

# Overview - Nanoparticulate Dry (Flame) Synthesis & Applications

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## ABSTRACT

Flame synthesis is a scalable technology that was developed largely by valiant evolutionary research for manufacture of commodities (e.g. carbon blacks, fumed silica and pigments). In the last 5-10 years, however, major advances in the scientific understanding of combustion and aerosol formation and growth allow now optimal reactor design and flame production of sophisticated inorganic nanoparticles with controlled composition, size and morphology. This leads to a series of new products such as highly selective (TiO<sub>2</sub>-spot-coated SiO<sub>2</sub>) epoxidation catalysts or V<sub>2</sub>O<sub>5</sub>-coated TiO<sub>2</sub> for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> at lower temperatures than conventional catalysts that can lead to better fuel utilization and/or effective pollutant (e.g. Hg) removal during incineration.

Furthermore, this understanding allows now the creation of new processes like liquid-fed flame reactors making possible the manufacture of a much broader spectrum of products such as efficient Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for synthesis of chiral molecules for pharmaceuticals. Specialty oxides like stable CeO<sub>2</sub> for catalytic or planarization applications can be readily made as well as stable ZnO quantum dots (1-8 nm in diameter) that exhibit the blue shift of UV light. Carbon-coated silica or titania nanoparticles have been made that could either better blend in a polymer without requiring functionalization with surfactants or facilitate the formation of electrodes for a Li-battery. Very recently, biomaterials have been made by these processes creating some unprecedented opportunities for orthopedics.

Non-agglomerated fumed silica (50-90 nm in diameter) that are blended with dimethylacrylate contributes to the development of nanocomposites for novel dental fillings that could replace current ones based on polymeric resins. A new flame-nozzle process is developed that freezes particle growth and allows formation of non-agglomerated and even blue titania (5-10 nm in diameter). Scale-up relationships for flame aerosol reactors are developed and validated with a large body of data allowing a systematic design and operation of industrial units. With this technology inorganic nanoparticles with closely controlled morphology and composition are made exhibiting unique performance in a field that has been dominated by wet chemistry for years.

Summarizing, dry (flame) aerosol technology offers a proven and rather inexpensive route for large-scale production of nanoparticles. The field is expanding from synthesis of simple oxides to more complex, functional

nanoparticles. The extension of classical flame aerosol synthesis to new processes allows the manufacture of new, high value products. Flame-made materials emerge into other engineering areas such as heterogeneous catalysis, biomaterials, dental materials, fuel cell membrane production and electroceramics fabrication. Early results in heterogeneous catalysis, in particular, indicate the potential of flame-made catalysts. Microelectronics and even medical applications will profit from these developments. New questions arise and underline the need for basic research in synthesis of mixed oxides with precisely controlled characteristics. Some of them include: scale-up for synthesis of particles with controlled functionalities; mesoscopic chemistry relationships that can be verified & used and nanothin coated nanoparticles made in mass. Whatever the direction, however, abundant new discoveries are awaiting on this rather unexplored interface of material and engineering science.

Aside from this potential of nanoparticles, there is significant concern for their health effects. Do the advanced material properties come with adverse health effects? Scattered data at academic and industrial laboratories imply a rather vague answer. Some public opinion groups seem eager to treat this technology as another "GMO" and even imply a moratorium on nanoparticle research. There is, however, plenty of information on the effects of nanoparticles on human health that has been completely overlooked. Humans have been in contact with nanoparticles for centuries and even with their manufacturing for over a hundred years. Clearly there is a great need to place the health effects of nanoparticles on a firm scientific basis to better protect the national investment in this field and, most importantly, guide researchers and even investors. Given the current advances of aerosol science in characterizing nanoparticles and the large body of anecdotal data regarding exposure to nanoparticle commodities (carbon black, fumed silica, pigmentary titania), there is also a great opportunity for systematic research on the health effects of nanoparticles at an international level.

