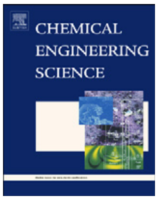
Chemical Engineering Science 92 (2013) 126–133

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces



Controlled droplet coalescence in miniemulsions to synthesize zinc oxide nanoparticles by precipitation

Marion Winkelmann [a,]*, Eva-Maria Grimm [a], Talita Comunian [a], Barbara Freudig [a], Yunfei Zhou [b], Wolfgang Gerlinger [b], Bernd Sachweh [b], Heike Petra Schuchmann [a]

[a] *Karlsruhe Institute of Technology (KIT), Food Process Engineering, Kaiserstr. 12, 76131 Karlsruhe, Germany*
[b] *BASF SE, 67056 Ludwigshafen, Germany*

HIGHLIGHTS

- ▸ We introduce a miniemulsion process to precipitate zinc oxide by droplet coalescence.
- ▸ We identified parameters to control coalescence in high pressure homogenization.
- ▸ The coalescence rate depends on the viscosity, pressure and valve geometry.
- ▸ Particle size depends on the coalescence rate and precursor concentration.

ARTICLE INFO

Article history:
Received 26 July 2012
Received in revised form
29 November 2012
Accepted 20 December 2012
Available online 16 January 2013

Keywords:
Droplet coalescence
Zinc oxide
Precipitation
Nanoparticles
Miniemulsion
High pressure homogenization

ABSTRACT

The precipitation of zinc oxide with a coalescence controlled emulsion technique is introduced. This technique involves the preparation of two stable water-in-oil submicron sized emulsions (miniemulsions). Each emulsion contains one water soluble precipitation precursor. In a second high pressure emulsification step droplet coalescence is induced leading to particle precipitation. In this contribution we present parameters influencing droplet coalescence rate such as emulsifier and emulsifier content as well as local flow conditions. Considering the precipitation of zinc oxide we furthermore investigate the influence of droplet coalescence rate on the size and composition of the particles synthesized. The results approve the importance of full coalescence of droplets prior to particle synthesis: Remaining uncoalesced droplets lead to a wide particle size distribution with a fraction of larger particles. If all droplets coalesce to some extent, we observe a decrease in particle size with increasing reactant concentration depicting a precipitation process dominated by homogeneous nucleation.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The demand for stable nanoparticle-suspensions has dramatically increased during the last years. Nanoparticles enjoy great popularity in chemical, pharmaceutical, cosmetic and textile industry due to their unique properties related to the small particle size ($x < 100$ nm) or high specific surface area. Nano-sized zinc oxide finds its application in optical, electrical, catalytic and photocatalytic devices (Peppley et al., 1999; Yoshida et al., 2003; Huang et al., 2001; Hoffman et al., 2003). Zinc oxide can be synthesized by precipitation as described in (Bahnemann et al., 1987; Wong et al., 1998; Taubert et al., 2002; Spanhel and Anderson, 1991; Yamabi and Imai, 2002). In addition, the precipiation of zinc oxide in a two-phase system (Vorobyova et al., 2004), with an emulsion (Hoshi et al., 1997) and a microemulsion approach are described in (Li et al., 2009; Yildirim and Durucan, 2010; Moleski et al., 2006). Microemulsions are considered to be thermodynamically stable (Paul and Moulik, 2001). Regarding the microemulsion approach, the particle precipitation is based on micellare exchange processes.

In Hoshi et al. (1997), the authors compare the emulsion technique with the conventional batch-process to precipitate zinc oxide. The emulsion approach proves to obtain significant advantages compared to conventional batch processes: It allows for synthesizing spherical, homogeneous submicron ZnO of smaller particle size and particle size distribution (Hoshi et al., 1997).

Nevertheless, a challenge with the precipitation in batch processes and with the microemulsion approach is to selectively initiate and control particle growth. A reaction medium that enables to control both particle precipitation as well as particle growth is a water-in-oil miniemulsion droplet of mean diameter in the range of $d = 100$–1000 nm (Landfester, 2003; Gedrat et al.,

---

* Corresponding author. Tel.: +49 721 608 43723; fax: +49 721 608 45967.
E-mail address: marion.winkelmann@kit.edu (M. Winkelmann).

0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2012.12.049

2011; Winkelmann and Schuchmann, 2011). Each droplet serves as an individual nanoreactor limiting the resulting particle size by the droplet volume and the reactant concentration provided therein.

Miniemulsions are in comparison to microemulsions thermodynamically unstable. Accordingly, particle precipitation is not a result of micellar exchange process or exchange of matter via the continuous phase of the emulsions. In miniemulsions, particle precipitation is accomplished by controlled coalescence of droplets containing water-soluble precursors (Gedrat et al., 2011; Sotowa et al., 2007; Tokumitsu et al., 1999). Coalescence of the droplets containing the precipitation reactants results in a product of low solubility and thus particle synthesis. Growth of the particles is then limited by the reactant concentration in the miniemulsion droplet. Former work showed, that only in case of an increase of droplet size in the second emulsification step, precipitant can be detected (Gedrat et al., 2011).

Processes applied to produce miniemulsions are generally ultrasonication and high pressure homogenization (Landfester et al., 2003; Hecht et al., 2011). In our work we focus on high pressure homogenization, as it is an easily scalable process applied in technical emulsification processes with throughput of industrial relevance.

