1300°C) and shorter residence times. The established vapor flame method for the
production of silica and titania clearly showed the advantages of high temperature and large temperature gradients and their control [23]. This led to the development of vapor(gaseous)-flame-supported spray pyrolysis (VFSP). In VFSP, the energy is supplied by a vapor flame where a fuel (mainly hydrogen, methane or propene) reacts with air or oxygen, forming the reaction and particle formation zone. The precursor is sprayed directly into the flame. Most of the precursor reactions are endothermal and since mainly aqueous solutions are used to dissolve the precursor (e.g. nitrates), the spray itself also cools the flame.

One of the first applications of this technique was the synthesis of YBaCuO high T_c superconductors [56, 57]. Three years earlier, Kodas et al. [58] used spray pyrolysis in a tubular reactor to decompose the nitrate salts. Their product showed chemically homogeneous micron-sized particles of high purity and superconductivity at 90 K when produced at high temperature (1000°C) with a post-calcination step. The flame reactor offered the possibility of synthesis without an additional post-calcination step. Different flame reactor configurations and conditions were tested, and it was shown that a diffusion flame in which particles do not pass through the flame front was the best way to control the temperature in order to avoid preferential volatilization while minimizing water vapor content [56, 57]. The VFSP-produced powder displayed superconductivity at 92 K without post-processing.

Aggregated ultrafine spinel powders of NiMn_2O_4 and SrMnO_3 were obtained by dissolving the carbonate precursors in dilute acetic acid and spraying this solution into a hydrogen/oxygen diffusion flame [59]. The successful preparation of nano-grained ternary oxides in the flame process similar to established methods for titania and silica was a major step towards the aerosol-based, large-scale production of functional nanoparticles. Kriegel et al. [59] further demonstrated that the prepared β-SrMnO_3 powders were catalytically active (temperature-dependent CO_2 formation from methane) and had higher conversion rates compared with powders derived using a conventional solid-state reaction. This performance was mainly attributed to the high specific surface area in the absence of micropores of the aerosol-derived powder. The same technique was used for the production of ultrafine γ-Fe_2O_3 from iron(III) acetylacetonate dissolved in ethanol or toluene by Grimm et al. [60]. The authors compared their results with the established and patented combustion of the volatile Fe(CO)_5 and found no significant difference. They further studied the development of the iron-oxide crystalline phases by varying the reactor conditions (oxygen content within the flame) and highlighted the importance of high maximum temperatures and steep temperature gradients during synthesis of the γ-Fe_2O_3 phase, while higher residence times were necessary to obtain the α-Fe_2O_3 phase. It is worth noting that in this study, the precursor solution itself supplied thermal energy to the process upon evaporation and reaction. The authors reported only the formation of ultrafine particles which most probably left the droplet environment during particle formation.

Metal nanoparticles were also produced in the VSFP process for glass coloring (Co, Cu, Ag) [65] or catalytic applications (Pt nanopowders) [66], but no distinct testing was reported. The process of spraying a precursor solution into a hydrogen/oxygen flame was characterized with respect to the atomization of the liquid feedstock, characterization of the flame, and flame droplet interaction by Tikkanen et al. [67]. Laser diffraction anemometry was used to obtain the droplet size distribution of the spray within the flame, laser doppler velocimetry traced the droplet velocity, the flame temperatures were measured with pulsed...
laser Rayleigh backscattering, and Schlieren photography determined the flame structure. Significantly, Tikkanen et al. [67] showed how the solvent affected the flame structure especially when using water instead of organic solvents. Detailed measurements of this kind, together with particle dynamic models (as done for vapor flame reactors [24]) would give detailed insights into the particle formation mechanisms and particle growth dynamics in VFSP flame reactors.

