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Short communication

Precipitation of metal oxide nanoparticles using a miniemulsion technique

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ABSTRACT

A method to precipitate nanoparticles using a miniemulsion technique is described, in which miniemulsion droplets between 100 and 1000 nm in size serve as nanoreactors enabling both the control of particle formation and particle growth. The application of miniemulsion droplets to synthesise nanoparticles comprises three advantages: first, the size of the precipitated particles is limited by the reactant concentration within the emulsion droplet; second, particle agglomeration is prevented as nanoparticle collision outside the nanoreactor is avoided; and third, easy technical scale up can be realized by increasing emulsion volume and thus the number of nanoreactors, while local conditions within the reactors are not changed. The miniemulsion technique is an easy scalable process which allows defined synthesis of particles by precipitation reactions. The miniemulsion technique involves first the preparation of a stable water-in-oil miniemulsion by high pressure homogenisation. Whereas a water soluble reactant is provided within the aqueous droplets, another oil- as well as water-soluble reactant can be introduced to the emulsion after homogenisation. The precipitation reaction is induced by the diffusion of the second reactant into the emulsion droplet. Together with this contribution, a method is described and discussed which uses a high pressure homogenisation process to produce stable water-in-oil miniemulsions serving as a reaction medium to precipitate metal oxides.

1. Introduction

Nanoparticles enjoy great popularity in chemical, pharmaceutical, cosmetic and textile industries due to their unique properties related to their small particle size ($x < 100$ nm). In principle, there are two ways to produce nanoscaled particles: the top-down methods involving grinding to break up large particles into smaller ones (Breitung-Faes & Kwade, 2008) and the bottom-up methods dealing with the build-up of nanoparticles via nucleation processes. The bottom-up methods include a variety of different procedures such as the sol–gel processes (Jauregui-Rosas, Perez, Jia, Vasquez, & Angelats, 2009) and precipitation of nanoparticles with a Y-Mixer set-up (Kucher, Babic, & Kind, 2006). In both the top-down and bottom-up approaches, prevention of nanoparticle agglomeration plays an important role. Reactors that control both particle growth and particle agglomeration and furthermore allow simple scale up are droplets of submicron sizes (Gedrat & Schuchmann, 2009). These are found in water-in-oil miniemulsions (typical mean droplet size $x_{1,2} = 100$–1000 nm). The application of a water-in-oil miniemulsion as a reaction medium to synthesise nanoparticles requires the diffusion of an oil soluble reactant R1 into the emulsion droplet which contains the second precipitation reactant, water-soluble R2, as shown in Fig. 1.

The reaction results in a product of low solubility and, caused by supersaturation, nucleation is induced. Nucleation and growth of the particles are furthermore limited by the reactant concentration in the miniemulsion droplet. The isolated nanodroplets protect the particles from agglomeration, as often found in bulk precipitation. Easy technical scale up can be realized by increasing the emulsion volume. Conventional emulsification scaling rules can be applied resulting in an increased number of the nanoreactors, while local conditions within the emulsion droplets, that is, the nanoreactors, are not changed.

Much research has been carried out in the field of precipitation in microemulsions (Adityawarman, Niemann, & Sundmacher, 2008) as well as miniemulsions (Liu, Yang, Yao, Du, & Liu 2006; Vidal-Vidal, Rivas, & Lopez-Quintela, 2006). A great advantage of the miniemulsion method in contrast to the microemulsion technique is the little demand of surfactant (about one tenth) and thus easier downstream processing in regard to purification of the nanosuspension. In cited publications, authors have used typical laboratory equipment for miniemulsion preparation, e.g., ultrasonication or rotor–stator devices. For the work presented here, a method is described and discussed which uses a high pressure

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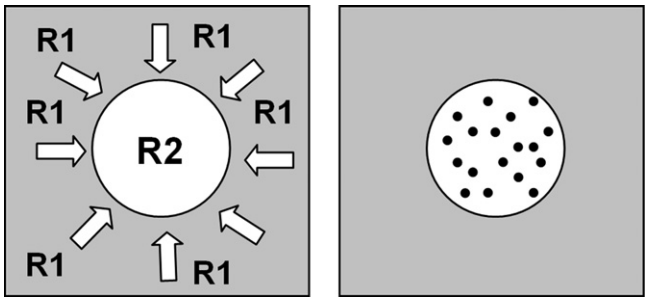

Fig. 1. Schematic of precipitating nanoparticles in a miniemulsion droplet. Oil-soluble amine (R1) dispersed in the continuous phase, diffuses into the miniemulsion droplet, to react with water-soluble reactant (R2), and thereby induces nucleation.

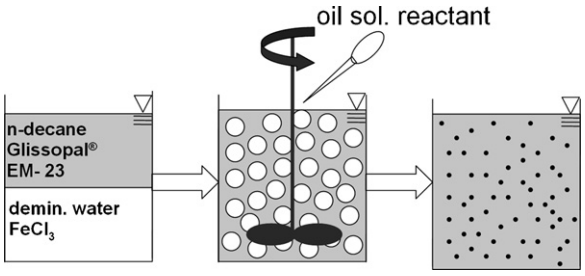

Fig. 2. Schematic procedure to precipitate nanoparticles via the miniemulsion technique. The miniemulsion was produced by a high pressure homogenisation process. Then the oil soluble reactant was added to transform the miniemulsion into a stable nanosuspension.

homogenisation process to produce stable water-in-oil miniemulsions to serve as reaction media to precipitate iron oxides. High pressure homogenisation is a well scalable technical process and has been thoroughly discussed in literature (Freudig, Aguilar, & Schubert, 2004; Vankova et al., 2007; Walstra, 1993). It further allows for process intensification with respect to combining the two unit operations, homogenisation and mixing (Koehler et al., 2007), and is thus a promising approach regarding the precipitation of nanoparticles in emulsions.

