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Production of metal oxide nanoparticles by supercritical emulsion reaction

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ABSTRACT

A technique derived from SAS is proposed for the production of silicon, tungsten and molybdenum oxides nanoparticles in which supercritical CO_2 plays a double role, acting as antisolvent and as reactant. A liquid mixture, that will be used as the continuous phase, containing i-octane, n-heptane, cyclohexane or ethyl acetate and sodium bis (2-ethylhexyl) sulfosuccinate (AOT) or Tween80 as surfactant is first prepared. Then, a solution of sodium metal hydrate in water is added to the above mixture, to form a reverse micellar solution. Oxide nanoparticles of various materials are synthesized in the reverse micelles by reaction with CO_2; in the meanwhile, the organic solvent is solubilized in CO_2. At the end of the process, the residual components are eliminated by continuous purging with CO_2 in a washing step. Semi-continuous SAS-like process has been adopted and process parameters affecting nanoparticles production have been studied such as emulsioning conditions, pressure, water and surfactant concentration. Various recovery methods of the precipitated nanoparticles have been explored such us ultrafiltration (UF) or separation by ultrasonic probe. Nanoparticles have been characterized by Field Emission Electron Microscopy (FE-SEM) and Energy Dispersive X-ray Analysis (EDX). The results show that particles dimensions can be easily controlled by tuning the process parameters. Nanoparticles can be obtained with a narrow particle size distribution and with a mean diameter as small as 29 nm.

1. Introduction

There is an enormous interest in the production of metallic or non-metallic oxide nanoparticles, in the approximate size range 1–100 nm. These particles are used in a variety of applications; the most important of which are catalysis and pharmaceuticals. Industrial processes such as petroleum reforming depend on catalytic metal nanoparticles and it is possible to detect cancer with silica nanoparticles [1–3]. Metal oxide nanoparticles are also used in other applications, including the labeling of biological samples and hydrogen storage. One of the challenges in this field is to make the particles as small as possible, with a narrow particle size distribution (PSD).

Numerous methods for the preparation of fine powders and thin layers of nanoparticles have been proposed; they include: cathodic arc deposition, gas-phase adsorption in a fluidized-bed reactor, laser vaporization, chemical vapor deposition (CVD) from metallorganic precursors, magnetron sputtering, electrochemical deposition, wet chemical deposition, sol–gel process, hydrothermal reactions [4–8]. Sonochemical decomposition of volatile metal carbonyls has been recently proposed as a means to obtain nanosized materials. The major limits of these techniques are the complex multistep processes and the low yield. For these reasons, the development of simple and effective methods for nanoparticles preparation is of practical interest [9–11].

The production of silicon oxide (SiO_2) nanoparticles using SC-CO_2 as reactant and antisolvent, has been proposed for the first time by Chattopadhyay and Gupta [12] starting from an aqueous sodium silicate solution ($NaOH{\cdot}SiO_2$). This process is very similar to the supercritical antisolvent micronization (SAS) that has been widely used to produce micro and nanoparticles of several kinds of organic compounds [13,14]. During SAS, a liquid solution is continuously atomized in a precipitator and the presence of SC-CO_2 induces the formation of micro and nanosized solids by the fast elimination of the liquid solvent. The process proposed by Chattopadhyay and Gupta (that we will call SAS-ER: SAS plus Emulsion Reaction) differs from the standard SAS for the fact that a water-in-oil (W/O) emulsion/microemulsion is injected in the precipitator instead of the liquid solution and that CO_2 reacts with the solute contained in the emulsions. The cited authors propose this reaction when an aqueous salt solution is used:

$$2NaOH{\cdot}SiO_2 + CO_2 \rightarrow Na_2CO_3 + 2SiO_2 + H_2O$$

that explains the formation of SiO_2. The emulsion was formed using n-heptane or i-octane as solvents and AOT as surfactant. The

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emulsion droplets act as micro or nanoreactors and, depending on their diameter, micro or nanoparticles are formed when the solid reaction product is obtained. In a first work, these authors used a discontinuous process without the atomization step [12]. In a subsequent work Thakur and Gupta [15] used the standard SAS semi-continuous process obtaining the coating of SiO_2 on gold nanoparticles added in the droplets. The same process has also been used by Zhang et al. [16] to induce the precipitation of SiO_2 on TiO_2 nanoparticles. Therefore, SAS-ER process has been demonstrated to be feasible; but, until now, it has been applied only to the production of the SiO_2 nanoparticles.

In the present work we, propose the extension of the range of applicability of SAS-ER to other metal oxides (namely tungsten oxide WO_3 and molybdenum oxide MoO_3) and will try to evaluate the capacity of this process to control particle size and distribution. The advantages with respect to the traditional processes will be the reduction of the aging times from several days to a few minutes, the reduction of the processing times, the use of mild operative conditions such as low temperatures (35–60 °C) and relatively low pressures (70–150 bar). This technique can also allow a good process yield of the produced nanoparticles that precipitate together with surfactant residues. Systematic experiments were performed varying the method of preparation of the emulsions and the process pressure. Metal oxide nanoparticles were analyzed using FE-SEM and EDX.