**Keywords:** Flame synthesis, nanoparticles, catalysis, sensors, biomaterials

## 1 INTRODUCTION

Methods to produce nanoparticles are many, however, only few can produce ton quantities. Flame aerosol technology has been used since prehistoric times to make

carbon nanoparticles for artwork inks in China and black- or red-faced vases in ancient Greece. Today it is used for large scale manufacture of simple commodities such as carbon black [1], pigmentary titania, fumed silica and alumina [2], and even optical fiber preforms [3]. Production rates of these materials can be in the order of 25 t/h and the corresponding reactors resemble best the rockets of the space shuttle departing from Cape Kennedy. Product value ranges between \$0.5/kg for carbon black to \$500/kg for cermets or even \$20,000/kg for Pt catalysts. While titania, for example, was mainly produced by wet-phase chemistry in the early 60s, entailing huge amounts of sulfuric acid waste, the development of the dry “chloride” process was solvent free and produced few by-products. Likewise, in the late 70s flame technology contributed decisively to the manufacture of ultrapure silica fiber to be used as a lightguide in telecommunications [4].

Industry led this research with Cabot in carbon blacks [5] while Degussa discovered fumed silica in the 1940s [6]. Parallel to this, intensive research was carried out, especially at DuPont, for flame synthesis of TiO<sub>2</sub> [7]. This research, however, was rather Edisonian than based on the fundamental principles of combustion and aerosol engineering. As a result, the design of these reactors was rather evolutionary making difficult today their modification for flexible synthesis of other simple or mixed oxide nanoparticles. So it is not surprising that only recently these manufacturers have entered the field either with their own R&D (e.g. Degussa) or by acquisition of small start-up companies (Cabot, DuPont).

Academia has paid close attention to flame synthesis of nanoparticles contributing a number of discoveries from first class university laboratories that have substantially advanced the current understanding of particle formation at high temperatures. Major contributions include the use of thermophoretic sampling [8] and the direct temperature measurement of these particle-laden flames e.g. by FTIR [9] to unravel the particle growth history in a flame. In addition the morphology of flame-made ceramic particles is related quantitatively to their sintering history in the flame [10]. When such data are coupled with fluid-particle dynamics models [11], it becomes clear that product particle characteristics (size, crystallinity and morphology) are determined largely by maximum flame temperature, cooling rate and precursor concentration in a given reactor [12, 13]. Of course many other parameters beyond the above core ones such as reactor design, additives, electric fields etc can influence particle characteristics.

Having this understanding allows now a fresh look in flame technology so to use it for making a series of new products such as catalysts, quantum dots, nanocomposites that are made conventionally by tedious wet chemistry, to highlight just a few as Gael Ulrich [14] had pointed out since 1984! (I require every one of my new students to read that article [14] on their first day in the lab). In general flame reactors are advantageous as they do not involve the many process steps of wet chemistry, have no moving parts

and can produce high purity particles (e.g. as exemplified with optical fibers) that can be readily separated from their carrier gases. Most importantly, there is a good understanding of flame technology in the engineering community so one should not have hard time to attract personnel to operate such a process [2].

## 2 HETEROGENEOUS CATALYSIS

### 2.1 Mixed metal oxide catalysts

Today, most industrial chemical processes heavily rely on catalysis to make high value products such as polymers or pharmaceuticals. Typically, catalysts are prepared by wet-phase chemistry, followed by filtration, drying and calcination to remove undesired residuals and homogenize the surface. Alternatively, flame technology may provide a direct, continuous process with few waste and by-product generation [4].