2. Materials and methods

The miniemulsion technique calls for a water soluble reactant inside the water droplets. As another reactant, an oil- as well as water-soluble precursor is required which can diffuse through the continuous oil phase to the droplet interface and then into the emulsion droplet. We focus on the formation of iron oxide nanoparticles inside the emulsion. The precursors for synthesising iron oxide were iron(III) chloride (Merck Schuchardt OHG, Germany) and an oil- as well as water-soluble amine which dissociates in the presence of water to form an amino cation and a hydroxide anion (see Eq. (1)). Then, the latter reacts with iron chloride to precipitate iron oxide (see Eq. (2)).

$$\text{R-NH}_2 + \text{H}_2\text{O} \leftrightarrow \text{R-NH}_3^+ + \text{OH}^- \quad (1)$$

$$\text{MeX} + \text{OH}^- \leftrightarrow \text{MeO} + \text{HX} \quad (2)$$

The continuous phase of the emulsion is the paraffin n-decane (VWR, Germany) whereas a water based iron(III) chloride suspension serves as the dispersed phase. As a stabilizer the emulsifier Glissopal® EM-23 (BASF, Germany) was used. All chemicals were used as received without further purification.

The emulsion was prepared with a high pressure device (M-110Y Microfluidizer®, Microfluidics, USA). Stability of the droplets against coalescence is strictly required as a change in droplet size, that is, nanoreactor size, during experiments may lead to uncontrollable precipitation, thus generating undesirable results. Therefore, it was important first to ensure emulsion stability. Following high pressure homogenisation, the oil as well as the water-soluble reactant was added to the stable miniemulsion to induce the precipitation reaction and particle formation. Then, water was removed by azeotropic distillation to obtain a nanosuspension. Fig. 2 illustrates schematically the process of precipitating nanoparticles with the miniemulsion technique.

The droplet size distribution of the miniemulsion was determined by laser diffraction (Mastersizer X, Malvern Instruments GmbH, Germany), and the nanosuspension obtained after azeotropic distillation was analysed by dynamic light scattering (Nanotrac™, Microtrac, USA). For further analysis by transmission electron microscopy (LEO 922, Omega, Germany) the sample was prepared as described by Schmidt, Guesdon, and Schomäcker (1999). The dispersed phase fraction was kept constant at 40% (w/w) throughout the experiments. The homogenisation pressure was varied between 400 and 1000 bar, and two emulsifier contents, 2 and 3% (w/w), were studied to investigate operational influence on resulting droplet size. In order to study the influence of the reactant concentration of the amine on resulting particle size, three amine concentrations were considered, that is, equimolecular, threefold and sixfold iron(III) chloride concentration. The iron(III) chloride concentration was kept constant at $c_{\text{iron(III) chloride}} = 0.04$ mol/L.

3. Results and discussion

Fig. 3 shows the cumulative droplet size distributions of miniemulsions obtained after high pressure homogenisation. While emulsifier concentration, always above the critical micelle concentration, does not show any significant effect on the obtained emulsion droplet sizes, homogenisation pressure is shown to influence droplet (nanoreactor) size distribution. With an increase of homogenisation pressure Δp from 400 to 1000 bar, the droplet sizes can be considerably reduced, depicting a disruption-controlled emulsification process. Less than 5 vol% of the disperse phase is found in droplets of size > 1 μm. A surfactant concentration of 2% (w/w) proves to be adequate to stabilize the miniemulsions.

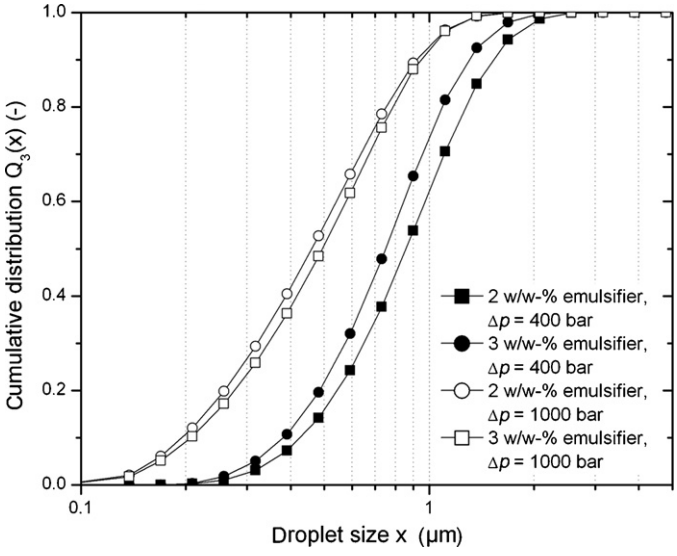

Fig. 3. Cumulative droplet size distributions of miniemulsions after high pressure homogenisation, measured by laser diffraction.