

6th International Symposium on Gas-Phase Synthesis of Functional Nanomaterials 2024

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Light extinction and scattering to determine nanoparticle formation rates during droplet jetting in aluminum dust flames

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Aluminum (Al) powder gains increasing interest as a carbon-free energy carrier. The powder is combusted in air to generate heat and electricity where and when needed. The aluminum oxide (Al_2O_3) particles are subsequently reduced to recycle the metal powder [1].

Micrometer-sized Al particles are aerosolized and transported into a lean premixed flame above a modified McKenna burner [2]. Once ignited, each evaporating Al droplet produces a thin spherical flame sheet containing nano- and micrometer-sized Al_2O_3 particles. However, this ‘symmetrical’ combustion phase is frequently interrupted when Al_2O_3 product particles collide with the Al droplet. This causes intense and local boiling of Al with subsequent ejection of Al vapor. The thrust accelerates the liquid droplet which then leaves behind a condensation trail of Al_2O_3 particles [3], as shown in Figure 1a. The high frequency of this jetting event in the dust flame makes it responsible for a large part of the heat release during Al combustion. However, the rate at which Al evaporates and Al_2O_3 forms (and heat is released) during the droplet jetting is still unknown. To infer these rates, light extinction, I_e , and scattering, I_s , are quasi-simultaneously imaged with two pulsed LEDs and a high-speed camera at 200 kHz.

Figure 1a shows the correction of light scattering in the total light extinction which yields the absorption, I_a , of light by Al_2O_3 particles. Supported by scanning electron microscopy images of the sampled product, we assume that the particles in the trail follow the Rayleigh-Debye-Gans approximation, so that the total volume of Al_2O_3 nanoparticles can be quantified. The difference in volume between two subsequent images then yields the Al_2O_3 formation rate and the evaporation rate of the Al droplet. Figure 1b shows the ratio of scattering and extinction ($\frac{\tau_s}{\tau_e}$), the single-scattering albedo, which increases with the particle size. The albedo increases with increasing distance to the Al droplet, qualitatively indicating the growth of the particles along the trail. However, this also implies a strong sensitivity in the scattered-light correction and the inferred Al_2O_3 volume.

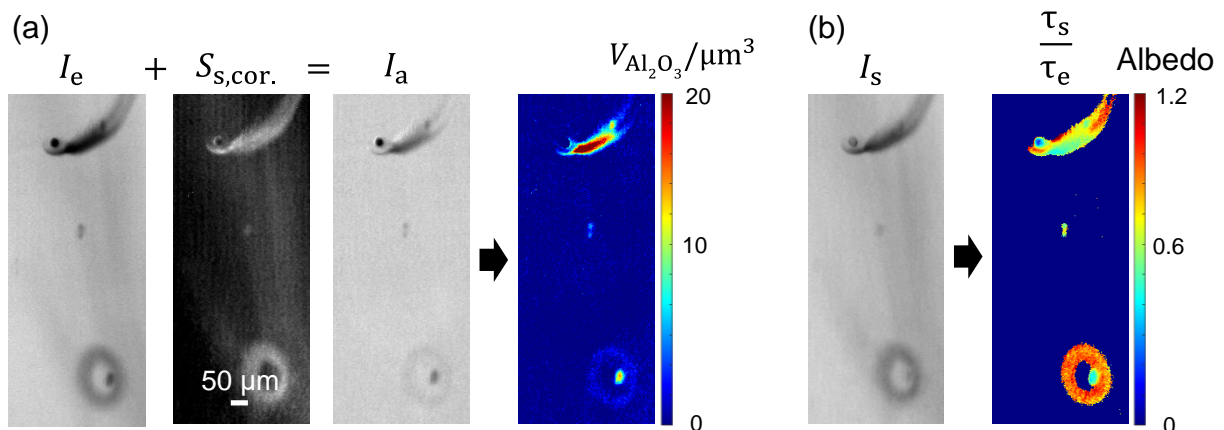


Figure 1: (a) Scattered-light correction from light extinction to infer light absorption and Al_2O_3 nanoparticle volume, (b) Single-scattering albedo derived from light scattering and extinction.

[1] J.M. Bergthorson, *Prog. Energy Combust. Sci.* **68**, 169 (2018).

[2] C. Ruan, Z. Wu, J. Sun, et al., *Proc. Combust. Inst.* **40**, 105596 (2024).

[3] J. Zhang, Z. Xia, L. Ma, et al., *Energy* **214**, 118889 (2021).

Phase changes in burning precursor-laden single droplets leading to puffing and micro-explosion

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In flame spray pyrolysis for the production of metal-oxide nanoparticles, precursor laden droplets are ignited and undergo thermally-induced disintegration, called ‘puffing’ and ‘micro-explosion’. In a manner that is not fully understood, these processes are associated with the formation of dispersed phases in the droplets.

Ethanol (EtOH) and 2 ethylhexanoic acid (EHA) solutions containing iron(III) nitrate nonahydrate (INN) were dispersed into single droplets with a diameter of about 75 μm that were then ignited. Purpose-optimized diffuse LED lighting allowed trans-illumination and microscopic imaging of almost the entire droplet interior onto a high speed camera with about 2 μm resolution in a 0.24 x 1.38 mm² field of view (FOV). This allowed observing rapid transformations such as shell formation and droplet breakup, and small-scale phase changes such as bubble nucleation and growth. All droplets undergo thermal disruption, but we find several routes with different phenomena that lead there.

Fig. 1 shows a sequence of an LED-illuminated burning droplet containing 0.1 mol/l INN.

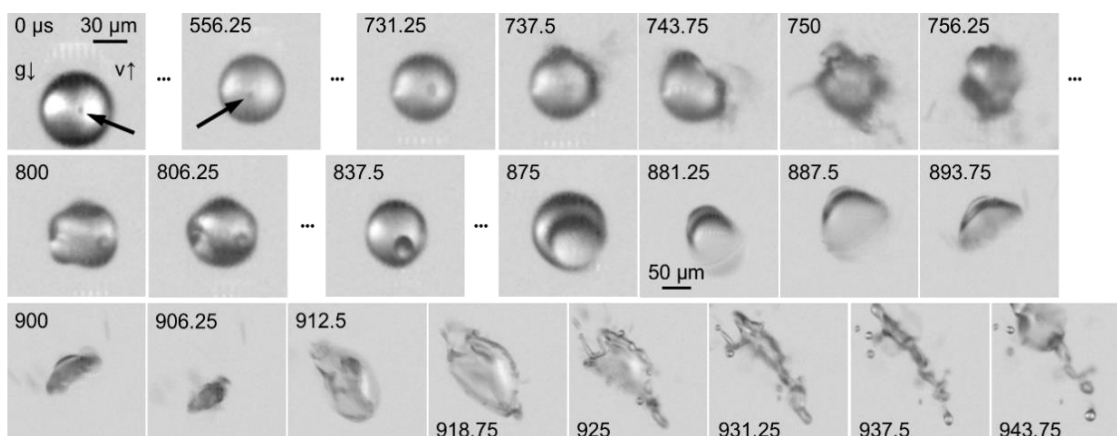


Fig. 1. Micro-explosion of an EtOH/EHA droplet containing 0.1 mol/l INN: Bubble onset, puffing, and bubble growth before micro-explosion. FOV is larger from 881,35 μs onward. Three dots indicate that frames have been omitted.

At 0 μs , a bubble of about 5 μm in size is visible in the center of the droplet.

It remains at constant size and near the center for over 700 μs . At 731.25 μs , the bubble expands slightly, which is followed by the droplet puffing, oscillating, and ejecting small droplets and ligaments until 756.25 μs . Between 837.5 and 893.75 μs , the bubble rapidly expands causes a micro-explosion into a chain of liquid ligaments and secondary droplets that then further disrupt.

Besides bubbles the surface of some droplets increasingly acquires spatial modulations in brightness, i.e., undulations that may be a ‘viscous shell’ [1].

In-situ measurements of the spectral absorption function for flame-made TiO₂ nanoparticles via light emission and Laser-induced incandescence: new results and open questions

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In a recent work by Yi et al [1], a new approach has been proposed to determine the spectral evolution of the absorption function $E(m\lambda)$ of flame-made TiO₂ nanoparticles subjected to Laser-induced incandescence (LII).

Complementary to these measurements, in this work, new results of the spectral absorption function are obtained by combining light emission measurements and information from computational fluid dynamic simulations. The spectral evolution of $E(m\lambda)$ is obtained at three heights above the burner using LII and light emission. Three different delay times are considered for LII measurements.

The curves of $E(m\lambda)$ of TiO₂ nanoparticles subjected to LII collapse for all HABs and delay times. On the contrary, the spectral absorption function varies with the HAB, indicating that the optical properties of the particles may vary along their trajectory in the flame.

Different curves are obtained when comparing light emission to LII measurements, signifying that the properties of the particles under study are likely to be modified during the LII process.

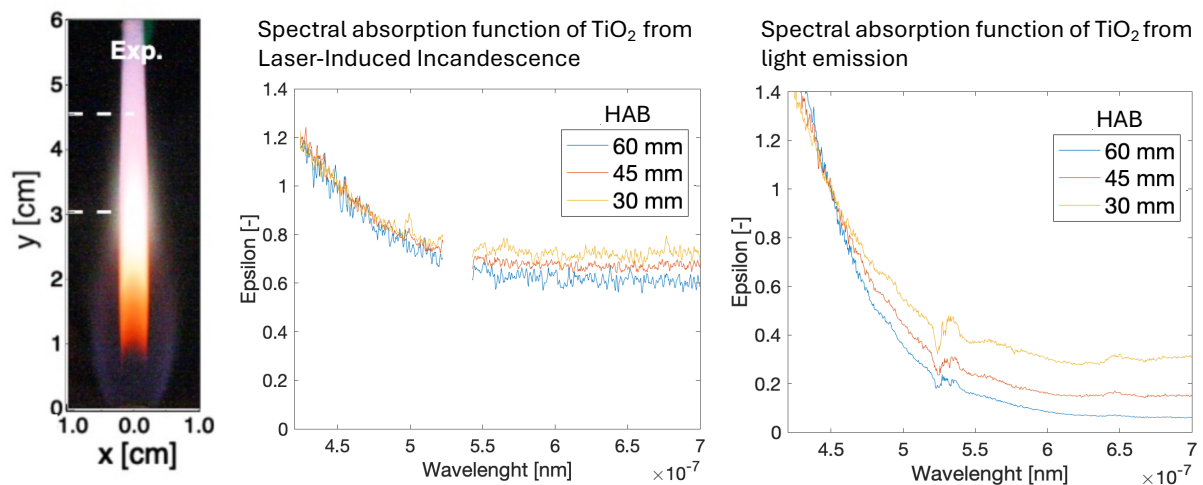


Figure 1 Spectral absorption function of flame-made TiO₂ at different heights above the burner (HAB) using in-situ measurements (laser-induced incandescence) and light emission.

[1] J. Yi, C. Betrancourt, N. Darabiha, B. Franzelli, *Appl. Phys. B.* **129**, 179 (2023).

Optical in situ diagnostics of iron nanoparticle aerosols in microwave plasma

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Microwave plasma synthesis of iron nanoparticles is a complex process involving the nucleation and growth of particles and phase transitions, e.g., in between solid and liquid state. Accurate diagnostics are essential for understanding this process, though estimating the optical properties of the nanoparticles can be challenging. In this study, we employ optical *in situ* diagnostics, including line-of-sight attenuation, optical emission spectroscopy, and two-color thermometry, to investigate the synthesis process. We evaluate the effects of different nanoparticle sizes and phases on the diagnostics. Our results demonstrate that while nanoparticle size and phase have a limited effect on pyrometric temperature measurements, size variations can introduce significant errors in volume fraction measurements. The particle distribution across the plasma off-gas is measured and discussed. Moreover, we observe that an increase in precursor flow rate yields a higher nanoparticle count but results in smaller nanoparticle size, lower nanoparticle temperature, and a more strongly focused nanoparticle stream. Optical emission spectroscopy confirms the presence of gas-phase Fe* and the observed thermal radiation indicates successful nanoparticle generation within the plasma zone. This research contributes valuable insight into the process of iron nanoparticle formation and the associated diagnostics.