In fact, flame technology has been identified early on as an effective process for catalyst manufacture [15]. Degussa capitalized in that by developing the oxy-hydrogen flame process for synthesis of titania, thus creating a product (Degussa P25) that is routinely used in the exploding field of photocatalysis today as well as in cosmetics and other specialty products. There is now interest of developing mixed oxide catalysts in flames. Stark et al. [16] prepared in one step non-porous vanadia/titania catalytic nanoparticles of high surface area (100+ m<sup>2</sup>/g) in a diffusion flame aerosol reactor. These particles had a smooth monolayer of vanadia on top of anatase titania by taking advantage of the vast difference in boiling points between the two oxides. This catalyst converted NO to N<sub>2</sub> by selective catalytic reduction by NH<sub>3</sub> at 30 to 40 °C lower than conventionally prepared catalysts (Figure 1). This is very important for energy utilization as more energy can be extracted from the off-gases prior to scrubbing them through a treatment unit of a power plant. The open morphology of these particles gives good NO access to the catalyst surface so pore diffusion does not limit the reaction rate. Even though vanadia and titania show a series of complex mixed oxides in the phase diagram, none was observed in flame made powders. High temperature and high gas exit velocity favor rapid reaction and limit the high temperature residence time, thus reducing the probability to react further to mixed phases. Furthermore, this process was scaled-up from a few grams to several hundred grams per hour production rates and its catalytic performance was independently tested at the University of Duisburg-Essen in Germany [17] and found to be consistent with the early laboratory studies [16] and Figure 1.

Vapor-fed flame technology was used also to prepare mixed titania/silica oxide catalysts for liquid phase oxidations [18]. Depending on the synthesis conditions, catalysts with improved selectivity (above 90%) compared to wet-phase made ones (around 65%) are obtained. Figure 2 compares the selectivity of commercial epoxidation

catalysts to that of flame-made ones at different production scales.

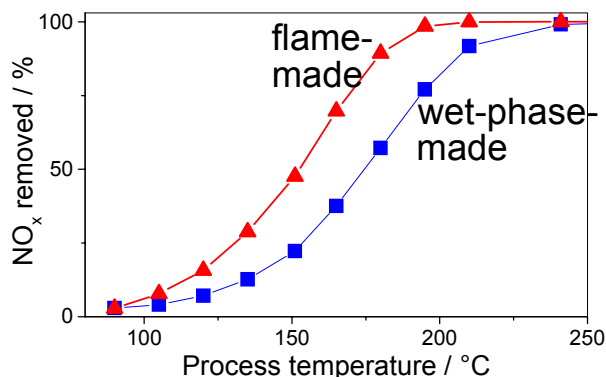


Figure 1: Conversion of NO to N<sub>2</sub> by selective catalytic reduction with ammonia using either flame-made or wet-made vanadia-coated titania catalysts. The flame made catalysts achieve the same conversion but at 30-40 C lower than the conventional ones leading to better energy utilization before gas scrubbing (adapted from Stark et al. [16]).

It is fascinating to see that the flame-made catalysts retain their superior performance over wet-made ones even when produced at relatively high production rates. In these catalysts, the titania is distributed within the surface of a silica matrix in the form of isolated Ti ions as determined by UV-VIS and diffuse reflectance FTIR spectroscopy which is identical to that seen with wet-phase made catalysts. Very recently, we discovered by in situ X-ray absorption near edge structure (XANES) analysis that flame-made catalysts have a considerably higher content of the active species (4-atom coordinated Ti) than conventionally-made ones [19]. It is likely that as TiO<sub>2</sub> condenses onto the 4-atom coordinated silica so that structure is forced on Ti by the substrate. Today, these reactors have been scaled also to 500 g/h [20, 21] and such catalysts are evaluated by industry even for manufacture of organic products.

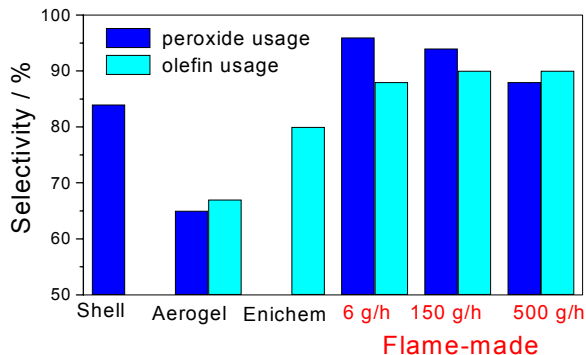


Figure 2: Comparison of the selectivity of flame-made titania-doped silica catalysts for olefin epoxidation with that of aerogel, and commercially available ones (adapted from

Stark et al. [21]. The flame-made ones are superior as they contain a higher fraction of the active site: 4-atom coordinated titanium [19].

