New Product Development for Nanomaterials Systems and Solutions

G. Varga, M. Kröll;
Degussa AG, Advanced Nanomaterials
Rodenbacher Chaussee 4, Geb.1040-004, Hanau, Germany

ABSTRACT

In the past several years there has been a tremendous increase of activitiy in the field of Nanomaterials Technology. This recent increase is in part a result of improved analytical methods which allow scientists and engineers to custom tailor nanoscale features into products which result in completely new functionalities. Realizing the intended functionalities of these materials most often requires that they undergo post-synthesis treatment and modification, and integration into dispersions and formulations. These developments will allow for the intended benefits to be realized in many different areas of application including energy, electronics, information technology, and optics. In this paper we present the synthesis techniques of our new nanoscaled products, their physical and chemical properties, and their further processing into systems which are tailored for use in specific applications.

Keywords: nanomaterials, synthesis, modeling, modification, dispersions

1 R&D APPROACH

Degussa's core competence of gas-phase synthesis of Nanomaterials was extended in a three-year strategic R&D project known as the Projechouse Nanomaterials. The goal of the project was to understand and control the important characteristics of these materials starting with particle morphology, which refers to the primary particle size and shape and also the aggregate structure of the materials, and also to understand and control other important characteristics which are established during synthesis, such as crystallinity, porosity, surface features and surface chemistry. It is necessary to control morphology with processing conditions which are optimiZed with regard to economics.

2 THE SCIENCE OF PARTICLE FORMATION

Synthesis processes involving gas-to-particle conversion allow for the production of particles having controlled nanometer-scale dimensions, which are built up from atomic or molecular size in the gas phase to the desired particle size. This general approach has been used for decades by Degussa and other companies to produce various nanoscale materials such as aluminum oxide, titanium dioxide, fumed silica and carbon black on a commercial scale. Although a number of variations exist for gas-phase processes, they all have in common the fundamental processes of particle dynamics which occur once the product species is generated [1]. As the superheated vapor cools, the saturation ratio of the vapor builds up and leads to the nucleation of thermodynamically stable clusters. These clusters can grow by collision and coalescence (collision-controlled growth), by vapor condensation (condensation-evaporation-controlled growth) or by surface reaction, in which the precursor reacts on the cluster surface. The clusters can grow further to a size where they are considered particles by collisions with other product particles, which leads to coagulation, or with product molecules, which results in a condensation, or by reaction of the precursor on the particle surface. Collisions between small particles at high temperatures lead to complete coalescence to form spherical particles. As the temperature decreases and particle coagulation continues, further collisions result in hard or soft agglomerates.

The most common reactor design used for the manufacturing of commercial quantities of nanoparticles such as SiO_2, TiO_2 or Al_2O_3 is the flame reactor. Flame reactor technology allows for current production rates typically in the range of several hundred to several thousand tons per year for each individual reactor, depending on the nanoscale oxide being produced. Such high temperature gas-phase synthesis typically leads to a product powder consisting of aggregates composed of up to several hundred primary particles. The structure of the aggregates and the product particle size distribution are determined by the particle formation processes occurring in the reactor. Three mechanisms dominate particle formation in flame reactors:

- Chemical reaction of the precursor: This leads to formation of product monomers (clusters) by *nucleation* and to the growth of particles by reaction of precursor molecules on the surface of newly formed particles, which is called *surface growth* [2].
- Coagulation: A critical level of particle concentration in the reactor leads to collisions of the product particles with other particles or with product monomers, which results in coagulation if the particles stick to each other [3]. Coagulation may occur in the *free-molecular regime* (particle diameter much smaller than the mean free path of the surrounding gas) or in the *continuum regime*, where the particles are larger than the mean free path.
- Sintering: In the high temperature zone of the flame reactor, coalescence and fusion are sufficiently fast which results in a reduction in the level of aggregation or the formation of spherical particles due to *sintering* processes [4].

2.1 Modeling and Simulation of Gas-Phase Synthesis Processes

Mathematical modeling and simulation of these production processes can improve product quality and performance characteristics of nanoparticles, since these often depend on the particle size distribution, morphology, and the degree of aggregation of the particles. The ultimate characteristics of the powder are determined by fluid mechanics and particle dynamics within a few milliseconds at the very early stages of flame synthesis. Therefore the product quality can be influenced by an intelligent selection of the process parameters. Process simulations can improve the understanding of the physical and chemical fundamentals of gas phase synthesis by connecting process parameters, such as temperature, reactant state or reactor geometry, to particle characteristics. The calculated particle size evolution is compared to experimental data obtained by thermophoretic sampling. Particle sizes and morphology can be measured directly in the flame at various distances (residence times) from the burner by shooting a probe into the flame, which collects particles by thermophoresis on a TEM-grid [5]. The resulting understanding and control of particle formation enables the production of tailor-made morphology and composition including nanocomposite particle structures. One example is a nanocomposite particle structure consisting of superparamagnetic iron oxide domains encased within an SiO_2 particle matrix.

