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Hydrothermal synthesis nanoparticle bysupercritical fluid

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ABSTRACT: Supercritical fluid (SCF) technology has become an important tool of materials processing in the last two decades. Supercritical CO_2 and H_2O are extensively being used in the preparation of a great variety of nanomaterials. The greatest requirement in the application of nanomaterials is its size and morphology control, which determine the application potential of the nanoparticles, as their properties vary significantly with size. Although significance of SCF technology has been described earlier by various authors, the importance of this technology for the fabrication of inorganic and hybrid nanomaterials in biomedical applications has not been discussed thoroughly. The interest in the preparation and application of nanometer size materials is increasing since they can exhibit properties of great industrial interest. Several techniques have been proposed to produce nanomaterials using supercritical fluids. These processes, taking advantage of the specific properties of supercritical fluids, are generally flexible, more simplified and with a reduced environmental impact. The result is that nanomaterials with potentially better performances have been obtained. In this study, the hydrothermal synthesis was investigated.

Keywords:*Hydrothermal; Nanostructure; Supercritical fluid; Synthesis; Water.*

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INTRODUCTION

There is a great interest in the preparation and application of nanometer size materials since they can exhibit new properties of industrial interest. Mainly the properties related to the ratio between surface and volume: at nanoscale, surface properties become relevant with respect to volume properties (Hakuta, *et al.,* 1998). For example, surface molecules can impart high hardness to metals and higher energy to propellants and explosives; electronic devices and pharmaceuticals with improved performance can also be produced (Hu, *et al.,* 1999). Different interpretations of the dimensions that set the boundary between normal materials and nanomaterials have been proposed. In this work, we assume that a nanoproduct should have at least one dimension smaller than 200 nm; though, more restrictive definitions have been proposed that set the upper limit at 100 nm. Nanoparticles, nanofilms and nanowires are nanometric along three, two and one dimension,respectively. In the case of nanostructured materials, at least one of the components has barometric dimensions (Adschiri, *et al.,* 2000).The various processes that have been proposed to obtain nanomaterials follow two main approaches: top down and bottom up (Li, *et al.,* 2002). Top-down is characterized by the production of nanoproducts departing from normal size materials; i.e., reducing the dimensions of the original material; for example, using special size reduction techniques. Bottom-up approach is related to the "synthesis" of nanosized materials, starting from the molecular scale; for example, the formation of particles by precipitation from a fluid phase. Supercritical fluids (SCFs) have also been proposed as media to produce nanomaterials (Cabbanas, *et al.,* 2001). The properties that make supercritical fluids particularly attractive, as a rule, are gas-like diffusivities, the continuously tunable solvent power/selectivity and the possibility of complete elimination at the end of the process. Particularly, the mix of gas-like and liquid-like properties can be useful in many applications related to nanotechnologies (Adschiri, *et al.,* 2000). The most widely used supercritical fluid is carbon dioxide (CO_2), that is cheap and non-polluting, and whose critical parameters are simple to be obtained in an industrial apparatus. However, ammonia, alcohols, light hydrocarbons and water have been proposed, among the others, for nanomaterials production at supercritical conditions. Among all the nanoproducts that can be envisaged, two main areas have been explored using supercritical fluids: nanoparticles and nanostructured materials. Nanoparticles cover a wide range of applications; it will be possible to produce explosives with a higher potential; i.e., approaching the ideal detonation; coloring matter with brighter colors; toners with a higher resolution; polymers and biopolymers with improved functional and structural properties (Cote, *et al.,* 2002). Moreover, pharmaceutical products can be designed that have enhanced pharmaceutical activity or that use different delivery routes and/or overcome human body internal barriers. Metals, metal oxides and ceramic compounds at nanodimensions can exhibit unusual strength and/or can be used as fillers in nanostructured materials. Composite nanospheres and nanocapsules can be used, for example, in pharmaceutical applications for controlled and sustained release of drugs (Viswanatha and Gupta*,* 2003). The production of nanowires, nanofilms and nanotubes has also been considered in supercritical fluid assisted processes (Zhang, *et al.,* 2001). Nanostructured polymers can be generated in form of nanocellular foams and membranes. For example, nanocomposite polymers can be obtained modification the host polymer properties using nanofillers (nanoparticles, nanoclays). However, nanostructured polymers will not be treated in this work since they have been the subject of a recent excellent review (Holmes, *et al.,* 2003). Several supercritical based techniques have been proposed in the literature for the production of micro and nano materials, since several processes can operate in the micronic or in the nanometric domain depending on the operating conditions and on the process arrangement. For what concerns micrometric and sub-micrometric particles generation by supercritical assisted processes, some good reviews are available in literature (Ji, *et al.,* 1999). A large number of papers in the literature claims the production of nanomaterials by supercritical fluids assisted processes; but, the dimensions of materials described are in several cases more properly in the range of sub-micronic products. Therefore, in this work we performed a first selection of the papers to be discussed on the basis of the “nano” definition previously proposed; i.e., papers related to materials with characteristic dimensions larger than 200 nm have not been considered. A critical analysis is proposed that highlights the most relevant positive and negative characteristic of each process and the kind of nanomaterial that can be produced (Chattopadhyay and Gupta, 2000).In this study, the application of supercritical water and carbon dioxide in synthesis of various nanoparticles was investigated. The various process i.e. RESS, SAS, ASES, SEDS, PGSS and hydrothermal synthesis was introduced and the processes based on hydrothermal synthesis was discussed in details.

