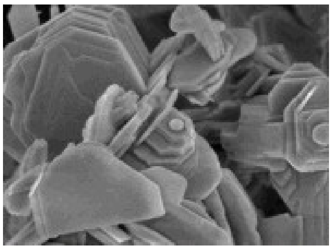
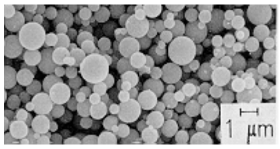
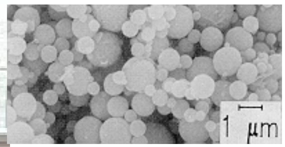
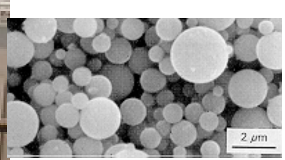
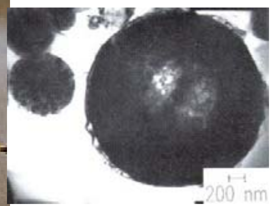


Aerosol processes









Gas phase powder synthesis

- Do not involve large volumes of liquid (compared to wet processes)
- Time scale very short
- High purity, high yield, high throughput
- Multicomponent and nanophase materials possible

Produced: titania, silica, carbon black… millions of tons/year

The aerosil process: (1942, Degussa)
Flame hydrolysis:

$$2H_2 + O_2 \rightarrow H_2O$$
$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

total: $SiCl4 + 2H2 + O2 \rightarrow SiO2 + 4HCl$

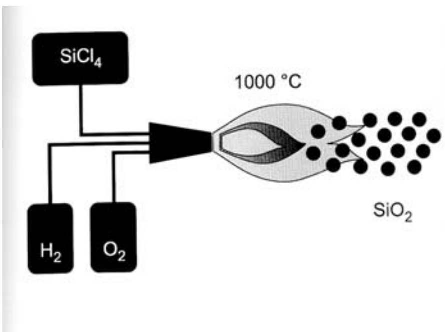


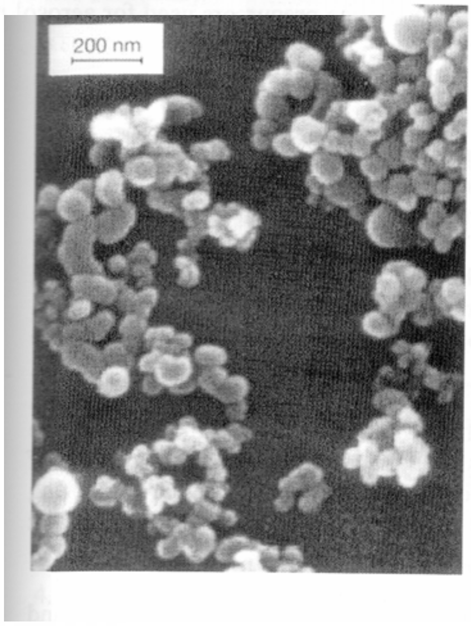
Figure 3-27. Formation of silica by the Aerosil process.

Aerosil

Product: 7-40 nm particles,
Surface area: 50-400m2/g,
S = 6/(d*ρ)
(surface, not pores)
200L ~ 10 kg

Fumed titania also produced (pigments)

Figure 3-29. Scanning electron micrograph of fumed silica with a primary particle size of 40 nm and a specific surface area of 50±15 $m^2 \cdot g^{-1}$ (Aerosil® OX 50 of Degussa–Huels).



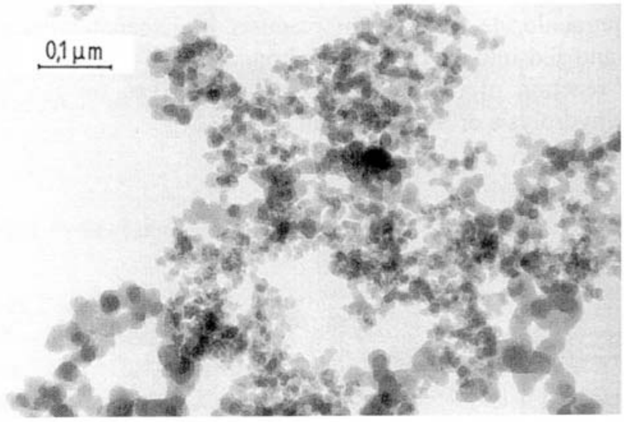


Figure 3-28. Transmission electron micrograph of fumed silica with a primary particle size of 16 nm and a specific surface area of 130 ± 25 $m^2 \cdot g^{-1}$ (Aerosil® 130 of Degussa–Huels).

