

Nanoparticles: Synthesis, technology and applications

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Abstract

This lecture addresses nanoparticle synthesis from gases highlighting flame technology as it dominates industrial manufacture of nanoparticles. Interfacing computational fluid dynamics with particle dynamics is used to better understand the fundamental processes and to optimally design reactors. Specific applications will be discussed also with emphasis on catalysis while future research needs will be outlined.

Definitions & Process Classification

Nanoparticles are either single particles of size 1 to 100 nm or the individual members (primary particles or grains or crystals) of large aggregates or agglomerates. In the last few years the scientific community has cherished the potential of nanoparticles. These entities have distinctly different properties than bulk material because the number of atoms or molecules on their surface can become comparable to that inside the particles. Some people even believe that nanosize particles may constitute another state of matter! With nanoparticles the particle melting point decreases, light absorption increases, and electromagnetic and other properties change, compared with those of the bulk material. Nanoparticles can also be used for catalysts with very high surface areas and a large density of active sites [1].

Typically, nanoparticles are made by gas-phase processes and wet chemical processes. The former are advantageous for inorganic (ceramic and metal) nanoparticle manufacture since they do not involve the tedious steps, high liquid volumes and surfactants of wet chemistry processes. Gas-phase processes for synthesis of nanoparticles are classified as gas-to-particle and droplet-to particle conversion processes depending on how particles are made [2].

In the gas-to-particle route nanoparticles are made by "building" them from individual molecules all the way up to the desired size. The particle formation process is driven by the generation of molecules by chemical reaction from precursor gases or by the rapid cooling of a superheated vapor. High temperatures are usually required to accomplish the reaction or to bring the vapor to the superheated state. Depending on the thermodynamics of the process, the product molecules can form particles either by uninhibited collisions (collision-controlled nucleation) or by balanced condensation and evaporation to and from molecular clusters (condensation-evaporation-controlled nucleation). The newly formed particles grow further by collision with product molecules (condensation or reaction on the particle surface) and/or particles (coagulation). When the rate of particle collision is faster than that of particle coalescence (fusion), aggregates of primary particles are formed. These are termed hard or soft aggregates (or agglomerates)

depending on how easy it is to break the bonds connecting the primary particles. Powders made by gas-to-particle conversion have relatively narrow size distributions and consist of nonporous spherical primary particles. The primary advantages of gas-to-particle conversion processes are: small particle size, narrow particle size distribution, solid particles and high purity. Disadvantages include difficulties in producing multicomponent materials, and problems in handling hazardous gases. Examples of these processes include flame[3], hot-wall, evaporation-condensation[4], plasma, laser and sputtering to name a few.

In the droplet-to-particle route, solution or slurry droplets are suspended in gases by liquid atomization or by condensation of a superheated vapor. This is followed by evaporation of solvent from droplets, initial crystallization of the solute in the droplet and further solvent evaporation from the droplet along with further solute crystallization to form a dried particle undergoing solid state reactions and morphology changes upon heating. The droplet-to-powder processes are typically operated at atmospheric pressure and involve particles in the 0.1 to 100 micrometer range consisting of nanosize crystallite or grains. In general, the advantages of these processes are: the ability to process organic and inorganic materials, to form a variety of multicomponent materials, simplicity, many choices for inexpensive liquid phase precursors, scale-up has been already demonstrated to ton quantities and relatively safe process since volatile precursors are not required. The disadvantages for these processes are: porous or hollow particles can be formed at certain conditions and the spread of particle sizes is limited by the spread of the starting droplets. The product powder distribution is determined primarily by the droplet distribution and in some cases by particle break-up during pyrolysis or drying. Powders made by this route are rarely aggregated but can be porous depending on precursor solute concentration and drying rate. Spray drying and pyrolysis are typical industrial processes employing droplet to powder conversion and can be used for manufacture of nanoparticles. Other droplet-to-particle processes for nanoparticle production are electrosprays and freeze drying.

