ADVANCED MATERIALS

DOI: 10.1002/adma.200((Please insert last 6 DOI digits))

Nanomaterial growth dynamics in jet flames**

By Rainer Jossen, Gregory Beaucage*, Martin C. Heine, Theyencheri Narayanan and Sotiris E. Pratsinis

Nanomaterial nucleation and growth in liquid spray jets subject to combustion is of interest to a wide range of researchers ranging from those interested in synthesis of nanopowders for catalysts and sensors to those interested in the unintentional production of nano-pollutants in diesel engines. Such nucleation and growth processes occur in spray flames in a few milliseconds at temperatures in excess of 2000 °C, in turbulent sonic jets with high optical emissions. We have recently been able to map this nanoparticle growth using a third-generation synchrotron source and small-angle x-ray scattering (SAXS). These in situ SAXS observations show droplet evaporation, nano-particle nucleation, growth and aggregation processes directly in the spray flame for the first time. Such information allows for control and understanding of this increasingly important synthetic process for nanomaterials.

Nanomaterial formation requires conditions far from equilibrium since phase size decreases with increasing supersaturation in temperature, partial pressure and concentration as described by Gibbs & Thompson^[1,2]. An ideal process for the formation of nanomaterials is a continuous process with extremely short residence time, to lock-in the earliest stages of growth, with high temperatures, and high concentrations of supersaturated vapors and uniform conditions to produce a narrow size distribution. Versatility in precursor composition is needed to produce a wide range of nanomaterials. These conditions are achieved in a narrow jet flame produced from the nebulized spray of a combustible liquid, flame spray pyrolysis (FSP). Flame spray pyrolysis (FSP) has been used for synthesis of a broad spectrum of inorganic nanoparticles^[3-11] from titania^[3] to yttrium aluminum garnet for solid state lasers^[11] and even catalysts such as Al₂O₃ supported Pt^[10]. In FSP, micron-scale droplets evaporate, followed by combustion, particle formation & growth and eventual aggregation^[12]. Compared to vapor-fed flames^[13], liquidfed spray flames have much higher gas velocities ^[14] and somewhat higher maximum temperatures. High temperature residence time is ~ 1 ms compared to 1 s in vapor-fed flames. Despite the speed of growth, FSP results in highly homogeneous particle morphologies^[9] and composition^[7].

Small angle X-ray scattering (SAXS) is the only *in situ* technique that can unravel structures from nano- to microscale in spray flames. Third-generation synchrotron X-ray sources, such as the European Synchrotron Research Facility (ESRF), yield sufficient photon flux to probe time resolved scattering signal in particle-laden flames even at low volume fraction (10^{-6}) with short acquisition time (< 0.1 second) ^[13,15,16]. Here, particle and aggregation dynamics are studied by SAXS for the first time *in situ* in a spray flame reactor^[17]. Results cover the whole size range from primary particles of about 2 nm to aggregates up to 300 nm in diameter and even micron-size droplets. Comparison is made with *ex-situ* product powder properties. The spray flame

apparatus described in [17] was used with a liquid feed of 70% zirconium n-propoxide (Zr(C₃H₇O)₄ in n-propanol for a 0.5 M feed at 4 ml/min producing 15 g/h ZrO2 using an O2 dispersion gas at 5 l/min. Droplet velocities and diameters were measured using a 2D-phase Doppler anemometer (PDA) described in reference^[14]. Spray flame temperatures were measured by emission/transmission spectroscopy^[18-21]. In situ particle growth during FSP was measured using small-angle X-ray scattering (SAXS) at the European Synchrotron Radiation Facility (ESRF, beam line ID02) in Grenoble^[22]. Data were corrected by a procedure reported elsewhere^[23] including subtraction of background measurements made on a similar flame in the absence of the zirconia precursor (pure propanol). The Sauter mean diameter, $d_{V/S}$, & the geometric standard deviation, σ_{g} , can be obtained in the range of 0.1 to 500 nm form the SAXS pattern as described in [24-29]