2.3 Emulsion combustion method (ECM)

A further step of applying the energy source in closer proximity to the reaction zone is the embedding of the aqueous precursor solution (mainly derived from nitrates) in a combustible droplet environment. This was achieved by preparing a water (with precursor) in oil (fuel) emulsion which was atomized into micron-sized droplets and subsequently ignited. This self-sustaining spray flame method is called the emulsion combustion method (ECM). Developed at Toyota labs in 1997 [68], this technique has been successfully applied to titania, silica, alumina, zirconia, barium titanate and zirconia-ceria, as well as electronic, catalytic and ceramic applications [69, 70]. A major limitation of this method can be the lack of control with respect to product morphology (e.g. hollow particles are often produced). A comparison between the ECM method and the flame spray pyrolysis (FSP) method (discussed in the next paragraph) revealed enhanced gas-phase mixing and reaction in the latter case [71]. The ECM was also used for the synthesis of gold coatings by flame spraying a micro-emulsion of an aqueous solution of HAuCl₄·H₂O and a surfactant solution in hexane [72]. The authors report nanoparticles of up to several nanometers in size with good control of size and shape but do not identify specific applications of their product.

2.4 Flame spray pyrolysis (FSP)

It was previously mentioned that endothermic precursor reaction pathways often lead to hollow or fragmented product particles [36, 37]. The utilization of the endothermic species (mainly metal-nitrates and metal-chlorides dissolved in water) is driven by low cost, availability and solubility (achievement of high concentrations). However, when using these precursors, the final product particle formation takes place very often within the droplet due to insufficient energy needed to vaporize, sublime or disruptively decompose the precursor, in order to facilitate reaction and particle formation in the gas phase surrounding the droplet. In most of the processes and applications introduced so far, the sprayed precursor solutions contained species which require external energy for their reaction. In EMC, the very high energy content of the kerosene in close proximity to the endothermic-reacting precursor (less than a micrometer) could not avoid the formation of hollow particles [69].

Taking this into account leads to the exclusive use of exothermic-reacting species and the design of self-sustaining spray flames that provide the temperature and the residence time profiles intrinsically similar to vapor flame reactors [23]. This similarity is illustrated in Figure 3 which shows a comparison between the temperature profiles of a premixed vapor flame (open symbols) and a spray flame reactor (full symbols), each producing silica at similar production rates. One of the first studies using these principles was the formation of ceramic Al₂O₃ aerosol from aluminium(III) acetylacetonate dissolved in an azeotropic mixture of benzene and ethyl alcohol [73]. The mixture was sprayed and combusted with no soot formation giving ultrafine (3-100 nm) alumina particles. In this profound work, the authors investigated parameters influencing the crystal structure of alumina and targeted studies for the synthesis of α-alumina in flames. The authors demonstrated that an increase in the water vapor content decreases the formation of the...
This was implemented commercially with the vapor flame approach using vaporized \( \text{AlCl}_3 \) in carbon monoxide (Degussa, EP0395925, 1990).

It took twenty years to follow up on this initial idea of flame spray pyrolysis when Bickmore et al. [29] and Karthikeyan et al. [75] reported on the formation of MgO, Al\(_2\)O\(_3\), ZrO\(_2\) and YSZ ceramics. Ultrafine particles were mainly produced from organic precursors and solvents (exothermic), while nitrates dissolved in water (endothermic) resulted in larger particles. This was also reported for the FSP preparation of yttria-stabilized zirconia (YSZ) powders from zirconium n-propoxide and ytterbium nitrate (with crystal water) [76].