3 ORGANIZATIONAL APPROACH TO NEW BUSINESS DEVELOPMENT

In order to generate new business we must make the transition from supplying simple nano powders to suppling highly functional specialized Nanomaterials and solutions. This includes tailoring materials with respect to composition, crystallinity and morphology, but also applying post-processing, surface modification, and forward integration of these materials into rheological or pH-stable dispersions or coating formulations in order to match a customer system.

Our organizational approach is to address the opportunities as an internal corporate venture, or an internal Start-up. The goal of this approach is to combine the agility, the flexibility and the innovative atmosphere of a Start-up together with the advantages of our more established internal business unit partners. We seek to leverage our technical innovation together with Degussa business units having the required production infrastructure for fast, effective, low-cost scale up of processes; the relevant applied tech expertise needed to thoroughly understand the customers' needs; or most importantly market access- preferably higher up in the value chain.

4 TAILOR-MADE SOLUTIONS

4.1 Custom Synthesis

The example of custom-tailored nanocomposite particles made up of superparamagnetic iron oxide in a silica matrix enables customers in the adhesives industry to remotely heat their formulations containing these particles using an AC magnetic field. Using this approach, parts can be bonded and de-bonded quickly, without heating the parts that are to be joined. In this case, the silica matrix provides rheological functionalities while the superparamagnetic domains contained within the silica provide the further functionality of remote heating, enabling efficient bonding and de-bonding processes. The ability to produce such multi-functional composite particles is a result of a thorough understanding of the science of particle formation.

4.2 Post-processing and Modification

Often times, materials are made more suitable for specific applications by realizing new characteristics and functionalities of standard products. These are achieved through post-processing or modification of standard, as-synthesized nanomaterials. One example is the thermal reduction of indium-tin-oxide nanoparticles in order to increase the density of highly mobile charge carriers. This post processing results in a significant increase in both the electrical conductivity and the IR absorption coefficient of the material, leading to higher effectiveness in anti-static and IR shielding applications in coating formulations containing the nanoscale particulate indium-tin-oxide. Another example is the granulation of nanoscale silica, which imparts free-flowing behavior into the product while maintaining high specific surface area, making it compatible with the material handling processes of certain customers. A third and very important example of particle modification is the hydrophobization of hydrophilic oxide nanomaterials, in order to improve dispersion characteristics, compatibility, and performance in various formulations and systems. In the case of sunscreen applications, hydrophobization of Zinc Oxide and Titania improves skin feel and suppresses photo catalytic activity.

4.3 Dispersions and Formulations

Often times, it is desirable to forward integrate these custom-synthesized and/or modified nanomaterials into dispersions and formulations. In some cases, customers prefer to utilize their know-how in these areas and profit from these value-added steps themselves. However, in other cases this opportunity can be realized by the nanomaterial supplier in order to increase margins by providing ready-to-go systems for customers in the fields of coatings, CMP, polymers, and printed films. Even in cases where the customer is willing to prepare their own dispersions and formulations, the material supplier often requires these competencies in order to show a proof-of-concept or to provide application guidance. Such competencies can also assist the particle design efforts in the synthesis of materials which are compatible with a given dispersion or formulation system. In these cases, a thorough understanding of the challenges facing customers one or more steps up the value chain can assist in the design of nanomaterials which are most suitable for a given system, providing an advantage over competing suppliers. In the case of inorganic nanomaterials for use in sunscreens, the desired transparency to visible wavelengths not only requires the appropriate particle morphology, but also the effective dispersion of the particles so that visible light is not scattered. Without the proper dispersion methods, transparency cannot be achieved. This also holds true for UV-resistant coatings on other surfaces such as wood or in polymer films. In the case of CMP, particle design is the first critical step, but the incorporation of the particles into a suitable and stable dispersion is just as critical to achieving the requirements of the IC wafer polishing process. The combination of high removal rate, a low defect or scratch rate, high degree of planarity, favorable selectivity between polishing different materials, and dispersion stability requires an in-depth knowledge of dispersions and formulations.

5 SUMMARY

In summary, developing new business in the field of nanomaterials technology requires a broad range of technical competencies. This starts with the understanding and ability to control a cost-effective, scaleable synthesis technology. Furthermore, winning new business often requires the synthesis of materials which are tailored, modified, or incorporated into a system intended for a specific application field. As a raw material supplier, significant opportunities for new business and higher profit margins can be realized through vertical integration up the value chain. But even to succeed as a material supplier, it is important to have a high degree of understanding of the entire value chain so that new products can be properly designed for specific applications which deliver the advantages and benefits that customers demand.

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