In high pressure emulsification processes, a coarse pre-emulsion (premix) is exposed to a pressure p of up to several hundred-to-thousand bars (conventional machines work at up to 2000 bar). The fluid pressure is released via a homogenization valve resulting in high flow velocities, turbulences and cavitational effects. Droplet deformation and break-up in homogenizing valves are intensely investigated by Walstra (1993), Tesch et al. (2003), Freudig et al. (2003). Both depend on local flow conditions, being influenced by the valve geometry and homogenization pressure (Walstra, 1993; Phipps, 1971; Treiber and Kiefer, 1976; Aguilar et al., 2004). A wide variation of different homogenization valves is available such as radial diffusers, impinging jet valves and standard orifices, the latter being basically a hole of defined diameter and length. Here, droplets are stretched to filaments when entering and passing the hole. These filaments break due to the laminar shear and elongational stresses as well as Reynolds stresses released in the free jet formed thereafter, the so-called laminar–turbulent transition area (Schubert, 2005; Kissling et al., 2011).

Disruption units increasing local turbulences and thus enforcing droplet break-up are two beam jet valves. The impact of the two jets induces local turbulences and thus increases the turbulent kinetic energy (Aguilar et al., 2004). Whether droplet breakage is caused by a turbulent viscous or turbulent inertial regime is, as proposed by Vankova et al. (2007), a material matter . It also depends on process parameters (Aguilar et al., 2008).

Once droplets are disrupted they need to be stabilized by adsorbing emulsifier molecules, a process taking some time depending on emulsifier molecule structure and chemical nature of the phases (Miller, 1990). Regarding droplet coalescence in turbulent flow regimes, Chesters (1991) provides the following theory: prior requirement for coalescence is the collision of droplets. The collision frequency C in respect of turbulent flow can be calculated with Eq. (1),

$$C = kud_{3,2}^2 n^2 \tag{1}$$

where k is the velocity constant and u the droplet velocity, $d_{3,2}$ accounts to the Sauter mean diameter and n to the number of droplets per unit volume. The velocity constant and the droplet velocity can be calculated according to the following equations:

$$k = \sqrt{\frac{2\pi}{15}} \tag{2}$$

$$u = \sqrt{\frac{\varepsilon}{\nu_C}} \times d \tag{3}$$

where ε is the turbulent energy dissipation rate per unit mass, and ν_C the kinematic viscosity of the continuous phase.

The Sauter mean diameter $d_{3,2}$ is defined as the diameter of a sphere that has the same volume to surface area ratio as the considered particle and is given by:

$$d_{3,2} = 6\frac{V_P}{A_P} \tag{4}$$

where V_P is the volume and A_P the surface area of the particle.

There are three scenarios which can occur once droplets collide (Ivanov and Kralchevsky, 1997): When the film between the collided droplets is stable, flocks of attached droplets can be formed. Colliding droplets will rebound in case of repulsive forces. Unstable films due to predominant attractive forces between the droplets will rupture which will result in droplet coalescence.

The coalescence rate Ω depends on the collision frequency C and the probability of coalescence p_{coal}.

$$\Omega = p_{\mathrm{coal}} C \tag{5}$$

The coalescence probability depends on droplet–droplet interaction forces (Schubert, 2005), the ratio of the film drainage time and the contact time of the droplets (Chesters, 1991), the latter depending on the viscosity of the continuous phase (Vankova et al., 2007; Davies, 1985).

In orifice valve high pressure homogenization no coalescence has been found in the orifice valve outlet until the free jet again turns into laminar flow conditions and resultantly the contact time between droplets increases (Kempa et al., 2006).

The influence of dispersed phase fraction and energy release on droplet coalescence rate is discussed in Gedrat et al. (2011). In this work we deliberately enforce droplet coalescence. For this reason we first focus on identifying appropriate emulsifiers and emulsifier contents. Furthermore we investigate the influence of the viscosity of the continuous phase, the geometry of the disruption unit and the homogenization pressure on droplet coalescence. In addition we study the impact of droplet coalescence rate on the characteristics of zinc oxide particles precipitated.

2. Materials and methods

The experimental procedure is illustrated in Fig. 1. The procedure involves the production of two precursor miniemulsions each loaded with different reactants. In a second homogenization step droplet coalescence and thus precipitation of zinc oxide is induced.

The emulsion consisted of n-decane (VWR, Germany) as lipophilic continuous phase. As dispersed phases two water based precursor solutions were prepared, containing zinc sulfate ($ZnSO_4$) and potassium hydroxide (NaOH) as reactants, respectively. The dispersed phase fraction was kept constant throughout the experiments at 40 w/w%.

The precursors $ZnSO_4$ (Merck, Germany) and NaOH (Merck, Germany) react to zinc hydroxide according to the following equation:

$$ZnSO_4 + 2\ NaOH \rightarrow Zn(OH)_2 \downarrow + Na_2SO_4 \tag{6}$$

In order to obtain zinc oxide a calcination step is required. According to (Bahnemann et al., 1987; Wong et al., 1998) the calcination of zinc hydroxide to zinc oxide is achieved when keeping the suspension at a temperature of 65 °C for two hours. In our work, the calcincation was accomplished by tempering the emulsion for 2 h at 72 °C.

Download English Version:

https://daneshyari.com/en/article/155308

Download Persian Version:

https://daneshyari.com/article/155308

Daneshyari.com