SPP1980
SPRAYSYN
NANOPARTIKELSYNTHESE
IN SPRAYFLAMMEN

FOR2284
MODELLBASIERTE SKALIERBARE
GASPHASENSYNTHESE KOMPLEXER NANOPARTIKEL

UNIVERSITÄT
DUISBURG
ESSEN
*Offen im Denken*

# GAS-PHASE SYNTHESIS OF FUNCTIONAL NANOMATERIALS:

## Fundamental Understanding, Modeling and Simulation, Scale-up and Application

## BOOK OF ABSTRACTS

University of Duisburg-Essen / NETZ – NanoEnergyTechnologyCenter / Carl-Benz-Str. 199 / 47057 Duisburg

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# Gas-Phase Synthesis of Functional Nanomaterials

## Fundamental Understanding, Modeling and Simulation, Scale-up and Application

**September 25–26, 2018**
Venue: NETZ, Room 2.42, University of Duisburg-Essen, Carl-Benz-Str. 199, 47057 Duisburg
Directions: https://www.uni-due.de/cenide/directions.php)

## Tuesday, September 25, 2018

| | |
|---|---|
| 12:00–12:30 | **Arrival and Lunch** |
| 12:30–12:50 | **Welcome**<br>Christof Schulz (University of Duisburg-Essen)<br>Lutz Mädler (University of Bremen) |

### **Keynote** (Chair: Christof Schulz)

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|---|---|
| 12:50–13:20 | **Improving the performance of functional particles by gas-phase structuring**<br>Alfred Weber, Technical University Clausthal |

### **Fundamentals of Particle Formation and Growth** (Chair: Christof Schulz)

| | |
|---|---|
| 13:20–13:50 | **Gas-phase synthesis of metal oxides – from molecules to particles**<br>Hartmut Wiggers, University of Duisburg-Essen |
| 13:50–14:10 | Production of manganese oxide nanoparticles in premixed flames with selectivity in manganese oxidation state<br>Joaquin Camacho, San Diego State University |
| 14:10–14:30 | Mass spectrometric investigation of key intermediates in synthesis flames<br>Yasin Karakaya, University of Duisburg-Essen |
| 14:30–14:50 | Carbon encapsulation of elemental particles by spark discharge<br>Tayfur Öztürk, Middle East Technical University, Ankara |
| 14:50–15:10 | High-temperature rate constants for the reaction of H atoms with tetramethoxysilane and reactivity analogies between silanes and oxygenated hydrocarbons<br>Sebastian Peukert, University of Duisburg-Essen |
| 15:10–15:30 | Reactive dimerization of small aromatics drives soot nucleation<br>Reza Kholghy, ETH Zurich |
| 15:30–15:50 | Effect of 2-ethylhexanoic acid in the liquid-fed flame synthesis of poorly volatile precursors<br>Jili Wei, Tsinghua University, Beijing |
| 15:50–16:20 | **Coffee Break and Posters** |

### **Modeling and Simulation** (Chair: Andreas Kempf)

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|---|---|
| 16:20–16:40 | Coupling particle size distribution dynamics with gas and solid phase interactions resolved using detailed chemical kinetics<br>Peter Lindstedt, Imperial College, London |

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|---|---|
| 16:40–17:00 | Sectional and monodisperse LES modeling of the SpraySyn flame for nanoparticle synthesis<br>Johannes Sellmann, University of Duisburg-Essen |
| 17:00–17:20 | Soot light absorption and refractive index during agglomeration and surface growth<br>Georgios Kelesidis, ETH Zurich |
| 17:20–17:40 | Structure of laminar, nanoparticle-forming flames: Silica and iron oxide<br>Irenaeus Wlokas, University of Duisburg-Essen |
| 17:40–18:00 | Discussion: Open research needs |
| 19:00 | **Conference Dinner at the Webster Brauhaus** (https://www.webster-brauhaus.de) |

## Wednesday, September 26, 2018

### **Diagnostics** (Chair: Thomas Dreier)

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|---|---|
| 8:30–9:00 | **Flame synthesis of iron oxide nanoparticles: laser-based diagnostics, particle mass spectrometry and modeling**<br>Igor Rahinov, Open University of Israel |
| 9:00–9:20 | Simultaneous OH-PLIF and PS-LIBS measurements of a turbulent flame synthesis reactor<br>Shuiqing Li, Tsinghua University |
| 9:20-9:40 | Measurements of aerosol size and structure at low-pressure reactors: sampling issues and measurements using a differential aerodynamic particle sizer<br>Einar Kruis, University of Duisburg-Essen |

### **Scale-up and Application** (Chair: Lutz Mädler)

| | |
|---|---|
| 9:40–10:10 | **Processing and functionalization of nanopowders in fluidized bed reactors**,<br>Dr. Martin Seipenbusch, ParteQ GmbH |
| 10:10–10:40 | **Coffee Break and Posters** |
| 10:40–11:00 | Flame-synthesized $Li_4Ti_5O_{12}$ anode materials for high-power Li-ion batteries<br>Tommi Karhunen, University of Eastern Finland, Kuopio |
| 11:00–11:20 | **Flame synthesized silica/ceria catalyst supports for the valorization of carbon dioxide**<br>Emma Lovell, University of New South Wales, Sydney |
| 11:20–11:40 | Large-scale manufacturing of fullerenes, single-walled carbon nanotubes, their derivatives and dispersions for energy and electronic applications<br>Henning Richter, Hossein Ghiassi, Nano-C, Inc., Westwood |
| 11:40–12:00 | **Scale-up of nanomaterials synthesis from the lab to the pilot-plant scale: challenges and results**<br>Tim Hülser, Institut für Energie- und Umwelttechnik e.V., IUTA, Duisburg |
| 12:00–13:30 | **Lunch and Posters** |
| 13:30–15:00 | Lab tour NETZ |

# ABSTRACTS

## ORAL PRESENTATIONS

# KEYNOTE

# Improving the performance of functional particles by gas-phase structuring

*A. P. Weber*

Institute of Particle Technology, TU Clausthal, Clausthal, Germany

Functional particles can be produced with gas phase processes in a large variety of materials and morphologies. However, depending on the intended application, modifications of the particle structure and surface properties may enhance their performance further. In this contribution it will be shown first how the chemical surface character of aerosol nanoparticles can be changed to cope with requirements regarding their hydrophilic/hydrophobic behavior. The employed gas phase methods are to a large extent generic, i.e. they may be applied to different particle materials without changing their shape. In addition, the two methods, namely post-plasma induced silica coating and UV induced photopolymer coating, operate at ambient pressure and temperature thereby representing mild coating techniques which are also applicable to sensitive materials such as pharmaceuticals.

In the second part template induced structuring of the particles will be outlined. As templates polystyrene and salt mixtures are used in order to control the pore system of the particles. As examples cobalt catalysts supported on porous silica particles for the Fischer-Tropsch- synthesis and ibuprofen loaded porous silica particles for controlled drug release will be discussed. For the cobalt/silica particles it will be shown that pore size, metal catalyst size and catalyst loading can be varied independently offering the potential for systematic studies on the influence of these parameters on activity and selectivity of the catalyst. For the ibuprofen/silica particles the pore size distribution is controlled via the amount and the composition of the salt mixture in Salt Assisted Spray Pyrolysis (SASP) experiments. The resulting pore system will influence the drug storage capacity and the release rate as determined from dissolution measurements.

# FUNDAMENTALS OF PARTICLE FORMATION AND GROWTH

## Gas-phase synthesis of metal oxides – from molecules to particles

*H. Wiggers*

Institute for Combustion and Gas Dynamics – Reactive Fluids and CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany

Gas-phase synthesis of nanoparticles allows to generate high-purity materials with well-controlled properties in continuous flow processes. It is an established technology for a couple of – mostly inorganic – commodities with more or less specific materials characteristics. However, for the synthesis of materials with desired properties, the reaction conditions must be well controlled and the underlying processes understood. The targeted synthesis of materials requires to understand the decomposition kinetics of vaporized precursor compounds and their potential interaction with bath gases, as well as the subsequent formation of clusters and at least particles.

The characterization of temperature and species concentration in flow reactors with laser-based detection as well as molecular-beam sampling techniques allows to gather valuable information with a view to process modelling and development. The paper will present methods and results that allow for a detailed characterization of intermediate and final species starting from simple molecules to the point of nucleation and growth of stable particles. When knowing the boundary conditions with respect to the final particle characteristics (stoichiometry, size, crystal structure), the synthesis process can thus be designed according to the requirements for the formation of specific materials. A few examples concerning the formation of selected materials from different kinds of gas phase reactors will be given.