## 2.2 Supported noble metal catalysts

A new liquid-fed flame reactor has been developed to overcome the constraints of conventional vapor-fed flames in synthesis of catalytic particles [22]. More specifically, flame spray pyrolysis (FSP) has been used for production of various supported noble metal catalysts. In the case of Pt/Al<sub>2</sub>O<sub>3</sub>, the specific surface area of the powders ranged from 70 to 140 m<sup>2</sup>/g depending on the oxygen and precursor flow rates [23]. Platinum was well dispersed and confined to the alumina surface (Figure 2). Platinum dispersion strongly depended on the platinum loading decreasing from ca. 77% to 24% when the loading was increased from 0.1 to 0.9 mg<sub>Pt</sub>/m<sup>2</sup>. These FSP-made catalysts showed higher activity for the enantioselective hydrogenation of ethyl pyruvate than a standard commercial platinum/alumina catalyst (E4759) with about the same platinum loading. Enantiomeric excess of (*R*)-ethyl lactate formation reached 87% at 100% conversion for FSP-derived catalysts pretreated in hydrogen. Turnover frequency increased with higher platinum loading, i.e. lower dispersion, indicating structure sensitivity of the reaction. In contrast enantiomeric excess was virtually independent on platinum loading in the range 0.2 – 0.9 mg<sub>Pt</sub>/m<sup>2</sup>. The porous-free flame-made catalysts were superior to the commercial ones as they exhibited less mass transfer limitations. The Pt nanoparticles had a narrow distribution as they were formed by nucleation-condensation after alumina particles had been formed by coagulation and sintering earlier on in the flame as was seen with gold nanoparticles made on titania or silica by flame spray pyrolysis also [24].

Similar to the Pt/Al<sub>2</sub>O<sub>3</sub> catalysts the flame spray pyrolysis method has been successfully applied for the synthesis of Pd/Al<sub>2</sub>O<sub>3</sub> hydrogenation catalysts [25]. Materials with good catalytic performance in enantioselective hydrogenation of could be produced in a single-step flame synthesis process. The catalysts are made up of small palladium particles (1–5 nm) attached to the surface of agglomerated, nonporous alumina particles (10–30 nm) and exhibit high thermal stability. Hydrogen pretreatment at elevated temperatures improved drastically the catalytic properties (TOF, ee, chemoselectivity) of flame-made catalysts in the hydrogenation of 4-methoxy-6-methyl-2-pyrone. After pretreatment flame-made catalysts showed higher activity and enantioselectivity than reference catalysts prepared by conventional methods. The flame-made catalysts with different Pd particle sizes revealed a significant structure sensitivity of the reaction.

As flame-made materials are nonporous they exhibit very often excellent thermal stability. In catalysis numerous processes operating at high temperatures exist where catalytic materials with high resistance against deactivation

and sintering are needed. One example is the catalytic combustion of natural gas in gas turbines. Flame-spray pyrolysis was applied for the one-step synthesis of Pd catalysts supported on La-stabilized  $\text{Al}_2\text{O}_3$  [26]. The addition of lanthanum resulted in materials with excellent thermal stability as judged from the loss in specific surface area and the transformation of  $\gamma$ - into  $\alpha$ -alumina. The catalysts were tested for their performance in the combustion of methane and compared to corresponding impregnated reference catalysts. After restructuring and sintering of palladium during an initial temperature cycle under reacting conditions (200-1000 °C) all catalysts showed similar activities that slowly decayed during the following cycles. It seemed that after this conditioning the catalytic performance is independent of preparation method, lanthanum content and specific surface area of the catalyst, indicating a very low metal-support interaction after palladium sintering and restructuring.