An important step toward the economic application of spray flame pyrolysis for the production of functional and complex nanoparticles was the work by Bickmore et al. [29], where they report the preparation of ultrafine crystalline spinel powders (MgAl\(_2\)O\(_4\)). The authors realized the importance of the precursor formulation and accordingly prepared stoichiometric amounts of Al(OH)\(_3\) and MgO with the amine base, tri-ethanolamine in ethylene glycol. The as-produced precursor (including ethylene glycol) was diluted with dry ethanol. With this dilution, they adjusted the metal content and the viscosity for good atomization while at the same time the ethanol served as the fuel source for combustion. The spray was atomized with oxygen and ignited with a natural gas/oxygen torch. Production rates were up to 100 g/h and the minimum average particle diameter obtained from specific surface area measurements of the products was 25 nm. This precursor preparation/FSP process was further investigated for the production of titania from titanium tetrachloride that forms titanatrane glycolate when reacting the hydrosol in triethanolamine and ethylene glycol. The derived precursor was diluted in different alcohols, and products with specific surface areas up to 45 m\(^2\)/g and a 9:1 anatase to rutile composition were produced. The materials had similar characteristics to commercial products of flame-made TiO\(_2\) [77]. Another example of the success of this precursor strategy (triethanolamine and ethylene glycol) is the preparation of Na\(_{x}\)Al\(_{1-x}\)O\(_2\) \( (x=0.5, 0.7) \) called \( \beta'' \)-alumina (Na\(_2\)O-x Al\(_2\)O\(_3\)) serving as a high-temperature solid electrolyte [78, 79]. The flame-spray-pyrolyzed nanopowder expressed preferentially the \( \beta'' \)-phase, which was attributed to the rapid heating and cooling within the flame spray reactor favoring this specific reaction pathway. Further examples are group II metal aluminates (MeAl\(_2\)O\(_3\)) with Me = Mg, Ca, Ba, Sr [80] as well as 3 Al\(_2\)O\(_3\) · 2 SiO\(_2\) [81, 82], CeO\(_2\) and SrO · Al\(_2\)O\(_3\) · 2 SiO\(_2\) [82], n-phosphors \( (Y_{1-x-y}Yb_xRe_y)_2O_3 \) with Re = Er, Tm and Pr [83] and CeO\(_2\)/ZrO\(_2\) [83, 84]. The complexity and functionality for very different applications of the products summarized in this paragraph is worth noting. All the products are characterized by an average particle diameter below 100 nm derived from specific surface area measurements, and no hollow structures are reported.

Commercial organic precursors (aluminum-sec-butoxide) (zirconium-n-butoxide and zirconium-n-propoxide) dissolved/diluted in their parent alcohols were used in a high-production-rate flame spray process (180 g/h) for nano-scale alumina and zirconia [85]. Use of the rather volatile exothermal-reacting species resulted in spherical nanoparticles typical for flame processes [23]. Particle diameters ranged from 4 – 100 nm with an average of about 40 nm.

The control of primary particle size, crystal size, morphology and composition using the options of the spray flame reactor similar to vapor flame reactors was first investigated for silica [74] and then later for a variety of functional products such as zinc oxide [86] and bismuth oxide [87]. It was shown that the decomposition behavior and the subsequent reaction path of the precursor/solvent systems influences the morphology and homogeneity of the products. Using ethanol and nitric acid as the solvent of the nitrate precursor resulted in the formation of hollow (1 \( \mu \)m in diameter) and sintered dense spheres (50 – 100 nm in diameter) as well as aggregates of primary particles, each of 10 nm in diameter. In contrast, dissolution of the bismuth nitrate in acetic acid led to synthesis of solid nanoparticles. The acetic acid solvent may have favored the formation of an aceto-bismuth complex, facilitating enhanced precursor evaporation and gas-phase formation of the oxide particles [87]. The importance of the precursor mixture was further demonstrated when producing ceria in the FSP process. Here, the addition of iso-octane/2-butanol to the acetic acid/acetate solution accelerated precursor evaporation and gas-phase reaction, resulting in homogeneous powders [88]. Powders with an average BET diameter as small as 5 nm were produced. Similar studies were performed for the alumina system [89]. It was further shown that in mixed-oxide systems, control of the product structure and morphology can be obtained in flame spray pyrolysis such as for ZnO/silica [90], zinc silicate [91] and ceria/zirconia [92]. Especially in the latter example, Stark et al. [92] highlighted the importance and specifics of the exothermal reaction of the precursor solution when using carboxylic acid mixtures, where
the precursor composition offered a very fast precursor delivery by the sudden onset of decarboxylation. The ceria/zirconia system was tested for its oxygen exchange capacity [93] and was later modified with dopants [94]. Precise control of process and product powder characteristics enabled the formation of zinc-oxide quantum dots [95] and the simultaneous deposition of noble metals on the formed ceramic particles, for example, gold on silica and titania [96] and platinum or palladium on alumina and titania [45, 97, 98] (see Figure 4). It was further shown that precise control is not restricted to lab-scale reactors and that even at production rates up to 1.1 kg/h, particle sizes and morphology can be closely controlled [99, 100] (see Figure 5).

