4.2 Generation of Particles by Reactions

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4.2.1 Gas-Phase (Aerosol) Techniques

Making particles by gas phase chemical reactions is a fascinating process. It makes some of the most widely used fine particulate commodities (carbon black, pigmentary titania, optical fibers, filamentary Ni, ferrites, fumed silica, etc.) and sophisticated nanomaterials (e.g. nanosilver, biomedical carbon-coated cobalt particles selling for \$200/g). At the same time, this process is responsible for generation of air pollutants (e.g. soot) with profound effects on human health and environment (climate, visibility). As a result, it attracts keen interest from various scientific fields and many sectors of applications.

In the context of classic particle technology and chemical reaction engineering, the reactors employed for synthesis of these powders are most closely related to lean phase fluidization with pneumatic transport as the solids volume fraction is very low, less than 10⁻³ even at production rates¹ of 25 t/h. The text by Friedlander² provides a lucid account of the fundamentals while the book of Kodas and Hampden-Smith³ details various processes for aerosol synthesis of materials. The history of industrial development of the above commodities has been summarized⁴ and the in-situ (laser) diagnostics for characterization of such particles have been reviewed⁵. A summary of processes for gas-phase synthesis of materials has been given⁶ while the fundamentals for multi-scale design of such processes have been presented quantitatively⁷. Athanassiou et al.⁸ have shown how chemical engineering facilitates gas-phase synthesis of nanoparticles. The impact of aerosol processing in heterogeneous catalysis has been brought forward by a review⁹ of nearly 500 articles with Koirala et al.¹⁰ highlighting the role of scalable flame aerosol technology in catalyst synthesis and Fujiwara et al.¹¹ pointing out the significance of strong metal-support interactions in such catalysts. Aerosol particle technology is attractive for the assembly of devices¹² (nanogenerators, battery and fuel cell electrodes) and most notably for highly selective chemoresistive gas sensors for breath analysis¹³.

Here a summary of the fundamental phenomena and main processes for particle synthesis by gasphase reactions is provided along with references for more detailed coverage of specific aspects.

4.2.2 Advantages and Disadvantages

Making particles in the gas phase has distinct advantages¹⁴:

- 1. Liquid byproducts are not generated requiring costly cleaning and disposal (e.g. "chloride" vs. "sulfate" process for manufacture of pigmentary TiO₂).
- 2. Collection of particles from gases is easier and less expensive than from liquids.
- 3. Fewer unit operations are required than wet-chemistry ones.
- 4. Ultrapure products can be made (e.g. optical fibers)
- 5. Materials with unique (e.g. filamentary) morphology can be made.
- 6. Stable synthesis of metastable phases is possible.
- 7. Operating in the gas-phase facilitates process design from first principles.
- 8. Scale-up to tons/h is proven.

There are however certain disadvantages^{3,10}:

- 1. Capital investment is needed even for simple exploration of tiny quantities (hoods, controls, filters etc.)
- 2. Safety must be closely observed as particles in gases can easily escape and be inhaled while operating at high temperatures requires close attention.
- 3. Low-cost precursor availability, preparation and handling is not always trivial.
- 4. Assuring product composition and uniformity requires thorough process design as on-line monitoring of particle characteristics is practically impossible during their large scale manufacture
- 5. Particles are typically more polydisperse than those made by wet-chemistry processes.

Exploiting the advantages while suppressing or, at least, mitigating the disadvantages, determines success for a particular product and process.

4.2.3 Particle Formation

Particles can be made by chemical reactions either in the gas-phase, the so-called gas-to-powder conversion route (Figure 1), or within suspended aerosol droplets in gases, the so-called droplet-to-powder conversion route. In either case, to initiate and/or sustain the chemical reactions heat is provided by various means (electric, chemical, laser, plasma) that define the actual reactor configuration as discussed below in more detail. The route affects distinctly the product particle characteristics. In gas-to-powder conversion, particles are made by a bottom-up sequence (molecules \rightarrow clusters \rightarrow particles) that results in compact or ramified (fractal-like) solid particles. In the droplet-to-powder route a top-down sequence takes place (droplets \rightarrow particles) resulting in solid, fibrous, porous, hollow or shell-like particles.