# Production of manganese oxide nanoparticles in premixed flames with selectivity in manganese oxidation state

*W. Wood, S. Dasappa, J. Camacho*

Mechanical Engineering Department, San Diego State University, San Diego, USA

Manganese oxide nanoparticles are synthesized in the current work from premixed flames doped with vaporized organometallic precursor, manganese methylcyclopentadienyl tricarbonyl (MMT). Premixed ethylene-oxygen-argon flames stabilized by flow stretch are used as the flame-synthesis configuration. The simple, well-characterized flow and temperature fields of this configuration enable systematic control of manganese oxidation conditions. Namely, the equivalence ratio of the unburned mixture and reaction time in the post-flame region largely control the extent of oxidation observed in the manganese oxide nanoparticle products. Nano-scale Mn(II) oxide was observed as a product from fuel rich flames (phi = 1.6) having maximum flame temperature of 2350K and growth time on the order of 10 ms. Flames with increased oxygen content, temperature and growth time lead to mixed or phase pure products of oxides with Mn(II), Mn(II,III) and Mn(IV). Proposed methods to extract manganese oxidation kinetics from the observed products are discussed.

# Mass spectrometric investigation of key intermediates in synthesis flames

*Y. Karakaya, T. Kasper*

IVG, Mass Spectrometry in Reacting Flows – Thermodynamics, and CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany

Every year, million tons of silicon dioxide and iron oxide nanoparticles are produced in flame reactors for a variety of applications in medical technology and pharmaceutical industry. The synthesis in a flame reactor is particularly attractive since it produces high-purity nanoparticles at scalable production rates in a continuous gas-phase synthesis process. The network of chemical reactions of the precursors are embedded in the flame chemistry, consequently the fundamental understanding of the decomposition of the precursor to intermediates and stable products and the start of cluster formation during flame synthesis is a great challenge. Laminar, low-pressure flames stabilized on model burners are valuable tools for the investigation of combustion kinetics. They are used to investigate the decomposition of tetramethylsilane (TMS) and iron pentacarbonyl, and cluster growth from these precursors in flat, premixed, laminar $H_2/O_2/Ar$ low-pressure flames by molecular-beam mass spectrometry (MBMS).

During the sampling process, condensing material like iron oxide species can block the nozzle and reduce the sampling efficiency. Consequently, in iron oxide synthesis flames iron-containing species are hard to detect. Sampling naturally occurring charged species from doped flames improves sampling efficiency for iron-containing key intermediates and allows measurement of species, which often elude detection in molecular-beam sampling systems.

Data sets including concentration profiles of key intermediates have been obtained for iron oxide and silicon dioxide synthesis flames, which are needed to validate kinetic reaction mechanisms in combustion synthesis processes.

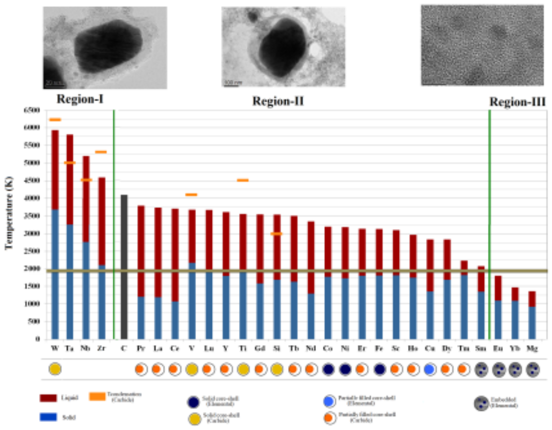
# Carbon encapsulation of elemental nanoparticles by spark discharge

*P. Livan, T. Öztürk*

ENDAM, Center for Energy Materials and Storage Devices, and Department of Metallurgical & Materials Engineering, METU, Ankara, Turkey

A study was carried out on the carbon encapsulation of a number of elements using a spark discharge generator. The study showed that elements W, V, Ti, and Si formed carbides which were encapsulated successfully by graphitic layers forming a sound core-shell structure. Copper formed a partially filled core-shell structure, attributed to its relatively low condensation temperature, where considerable shrinkage seemed to have occurred after the encapsulation. Mg could not be encapsulated in a core-shell form but rather yielded an embedded structure where Mg is condensed onto already condensed carbonaceous material

Analysis of current observations coupled with those already reported data imply a simple mechanism for encapsulation. Metals/compounds that are solid above the condensation temperature of carbon give rise to a sound core-shell structure. Elements whose condensation temperature is less than that of carbon could still produce core-shell particles but they may be partially filled. It is estimated that the process of graphitic encapsulation may be complete around 1900 K and partially filled core-shell structure might develop depending on the volume shrinkage upon cooling to room temperature. Elements/compounds whose condensation temperature is below the encapsulation temperature fail to develop core-shell structure. Instead they form embedded composite structure.



Regions of different encapsulation behavior. Elements are ordered based on their condensation temperature. Horizontal line drawn at 1900 K is the estimated temperature for carbon shell formation.

# High-temperature rate constants for the reaction of H atoms with tetramethoxy-silane and reactivity analogies between silanes and oxygenated hydrocarbons

*S. Peukert, P. Yatsenko, M. Fikri, C. Schulz*

IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids and CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany

Tetramethoxysilane ($Si(OCH_3)_4$, TMOS) is the simplest homolog in the group of the alkoxylsilanes, Si(OR)4, and is used as a precursor for SiO2 coatings deposited through chemical vapor deposition (CVD) and for flame-based nanoparticle synthesis. For process development and optimization, an in-depth understanding of the reaction mechanism is required. Since H-atom-abstractions are an important reaction class within the thermal degradation of silicon-organic compounds, the shock-tube technique has been used to investigate the H-abstraction reaction H + $Si(OCH_3)_4$ behind reflected shock waves. The experiments covered a temperature range of 1111–1238 K, and pressures of 1.3–1.4 bar. H-atom concentrations were monitored with Atomic Resonance Absorption Spectrometry (ARAS). Fits to the temporal H-atom concentration profiles based on a developed chemical kinetics reaction mechanism were used for determining bimolecular rate constants. Experimental total H-abstraction rate constants were well represented by the Arrhenius equation $k\mathrm{total}(T) = 10^{-9.16\pm0.24} \exp(-25.5\pm5.6\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{cm^3 s^{-1}}$. Transition state theory (TST) calculations based on the G4 level of theory show excellent agreement with experimentally obtained rate constants, i.e., the theory values of $k(T)$ deviate by less than 25% from the experimental results. Regarding H abstractions, we have compared the reactivity of C-H bonds in $Si(OCH_3)_4$ with the reactivity of C-H bonds in dimethyl ether ($CH_3OCH_3$). Present experimental and theoretical results indicate that at high temperatures, i.e., $T > 500$ K, $CH_3OCH_3$ is a good reactivity analog to $Si(OCH_3)_4$, i.e., $k_{\mathrm{H+Si(OCH3)4}}(T)\sim1.5\times k_{\mathrm{H+CH3OCH3}}(T)$. Based on these results, we discuss the possibility of drawing reactivity analogies between oxygenated silanes and oxygenated hydrocarbons.

## Reactive dimerization of small aromatics drives soot nucleation

*M. R. Kholghy, G. A. Kelesidis, S. E. Pratsinis*

Particle Technology Laboratory, ETH Zurich, Switzerland

Nucleation is an important, yet poorly understood step in soot formation. The exact mechanism as well as the species involved in soot nucleation are still unknown. Dimerization of Polycyclic Aromatic Hydrocarbons (PAHs) are traditionally considered for soot nucleation because of their thermodynamic stability at flame temperatures as well as observed Bragg diffractions from stacked PAH crystallites. Here, the importance of reactive PAH dimerization in reducing soot nucleation reversibility is investigated by simulating soot formation in a so-called “nucleation” flame. There, inception of soot particles is prolonged at minimal subsequent growth. With only reversible PAH dimerization, the simulated soot concentration is negligible. Accounting however for PAH chemical bond formation after physical dimerization, stabilizes dimers by covalent bonds and increases the soot concentration by four orders of magnitude, in good agreement with Laser Induced Incandescence measurements. In particular, dimers of benzene with benzene, phenylacetylene, naphthalene, toluene, acenaphthylene and cyclopentapyrene make significant contributions to the total soot concentration. The abundance of dimers with small PAHs highlights the dominant role of PAH concentration over their size and dispersion forces on dimer formation. Higher collision factors are used for irreversible dimerization models using larger PAHs because of their lower concentrations and not their larger dispersion forces leading to reduced reversibility and more stable dimers. The qualitative trend of main peaks agrees well with stochastic simulations and aerosol mass spectra measured in the above “nucleation” as well as premixed flames4 highlighting the abundance of PAHs with five-membered rings and substituted aliphatic chains in incipient soot. The predicted number of trimers is very low, i.e. less than 3% of the total soot nuclei formed, indicating that covalently bonded PAH dimers can be the main contributors to soot nucleation.

