Nucleation and Nanoparticle Growth in Flame Aerosol Process by USAXS

Nikhil Agashe, Greg Beaucage, Doug Kohls – *Dept. of Chemical and Materials Engineering, University of Cincinnati.*
Hendrik Kammler, Rainer Jossen, Sotiris Pratsinis – *Institute of Process Engineering, ETH-Zurich.*
Pete Jemian, Jan Ilavsky – *UNICAT, APS, Argonne.* **Theyencheri Narayanan** – *High Brilliance Beamline ID02, ESRF, Grenoble.*

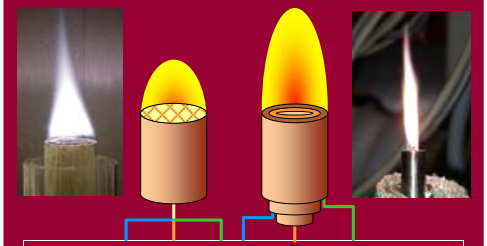
Abstract

Ultra small angle x-ray scattering (USAXS) is used as an in-situ technique to characterize titania particles made by high temperature flame method. Due to the extremely fast nature of the reaction and low concentrations associated with this process, it is difficult to accurately observe the formation of nuclei and their growth to form aggregated nanoparticles by thermophoretic sampling. The high brilliance of synchrotron radiation provides a method to study in situ particles at low concentrations. The Bonse-Hart camera of the USAXS instrument at UNICAT (APS, Argonne) and the pinhole camera of the SAXS instrument at beamline ID-02 (ESRF, Grenoble) can measure a wide range of size from nanometer (10^{-9} m) to micrometer (10^{-6} m) and make it possible to simultaneously examine evolution and morphology of these particles. Particle characteristics like the titania volume fraction, primary particle size, polydispersity in this particle size, number concentration, aggregate size and mass fractal dimension (d_f) are presented along the flame axis. The aggregates have complex mass fractal shapes which are joined by partial coalescence, ionic bonds and van der Waals forces.

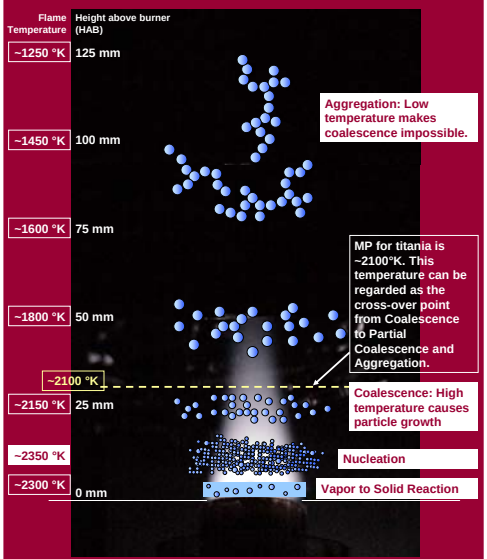
Nucleation and Particle Growth in Flame

Premixed Flame
Single Tube Reactor

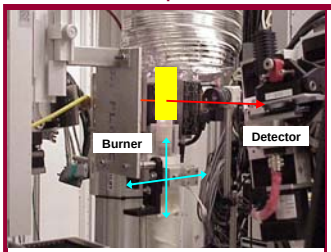
Diffusion Flame
Concentric Multitube Reactor



Reactants – Precursor, Fuel, O_2/Air, N_2 (diluent)



Burner Setup for In-situ Measurement



Bonse-Hart camera was used for in-situ measurements at UNICAT. Beam was 2mm wide by 0.4mm high. At ESRF, pinhole SAXS camera was used. Beam was 0.4 mm in diameter

Advantages of In-situ Study:

Insitu SAXS measurement serves as a better tool than thermophoretic sampling for study of nucleation and particle growth in flames.

The temperature of the flame is generally greater than the melting point of titania, and hence thermophoretic sampling does not guarantee that the collected particles are representative of the conditions in the flame.

USAXS Data Analysis – Unified Function

Power Law Decay – corresponds to the mass fractal aggregates; here d_f is the fractal dimension

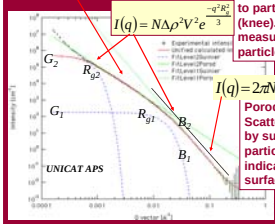
$$I(q) = Bq^{-d_f}$$

Guinier Regimes – Scattering due to particles (knee). R_g is a measure of particle size

$$I(q) = N\Delta\rho^2 V^2 e^{\frac{-q^2R_g^2}{3}}$$

Porod Law – Scattering caused by surface of particles. –4 Slope indicates smooth surface

$$I(q) = 2\pi N\Delta\rho^2 Sq^{-4}$$



$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

$$ParticleSize, R \sim \frac{1}{q}$$

$$d_{gs}(nm) = \frac{6000}{S/V} = \frac{6000}{\pi B_1/Q}$$

$$d_{g2}(nm) = 0.26R_{g2}$$

$$N = \frac{Q^2}{\Delta\rho^2 4\pi^2 G}$$

$$p = \left(\frac{R_s}{R}\right)^{d_f/c} = \left(\frac{R_s}{R}\right)^{d_{min}}$$

$$PDI = \frac{BR_g^4}{1.62G}$$

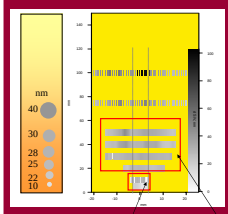
Unified Function yields 7 parameters: G_1, Rg_1, B_1, G_2, R_{g2}, B_2 and d_f. These values are used to calculate the particle size, polydispersity and number density of primary particles.

