Processes for the production of nanoparticles

Production processes

in a liquid phase

Precipitation process
- in homogeneous solution
- in surfactant based systems

Sol-gel process

Hydrothermal process

in a gaseous phase

Aerosol process
- Flame hydrolysis
- Spray pyrolysis
Educts

Nucleus formation

Critical supersaturation
Mixing of educts, temperature, etc.

Nucleus

Growth

Integration or diffusion-limited particle growth

Primary particle

Agglomeration
Deagglomeration

Transport mechanism
diffusion or convection-controlled
Particle interaction
van-der-Waals attraction
electrostatical / steric repulsion
Agglomerate structure
Euclidical geometry, fractals

Agglomerate

Stabilisation of the nanoparticles against agglomeration!
**Thermodynamics of nanoparticle formation**

**Gibbs energy** $\Delta g$

\[ \Delta g_{\text{surf}} = 4 \pi r^2 \sigma \]

\[ \Delta g_{\text{max}} = \frac{1}{3} \Delta g_{\text{surf}} \]

1. $r < r^*$ nuclei dissolve
2. $r > r^*$ nuclei are able to reduce Gibbs energy by growing

**Critical radius of nucleus:**

\[ r^* = \frac{2 \sigma}{RT \ln S} \frac{M}{\rho} \]

**Concentration of critical nuclei:**

\[ N^* = N_0 \exp \left( -\frac{16 \pi \sigma^3 M^2}{3 kT \rho^2 (RT \ln S)^2} \right) \]
Model of LaMer and Dinegar (1950)

- Fast homogeneous nucleation
- Critical supersaturation $C_0$
- Growth process by diffusion
- Supersaturation
- Saturation concentration $C_S$

$C_0$

$C_S$

Process time
Different approaches to synthesise nanoparticles in liquids

- Organic monomers
  - Polymerisation as emulsion
  - Polymerisation as suspension
  - Latex

- Inorganic salts
  - Hydrolysis
  - Sol

- Inorganic monomers
  - Oligomerisation
  - Polycondensation
  - Sol

- Metal organic compounds
  - Polycondensation
  - Sol

Examples:
- PS: 0.1 - 1000 μm
- PMMA: 0.3 - 1000 μm
- MF: 1.0 - 1000 μm
- Al₂O₃
- TiO₂
- ZrO₂
- Fe₂O₃

- Monomer, ions etc.
  - Nucleation
  - Growth
  - Primary particles
  - Ostwald ripening
  - Agglomeration and redispersion
  - Agglomerates

Microparticles GmbH
Chemical and physical processes for nano particle synthesis

Process: precipitation – in homogeneous solution
synthesis of silver bromide

Chemical reaction:

\[ \text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr} \]

Principle: precipitation (Controlled double jet precipitation CDJP - technique)

Precipitation homogeneous solution - controlled double jet precipitation CDJP
nucleus formation, followed by growth reaction and Ostwald ripening

Particle size: \( \text{AgBr : 7 nm - 60 nm, particle system dependent} \)
a lot of syntheses on a laboratory scale

T. Sugimoto: J. Colloid Interface Sci. 150 (1992) 208 - 225
Precipitation reactions in homogeneous solution

AgBr – nanoparticle, produced by CDJ - technique at pBr 2.0 (a), 2.8 (b), 4.0 (c)

Images (scanning electron microscopy) of typical monodisperse nanoscale oxides by conversion of metal alkoxides in alcoholic solution
Precipitation reactions in homogeneous solution

Images (transmission electron microscopy left - scanning electron microscopy right) of CdS – nanoparticles, produced in homogeneous solution at 26°C by CDJ - technique

Image (scanning electron microscopy) of PbS – nanoparticles, produced in homogeneous solution at 26°C by CDJ - technique
Precipitation reactions in homogenous solutions

Scanning electron microscopy image of aluminium(III)-oxide, 100°C, left
Transmission electron microscopy image of chromium(III)-oxide, 75°C, right,
produced by precipitation reaction in homogeneous solution

Images (scanning electron microscopy) of zinc oxide, 90°C, pH 8,8 (left) and 150°C, pH 13,3 (right), produced by precipitation reaction in homogeneous solution
Generation of nanoscaled barium sulphate

Process: Precipitation in homogeneous solution \[ \text{Nucleation - Growth} \]

Goal: Nanoscaled particle size distribution (as monodisperse as possible, stabilised)

Theoretical basics and experimental approach:

Chemical reaction:

\[
\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4
\]

Concentration of reactants:

\[ 0.01 \text{ mol/L} \ldots 0.5 \text{ mol/L} \]

\[
S_c = \sqrt{\frac{c_{\text{Ba}^{2+}} \cdot c_{\text{SO}_4^{2-}}}{K_L}}
\]

Concentration based initial supersaturation \( S_c \): \(500 \ldots 25,000\)