# Effect of 2-ethylhexanoic acid in the liquid-fed flame synthesis of poorly volatile precursors

*Jili Wei, Yihua Ren, Shuiqing Li*

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Energy and Power Engineering, Tsinghua University, Beijing, China

Liquid-fed flame synthesis is a versatile and manufacturing technique for synthesizing a variety of nanopowders. As the precursor and solvent account for a majority of the production costs of this process, low-cost metal nitrates are considered attractive for industrial application. However, due to the poor volatility and relatively low decomposition temperature of metal nitrates, large residual particles are produced via the droplet-to-particle conversion route. In this work, the effect of additional 2-ethylhexanoic acid (EHA) in precursor solution has been investigated with a lab-scale modified flat flame burner. Here, we define the stoichiometric amount of EHA as the volume concentration for converting all the nitrates to 2-ethylhexanotes in the precursor solution, which is 20% for producing yttrium-aluminum oxides. By varying EHA volume concentrations from 0% to 50%, the particle morphology gradually transits from the coexistence of both large particles (via droplet-to-particle) and small particles (via gas-to-particle) to pure small nanoparticles when the EHA concentration exceeds the stoichiometric volume concentration. Similar experiments are performed on yttria drawing the same conclusion. The precursor formulated mechanism is further verified with a pilot-scale swirl-stabilized burner, demonstrating the vast potential to manipulate the quality of aerosol-produced powders at industrial scales.

# MODELING AND SIMULATION

# Coupling particle size distribution dynamics with gas and solid phase interactions resolved using detailed chemical kinetics

*R. P. Lindstedt*

Department of Mechanical Engineering, Imperial College, Exhibition Road, London, UK

Theoretical models for the size-evolution of chemically reactive nano-scale particles typically feature moment-based methods. However, the need to describe the dynamics of the full particle size distribution (PSD) is becoming apparent due to the complexities of the evolution from uni-modal or multi-modal PSDs to fractal aggregates in chemically reacting environments. The current talk will outline progress made on the inclusion of detailed chemical mechanisms for heterogeneous surface reactions coupled with detailed gas phase chemistry descriptions for such processes. In particular, the prospects for extending Variational Transition State Theory (VTST) based approaches from noble transition metals such as Pt and Rh to systems such as Zn/ZnO will be discussed. The former have recently been studied using mechanisms that are self-consistent and derived using a reaction class-based framework comprising VTST and two-dimensional collision theory for the calculation of pre-exponential factors. Barrier heights were obtained using the unity bond index−quadratic exponential potential (UBI−QEP) method. Transition-state theory estimates were derived for reaction classes describing adsorption/desorption and Eley-Rideal processes by combining the M06 family of density functionals with the Stuttgart/Dresden effective core potential for metal atoms. The resulting surface reaction mechanisms are fairly complex (e.g. 35 adsorbed species and 284 reversible chemical reactions). However, such mechanism can now in principle be combined with detailed gas phase chemistry and sectional models that describe the full PSD evolution also for turbulent flows using calculation methods that permit a closed form coupling to the gas phase. Illustrative examples will also be given for carbonbased nanoparticles where simplified, closed form, surface chemistry descriptions are used to approximate the creation and destruction of reactive surface sites. The need for detailed experimental data and improved understanding of particle transition regimes will also be outlined. The overall aim of the contribution is to promote discussion on the prospects of enhanced detailed studies that support the gradual removal of empiricism from the design/optimisation of practical processes.

# Sectional and monodisperse LES modeling of the SpraySyn flame for nanoparticle synthesis

*J. Sellmann, E. Borukhovich, T. Helmig, A. Rittler, I. Wlokas, A. Kempf*

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Large eddy simulation (LES) of a nanoparticle synthesis flame enables the detailed investigation of the gas-phase synthesis of nanoparticles in resolved interaction of chemical kinetics, particle formation, coagulation and turbulent mixing. Highly resolved LES results are presented for the silica particle synthesis from a spray flame of hexamethyldisiloxane dissolved in ethanol. The simulations are performed for the new SpraySyn burner featuring a spray nozzle and dispersion gas inlet and a sintered matrix as inlet for a premixed pilot flame and a co-flow of shield gas. A Lagrangian-Eulerian and Eulerian treatment is used to describe the spray-, gas- and particle phases. Gas phase combustion is modelled with tabulated chemistry based on the flamelet generated manifold (FGM) approach, with two element mass fractions and a joint progress variable as control parameters. The primary objectives are a) to investigate the particle evolution in the new burner and b) to compare two population balance equations models of different computational cost: a polydisperse sectional model, which accounts for particle formation by nucleation and growth by coagulation and a monodisperse model that accounts for nucleation, coagulation and sintering. The performance of the sectional model and the monodisperse model is investigated based on detailed comparisons of particle diameters, number concentrations and particle size distributions. A parameter is introduced to indicate where the more costly sectional modelling is required and where the simpler model will suffice and particle size distributions at different points of the flame are presented to indicate where certain particle sizes should be extracted.

## Soot light absorption and refractive index during agglomeration and surface growth

*G. A. Kelesidis, S. E. Pratsinis*

Particle Technology Laboratory, Institute of Process Engineering, Department of Mechanical & Process Engineering, ETH Zurich, Switzerland

Optical characterization of soot by light absorption (e.g., Laser Induced Incandescence, LII) and its impact on climate largely depend on light absorption. As soot grows, its morphology changes[1] affecting its optical or radiative properties. Here, the impact of soot maturity on its light absorption is investigated by coupling Discrete Element Modeling (DEM)[2] with Discrete Dipole Approximation (DDA)[3] during soot surface growth and agglomeration. The absorption function, <*E*>, of nascent and mature soot agglomerates is estimated by DDA and validated against atomistic point dipole interactions and mesoscale DDA calculations. Using a refractive index, *RI*, for mature soot yields constant average <*MAC*> and absorption function <*E*> overestimating the nascent soot light absorption up to 75 %. Interpolating *RI* between those of nascent and mature soot for wavelengths, $\lambda$ = 532 and 1064 nm to account for quantum confinement and evolving number of clustered sp$^2$-bonded rings affecting the optical band gap, $E_g$, results in excellent agreement of the DEM-derived evolutions of <*MAC*>, <*E*> and ratio $R = \frac{< E(\lambda = 532 \text{ nm}) >}{< E(\lambda = 1064 \text{ nm}) >}$ with the corresponding LII measurements in methane[4] and ethylene premixed flames.[5] The nascent soot $E_g$ decreases during aging and agglomeration, increasing <*MAC*> and <*E*> by 65 %. The *R* decreases from 1.34 to 0.95 by aging and coagulation and slowly converges to the asymptotic 0.89 of mature soot measured in diffusion flames. The good agreement between DEM and LII data confirms that soot dynamics by surface growth and agglomeration strongly correlate with soot maturity, composition and *RI* that are essential for quantifying soot light absorption and scattering.

[1] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E., Morphology and mobility diameter of carbonaceous aerosols during agglomeration and surface growth. Carbon 2017, 121, 527-535.

[2] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E., Flame synthesis of functional nanostructured materials and devices: Surface growth and aggregation. Proc Combust Inst 2017, 36, 29-50.

[3] Kelesidis, G. A.; Pratsinis, S. E., Soot light absorption and refractive index during agglomeration and surface growth. Proc Combust Inst 2018, 37, in press.

[4] Bejaoui, S.; Batut, S.; Therssen, E.; Lamoureux, N.; Desgroux, P.; Liu, F.S., Measurements and modeling of laser-induced incandescence of soot at different heights in a flat premixed flame. Appl Phys B 2015, 118, 449-469.

[5] Olofsson, N.E.; Simonsson, J.; Torok, S.; Bladh, H.; Bengtsson, P.E., Evolution of properties for aging soot in premixed flat flames studied by laser-induced incandescence and elastic light scattering. Appl Phys B 2015, 119, 669-683.

## Structure of laminar, nanoparticle forming flames: silica and iron oxide

*I. Wlokas, J. Sellmann, H. Jünger, I. Rahinov, T. Dreier, H. Wiggers, C. Schulz, A. Kempf*

Institute for Combustion and Gas Dynamics, and CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany

The knowledge of the spatial structure of a laminar, premixed flame is essential for the understanding of the combustion process and for the development of models, either for reaction kinetics schemes based on experimental evidence or modelling of turbulence-chemistry interaction based on tabulation of pre-calculated flamelets. The nanoparticle synthesis form premixed flames is often assumed to be straight forward, beginning with a pure gas phase, in the premixed flat flame usually found in the small region close to the burner, followed by late particle formation and growth during cooling of the burned gases. The flame front and the zone of particle formation are therefore assumed to be spatially separated and distinguishable. Nevertheless, large concentrations of precursor species in the premixed gases may cause early particle formation with implications to the modeling of the process.

We discuss two popular systems in the gas phase synthesis of nanoparticles: iron oxide and silica. In the case of iron oxide it has recently been shown, that premixed flames doped with iron pentacarbonyl, produce a notable amount of condensable matter, likely iron particles, in the pre-heating zone and in the flame itself. Similar observation was made in silica forming flames, however, indirectly indicated by production and consumption of the SiO molecule. Based on these experiments and complementary CFD simulations we could verify the hypothesis of early inorganic particle formation (and decay) in iron oxide and silica particle forming flames, leading to an extended and improved view of the metal oxide particle synthesis process.