Transition from laser-induced incandescence to phase-selective laser-induced breakdown spectroscopy for various materials systems

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Laser optical diagnostics play a crucial role for the *in situ* analysis of nanoparticle synthesis processes. Especially for carbon-based nanoparticles time-resolved laser-induced incandescence (LII) has been proven to be beneficial for the determination of the mean primary particle diameter [1]. Through the years, the interest shifted toward synthetic non-carbonaceous nanoparticles. Although the species composition of the nanoparticles is better known for synthetic nanoparticles other questions arise, such like the validity of spectroscopic models (Mie-theory and complex dielectric function), laser-particle interaction and the formation of microplasmas with its parasitic emissions.

Through a wide variation of the applied additional materials properties could be accessed. One example is the inference of Clausius-Clapeyron parameters for silicon and germanium in the superheated state [2]. In fluence ranges, where the particle mass significantly evaporates, additional emission lines could be measured [3] – the invention of phase-selective laser-induced breakdown spectroscopy (PS-LIBS). Despite its advantages, this approach poses several challenges, particularly in the accurate interpretation of spectral emissions. One of the primary difficulties lies in the observation of additional emission lines that do not exhibit a straightforward, linear relationship with the applied laser energy. These nonlinear emissions can arise due to various complex interactions within the plasma generated by the laser, making it difficult to directly correlate the spectral signals with the concentration of elements present in the nanoparticles.

To address these challenges, it is crucial to develop comprehensive models that can accurately simulate the PS-LIBS signals. Such models require a deep understanding of several key parameters [2], including the evaporation characteristics of the nanoparticles, which dictate how material evaporated and ionized; Einstein coefficients, which influence the probability of spontaneous emission; and the spatial and temporal profile of the laser pulse, which affects energy deposition in the sample and the plasma. Additionally, factors such as plasma temperature and density, and the potential effects of particle size and distribution must also be considered. It is not clear yet whether a local thermodynamic equilibrium (LTE) can be assumed with excited-state lifetimes close to the mean collision times of the gas-phase species.

By accurately simulating these parameters, researchers can improve the reliability of LIBS as a diagnostic tool for nanoparticles, enabling more precise quantitative analyses and a better understanding of the underlying physical processes. This will ultimately lead to more effective applications of LIBS in various fields, including materials science and nanotechnology.

[1] C. Schulz, B.F. Kock, M. Hofmann, et al., *Appl. Phys. B* **83**, 333 (2006).

[2] J. Menser, K.J. Daun, T. Dreier, C. Schulz, *Appl. Opt.* **56**, E50 (2017).

[3] G. Xiong, Y. Zhang, C. Schulz, S.D. Tse, *Appl. Spec.* **76**, 569 (2022).

Flame-Spray Pyrolysis Characterisation using Tomographic Imaging using Multi-simultaneous Measurements (TIMes): Volumetric Emission, Refractive Index, and Temperature Fields

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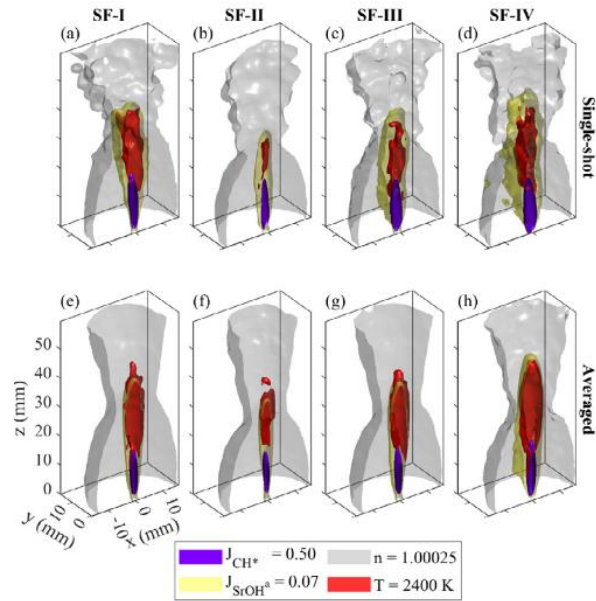
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Tomographic imaging using multi-simultaneous measurements (TIMes) [1,2] was performed on a series of turbulent flames generated from the second version of the SpraySyn burner [3] (SpraySyn 2.0). The standard lab-scale burner was designed to study flame-spray pyrolysis [4] to better understand the complex physicochemical mechanisms involved and to facilitate collaborative investigation between different research groups as part of the SPP1980 priority program. TIMes was employed to obtain single-shot and time-averaged 3D fields of CH* chemiluminescence (flame front indicator), SrOH emission from trace amounts of Sr(NO₃)₂ added to the liquid precursor solution (indicating hot spray-flame products), refractive index (which reflect changes in temperature, pressure and species concentration) and temperature [5]. The emission and refractive index fields were obtained using computed tomography of light emission and background oriented schlieren (BOS) tomography, respectively [6,7]. The temperature fields were obtained based on salt-emission thermometry, which was extended to volumetric measurements tomographically [5]. Voxel-wise intensity ratio of the reconstructed thermally-excited SrOH signals at two regions in the visible spectrum were converted to temperature based on a single calibration curve that was generated using multi-line OH planar laser induced fluorescence (PLIF). The combined measurements of the different fields revealed detailed 3D flame structure and showed the interaction between the flame front, spray stream and the hot gas regions. The characteristics of the spray flame were quantitatively examined, including temperature, height, width, 3D tilt angle and spreading half-angle of the flame plume. The temperature measurements were shown to be robust despite changes in the fuel/oxidiser equivalence ratio for the four investigated operating conditions.



Single shot (top row) and time-averaged (bottom row) 3D isosurface plots of refractive index n , CH^* emission signal J_{CH^*} , SrOH emission signal J_{SrOH} and temperature for four investigated operating conditions of the SpraySyn 2.0 burner [5].

- [1] C. T. Foo, A. Unterberger, J. Menser, K. Mohri, *Opt. Express.* **29**, 244 (2021).
- [2] C. T. Foo, A. Unterberger, F. J. W. A. Martins, M. M. Prenting, C. Schulz, K. Mohri, *Opt. Express.* **30**, 15524 (2022).
- [3] F. Schneider, S. Suleiman, J. Menser, E. Borukhovich, I. Wlokas, A. Kempf, H. Wiggers, C. Schulz, *Rev. Sci. Instrum.* **90**, 085108 (2019).
- [4] F. Meierhofer, U. Fritsching, *Energy Fuels.* **35**, 5495–5537 (2021).
- [5] F. J. W. A. Martins, C. T. Foo, A. Unterberger, S. Karaminejad, T. Endres, K. Mohri, *Appl. Energy Combust. Sci.* **16**, 100213 (2023).
- [6] A. Unterberger, K. Mohri, *Opt. Express.* **30**, 8592 (2022).
- [7] S. J. Grauer, K. Mohri, T. Yu, H. Liu, W. Cai, *Prog. Energy Combust.* **94**, 101024 (2023).

On-line, real-time control concept for nanoparticle synthesis by electrical discharges

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The product parameters of nanoparticle agglomerates and aggregates formed in the gas phase change dynamically in reactors with a non-constant delivery of monomers and variable temperature-time histories (e.g. spark ablation, arc discharge) and depend on the process conditions [1,2]. Therefore, such reactors fail to produce a high throughput of particles with uniform properties without utilizing a suitable control system. A suitable approach aims to correlate the key performance indicators (KPIs) of the system to the process parameters in a data-driven approach.

The control variables are chosen as the charging current, discharge-voltage (controlled by the electrode distance) and gas flowrate. Those have direct and coupled impact on the KPIs, which are chosen as two descriptors for the aggregate morphology (mean primary particle size and number of primary particles per aggregate) and particle production rate. The KPIs are measured and predicted on-line in real-time.

The combination of electrical mobility and aerodynamic size distribution measurements allows the calculation of the morphological properties under the assumption of a constant surface-equivalent primary particle size for the whole distribution and the absence of sinter-necks (see poster abstract "Rapid determination of nanoparticle agglomerate morphology by mobility and aerodynamic measurements"). For measurement of the aerodynamic particle size distribution an Electrical Low-Pressure Impactor (ELPI+, Dekati Ltd., Tampere, Finland) is used at a sampling rate of 1 Hz. A Scanning Mobility Particle Sizer (SMPS, TSI GmbH, Minneapolis, USA) scans the electrical mobility distribution in a span of 2.5 min. To accelerate the measurement of electrical mobility the cost-effective sensor Partector 2 (Naneos Particle Solutions GmbH, Windisch, Switzerland) is used giving the geometric mean electrical mobility diameter at a sampling rate of 1 Hz. The latter measurement is corrected in real-time by a neural network trained with SMPS measurements to provide an accurate estimation. The on-line, real-time measurement of the KPIs serves to close a meaningful feedback loop for the control system.

A particle formation model assuming monodisperse fractal-like growth by coagulation and a reduction of surface-area by sintering [3] lays the base for predicting the KPIs. This model falls short for monitoring and control of the process due to incomplete knowledge and inherent simplifications. Recent developments in machine learning allow utilizing advanced machine learning techniques to enhance process modelling, monitoring and control [4,5]. Control theory informed machine learning (CTIML) incorporates control-theoretic pre knowledge and integrates kernel-based methods with neural networks improving the accuracy and reliability of the model. The designed framework describes the system dynamics without approximation, independent of the existence of any type of uncertainties such as process fluctuations and sensor uncertainties and is capable of on-line running.

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Antagonistic impact of iron pentacarbonyl addition on the temperature and hydroxyl radical concentration in iron oxide synthesis flames

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Flame synthesis is a convenient route for fabrication of lucrative inorganic nanomaterials with tailored functionalities. Iron oxide synthesis system is actively studied due to applications of iron oxide nanoparticles in targeted drug delivery, wastewater treatment, energy storage as well as sensors and heterogeneous catalysts. Iron-pentacarbonyl ($\text{Fe}(\text{CO})_5$) doped flames provide a convenient testing ground for studies of the intricate interaction of iron-species chemistry with flame chemistry leading both to significant alteration of flame temperature and concentration of flame radicals such as hydroxyl, oxygen and hydrogen atoms, which in turn has an impact on particle evolution and final properties of the target nanomaterial [1].

Surprisingly, to the best of our knowledge, no systematic studies of the correlation between active species concentration and flame temperature dependence on addition of $\text{Fe}(\text{CO})_5$ and their dependence on flame equivalence ratio have been performed. In this study we report Planar Laser induced Fluorescence (PLIF) measurements of flame temperature and OH radical mole fraction in broad range of flame equivalence ratios (0.25-1.5) in $\text{H}_2/\text{O}_2/\text{Ar}$ low-pressure flames and their dependence on concurrent iron chemistry under typical particle synthesis conditions (500 ppm $\text{Fe}(\text{CO})_5$ dopant).

These results are compared to results of kinetic simulations based on state-of-the-art mechanisms of iron oxidation [2,3]. We perform both 2D-simulation with reduced mechanism, using a solver based on the open source CFD-library OpenFOAM to extract the velocity and temperature fields as well as 1D simulations with detailed mechanisms using the inputs from 2D simulations. Detailed flame structure studies that reveal key trends in $\text{Fe}(\text{CO})_5$ impact on flame temperature and OH mole fraction, are performed for generic laminar flame configurations.

Our findings indicate that the temperature elevation induced by $\text{Fe}(\text{CO})_5$ addition favors the enhancement of OH concentration while reactions with iron species, both in the gas-phase and likely, on the particle surface, lead to scavenging of hydroxyl radicals. The balance between these two antagonistic effects of $\text{Fe}(\text{CO})_5$ doping depends sensitively on flame equivalence ratio.

