CERAMIC AND COLLOIDAL PROCESSING - EXERCISES

Dr. Andrea Testino
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Exercises 4 - Solutions

1. What are the different nucleation mechanisms possible in a stirred tank reactor?

Homogeneous nucleation: takes place in the absence of a solid interface and is a direct result of the supersaturation.
- primary heterogeneous nucleation: it takes place on the surface of solids.
- true secondary nucleation: it occurs when using fine particles that act as seeds.
- apparent secondary nucleation: it occurs when small fragments are detached from the surface of the seeds or particles thus creating additional seeds.
- secondary contact nucleation: this occurs when precipitated fragments come off a particle on contact with the reactor, stirrer or even other particles.

2. What is the significance of the critical size of a seed/embryo of a crystal in a precipitation system?

- Above the critical size of the embryo/seed, the particle become thermodynamically stable and will grow spontaneously i.e. ΔG decreases ↓ when r increases ↑
- Below this critical size, the seeds/embryos become unstable and can dissolve, i.e. ΔG decreases ↓ when r decreases ↓

3. For the precipitation of a calcite powder at room temperature (25 ° C) calculate the critical size for 2 different supersaturation ratios; ln (SR) = 2.0 and 7.76; discuss the validity of the results.
(Vm = 6.13 x 10^{-29} m^3 / molecule, γ = 0.127 N / m2 βV = 4π / 3and βA = 4π).

Precipitation of a calcite powder:
Critical size :

Mathematical Application :

i) $R^* = \frac{2 \cdot 0.127 \cdot 6.13 \cdot 10^{-29}}{1.38 \cdot 10^{-23} \cdot 298 \cdot 2.0} = 1.89 \cdot 10^{-9} m = 1.89 nm$ (for ln (SR) = 2)

ii) $R^* = \frac{2 \cdot 0.127 \cdot 6.13 \cdot 10^{-29}}{1.38 \cdot 10^{-23} \cdot 298 \cdot 7.76} = 4.88 \cdot 10^{-10} m = 0.49 nm$ (for ln (SR) = 7.76)

When R* is very small (≤1nm) this calculation of the critical size is no longer valid. Indeed, the concept of surface free energy and the definition of surface energy (from which the relation giving R* results) are no longer always valid

4. What are the different methods for producing a powder from gaseous reactants? Give a typical example.

a) spray-pyrolysis: This method is useful for producing multi-component oxide powders. A solution (e.g. metal chlorides) is atomized (pulverized) into droplets and then water is evaporated by passing through an oven. During evaporation, the metal chloride precipitates and decomposes into oxides as the droplets reach the hottest part of the furnace.
Example: powder $La_{0.6}$ Sr 0.4 Fe0.8Co0.2

b) vapor phase synthesis:
- flame ; -plasma ; -oven ; -laser
The basic principles are similar to the spray pyrolysis method (see above). The major difference is that a reactive vapor is produced in molecular form and decomposed in a hot zone. Reagents are also often metal chlorides.
Example: TiO2 powder
The steps of such a synthesis method are therefore:
-the decomposition of products (from a mixture of vapor + air)
-nucleation of precipitates-partilces
-growth (see coalescence, that is to say melting of precipitates, condensation), agglomeration and / or sintering

5.- Give three methods of synthesis of a ceramic powder and give advantages and disadvantages of these methods.

i) Hydrothermal synthesis:
(+ ve) - can precipitate phases at high temperature and pressure which are thermodynamically unstable at ambient conditions, that is to say, a ceramic powder directly.
- allows the production of a fine powder of high purity and not a precipitated precursor of ceramics for which a heat treatment is required thereafter.
(-ve) - difficulty drying fine powders without the formation of hard agglomerates.
High pressures and operating temperatures generate high costs.
-security
-Thermodynamic data are not always available for modeling of formation mechanisms.

ii) Spray Pyrolysis:
(+ ve) - allows large productions of complex mixed oxides
(-) - if the relative solubilities of each component are too different, segregation and molecular mixing of the components will be imperfect, secondary phases can therefore be produced.
- agglomeration often present
- irregular particle shapes
- chemistry limited by the availability of suitable soluble salts.

iii) Vapor phase synthesis:
(+ ve) - allows the synthesis of powder with high specific surface
(-ve) - poor control of agglomeration (coagulation → strong agglomeration, condensation → weak agglomeration)
- limited with chemistry (difficult to make complex mixtures, more suited to single phases e.g. TiO_2, SiO_2, Al_2O_3, etc.)