Aerosol process routes

1. Gas-to-particle conversion. High temperature reaction between gases
2. Spray pyrolysis. Precursor particles or droplets are converted to powder product. Reaction with gaseous species or pyrolysis.

Precursors often similar to those used in CVD and PVD

- **Coagulation**: Attachment of two particles when they collide
- **Coalescence**: Fusion (sintering) of two particles
- **Agglomerates**: Assemblies of primary particles physically held together by weak interactions. (Soft agglomerates)
- **Aggregates**: Assemblies of primary particles held together by stronger chemical bonds. Hard agglomerates.

Gas-to-particle conversion

1. Homogeneous gas phase reactions. Formation of molecular or cluster compounds
2. Nucleation. Formed from supersaturated vapour. Homogeneous nucleation from molecules or clusters.
3. Particle growth. Nuclei grow by several mechanisms. E.g. condensation, surface reactions, coagulation… The relative rates of particle collision, coalescence and sintering are important for the shape of the obtained particles.

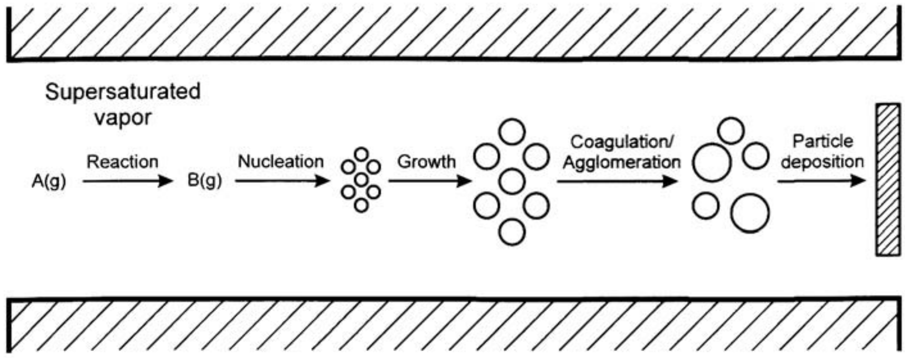


Figure 3-30. Particle generation by gas-to-particle conversion.

Spray pyrolysis

A solution or slurry is atomized and passes through a heated area.
Solvents evaporate, particles pyrolyze or react to form the product powder.
The size of the particles depends on the size of the droplets and the concentration
Often hollow spheres are formed.

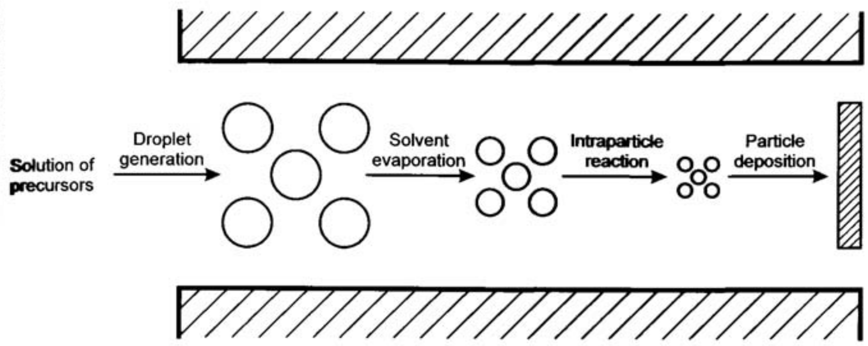


Figure 3-31. Particle generation by spray pyrolysis.

Spray pyrolysis

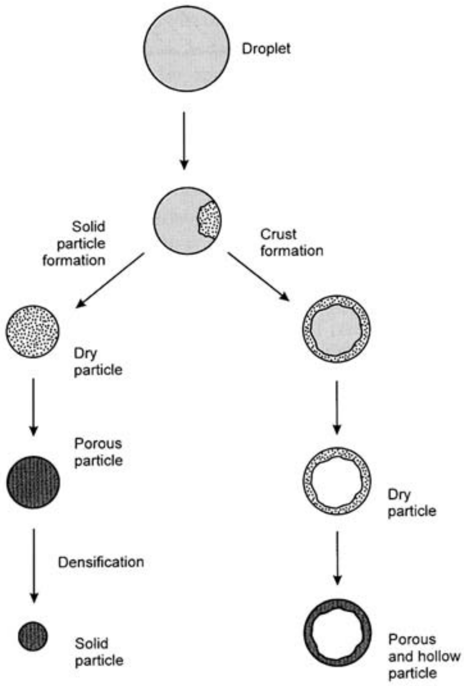


Figure 3-32. Formation of dense (left) and hollow particles (right) by spray pyrolysis.