2.5 Plasma-supported spray processes for nanoparticle synthesis

One important technique for pyrolyzing liquid precursor droplets to obtain nano-structured materials is plasma assisted droplet to particle conversion. These processes differ from the previous methods in terms of a closed (non-ambient) reactor design and significantly higher set-up expenditure and will therefore be mentioned only briefly here. Similar to conventional spray pyrolysis, the energy source is located externally of the reactor (mainly radio frequency inductively coupled or microwave cavity plasmas). Although the external energy source enables the utilization of a wide range (mainly aqueous) of precursor solutions, at the same time high energy densities from the plasma are required, leading to solvent evaporation (or droplet disruption), precursor conversion and particle formation. Consequently, all reported products are nano-grained powders with high crystallinity comprising a wide range of metal ceramics. Detailed overviews of the technique are given by Suzuki et al. [16], Vollath and Sickafus [101] and Hasegawa et al. [102]. The technology is also used commercially (e.g. for zinc oxide), while the reactor design focuses mainly on the utilization of pure metal precursors rather than spraying metal-containing solutions.

3 Applications of powders produced by spray pyrolysis methods

Spray pyrolysis in its different forms as introduced in Sections 2.1 to 2.4 finds application in various fields of modern technology. The high specific surface area, texture, morphology, crystal structure, composition, purity and environmental benefits (minimal liquid wastes) can be advantageous compared with powders prepared by wet chemical methods. Furthermore, the ability to produce nano-structured materials of single oxides, mixed oxides, and noble metals on ceramic supports has broadened the potential range of applications. Table 1 gives a structured overview of the application for the examples described in Sections 2.1 to 2.4. Applications are categorized in the fields of ceramics, electronics, optics and catalysis. The morphology of the powders, mainly divided here into hollow and solid particles, is crucial for most of the applications and special attention is paid to this property in Table 1.

There is a broad variety of applications and specific powders made by ambient pressure spray processes, and only a small selection is given in Table 1.
Table 1: Summary of Sections 2.1—2.4