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Evaluation of the spatiotemporal spray evolution from the SpraySyn II burner configuration in the FSP process

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The industrial application of functional nanomaterials requires tailored nanoparticle size, composition and morphology. For this purpose, a full understanding of the process chain of the synthesis routes is inevitable. In **flame spray pyrolysis** (FSP), which has proven to be a promising nanoparticle synthesis process, several nozzle designs have been introduced within the last decades to further improve flame stability and, thus nanoparticle quality. Recently, a new version of the SpraySyn I burner [1] has been presented by Karaminejad et al. [2]. The so-called **SpraySyn Config. D burner** presents, instead of a coaxially aligned dispersion gas outlet, an angled dispersion gas outlet in order to increase the radial momentum of liquid lumps during primary and secondary atomization to bridge the gap of the liquid jet to the pilot flame.

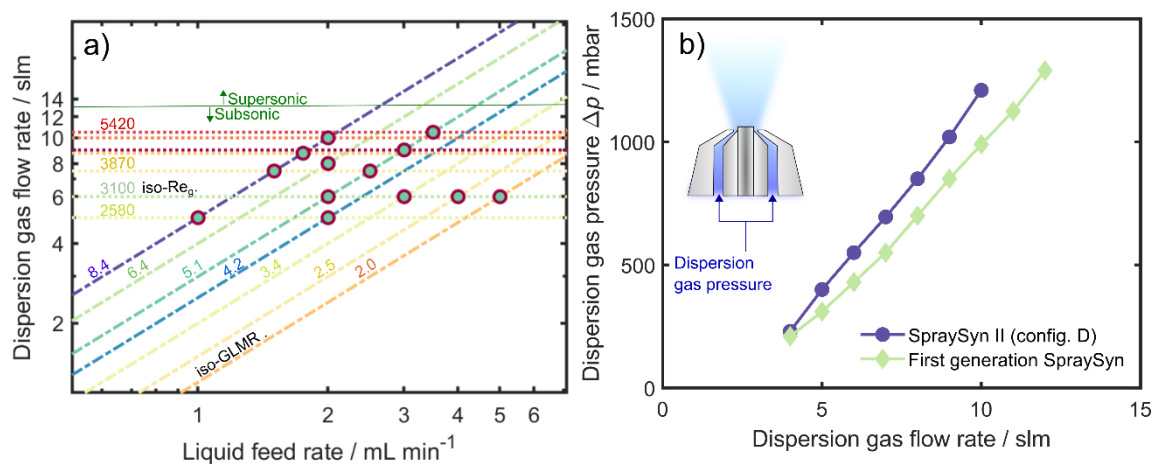


Figure 1: a) Diagram of the operating conditions used at either constant Re_g or GLMR; b) Dispersion gas pressure Δp as a function of the dispersion gas flow rate for both SpraySyn burner versions.

In the present work, extensive measurements to characterize the spray formation and spray evolution under reactive conditions of the second-generation SpraySyn burner (Config D) are conducted. To identify proper operating conditions, the study is carried out with systematically varying jet Reynolds numbers (Re_g), gas-liquid-mass ratios (GLMR) and dispersion gas pressures Δp , as shown in Figure 1. Locally sampled droplet velocities by phase-Doppler anemometry (PDA) measurements are used to derive droplet flight times to estimate flame residence times. Attention is also drawn to the correlation between droplet clusters, which might induce fluctuations in the release of fuel, and spray flame instabilities. The droplet time scales are correlated to photographically determined macroscopic spray flame heights. The

correlation of flame height and droplet flight times allows for an estimation of spray combustion kinetics that is controlled by the initial conditions set by the operating conditions.

Acknowledgement:

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Visualization techniques for aerosol/aerosol mixing in a generic flow configuration

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In mixing different aerosols, key quantities are the spatial distributions, velocities, and maybe temperatures of the disperse phases and the gas phases. Here, we use laser-induced fluorescence (LIF), Mie-scattering, and luminescence of “thermographic phosphors” to obtain some of these parameters in a generic flow configuration. This is a round, coflowing laminar jet in which vortex rings are created by acoustic modulation. The diameter of the jet is 3.8 mm, and the Reynolds number is $Re = 273$. The jet and the coflow are two different aerosols, and the aim of our experiments is to investigate the mixing of these two streams in the repeatable vortex rings by laser imaging. A key challenge for the diagnostics is achieving a spatial resolution that allows visualizing the scalar gradients that are the driver for local mixing.

A double-pulse Nd:YAG laser beam at 532 nm and 266 nm is formed into a 26 mm tall and 0.5 mm thick light sheet. Both lightsheets are separately conditioned to reduce chromatic aberration. On each side of the resulting lightsheet, a camera is placed.

Air is the carrier gas in both streams. In one set of experiments, the jet is seeded with very small amounts of fluorescent gaseous anisole, the coflow is seeded with oil droplets. In a second set, the two streams are seeded with different “thermographic phosphors”. Figure 1 shows example images.

The anisole in the jet’s gas phase is excited by the 266 nm laser to fluoresce at around 285 nm. With suitable calibration, the local gas-phase jet mixture fraction can be determined throughout the images acquired on an image-intensified UV sensitive camera. The spatial resolution that can be achieved with this camera type and the available UV optics is somewhat limited, but the gradients in the gas phase are also not as sharp as in the disperse phase.

The Mie-scattering of the 532 nm laser by droplets dispersed in the coflow is imaged on an unintensified sCMOS camera, showing the presence of each droplet. Additionally, the local velocity of that phase can be obtained by particle image velocimetry (PIV), leveraging the double-pulse feature of laser and camera. Excellent spatial resolution can be achieved since for the visible wavelength used here, highly corrected macro lenses and a high-resolution sensor are available. However, Mie-scattering is not specific to the scatterer. If both flows are aerosols, a different technique is needed to differentiate the two disperse phases.

Here, -in a different set of experiments- this differentiation was achieved by using two different so-called “thermographic phosphors” as the disperse phases in the two aerosols. These are rare earth materials that upon excitation by the 266 nm laser sheet emit light at a wavelength specific the phosphor (and the temperature, but the current flow is isothermal). Each camera captures an image of the distribution of one of the disperse phases. However, with solid particles, achieving the desired constant seeding density can be difficult, especially at low flow rates. Also, the luminescence signals are relatively weak and partially in the UV, again requiring resolution-degrading UV optics.

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Rapid determination of nanoparticle agglomerate morphology by mobility and aerodynamic measurements

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The size and morphology of nanoparticle clusters (agglomerates) formed in the gas phase determines their performance in various applications, including catalysis, drug delivery, and energy storage. The agglomerate morphology (quantified here by the surface-equivalent mean primary particle diameter d_{va}) changes dynamically in reactors with a non-constant delivery of monomers (e.g. spark ablation, arc discharge) and depends on the process conditions [1,2]. Here, a rapid method for on-line characterization of d_{va} is developed by interfacing discrete element modeling (DEM) for agglomerate formation in the free-molecular and transition regime in the absence of sintering [3,4] with mobility (d_m) and aerodynamic (d_a) size distribution measurements. The morphology of DEM-derived agglomerates of monodisperse and polydisperse primary particles is validated with experimental data of soot agglomerates and easy-to-use relations between d_m and d_a are obtained from the power law scaling of particle mass-mobility [5], the definition of effective density [6] and the correlation between particle relaxation time and d_a [7].

$$\frac{d_a}{d_{va}} = \sqrt{\frac{C_c(d_m) \rho_{bulk}}{C_c(d_a) \rho_0} k_{fm} \left(\frac{d_m}{d_{va}}\right)^{D_{fm}-1}} \quad (1)$$

Figure 1 validates the relation (broken lines) by comparing to the corresponding DEM data (solid lines) revealing a slope dependence on geometric mean diameter d_{pg} and geometric standard deviation σ_{gp} despite normalization with d_{va} . The relation is coupled with d_m and d_a distribution measurements for spark ablation-synthesized iron oxide agglomerates to on-line monitor d_{va} by utilizing the sensitive relation in equation (1) finding good agreement with microscopy and literature data assuming ballistic cluster-cluster agglomeration in absence of sintering as the main growth mechanism.

The d_a distribution is measured every second by an Electrical Low-Pressure Impactor (ELPI+, Dekati Ltd., Tampere, Finland), while a Scanning Mobility Particle Sizer (SMPS 3938, TSI GmbH, Minneapolis, USA) provides the d_m distribution in 2.5 min in parallel, which

defines the limit of the present method's time resolution. Therefore, it is at least 90% faster than existing on-line methods based on mass-mobility measurements [8,9] and can be used to facilitate the process monitoring and optimization of gas phase synthesis reactors.

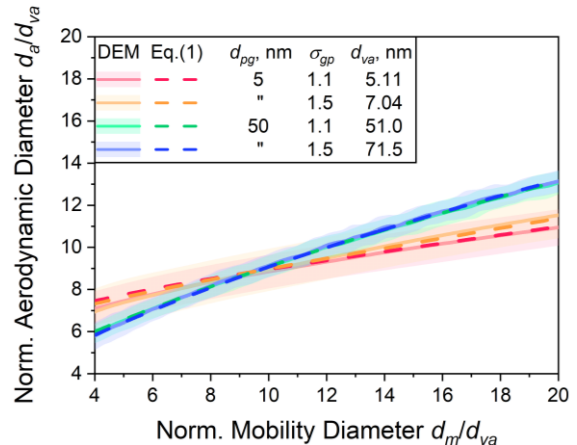


Figure 1. d_a vs d_m data normalized by d_{va} from DEM generated agglomerates (solid lines) and the predicted relationship from equation 1 for the specific d_{va} values (broken lines) for 2 different d_{pg} and 2 different σ_{gp} .

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Combustion of single droplets in a confined 2-D microreactor

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Single droplet experiments have been designed to study specifically the reaction and nanoparticles formation from metal-precursor-laden droplets that combust in air or pure oxygen. With the support of these experiments, physicochemical mechanisms in nanoparticle producing spray flames can be deduced. The single burning droplets themselves can be viewed as spatially confined microreactors, with numerous mechanistic pathways involved in attaining the final product particle size, composition, and morphology.

In this work, the burning droplets are further confined in a 2-D microfluidic channel, thereby examining a novel arrangement of burning micrometer-sized droplets within a microreactor, allowing precise control and fundamental investigation of the variations in chemical properties and physical dynamics for initially same-sized burning droplets. For this purpose, various confined microreactor systems with different gap sizes were set up and tested with solvent droplets and droplets from solvent mixtures.

To first investigate the influence of the confinement on fundamental burning phenomena, here, droplets of a solvent mixture of ethanol and xylene are combusted in different confined microreactor systems with gap sizes, ranging from 500 μm to 2 mm. Both the flame dynamics of the droplets and the droplet histories were analyzed using high-speed imaging techniques. Studying the droplet and flame dynamics shows that the flame sizes change with increasing confinement, leading to different histories of the flame-to-droplet ratios.

Optical Properties of Young Soot Formed in a Shock Tube: Simultaneous Reaction Time-resolved Laser-Induced Emission, UV-Vis Absorption, and Laser Extinction Measurements

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Abstract

Soot inception is still the most mysterious part of the entire soot formation process. Detailed knowledge of the optical properties of young soot particles is required for understanding the inception process and is also a prerequisite for accurate measurements of the soot volume fraction in the combustion environment. This study addressed the optical properties of young soot particles generated by toluene pyrolysis in a shock-tube facility. Reaction time-resolved and spectrally-resolved measurements of laser-induced signal excited at either 266, 355, 532, or 1064 nm were carried out after the reflected shock arrival. These measurements capture the transition from the step-wise red-shifted laser-induced fluorescence (LIF) during toluene decomposition, polycyclic aromatic hydrocarbon formation, to young soot formation to laser-induced incandescence from early refractory soot. Different from matured soot, the emission of young soot is dominated by the LIF signal in the visible region. Time-resolved UV-Vis absorption spectroscopy measurements were conducted simultaneously during the transition from PAH to young soot. Laser extinction at 633 nm was used in parallel to determine the soot yield as a function of reaction time for various reaction conditions.

