DFG Priority Program SPP1980

Nanoparticle Synthesis in Spray Flames
SpraySyn: Measurement, Simulation, Processes

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1 Summary

Spray-flame synthesis offers a promising approach for the production of functional nanomaterials. The viability of this route has already been proven for a wide range of materials on the laboratory scale. Compared to existing large-scale methods for nanomaterials synthesis in pure gas-phase processes, spray-flame synthesis provides access to a wealth of additional materials that cannot be produced with other processes. Industrial applications of spray-flame synthesis have not been developed so far due to the necessity of expensive precursor materials and a lack of process understanding. This situation should be overcome by an interdisciplinary research approach within the SPP1980 that will lay the foundations for practical applications of spray-flame synthesis. The prospects are excellent via an interdisciplinary collaborative network that links recent developments on experimental, theoretical, and simulation techniques that have been previously used in their individual research disciplines. Their combination will allow to analyze and describe the underlying sub-processes that are relevant in the context of spray-flame synthesis. Sub-processes will be analyzed and their understanding will be integrated into comprehensive models that provides the chance for the development of processes that are based on inexpensive starting materials and that can be scaled-up to an industrial scale for the targeted production of materials with a wide range of characteristics.

This approach is based on the development and application of specific *in situ* analytical methods, the preparation of chemical mechanisms by fundamental kinetics experiments and theoretical calculations, and a comprehensive simulation of the underlying process chain: precursor solution – spray – flame – particles. Of central importance are the development and application of a standardized experiment – the so-called SpraySyn burner – which is to be established as a reference experiment with a comprehensive validation data set. It will serve as an anchor point for the research and development of particle synthesis in spray flames.

Downstream processes for morphological modification of the product initially formed and the study of isolated individual aspects are not part of SPP.

The Priority Program is divided into thematic blocks

- *In situ* diagnostics
- Theory and simulation
- Processes

Connecting elements are a common experimental configuration (the SpraySyn burner) and the focus on predefined materials systems. All projects are immediately influenced by these definitions, thus ensuring the coherence of the research in SPP1980.

2 Background

The synthesis of specific nanomaterials by atomization and combustion of solutions of appropriate precursor mixtures in spray flames has a high potential. This strategy enables continuous generation of complex and high-purity nanomaterials in the exhaust gas of the spray flame based on inexpensive starting materials. The spray-flame method can be applied to a wide range of chemical elements. This distinguishes the spray flames process from the industrially established particle production in gas burners. With appropriate process control, the production of materials with a defined composition, particle size, and morphology can be achieved – even beyond the thermodynamic stability limits and therefore outside the range of materials that can be synthesized in liquid-phase processes. Precursor mixtures can be easily used in spray-flame synthesis to generate nanoscopic mixtures and composites of different materials systems. Such materials are of great practical and commercial interest in a wide range of applications, e.g., catalysis, battery storage, and photovoltaic materials. More than 600 publications published in recent years describe the spray-flame synthesis of some 300 different materials. Thus, demonstrated the fundamental feasibility of this approach has been demonstrated in about 30 academic research groups worldwide.

The scalability of gas-phase synthesis of nanomaterials is shown by established industrial processes for producing SiO_2 (fumed silica), TiO_2, and carbon black. Even first small-scale plants for spray-flame synthesis of nanomaterials have recently become commercially available. A transfer to the industrial scale and an associated application of the generated highly attractive materials has so far only partly taken place. As a result, it was not yet possible to further investigate applications because the necessary materials for further processing and product development have not been available. The large-scale use of spray-flame synthesis was often hindered because – with the present state of knowledge – often expensive specialty chemicals (organometallic precursors) and expensive solvents (xylene, etc.) must be used. Also, central processes such as the transfer of the substances from the spray droplets to the gas phase, as well as the reaction and the interaction of the primary decomposition products with the flame are so far not sufficiently understood. Understanding these sub-processes will form the basis to develop new processes with reduced cost, for example by using of solutions of nitrate or carbonates with conventional solvents (aliphatic hydrocarbons, alcohols, or even water). Overcoming this hurdle will require a significant expansion of the detailed understanding of the process chain of solution stabilization – spray formation and vaporization – interaction of precursors and metal atoms with the flame chemistry – and particle formation and growth in a complex turbulent reactive flow field. So far, difficulties are for example the premature hydrolysis of non-vaporized starting materials, the formation of large solid particles during droplet evaporation, the contamination of the product by soot due to a locally incomplete combustion, or the formation of a broad distribution of the materials characteristics due to variable paths of the reactive media through vortices in the reactor. Many of these problems can be attributed to undesirable inhomogeneities back-mixing or uncoordinated reaction kinetics that are not yet under control.