Scattering can yield certain statistical information concerning the nature of aggregates. It has long been known that scattering can yield directly the mass fractal dimension, d_{f_2} and aggregate mass, z, where^[30,31],

$$z \sim \left(d_{agg} / d_{S/V} \right)^{d_f} = G_{agg} / G_{primary} \tag{1}$$

where d_{agg} is the aggregate diameter and G is the extrapolated scattering intensity at zero scattering angle. z is known to be a mass average when calculated by the last expression. By considering the shape of the aggregate scattering pattern as a whole is it possible to determine another dimension pertaining to the mass-fractal dimension of a linear or conducting pathway, p, stepping along an aggregates structure^[25]. This minimum dimension would be the observed mass fractal dimension if the

F-4-7	
[^]	Prof. G. Beaucage
	Department of Chemical and Materials Engineering
	University of Cincinnati
	Cincinnati OH 45221-0012 (USA)
	E-mail: beaucag@uc.edu
	Prof. S. E. Pratsinis, Dr. R. Jossen, Dr. M. C. Heine
	Particle Technology Laboratory
	Department of Mechanical and Process Engineering
	ETH Zurich
	CH-8092 Zurich (Switzerland)
	Dr. T. Narayanan
	European Synchrotron Research Facility (ESRF)
	F-38043 Grenoble (France)

[**] This work was supported by the TH Gesuch No. 34/02-3, the Swiss National Science Foundation (Grant No. 200021-101901/1), the synchrotron facilities at ESRF (beam time allocation ME-628) and the U.S. National Science Foundation (Grant No. CTS-0626063). We thank J. Gorini and H.K. Kammler & R. Mueller for stimulating discussions. branches could be removed from the aggregate. Using this dimension, d_{min} , it is possible to estimate the linearity of an aggregate structure through the connectivity ratio, $c = d_f/d_{min}$. For an unbranched structure c = 1 and in the presence of branching $1 < c \leq d_f$. From scattering we can determine the molar fraction branches ϕ_{Br} ,

$$\phi_{Br} = (z - p)/z = 1 - z^{(1/c - 1)}$$
⁽²⁾

which is the mole fraction of particles that branch off a pathway through the structure $[^{25]}$.

In the flames, Doppler anemometry shows the gas is accelerated by droplet combustion and thermal expansion until 14 mm height above the nozzle $(HAN)^{[12]}$ where the maximum gas velocity of 170 m/s is reached. Then this velocity decays to 59 m/s at HAN 45 mm due to thermal contraction and nanoparticle formation. Beyond this height droplets are not present by anemometry. The maximum gas temperature is 2620 K at 0.05 ms (3 mm HAN). At 0.2 ms the cooling rate is 7·10⁶ K/s at 18 mm HAN and thereafter decreases by about one order of magnitude to 7·10⁵ K/s for a residence time of 0.4 ms.

Figure 1 shows the intensity of the SAXS measurements as a function of scattering vector, $q = 4\pi/\lambda \sin(\theta/2)$, where θ is the scattering angle. From 0.16 ms (1 mm HAN, circles) to 0.25 ms (7 mm HAN, squares), both droplets ($q < 0.02 \text{ Å}^{-1}$) and particle ($q > 0.04 \text{ Å}^{-1}$) structures can be seen. Droplets are in the range of micrometers and therefore present at low q while the nanosized particles are present at high q values since $q \sim 1/d$. The -4 slope at low q corresponds to Porod's law^[32,33] that indicates smooth sharp surfaces of micrometer size droplets in the spray (Fig. 1). The low-q arrow indicates the evaporation of droplets in the flame. At high-q nanostructure growth shows first single particles 0.16 ms, and later aggregated particles as evidenced by a weak power-law regime in the 1.85 ms data between 0.004 and 0.013 Å⁻¹.



Figure 1. Scattering intensity as a function of the scattering vector, q, for flame A. At t < 0.25 ms droplets are detected in the low q range (< 0.02 Å⁻¹) while in the high q range (> 0.04 Å⁻¹) the nanosized particles are detected. For t > 0.25 ms no droplets are detected.