Figure 1

Sometimes precursors are fed as droplets that fully evaporate so particles are formed solely gas-topowder conversion (e.g. carbon black the so-called "furnace process). In development of new products, however, is not uncommon to form particles by both routes when droplets are fed to a reactor. This is usually quite undesirable and should be avoided by appropriate process design and operation.

4.2.3.1 Gas-to-powder conversion

Figure 1 shows a schematic of particle formation by gas-to-powder conversion overlaid on a flame. This is typical for manufacture of most of the above commodities and new materials. Usually such particles are formed by gas-phase reactions such as decomposition, oxidation, reduction, nitridation etc. of a precursor (hydrocarbon, SiCl₄, TiCl₄ or Ni(CO)₄ etc.) at high temperatures. Initially numerous chemical species (radicals, oxychlorides, aliphatics, aromatics etc.) are generated leading to creation of a multitude of molecular clusters and/or nuclei that rapidly grow into particles by collisions with each other (coagulation) and chemical reactions with gaseous species (e.g. condensation, surface or epitaxial growth).

At the initial stages of particle formation, small and rather compact particles are created (few nm in diameter). As particles grow larger and/or process temperature drops, their coalescence (sintering or fusion) rate slows down and can become comparable (typically within a factor of 10) to their (ongoing) coagulation rate. Then partially-fused or dumbbell-shaped structures (Fig. 1a) are formed as the colliding particles are held together by strong chemical forces (e.g. covalent, ionic bonds). The resulting structures are called aggregates while their constituent particles, primary particles (PPs). When coalescence stops completely and/or gaseous precursors are exhausted, colliding particles (single or aggregated PPs) can be held together by weak physical forces (van der Waals, electrostatic, magnetic etc.) resulting in the so-called agglomerates (Fig. 1b). When the number of constituent PPs follows a power law with the agglomerate radius of gyration (or mobility radius), they are referred as fractal-like particles.

Agglomerates are attractive for suspensions (e.g. paints, slurries) and polymer nanocomposites because they can be broken readily into their constituent smaller aggregates and/or PPs by ultrasonication, high-pressure dispersion etc. On the other hand, aggregates are most attractive for electroceramics (sensors, battery or fuel cell electrodes) as they do not suffer electric losses by contact resistance. They are also attractive for catalysts and lightguides as upon assembly of pellets and preforms, respectively, aggregates form large openings (interparticle pores) facilitating transport of fluids to/from the particle surface.

4.2.3.2 Droplet-to-powder conversion

Manufacture of micron to submicron sized ceramic particles and most notably ferrites is typically carried out by this route which is similar to spray drying or granulation. In the literature this is referred as spray pyrolysis or spray roasting or aerosol decomposition. Typically precursor droplets (generated by any of the processes given in the previous chapter) flow through a high temperature chamber to drive the chemical reactions within the droplet components and/or the carrier gas. Particle formation takes place within the droplet as it evaporates. If nucleation and precipitation takes place at the droplet surface, hollow or cenosphere-like particles are formed that can rupture into shell-like fragments. Otherwise solid particles are formed that can have with a highly porous surface. A characteristic of this route is that the droplet size affects the size of product particles that tends to be polycrystalline unless high temperatures and long residence times are involved. The textbook of Kodas and Hampden-Smith³ has provided a thorough account of droplet-to-powder conversion processes.

4.2.4 Control of Particle Size Distribution and Morphology

As in every chemical reactor, product characteristics (e.g. size distribution, morphology, crystallinity etc.) are determined by reactant concentrations and reactor residence time (that depends on the process temperature and velocity profiles). So their impact on chemical reaction rate, coalescence and coagulation rate determines product particle characteristics. In particle synthesis by gas-to-powder conversion typically high temperatures, steep temperature gradients and high particle concentrations are involved.

