Synthesis of different nanostructures by precipitation reactions in a technical w/o-microemulsion

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Motivation and Objectives

- Nanometer sized particles are of interest for an increasing number of applications (catalysis, additives for polymers, etc.)
- Producing high-value nanoparticles with defined size and shape in large quantities is a current challenge
- Applying w/o-microemulsions as structured reaction media (see Fig. 1) on a technical scale for the synthesis of nanoparticles
- Identification of the determining process conditions using experimental and theoretical tools to produce nanoparticles in a controlled manner

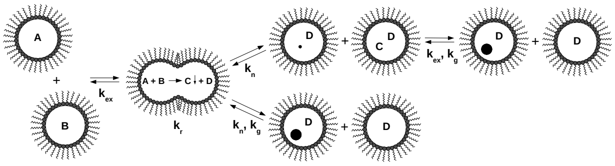

Figure 1: Suggested mechanism of particle precipitation in microemulsion droplets with the governing rate constants for droplet exchange k_{ex}, chemical reaction k_r, nucleation k_n and particle growth k_g.

Approach

- Selection and characterization of a technical w/o-microemulsion and identification of suitable regions for particle synthesis [1]
- Experimental investigation of important process and operational parameters for the $CaCO_3$ and $BaSO_4$ particle formation process
- Modelling and simulation of the precipitation process in microemulsion droplets using a Monte-Carlo method

Experimental Results

- Precipitation of $CaCO_3$ nanoparticles is only slightly influenced by the droplet diameter and the initial reactant concentration (Fig. 2)

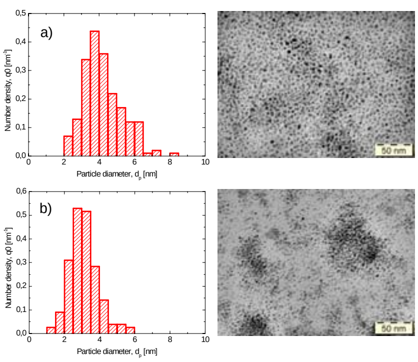

Figure 2: TEM images of amorphous $CaCO_3$ nanoparticles precipitated in a w/o-microemulsion at a temperature of T = 40 °C and an initial reactant concentration of 0.1 M.
a) Microemulsion with a droplet diameter of d ≈ 46 nm;
b) Microemulsion with a droplet diameter of d ≈ 18 nm.

- Prolongation of residence time leads in case of $CaCO_3$ to the formation of crystalline needle-like particles with a high aspect ratio (see Fig. 3)

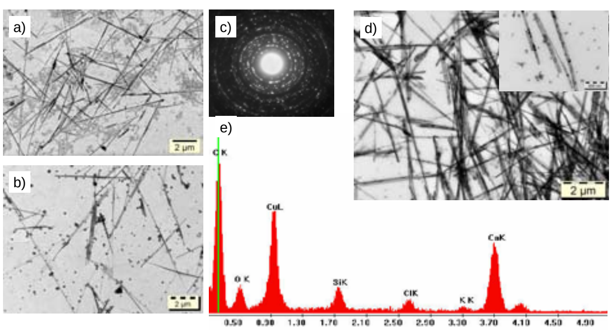

Figure 3: TEM images of $CaCO_3$ particles precipitated in a w/o-microemulsion (T = 40 °C, c_0 = 0,1 M). a) After 4 h residence time. b) After 6 h residence time. c) Electron diffraction pattern of particles obtained after 24 h. d) Needle-like particles after 24 h residence time. e) X-ray spectrum of needle-like particles (EDX-analysis).

- Changing the initial reactant concentration (0.01M to 0.1 M) or the concentration ratio showed no significant effect on the $CaCO_3$ particle formation process
- Precipitation of $BaSO_4$ using an identical w/o-microemulsion results in stable crystalline nanoparticles [2] where the particle size and shape is strongly affected by the initial reactant concentration (see Figs. 4 and 5)

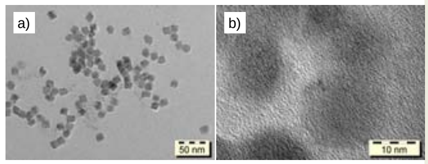

Figure 4: a) TEM image of $BaSO_4$ particles precipitated in a w/o-microemulsion. For a temperature of T = 25 °C, an oil content of 96%, a surfactant content of 15% and an initial reactant concentration of 0.1 M $CaCl_2$ and 0.01 M K_2SO_4.
b) HRTEM image of $BaSO_4$ particles.

- Experiments where one microemulsion with the corresponding reactant was added with an extremely low feeding rate lead to the formation of crystalline $CaCO_3$ and $BaSO_4$ nanoparticles (see Fig. 5)
- Experimental findings indicate, that a stabilizing effect exists for crystalline nanoparticles formed in microemulsions
- Amorphous $CaCO_3$ nanoparticles could undergo a transformation process leading to relatively large crystals (compare Fig. 2)

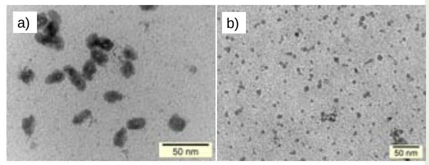

Figure 5: TEM images of a) $BaSO_4$ and b) $CaCO_3$ particles precipitated by adding K_2SO_4/Na_2CO_3 containing microemulsion with a low feeding rate (2 ml/min).
For T = 25 °C, an oil content of 96 %, a surfactant content of 15 % and an initial concentration of 0.1 M.

Monte-Carlo Simulation

- A discrete MC model was formulated to study the influence of droplet size, feeding rate and initial reactant concentration [3]
- Variation of droplet size leads to a significantly broader particle size distribution whereas the mean size is only slightly increased (see Fig. 6)
- A qualitatively good agreement between experiments and theoretical results was found for the formation of nanoparticles in microemulsions with different droplet sizes

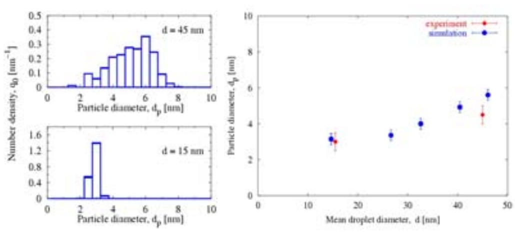

Figure 6: Left: Simulated particle size distribution for two different droplet sizes (d = 15 nm, d = 45 nm) corresponding to the experimental data (see Fig. 2). Right: Experimental and simulated mean particle size vs. droplet diameter.

Conclusion and Outlook

- Different nanoparticle sizes and morphologies are obtainable using identical microemulsions and parameters
- Depending on the precipitation system the particle synthesis could be influenced by different process parameters (e.g. concentration, residence time)
- MC simulations are an effective tool to describe qualitatively and quantitatively the particle formation in microemulsions
- Closer investigation of the $CaCO_3$ needle formation process by combining experimental and theoretical means

References

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