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New insights into the formation of submicron silica particles using CO_2 as anti-solvent

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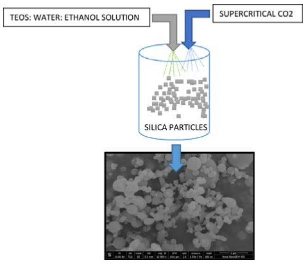
GRAPHICAL ABSTRACT



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ABSTRACT

A supercritical anti-solvent (SAS) process was carried out to obtain micron and submicron particles (0.35–1.78 μm) of silica from a solution with a silica precursor. The effects of different parameters such as pressure (120 and 150 bar), temperature (323 and 333 K), CO_2 flow rate (20 and 35 g/min), liquid solution flow rate (4 and 8 mL/min) and nozzle diameter (0.1 and 0.2 μm) on the outcome of the SAS process were analyzed. The TEOS: water molar ratio (1:4–1:17) was also evaluated and seems to play a major role in the precipitation of particles, especially in terms of agglomeration and morphology in that a higher amount of water leads to lower agglomeration of particles. Higher CO_2 and lower liquid solution flow rates are recommended to obtain a smaller particle size with narrow particle size distribution (0.35 ± 0.17 μm). Lower temperatures are recommended to reduce the particle size. The rest of the assayed variables did not have a significant influence on particle size and size distribution. As far as the textural properties are concerned, silica particles with low porosity (1.41–10.22 m^2/g) and certain hydrophilic character were generally produced.

1. Introduction

Silica particles are of great interest for numerous applications, e.g. in the medical field, the pharmaceutical industry, and colloidal chemistry [1]. Precipitated silica is mainly produced by the acidification of solutions of sodium silicate with sulfuric acid. In this procedure it is necessary to wash the resulting gel and then dehydrate it to produce colorless microporous silica [2]. In the conventional sol-gel process the sol is left to dry in air for several days for the hydrolysis and condensation of silica to occur and for the xerogel to form. Another alternative is the supercritical drying process often used to obtain aerogels [3–5]. Capillary forces act due to the existence of a solid-liquid-gas interface inside the pores within the solid phase network and these forces rupture the microstructure of the particles. A supercritical fluid

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drying process is employed to avoid the collapse of the microstructure [6]. In addition, the removal of ethanol must be carried out very slowly to avoid the fracture of the aerogels. Precipitation by the supercritical anti-solvent process (SAS) using carbon dioxide ($scCO_2$) can be applied to obtain SiO_2 particles [7]. In relation to the specific properties of the SCF, such as the high diffusivity as a consequence of the low viscosity and high density, the aforementioned fluids can provide a way to achieve nucleation of SiO_2 particles. Therefore, a precursor solution is made by mixing TEOS/water and ethanol was used to obtain SiO_2 particles.

The main advantages of using an SAS process are that the washing and dehydration steps are not required because the silica precipitated by SAS does not need any subsequent treatment. The faster nucleation means that a high added value silica with a particle size in the submicron range and a narrow particle size distribution is obtained. Moreover, by tuning the operating conditions it is possible obtain a silica with selected features. Furthermore, this is a green technology and the use of organic solvents is reduced.

The objective of the study described here was to generate fine particles by a supercritical anti-solvent process (SAS) using supercritical carbon dioxide ($scCO_2$). The precipitation with a compressed fluid, such as an anti-solvent, is one of the most promising supercritical techniques to produce controlled micronic and submicronic particles. This process starts with liquid crystallization through an increase in the molar volume of solution that induces a decrease in the solvent power to the solute when a liquid antisolvent is added [8]. Indeed, in the SAS technique the supercritical fluid replaces the liquid anti-solvent and this leads to the precipitation of solute since it forms a solution with the primary solvent. Therefore, a prerequisite for an SAS process is that it must be performed at temperature and pressure conditions in which complete miscibility exists between the primary solvent and the supercritical anti-solvent. A distinctive characteristic of supercritical fluids is their diffusivity, which can be up to two orders of magnitude higher than that of liquids. Therefore, the diffusion of the supercritical fluid into a liquid solvent can produce a fast supersaturation of a solute dissolved in the liquid and the precipitation of the solute as micronized particles. Moreover, this process allows control of particle size distribution and morphology.

In such a semi-continuous processing mode, the mixing between the solvent and anti-solvent is achieved by spraying an organic solution of the solute through a nozzle into the flowing stream of $scCO_2$. An injector is used to produce a liquid jet to form small droplets that expand in the precipitator [9]. SAS processes have been widely used for the last ten years in a variety of different fields: e.g., pharmaceuticals [10,11], explosives [12], polymers [13], coloring matter [14,15], fullerene [16], superconductors [17] and catalysts [18,19].