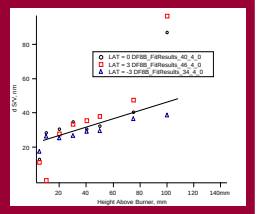
d_{min} and PDI give accurate estimate of polydispersity and aggregate structure

Reference:
Beaucage, G., *Journal of Applied Crystallography* **28** 717 (1995).
Beaucage, G., *Journal of Applied Crystallography* **29** 134 (1996).

Silica Diffusion Flame – ESRF

Particle Size

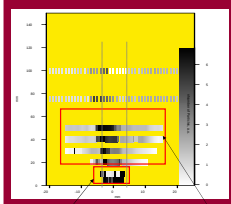


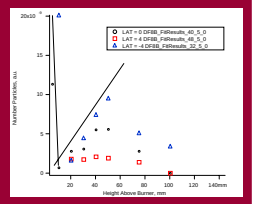


Particles grow in the flame due to coalescence at high temperatures.

Particles show linear growth outside the flame. Final particle size is about 60 to 80 nm.

Number Concentration

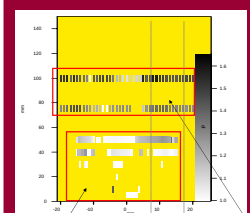


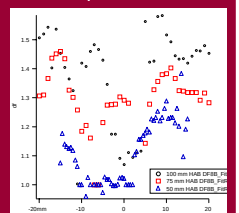


Nucleation can be seen at 2 mm HAB. This is seen by the spike in the number concentration at 2 mm HAB. This also results in lowering the average particle size.

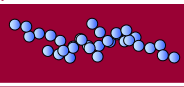
Secondary Nucleation takes place at 50 mm HAB.
The number density is also higher laterally outside the flame than that at the central axis.
Decrease in Number Concentration is due to combined effect of coalescence and lateral diffusion outside the flame..

Fractal Dimension (d_f)





Particles in the flame are linear and non-aggregated indicating sintering and coalescence. Coalescence results in complete joining of particles to form a bigger particle.



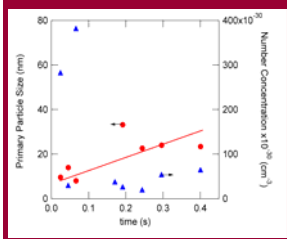
The aggregate dimension increases further outside the flame. This is because in this zone aggregation dominates coalescence.

d_f also increases in the lateral direction. As the particles diffuse laterally outside the flame, they experience lower temperatures resulting in partial coalescence and aggregation

Titania Premixed Flame – UNICAT/APS

Height above burner (HAB) can be converted to residence time of the particles in the flame by using total initial flow rate and flame temperature. Results in this section are presented vs. residence time of particles in flame as opposed to HAB as is the convention.

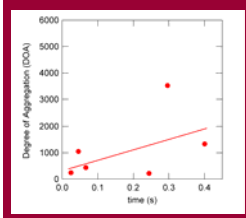
Particle Size & Number Concentration



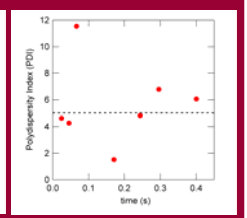
Primary particle grows steadily with time in the flame. from 10 nm initially to about 35 nm. Final particle size was 25 nm.

The sudden increase in Number Concentration denotes the nucleation event. (Note the corresponding decrease in average particle size). Decrease in number density is due to Coalescence and lateral diffusion.

Degree of Aggregation



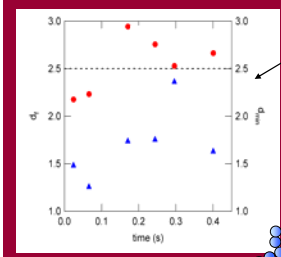
Polydispersity Index



DOA remains low at first in the high temperature region of the flame (Coalescence); it increases high above in the flame where the particles experience lower temperatures (Aggregation).

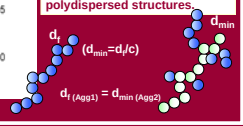
Polydispersity Index (PDI) is high initially (Nucleation leads to formation of nuclei of different sizes). But PDI then decreases with time as we go higher in the flame (Sintering).

Fractal and Minimum Dimension

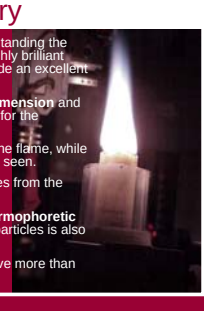


Powder Aggregates are mass fractal in nature. Fractal dimension remains around 2.5

Aggregates are linear and polydisperse low in the flame. They then coalesce to form branched monodispersed structures. Outside the flame, the particles again form linear polydispersed structures.



Summary



- **In situ studies** are very important in understanding the behavior of the particle in the flame. The highly brilliant beams at the APS and ESRF facilities provide an excellent opportunity to carry out these studies.
- **Nucleation, particle growth, aggregate dimension** and **aggregate characteristics** were evaluated for the important zones in the flame.
- **Particle growth** takes place completely in the flame, while further out **aggregation** of these particles is seen.
- **Lateral diffusion** of particles and aggregates from the center of the flame is also observed.
- **In-situ method is more effective than thermophoretic sampling**, as really low number density of particles is also detected.
- This is a **modern technique** that can achieve more than thermophoretic sampling.

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