Porosity of the product is controlled e.g. by concentration and thermal profile

Flame reactors: A combustion reaction is used to heat the spray. Short residence time, maximum use of energy. Risk of contamination by combustion reactants.
Heating reactors: Spray into a hot furnace. Good control of temperature and residence time. Growth on walls, formatio n of hard aggregates.
Laser reactors: Heated by a laser; efficient transfer of heat to gaseous species.
Plasma reactors.

Products

Large scale: Titania, silica, alumina powders. (from the chlorides by flame pyrolysis)
Smaller scale: Bi_2O_3, Cr_2O_3, Fe_2O_3, GeO_2, NiO, MoO_2, SnO_2, V_2O_5, WO_3, ZrO_2, $AlBO_3$, Al_2TiO_5, $AlPO_4$…
Nitrides, carbides, borides, silicides….
Metal synthesis: $SiCl_4(g) + 4Na(g) \rightarrow Si + 4NaCl$
$2NbCl_5(g) + 5\ Mg \rightarrow 2Nb + 5gCl_2$

Table 3-3. Examples of non-oxide powders prepared by aerosol methods.

Product	*Method*	*Reactants*
Carbides		
B_4C	Plasma/Laser	$BCl_3 + CH_4$
B_4C	Thermal	$B_2O_3 + C$
SiC	Laser/Plasma/Thermal	$SiH_4 + CH_4$
SiC	Plasma	$SiCl_4$ or SiO_2 or $SiO + CH_4$
SiC	Plasma/Thermal	$SiMe_4$
SiC	Laser/Plasma	$SiO_2 + C$
SiC	Laser	$H_2SiCl_2 + C_2H_4$
TiC	Plasma/Thermal	$TiCl_4 + CH_4$
Mo_2C	Thermal	$MoCl_5$ or $MoO_3 + CH_4$
WC, W_2C	Plasma/Thermal	WCl_6 or $W + CH_4$
Nitrides		
BN	Laser/Thermal	$BCl_3 + NH_3 + N_2$
AlN	Plasma/Thermal	$Al + N_2$ [$+ NH_3$]
AlN	Thermal	$AlCl_3 + NH_3 + H_2$
AlN	Thermal	$Al_2Et_6 + NH_3$
Si_3N_4	Laser/Plasma/Thermal	$SiH_4 + NH_3$
Si_3N_4	Laser/Plasma/Thermal	$SiCl_4 + NH_3 + H_2$
Si_3N_4	Plasma	$Si + NH_3$ or N_2
Si_3N_4	Thermal	polysilazanes $+ NH_3 + N_2 + H_2$
SiAlON	Plasma	$Si + Al + NH_3 + O_2$
TiN	Plasma	$Ti + N_2$ [$+ H_2$]
TiN, ZrN	Thermal	$TiCl_4/ZrCl_4 + NH_3 + N_2 + H_2$
VN_x	Thermal	$VCl_5 + NH_3 + N_2 + H_2$
Borides and Silicides		
B_4Si	Plasma	$B_2H_6 + SiH_4$
$TiSi_2$	Laser	$TiCl_4 + SiH_4$
TiB_2	Laser	$TiCl_4 + B_2H_6$
TiB_2	Thermal	$TiCl_4 + BCl_3 + Na$ or H_2
WSi_2	Plasma	$WF_6 + SiH_4$

Film deposition

Spray pyrolysis (droplet deposition). Evaporation of substrate
Aerosol Assisted chemical vapour deposition, AACVD. Up to 5 μm/min
Particle deposition. 1-5 μm/min

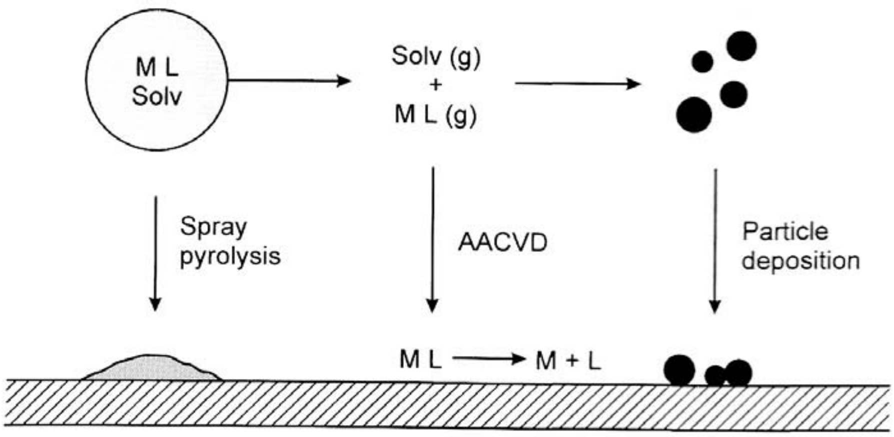


Figure 3-33. Comparison of processes for film formation during aerosol syntheses.