4.2.4.1 Residence Time.

As particle growth takes place in high temperatures, the residence time there, the so-called high temperature particle residence time (HTPRT), is of importance⁷. For example, the mean TiO₂ PP diameter (or specific surface area, SSA) is determined when chemical reaction, coalescence and coagulation take place. When only coagulation takes place, agglomerates are formed that can be re-dispersed to their constituent PPs and aggregates (e.g. by ultrasonication or high pressure dispersion). So the HTPRT for the primary particle size during gas-phase synthesis of TiO₂ starts with onset of particle formation and ceases with the end of sintering or coalescence. The start of HTPRT can be defined by the onset of precursor conversion (TiCl₄ oxidation) as determined by monitoring the infrared signal of TiCl₄. The end of HTPRT can be determined by monitoring it by small angle X-ray spectroscopy or thermophoretic sampling and microscopy (or by nitrogen adsorption). Now if the goal is to attain a specific crystal size and composition, the HTPRT could be different and

typically longer than the above for the PP size. This is a reason, for example, that amorphous fumed SiO_2 reactors (for PP size 5-50 nm) are few meters long while those of pigmentary rutile TiO_2 (PP diameter 200-250 nm) are much longer (e.g. 100 m)⁴.

Controlling the HTPRT controls product particle sizes, morphology and composition. For example, increasing precursor concentration, process temperature and pressure will always increase agglomerate size but PP and aggregate sizes will only increase as long as gas phase reactions and/or coalescence take place also. Suppression of aggregate formation is possible by drastic change of the ratio of characteristic times for particle coagulation to coalescence e.g. by steep cooling rates at constant particle concentration¹⁵ or steep reduction of particle concentration at constant cooling rate¹⁶. Other process variables (e.g. doping, electric fields) that affect these characteristic times can have similar effects as has been demonstrated in gas-to-powder conversion reactors (flame, hot-wall and plasma).

4.2.4.2 Size Distribution and Structure

Besides average particle size, particle growth by rapid coagulation facilitates rapidly attainment of their self-preserving size distribution (SPSD).¹⁷ This means that particles grow but the shape of their size distribution is intact. For instantly-coalescing upon collision spherical particles, the number-based geometric standard deviation, σ_g , is about 1.45.¹⁸ This holds also for the primary particle (PP) size of agglomerates. For example, Granqvist and Buhrman¹⁹ made a dozen metallic particles by inert gas condensation and found the σ_g , of PPs to be 1.48 ± 0.12 regardless of composition! In contrast, for aggregates with significant necking between PPs, the σ_g of PPs can become much narrower, nearly monodisperse.²⁰ Coalescence is faster for smaller particles similar to condensation, red-shifting the small tail of the size distribution and making such powders to exhibit quantum dot behavior.²¹

For agglomerates the σ_g of their SPSD is larger than the above of spherical particles, 2 or 2.3, based on their mobility radius or radius of gyration, respectively, in the free-molecular regime.²² The SPSD is attained when the average particle size becomes 2-3 times the initial particle size or that reached at the end of new particle formation¹⁸. The SPSD facilitates enormously the quantitative description of particle growth by coagulation as the total particle concentration, N, can be obtained by assuming a unimodal (e.g. monodisperse) size distribution:

 $dN/dt = -\beta N^2$.

The collision frequency, k, depends on particle size, shape, temperature and pressure and detailed expressions can be found in textbooks.² The simplest is for spherical particles in the continuum regime, $\beta =$

 $4k_BT/3\mu$, where k_B is the Boltzmann constant, T the temperature in K and μ the gas viscosity. For particles having attained the SPSD, one has to replace 4 by 4.3 in β .

By a mass balance, the average particle size can be determined from N while the entire size distribution can be obtained by scaling to that size the corresponding SPSD for that size regime (continuum or free molecular) and particle shape (sphere or fractal-like). Kruis et al.²³ have developed a monodisperse model for fractal-like particle coagulation-coalescence from the free molecule to continuum regime that has been used for aerosol reactor design for a wide array of ceramic and metallic particle compositions.