The authors gratefully acknowledge the financial support by DFG through FOR2284.

# DIAGNOSTICS

# Flame synthesis of iron oxide nanoparticles: laser-based diagnostics, particle mass spectrometry and modeling

*I. Rahinov[2], J. Sellmann[1], S. Kluge[1], H. Jünger, A. Fomin[2], M.R. Lalanne[2], S. Cheskis[3], C. Schulz[1], H. Wiggers[1], A. Kempf[1], I. Wlokas[1]*

[1]IVG, Institute for Combustion and Gas Dynamics and CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany
[2]Department of Natural Sciences, The Open University of Israel, Raanana, Israel
[3]School of Chemistry, Tel Aviv University, Tel Aviv, Israel

Production of the iron oxide nanoparticles with tailored properties by flame-assisted synthesis should rely on detailed understanding of the mechanisms governing their formation and nucleation from the gas phase. Well-defined experiments able to make direct contact with simulations are important prerequisite to elucidating the mechanistic details of particle formation. In this talk I will present our collaborative work comprising experiments and simulations for the synthesis of iron oxide nanoparticles from premixed iron-pentacarbonyldoped hydrogen/methane/oxygen flat flames [1-5]. The experiments apply molecular-beam sampling with a particle mass spectrometer to measure particle sizes and a quartz microbalance to detect the presence of condensed matter [1]. Laser-Induced Fluorescence (LIF) and Intracavity Laser Absorption Spectroscopy (ICLAS) were applied to monitor gas-phase Fe and FeO, respectively [2,4]. The simulations rely on a finite-rate chemistry approach with detailed diffusion, particle dynamics are described by a bi-modal population balance model. We observe rich and complex flame structure where "prompt" nucleation zone occurs for precursor loads above ~70 ppm – most probably iron clusters [3,4]. These clusters then evaporate and oxidize and giving rize to second, "late" nucleation zone, presumably preceded by FeOOH and $Fe(OH)_2$ species. We also study how the temperature history can be intentionally modified by orienting flames either in an upward-firing or downward-firing configuration [5]. The results revealed a strong impact of the reactor orientation on the velocity field. It is demonstrated that the downward-burning flame forms a detached stagnation point, causing longer residence times at elevated temperature than an upward- or horizontally firing flame, permitting the growth of larger particles.

[1] A. Fomin, M. Poliak, I. Rahinov, V. Tsionsky, S. Cheskis, Combined particle mass spectrometer–Quartz crystal microbalance apparatus for in situ nanoparticle monitoring during flame assisted synthesis. Combust. Flame, 160, 2131-2140 (2013).
[2] I. Rahinov, A. Fomin, M. Poliak, S. Cheskis, Absorption electronic spectrum of gaseous FeO: in situ detection with intracavity laser absorption spectroscopy in a nanoparticle-generating flame reactor, Appl. Phys. B 117, 317- 323 (2014).
[3] M. Poliak, A. Fomin, V. Tsionsky, S. Cheskis, I. Wlokas, I. Rahinov, On the mechanism of nanoparticle formation in a flame doped by iron pentacarbonyl Phys. Chem. Chem. Phys. 17, 680-685 (2015).
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[5] J. Sellmann, I. Rahinov, S. Kluge, H. Jünger, A. Fomin, S. Cheskis, C. Schulz, H. Wiggers, A. Kempf, I. Wlokas, Detailed simulation of iron oxide nanoparticle forming flames: Buoyancy and probe effects, Proc. Combust. Inst. 37 (2019) https://doi.org/10.1016/j.proci.2018.06.041

## Simultaneous OH-PLIF and PS-LIBS measurements of a turbulent flame synthesis reactor

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Simultaneous single-shot measurements of OH radicals by planar laser-induced fluorescence (PLIF) and $TiO_2$ nanoparticles by phase-selective laser-induced breakdown spectroscopy (PS-LIBS) have been developed to investigate nanoparticle formation and transport during turbulent flame synthesis in a turbulent jet-diffusion flame. By collecting the atomic spectra of titanium near 480 nm from nano-sized plasmas after the second laser-induced fluorescence excitation by the laser pulse with a wavelength of 355 nm, we can reveal the particle information without elastic scatterings or Bremsstrahlung. Direct comparison between the OH-PLIF and $TiO_2$ particle volume fraction can well describe how the nanoparticles form and transport in the turbulent flame synthesis reactor, which can be used in validating numerical models.

# Measurements of aerosol size and structure at low-pressure reactors: sampling issues and measurements using a differential aerodynamic particle sizer

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Online measurements of nanoparticles at the outlet of aerosol reactors are necessary when rapid information about the particle size, density or fractal dimension is required. At low-pressure conditions, the application of online measurement techniques with the commonly used instruments such as SMPS, CPMA and ELPI+ is currently not possible. A continuous sampling procedure from low-pressure into ambient pressure would be of great advantage for online methods. In this work, a commercial vacuum ejector is investigated as a simple tool to transfer nanoparticles from a low-pressure region to atmospheric pressure. Commonly, vacuum ejectors are used to generate up to 98 % vacuum on the basis of the Venturi principle. A driving gas with a high velocity provides the driving force to entrain a side gas, usually the gas to be sucked in, by the use of a converging nozzle. In a diverging diffuser section, the mixed gas is slowed down so that the pressure increases. The final pressure of the mixed gas is in between that of the driving gas and the sampling gas. The vacuum ejector is tested for different process pressures between 120 to 170 mbar in the size range from 10-100 nm, using size-selected aerosols with well-known number concentrations. The gas and particle dilution factors as well as the particle losses are determined, so that quantitative aerosol size distribution can be obtained.

Measurement of two different equivalent particle diameters can allow to determine structure parameters such as fractal dimension. The therefore required high resolution is best obtained by fractionating sizing techniques. Size-fractionation based on electric mobility is well known, but until now it was not possible to obtain a high-resolution aerodynamic diameter distribution. Here, we apply a novel measurement called the Differential Aerodynamic Particle Sizer (DAPS), which measures the number concentrations of narrow size fractions, which are generated by aerodynamic focusing. Here, applying low pressure allows to reach sizes relevant in aerosol reactor engineering. Applications of this instrument for aerosol structure determination will be shown.

The authors acknowledge the support by the Deutsche Forschungsgemeinschaft (DFG) in scope of the research group 2284 “Model-based scalable gas-phase synthesis of complex nanoparticles” and the joint research program “Multi parameter characterization of functional particle based materials by innovative online measurement techniques (PAK688)”

T. Rosenberger, A. Münzer, D. Kiesler, H. Wiggers, F.E. Kruis, Ejector-based sampling from low-pressure aerosol reactors, Journal of Aerosol Science, 123, 105-115 (2018).

# SCALE-UP AND APPLICATION

## Processing and functionalization of nanopowders in fluidized bed reactors

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The need for scale up of an aerosol process for the functionalization of nano-scaled oxide particles (led to the development of a fluidized bed reactor. Fluidization of nanopowders is not trivial and requires special measures to overcome the dominating interparticle forces. We used two established approaches to this problem. One is the use of a secondary high velocity flow in addition to the primary fluidization gas (see fig. 1). The second approach is a vibration activated fluidized bed, which was used for Geldart C-type powders, such as $TiO_2$. Precursors for functionalization are vaporized and introduced into the fluidized bed using a heated lance to prevent condensation or resublimation. The reactor is equipped with electrical heating and can be heated up to 200°C. Coating experiments were carried out with Molybdenum hexacarbonyl and TEOS as precursors to generate core-shell structures of alumina- , silica and $TiO_2$ particles. Figure 2 exemplarily shows the course of a coating experiment of MoOx/$SiO_2$. The reactor temperature was kept at 130°C, images were taken every 30 minutes. The characterization of the coatings in the electron microscope and by zeta-potential measurements showed very thin but closed films of MoOx on alumina.The functional properties of the nanocomposites produced by FB-CVD were analysed by means of their photocatalytic properties.

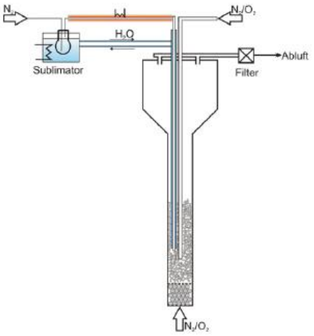

Figure 1. Fluidized bed reactor
Several oxide materials were successfully fuidized using these systems.

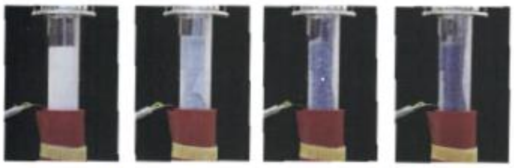

Figure 2. FB-CVD coating of silica NP with MoOx. Total duration: 90 min.

