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Silica microparticles precipitation by two processes using supercritical fluids

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ABSTRACT

Silica microspheres are of great interest for several applications in areas such as medicine, biochemistry, colloidal chemistry and aerosol research. In this work, the sol–gel method was used to obtain such microparticles in two different ways. One of the methods applied was supercritical reaction; a high temperature process using ethanol as a supercritical fluid (SCF reaction). Another approach to obtaining silica microparticles was Supercritical AntiSolvent (SAS) process, as a low temperature process, using supercritical carbon dioxide ($scCO_2$). A tetraethyl orthosilicate (TEOS) and water solution (1:4 molar ratio) was dissolved in ethanol and then pumped into an autoclave at 100 bar and 523 K for the SCF reaction process, and at 120 bar and 313 K in the case of the SAS process. All the experiments led to a successful precipitation of silica microparticles, in the micrometer range. In all cases spherical morphology and no agglomeration was found. Furthermore, the main textural characteristics of such powders were obtained by nitrogen physisorption experiments. Results reveal spherical microparticles with nanopores smaller than 1 nm in size when using supercritical ethanol, and bulky microparticles with smooth surfaces when using $scCO_2$.

1. Introduction

Silica microspheres are of great interest for several applications in medicine, biochemistry, colloidal chemistry, aerosol research, drug delivery, and used for proteins encapsulations [1,2].

The sol–gel method is often used to obtain aerogels, by supercritical drying processes [3–5]. It is possible to avoid the collapse of the microstructure due to the capillary forces that are acting from the existence of a solid liquid gas interface inside the pores among the solid phase network, using supercritical fluids due to SCF drying circumvents the liquid–gas interface [6]. Moreover, the sol–gel method can also be used to precipitate SiO_2 microparticles using supercritical fluids (SCF). Given the specific properties of SCF, such as their high diffusivity as a consequence of their low viscosity and high density, the aforementioned fluids can provide a way to achieve nucleation of SiO_2 particles. Therefore, a precursor solution made by mixing TEOS/water and ethanol was used to obtain SiO_2 microparticles.

In this work SiO_2 particles were obtained by two processes, namely reaction with supercritical ethanol (SCF reaction process) and precipitation by supercritical antisolvent process (SAS) using supercritical carbon dioxide ($scCO_2$).

To precipitate SiO_2 microparticles by supercritical reaction, the aforementioned ethanol mixture is placed in an autoclave. During heating the liquid expands inside the autoclave reaching the supercritical point of ethanol. The SCF reaction process can be described as follows: reactions take place inside the autoclave, and the precursors dissolve in the SCF. The subsequent isothermal venting off causes SiO_2 to precipitate as microspheres. Particles nucleate in the liquid phase during heating and grow further in the SCF. Previous studies carried out by Moner-Girona et al. [7] proposed the condensation of silica microparticles from silicon alkoxides submitted to a stream of SCF (CO_2, EtOH or acetone), based on the Stöber method [8]. The authors found a correlation between particle size and hydrolysis parameter (i.e. TEOS/water molar ratio) as well as with the residence time in supercritical conditions before evacuation.

SAS is a semi-continuous precipitation technique developed to produce micrometric and sub-micrometric particles using a SCF as an antisolvent. The SAS process exploits the fast diffusion of the supercritical fluid, normally CO_2, into the organic solvent in which the solute is dissolved. This generates a high volumetric expansion of the solvent thus reducing the solvation capacity of the solvent. As a consequence, a high degree of uniform super-saturation is produced, promoting the precipitation of the solute as particles in the micrometer and nanometer size ranges. Moreover, this process allows control of particle size distribution and morphology. In such a semi-continuous processing mode, the mixing between the solvent and antisolvent is achieved, basically by spraying the organic

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solution of the solute via a nozzle into the flowing stream of $scCO_2$. SAS processes have been widely used for the last ten years in a variety of different fields: pharmaceuticals, explosives [9], polymers [10], coloring matter [11,12], superconductors [13], catalysts [14,15] and inorganic compounds [16], among others.

However, very little is known about silica microparticles formation by SAS process. In this way, Chattopadhyay and Gupta [17] and Zhang et al. [18] developed a method for precipitation of silica nanoparticles using $scCO_2$ acting as both an antisolvent and a reactant. Precipitation of silica nanoparticles was carried out using microemulsions of aqueous sodium silicate in organic solvents, obtaining silica nanoparticles with mean sizes ranging between 20–800 nm and 3–15 nm, respectively.

In both processes, SCF reaction and SAS processes, the wall of the autoclave becomes totally covered with SiO_2 powder, revealing an effective hydrolysis rate and generating a multinucleation mechanism that avoids growth of bigger particles.

Therefore, the objective of this work is to achieve an effective silica precipitation by supercritical ethanol reaction and SAS process. The two different processes were examined, focusing on particle size, particle size distribution and textural parameters, in order to assess their feasibility.

2. Materials and methods

Tetraethyl orthosilicate (TEOS) (≥99% purity) and ethanol (EtOH) (99.5% purity) were purchased from Sigma–Aldrich Chemical (Madrid, Spain). Carbon dioxide with a minimum purity of 99.8% was supplied by Linde (Spain). For both processes a 14 mL of TEOS and acid water mixture (100 mM), with a molar ratio of 1:4 and pH = 1 diluted in ethanol (total volume of 200 mL) was prepared. For the SCF reaction method, the mixture was placed in an autoclave freshly prepared, whereas for SAS several aging times were taken into account (3, 8 and 21 days). The samples were aged at 277 K in air at atmospheric pressure.