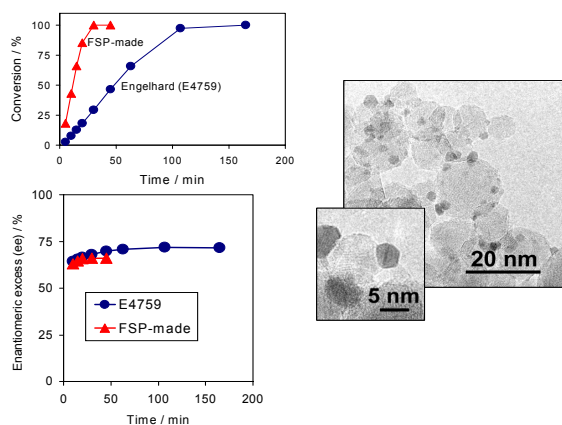


Figure 3: Narrowly distributed Pt nanoparticles (black/grey dots on the pictures) on alumina nanostructured aggregates made simultaneously by flame spray pyrolysis (FSP). This flame-made  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst exhibited similar selectivity (enantiomeric excess) with conventional (E4759) catalysts for synthesis of chiral molecules but much higher activity (2-3 times faster conversion) as its open structure did not exhibit mass transfer limitations that are typically encountered in porous structures. Adapted from Strobel et al. [23].

To stabilize not only the supporting material  $\text{Al}_2\text{O}_3$  but also the noble metal particles bimetallic Pd-Pt catalysts were prepared by FSP [27]. These catalysts were also tested in the combustion of methane in the temperature range up to 1000 °C. The as-prepared materials consisted of agglomerated alumina nanoparticles on which the metal components are well-dispersed. The metal constituents formed small bimetallic particles supported on alumina. EDX and EXAFS measurements indicated that the metal particles are alloyed (Figure 4). Platinum influenced the  $\text{PdO} \leftrightarrow \text{Pd}$  transformation, favoring palladium in its

reduced form. Furthermore, added in small amounts (Pt mass fraction <10%), platinum increased the resistance of the metal particles towards sintering at high temperatures. This stabilization by Pt improved the behavior of the catalysts in the combustion of methane.

Overall, high temperature preparation favors the distribution of an active component on the surface of the catalyst and often leads to narrow site distribution and consequently enhanced selectivity thus reducing by-product and waste formation. Today, the production of sizable quantities of flame made catalysts has been achieved in a pilot scale flame aerosol reactor in Zurich and making, thus, dry-made catalysts accessible on an application scale [28].

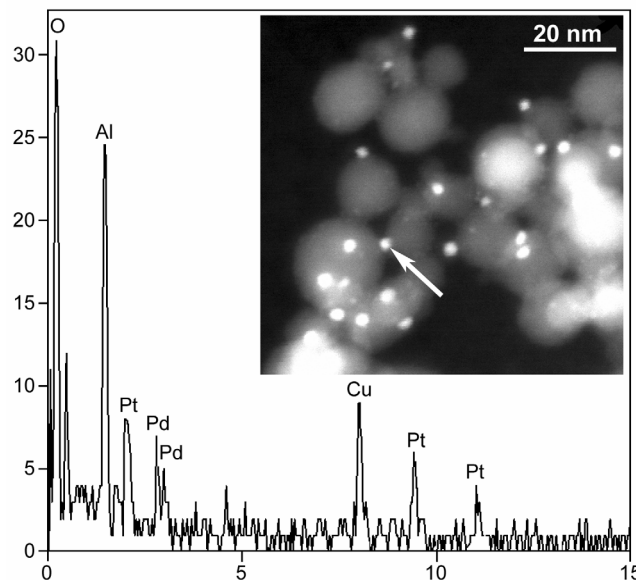


Figure 4: EDX analysis of a single Pd-Pt particle (3 nm) revealed the direct formation of alloyed Pt-Pd particles by one step flame spray pyrolysis. These bimetallic particles exhibited an increase thermal stability in the catalytic combustion of methane (adapted from Strobel et al. [27]).