Figure 2a shows the evolution of the Sauter mean diameter along the centerline of spray flame for primary particles as determined from the SAXS $d_{V/S}$ (circles)^[26,27]. First measurements

are made at 0.04 ms (0.4 mm) where $d_{V/S}$ is 6 nm, then $d_{V/S}$ decreases to 2.5 nm at 0.22 ms (3 mm HAN) before it increases



Figure 2. a) Evolution of primary particle size, $d_{V/S}$, obtained from *in situ* SAXS technique as a function of the flame residence time, t (circles). $d_{V/S}$ is calculated from the volume to surface ratio. The filter particle size obtained with BET (triangle), SAXS (circles) and TEM-image analysis are also shown (squares). b) Evolution of the geometric standard deviation, σ_g (circles), and zirconia volume fraction (triangles) as a function of the residence time (circles) compared to the filter powder (squares).

again to about 10 nm at 0.68 ms (50 mm HAN). The particle size of 2.5 nm is the smallest in situ flame-made particle diameter ever measured. At the beginning of the process (0.04 ms), the

supersaturation is low resulting in formation of relative large critical clusters by nucleation following Gibbs-Thompson theory^[1,2]. As temperature increases and more condensable species are formed, supersaturation is increased (Fig. 2b) leading to smaller critical clusters and a smaller Sauter mean diameter^[34]. This decrease in particle size at the early stage of the flame was also seen by Kammler et al.^[15] in premixed vapor-fed flames & by Beaucage et al. in TiCl₄ flames [16]. The particle growth rate between about 0.25 and 0.6 ms is about 6.1 nm/ms (or μ m/s) as indicated by the line connecting points in this region of Fig. 2a.

Primary particle growth stops at 0.68 ms (50 mm HAN) with $d_{V/S} \sim 10.8$ nm where the gas temperature is about 1620 K, consistent with Mueller et al.^[12]. The primary particle distribution is indicated by the geometric standard deviation in Figure 2b, left axis and is essentially frozen beyond the point where the Sauter mean diameter stops growing, 0.68 ms. Figure 2a shows also that FSP-made particles collected on the filter have a $d_{V/S}$ (last circle) and d_{BET} (triangle) of 11.7 nm and 10 nm, respectively. The Sauter mean diameter from TEM images of particles collected on the filter is 10.6 nm (Fig. 2a, square).

In situ wide angle X-ray scattering (WAXS) was also used to explore the evolution of crystal structure^[35]. Only amorphous patterns were detected by in situ WAXS at all HAN's observed, indicating that zirconia was not crystalline in the flame despite a melting point of about 2700 K for bulk zirconia. It must be assumed that particles are supercooled liquids above 1600 K since they appear to coalesce as indicated by a drop in number density and an increase in particle size. Particles collected on the filter show a metastable tetragonal structure^[36]. Despite the absence of crystallinity the nanoparticles do not coalesce at temperatures below 1600 K on the time scale of aggregation.

Figure 2b shows the evolution of geometric number-based standard deviation, σ_{g} (circles and left axis), of the primary particle size distribution (PPSD) assuming spherical particles and a lognormal distribution^[26]. At 0.04 ms (0.4 mm HAN) σ_{g} is initially 1.49 and increases to 1.71 at 0.17 ms (1 mm HAN) and then σ_{σ} decreases continuously to 1.48 at 0.59 ms which is close to the self-preserving limit, for the free molecular regime $(1.45^{[37]})$. At 0.68 ms (50 mm HAN), aggregates are formed as indicated by the appearance of fractal scattering as seen in figure 1, weak power law decay between 0.003 and 0.015 for top two curves. σ_{σ} decreases to 1.35 after the particles start to aggregate, which is significantly below the self-preserving limit. At the end of the flame (1.85 ms; 100 mm HAN) $\sigma_g = 1.31$ while for the filter powder a higher value of $\sigma_g = 1.47$ is detected. The increased σ_g of the filter powder may be affected by sintering on the filter or other post synthetic factors. High polydispersity near the nozzle tip may be caused by nucleation of new particles under rapidly changing conditions near the critical volume fraction for homogeneous nucleation^[1,2,14].

