From agglomerates to aggregates by sintering – coalescence

Sotiris E. Pratsinis
Particle Technology Laboratory
Department of Mechanical and Process Engineering, ETH Zürich, Switzerland
www.ptl.ethz.ch

Sponsored by
European Research Council,
U.S. and Swiss National Science Foundation,
Swiss Commission for Technology and Innovation
Aerosol-made nanostructured materials

Tires (~30 wt%)

Carbon Black

Paints

Optical fibers

TiO$_2$

Inks

Ni for batteries

4 - 8 m$^2$/g

ZnO as vulcanizing agent

Flowing aid

SiO$_2$

Courtesy of Umicore

Courtesy of Dupont

Courtesy of Inco

Courtesy of Cabot
Volcanic Aerosols


Iceland, April, 2010

Exhaust aerosols

Power Plant Ply ash

AluminoSilicate, by Esther Coz of CIEMAT/IDAEA-CSIC at RJ Lee Group, Inc.
Advantages of aerosol synthesis of materials

1. No liquid by-products

2. Easier particle collection from gases than liquids

3. High purity products

4. Special morphology facilitating reactant & product transport to & from the catalyst surface

5. Efficiency: Few and fast unit operations
Synthesis of heterogeneous catalysts

1. Process Efficiency

2. Novel (e.g. metastable) materials

Advantages of aerosols in materials synthesis


1. No liquid by-products
2. Easier particle collection from gases than liquids
3. High purity products
4. Special morphology (fillers in composites)
5. Efficiency: Few and fast unit operations
6. Unique metastable phases by rapid heating-cooling
7. Transport (e.g. diffusion) in gases is better understood facilitating process design from *first principles*. 
Sensors

Some future aerosol-made materials

Catalysts

Flame aerosol synthesis of smart nanostructured materials *J. Mater. Chem.* 17, 4743 - 56 (2007)
Micropatterning Layers by Flame Aerosol Deposition - Annealing


Wafer-level flame-spray-pyrolysis deposition of gas-sensitive layers on microsensors J.
Diabetes monitoring by acetone breath analysis


ETH Zurich & Innsbruck Medical Univ.
Dental fillers & bone replacement

Catalysts

Sensors

Advanced Pigments

some future aerosol - made materials

C-LiFePO₄

Flame aerosol synthesis of smart nanostructured materials J. Mater. Chem. 17, 4743 - 56 (2007)

Batteries

Phosphors

Nutrition

SPION/Ag
**Magnetization of silica-coated Ag/Fe$_2$O$_3$**

- Comparable magnetization for pure flame-made Fe$_2$O$_3$\(^1\)
- Lower magnetization for \(x = 50\) wt% Ag
  - Higher \(\alpha\)-Fe$_2$O$_3$ content
- Near superparamagnetic behavior

---

Flame aerosol reactors for synthesis up to 1 kg/h of Nanocomposite particles

Flame Spray Pyrolysis Reactor & Control Unit

Baghouse filter

Flame aerosol synthesis of smart nanostructured materials *J. Mater. Chem.*, 17, 4743 (2007)
Biofunctionalization – Cell detection

Absorbance, a.u.

Wavelength, nm

400 450 500

Δλ

35Ag/Fe$_2$O$_3$

SiO$_2$

Ag

Fe$_2$O$_3$

Raji cells

Untagged Raji + labeled particles

Tagged Raji + labeled particles

Tagged HeLa + labeled particles

20 μm

20 μm

20 μm

20 μm

Dl

35Ag/Fe$_2$O$_3$

10 nm


Flame reactor pilot plant, Johnson Matthey Research Center, Reading, UK

Aggregates and Agglomerates

Chemical or Sinter-forces

Catalysts, lightguides, devices
Less toxic?

Nanocomposites, paints
Potentially toxic?

Physical (e.g. vdW) forces

Current instruments cannot distinguish them

Flame-made SiO$_2$ agglomerates and aggregates

The Structure of Agglomerates consisting of Polydisperse Particles

The Structure of Agglomerates consisting of Polydisperse Particles

Scaling of Agglomerate Structure

\[ m \propto r^3 \]

\[ m \propto r^D \]
Characteristic Agglomerate Radius

Mass fractal dimension\(^1\),
\[
D_f = \frac{m}{m_p} = k_n \left( \frac{r_g}{r_p} \right)^{D_f}
\]

Mass-mobility exponent\(^3\),
\[
D_{fm} = \frac{m}{m_p} = k_m \left( \frac{r_m}{r_p} \right)^{D_{fm}}
\]

Radius of gyration

Cluster-cluster\(^2\):
\[D_f \approx 1.8\]

Mobility radius
\[
r_m = \sqrt{\frac{a_a}{\pi}}
\]

Cluster-cluster\(^2\):
\[D_{fm} \approx 2.15\]