## 2.3 Exhaust gas catalysts

Ceria is an attractive basis material for automotive catalysts (three way) as well chemical mechanical planarization. Classical vapor flame synthesis cannot be used for ceria since no readily volatile ceria precursors exist. Mädler et al. [29] prepared ceria nanoparticles in a spray flame and compared the product to precipitation-made ceria in terms of sintering stability. With the addition of an iso-octane/2-butanol mixture to that solution, homogeneous  $\text{CeO}_2$  nanoparticles were obtained. The specific surface area of the powders ranged from 240 to 100  $\text{m}^2/\text{g}$  by controlling the oxygen dispersion and liquid precursor flow rates through the flame. Furthermore, for production rates from 2 to 10 g/h a constant average primary particle size could be obtained at selected process parameters. The ceria showed high crystallinity and primary particles with a stepped surface. The powder

exhibited good thermal stability and conserved up to 40% of its initial specific surface area when calcinated for 2 h at 900 degrees C. This shows the potential of FSP made ceria for high-temperature applications as in three-way catalysts or fuel cells. In particular, the stepped surface of this flame-made ceria should be quite attractive for rapid planarization applications.

Spraying cerium and zirconium precursors dissolved in carboxylic acids into a methane-oxygen flame resulted in nanocrystalline solid-solutions of ceria-zirconia mixed oxides with high temperature stability and surface area [30]. Recently, Stark et al. [31] prepared Pt supported on  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  by flame spray pyrolysis. The as-prepared material showed excellent thermal stability. Compared to a conventionally prepared material the flame made Pt/Pt/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  showed no deactivation in the low temperature oxygen storage capacity after exposure to very high temperatures.

### 3 SENSORS

Flame spray pyrolysis (FSP) has been used to synthesize tin oxide nanoparticles from the ethylhexanoate precursor in ethanol [32]. The particles were highly crystalline having a primary particle and crystallite size of 17 nm. The single crystalline particles were only slightly aggregated and directly used for thick film sensor deposition by drop coating. The flame made  $\text{SnO}_2$  nanoparticles showed high and fast response to both reducing (propanal) and oxidizing ( $\text{NO}_2$ ) gases.

$\text{SnO}_2$  and Pt doped  $\text{SnO}_2$  sensors were further prepared by flame spray pyrolysis. Nano-crystalline tin-oxide can be directly *in-situ* deposited as porous films onto alumina sensor substrates by thermophoresis [33]. The as-obtained sensors exhibit extremely good homogeneity of the sensing film and good sensor performance. This innovative process has obvious advantages such as superior control over the microstructure and morphology of the nano-powders compared to classical wet-chemistry methods. Furthermore, the process is clean and fast (minutes compared to days for comparable quantities) and also allows for *in-situ* functionalization. The direct deposition resulted in fully formed functionalized sensing films. The *in-situ* prepared sensors of pure  $\text{SnO}_2$  and Pt doped  $\text{SnO}_2$  are reproducible and have very low detection limit for CO (down to 1 ppm) with high sensor response.

### 4 NANOCOMPOSITES

The degree of agglomeration is an important quality index in a number of applications. For example, agglomerated nanostructured particles are needed in manufacture of fillers, catalysts, lightguide preforms and for filamentary nickel. In contrast, non-agglomerated nanoparticles ( $d_p < 200$  nm) are needed in ceramics, composites and electronics. Non-agglomerated spherical silica particles of  $d_p = 44\text{--}78$  nm were made in a standard

diffusion flame reactor that can be readily scaled-up by variation of the  $\text{O}_2$  flow rate using 2.5–8.5 l/min  $\text{O}_2$  at powder production rates of 17 g/h [34]. By reducing the particle concentration, non-agglomerated tailor-made silica particles were synthesized at all  $\text{O}_2$  flow rates with diameters ranging from 18 to 85 nm. Non-agglomerated particles were formed when gas-to-particle conversion was completed or the residence time at high temperature (as defined by the onset of steep cooling) was larger than the characteristic time for sintering or coalescence. These non-agglomerated particles were well dispersed in a polymer matrix resulting in nanocomposites with increased elastic modulus.