This work was supported by JointLab IP3, a collaboration of KIT and BASF.

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## Flame-synthesised $Li_4Ti_5O_{12}$ anode materials for high-power Li-ion batteries

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Increased renewable energy production and electrification of the transport sector are required to abate climate change. However, the limitation in current rechargeable batteries form a significant bottleneck in both fields. At the moment, Li-ion secondary cells are one of the most advanced energy storage systems available. Lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) is recognized as a promising material for the negative electrode of Li-ion batteries as it is cheap and safe, and has an excellent cycle. However, the major drawback of LTO is its low electronic conductivity. To overcome this problem the particle size can be reduced to the nanoscale. Another solution is to use transition metal dopants (e.g., Cu, Ag).

In the standard FSP process the quenching of the particle sintering is very efficient. As such, the primary particle size remains small. However, it also stops the growth and ordering of the crystallite structures. This can lead to retardation of the Li-ion diffusion within the crystallites reported by Kavan et al. In order to promote further crystallisation the entrainment of surrounding air was limited by enclosing the flame. The system was also scaled up to produce up to produce kilograms of nanopowders.

For the liquid precursor organometallic Li and Ti were dissolved in stoichiometric ratio (4:5) into organic solvent, resulting in a solution with a total metal concentration of 1 M. The silver doping was realised by adding organometallic silver directly into the precursor solution. The mass fraction of dopant metal was 1% of the calculated LTO mass. The resulting particles were found to be high-purity (99%), single crystalline nanoparticles with a primary particle size of about 30 nm. The silver dopant nucleated separately and deposited uniformly onto the LTO particles.

The electrochemical performance of the material was tested in Li-ion half-cells. It was found that the improved performance compared to the undoped version and to commercial LTO was obtained. In particular, the capacity at high C-rates was found to be excellent, 75% of theoretical maximum even at 20C. In summary, doped LTO synthesised with the increased high-temperature residence time is a good alternative for battery application where high-power performance and long cycle-life is required.

This work was supported by the Finnish Funding Agency for Technology and Innovation (grant 40051/09), Fortum Foundation (12-072), the Finnish Cultural Foundation (65171599), and the strategic funding of University of Eastern Finland (931057).

# Flame synthesised silica/ceria catalyst supports for the valorisation of carbon dioxide

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The conversion of carbon dioxide to methane, through the Sabatier reaction as well as the carbon dioxide reforming of methane, poses promising routes for the mitigation of carbon dioxide emissions whilst simultaneously producing valuable chemicals. For the activation of carbon dioxide, the vacancy-rich surface of ceria supports has been extensively studied as a route to enhance catalyst activity and selectivity. Silica, as an inert support, is thermally stable and has a high surface area which are desirable for thermal catalytic reactions. Ultimately, the rapid and scalable synthesis of catalyst supports is essential for the implementation on carbon dioxide valorisation reactions on an industrial scale.

In this work, we first examined the formation of silica during flame spray pyrolysis (FSP) synthesis and revealed that, at low precursor concentration (<1.5 M tetraethyl orthosilicate in xylenes), silica forms uniquely within the flame. Explicitly increasing the precursor feed rate resulted in an increase in the specific surface area (for example at 0.5 M tetraethyl orthosilicate, the surface area increased from 217 $m^2$/g at 3 ml/min to 363 $m^2$/g at 7 ml/min). With this understanding of the formation of silica, we examined the use of an asymmetrically variable double FSP (DFSP) to design silica/ceria-zirconia composites for their use as supports for the dry reforming of methane. Further, to design silica/ceria composites for the Sabatier reaction, the ratio of silica and ceria were varied to give rise to impressive variations in material performance.

# Large-scale manufacturing of fullerenes, single-walled carbon nanotubes, their derivatives and dispersions for energy and electronic applications

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The availability at industrial scale of high quality fullerenes, particularly C60 and C70, and single-walled carbon nanotubes (SWCNT) with consistent characteristics is essential for the commercial development of many nanoscale devices such as organic photovoltaics (OPV) and photodetectors; transparent conducting films; non-volatile memory; and optical, chemical or biological sensors.

Premixed hydrocarbon combustion is a particularly appealing approach for the large-scale manufacturing of these carbonaceous nanomaterials. It is exothermic, scalable and, most importantly, allows, depending on the process parameters, for the selective formation of either fullerenes or SWCNT. The fuel-rich combustion of aromatic hydrocarbons at reduced pressure results in the targeted synthesis of fullerenes whereas low-pressure combustion below the sooting threshold of aliphatic and other simple hydrocarbons in presence of a continuously supplied catalyst precursor enables the efficient formation of exclusively SWCNT.

In this presentation, the path from first observations of fullerenes in flames to the industrial manufacturing of fullerenes and SWCNT, now in place at Nano-C, will be described. Correlations between reactor design; operating parameters such as pressure, fuel-to-oxygen ratio and residence time; and characteristics of the generated fullerenes or SWCNT determined by means of a range of analytical techniques will be discussed.

The further refining of the products of Nano-C’s combustion processes, in the case of many applications necessary prior to their use, will be outlined. The purification of fullerenes resulting in isolated C60 and C70, as well as the use of chemical functionalization targeting specific electronic and physical (e.g., solubility in a given solvent) properties will be described. Methods implemented for the purification of SWCNT and their further use, e.g., in dispersions, will be discussed. Major applications, currently at the edge of accelerated commercialization, will be described and future improvements in the efficiency of the combustion synthesis of carbonaceous nanostructures will be discussed.

# Scale-up of nanomaterials synthesis from the lab to the pilot-plant scale: challenges and results

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The synthesis of nanomaterials has a long history in science. The size-dependent properties of particles have led to astonishing discoveries in recent decades. Synthesis takes place mainly through wet-chemical or gas-phase processes. Especially gas-phase synthesis allows the production of particularly pure and well-defined particles in scalable processes, so that new materials can be provided for industrial development in sufficient quantities. While the gas-phase synthesis of highly-specific particles is currently very successful on a laboratory scale, even the first scaling stage on a pre-industrial level requires remarkable effort. To investigate this step, a pilot plant with a microwave-assisted plasma reactor (PLR), hot-wall reactor (HWR) and flame reactor (FLR) was set up at IUTA ten years ago. We present the challenges to enable each reactor system for stable short- and long-term operation and the properties of the nanoparticulate materials produced during the experiments.

The reference materials for the synthesis in hot-wall and plasma reactors is silicon. Production rates of 1.0 kg/h and higher in the hot-wall reactor require specific nozzle design and good process control to avoid the accumulation of particles on the inner tube of the reactor. We demonstrated the long-term stability of the silicon production process for more than 30 h using a double filter system to enable continuous production. We show the continuous synthesis of silicon nanomaterial in the plasma reactor with a production rate of 200 g/h with stable material properties. For the plasma reactor we will present details of the synthesis for particles in the regime from 15–50 nm and major differences between lab and pilot-plant scale during the agglomeration of particles for higher precursor concentrations. In the flame reactor, cerium oxide will be shown as an example for the production of metal oxide nanomaterials. Here, the incorporation of dopants with various concentrations will be discussed and challenges of precursor preparation and handling is shown.

# POSTER PRESENTATIONS

# P1

# Spray-flame synthesis (SFS) of the nanosized $LaMO_3$ (M = Fe, Co) perovskites from metal nitrate precursors: Influence of the mixture of ethanol and 2-ethylhexanoic acid on the materials homogeneity

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Perovskite nanomaterials composed of $LaMO_3$ (M = Fe, Co) are of current interest for environmental catalysis applications, e.g., oxidation of CO and $CH_4$, and for catalytic energy conversion reactions such as water splitting. The synthesis of such compounds is commonly done in time and energy consuming batch processes. Alternatively, spray-flame synthesis (SFS) allows the formation of functional perovskite nanoparticles in a single step. Cost-efficient production requires the utilization of cheap and abundant precursors such as metal nitrates, which are more attractive than the organometallic precursors (acetates, carboxylates). However, the use of metal nitrates in SFS is often associated with the formation of particles non-homogeneous in size[1]. Furthermore, the different melting/decomposition mechanisms and their different solubility in solvents such as ethanol cause the formation of undesired phases, e.g., $La_2CoO_4$, $La_2O_3$ and $Co_3O_4$, which are often obtained in parallel to the main perovskite phase.

In order to improve the perovskite homogeneity in size and composition, mixtures containing the metal nitrate precursors and two different solvents, ethanol and 2-ethylhexanoic acid (2-EHA), were employed in this study. The incorporation of 2-EHA has been previously investigated and a positive effect toward narrow particle-size distributions has been observed. It is suggested that the addition of 2-EHA leads to the formation of micro-explosions in the droplets through superheating of ethanol and the formation of volatile metal carboxylates[2], which is investigated in this study.