The development of the currently existing methods of spray-flame synthesis was hitherto largely phenomenological with the focus on the characteristics of the materials produced. The approach was based generally on *ex situ* characterization of the materials and largely empirical variation of starting materials, reaction conditions, and burner geometries. This development was often decoupled from the advancement in related topics, in particular combustion research, the spray formation, the interaction of precursors and fuels, solution stabilization and vaporization, diagnostics capabilities for reacting multi-phase flows, and their numerical description. Therefore – despite the demonstrated successes – evident that through the synergetic use of the previous experience in the area of the burner design, nanoparticle synthesis in premixed gas-phase systems, new *in situ* measurement methods [1], and simulation approaches for reactive flows, the improved mechanistic understanding of combustion processes and the new possibilities for the theoretical description of the properties of the solutions of precursors in solvents is the first time a realistic chance to overcome the obstacles mentioned above.

3 Research approach

The synthesis of nanoparticles in spray flames passes through a sequence of processes that are determined to a great extent of interactions at the molecular level and of ultrafast physical and chemical processes. This process chain includes elementary processes in the spray (largely dominated by molecular interaction and fluid properties), in the flame (dominated by ultrafast radical reactions and their interaction with flow processes), and the particles (surface growth, coalescence, and aggregation). In a spray flame, these processes are not fully separated in space and time. Due to the different time scales of spray formation and vaporization (slow), precursor decomposition (fast), flame chemistry (ultra-fast), and particle formation (with temperature-dependent competition of coalescence and aggregation) the respective processes overlap and interact. Therefore, spray-flame synthesis provides a much higher degree of complexity than flame synthesis of nanomaterials based on homogeneously premixed gases. Moreover, precursor- and flame chemistry are strongly coupled through the catalytic effects of many metal species and reactive particle surfaces. These effects are relevant due to turbulence and recirculating flows and this interaction further complicates the prediction of local temperature variations. Therefore, only a coupled experimental/numerical approach that is at the core of the SPP1980 can lead to success.

For the successful description of the overall process, close collaboration of various disciplines is required. The individual projects target complementary – but closely interlinked – topics within the Priority Program. Many of these issues are for the first time considered in the context of particle synthesis and thus connected in the context of this topic.

3.1 The overarching objectives:

- Comprehensive understanding of spray-flame synthesis based on a physically sound modeling of the sub-processes
- Creation of methods for multi-scale simulation for designing, scaling, and optimizing spray-flame synthesis systems
- Design of economic and sustainable processes by substituting raw materials towards metal salts instead of organometallic substances, and inexpensive solvents (possibly also water)
- Upgrading the spray-flame synthesis for the inexpensive production of highly specific the nanoscale materials on an industrial scale

3.2 Project goals

- Developing and establishing a standard experiment configuration (SpraySyn burner) considering the practical relevance, reproducible production, measurability, and simulation capability
- Building an extensive, well-documented and publicly available data set for selected operating conditions (benchmarking)
- Developing and providing metrological approaches
- Development and deployment of simulation methods
- Understand central sub-processes:
    - Spray formation and evaporation precursor-laden droplets
    - Interaction of the precursors with the flame chemistry: Investigation of atomic/molecular intermediates and their influence on the reaction mechanisms
    - Impact of droplets and particle loading on the turbulent flow

- Implementation and use of a database for the long-term documentation of the results of the entire SPP
- Use of the SpraySyn approach to the design of optimized and scaled synthesis plants that are then used to validate the simulation method
- Use of the SpraySyn approach for modular and combined synthesis pathways towards the generation of complex materials

3.3 Long-term goals (visions)

- Development of process design rules for industrial implementation
- Developing integrated spray-flame processes, such as by supporting the spray flame synthesis by plasma processes
- Evaluating the possibility of a carbon-free spray-flame synthesis to fully exclude the formation of carbides and carbon impurities
- Transfer and generalize the scheme of interaction between theory and experiment as developed in SPP1980 towards more complex issues of material synthesis not limited to spray-flame synthesis
- The SpraySyn database acts as a standard and reference beyond the project duration SPP in order to advance the research and development of spray-flame based nanoparticle synthesis