#### 4.1 Dental materials

Mixed  $\text{Ta}_2\text{O}_5$ -containing  $\text{SiO}_2$  particles, 6-14 nm in diameter, with closely controlled refractive index, transparency, and crystallinity are prepared via flame spray pyrolysis (FSP) at production rates of 6.7-100 g/h [35]. The refractive index of these particles could be controlled from 1.44 to more than 1.80 by varying the  $\text{Ta}_2\text{O}_5$  content. Excellent composite transparency was observed for high transparencies of the filler itself. The composite transparency increased for  $\text{Ta}_2\text{O}_5$  contents in the ceramic filler up to 35 wt%. For higher  $\text{Ta}_2\text{O}_5$  content, the composite transparency decreased drastically. High composite transparency is attributed to a high powder (filler) transparency, the amorphous nature of the mixed ceramic oxides, the high dispersity of Ta within the  $\text{SiO}_2$  matrix, and a matching refractive index between filler and polymer. Composites with a high  $\text{Ta}_2\text{O}_5$  content in the filler particles (35 wt%) coupled with a high transparency (86%) are best for dental-restoration applications, optical caries detection, and X-ray detection of the filling.

#### 4.2 Biomaterials

Calcium phosphate biomaterials have attracted tremendous interest in clinical medicine. Both hydroxyapatite (HAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) and tricalcium phosphate (TCP,  $\text{Ca}_3(\text{PO}_4)_2$ ) exhibit excellent biocompatibility and osteoconductivity. The extension of flame spray pyrolysis to complex salt nanoparticles was demonstrated for the preparation of different calcium phosphates [36]. The synthesis of amorphous calcium phosphate with a broad range of compositions and optional doping with additional metals resulted in salt nanoparticles of 10-50-nm size. Phase-pure  $\alpha$ - or  $\beta$ -tricalcium phosphate was obtained after calcination of the amorphous particles for a precursor calcium to phosphorus molar ratio of 1.52. Excess phosphorus ( $\text{Ca/P} < 1.5$ ) promoted the formation of dicalcium pyrophosphate. Hydroxyapatite is formed from corresponding calcium-rich precursors. As-prepared amorphous apatite ( $\text{Ca/P} = 1.67$ ) contained 3.9 wt % carbonate  $\text{CO}_3^{2-}$  and crystallizes above 600 °C. Fluoro-apatite nanoparticles resulted from the addition of fluoride

to the precursor mixture. After sintering, such materials exhibit a highly regular open structure with interconnecting pores. Facile substitution of anions ( $F^-$ ) and cations ( $Mg^{2+}$  or  $Zn^{2+}$ ) in calcium phosphate combined with a high degree of flexibility in morphology, crystallinity, and phase composition offer a versatile production tool to biomaterials engineering.

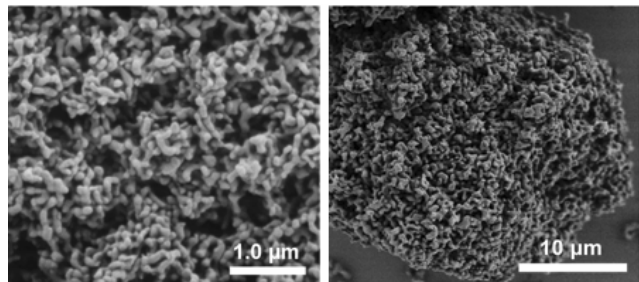


Figure 5: Scanning electron microscopy images of calcium phosphate. Metastable  $\alpha$ -tricalcium phosphate resulting from calcination (30 min) at  $700^\circ C$  (left).  $\beta$ -tricalcium phosphate is formed after calcination at  $900^\circ C$  (right). The highly regular, open structure of flame-made calcium phosphate results from sintering the low-density aerosol. Interconnecting pores facilitate liquid circulation through the samples (adapted from Loher et al [36]).