| Application | Process/Morphology | Reference |
|-------------|--------------------|-----------|
| Ceramic Al2O3, CaAl2O4 | SP/m | Roy et al. [33] |
| Ceramic Al2O3 | FSP/n | Sokolowski et al. [73] |
| Ceramic MgO | SP/m | Gardner and Messing [35] |
| Ceramic YSZ | SP/m | Febler [58] |
| Ceramic MgAl2O4 | FSP/u | Bickmore et al. [29] |
| Ceramic MgO, ZrO2, YSZ | FSP/m,u,n | Karthikeyan et al. [75] |
| Ceramic (MeAl2O4) with Me=Mg, Ca, Ba, Sr | FSP/m,u | Narayanan and Laine [80] |
| Ceramic YSZ | FSP/m | Yuan et al. [76] |
| Ceramic TiO2 | FSP/u | Bickmore et al. [77] |
| Ceramic MgO, YSZ; sugar solution | VFSP/n | Helble [30] |
| Ceramic ZrO2, Al2O3 | ECM/m/h | Takatori et al. [68] |
| Ceramic SrO · Al2O3 · 2 SiO2 | FSP/u | Laine et al. [82] |
| Ceramic 3 Al2O3 · 2 SiO2 | FSP/u | Baranwal et al. [81] |
| Ceramic ZrO2, Al2O3; high production rate | FSP/u | Kilian and Morse [85] |
| Ceramic ZrO2 | VFSP/u/n | Limaye and Helble [62] |
| Ceramic SiO2 | FSP/n | Mädl er et al. [74] |
| Ceramic SiO2; high production rate | FSP/n | Mueller et al. [59] |
| Electronic Ferrite and chromite powders | SP/m/u/n | Ruthner [34] |
| Electronic YBaCuO | SP/m | Kodas et al. [58] |
| Electronic BaTiO3, SrTiO3 | SP/m | Nonaka et al. [40] |
| Electronic YBaCuO | VFSP/m | Zachariah and Huzahewicz [57] |
| Electronic γ-Fe2O3 | SP/h/u/n | Gonzalez-Carreno et al. [37] |
| Electronic γ-Fe2O3; energy supply from the liquid | VFSP/n | Grimm et al. [60] |
| Electronic BaTiO3 | VFSP/m/u | Brewster and Kodas [61] |
| Electronic Na1.67Al10.67Li0.33O16.33 | FSP/u | Treadwell et al. [78] |
| Electronic Au | ECM/n | Bonini et al. [72] |
| Electronic ZnO | FSP/n | Mädl er et al. [86] |
| Electronic ZnO/3SiO2 | FSP/n | Mädl er and Pratsinis [87] |
| Electronic ZnO/SiO2 | FSP/n | Tani et al. [90] |
| Electronic Au on TiO2 and SiO2 | FSP/n | Mädl er et al. [96] |
| Electronic SnO2 | FSP/n | Sahm et al. [47] |
| Optics Y2O3 : Eu | SP/m | Kang et al. [42] |
| Optics Y2SiO5 : Tb | SP/m | Kang et al. [41] |
| Optics Co, Cu, Ag | VFSP/m/h | Gross et al. [55] |
| Optics Y2O3 : Eu | VFSP/m | Kang et al. [63] |
| Optics SrTiO3 : Pr | VFSP/m | Kang et al. [64] |
| Optics Zn2SiO4 : Mn | SP/m | Leugger et al. [43] |
| Optics (Y2/3, Yb)2O3 with Re=Er, Tm and Pr | VFSP/u | Laine et al. [83] |
| Catalysis NiMn2O4, SrMnO3 | VFSP/n | Kriegel et al. [59] |
| Catalysis Pt, Ag, Ir, Sn on Al2O3 | SP/m | Moser et al. [44] |
| Catalysis CeO2 | SP/m | Vallet Regi et al. [48] |
| Catalysis Ce2Zr1-xO3 | ECM/m/h | Takatori et al. [68] |
| Catalysis SiO2, specific topology | SP/m | Lu et al. [51] |
| Catalysis CeO2 | FSP/u | Laine et al. [82] |
| Catalysis CeO2, salt-assisted | SP/u/n | Xia et al. [49] |
| Catalysis Pt | VFSP/n | Oljaca et al. [66] |
| Catalysis CeO2 | FSP/n | Mädl er et al. [88] |
| Catalysis Pt on TiO2 | FSP/n | Stark et al. [97] |
| Catalysis Ce2Zr1-xO3 | FSP/u | Sutorik and Baliat [84] |
| Catalysis Ce3Zr1-xO2 | FSP/n | Stark et al. [92] |
| Catalysis SiO2, Al2O3/Ce3Zr1-xO2 | FSP/n | Schulz et al. [94] |
| Catalysis Pt on Al2O3 | FSP/n | Strobel et al. [45] |
| Catalysis Pd on Al2O3 | FSP/n | Strobel et al. [98] |

1SP=Spray pyrolysis using tubular reactor; VFSP=Vapor-flame-supported spray pyrolysis; ECM=Emulsion combustion method; FSP=Flame spray pyrolysis; m=micron-sized aggregate (larger than 500 nm) composed of nano-crystallites (smaller than 100 nm); h=hollow particles; u=powders with distinct primary particles below 100 nm; n=powders with distinct primary particles below 20 nm
ever, the list shows that all spray techniques introduced in Section 2 are used for many different applications. All techniques are capable of producing metal oxides, mixed metal oxides and noble metal on metal oxides. It should be noted that powders with distinct primary particles below 20 nm are only produced when the liquid feed supplies the reaction energy to the reactor, as for example in exceptional cases of VFSP by Kriegel et al. [59], Grimm et al. [60], and more generally in FSP. Another point to note is that most of the techniques were first introduced 30 years ago, while it is only in the last four years that research has intensified in this area, driven by the increasing demand for functional nano-structured materials. This can further be seen in the pertinent patent literature (not reviewed here) as well as in the flourishing of commercial activity in this area.

