Functional Nanoparticles made in Flames: Synthesis of Core-Shell Nanoparticles

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Overview

Aggregates & Agglomerates

Core-Shell Nanoparticles

Summary & Research Opportunities
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. Unique metastable phases by rapid heating-cooling (e.g. low T BaCO$_3$ for NOx storage-reduction)

6. Efficiency: Few and fast unit operations
Synthesis of Pt/Al₂O₃ catalysts

Catalysts

Fuel Cells

Batteries

Sensors

Advanced Pigments

Nutrition

some future aerosol - made materials

Phosphors

Bio: dental fillers & bone replacement
Flame aerosol reactors for synthesis up to 1 kg/h of Nanocomposite particles

Flame Spray Pyrolysis Reactor & Control Unit

Baghouse filter

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Aggregates and Agglomerates

Chemical or Sinter-forces

Catalysts, lightguides

Less toxic?

Current aerosol instruments cannot distinguish them

Nanocomposites, paints

Potentially toxic?
Fumed SiO₂ by Flame Hydrolysis of SiCl₄

\[ SiCl₄ \rightarrow O_2, H_2 \rightarrow \text{Hydrolysis (endothermic) + cooling} \]

Solid fraction \[ \phi \sim 10^{-4} \]
Nucleation, Coagulation and Sintering

Agglomerate Number:

Total Surface area:

\[
\frac{dN}{dt} = N_{i-1} \sum_{j=1}^{i-2} 2^{j-i+1} \beta_{i-1,j} N_j + \frac{1}{2} \beta_{i-1,i-1} N_{i-1}^2 - N_i \sum_{j=1}^{i-1} 2^{j-i} \beta_{i,j} N_j - N_i \sum_{j=i}^{\text{max}} \beta_{i,j} N_j
\]

\[
\frac{dA}{dt} = \sum_{j=1}^{i-2} \beta_{i-1,j} w_{i-1,j} \left( A_j N_{i-1} + N_j A_{i-1} \right) + \beta_{i-1,i-1} A_{i-1} N_{i-1}
\]

\[
- \sum_{j=1}^{i-1} \beta_{i,j} \left( w_{i,j} N_j A_i - (1 - w_{i,j}) A_j N_i \right) - A_i \sum_{j=i}^{\text{max}} \beta_{i,j} N_j - \frac{1}{\tau_{s,i}} (A_i - N_i \alpha_{i,s})
\]

\[
w_{i,j} = \frac{2^j}{2^{j-1} + 2^{i-2}}
\]

Coagulation
(Hounslow et al. 1988; Prakash et al. 2003)

Sintering
(Koch & Friedlander, 1990)
Monodisperse Silica Aerosol Dynamics for SiCl$_4$ Oxidation, Coagulation and Sintering

Total Number Concentration
\[
\frac{dN}{dt} = - \frac{1}{2} \beta N^2 \rho_g - \frac{d[\text{SiCl}_4]}{dt}
\]

Total Surface Area Concentration
\[
\frac{dA}{dt} = - \frac{d[\text{SiCl}_4]}{dt} \alpha_m - \frac{1}{\tau_s} (A - N \cdot \alpha_s)
\]

Total Volume Concentration
\[
\frac{dV}{dt} = - \frac{d[\text{SiCl}_4]}{dt} v_m
\]

Particle Size Evolution during SiO₂ Synthesis

Comparison with data of non-aggregated TiO$_2$

![Graph showing comparison with data of non-aggregated TiO$_2$]
High Effective Agglomerate Volume Fraction

Collision diameter, $d_c$ (nm)
Primary particle diameter, $d_p$ (nm)
Effective agglomerate volume fraction, $\phi_{eff}$ (%)

$D_f = 1.8$

$\phi_{eff} = N \frac{\pi}{6} d_c^3 \geq \phi_s$

$\phi_s < 0.01\%$

Derivation of the Collision Frequency Function
(Brownian Continuum Regime)

Model assumptions:
- Equilibrium particle concentration profile
- Sufficiently dilute concentrations

\[ \beta_{i,j} = 2\pi (d_i + d_j)(D_i + D_j) \]

At high particle concentrations the key model assumptions are no longer valid

M. Smoluchowski (1917)
Langevin Dynamics (LD) Simulations

**Equation of particle motion:**

\[ m_i \ddot{v} + \frac{3\pi \eta d_i}{C_i} v + F_{\text{Brownian}} = 0 \]

**Numerical solution procedure:**

Ermak and Buckholz (1980)
Gutsch et al. (1995)

**Validation of particle trajectories:**

3 dimensional particle trajectories allow calculation of the diffusion coefficient \( D \)

\[ 3D = \frac{\langle x^2 \rangle}{2t} \]

\( D \) is identical to theoretical value (±0.01%)
Polydispersity for Dilute Concentrations

Langevin dynamics simulations:
\[ \sigma_n \approx 1.45 \]
\[ \sigma_v \approx 1.30 \]

Vemury et al. (1994)
\[ \sigma_n = 1.445 \]
\[ \sigma_v = 1.28 \]

Xiong & Pratsinis (1991)
Validation: Attainment of Self-preserving Size Distribution

CONDITIONS:
T = 293 K
p = 1 bar

2000 monodisperse particles
D_f = 3
d_0 = 1 μm
ρ_p = 1 g/cm^3
N_0 = 2 x 10^9 #/cm^3

Brownian Continuum Regime
Polydispersity of Coagulating Aerosols at High Concentrations

$\phi_s = 20\%$

$\sigma_n$

$\sigma_v$

Geometric standard deviation, $\sigma$

Normalized geometric mean diameter, $d_n/d_0$

Run 1
Run 2
Run 3
Dilute limit

Self-preserving Size Distribution broadens with increasing volume fraction $\phi_s$