Keywords: Shock-tube; Laser-induced emission, UV-Vis absorption, extinction, young soot

Background-AIM

Soot inception is still the most mysterious part of the entire soot formation process. Detailed knowledge of the optical properties of young soot particles is required for understanding the inception process and is also a prerequisite for accurate measurements of the soot volume fraction in the combustion environment.

Method

This study addressed the optical properties of young soot particles generated by toluene pyrolysis in a shock-tube facility. Reaction time-resolved and spectrally-resolved measurements of laser-induced signal excited at either 266, 355, 532, or 1064 nm were carried out after the reflected shock arrival. Laser extinction at 633 nm was used in parallel to determine the soot yield as a function of reaction time for various reaction conditions.

Results

These measurements capture the transition from the step-wise red-shifted laser-induced fluorescence (LIF) during toluene decomposition, polycyclic aromatic hydrocarbon formation, to young soot formation to laser-induced incandescence from early refractory soot. Different from matured soot, the emission of young soot is dominated by the LIF signal in the visible region. Time-resolved UV-Vis absorption spectroscopy measurements were conducted simultaneously during the transition from PAH to young soot.

Conclusions

This work gives a detailed investigation of the optical properties of young soot particles including laser-induced emission, UV-Vis absorption, and extinction, which are significantly different from mature soot particles.

Flame structure of single aluminum droplets burning in hot steam-dominated flows

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Aluminum (Al) has recently been proposed as a carbon-free energy carrier [1]. Specifically, the combustion of Al in steam offers a novel method for the simultaneous production of hydrogen and heat through the reaction $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2 + \text{Q}(\text{heat})$, which is inherently carbon-free.

The current study presents a novel experimental system enabling systematic observation of the combustion of single-micron-sized aluminum droplets in hot steam-dominated flows [2]. A specially designed flame is anchored on a modified burner, where a diffusion H_2/O_2 flame in the center provides a locally high temperature ($> 2325 \text{ K}$) region for Al ignition, and a co-flow of premixed $\text{H}_2/\text{O}_2/\text{N}_2$ flame generates an adjustable oxidizing environment for Al combustion. Single-burning Al droplets are produced from the breakup of Al wires when placed in the burner center. The design allows the generation of individual Al droplets with varying diameters, ranging from 100 to 550 μm , which burn in different oxidizing environments adjustable from $\text{H}_2\text{O}/\text{N}_2$ to $\text{O}_2/\text{H}_2\text{O}/\text{N}_2$ mixture.

The transient burning behaviors of Al droplets of different sizes are characterized by simultaneously visualizing the flame incandescence and droplet shadowgraphs with two high-speed cameras at high magnification. Figure 1 shows a representative sequence of ignition and combustion of the 250 μm Al wire in the steam case. The top row of each stage shows the incandescence images, and the corresponding shadowgraph images are shown beneath. It is found that the combustion process can be divided into two stages: Al ignition and droplet generation, flame development and steady combustion. During the steady combustion stage, the flame structure of a burning Al droplet, such as flame Standoff ratio, flame thickness, and Al droplet evaporation rate, are quantitatively determined under varying surrounding conditions. The experimental findings and quantitative analyses provide novel datasets for model development, deepening the understanding of Al droplet combustion.

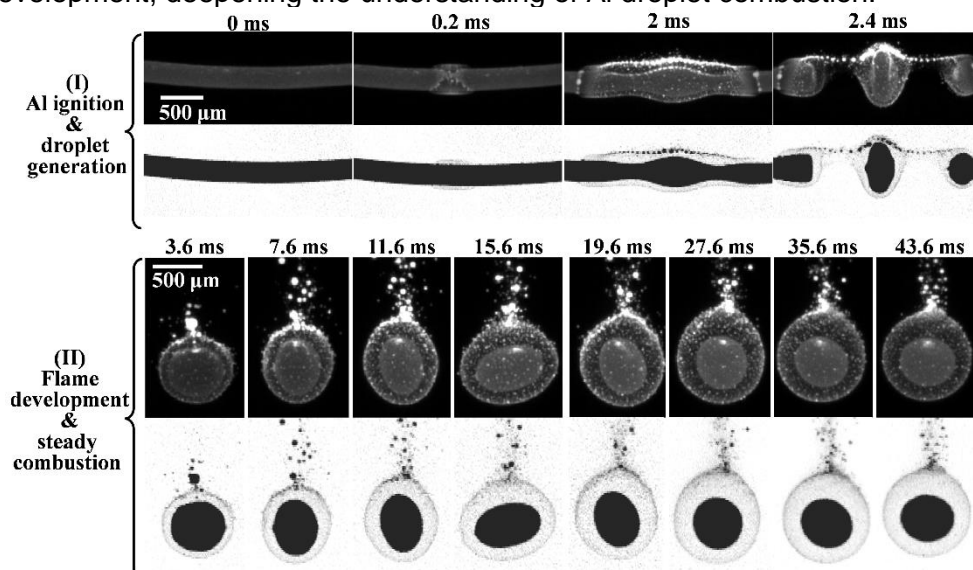


Figure 1: Ignition and combustion sequences of the 250 μm Al wire in steam from the simultaneous recording of incandescence (top row) and shadowgraph (bottom row).

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Black is the New Orange: Inline Synthesis of Silica-coated Iron Oxide Nanoparticles Produced via Gas-Phase in a Matrix Burner

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Superparamagnetic iron oxide nanoparticles (IONPs) have a large range of applications, such as pollutant removal and inductive heating. Some of these applications have shown to benefit from coating IONPs with silica (SiO_2) to conserve their properties and/or prevent their aggregation; yet, the habitual synthesis methodologies require several steps, which limit their industrial scalability. In this work, we explore the capability to synthesize and stabilize oxidation-sensitive phases of IONPs via gas-phase flame synthesis as an alternative methodology that enables continuous operation. The addition of an inline quench gas nozzle – to avoid aggregation/agglomeration – and a coating nozzle is investigated to clarify which role they play on the properties of the resultant coated IONPs. Three different quench and coating configuration heights above burner (HAB) are studied. The resultant synthesized $\text{Fe}_x\text{O}_y|\text{SiO}_2$ core-shell nanoparticles are characterized using (Scanning) Transmission Electron Microscopy ((S)TEM), X-Ray Diffraction (XRD), Fourier-Transform InfraRed spectroscopy (FTIR), Elemental analysis, Dynamic Light Scattering (DLS), Mössbauer spectroscopy, magnetometry, and Energy-dispersive X-ray spectroscopy (EDX) from scanning electron microscopy (SEM).

The results show that the synthesized nanoparticles presented a mixture of oxidation states – mainly the magnetic phases magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) – and a narrow primary particle size distribution. Quenching the IONPs early decreased nanoparticle agglomeration/aggregation up to one order of magnitude. Moreover, homogeneous coating was achieved in all cases. Increasing the coating thickness showed to help reduce oxygen diffusion to the iron oxide core of the coated IONPs, conserving more magnetite phase in the coated IONPs cores. These insights allow us to conclude that targeted coated IONPs can be successfully produced through gas-phase synthesis using a flame reactor. In the near future, long-term stability of the IONPs properties using this inline coating will be explored.

Characterization of adsorbed polycyclic aromatic molecules on gas-phase synthesized carbon nanomaterials

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Since its discovery in 2004, graphene triggered remarkable interest in many different research fields due to its unique properties. Graphene flakes are a promising component of various composites, e.g., for improving the electrochemical performance of batteries and supercapacitors and for altering the thermal, electrical and mechanical properties of polymers. For commercialization, reliable high-throughput synthesis methods are needed to satisfy the demand for graphene (powder). Typical methods for producing freestanding graphene are usually thermal or wet-chemical exfoliation of graphene oxide. These methods are usually troubled by their non-continuous approach and the requirement for costly and aggressive chemicals.

A simple and scalable alternative is the direct gas-phase synthesis of freestanding few-layer graphene (FLG) by the decomposition of hydrocarbons in a plasma. The formation of FLG compared to other types of carbon particular matter has been found to be sensitive to the reactant concentration [1]. Furthermore, previous works were able to show that the first FLG particles can contain monolayers of graphene which start to crumble and self-fold while travelling downstream of the inception zone [2]. However, it is still unclear whether specific polycyclic aromatic hydrocarbon (PAH) molecules play a role as precursor molecules for the first (graphene) particle inception and whether there are distinct differences to the inception of soot-like particles.

The aim of this work is to gain insight into the carbon particle formation process by characterizing the PAH molecules adsorbed on the particle surface. For this purpose, three different carbon materials are produced: one containing mostly few-layer graphene, another with mixtures of FLG and soot-like particles, and a third containing mostly soot-like or graphitic particles. All of these particle mixtures are generated with ethylene as reactant while only its concentration is altered. These particle mixtures are characterized by extensive *ex situ* analysis including laser desorption ionization-time of flight mass spectroscopy (LDI-TOFMS) [3] and gas-chromatography mass spectrometry (GC-MS) following dichloromethane (DCM) extraction [4].

The results show that all obtained particle mixtures contain aromatic moieties soluble in DCM. Their concentration scales with the amount of reactant supplied for the particle generation and increases from the mostly FLG to the mostly soot-like particle sample. For FLG the adsorbed amount is <1wt% of the particle mass while it increases up to ~6wt% when mostly soot-like particles are generated. Fourier analysis of LDI-TOFMS [5] suggest that the adsorbed moieties don't differ between the particle mixtures and largely contain CH₂ containing species such as in cyclopenta-containing aromatic moieties. Characterizing the DCM extract via GC-MS shows the presence of aromatic molecules containing up to 5-membered rings in the form of benzopyrene. While FLG shows lower relative concentrations for some intermediate sized (2–4 membered) PAH molecules, no significant difference is observed compared to the other samples showing the presence also of larger PAHs. The results may indicate that overall, the type of formed PAH molecules is not driving the transition from FLG to soot formation, but mostly their local concentration in the particle inception region.

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The Influence of Metal Release Mechanisms and Micro-Explosions on Nanoparticle Formation in Single-Droplet Combustions

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FSP is a versatile technique that has been proven to produce tailor-made nanoparticles, especially multi-component nanoparticles. Therefore, a comprehensive understanding of the fundamental mechanisms governing nanoparticle formation in flame spray pyrolysis (FSP) is essential. Single-droplet combustion experiments have been shown to reveal the physicochemical processes and combustion behavior of liquid metal precursors. A major finding of single-droplet combustion analysis was the occurrence of micro-explosions, which were further correlated with the formation of homogeneous nanoparticles. Recent direct observations of micro-explosions in the FSP process highlight their crucial role in nanoparticle formation [1,2,3].

To further investigate the nanoparticle formation process in detail, a novel method combining flame emission spectroscopy and high-speed imaging has been developed. This technique allows the analysis of metal release and subsequent nanoparticle formation during single-droplet combustion. Initial investigations confirmed the gas-to-particle synthesis pathway for nanoparticle formation in droplet/spray flame combustion. Furthermore, by observing metal release into the flame front immediately before and primarily during micro-explosions, a direct correlation between micro-explosions and nanoparticle formation was established [4].

The present work extends upon these findings by investigating how differences in the release mechanisms of metal components into the flame affect the formation of multi-metal nanoparticles. Specifically, how variations in the release mechanisms of different metal components within the precursor affect the composition, structure, and phases of the resulting multi-metal nanoparticles. As examples, two metal precursors were studied, both containing the same non-volatile copper compound (copper naphthenate) but different iron components. One precursor employed a volatile iron source (ferrocene), while the other used a non-volatile source (iron naphthenate). The precursor with non-volatile metal components (iron/copper naphthenate) exhibited simultaneous metal release into the combustion process via micro-explosions, resulting in the formation of homogeneous nanoparticles. In contrast, the release of a metal component prior to the micro-explosions, observed with the volatile iron source, resulted in heterogeneous particle formation, as evidenced by the presence of different phases (according to X-ray diffraction) and Fe/Cu distributions within the particles (as observed by transmission electron microscopy).