$LaCoO_3$ and $LaFeO_3$ nanoparticles were synthesized from solutions of the respective nitrates in ethanol/2-EHA. To understand the effect of 2-EHA on the product properties, temperature-dependent liquid-phase ATR-FTIR studies were performed. It was found that an esterification of 2-EHA with ethanol occurred forming ethyl-2-ethylhexanoate (verified by GC/MS). We assume that the metal nitrates act as catalysts as reported for similar reactions[3,4]. The nanoparticle products were characterized using XRD, XPS, TEM, SAXS, and Mößbauer spectroscopy. The measurements confirm that the incorporation of 2-EHA in the solution was effective for obtaining homogeneous, single-phase, and high-surface-area products ($LaCoO_3$: $d_p = 11$ nm, SSA $> 90$ m$^2$/g, $LaFeO_3$: $d_p = 15$ nm, SSA $> 88$ m$^2$/g). The $LaFeO_3$ and $LaCoO_3$ perovskites were evaluated for the catalytic oxidation of carbon monoxide, reaching temperatures lower than 206°C for the 50% CO conversion.

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## P2

# Characterisation of the SpraySyn burner by LES calculations

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The SpraySyn burner has been developed from previously available burners for spray synthesis to permit a more effective and less costly treatment of inlet boundaries. The present poster contributes to the initial characterization before in the later project stage the burner is used for studies of nano particle syntesis by pyrolysis. As the first step, simulations on flow and combustion in the burner‘s pilot and spray flames are performed based on the Large Eddy Simulation (LES) technique combined with the Artificial Thickened Flame (ATF) and the Flamelet Generated Manifold (FGM) approaches. For the generation of the tabulated chemistry data used within the FGM, an existing ethanol mechanism published by Marinov has been used (Marinov, Int. J. Chem. Kinet. 31, 1999, 183-220). The simulation results are compared against available experimental data.

P3

# Synthesis of $Fe_xO_y$ nanoparticles by spray flame. A study of the reaction parameters

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FexOy nanoparticles were prepared by spray flame synthesis employing several reaction conditions. Different dispersion gas flows, liquid precursor flows and assistant flame fuels were tested in order to correlate reactive environment conditions to composition, crystalline phases, shape, and size. Moreover, residues adsorbed on the particles' surface originated from (incomplete) combustion were investigated. In fact, an overview of synthesis parameters effects on materials properties is a useful tool aiming to design materials with several compositions and morphologies

Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and magnetometry measurements were used to determine main material features. Powders with different compositions including hematite ($\alpha$-$Fe_2O_3$), maghemite ($\gamma$-$Fe_2O_3$) and magnetite ($Fe_3O_4$) crystalline phases were obtained depending on reaction parameters. More reducing environments, as those with higher liquid feeds or lower dispersion gas flows contributed to the magnetite formation, while high hematite amount was obtained at oxidizing conditions with high temperatures. Determined residues percentages were found to be between 10 and 35%, taking into account non-consumed precursor materials and soot formation. In terms of samples composition, those with higher magnetite content where the same showing elevated soot formation and the one with the highest hematite content exhibited less than 1.5% of carbonaceous residues. About shape, spherical and facetted particles were observed with particle size distributions mainly centered between 15 nm and 25 nm. Saturation magnetization values were found to be between 26 emu/g to 32 emu/g, allowing to identify the magnetite effect content and particle size in the magnetic behavior.

## P4

# Modular plasma activation and functionalization of nanoparticles from gas-phase synthesis

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Nanoparticles have shown promising opportunities concerning their suitability in a plethora of applications, e.g., coatings, sensor technology, and photocatalysis. Due to their high surface-to-volume ratio, the properties of nanoparticles highly relate on their surface properties and can thus be modified by means of surface functionalization to suit for specific applications. Gas-phase synthesized nanomaterials have already proven to be contaminant-free from stabilizers and functionalization agents. However, this can lead to high reactivity resulting in unwanted surface reactions and surface treatment is often required with respect to nanoparticle processing, thus allowing to tune their processability for developing innovative processes and products.

This work aims to design a modular system that aids in direct functionalization/stabilization of gas-phase made particles and their transfer into a liquid phase immediately after particle production. Therefore, nanoparticles from a spray-flame reactor are directly subjected to an AC/DC plasma discharge for inline activation and functionalization. Preliminary work introducing a plasma-assisted coating with $SiO_2$ using hexamethyldisiloxane (HMDSO) as gaseous coating precursor has shown promising results concerning tuning the processability of flame-made nanoparticles. This work focuses on the functionalization of $TiO_2$ as there have been innumerable investigations on surface modification of $TiO_2$ and its application. The combination of $TiO_2$ flame synthesis and subsequent functionalization is aimed to directly transfer particles from the gas phase into a liquid to form stable dispersions using a variety of liquids. First results concerning particle formation will be shown.

# P5

# Laser-induced incandescence measurements for nanoparticle size monitoring in spray-flame synthesis

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Flame spray pyrolysis (FSP) is considered a powerful method to produce nanoparticles oxides with different properties. In particular, the possibility to change the experimental conditions in the flame can be very helpful for the synthesis of single- and multi-component nanoparticles with specific and tailored characteristics. Properties such as crystallite size, crystalline phase, degree of aggregation and agglomeration, surface area and porosity can be very challenging in different applications including catalysis, gas sensors as well as energy storage. In particular, particle size is a key parameter in nanopowder characterization being particle properties strictly related to surface/volume ratio. In this context, monitoring particle size during flame synthesis can be particularly attractive for the production of tailored size nanoparticles.

In this work laser-induced incandescence (LII) of nanoparticles oxides is proposed as a powerful tool to follow particle formation and size during the synthesis in flame.

The spray-flame synthesis apparatus developed in CNR Milano laboratory consists of an oxygen-assisted spray used to inject the liquid precursor, which is normally feed by a syringe pump. A pilot flame, positioned coaxially to the flame spray, allows starting combustion reactions.

The apparatus has been designed and developed in order to produce nanoparticles in powder as well as in film. In fact, the availability of powder supported deposits is very useful especially for catalytic applications (e.g., air and water treatment), to overcome several problems of process design and implementation. As a first analysis, LII measurements have been performed on filter-deposited nanoparticles to investigate the influence on the incandescence signal of laser fluence and delay time with respect to the laser beam. To this purpose, both single shot spectral analysis and two wavelengths time-resolved measurements have been carried out. A characteristic time and fluence threshold for fluorescence and incandescence signals have been observed.

The same LII optical apparatus for spectral and time-resolved measurements have been then applied directly in the flame spray pyrolysis apparatus to follow particles synthesis along the flame.

The results prove the ability of monitoring synthesis and sizing of particles in flame.

## P6

## Spray characterization of the SpraySyn burner using high-fidelity simulations

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Flame spray pyrolysis (FSP) is a promising approach for production of nanoparticles with tailored functionalities. Those functionalities are determined by the particle properties (e.g. size, morphology, homogeneity, configuration, crystallite properties), which are controlled by the temperature, concentration distribution inside the reactor, and the residence time of particles in certain regions. The complex multiscale, multiphysics FSP can usually be divided into three zones: the spray zone, the combustion zone, and the particle formation zone. The local conditions in these zones are governed by zone corresponding sub-processes and their interactions. It was shown that the spray characteristics influence the particle formation [1], which may be used to tailor particle properties. However, this requires a comprehensive knowledge of the impact of spray formation on the particle formation. In order to overcome the lack of knowledge, a detailed and accurate characterization of the spray formation is necessary. For that, modern high-fidelity simulation methods and detailed experiments are suited.

In this work, the spray formation of the SpraySyn standard configuration is studied using high-fidelity simulations in order to understand the influence of the dispersion gas flow on the spray characteristics. Coupled simulations of the turbulent internal nozzle flow of the dispersion gas and primary breakup are used. Coupling is achieved by forcing the unsteady velocity field of the nozzle outlet plane as inlet conditions for the interface resolving primary breakup simulations. The internal nozzle flow is computed in a large-eddy simulation (LES) using a structured, high-order finite-difference in-house code, called CIAO, which solves the fully compressible, filtered Navier-Stokes equations explicitly. The primary breakup is computed as direct numerical simulation (DNS) with a 2nd order coupled 3D unsplit Volume of Fluid/Level-Set method, which employs a hybrid Lagrangian/Eulerian discretization of the convective terms and pressure projection. Simulations of the real SpraySyn nozzle geometry and a fully developed turbulent pipe with SpraySyn nozzle outlet geometry are performed and the resulting spray characteristics are compared.

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# P7

# Reactions of the precursors for the spray-flame synthesis of nanoparticles in partial spray evaporation

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The wide application of nanoparticles in industry, especially in materials science, imposes strict requirements on their geometric characteristics because the physical properties of the final material directly depend on the size. One of the main methods of nanoparticles synthesis is “Spray Flame Synthesis”. The SPP1980 uses a standardized Spray-Syn Burner, to investigate all aspects of the nano particle formation process. However, in the experimental study of the chemical transformation of precursors to particles in the flame it is problematic to separate contributions of the thermal decomposition and oxidation from spray formation. This project focusses on the investigation of the chemical reactions occurring during spray formation. This information is necessary for the creation and verification of a chemical mechanism for simulation of the nanoparticle formation.