4 Scientific focus

The Priority Program of the SPP1980 is divided into the following three thematic blocks:

- Theory and simulation (molecular interaction, reaction, particle interaction, interactions with the (turbulent) flow)
- *In situ* measurement technology (spray, particles, gas-phase concentrations and temperatures, velocities)
- Processes (spray, burners, gas mixing)

4.1 Theory and simulation

- Molecular interaction of precursor and solvent
- Chemical reaction: Decomposition kinetics of solution-based precursor systems, reaction mechanisms of precursors and mechanistic description of the interaction of precursor- and flame chemistry, competition with soot formation
- Interaction in turbulent reactive multiphase flows: Spray combustion of complex solutions, reactive turbulent multiphase flows
- Particle dynamics: Homogeneous particle formation, growth, and interaction

4.2 *In situ* diagnostics

- Liquid phase: Droplet sizes, velocities, temperature, and vaporization, reactions and phase transformation within the droplets
- Gas phase: Velocities, temperature distribution and concentration distribution of selected species; time- and spatially-resolved (LIF, Raman), species concentrations of exotic species; line-of-sight integrated (FTIR), process measurement technology (TDLAS)

- Particle phase: Particle size, particle volume fraction, phase composition, surface layers, morphology; angle-resolved light scattering, Raman scattering, laser-induced incandescence, X-ray small angle scattering

4.3 Processes

- Spray: Spray atomization, precursor feed, pulsed feed
- Burner: Compactness of the flame, suppressing/generating fluctuations, modification of the temperature field, influence of the fuel, modifying the temperature distribution, carbon-free fuels
- Alternative energy intake: Plasma support, non-carbonaceous fuels and solvent
- Media pathways: Nozzle concepts, mixing concepts, feeding and conveying concepts

4.4 Not part of the work program are

- Generation of carbon particles (unless soot occurs as an impurity in combination with the formation of non-carbon particles)
- Modification of the particle morphology downstream of the spray-flame synthesis
- Consideration of isolated individual processes without integration into the overall concept

5 Coherence of the planned research activities

As a connecting element are a common model configuration and the definition of materials systems. This eliminates a time-consuming initiation phase and ensures coherent cooperation. All projects are directly affected by one of the two specifications for model configuration and the materials system.

5.1 Definition of a model configuration

A key element of the Priority Program is the design and use of a standard burner, the so-called SpraySyn burner [2]. A standard configuration enables a comprehensive characterization of the spray-flame synthesis with a variety of *in situ* and *ex situ* measurement methods and the implementation and integration of sub-models with the aim of a validated overall simulation. The SpraySyn burner should bevome an internationally recognized standard with long-term significance. This required the development of a burner that is ideal for measurement and simulation, reproducible, relatively inexpensive, and that requires little effort in the simulation for the correct treatment of boundary conditions. In addition, the burner should be designed so that it can be integrated in a chamber to enable the variation of the pressure and the composition of the atmosphere (especially oxygen content).

5.2 Definition of materials systems

The materials considered are selected in order to investigate the overall system with different and increasing complexity.

Iron oxides: This is a system in which already comparatively many basics are known. Due to the various oxidation states and phases, targeted synthesis is challenging and the materials class therefore provides a critical test case for the simulation of the spray-flame synthesis.

Barium/strontium oxides: These substances tend to form carbonates and therefore require detailed understanding of the process with respect to the temperature distribution and back flow of combustion exhaust gases.

Barium/titanium oxides: The starting materials (such as TTIP) are highly susceptible to hydrolysis and therefore require detailed understanding of the process regarding the backflow of the combustion-generated water.

Cerium/aluminum oxides: These materials can so far be generated in flames only from very expensive precursors. The goal here is the substitution of these precursors by salts. This requires a good understanding of the spray formation and evaporation, in order to avoid contamination of the products by large particles that are produced by incomplete spray evaporation.

Bismuth: It is of particular interest to reduce Bismuth particles in the flame to the metal. To achieve this without the simultaneous formation of soot, requires detailed understanding and possibly an adjustment of the composition of the solvent.

[1] T. Dreier, C. Schulz: Powder Technol. **287**, 226 (2016)
[2] F. Schneider, S. Suleiman, J. Menser, E. Borukhovich, I. Wlokas, A. Kempf, H. Wiggers, C. Schulz: Rev. Sci. Instrum. **90**, 085108 (2019)