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Towards complete understanding of a prototypical iron oxide synthesis flame: the roadmap of the challenges ahead

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The gas-phase synthesis of transition metal oxide particles has emerged as a highly versatile and scalable process. Among the various materials studied, iron oxide stands out as a particularly compelling subject for both experimental and numerical investigations. Iron pentacarbonyl ($\text{Fe}(\text{CO})_5$, IPC), the precursor, possesses a high vapor pressure, allowing its use across a broad range of flame dopant concentrations. Furthermore, iron species in the gas phase exhibit strong interactions with flame kinetics. Since the early 2000s, the gas-phase kinetics of this system were presumed to be "well understood," enabling accurate modeling of laminar flame structures [1]. These models have been validated against several experimental studies.

Over the past 15 years, the system has been extensively explored using advanced optical diagnostics and in-situ probing techniques. Laser-Induced Fluorescence (LIF) has been employed to measure flame temperatures and Fe-atom concentrations, providing insights into the flame dynamics. Mass spectrometry has offered spatially resolved species concentration measurements, enhancing the understanding of chemical processes within the flame. Probing of condensed matter (PMS, QCMB) from the flame has allowed to map the regions of particle formation within the flame with spatial resolution. These experimental findings have significantly advanced our understanding of the particle formation process and have been successfully replicated in simulations [2].

However, recent developments have necessitated a reevaluation of the established models. Observations of grey body radiation by Rahinov's group at the Open University of Israel have challenged previous assumptions about the formation pathway of early particles and required the modeling at molecular scales [3,4]. These findings indicate that early-stage particles may interact more significantly with flame kinetics than previously thought, a factor that should not be overlooked in gas-phase kinetic models. Additionally, recent quantitative measurements of the OH radical as well as Fe and FeO species concentrations have revealed discrepancies in the existing models. While the models accurately predict flame temperature, they fall short in quantitatively predicting OH concentrations.

These new insights underscore the complexity of iron oxide formation in flames and highlight the need for further research to refine our models and fully understand the interplay between flame kinetics and particle formation. In our presentation, we sketch the roadmap of challenges to be solved next, in order to develop the next generation of models for iron oxide nanoparticle synthesis in particular and transition metal oxides in general.

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Influence of Dispersion Gas and Resulting Reaction Zone on the Particle Formation in Spray Flame Synthesis

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Introduction

The spray flame synthesis (SFS) of nanoparticles enables the production of industrially relevant materials with novel properties. Compared to other synthesis methods, this approach offers several advantages as such large specific surface area, high purity and crystallinity of the materials (Teoh *et al.*, 2010). However, the SFS process involves numerous simultaneous physical and chemical sub-processes, contributing to a high degree of complexity. The initial step is the atomization of a liquid precursor mixture through a nozzle into a self-sustaining gaseous pilot flame. This is followed by the evaporation and ignition of the droplets in the gas phase. Within the reactive and highly turbulent flame, the interplay of nucleation, coagulation, and sintering ultimately leads to the tuneable formation of fractal, specific particle structures. Due to the high process complexity, several key factors are not fully understood in terms of tailoring the final properties. This study aims to elucidate the impact of atomization on the morphology, shape, size distribution, and crystallinity of nanoparticles, as well as the material residue content in the product during the SFS of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) using the so-called SpraySyn burner. In the present investigation, the focus was the dispersion gas flow variation (6, 8, 10, and 12 L/min) while characterizing droplet dynamic and mean droplet size directly in the spray flame using Phase Doppler Anemometry (PDA), and subsequently, its impact on particle formation. Additionally, the overlap of the liquid precursor atomization, droplet evaporation and reaction zone formation was qualitatively observed by means of schlieren and OH* chemiluminescence. The inline size distribution of aggregates/agglomerates extracted via a sampling probe called Hole in a Tube was measured with a Scanning Mobility Particle Sizer (SMPS). Thermogravimetric analysis coupled with mass spectrometry (TGA-MS), transmission electron microscopy (TEM), and X-ray diffraction (XRD) were used to characterize the materials.

Key Findings

The PDA measurements show that increasing the dispersion gas flow leads to a decrease in mean droplet size along the flame axis. Thus, the atomization and evaporation of the liquid precursor are more effective at higher dispersion gas flows. There is a strong relationship between dispersion gas flow, spray flame shape, and height, which in turn influences the high-temperature droplet/particle residence time in the spray flame (HTPRT). Since nanoparticle growth is governed by HTPRT, increasing the dispersion gas flow impacts directly the nanoparticle size. TEM images reveal a reduction in primary nanoparticle size by approximately 50% as the dispersion gas flow increases from 6 to 12 L/min. Additionally, the nanoparticles' diameters were found to be homogeneous and polydisperse, primarily following the gas-to-particle pathway. BET and XRD analyses corroborate the observations made from the TEM images. TGA-MS measurements revealed an increase in carbonaceous species in the samples, indicating that less pure maghemite particles were synthesized. Despite the finer atomization due to dispersion gas flow increase mentioned above, it is suspected that droplets exited the spray flame unburned and deposited on the material surface. Consequently, it is assumed that evaporation was not completely finished, leading to incomplete precursor conversion into maghemite.

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The role of silanol in the formation of silica aggregates in TMS/H₂/O₂/Ar-flames

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Nanomaterials are used in many applications because of their size-dependent properties. The physical, chemical, and biological properties change due to their large surface-to-volume ratios, which lead to higher reactivity, chemical stability and increased mechanical strength.

For the model-based synthesis of silica nanomaterials, the understanding of the following sequential processes is essential: Precursor decomposition, oxidation reactions, silica aggregation, and metastable particles. The processes and reactions were considered in a reaction kinetic model during flame synthesis from tetramethylsilane (TMS) in our previous work [1]. Silica aggregation initiated by silanols is not yet fully captured in this model.

Reactive molecular dynamics simulations (RMDS) with the ReaxFF force field are used decoupled from the reaction kinetic model to investigate the fate of silanol (Si1) under high-temperature conditions. The MD-simulations show that the initial step is the destruction to smaller molecules by loss of H, OH and water, followed by aggregation in a second step. Depending on duration, temperature, density, and the absolute number of molecules in the simulation, aggregation starts with dimers Si₂, followed Si₃ and Si₄ aggregates which continue to grow in size until up to 30-50% of the silicon atoms are found in aggregates with more than 10 Si atoms. In all structures oxygen and hydrogen are present leading to sum formulas of Si_xO_yH_z with over- and sub-stoichiometric oxygen content compared to SiO₂. With increasing temperature from 3000-5000 K more silanol is consumed and more OH radicals are formed in the process. From comparison of the ratios of reacted silanol to present OH radicals ((Si₀-Si)/OH), which decreases with increasing temperature, it can be concluded that also more OH radicals are consumed in other reactions. The maximum of reacted silanol to Si₂ ((Si₀-Si)/Si₂) coincides with the maximum gradient in the change of the ((Si₀-Si)/OH) ratio. This observation suggests that OH radicals take part in the initial aggregation to Si₂. Typical structures such as rings or bulb-like aggregates are formed. Reactions can be identified from the molecular trajectories of the particles. While some of these reactions correspond to typical elementary reactions, e.g., loss of OH radicals from the silanol or from larger aggregates, some reactions are not typically considered in classic chemical reaction mechanisms, e.g., three particle interactions in which one particle assists rearrangement, condensation or decomposition of the other two particles, but leaves the reaction space without rearrangement itself.

It will be discussed how comparable results are to the known reactions in the TMS reaction mechanism and if/how these reaction types of silica aggregation could be implemented in future reaction kinetics models.

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Gas-phase Si-hemiketal reactions: A novel molecular growth pathway in flame synthesis of SiO_x using siloxane precursor

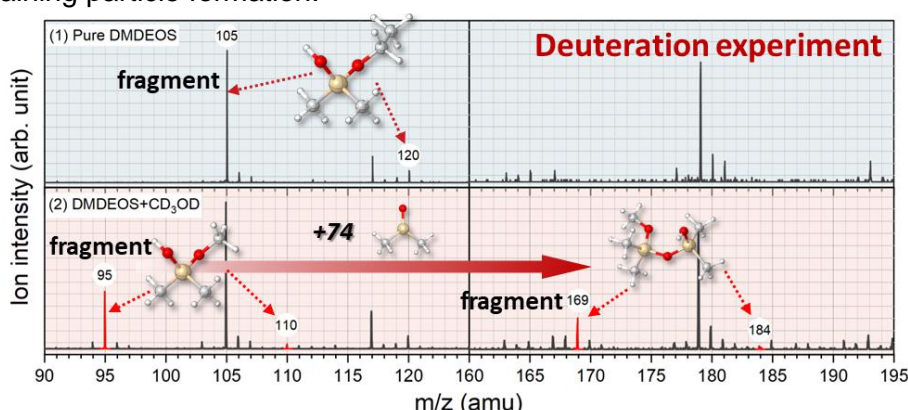
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Silicon-containing nanoparticles are widely used in various fields as important industrial particles. They are usually synthesized by thermochemical methods such as flame spray pyrolysis and chemical vapor deposition. However, the transition from gaseous siloxane precursors to silicious nanoparticles under high-temperature conditions remains mysterious [1]. Due to the lack of high-resolution information on silicon-containing intermediates, the primary precursors of high-temperature silicon-containing nanoparticle formation and the molecular pathways that trigger nanoparticle formation are currently unknown [2]. Herein, we report a novel molecular growth mechanism involving successive Si-hemiketal reactions between silanols and siliconyl intermediates (R-Si(=O)-R'). Theoretical calculations reveal that silanols can react with siliconyl intermediates to form covalently bound complexes and regenerate larger silanols through low-barrier transition states. Experimental evidences are found in the flow reactor pyrolysis of dimethyldiethoxysilane (DMDEOS), which is a typical precursor of silica nanoparticles, using synchrotron vacuum ultraviolet photoionization mass spectrometry. Mass signals support the evolution from small silanols such as HOSi(CH₃)₂OC₂H₅, HOSi(CH₃)₂OC₂H₃, and HOSi(CH₃)₂OH to large silanols such as H-[OSi(CH₃)₂]_x-OC₂H₅, H-[OSi(CH₃)₂]_y-OC₂H₃, and H-[OSi(CH₃)₂]_z-OH (x, y, z = 2~8). Through the deuteration experiments, we found that successive O=Si(CH₃)₂ addition via Si-hemiketal reactions drives the formation and growth of large silanols. Further evidence can be found in the pyrolysis of other precursors such as tetraethoxysilane (TEOS) and methyltriethoxysilane (MTrEOS) through successive O=Si(OC₂H₅)₂ and CH₃-Si(=O)-OC₂H₅ addition, respectively. These observations demonstrate the universality of the Si-hemiketal mechanism in triggering silicon-containing particle formation.



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Shock tube TOF-MS study of the decomposition of hexamethyldisiloxane

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Research into the gas-phase reaction kinetics of organosilicones has been increasing due to their use as precursors for synthesizing silica products such as nano-particles and surface coatings [1] and fouling of gas turbines generating power from landfill biogas [2,3]. Experimental studies on the elementary chemistry of siloxanes and silanols is limited, especially at the elevated temperatures and pressures relevant to practical applications. In this work, we have studied the pyrolysis of the smallest methylated siloxane hexamethyldisiloxane (HMDSO). This compound is of interest as nanoparticle precursors in flame spray pyrolysis processes and prevalent in biogas. The pyrolyses of HMDSO was studied in two shock tubes with molecular beam sampling and time-of-flight mass spectrometric detection. One set of experiments was conducted at the Advanced Light Source – Lawrence Berkeley National Laboratory with VUV-photoionization. The other set were performed at Argonne National Laboratory using electron impact ionization. The two ionization techniques yield complementary information, allowing a more detailed picture of the pyrolysis products to be obtained.

The data collected in this study are intended to guide on-going mechanism development efforts to define the pyrolysis and combustion chemistry of HMDSO. Contrary to the growth behaviour observed in the low temperature and long residence time flow reactor experiments of HMDSO [4,5], the high-temperature shock tube studies showed a rapid conversion to silicon-oxide based particles. This combined with observations of H₂ and C₂ species in the gas-phase products indicates rapid reaction through highly reactive intermediates. These observations support hypotheses that the leading decomposition pathways are direct molecular channels that include dimethylsilanone (O=Si(CH₃)₂) or 2-siliasobutene (CH₂=Si(CH₃)₂), each of which would readily decompose into the observed products[6].