4 Future directions

The capabilities and know-how of gas-phase synthesis were successfully transferred from classic vapor-fed flames to liquid-fed aerosol reactors, enabling the one-step production of demanding and highly functional products. Such aerosol-derived nano-structured metal oxides, mixed metal oxides and metals on metal oxides find application in the fields of catalysis, sensors, fillers, and electronics, and have advanced the research and development of these reactors in recent years. However, in the process of synthesizing these materials and controlling their functionality, many questions remain open. Examples include the formation mechanisms of mixed structures, such as two or multiple mixed oxides or metals on a metal oxide, further the formation of hollow structures in comparison with solid ones. Current research is addressing these questions with spatially resolved diagnostic methods to obtain droplet, gas and product kinetics in these complex multiphase systems. Such understanding will only be achieved by the combination of theoretical analysis and experimental data. In theoretical research, the challenge is the adaptation of established models, such as for nanoparticle growth in vapor(gas)-fed flames or droplet combustion in engines. The chemistry involved during the transformation of the dissolved precursor to the first stable clusters is probably one of the keys in further understanding this technology.

For numerous applications, coatings are applied to nanoparticles in order to improve their functionality. Modern sun creams make use of titania nanoparticles which absorb light in the ultraviolet region of the sun-light spectrum and are small enough in size to avoid the scattering of visible light. However, in order to reduce photocatalytic activity and to improve the compatibility of the particle surface when immersed in liquid or solid matrices, silica coatings are added. New protective coatings for optical filtering and thermal barriers, nano-structured polymers, and catalysts are already starting to enter the market. Nano-structured coatings show good corrosion/erosion resistance and could be used as possible replacements for environmentally troublesome chromium-based coatings. Coatings also assist the blending of materials such as boron nitride which has a very high thermal conductivity, making nanoparticles of this kind of material interesting for heat conduction in electronic devices. Here, the surface inertness has to be overcome by an alumina surface coating before embedding into the epoxy matrix.

Another largely unexploited field in this area is the direct utilization of as-produced particles being suspended and well-dispersed as an aerosol. Further processes such as immobilization and controlled deposition offer many exciting possibilities for further modifying the particles and new technologies of this kind are close at hand.

5 Summary

The utilization of liquid-fed reactors for the aerosol-based production of nano-sized powders has been reviewed. Growing awareness of the potential of aerosol processes and the increasing demand for functional metal oxides, mixed metal oxides and metals on metal oxides has driven the research and development of these reactors in recent years. The four main spray methods, namely spray pyrolysis in a tubular reactor (SP), spray pyrolysis using a vapor flame reactor (VFSP), the emulsion combustion method (ECM) and flame spray pyrolysis (FSP), were discussed and main concepts were compared such as the energy source driving the solvent/fuel evaporation and precursor reaction. Strategies for the production of homogeneous products were presented in context with existing methods and specific applications.

Acknowledgement

Stimulating discussions with Prof. S.E. Pratsinis, H.K. Kammler and M.J. Height (ETH Zurich) are gratefully acknowledged.
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Author’s short biography

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Lutz Mädler studied Technical Physics at the Technical University of Zwickau, Germany, from 1991 to 1996 and received an engineering diploma in Physics. He also holds Diploma and Doctoral degrees in Process Engineering from the Technical University of Freiberg, Germany. From 1996 till 1999 he worked for the Fraunhofer Institute of Toxicology and Aerosol Research Hannover, Germany, in the field of particle characterization and particulate source apportionment. In 1999 he joined the Particle Technology Group at the Swiss Federal Institute of Technology (ETH) Zurich. He received his Habilitation from ETH Zurich in 2003 and serves as Privatdozent (senior lecturer) for Particulate Processes. His research developed the area of spray processes for materials manufacture. He focuses on the design, control, and theoretical understanding of spray flame reactors for the production of functional and tailor-made nanoparticles for applications in composites, sensors, catalysts, and electronic materials.