Figure 2b also shows the total zirconia volume fraction (triangles) as a function of the residence time along the burner centerline. The volume fraction increases rapidly to about 1.7×10^{-6} at 0.19 ms (15 mm HAN) and then to $3.22 \cdot 10^{-6}$ at 0.68 ms (50 mm HAN). In contrast to vapor flames there is almost no entrainment or dilution of the spray flame.

Figure 3b shows the number density of zirconia primary particles (triangles) in the spray flame as a function of the residence time above the nozzle. A sharp increase in number density is observed and has its maximum at 0.22 ms (3 mm HAN) indicating a nucleation event. The maximum value of σ_g is observed at the same residence time, 0.22 ms (1 mm HAN, Fig. 5) where the minimum in particle size occurs of $d_{V/S} = 2.5$ nm. The combination of a minimum in particle size, a maximum in σ_g and a rapid increase in particle number concentration^[34] indicates a

nucleation event at 0.22 ms. The critical volume fraction associated with this nucleation event is $1 \cdot x \ 10^{-6}$ (arrow in Fig. 2b). At slightly longer residence times the number concentration decreases while the particle size increases (Fig. 2a) indicating coalescence. The particle number concentration at t > 0.68 ms (50 mm HAN) remains almost constant as growth stops (Fig. 2a).



Figure 3. a) Evolution of the mass-fractal dimension, d_r (triangles), d_{min} (diamonds) connectivity dimension c (squares) and branch fraction (filled circles) as a function of residence time above the nozzle obtained by *in situ* SAXS measurements along the centerline. Data from the filter powder are also shown. Below 0.68 ms residence time no data are shown as particles are non-aggregated. b) Evolution of the radius of gyration of the aggregates, R_g (circles), particles per aggregate, z (squares), and number concentration (triangles) as a function of the residence time obtained form *in situ* SAXS measurements along the centerline (circles). Aggregates are only formed after 0.68 ms.

A slight discontinuity in particle size at about 50 mm HAN in Figure 2a corresponds with the onset of aggregation in the FSP. Figure 3a shows the evolution of d_f (triangles), d_{min} (diamonds), c

(squares) and ϕ_{Br} (circles) above the burner. At t < 0.68 ms (50 mm HAN) aggregates are not detected. Above 0.68 ms the gas temperature is below 1600 K and a cessation of particle growth is observed, Fig. 2a. At 0.68 ms, $d_f = 1.2$, and d_f increases to 1.47 at 1.85 ms (100 mm HAN) and finally to 1.53 at the filter. Between 0.68 and 1 ms, d_f and d_{min} are similar so c is close to one and ϕ_{BR} close to zero. This indicates that the first aggregates in the spray flame are linear structures with no branches which are just slightly kinked. This dramatically differs from the initial aggregation process in vapor flames and in most models for aggregation in the literature and might be associated with the rapid growth and turbulent environment of the spray flame. After 1 ms branching increases as c and ϕ_{Br} increase. The value of $\phi_{Br} \sim 0.3$ and c ~ 1.2 are extremely low values for flame-made aggregates. Even for the final FSP aggregates the structures are close to linear especially in comparison to solution route and vapor flame aggregates^[25]. z is also lower than usual flame-made aggregates (Fig. 3b).

Figure 3b also shows the evolution of the radius of gyration of the aggregates R_g (circles). At t > 0.68 ms aggregation starts with aggregates of about 30 nm R_g. R_g stays constant till the end of the spray flame. R_g of the filter powder aggregates is about 140 nm. This is about 5 times larger than that measured at 1.85 ms (100 mm HAN), indicating aggregation on the filter.