State of affairs in industry

Flame processes are by far the most widely used ones for manufacture of commercial quantities of nanoparticles, the most important of which are carbon blacks (Cabot, Degussa, Columbia etc.), fumed silica (Cabot, Degussa) and pigmentary titania (DuPont, Millenium, Kerr-McGee, Ishihara) and optical fibers (Lucent, Corning, Sumitomo, Heraeus). The annual production volume of the flame industry is several million metric tons at a rate of 100 metric tons per day [6]. Hot-wall reactors are used on an industrial scale for synthesis of filamentary (nanostructured) nickel and iron powders from decomposition of the corresponding metal carbonyls (BASF, INCO). In addition these reactors have been used for commercial synthesis of nanostructured carbides, nitrides, borides and other non-oxide ceramics (Dow, H.C. Stark)). Rather recently, the inert gas condensation technique has been scaled up by new companies (Nanophase) for manufacture of rather costly (about \$100/kg) nanostructured metals and ceramics powders. With respect to droplet-to-particle conversion processes, spray pyrolysis technologies are used primarily by small companies (Particle Technology, Nanochem, SSC) for manufacture of precious metal, ceramic and especially nanostructured composite ceramic powders from nitrate, organic and other solutions.

The control of particle growth during synthesis is crucial because the properties of materials made from nanosize particles depend on size and size distribution, morphology, extent of agglomeration and chemical and phase composition. For example, in manufacture of titania pigments, the goal is to produce nearly monodisperse rutile particles lying between 150 ~ 250 nm to obtain the maximum hiding power per unit mass. In contrast, in manufacture of powders for structural ceramics, particle size may not be so

important though the size distribution may affect powder flow and packing prior to compaction. There, agglomerates should be avoided since they result in flaws during sintering.

Despite the age and significance of industrial gas-phase processes, their design and operation rely heavily on experience and empiricism. As a result, it is nearly impossible for existing industrial units to address synthesis of nanosize powders without going through the laborious "trial and error" development that was followed for the development of the current units and processes. However, in contrast to the state of affairs in industry, substantial work has been done in academe on a laboratory scale towards understanding the fundamentals of aerosol formation and growth at high temperatures. Today, much of the pertinent aerosol research has been developed in connection with aerosols and the environment, but little has been applied to powder processing in the chemical and material industries.

Computational Fluid and Particle Dynamics

There is a strong interest for the development of simulators for aerosol manufacture of nanoparticles. More specifically mathematical models relating the characteristics of the product powder (average aggregate and primary particle diameter (dp), polydispersity, specific surface area (SSA), crystallinity and morphology) to the process variables (reactant state, composition and flowrate as well as reactor geometry) are needed that are based on sound understanding of particle formation and growth. This is best accomplished by interfacing models for computational fluid dynamics with models for particle dynamics assuming that the chemistry is fast as it is typically with high temperature processes dominated by coagulation.

The construction of such a simulator starts with the velocity and temperature profiles in the reactor that can be readily calculated even by commercial software such as CFX or Fluent. Regarding particle dynamics, moment and sectional representations of the size distribution are employed depending on the required product particle specifications. Typically the specific surface area or an average particle diameter and polydispersity are key characteristics that are desirable. As such monodisperse models are quite attractive for the SSA and dp while for the polydispersity either a sectional or lognormal moment model are required. Typically monodisperse model offer computational simplicity while sectional provide detail. Models that distinguish between primary and aggregate particles are attractive and are widely used [7]. Very recently, rapid sectional models accounting for coagulation and sintering giving both primary and aggregate particle size distribution have been developed [8] that are substantially faster than earlier ones.

Running these simulators can be quite revealing as they can identify problematic regions in the reactors involving either hot spots or dead volumes. As the volume fraction of particles in the suspension is, typically, in the order of 0.0001, the fluid and particle dynamics can be decoupled. If the chemistry is fast as it is with high temperature processes it can be neglected and the particle dynamics can be superimposed on the velocity temperature profiles. This was successfully done for synthesis of titania in hot wall reactors [9], in flame synthesis of alumina [10] and titania [10, 11] using the simple monodisperse model for aggregate dynamics by coagulation and sintering [3]. These models have been quite successful in industry as they can predict the product specific surface area within 3% [12].