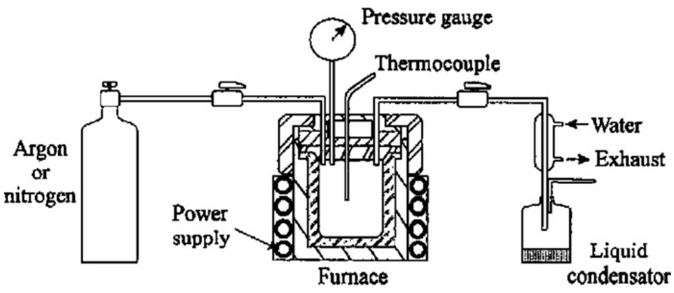

Fig. 1. Schematic diagram of SCF reaction process.

For the SCF reaction process, a 200 mL TEOS/water mixture diluted in ethanol was stored in a 500 mL-autoclave and slowly heated (1 °C/min) up to 523 K and at a pressure of 100 bar reaching the supercritical conditions of ethanol. Then, the ethanol was isothermally evacuated causing the formation of silica particles. A schematic diagram of the apparatus is shown in Fig. 1.

On the other hand, the SAS experiment was carried out in a pilot plant developed by Thar Technologies® (model SAS 200). A schematic diagram of the equipment, described in detail in a previous work [19], is shown in Fig. 2. The SAS 200 system comprises the following main components: two high-pressure pumps, one for the CO_2 (P1) and the other for the solution (P2); a stainless steel precipitator vessel (V1) with a 2-L volume, consisting of two parts, the main body and the frit, all surrounded by an electrical heating jacket (V1-HJ1); an automated high precision back-pressure regulator (ABPR1), attached to a motor controller with a position indicator; and a jacketed (CS1-HJ1) stainless steel cyclone separator (CS1) with 0.5-L volume, to separate the solvent and CO_2 once the pressure is released by the manual back-pressure regulator (MBPR1). The following auxiliary elements were also necessary: a low pressure heat exchanger (HE1), cooling lines, and a cooling bath (CWB1) to keep the CO_2 inlet pump cold and to chill the pump heads; an electrical high-pressure heat exchanger (HE2) to preheat rapidly the CO_2 in the precipitator vessel to the required temperature; thermocouples placed inside (V1-TS2) and outside (V1-TS1) the precipitator vessel, inside the cyclone separator

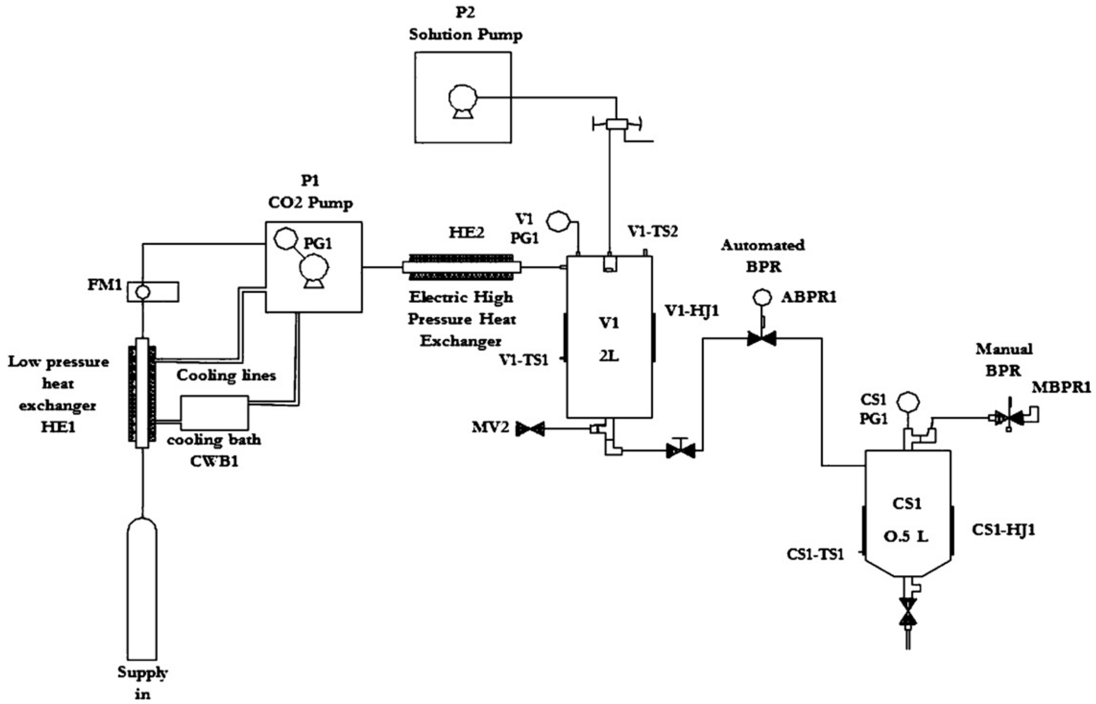

Fig. 2. Schematic diagram of pilot plant SAS200.