Sintering by Viscous Flow

1. Energy balance\(^1\)
\[ \gamma \frac{dA_i}{dt} = \iiint 3\eta \dot{\varepsilon}^2 \, dV_i = 3\eta \dot{\varepsilon}^2 V_i \]

Change in surface energy = viscous dissipation

2. Mass balance\(^2\)
\[ \frac{dV_i}{dt} = 0 \]

Sintering - Coaleascence
Evolution of $D_f$ & $D_{fm}$

Ensemble average over 200 clusters with 16-512 PPs

Projected Area of Aggregate\textsuperscript{1} during Sintering

\[ n_{va} = k_a \left( \frac{a_a}{a_{va}} \right)^{D_a} \]

\( a_a \): projected area

\( d_{va} \): average PP diameter

\[ d_{va} = d_{BET} = \frac{6v}{a} \]

\( n_{va} \): average number of PPs

\[ n_{va} = \frac{v}{\pi d_{va}^3 / 6} \]

Projected Aggregate\textsuperscript{1} Area during Sintering

\[ n_{va} = k_{a} \left( \frac{a_{a}}{a_{va}} \right)^{D_{a}} \]

1. A.I. Medalia, J. Colloid Interface Sci. \textbf{24} 393-404 (1967).
Projected Aggregate\textsuperscript{1} Area during Sintering

\[ k_a = 1 \text{ & } D_\alpha = 1.07 \text{ are practically independent of sintering mechanism} \]

grain boundary diffusion\textsuperscript{3}

viscous flow sintering\textsuperscript{2}

\[ n_{va} = k_a \left( \frac{a_a}{a_{va}} \right)^{D_\alpha} \]

### Mass - Mobility Relation

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface area mean diameter</strong>:</td>
<td></td>
</tr>
<tr>
<td>( d_{va} = \frac{6v}{a} )</td>
<td></td>
</tr>
<tr>
<td><strong>Average number of primary particles</strong>:</td>
<td></td>
</tr>
<tr>
<td>( n_{va} = \frac{v}{v_{va}} )</td>
<td></td>
</tr>
<tr>
<td><strong>Scaling of projected aggregate area</strong>:</td>
<td></td>
</tr>
<tr>
<td>( n_{va} = k_{a} \left( \frac{a_{a}}{a_{p}} \right)^{D_{a}} )</td>
<td></td>
</tr>
<tr>
<td>( a_{a} = \text{projected aggregate area} )</td>
<td></td>
</tr>
<tr>
<td><strong>Mobility in free molecular and transition regime</strong>:</td>
<td></td>
</tr>
<tr>
<td>( d_{m} = \sqrt{\frac{4a_{a}}{\pi}} )</td>
<td></td>
</tr>
</tbody>
</table>

**Surface area mean diameter from mobility size and volume**

\[
d_{va} = \left( \frac{\pi k_{a}}{6v} \left( d_{m} \right)^{2D_{a}} \right)^{1/(2D_{a}-3)}
\]

Characterization of ZrO$_2$ Nanoparticles

Measure:

\[ d_{\text{BET}} \]

\[ d_p \]

\[ d_m \]

\[ m \]

\[ d_{va} = \left( \frac{\pi k_a}{6v} \left( d_m \right)^{2D_a} \right)^{1/3D_a} \]

Reality Check: Effect of Liquid Precursor Feed Rate on $d_p$ & $D_f$

**X/Y Flame**

X: precursor feed liquid (ml/min)
Y: dispersion gas (l/min)

Increasing liquid precursor feed rate results in faster sintering & coagulation.¹

---

Effect of Precursor Feed Rate: Mass-Mobility

\[ D_{fm} \approx 2.15: \text{agglomerates or aggregates at beginning of sintering} \]

Effect of Liquid Precursor Feed Rate: $d_{va}$

$d_{va}$ can be rapidly determined during nanoparticle production by DMA-APM measurements.

\[
d_{va} = \left( \frac{\pi k_a}{6v} \left( d_m \right)^{2D_a} \right)^{1/(2D_a-3)}
\]

Increasing $O_2$ flow rate dilutes the aerosol & shortens the high temperature particle residence time resulting in smaller particles$^1$

$$d_{va} = \left(\frac{\pi k_a}{6v} (d_m)^{2D_a}\right)^{1/(2D_a-3)}$$


Formation & Filtration of Nanoparticles

Structures at $t_{cl}$ vs $Pe$

Increasing $\phi_{sd}$

Void conical structure

Conclusions

• The polydispersity of primary particles opens the structure of their agglomerates while, in contrast, sintering forms more compact aggregates.

• The primary particle diameter, \(d_{va}\), can be obtained online by mass-mobility measurements by

\[
d_{va} = \left(\frac{\pi k_a}{6v} \left( d_m \right)^{2D_a} \right)^{1/(2D_a - 3)}
\]

regardless of material composition or sintering rate, in agreement with ex-situ \(N_2\) adsorption & microscopy.

• Aggregates are distinguished from agglomerates.
Thank you for your attention