## 5 ADVANCED MATERIALS AND PROCESSES

### 5.1 Quantum dots

Quantum dots are one of the most promising nanosize materials that are made typically by wet chemistry. Major challenge are their a) stability, these particles tend to grow upon storage by Ostwald ripening, and b) size selectivity involving sometimes quite an elaborate fractionation process to attain the desired size. Zinc oxide nanocrystallites down to 1.5 nm in diameter, however, were made surprisingly by spray combustion of Zn/Si precursors [37]. The surprise is that flame produce broadly distributed particles (self-preserving size distribution) that could not exhibit the blue shift of UV light. In this system, however, silica prevented the sintering growth of ZnO crystallites “forcing” a specific ZnO crystallite size depending on silica concentration. These crystallites exhibit a quantum size effect: blue shift of light absorption with decreasing crystallite size. X-ray diffraction, high-resolution transmission electron microscopy, and nitrogen adsorption showed that the addition of controlled amounts of silica prevented the growth and stabilized the ZnO crystals. The blue shift of the ultraviolet-vis absorption edge with decreasing ZnO crystal size closely followed a correlation between optical band gap and crystallite size from the wet chemistry literature. The flame-made quantum size effect is

shifted to smaller particles than that of the wet-made ZnO as the stress of the silica matrix may affect the performance of the ZnO crystallites. The band-gap energy of these ZnO quantum dots increased with silica content in the spray and particles consistently. The as-prepared quantum dots were stable and did not require any post processing.

### 5.2 Freezing growth at the nano level

A process for close control of primary particle size morphology and crystallinity [38, 39] of flame made nanoparticles has been developed. According to this, freshly made titania aerosol nanoparticles are rapidly quenched in a critical flow nozzle essentially freezing particle growth at desired levels. The nanoparticles are produced in a methane/oxygen diffusion flame reactor by oxidation of titanium tetra isopropoxide (TTIP). Precise control of phase composition from 97 to 5 wt. % anatase (and the balance rutile) and average primary particle diameter from 5 to 60 nm is possible by positioning the quenching nozzle at the desired heights above the burner and controlling gas and precursor flow rates. The nozzle quenching also reduces the degree of agglomeration of the product particles. An operation diagram shows that the primary particle diameter and the phase composition can be independently controlled, making anatase or rutile nanoparticles with high or low specific surface area. This process has been used to make blue titania suboxides which can be protected from full oxidation by in-situ coating with silica preventing, thus, oxygen diffusion to suboxide. This process has worked well also for silica and alumina and has high potential to be used in high value nanoparticles (2-10 nm) for electronic and even cosmetic applications.

## 6 OUTLOOK AND RESEARCH NEEDS

There are a number of discoveries at the nano level that can be brought to broader use through efficient and economic manufacturing of nanoparticles. Flame aerosol technology offers a proven and rather inexpensive route for large-scale production of nanoparticles. A reasonably good understanding of particle formation and growth allows the combination of particle dynamics models and computational fluid dynamics for aerosol reactor engineering and product development. The field is expanding from synthesis of simple oxides to more complex, functional nanoparticles. The extension of classical flame aerosol synthesis to new processes allows the manufacture of new, high value products.

Today flame aerosol reactors can readily produce catalysts, nanocomposites, sensors and even quantum dots. These materials seemed impossible to make in the gas phase in mass just 3 or 4 years ago. Medical applications will profit from these developments and aerosol-made dielectrics provide new possibilities for microelectronics. There is concern, however, that the unique features of the

nanoscale are rather elusive when these materials are made in mass. In many instances, nanosized powders cannot be even transported, stored and used in air processing atmospheres without losing performance. Nanometals are pyrophoric and non-oxide ceramic nano-powders will oxidize readily in air. Critical research areas are the scale-up for synthesis of particles with controlled functionalities, mesoscopic chemistry relationships that can be verified, used and, finally, nanothin coated nanoparticles made in mass [40]. Whatever the direction, however, abundant new discoveries are awaiting on this rather unexplored interface of material and engineering science.

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