While the aggregate size remains fairly constant in the flame, the weight average number of primary particles per aggregate, z (squares), steadily increases at a rate of 4.3/ms. The aggregates at 0.68 ms (50 mm HAB) consist of about 4 particles each that increase to 14 at 1.85 ms (100 mm HAN). This indicates that aggregates form first a linear structure and then start branching as discussed above. The product powder has about 64 particles per aggregate.

Despite turbulent sonic flows, spray jet flames display exceedingly uniform nanomaterial growth due to the confinement of nanoparticulate streams to a narrow, none expanding stream of about 1 mm diameter and due to extremely high cooling rates as high as 10 million degrees K/second! These conditions are far from equilibrium and provide kinetic locking-in of transient nanostructure. Particles grow quickly with a particle growth rate of about 6 µm/s at temperatures higher than 1600 K. The primary particle size at the nucleation event is about 2.5 nm in Sauter mean diameter which is the smallest particle directly observed in a flame and serves to indicate the potential of spray flame technology to produce controlled particles approaching the size of molecular clusters. Aggregation is a major feature of the zirconia spray jets with primary particle addition rates of about 4000 per second. Initial growth is linear (unbranched) possibly due to high turbulence. Later in the flame, non-linear aggregates form. Such linear growth has not been previously reported in lower flow rate flames.

- [1] T. Sugimoto, *Monodisperse particles*. 2001, New York: Elsevier.
- [2] D. Kashchiev, *Nucleation: basic theory with applications.* 2000, Boston: Butterworth-Heinemann.
- [3] C.R. Bickmore, K.F. Waldner, R. Baranwal, T. Hinklin, D.R. Treadwell and R.M. Laine, J. European Ceram. Soc., 1998, 18, 287.
- [4] S. Grimm, M. Schultz, S. Barth and R. Muller, J. Mater. Sci., 1997, 32, 1083.
- [5] J.J. Helble, J. Aerosol. Sci., 1998, 29, 721.
- [6] C.R. Bickmore, K.F. Waldner, D.R. Treadwell and R.M. Laine, J. Am. Ceram. Soc., 1996, 79, 1419.
- [7] W.J. Stark, L. M\u00e4dler, M. Maciejewski, S.E. Pratsinis and A. Baiker, *Chem. Commun.*, 2003, 588.
- [8] H. Schulz, L. M\u00e4dler, S.E. Pratsinis, P. Burtscher and N. Moszner, Adv. Funct. Mater., 2005, 15, 830.
- [9] R. Jossen, R. Mueller, S.E. Pratsinis, M. Watson and M.K. Akhtar, *Nanotechnology*, **2005**, 16, S609.P.W. Morrison, R. Raghavan, A.J. Timpone, C.P. Artelt and S.E. Pratsinis, *Chem. Mat.*, **1997**, 9, 2702.