The scheme of the experiment is shown in Fig. 1. The spray was generated by the SpraySyn burner in the current design and with recommended flows with the exception that the pilot flame is not ignited to decouple chemical reactions in the spray from chemical reactions in the flame. Nitrogen (as an inert atmosphere) was used for all channels (supported gas, pilot gas, dispersion gas). For the pilot channel, there is the option of heating the initial flow (up to 250°C). The decomposition of the spray was carried out in the quartz flow reactor (diameter of 90 mm, length of 500 mm). The temperature of the total flow through the reactor can reach up to 900°C at the outlet of the reactor. Reactor design and characterization will be presented.

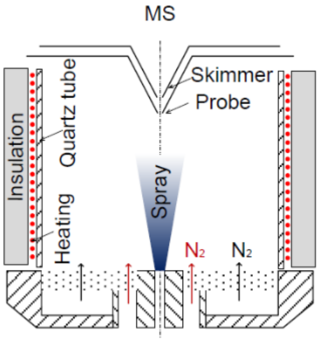

Fig. 1: The scheme of the experiment of spray decomposition

## P8
## Reaction kinetics model for silica precursors: TMS and HMDSO

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Tetramethysilane (TMS) and hexamethyldisiloxane (HMDSO) are promising precursors for flame assisted synthesis of silica ($SiO_2$) nanoparticles. Based on the previous studies proposing reaction mechanisms of silica formation from the oxidation of silanes and siloxanes and experimental observation, we developed a new reaction kinetic model for the combustion of TMS and HMDSO in H2/O2/Ar low-pressure flames. The kinetic model is based on combinatorial considerations and refined using spatially resolved Molecular-Beam-Mass-Spectrometry (MBMS) measurements and laser-induced fluorescence (LIF) diagnostics (Chrystie et al., Proc. Combust. Inst. 37, 2019) in the flame. The thermodynamic properties of the Si-C-H and the Si-C-O-H molecules were calculated in quantum chemical calculations at the G4 level of theory. The C-O-H sub-system is represented by the C1 mechanism of Li et al. (Int. J. Chem. Kin. 39, 2007). We employed a genetic-algorithm based global optimization procedure (Sikalo et al., Int. J. Chem. Kin. 47, 2015) using the experimentally determined flame structure and mixture properties as the evaluation criteria. The mechanism was able to reproduce the concentration profiles of selected major species showing in general good agreement with the experimental observations made via MBMS and LIF.

We gratefully acknowledge funding by DFG through FOR 2284.

## P9

# Impact of humidity on silica nanoparticle agglomerate morphology and size distribution

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Fractal-like agglomerates of physically-bonded single primary particles and/or chemically-bonded ones (aggregates) are typically formed by agglomeration during flame synthesis of carbon black and other nanostructured materials.[1] This ramified agglomerate morphology changes drastically during atmospheric aging,[2] storage or industrial processing by spray granulation[3] or fluidization[4] in the presence of humidity.

Here, flame-made agglomerates of silica nanoparticles are humidified at various saturation ratios and dried before characterization.[5] These agglomerates collapse into compact structures and follow a fractal scaling law. The hydrophilic surface of silica delays water evaporation and results in a critical saturation ratio larger than that of hydrophobic particles (e.g. soot[2]). Online diagnostics using a scaling law derived here from first principles are employed to monitor for the first time the aggregate size and its impact on agglomerate morphology after condensation-evaporation. The humidified-dried silica agglomerates are more porous than those of soot[2] due to their larger aggregate size. The method developed here[6] can facilitate handling, storage, processing and eventual performance of spray-dried[3] and fluidized nanoparticle granules[4] in different applications, such as batteries and fuel cells.

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## P10
# Soot morphology and light scattering

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Soot nanoparticles generated by combustion sources involving transportation, power generation and fires form fractal-like, porous clusters (agglomerates).[1] Yet, their optical properties are calculated using the Mie theory for spheres neglecting the ramified agglomerate morphology and impeding the accurate estimation of soot environmental impact, characterization by optical diagnostics and selective detection with fire sensors.

Here, the soot morphology and radiative properties are investigated experimentally and simulated during surface growth and agglomeration by Discrete Element Modeling (DEM)[2] coupled with Discrete Dipole Approximation (DDA).[3] The DEM-derived number of constituent primary particles (PPs), effective density and differential scattering cross-sections for vertically-, $C_v$, and horizontally-polarized incident light, $C_h$, are in excellent agreement with those measured here in different premixed ethylene flame conditions. In contrast, the Rayleigh Debye Gans (RDG) theory coupled with a scaling law for agglomerates with monodisperse, single, non-aggregated PPs[4] underestimates the DEM-derived $C_v$ and $C_h$ by 60 %. Thus, DEM-DDA can be used instead of the conventional RDG theory for the optimization of climate forcing estimations and soot optical diagnostics, as well as for selective detection by fire sensors.

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## P11

# The comparison of tin dioxide nanoparticles synthesized from single droplet combustion and from flame spray pyrolysis

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Tin dioxide ($SnO_2$) nanoparticles synthesized via flame spray pyrolysis (FSP) are attractive and promising for the gas-sensing applications. In this work, we used the same precursor-solvent solutions (Tin (II) 2-ethylhexanoate/xylene) with precursor molar concentration variations from 0.05, 0.1, 0.25, 0.5, 0.75 to 1 mol/l in order to synthesize nanoparticles via single droplet combustion as well as FSP experiments. The nanoparticles obtained from FSP were characterized by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET), and their morphology and size distributions were also be compared to nanoparticles from single droplet combustion via transmission electron microscopy (TEM).

## P12

# Gas-phase synthesis and inline coating of nanoparticles in a microwave plasma reactor

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Gas phase synthesis of nanoparticles (NPs) in plasma reactors is an established approach to produce pure and complex nanomaterials like composites (e.g., embedded structures) and core–shell materials in large quantities. As their properties are strongly depended on structure and composition, the combination of various compounds and their structuring is necessary to tune and develop materials with specific characteristics. We report on a promising, scalable and continuous microwave-based plasma method to manufacture highly specific nanomaterials and its utilization for a direct in-line coating. The process technology doesn't require a specific gas composition and has the potential for being transferred to pilot and industrial production scale. A few examples concerning the formation of different materials (iron oxide, silicon, graphene) are given:

As the gas phase composition in the microwave plasma reactor can be tuned individually, we were able to produce iron oxide ($Fe_xO_y$) nanoparticles with different stoichiometries depending on the Fe/O-ratio in the plasma reactor. Silicon nanoparticles with adjustable size are available by pyrolysis of different concentrations of monosilane while graphene is accessible via thermal decomposition of hydrocarbons. Because of plasma afterglow activation, it is possible to realize a direct inline coating of the nanoparticles downstream the particle-forming microwave plasma process. This was realized by subsequent injection of a coating precursor via a well-designed coating nozzle enabling a homogeneous intermixing with the particle-laden off gas. Ethylene and a few silica precursors (e.g. HMDSO, TMOS, TMDSO, and TEOS) have been successfully tested to form either a carbonaceous or a silica shell.

## P13

# Development of compact, skeletal reaction mechanisms for the combustion of n-butanol/air and o-xylene/air

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The n-butanol and o-xylene are popular solvents for metal-oxide nanoparticle precursors in spray flame pyrolysis process. While detailed reaction schemes for combustion of these fuels exist, which are too large in their number of species and reactions for application in simulation of the turbulent spray combustion. In this work we present new hybrid global-skeletal reaction schemes of n-butanol and of o-xylene combustion in air. The o-xylene combustion scheme consists of 22 species and 37 reactions and n-butanol mechanism consists of 23 species and 34 reactions, both developed using the global fuel breakdown approach. The general structure of the two presented mechanism comprises, the global, irreversible reaction steps leading to C2 intermediates and the combustion reactions of the C2 intermediates (o-xylene - Z. Luo et al. (Combust. Flame 159, 2012) and nbutanol – Zetterval et al. (Energy Fuels 30, 2016) and hydrogen mechanism by Li et al. (Int. J. Chem. Kin. 39, 2007)). The reactions rate coefficients of the mechanisms are optimized using genetic algorithm technique by Sikalo et al. (Int. J. Chem. Kin. 47, 2015). The optimization targets are combustion characteristics i.e., ignition delay and laminar flame speed over wide range of temperature and equivalence ratios at atmospheric pressure. The validation targets are detailed reaction mechanisms from literature sources (n-butanol - Veloo et al. (Combust. Flame 147, 2010) and o-xylene – Ranzi et al. (http://creckmodeling.chem.polimi.it/menu-kinetics/menu-kineticsdetailed- mechanisms/menu-kinetics-prf-pah-real-fuels-mechanism)) and the available experimental data (n-butanol - Veloo et al. (Combust. Flame 147, 2010) and o-xylene - Ji et al. (Combust. Flame 159, 2012)). The presented mechanisms are in good agreement with the reference data for laminar flame speed, ignition delay time, temperature profiles and concentration profiles of selected radicals and product species.