![Graph showing normalized particle diameter, $d_i/d_n$, against solid volume fraction, $\phi_s$, and geometric standard deviation, $\sigma$.]
Coagulation Rate of Highly Concentrated Polydisperse Aerosols

\[ \beta_{LD} \approx 1 + \frac{2.5}{1 - \phi} \left( -\log \phi \right)^{-2.7} \]

- This work
- This work, regression
- Vemury et al. (1994)

<table>
<thead>
<tr>
<th>Solid volume fraction, ( \phi_s ) (%)</th>
<th>( \beta_{LD}/\beta_{dilute} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01%</td>
<td>± 0%</td>
</tr>
<tr>
<td>0.1%</td>
<td>+ 8%</td>
</tr>
</tbody>
</table>

Fractal-like Particles: Volume Fraction during Coagulation

- Effective agglomerate volume fraction, $\phi_{\text{eff}}$
- Time, s

Graph showing $\phi_{\text{eff}}$ for $D_f = 1.8$ and $D_f = 3.0$

- $\phi_s = 0.03\%$
- $d_0 = 220 \text{ nm}$
- $N_0 = 5.4 \times 10^{10} \#/\text{cm}^3$
Rate of Coagulation of Fractal-like Particles

Light scattering measurements during aerogelation of fractal soot clusters:

Coagulation kinetics are more than 100 times faster than predicted by the classic dilute theory

(Sorensen et al., 1998)
“Gelation” is attained within 3 – 4 seconds.

Fluid flow, however, promotes restructuring & fragmentation

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Vapor-fed flame synthesis (chloride process) of pigmentary TiO$_2$:
~ 2 million tons/year$^{[1]}$

Segregation in co-oxidized SiO$_2$/Al$_2$O$_3$/TiO$_2$

Co-oxidation of Si/Ti precursors leads to segregation and separate SiO$_2$ and TiO$_2$ particles$^{[1]}$.

Apparatus for *in-situ* coating

![Diagram of the apparatus](image_url)

1. Si injection point
   - 20 wt% SiO₂, 15 l/min N₂
2. SiO₂ content
   - 15 l/min, 20 cm BRD
3. Mixing intensity
   - (N₂ flow rate)
4. Co-oxidized SiO₂/Al₂O₃/TiO₂
   - 15 l/min, 20 cm BRD
5. 25 g/h: 4 wt% Al₂O₃/TiO₂

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Particle Composition

Consistent precursor delivery and product composition

Photooxidation of isopropanol (IPA) to acetone

Photooxidation of isopropanol (IPA) to acetone

Photooxidation of isopropanol (IPA) to acetone

Premature Si injection results in separate SiO₂ and poorly-coated TiO₂.

The Mixing Intensity

15.8 l/min Si-laden N₂

$v_0 = 58$ m/s

The Mixing Intensity
15.8 l/min Si-laden N₂
\( v_0 = 58 \text{ m/s} \)

\[
\begin{align*}
35 & \quad 10.8 \text{ l/min} & \quad 40 \text{ m/s} \\
5.8 & \quad 21 \text{ m/s} \\
\end{align*}
\]
SiO$_2$ Content on Photoactivity

\[ \text{μg Acetone/ml IPA} \]

- **coating process**
- **co-oxidized**

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \]

\[ 0 \quad 50 \quad 100 \quad 150 \quad 200 \quad 250 \quad 300 \]

\[ \text{SiO}_2 \text{ wt\% fraction} \]
Increasing coating thickness

Theoretical coating thickness
5 wt% SiO$_2$: < 1 nm
20 wt% SiO$_2$: 2.7 nm
Homogeneous, Smooth Coatings – No separate SiO$_2$

20 wt% SiO$_2$
Aqueous suspensions of product particles

Zeta potential $\zeta$, mV

Isoelectric point (IEP)

- pH 1.7
- pH 7.7

pure Al/TiO$_2$

pure SiO$_2$
Coated particles: $\zeta$ Potential & SiO$_2$ Content

Very thin or partial coatings at 2.5 - 5 wt% SiO$_2$.

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Co-oxidized particles: $\zeta$ potential - SiO$_2$ Content

The IEP shifts towards lower pH as the SiO$_2$ content increases and large SiO$_2$ domains are formed.

August 14, 2008
Chemical structure of particle surface

Shift of the Si-O-Si 1100 cm\(^{-1}\) band and high intensity of 1225 cm\(^{-1}\) band attributed to Si-O-Si bond strain\([1,2]\).

The bond strain is reduced as coating thickness increases.

Conclusions

- A process was developed for *in-situ* coating of flame-made particles.
- Turbulent mixing, > 10 wt% SiO$_2$ and Si precursor vapor injection point above the TiO$_2$ formation zone led to smooth and homogeneous SiO$_2$ coatings 2 – 4 nm thick on TiO$_2$.
- SiO$_2$-coated TiO$_2$ particles exhibited limited photoactivity.
- The extent of SiO$_2$ surface coverage was determined electrophoretically.
- Overview

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- Coating of Particles

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Summary

Gas-phase synthesis contributes to new materials & processes

Synthesis of simple oxides is well understood for scale-up as primary particle and aggregate sizes made by coagulation and sintering can be determined from first principles.

Functional nanoparticles with tailor-made characteristics are made for catalysts, sensor & biomaterials.

Key concept: the high temperature residence time distribution of the particles (aggregates vs. agglomerates)
Research Opportunities

Understanding flame synthesis of mixed materials,
Tailored-morphology (solid or layered) particles,
Focus on performance-based characteristics
Health effects of flame-made materials
Thank you for your attention!

Saas Fe, March 2007