Molar ratio of reactants \( R \): \(1 \ldots 10\) (excess of \(\text{Ba}^{2+}\) ions)

Stabilisation: electrostatic (excess of \(\text{Ba}^{2+}\) ions)

Sterical (0.03 g dispersing agent / g \(\text{BaSO}_4\))

Dispersing agent: Melpers 0030:- 30 % w/w Polyethylenecarboxylate

Process parameter: concentration based initial supersaturation \( S_c \)

- molar ratio of reactants \( R \)
- feed rate and mixing
- concentration of dispersing agent

Discontinuous stirred tank reactor

- Stirrer rotational speed 800 min\(^{-1}\)
- Tank reactor volume 1000 ml

Characterisation of particle sizes

- Dynamic light scattering
- Scanning electron microscopy

**Particle size distributions during the precipitation process of BaSO₄**

Influence of the feed rate of potassium sulphate solution on the particle size distribution $Q_0(d)$ of the precipitated BaSO₄ particles

**Method:** Dynamic light scattering

**Instrument:** Horiba LB 500

**Educts:** 0.2 mol/L, $S_c=10,000$, $T=25°C$

0.03 g dispersing agent / g BaSO₄

**Mean agglomerate diameter $d_{50,0}$**

Feed rate of $K_2SO_4$

- 5 mL/min $d_{50,0} = 227.8$ nm
- 10 mL/min $d_{50,0} = 208.2$ nm
- 20 mL/min $d_{50,0} = 178.9$ nm
- 40 mL/min $d_{50,0} = 121.5$ nm
- 80 mL/min $d_{50,0} = 105.3$ nm

**Influence of the feed rate of potassium sulphate solution on the particle size distribution $Q_0(d)$ of the precipitated BaSO₄ particles**
**Particle size distributions during the precipitation process of BaSO₄**

**Method:** Dynamic light scattering  
**Instrument:** Horiba LB 500

**Educts:** 0.05 mol/L - 0.5 mol/L, R=1  
Sc = 2,500 … 25,000, 25°C  
0.03 g dispersing agent / g

**Mean agglomerate diameter:**

- **Sc = 2,500**  
  \[d_{50,0} = 208.9 \text{ nm}\]
- **Sc = 5,000**  
  \[d_{50,0} = 151.4 \text{ nm}\]
- **Sc = 10,000**  
  \[d_{50,0} = 123.9 \text{ nm}\]
- **Sc = 15,000**  
  \[d_{50,0} = 109.0 \text{ nm}\]
- **Sc = 20,000**  
  \[d_{50,0} = 101.4 \text{ nm}\]
- **Sc = 25,000**  
  \[d_{50,0} = 82.5 \text{ nm}\]
Particle size distribution during the precipitation process of BaSO₄

Influence of the molar ratio R on the particle size distribution \( Q_0(d) \) of the precipitated BaSO₄ particles

Method: Dynamic light scattering

Instrument: Horiba LB 500

Educts: 0.2 mol/L barium chloride

0.05 mol/L-0.5 mol/L sulphate

\( S_c = 2,500 \ldots S_c = 8,000, 25^\circ C \)

without dispersing agent

Mean agglomerate diameter:

\[
\begin{align*}
R = 1 & \quad d_{50,0} = 3,781.3 \text{ nm} \\
R = 2 & \quad d_{50,0} = 506.0 \text{ nm} \\
R = 4 & \quad d_{50,0} = 155.8 \text{ nm} \\
R = 6 & \quad d_{50,0} = 121.9 \text{ nm} \\
R = 8 & \quad d_{50,0} = 100.9 \text{ nm} \\
R = 10 & \quad d_{50,0} = 92.9 \text{ nm}
\end{align*}
\]
Structure of precipitated barium sulphate agglomerates

Scanning electron microscopy image of barium sulphate agglomerates (without dispersing agent)

Method: Scanning electron microscopy (SEM), concentration of reactants: 0.5 mol/L, R= 1, $S_c = 25,000$, $T = 25 \, ^\circ\text{C}$, addition of barium chloride to potassium sulphate, 80 mL/min, without dispersing agent
Particle size distributions during the precipitation process of BaSO4

Particle size distributions $Q_0(d)$ of precipitated BaSO4, with and without dispersing agent, sizes were determined with dynamic light scattering (DLS) and scanning electron microscopy (SEM).

Method: Dynamic light scattering
Scanning electron microscopy

Educts: 0.5 mol/L, R=1, $S_c =25,000$

$25 \degree C$, 80 mL/min

with/without dispersing agent (0.02 g/g)

Mean agglomerate diameter:

with dispersing agent: $d_{50,0} = 82.0$ nm

without dispersing agent: $d_{50,0} = 1,498.2$ nm (DLS)

$d_{50,0} = 79.0$ nm (SEM)