This early success of simulators has motivated research in further development of diagnostics for verification as well as more accurate models that account for the full size distribution and the detailed chemistry. This, however, adds a load of computational demands motivating research for efficient design of algorithms for these simulators.

Nevertheless, the availability of data describing the detailed evolution of particle size distribution by thermophoretic sampling and computerized image analysis coupled with accurate temperature and velocity measurements creates the foundation for rigorous testing of models and hypotheses.

Current Research State & Future Directions

Industrial laboratories led the research in synthesis of nanoparticles since the 19th century for manufacture of nanostructured carbon blacks followed by fumed silica in the mid-20th century. The latter research was motivated from the industrial importance of fumed silica which was first made in the 1940s and marketed under the name Aerosil [13]. Parallel to this, intensive research was carried out for synthesis of TiO₂ and Mezey [14] summarized the early patent race in flame technology for synthesis of TiO₂ and SiO₂. Ulrich [3] along with Formenti et al. [15] at the early 70s pioneered the investigations of flame synthesis of ceramic powders. Ulrich first recognized that coagulation rather than nucleation was the dominant particle formation mechanism and reported that the size distributions of the product particles were self-preserving. These early studies revealed also that the appearance of aggregates of primary particles results from the competition between particle collision and sintering.

Since the mid-80s research in this field has been accelerated when, in industry, flame reactors were introduced in large scale manufacture of optical fiber preforms [6]. For example, one of the most successful processes in Corning Glass includes the flame synthesis of optical fiber preforms. In the late seventies, Prof. Gleiter and his colleagues at the University of Saarbrücken, Germany sparked the interest of the materials community, and academics in general, in nanoparticles with his observations on the unique characteristics of nanograined ceramics. Of course, other communities including the aerosol, combustion and synthetic chemistry were focusing in this size range for different reasons. Today most oxides [16] like SiO₂, TiO₂, Al₂O₃, ZrO₂, GeO₂, V₂O₅ and metals (e.g. Fe, Ni, Cu, Pd) have been produced as nanoparticles [4].

Gas-phase technology is a particularly challenging technology, however, since powders are produced virtually *without control* at high temperatures and extremely short process residence times (less than a second). This makes very difficult representative particle sampling, model development and process control.

The early stage of particle formation is one of the areas that is ripe for better understanding as instruments that allow non-intrusive nanoparticle aerosol sizing such as infra-red spectroscopy are becoming available. Particularly intriguing is the role of gas or surface reaction on particle formation and growth since surface growth favors much narrower size distributions as compared to pure coagulation. It is well known, for example, that surface growth is an integral process for carbon black particle growth while its significance is less clear in the growth of silica, titania and other ceramic or metallic powders.

Reactant mixing is a critical variable in controlling process temperature and subsequently the chemistry, the aggregate and primary particle size and composition over a wide spectrum. Experimental and theoretical investigations of mixing based on the principles of chemical reaction engineering could provide the tools for better understanding and controlling the product characteristics. In certain systems such as titania and silica it seems that there is a reasonably good understanding of the role of additives for control of powder crystallinity such as through interstitial or substitutional defects in the titania lattice. However, the role of ionic additives affecting the particle collision, and possible coalescence, rate and subsequently the extent of aggregation are not well understood.

Aggregate characterization has not been standardized and various instrument readings are affected by particle structure further obscuring the effect of process variables on product particle characteristics. Direct visual observation by electron microscopy still provides the best assessment of particle structure though it is a laborious off-line process.

Using force fields may provide another tool for process control. At this point, it appears that electric fields provide one of the best means for precise control of primary particle size and crystallinity and even aggregate size though in a narrow range say within 50% of the average size but with just 1 or 2 nm variation! Last and most important, there is a pressing need for instrument development for in-situ measurements of temperature and particle size and composition distribution at high aerosol concentrations and temperatures.

Finally, the decisive step for this technology and even for the entire field is the development of commercially viable technologies involving nanoparticles for a broad range of applications. Once technologies become industrial processes there is an avalanche of research issues around them. Gas-phase technology produces some of the cheapest ceramic powders made today and it has high potential for synthesis of nanoparticles. Having a low cost starting material (nanoparticles) will certainly accelerate the development of nanotechnology in our market-driven society.

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