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Plasma Treatment of Electrode Surfaces coated with nanoparticles

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In the framework of H2Giga, a flagship initiative by the German Federal Ministry of Education and Research centered on hydrogen technologies, we have developed a nitrogen plasma treatment aimed at optimizing materials systems for electrodes [1].

A well-established approach to enhancing the electrochemical efficiency of materials is by increasing their active surface area [2]. Nickel foams are frequently utilized in academic research and certain applications due to their extensive surface area [3]; however, their higher cost and handling difficulties make them less favorable for industrial use compared to bulk nickel plates.

A remote plasma process was devised applicable to both pure nickel substrates and nickel surfaces coated with nanoparticle catalysts. A distinctive feature of this remote plasma process is that the substrate does not need to be positioned in the plasma's excitation zone but rather in the effluent. This configuration significantly reduces the thermal load on the substrate, allowing the treatment of more thermally sensitive samples.

The plasma-induced surface modification is rapid, typically requiring only a few minutes under low-pressure conditions. This treatment results in hierarchical surface structuring, which markedly enhances the active surface area. Additionally, the plasma process improves the adhesion of nanoparticle coatings to the substrate surfaces, potentially extending the electrodes' operational lifespan [4,5].

The surface is characterized using SEM and focused ion beam cross-sections. Due to the use of nitrogen plasma, nitridation is observed, confirmed by various analytical methods such as EDX, XRD and XPS.

The experimental results have led to the development of a first model of the restructuring mechanism based on diffusion effects like the Kirkendall effect. Analysis by OES shows that the key factors for the change are the supply of atomic nitrogen at the surface from the plasma and the diffusion of nickel in the substrate. Our findings indicate that in our experimental setup the process is diffusion-limited, with sufficient atomic nitrogen supply at the surface [4].

Moreover, the shown hierarchical structuring by nitrogen plasma is not confined to nickel surfaces; similar modifications have been observed on other substrate materials, such as copper and aluminum. To demonstrate the industrial applicability of this process, we have successfully scaled up the plasma treatment from a laboratory scale of 1 cm² to an industrial test scale of 100 cm² [4].

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Mass Spectrometric Investigation of the Influence of Water Vapour and Oxygen on Gas-Phase Reactions of Aluminium Acetylacetonate Using VUV-Synchrotron Radiation

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Thin alumina (Al_2O_3) layers are used, among other applications, for corrosion protection and as permeation barriers. One method for synthesising Al_2O_3 layers is metal-organic chemical vapour deposition (MOCVD), where a metal-containing precursor is vaporised and reacts on a surface to form the desired film. Metal β -diketonates are often-used precursors due to their relatively high vapour pressure at moderate temperatures and their thermal stability. Aluminium acetylacetonate ($\text{Al}(\text{AcAc})_3$), which is investigated in this study, is also used for producing Al_2O_3 layers. Understanding the mechanisms and kinetics of the chemical reactions involved is crucial for designing MOCVD processes and ensuring the resulting quality of the produced layers. From the literature it is known that different carrier gases or co-reactants affect the deposition rate and surface properties of the layers, although the causes of this behaviour are mostly unknown. Their influence on the gas phase composition is investigated here.

The gas-phase reactions of $\text{Al}(\text{AcAc})_3$ in Ar, O_2 , and H_2O were investigated using VUV synchrotron radiation in a heated quartz reactor with mass spectrometry. The concentration of the precursor (m/z 324) in the gas phase decreases more rapidly in the presence of H_2O than in pure argon, while the acetone concentration (m/z 58) increases more rapidly with water vapor. The concentration of m/z 100 (acetylacetone) also increases with rising temperature. This is in line with previous observations that H_2O as a carrier gas leads to higher deposition rates. The series of experiments with oxygen, which increases the deposition rates, reveals a surprising behaviour: the precursor maintains a constant concentration within the temperature range of 510 K to 690 K. Oxygen apparently induces a series of reactions within this temperature range, where the precursor is initially consumed and then regenerated. At temperatures above 690 K, the concentration of the precursor in oxygen decreases more sharply than in pure argon. The temperature-dependent profiles of other species are also presented and discussed.

A monodisperse model for binary hetero-aggregate formation in mixing aerosol streams

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The mixing of dispersed particle streams (aerosols) is a common path in hetero-aggregate production. The dispersed phase exhibits usually a small diffusion relative to the carrier gases but due to the large number concentration, it is conveniently described as a scalar field in the Eulerian frame. This limited diffusion leads to challenges in modeling, resulting in spatially under-resolved mixing layers. More critically, low resolution and numerical diffusion blur concentration gradients, and directly impact the particle collision rate [1]. In the simulation of hetero-aggregate formation from dispersed (nano-) particles the recently proposed Euler-Lagrangian decomposition method (ELD) is the cornerstone to reconstruct under-resolved concentration gradients [2,3] in mixing layers of two aerosol streams.

In this work, we present a new population balance equation (PBE) model to describe the growth of hetero-aggregates from two mixing particle streams. The new model builds upon the monodisperse model by Jeong and Choi [4] and is developed to be integrated within the ELD Method. The model is validated using the sectional model proposed by Shigeta and Watanabe [5] in a spatially zero-dimensional configuration for a binary material system, showing good accuracy and a far smaller algorithmic complexity than the sectional model. The low computational costs of the new model make it ideal for integration into the in-house computational fluid dynamics (CFD) code PsiPhi.

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Flame Spray Synthesis of nanooxide for energy application

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Abstract

Flame spray pyrolysis (FSP) is considered one of the most scalable and cost-effective technologies for preparing well-controlled nanooxides which find applications as catalysts, biomaterials, sensors, to cite a few [1-2]. Compared to other synthesis techniques such as solid-state reaction or wet methods, it has the advantage of avoiding detrimental steps (e.g. grinding, intensive milling, washing, or heat treatment). This method allows obtaining homogeneous nanoparticles as a nucleation process from the gas phase (gas-to-particle conversion). To this purpose economical precursors (e.g. nitrates) and solvents are used to synthesize a wide variety of possible material compositions with high production yields.

In the present work we investigate the relation between FSP solvents and particle formation focusing on solvent parameters such as boiling point, enthalpy of reaction and possibility for carboxylation. To this purpose, XRD, SEM and TEM analysis is performed to assess the impact of the solvent on particles size and crystallinity. Examples of the application of these flame-spray synthesized oxide nanoparticles in electrocatalysis for H₂ production are also presented.

Acknowledgement

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Investigation of the Reaction Kinetics of Precursor Systems in Shock-Tube and Flow-Reactor Experiments

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The present work comprises investigation of reaction kinetics of organosilicon compounds in a shock tube behind reflected shock waves and in a flow reactor. Silicon-containing precursors are typically applied to generate functional particles in the gas phase. Material properties can be controlled by selecting the precursor and the reaction conditions. However, the kinetics information of many precursors is rare. Through variation of the silicon-containing precursors by progressively changing alkyl groups structure activity relationships can be derived [1]. In the present work trimethylethoxysilane is presented as an example. Shock tubes are a well-established technique to study the high-temperature kinetics without interfering transport processes. For this study it is operated in single pulse mode. Speciation was effectuated by gas-chromatography coupled with mass spectrometry (GC/MS). Furthermore, a flow reactor for reaction kinetic studies for temperatures up to 1100 K and a pressure of 1 bar was used. The products were identified and quantified by GC/MS.

Trimethylethoxysilane was found to decompose to ethylene and silanol $\text{HO-Si}(\text{CH}_3)_3$ via four center elimination. At high temperature silanol further decompose leading to methane and D1 ($(\text{CH}_3)_2\text{SiO}$). This reaction was separately studied in the flow reactor. For both reactions Arrhenius equations were derived. The results of both shock tube and flow reactor can be very well represented by one Arrhenius expression which agrees also very well with an older shock tube study of Herzler et al. [2]. The results were also confirmed by quantum chemical calculations.

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Scalable manufacturing of nanostructured materials for energy and health applications using gas phase deposition

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Nanostructured solids (for example, core-shell nanoparticles or porous micro-particles containing nanoparticles) hold great potential for energy and health applications. However, to come from product design incorporating nanostructuring to actually making such materials at relevant scales is not trivial. Gas phase deposition using techniques such as chemical vapour deposition (CVD), atomic layer deposition (ALD), and molecular layer deposition (MLD) can be used to provide the surface of a particle with either an ultrathin continuous coating or a decoration of nanoclusters. This allows us to take benefit from the vast range of chemistries that has been developed over the years for CVD, ALD, and MLD.

Gas phase deposition is also attractive for manufacturing nanostructured particles on a large scale when implemented in a system where particles are suspended in the gas phase, such as a fluidized bed or a pneumatic transport reactor. Even nanopowders can be processed using this method, although they form very dilute agglomerates and are not fluidized as individual particles. Since we often process cohesive materials, an effort has been made to obtain proper dispersion of the particles.

In this presentation, experimental evidence will be given for the benefits of applying gas phase deposition to powders. The application to various areas will be discussed, such as TiO₂ modified with SiO₂ and Pt for photocatalysis [1], Pt electrocatalysts with an ultrathin SiO₂ coating for stable hydrogen production [2], and pharma particles coated with Al₂O₃ to get controlled release properties [3]. We conclude that combining gas phase deposition with suspending particles either in a fluidized bed reactor or in a pneumatic transport reactor is an attractive way to combine nanoscale precision with producing large amounts of functional materials.

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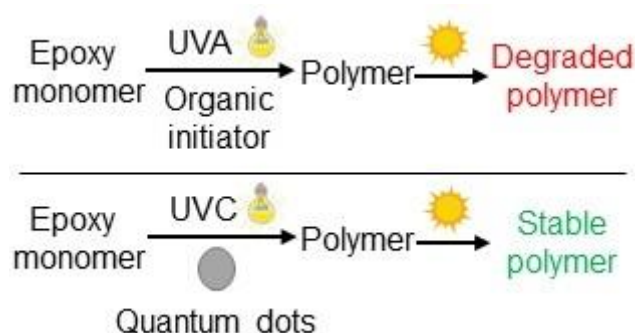
Photo-polymerization using flame-made quantum dots for stable epoxy coatings.

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Photo-polymerization is at the foundation of many industries such as dentistry, coating and stereolithography 3D printing. However, the organic cationic photo-initiators currently used are toxic, expensive, and difficult to tune with respect to the wavelength of light required to trigger polymerization reactions. For example, current stereolithography 3D printing resins are unstable under sunlight. Here [1], we demonstrate that cheaper and non-toxic titania quantum dots made via the scalable flame spray pyrolysis technology can photo-polymerize epoxy when exposed to UVC (not present in sunlight on Earth), while being insensitive to UVA (present in sunlight on Earth) leading to resins that are photo-stable during end use. We use NMR and FTIR to demonstrate that photo-polymerization is catalyzed under UVC but not UVA, and nanoindentation to monitor the mechanical stability of epoxy films during post-polymerization UVA exposure. This approach allows precise control over the wavelengths of light under which photo-polymerization can and cannot occur.



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CARBON-TiO₂ BASED MEMRISTIVE FILM FABRICATED THROUGH FLAME SYNTHESIS TECHNIQUE FOR POTENTIAL APPLICATIONS IN NON-VOLATILE MEMORY AND NEUROMORPHIC SYSTEMS.