2. Materials, apparatus and procedures

2.1. Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT; 99+% pure), polyoxyethylene sorbitan monoleate (Tween 80, 99+% pure), cyclohexane (99% pure), i-octane (2,2,4-trimethylpentane, 99.4% pure), and n-heptane (99.4% pure) were supplied by Fisher Scientific. Sodium silicate solution ($Na_2Si_3O_7 \cdot H_2O$ in aqueous solution: 14 wt% NaOH, 27% SiO_2, and 59% H_2O), Sodium Tungstate dihydrate $Na_2WO_4 \cdot 2H_2O$ ($\geq$99+% pure), Sodium molybdate dihydrate $Na_2MoO_4 \cdot 2H_2O$ ($\geq$99+% pure) were supplied by Sigma–Aldrich Chemicals. Sodium tungstate and sodium molybdate stable solutions were obtained by adding water as for the commercial sodium silicate solution. Ethyl Acetate (>99%) was supplied by Carlo Erba Reagenti. Carbon-dioxide (CO_2, purity 99%) was purchased from SON (Italy). All reagents were used without further purification.

2.2. Optimization of emulsions

Emulsion optimization is generally performed to obtain the minimum droplet size and/or the minimum polydispersity. In this work, W/O emulsion has been optimized for systems formed by AOT or Tween80 as surfactant, i-octane, n-heptane, cyclohexane and ethyl acetate as the continuous phase, and a disperse phase formed by a sodium metal solution. Emulsions formed using AOT have been prepared for different weight ratios between surfactant and hydrocarbon solvents (1, 1.6, 3.2%, w/w). In this case, the disperse phase was formed by water plus metallic sodium salts in aqueous solution (60/40%, w/w, respectively) with a ratio W_0 = water/surfactant of 10, 6, 3.

The emulsions formed using Tween80 were obtained using Ethyl Acetate as solvent and 1% by volume of Tween80 with respect to the continuous phase. Then, the system was studied by changing the ratio of the distilled water to the disperse phase, formed by metallic sodium salt solution (60/40%, w/w) with ratios W_0 = water/surfactant = 6, 8, 10. Ultrasonic treatment to obtain a semi-permanent emulsion was accomplished using a high-intensity ultrasonic probe (Branson Digital Sonifier Model 450, ½″ diameter micro-tip, 20 kHz). Temperature during sonication was kept at 30 °C. Different sonication cycles were adopted to control the droplet size.

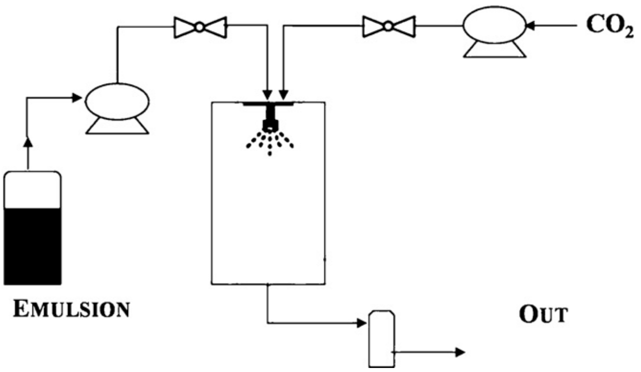

Fig. 1. Schematic representation of the SAS-ER apparatus.

2.3. Apparatus and procedures

The SAS-ER laboratory apparatus consists of a diaphram high-pressure pump (Milton Roy Mini Pump) used to deliver the liquid solution, and a diaphragm high-pressure pump (Milton Roy, mod. Milroyal B) used to deliver supercritical CO_2. A cylindrical vessel with an internal volume of 500 cm^3 is used as the precipitation chamber. The liquid mixture is delivered to the precipitator, through a thin wall 800 μm length and 200 μm diameter stainless steel nozzle. A second collection chamber operated at lower pressure and located downstream the precipitator is used to recover the liquid solvent. Further information on the apparatus has been given elsewhere [13,14] and a schematic representation is reported in Fig. 1. Typical liquid solution flow rates ranged between 1.5 and 2.0 mL/min and SC-CO_2 flow rates were correspondingly adapted to produce $X_{CO2} \approx 0.98$.

In each experiment, SC-CO_2 is injected into the precipitation chamber until the desired pressure is reached. Then, antisolvent steady flow is established, and a mixture of liquid solvent and surfactant (that does not contain the solute) is injected first, to obtain steady state fluid phase concentration conditions in the precipitator. When the steady state composition of solvent, surfactant and antisolvent is realized within the precipitator, the flow of the liquid solution is stopped and the emulsion is delivered through the nozzle producing the reaction and precipitation of the products. At the end of the liquid solution delivery, the chamber is purged with supercritical CO_2 to eliminate the residual solvent and surfactant solubilized in the supercritical antisolvent. More details about this procedure are given elsewhere [13,14].

2.4. Nanoparticles recovery

Nanoparticles recovery is still an open problem for many techniques. In the case of the SAS-ER, the direct recovery of the nanopowders is, instead, relatively simple. Residual surfactant, that has not been eliminated by washing with pure CO_2, is collected together with nanoparticles; it contributes to improve the nanoparticles collection producing a sticky product. A post-process treatment is used to obtain free nanoparticles. We used different recovery methods:

- We suspended the powders by ultrasonication in distilled water and used ultrafiltration (UF) on a membrane to eliminate the residual sodium carbonate that is soluble in water. Suspended solids are retained, while water and water soluble compound