- [10] R. Strobel, W.J. Stark, L. Mädler, S.E. Pratsinis and A. Baiker, *J. Catal.*, 2003, 213, 296.
 R.M. Laine, J.C. Marchal, H.P. Sun and X.O. Pan. *Nat. Mat.*, 2006, 5.
 - 710.
- [11] J. Marchal, T. John, R. Baranwal, T. Hinklin, R. M. Laine, *Chem. Mat.*, 2004, 16, 822.
 - R. M. Laine, J. Marchal, H. Sun, Z. Q. Pan, Adv. Mat., 2005, 17, 830.
- [12] R. Mueller, R. Jossen, H.K. Kammler, S.E. Pratsinis and M.K. Akhtar, *AIChE J.*, 2004, 50, 3085.
- [13] G. Beaucage, H.K. Kammler, R. Mueller, R. Strobel, N. Agashe, S.E. Pratsinis and T. Narayanan, *Nat. Mater.*, 2004, 3, 370.
- M.C. Heine and S.E. Pratsinis, *Ind. Eng. Chem. Res.*, 2005, 44, 6222.
 M.C. Heine, L. M\u00e4dler, R. Jossen and S.E. Pratsinis, *Combust. Flame*, 2006, 144, 809.
- [15] H.K. Kammler, G. Beaucage, D.J. Kohls, N. Agashe and J. Ilavsky, J. Appl. Phys., 2005, 97.
- [16] G. Beaucage, D. Londono, B. Diemer, Chem. Mat. 2007 (in Press).
- [17] L. Mädler, W.J. Stark and S.E. Pratsinis, *J. Mater. Res.*, 2002, 17, 1356.
 [18] P.E. Best, R.M. Carangelo, J.R. Markham and P.R. Solomon, *Combust.*
- Flame, 1986, 66, 47.
 [19] H.K. Kammler, S.E. Pratsinis, P.W. Morrison and B. Hemmerling, *Combust. Flame*, 2002, 128, 369.
- [20] P.R. Griffiths and J.A. Haseth, Fourier Transform Infrared Sprectroscopy. 1986, New York: John Wiley and Sons.
- [21] P.W. Morrison, R. Raghavan, A.J. Timpone, C.P. Artelt and S.E. Pratsinis, *Chem. Mat.*, **1997**, 9, 2702.
- [22] T. Narayanan, O. Diat and P. Bosecke, Nucl. Instrum. Methods Phys. Res. Sect. A-Accel. Spectrom. Dect. Assoc. Equip., 2001, 467, 1005.
- [23] D. Pontoni, T. Narayanan and A.R. Rennie, Langmuir, 2002, 18, 56.
- [24] G. Beaucage, J. Appl. Crystallogr., 1995, 28, 717.
- [25] G. Beaucage, Phys. Rev. E, 2004, 70, 031401.
- [26] G. Beaucage, H.K. Kammler and S.E. Pratsinis, J. Appl. Crystallogr., 2004, 37, 523.
- [27] H.K. Kammler, G. Beaucage, R. Mueller and S.E. Pratsinis, *Langmuir*, 2004, 20, 1915.
- [28] G. Beaucage, J. Appl. Crystallogr., 1996, 29, 134.
- [29] J. Hyeon-Lee, G. Beaucage, S. E. Pratsinis, Langmuir 1998, 14, 5751.
- [30] D. W. Schaefer, Science, 1989, 243, 1023.
- [31] R. Jullien and R. Botet, Aggregation and fractal aggregates. 1987, Singapore: World Scientific.
- [32] G. Porod (O. Glatter and O Kratky eds) in *Small-angle x-ray scattering*. 1982, London: Academic Press.
- [33] A. Guinier and G. Fournet, Small-Angle Scattering of X-Rays. 1955, New York: Wiley.
- [34] S.E. Pratsinis, T.T. Kodas, M.P. Dudukovic and S.K. Friedlander, Ind. Eng. Chem. Proc. Des. Dev., 1986, 25, 634.
- [35] D.O. de Zarate, C. Boissiere, D. Grosso, P.A. Albouy, H. Amenitsch, P. Amoros and C. Sanchez, *New J. Chem.*, 2005, 29, 141.
- [36] R. Mueller, R. Jossen, S.E. Pratsinis, M. Watson and M.K. Akhtar, J. Am. Ceram. Soc., 2004, 87, 197.
- [37] J.D. Landgrebe and S.E. Pratsinis, J. Colloid Interface Sci., 1990, 139, 63.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff)) Nanoparticle nucleation, growth and aggregation in liquid-feed flame spray pyrolysis is observed in situ using synchrotron radiation and small angle x-ray scattering. A well characterized nucleation event as well as linear growth rate and low-branch content aggregation are observed within the flame for the first time. The kinetics of nano-particle formation are observed on sub-millisecond time scales from sonic jets with heating and cooling rates on the order of 10^7 K/s.



COMMUNICATION

Growth of Nanoparticles in Liquid Spray Jets

Rainer Jossen, Gregory Beaucage*, Martin C. Heine, Theyencheri Narayanan and Sotiris E. Pratsinis

..... Page No. – Page No.

Nanomaterial growth dynamics in sonic jet spray flames