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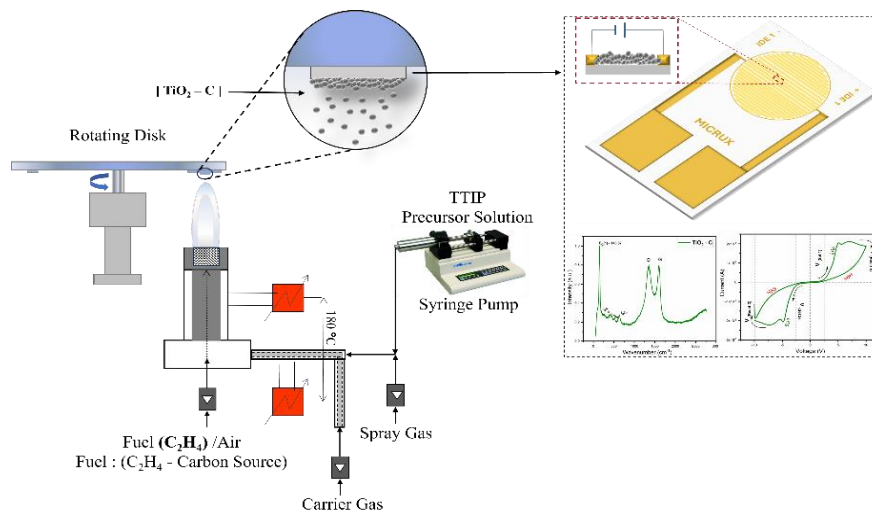
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The formulation of a memristor is a perspective route in the development of non-volatile memory for compact devices and neuromorphic systems [1]. In addition to the generally opted metal oxides (TiO₂, ZnO, HfO₂, NiO) for preparing memristors and other functional device [2], recently the carbon nanomaterials (carbon nanotubes, graphene oxide, and amorphous carbon) have been extensively investigated to be used as a functional material for the memristors due to their switching rate, chemical stability, and easy scalability [3]. In this work, a composite nanostructured thin film of TiO₂-C nanoparticles has been fabricated through a facile one-step flame-based nanoparticle synthesis using a customized honeycomb burner and then thermophoretic sampling for particle collection/deposition on different substrates for chemical, electrical, and topographic analysis. Titanium (IV) isopropoxide (TTIP) was used as a precursor for TiO₂ nanoparticles and ethylene/air-premixed gas was used as the fuel source of carbon compounds. Particle size distributions of the flame-generated nanoparticles were measured by differential mobility analysis. The chemical characteristics of the produced film were analyzed through Raman spectroscopy, where the E_{g(1)}, E_{g(2)}, B_{1g}, (B_{1g}/A_{1g}), and E_{g(3)} peaks of active anatase modes of TiO₂ and the D peak and G peak related to the carbon were observed. A slight blue shift in the spectrum was observed for the primary TiO₂ peak E_{g(1)}, suggesting the interaction between TiO₂ and carbon. The produced film was further investigated through AFM, and UV-Vis spectroscopy for the surface topography analysis and the optical bandgap identification respectively. The current-voltage (I-V) measurements showed the repeatable resistive switching phenomenon with consistent set/reset voltage values, as observed in the non-volatile memory and neuromorphic systems [4].

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A two-step strategy for production of spherical non-aggregated multi-component particles by suspension-fed spray flame

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For applications in optics, energy storage, and semiconductors etc., spherical non-aggregated particles are desired for better flowability, molding capability and homogeneous densification. Spray flame synthesis has attracted widespread attention with its excellent ability for atomic-level mixing/doping and good potential for scale-up production. However, spray flame synthesis usually produces aggregates due to the known collision-coalescence growth. In this paper, we propose a two-step strategy of suspension-fed spray-flame synthesis. The first step involves the synthesis of aggregated nanoparticles, followed by a second step where these aggregates are reconstructed into spherical non-aggregated particles while retaining the advantage of atomic-level homogeneous mixing. It is found that for aggregated Y_2O_3 nanoparticles, the critical point for reconstructing into spherical particles occurs when the flame temperature exceeds the melting point. The spherical particle size increases with the solid concentration of the suspension to a power of about 0.28. Assuming that droplets do not undergo micro-explosions and instead follow a one droplet to one particle route results in an overestimation of particle size by a factor of 6 to 8. This discrepancy suggests that micro-explosions may play certain role in the new suspension-fed flame synthesis, and largely reduces the final particle size. Furthermore, the Al_2O_3 - Y_2O_3 and MgO - Y_2O_3 particles are selected for the multicomponent suspension feed synthesis, representing the miscible and immiscible systems, respectively. The results show that for the Al_2O_3 - Y_2O_3 system, uniformly mixed spherical non-aggregated particles are obtained. For the MgO - Y_2O_3 system, both composite spherical particles with pinning structure and MgO nanoparticles are identified, indicating that for obtaining spherical multi-component non-agglomerates, the flame temperature needs to be higher than not only the eutectic component's melting point but also any single component's melting point. Overall, suspension-fed atomized flame synthesis opens up a new pathway for the low-cost industrial-scale production of spherical non-aggregated multi-component particles.

Scalable fabrication of catalysts for proton exchange membrane water electrolysis

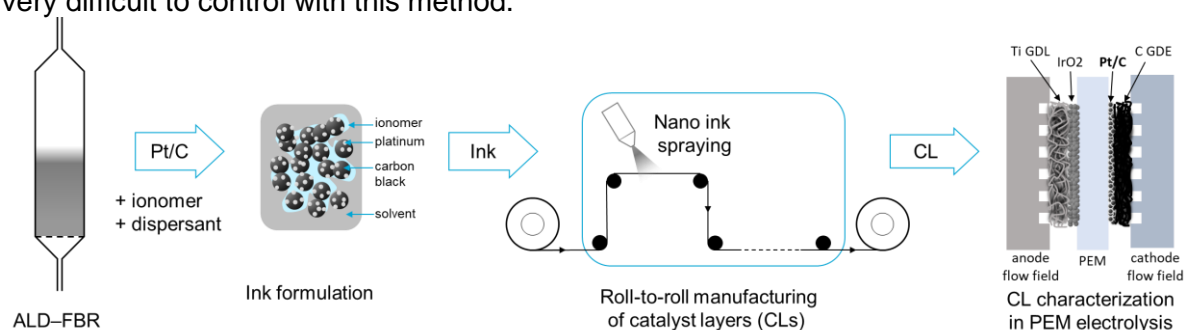
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The phenomenal growth in renewable power generation has even further increased research interest in the fields of energy storage and material conversion through electrolysis. A key element in any electrolysis process is a catalyst tailored to the targeted reaction, e.g., platinum group metals (PGMs) for water splitting. Due to the immense scale of the problem, and the cost and scarcity of PGMs, economical use of these materials is imperative. Hence, catalysts are typically dispersed on a support material, e.g., Pt-loaded carbon black (Pt/C) as cathode catalyst in proton exchange membrane water electrolysis (PEMWE). Compared to bulk Pt, a larger fraction of atoms is exposed at the surface thus leading to a higher catalytic activity per unit weight of Pt. Traditional fabrication methods for Pt/C, such as incipient wet impregnation, allow control over the amount of deposited Pt; however, the morphology and dispersion are very difficult to control with this method.



In this work, we propose an alternative and economically feasible fabrication route (see figure above) for Pt/C catalyst layers based on gas-phase synthesis via atomic layer deposition (ALD). We have previously shown that Pt/C can be fabricated via atmospheric pressure ALD on particles in a fluidized bed (ALD-FBR), which is readily scalable [1]. In contrast to traditional fabrication methods, we can control the morphology and achieve a finer dispersion of deposited Pt [1,2], enabling higher catalytic activity at reduced Pt loading. First, we use ALD-FBR to fabricate tailored Pt/C for PEMWE. Second, to establish the relationship between morphology and performance, we characterize the material using (HR)TEM and with respect to electrochemically active surface area (ECSA) as a relative indicator for performance. However, a full assessment of Pt/C requires testing in real-world applications, which is why we go one step beyond bare catalyst characterization and demonstrate the use of ALD-made Pt/C in lab-scale PEMWE cathodes. In conclusion, we demonstrate, for the first time, the fabrication of Pt/C via atmospheric pressure FBR-ALD, and its superior performance at reduced Pt loadings compared to conventional Pt/C in PEMWE cathodes.

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Improved stability and activity of Pt catalyst for sustainable hydrogen generation

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Green hydrogen is gaining increasing attention as a means of transport and energy storage worldwide. The proton exchange membrane water electrolyzer (PEMWE) is one of the promising methods for producing green hydrogen. In PEMWE, platinum group noble metals are commonly utilized to achieve high-efficiency hydrogen production. For example, Pt-loaded carbon black (Pt/C) is typically used as a catalyst at the cathode side, as no other catalysts can currently outperform Pt in hydrogen evolution reaction (HER) [1]. However, the cost and scarcity of Pt soon become a bottleneck when scaling up hydrogen production to relevant outputs to partially replace, e.g. fossil fuels.

One potential solution for the economical use of Pt is to minimize its loading in PEMWE while maintaining the performance of the cell. To maximize the utilization efficiency of Pt, better control of the morphology and dispersion of the catalyst should be ensured. Therefore, Pt/C has been synthesized with atomic layer deposition (ALD) to achieve lower loading and enhanced catalytic performance with smaller and more uniform particle sizes as compared to those produced by conventional incipient wet impregnation [2]. In this work, Pt/C catalysts were synthesized using ALD, with the platinum loading and particle size controlled by the number of ALD cycles. The catalytic activity of Pt/C was evaluated using rotating disk electrode (RDE) equipment. Additionally, the stability of these catalysts was assessed through 1000 cycles of cyclic voltammetry scanning. Our results demonstrate that by carefully selecting the number of ALD cycles, it is possible to achieve ALD Pt/C catalysts that are both more active and more stable compared to commercial benchmark Pt/C catalysts.

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Gas phase synthesis of SiN_x nanoparticles for battery application using a hot-wall reactor

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Silicon is considered to have great potential as an anode material for next generation lithium ion batteries (LIBs) and solid-state batteries, owing to its high theoretical capacity of 4200 mAh g⁻¹. Problems arising from volume expansion (300%) during cycling not only limit its commercial viability, but also open up research avenues to improve the performance already on the material level. Together with materials like SiO_x, conversion type silicon compounds such as silicon nitride (SiN_x) are shown to tackle these stability issues^[1]. The gas phase synthesis of SiN_x nanoparticles offers a simple, scalable, and flexible production approach for enhancing the stability and performance of LIB anodes.

In this study, nanostructured silicon-rich SiN_x is synthesized using a hot-wall reactor via the pyrolysis of the gaseous precursors monosilane (SiH₄) and ammonia (NH₃), which can produce SiN_x particles having average sizes from 55 nm to 250 nm depending on the reaction parameters. Process-property correlations within this reactor design are explored with elemental analysis, XRD, BET, and TEM.

Elemental analysis shows that nitrogen content in SiN_x increases with NH₃ concentration and holds a linear relation at high concentrations. A decrease in crystallinity with increasing nitrogen content that is conducive to the long-term stability of the materials can be observed from XRD of SiN_x. The stoichiometry of SiN_x can be tuned in the full range of $x = 0$ (pure silicon) to $x = 1.33$ (stoichiometric Si₃N₄), while typically the core of the particles is slightly more silicon rich. At specific synthesis conditions, core shell structures can be observed.

Electrochemical testing of the powders that have been processed into electrode layers is performed in liquid electrolyte half cells. Greater Coulombic efficiency loss is observed in powders with very small particle size because of their higher surface-to-volume ratio and reactivity. Higher nitrogen content in SiN_x yields better cyclic stability, yet at reduced capacity and first cycle efficiency. Formation of the c-Li₁₅Si₄ phase, which reacts with the electrolyte, is suppressed with increasing N content in SiN_x, as shown by the dQ/dV vs V plot. The battery performance in liquid electrolyte serves as a screening for further usage in solid state cells.