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## P14

## Numerical investigation of ethanol-water spray evaporation in counterflow spray flames

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Nanoparticle synthesis in spray flames requires the evaporation of a precursor solution and ist combustion resulting in a multiphase reacting flow. The evaporation of an ethanol/water spray in air is studied in a counterflow spray flame where the influence of the water on both the evaporation and the combustion characteristics of this flame is investigated in comparison with single-component ethanol sprays in air. The similarity transformation of the gas phase from two-dimensional into onedimensional coordinates makes the use of detailed chemical reactions computationally affordable. The use of these spray flame structures in the framework of spray flamelet modeling of turbulent spray combustion will enhance the knowledge of multi-component droplet evaporation and combustion in nanoparticle synthesis in spray flames. The numerical study concerns mono-disperse fuel/water droplets in air in the counterflow configuration where the spray and the carrier gas air are directed against a pure air stream. The strain rate on the spray side of the flame will be varied as well as the initial droplet size of the mono-disperse spray. A detailed chemical reaction scheme including 38 chemical species and 337 elementary reactions is used to describe the gas-phase reactions. Detailed flame structures as well as droplet evaporation characteristics are presented and discussed. The model will serve as base for the study of the evaporation and combustion of a precursor solution in the counterflow configuration which eventually may be used as a flamelet library in turbulent spray combustion.

## P15

# Kinetics of structure formation of complex nanoparticles in model flow reactors

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Sintering of aerosol particles is complex process due to their dependency of various particle properties, for example size, shape, agglomerate structure as well as the dependency of the process parameters like temperature and residence time in the reactor. For the validation of sinter models, precise experimental data of the particle structure formation are needed [1].

A model flow reactor, where the process parameters are simplified by using a laminar flow field with well-defined particle trajectories and a narrow residence time distribution, is used to this end. CFD simulations are required to calculate the temperature and residence time of the particles in the reaction zone. The model flow reactor itself is based on a vertical tube furnace with water-cooled gas in- and outlets. Particles are entering at the bottom of the reactor flow surrounded by a preheated sheath gas in the centre. Therefore, a small variation in residence time of the particle is achieved. The water-cooled in- and outlet are used to restrict the structure changes to the heated area. A setup for very short residence times around 100 ms in turbulent flows has already been presented [2]. In contrast, our new setup is designed for residence times of at least 1 s at atmospheric pressure.

An aerosol consisting of monodisperse iron agglomerates, which are classified by their electrical mobility, is sintered in the model flow reactor for different temperatures in the range of 400 K to 1300 K. The particle mass and size distribution is measured by a combination of different online measuring instruments such as SMPS, CPMA, DAPS and offline SEM analysis to detect structural changes of the particles [3]. It is currently not possible to validate the sinter models by measuring the particle structures with these online measuring instruments at low-pressure reactors [4]. In order to obtain rapid information about the particle structure, a commercial vacuum ejector was investigated as a simple tool for transferring nanoparticles from a low-pressure region (120-170 mbar) to atmospheric pressure. Additionally, the applicability of the vacuum ejector is tested by real-time measurements due to the direct transfer of the aerosol to atmospheric pressure during particle synthesis in a low-pressure microwave plasma reactor [5].

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**P16**

## The SpraySyn burner: A new standard burner for coordinated studies on material synthesis in spray flames

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In many scientific communities, the definition of standardized experiments has enabled major progress in process understanding. The investigation of the spray-flame synthesis of nanoparticles at a well-defined standard burner by experiment and simulation makes it possible to produce a comprehensive data set with various established and novel measuring methods. In this work, we introduce the design of the SpraySyn burner as a new standard that offers well-defined and simulations-friendly boundary conditions and geometries as well as accessibility for optical diagnostics. The premixed CH4/O2 pilot flame exits the SpraySyn burner through a sinter bronze. The flame is stabilized by a sheath gas flow of air that offers easy to calculate boundary conditions for simulations. The liquid precursor and solvent are fed through a capillary aerosolized with an additional oxygen dispersion gas flow into the pilot flame as a spray. This technique allows for a wider choice of fuel and precursors and much higher production rates than obtained in gaseous flame synthesis. Standard operating conditions for spray-flame synthesis are given and a parameter study of the flame performance for operation with ethanol, o-xylene and nbutanol is presented. For ensuring reproducible operation in many labs, we define a simple optical setup for flame characterization using a DSLR consumer camera. Post processing of the raw images allows to quantitatively describe the flame geometry under standard operating conditions, such as flame length, width, tilt angle, photometric distribution of visible flame chemiluminescence along the flame center axis and the characterization of the pilot flame hemisphere.

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## P17

# High-temperature gas-phase kinetics of the thermal decomposition of tetramethoxysilane

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Accurate measurements of the kinetics of Tetramethoxysilane (TMOS) in at high temperatures are a fundamental requirement for the understanding of the decomposition of alkoxylsilanes and to develop a kinetics model to control and optimize CVD and nanoparticle formation processes. The decomposition of TMOS has been studied in single-pulse shock tube over a temperature range of 1131–1610 K and pressures ranging from 1.9 to 2.3 bar. Here we measured the rate of decomposition of TMOS behind reflected shock waves using gas chromatography/mass spectrometry (GC/MS) and high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS). The primary decomposition step is a four-center elimination to form methanol and at elevated temperatures, TMOS also decomposes via a O–C bond scission forming methyl ($CH_3$) and $OSi(OCH_3)_3$ radicals. The main observed products were methane ($CH_4$), methanol ($CH_3OH$), ethylene ($C_2H_4$), and ethane ($C_2H_6$). The rate of decomposition can be expressed in Arrhenius form as follows:
$k_{\text{overall}}[\text{TMOS} \rightarrow \text{products}] = 2.9\times10^{11}\exp(-225\text{ kJ mol}^{-1}/RT)\text{s}^{-1}$

A kinetics mechanism from literature (Chu *et al*. 1995), which quantitatively accounts for the observed products during the decomposition of TMOS, was adopted and updated. The mechanism contains 13 silicon species and 24 reactions with silicon-containing species. It was combined with the methanol mechanism of Burke *et al*. (2006). The mechanism allows to predict TMOS as well as the formed products.

## P18

# Atmospheric-pressure particle mass spectrometry for inline detection of nanoparticles growth in spray-flame reactors

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Inline characterization of nanoparticle formation with particle mass spectrometry (PMS) is well established to investigate the evolution of particle size distributions during the nanoparticle synthesis in low-pressure gas-phase reactors. It is commonly used to investigate the synthesis of metal and metal oxide nanoparticles to determine the influence of process conditions (temperature, precursor concentration, pressure, fuel/oxygen equivalence ratio) on the particle growth. The method is based on molecular-beam sampling by vacuum expansion of the particle-laden gas at variable locations in the reaction chamber through a nozzle/skimmer system. The vacuum conditions immediately suppress further reactions and particle growth. The system is equipped with an electrostatic deflection unit and a Faraday cup detector to measure potential-energy-filtered currents of charged particles. Due to limitations in the achievable pumping rates and (too high) particle loading, conventional PMS systems with a two-step skimmer/nozzle arrangement are limited to sampling from low-pressure (< 100 mbar) environments at low particle number concentrations. There are only few reports on molecular-beam mass spectrometry (MBMS) of particles from atmospheric-pressure systems, mostly used for the investigation of sooting flames.

In this study, we present a newly designed PMS that can be operated at atmospheric pressure. It is based on a three-stage system that consists of the conventional nozzle/skimmer system combined with an additional expansion chamber in front of the PMS nozzle between reactor and PMS. The PMS is connected to the reactor via a thin pipe (1.7 mm inner diameter). Fluid-dynamic calculations as well as Schlieren measurements show that a supersonic expansion develops in the first chamber. Dependent on the length of the pipe, the supersonic expansion moves upstream. This enables the determination of the best skimmer position that ensures the charge preservation of the sampled particles by extracting them before interacting with the shock wave. Thus, the sampled aerosol is directly transferred into a particle-laden molecular beam, which than passes the nozzle and the skimmer of the PMS. The additional expansion chamber enables sampling with the PMS within a wide pressure range between 5 mbar and atmospheric pressure. Results concerning Schlieren measurements and spatially resolved investigation of nanoparticles from sooting flames as well as from a spray-flame nanoparticle reactor, both operated at ambient pressure, will be discussed.

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This international symposium is organized by the DFG Priority Program SPP1980 Nanoparticle Synthesis in Spray Flames SpraySyn and the DFG Research Unit (FOR 2284 Model-based scalable gas-phase synthesis of complex nanoparticles.