The high particle concentrations facilitate also the rapid attainment of the asymptotic, so-called fractallike structure (fractal dimension, D_f) of agglomerates. When agglomerates are made of monosdisperse PPs, the D_f of 1.91 or 1.78 is attained (in the free molecular and continuum regime, respectively) by the time the agglomerate grows to within 2-3 times the PP size (10-15 PPs per agglomerate). As the PPs distribution broadens, it takes longer to attain that D_f . For example, for spherical PPs having their SPSD (e.g. $\sigma_g = 1.45$), attainment of the above D_f requires agglomerates containing 35-50 PPs on the average.²²

4.2.5 Hot-wall flow reactors

In these reactors the required high temperature for driving the chemical reactions for particle formation is provided by external heating of the reactor walls³. These reactors and processes come with several names in the literature. For example, when the particle precursor is fed in the vapor form (e.g. by bubbling a carrier gas through its liquid) to the reactor, this process is called high temperature (aerosol) flow reactor, chemical vapor synthesis or condensation (a derivative from chemical vapor deposition widely used in film deposition). When droplets are fed to the reactor by the generators of the previous chapter and droplets fully evaporate, then the process is called spray pyrolysis or roasting or aerosol decomposition etc.

These reactors are most attractive for basic measurements (e.g. overall sintering²⁴ or reaction rates) as well as product development³ due to their well-defined temperature profiles and residence time distributions. Various commodities are made commercially in these reactors: ferrites by spray pyrolysis, lightguide preforms by modified chemical vapor deposition (MCVD), filamentary Ni by Ni(CO)₄ decomposition, WC for coating of drilling bits by the carbothermal reduction etc.. Typically precursor gases and/or droplets flow into an externally (e.g. electrically) heated tube (the hot-wall reactor) in which particles are formed by chemical reactions. Usually particles are collected downstream by baghouse filters or onto the reactor wall (e.g. lightguide preforms by MCVD). These reactors have been used for the laboratory-scale synthesis of an array of materials like Si for photovoltaic applications and SiC and AlN for

structural ceramics in addition to ultrafine alumina, zirconia, silica, and titania to name a few. These reactors are used also for extraction of basic properties for process design as, for example, overall reaction rates leading to particle formation: SiCl₄ oxidation for manufacture of optical fibers, and TiCl₄ or titanium tetra-iso-propoxide (TTIP) oxidation for particles or films. Such data facilitate the development of quantitative models for particle formation in every aerosol reactor without adjustable parameters as with the deposition efficiency of lightguide preforms made commercially in MCVD reactors²⁵ and the evolution of spherical titania particle size distribution²⁶.

4.2.6 Flame reactors

These reactors are used exclusively in manufacture of carbon blacks and fumed silica. They are the major processes also for manufacture of optical fibers, pigmentary and photocatalytic titania as well as other oxides dominating gas-phase synthesis of particles by volume and value. This due primarily to the relatively cost of the required energy. Here particle formation takes place usually by exothermic chemical reactions so an external energy source is not needed to sustain the process. Some reactants are preheated by oxidation of light hydrocarbon gases as in manufacture of carbon black and pigmentary TiO₂. When the precursor chemistry does not generate sufficient energy for this task, additional fuel is provided with the precursors to initiate and/or sustain the process.

Despite the broad use of these reactors, their understanding and development has been rather incremental driven by valiant Edisonian research.⁴ The complexity of the temperature and velocity profiles in the highly turbulent jets of industrial units (Re $\# \sim 10^6$) along with the ramified structure of the resulting particles have been the main obstacles for systematic understanding of these processes.

Flame reactors are classified according to the state of the particle precursor²⁷. Vapor-fed aerosol flame synthesis (VAFS) refers to oxidation or combustion (or hydrolysis) of volatile precursors (e.g. methane, ethylene, TiCl₄, TTIP, SiCl₄) by oxidant (air, oxygen) and particle formation by gas-to-powder conversion. The availability of volatile precursors at reasonable cost, however, drastically limits VAFS to only few materials.²⁷.

Non-volatile precursors can be used with liquid-fed aerosol flame synthesis (LAFS) that is employed in production of carbon black by the widely used furnace process in that industry. Usually a combustible precursor solution is sprayed and ignited to give the particle product by gas-to-powder conversion. Spraying is accomplished typically by solution atomization through air-assist nozzles as described in the last chapter. For a high enthalpy-content organic solution a rather small pilot flame is used to ignite and

sustain spray combustion. This is the so-called flame spray pyrolysis process (FSP). For a low enthalpycontent (*i.e.* aqueous) spray solution of inorganic precursors, an external flame is used as a heat source serving essentially as the hot walls of classic spray pyrolysis. This is the so-called flame-assisted spray pyrolysis (FASP).