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Synthesis and upscaling of silicon and a-SiC_x nanoparticles for lithium-ion batteries in a hot-wall reactor

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Small amounts of silicon are currently used to partly replace graphite as anode material in lithium-ion batteries to increase their energy density and fast charging capability. Ensuring mechanical integrity during charging and discharging as well as the production of suitable silicon-based materials on a large scale at acceptable costs still remains a challenge. Applying silicon as nanoparticles can greatly increase cycling stability, yet coulombic efficiency may be reduced due to the increased surface area. The addition of carbon as a hetero-element has been shown to greatly increase the cycling performance furthermore. The production of silicon and silicon compounds from monosilane is a well-studied process, yet the upscaling, especially of silicon-carbon compound materials is not well reported. In this work, the formation of silicon and a-SiC_x nanoparticles from the gas phase is analyzed to understand the process, identify key parameters regarding a suitable process technology, and resolve upscaling issues for transfer to the industrial pilot scale. The experimental findings are supported by simulations of fluid dynamics. Process conditions regarding the formation of pure as well carbon containing nanoparticles are studied and a successful transfer to an industrial pilot plant reactor is demonstrated ¹.

¹ Loewenich et al., J. Alloys and Compounds, 9886, (2024), 174061

Pilot-scale spray-flame synthesis of iron oxide nanoparticles: Investigation a hydrogen based burner concept

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The synthesis of nanoparticles in spray flames is a versatile approach to produce materials with different composition, morphology, and properties. For enabling the transition from lab-scale experiments to industrial application, investigations on the pilot-scale provide a crucial intermediate stage. In this study, a pilot-scale burner design based on a H₂/air pilot flame, stabilized by an electrically heated ring [1, 2], is used. By using H₂ and ethanol as a fuel, the burner enables the sustainable production of nanoparticles. The temperature distribution within the flame is an important parameter influencing the kinetics of precursor decomposition, particle nucleation and growth. To examine this in larger scales, we investigated the gas phase temperatures within the reactive zone using non-intrusive multi-line NO-LIF temperature measurement. The synthesis of iron oxide nanoparticles is carried out using a precursor solution of iron nitrate nonahydrate in ethanol. By targeted variation of the process conditions, which also includes changes to the type of fuel and dispersion gas as well as the flow rates, we are able to adjust product characteristics. The following methods are applied to characterize the products: electron microscopy to visualize the morphology and create particle size distributions, BET gas adsorption to determine the specific surface areas and X-ray diffraction to determine crystallite phases and sizes. Based on the particle analysis we could find and explain correlations between operating conditions, gas phase temperature, and product characteristics. It has been determined that although the dispersion gas mass flow changes the temperature distribution, it has only small effect on the maximum gas temperature and material characteristics. By varying the choice of process gases, higher flame temperatures can be set, which are advantageous for suppressing the often undesirable large particle fraction.

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Iron-based nanoparticles synthesized by Flame Spray Pyrolysis for strong magnetic properties

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Flame spray pyrolysis (FSP) is a versatile method for rapid and large-scale production of various nanomaterials usually oxides or, to a lesser extent, carbides, sulfides and even metallic phases, alloys and core-shell structures [1,2,3,4]. The liquid-fed aerosol is vaporized in a flame under a controlled atmosphere and the process of nucleation-growth of particles results directly from the capacity of vaporization of the precursors [4]. Key parameters such as the enthalpy of combustion of solvents and precursors, the atmosphere generated in the closed environment and the residence time in the flame influence the resulting product and its morphology. [5,6].

Among the materials of interest for magnetic applications, the choice of iron-based materials is motivated by their low toxicity and wide availability; more suitable for large-scale production. Apart from the chemical composition and the nature of the crystalline phase, magnetic properties of iron-based nanoparticles can be related to their size [7]. Thus, the optimization of these magnetic properties requires a precise control of the composition and morphology of the objects. Moreover, for iron-based materials, the carbide and nitride phases show strongly enhanced magnetic properties (including saturation magnetization $M_s \sim 130\text{-}200$ emu/g for bulk) [8, 9] when compared to the oxide phases ones ($M_s \sim 92$ emu/g) [9]. The challenging use of FSP to produce these non-oxide phases appears then of peculiar interest.

Here, we present our recent advances in the synthesis by FSP of iron oxide nanomaterials for the determination and optimization of reference magnetic properties. For these particles, magnetic measurements combined to XRD, SAXS and SEM characterization allowed to study the influence of the encountered phases and morphologies on their properties. First results concerning the formation of non-oxide phases are also reported.

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A semi-detailed Kinetic Model for the production of Carbon Nanotubes and H₂ from the thermo-catalytic pyrolysis of Methane

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Floating Catalyst Chemical Vapor Deposition (FCCVD) is a promising method for the continuous industrial scale production of hydrogen and carbon nanotubes (CNTs). Thanks to the remarkable properties of CNTs, the large-scale implementation of such technology would allow the production of hydrogen at a price that is comparable to the largely diffused steam reforming processes [1, 2]. However, the design of a suitable industrial reactor is still a challenge due to the complex interplay between the multiple chemical and physical phenomena involved. Starting from the chemistry side, a well-directed CNT kinetic model can be a game-changing tool to support reactor design and accelerate scale-up efforts.

This work proposes a CNT model describing the main chemical steps involved in FCCVD reactors. A discrete-section approach is applied to address the extreme complexity related to the different chemical routes of carbon formation, aggregation, and CNT growth. The surface kinetic model is combined with a validated gas-phase pyrolysis mechanism accounting for the competitive soot formation process [3], with a surface deposition mechanism [4] and with a kinetic model describing the decomposition of ferrocene into iron atoms and the subsequent nucleation and growth of the catalyst particles through agglomeration of the produced iron atoms. The model is used in one-dimensional numerical simulations of the FCCVD reactor.

To the best of our knowledge, this is the first semi-detailed chemical kinetic framework, hierarchical and modular in nature, able to describe the relationships between catalyst, reaction conditions and yields in the CNT production from thermo-catalytic pyrolysis of methane. Although, a thorough validation of the model requires further quantitative data, especially in terms of methane conversion, gas-phase species formation and nanotube yield. Results show good agreement with the limited number of experimental observations from the literature and with new experimental data recently acquired at IMDEA Materials Institute.

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Investigation of effects of different chemical mechanisms on formation of graphene during gas-phase synthesis

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The all-gas-phase synthesis of graphene using a microwave-assisted plasma reactor enables the effective decomposition of precursors into graphene layers. This method can operate at atmospheric pressure, eliminating the need for high vacuum or elevated temperatures. In this paper, the formation of graphene within a microwave plasma reactor was modeled by assuming the reactor operates as a 1D plug-flow system, with ethanol serving as the primary reactant. A sectional approach was employed in this study to predict both the yield and the number of graphene layers produced. The research focused on evaluating the influence of various kinetic mechanisms, including DLR, CALTECH, CRECK, KAUST, and ABF, on the properties of the graphene layers, specifically in terms of Feret Diameter (FD) and yield. It was shown that the different kinetic mechanisms exert a significant influence on the simulation results. This impact is particularly evident when comparing the predicted Feret Diameter and yield across the various mechanisms. Among these, the results obtained using the KAUST mechanism were found to be closest to the experimental data, suggesting its potential accuracy in modeling graphene formation under the given conditions. The KAUST mechanism also addressed the delayed onset of graphitic particle formation observed with other mechanisms. To further refine the analysis, a sensitivity analysis was conducted by varying the surface growth (SG) and inception (IN) parameters specifically for the KAUST mechanism. This analysis aimed to identify the parameter values that yield the most accurate simulation results. The findings revealed that for the KAUST mechanism, a specific value of $SG = 2500$ provided results that closely matched the experimental observations. This suggests that the KAUST kinetic mechanism may cause a more precise representation of the graphene formation process, enhancing the model's predictive accuracy.

Iron nanoparticle formation in resolved single microparticle simulations

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Metal fuels are gaining attention as sustainable energy carriers due to their carbon-free oxidation, recyclability, and high volumetric energy density. Among them, iron stands out due to its wide availability, cost-effectiveness, and compatibility with existing coal infrastructure. However, the formation of nanoparticles during the combustion of iron particles poses significant challenges for recycling and health. Nanoparticles are difficult to separate from gas exhaust and are respirable, which is why a comprehensive understanding of their formation is necessary.

Recent molecular dynamics simulations show that the nucleation of nanoparticles is caused by clustering of iron / iron oxide molecules forming nanoparticles that have the composition of FeO in high temperature regions [1]. In this study, a model for nanoparticle formation is introduced that considers the nucleation as condensation of supersaturated iron / iron oxide vapor. The model also includes the oxidation of the nanoparticles up to the maximum oxidation state of FeO, and condensation and oxidation heat release from the nanoparticles.

Recent in-situ optical measurements by Li et al. [1] have investigated the onset of nanoparticle formation and the characteristics of the nanoparticle cloud that is formed close to the burning iron microparticle. Resolved boundary layer simulations of single iron microparticles are conducted, and results are compared with the experimental data to validate the nanoparticle model. Additionally, key aspects of nanoparticle formation and cloud evolution are investigated, considering combustion characteristics and transport processes in the boundary layer. It is shown that the particle temperature is the most important parameter for nanoparticle formation and a precise prediction of particle temperature evolution is crucial for accurate nanoparticle prediction. Further analysis identifies convection and thermophoresis as the primary transport processes for the nanoparticle cloud, while diffusiophoresis is negligible.

This research is conducted within the framework of the Clean Circles project (www.tudarmstadt.de/clean-circles).

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Process Design for Gas Phase of Iron Nanoparticle from Iron Pentacarbonyl

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Iron nanoparticles (Fe NPs) are used in manufacturing of carbon nanotubes (CNTs) due to their low toxicity, abundance, and exceptional catalytic properties [1]. The concentration, polydispersity, and morphology of Fe NPs are critical in controlling CNT yield and physical characteristics (i.e., their diameter, length, and helicity) [2]. In this study, the gas-phase synthesis of Fe NPs by thermal decomposition of $\text{Fe}(\text{CO})_5$ is simulated. A simple monodisperse population balance model (MPBM) is coupled with global and detailed chemical kinetics of $\text{Fe}(\text{CO})_5$ decomposition to predict the evolution of agglomerate morphology and the primary particles diameter of Fe NPs by inception, surface growth, coagulation, and sintering of primary particles (PPs). A new characteristic time, τ_s , for the sintering of Fe NPs is proposed based on the particle size dependence on their melting temperature, and its performance in predicting PP size is benchmarked with data reported in the literature. The results of the PP size of Fe agglomerates are compared with TEM measurements available in literature on synthesis of Fe NPs. The model predictions are in good agreement with the measured d_p and concentration of Fe NPs produced by thermal decomposition of $\text{Fe}(\text{CO})_5$. Diagrams for degree of hard-agglomeration are developed in terms of the reactor initial precursor concentration, maximum temperature, cooling rate, and particle residence time. The proposed relation for τ_s in this study shows a significant enhancement (up to 65%) in predicting the evolution of the PP size of agglomerates at $T < 1073$ K, an important temperature range in the process design of CNTs by gas-phase synthesis with high throughput.

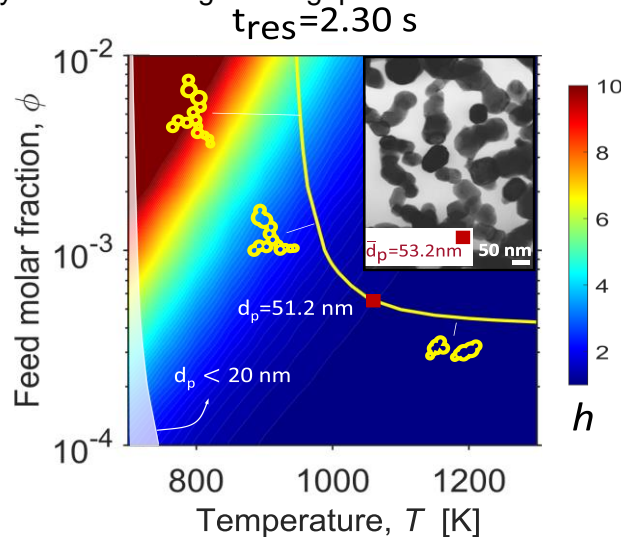


Figure 1. Hard-agglomeration map of Fe in terms of precursor molar fraction and maximum reactor temperature, along with isopleth of PP size and inset schematics showing aggregation of PPs.

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