Chattopadhyay and Gupta [20] and Zhang et al. [21] developed a method for the precipitation of silica nanoparticles using $scCO_2$ as both an anti-solvent and a reactant. The precipitation of silica nanoparticles was carried out using emulsions of aqueous sodium silicate in organic solvents to provide silica particles. In a previous study, silica microparticles were produced by an SAS process and by supercritical ethanol drying of a silica precursor solution [7]. The aging time was evaluated and it was concluded that the particle size remained unchanged during the first week. However, an exhaustive study of the main parameters that could affect morphology, particle size and particle size distribution of silica obtained by this process is lacking. In this work the influence that different parameters in the SAS process have on morphology, particle size, particle size distribution and textural parameters was evaluated. The objective was to ascertain the operating conditions in this process required to obtain porous spherical silica particles in the submicron range.

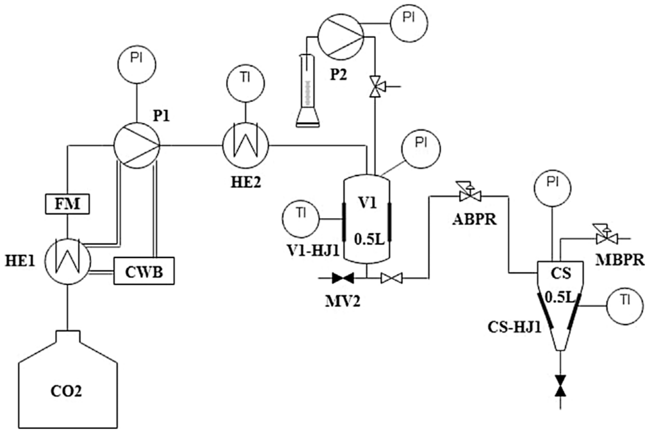

Fig. 1. SAS200 pilot plant scheme. (P1) high-pressure pumps for the CO_2; (P2) high-pressure pump for the solution, (V1) precipitator vessel surrounded by an electrical heating jacket (V1-HJ1); cyclone separator (CS1) surrounded by a jacketed (CS-HJ1); (MBPR) manual back-pressure regulator; (ABPR) automated back-pressure regulator; (HE1) low pressure heat exchanger; (CWB) cooling bath; (FM) mass flowmeter; (HE2) electrical high-pressure heat exchanger.

2. Materials and methods

2.1. Materials

The following substances were required for the SAS process. Carbon dioxide (CO_2) with a minimum purity of 99.8% was provided by Linde. Tetraethyl orthosilicate (TEOS) with a purity greater than or equal to 99% and ethanol (EtOH) with a purity of 99.5% were purchased from Sigma-Aldrich. In each experiment a sol based on 7 mL of TEOS and an acid/water mixture (100 mM HCl, pH = 1) in different molar ratios, diluted in ethanol (total volume of 100 mL), was prepared. The solution was pumped into the system after aging for 1 h.

2.2. Supercritical anti-solvent precipitation (SAS)

The Supercritical Fluid experiment was carried out in a pilot plant developed by Thar Technologies® (model SAS 200). A schematic diagram of the equipment is shown in Fig. 1. The plant was described in detail in a previous publication [10]. The construction of the plant includes the following main components: one high-pressure pump for the CO_2 (P1) and another for the solution (P2), a stainless-steel precipitator vessel of 0.5 L volume (V1), which is composed of a cylindrical main body with a frit at the bottom. The container in which the vessel is placed is surrounded by an electrical heating jacket (V1-HJ1). A stainless steel cyclone separator (CS1) with 0.5 L volume surrounded by a heated jacket (CS-HJ1) to separate the solvent and CO_2 once the pressure is released by the manual back-pressure regulator (MBPR). An automated high-precision back-pressure regulator (ABPR) is included to maintain a constant pressure. Auxiliary elements include a low pressure heat exchanger (HE1), cooling lines, and a cooling bath (CWB) to keep the CO_2 inlet pump cold and to chill the pump heads; a FlexCOR coriolis mass flowmeter (FM) to measure the CO_2 mass flow rate; an electrical high-pressure heat exchanger (HE2) to preheat the CO_2 in the precipitator vessel to the temperature set point; several thermocouples placed inside the precipitator vessel, the cyclone separator, and an electrical high pressure heat exchanger to obtain temperature measurements in real time.

The SAS process is semi-continuous. The experiments were carried out as follows: Once pressure and temperature set points were achieved in the precipitator, the previously prepared solution was injected into the vessel trough a nozzle device. Inside the reactor, the $scCO_2$ assumes the role of an anti-solvent, solubilizing into the nebulized drops of solvents, and therefore enhancing the precipitation of SiO_2 particles.