Flame-made particles are collected with baghouse filters and cyclones. When flame-made films are desired, particles can be deposited directly on a flat plate, tube, fiber or foam substrate. Such deposition can take place at different substrate temperatures with different particle morphologies affecting film structure and texture. Using masks during deposition allows preparation of films with well-defined patterns for catalytic microsystems and gas sensors.

Recent advances in combustion aerosol characterization and process simulations have improved the understanding of material synthesis by combustion of liquid precursors at kg/h (e.g. Gröhn et al.²⁸). As a result, a wealth of new catalysts, gas sensors and biomaterials have been created²⁷ from various precursors²⁹ and most recently reviewed by Mäkelä et al.³⁰. Especially, flame aerosol deposition of noble metal clusters and even, their single atoms on ceramics nanoparticle supports³¹ (Figure 2) opens new frontiers in catalysis and gas sensing as it drastically minimizes the cost of such materials since very small amounts of noble metals are used. In 2017 the German Science Foundation launched the SPP1980 initiative (~6 M Euros) supporting 20 PhDs across Germany for 6 years to advancing the fundamentals of FSP.³²

Figure 2

4.2.7 Plasma reactors

Plasma is a charged or ionized gas that created by direct (arc) or indirect (inductive) electric discharges using high voltages. Direct are more energy efficient than indirect but can contaminate the product from the erosion of electrodes. This is important for synthesis of nanoparticles having high surface area. Plasmas reach extreme temperatures (e.g. up to 10⁴ K) and decompose gases, droplets and even particle feeds down to atoms and radicals. Chemical reaction and/or condensation downstream of the plasma leads to particle formation (e.g. cooling of the plasma plume). Plasma reactors are used widely for deposition of films and hard coatings on commercial scale.³³ Mostly inductively coupled plasma reactors are used on laboratory scale for synthesis of an array of nanoparticles with narrow size distributions³³ with many promising applications but have been challenging for large scale production of powders. Plasma processes for synthesis of various particle compositions and morphologies have been reviewed by Vollath³⁴ and Phillips et al.³⁵. These reactors are quite attractive for synthesis of non-oxide particles. Recently plasma reactors

are looked closely for efficient and environmentally-friendly production of carbon black and H₂ by direct conversion of hydrocarbons in the absence of oxidation, reaching 100 % yields and reducing significantly CO₂ emissions ³⁶. This has led to creation of new carbon black industry (Monolith) testing them at the pilot scale for industrial scale manufacture of carbon black from natural gas.

4.2.8 Laser reactors

Lasers provide the required energy to drive chemical reactions for particle synthesis at precise locations. This is accomplished by absorption of the infrared laser energy by one of the precursors or by an inert photosensitizer (e.g. sulfur hexafluoride). Laser reactors reduce wall deposits and produce high-purity powders with a fairly narrow size distribution because they confine the reaction to a small region where high temperatures and short residence times prevail. As they do not need oxygen to generate the required heat (similar to plasma reactors), they are attractive for synthesis of metallic and nonoxide powders (e.g. carbide, nitride powders). Early research was done at MIT while significant effort has been done in TU Delft especially with process upscaling³⁷ that has been quite challenging. Focusing on synthesis of solar silicon, a commercial process was developed by Nanogram, that was acquired by Teijin. The focused energy of lasers has been used also to fuse in-situ agglomerates of flame-made particles³⁸. Lasers have been used also to evaporate materials from surfaces e.g. laser ablation. The resulting plume is brought in contact with reactants that can lead to new particle compositions.

Figure captions

Figure 1 Schematic depiction of particle formation by gas-to-particle conversion delineating the ongoing physical phenomena and particle morphology⁷ along with microscopic images of TiO_2 aggregates (a) and agglomerates (b) made by open and enclosed spray flames³¹, respectively.

Figure 2 Microscopic images of flame-made (a) Pt subnano-clusters (0.4 wt%), (b) Pt atoms (0.1 wt%) and (c) Ag clusters at very high loading (30 wt%) on TiO₂. Such small clusters (a) and even single atoms (b) are stable during annealing up to 600 C in ai,r taking advantage of strong metal-support interactions.¹¹

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