SUPERCRITICAL FLUID

Supercritical fluid (SCF) is a highly compressed gas that has a density similar to that of a liquid. Figure 1 shows the phase diagram of a pure substance. At the triple point (T_P) the three phases (gas, liquid and solid) of the substance coexist in thermodynamic equilibrium. As the temperature goes high, the substance coexists in two phases, i.e., gas and liquid. At the critical point (*CP*) and in the region the temperature and the pressure are above the critical temperature and pressure, the substance exists in a single gaseous phase (Chattopadhyay and Gupta, 2000). The substance in this region is defined as in the supercritical state where the density is liquid-like while the viscosity is gas-like, and the diffusivity is in between those of a liquid and a gas as shown in Table 1. It is expected that a supercritical fluid, which has the higher diffusivity and the lower viscosity than a liquid solvent, will function much better than a liquid solvent as an extracting and a mobile phase in extraction and chromatography (Ji, *et al.,* 1999). Technically, a SCF is a gas but not a vapor. The term “gas” refers to any phase which “will conform in volume to the space available”. A “vapor” is defined as “a gas whose temperature is less than the critical temperature”. This was the definition proposed by Thomas Andrews in 1869 and is still generally, but not universally, accepted today. In practice, however, the terms gas and vapor are often used interchangeably (Holmes, *et al.,* 2003).

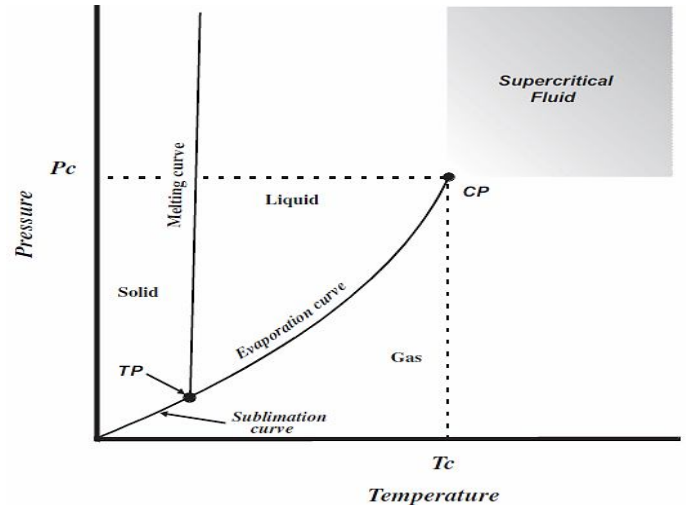

Fig. 1. Phase diagram of pure substance (Chattopadhyay and Gupta, 2000).

Table 1. Properties of gas, liquid and supercritical fluid (Zhang, *et al.,* 2001).

Supercritical fluid	**Liquid**	**Gas**	**Units**	**Property**
0.2-0.5	0.6-1.6	$0.6\text{-}2\times10^{-3}$	ρ (gr/cm^3)	Density
$0.5\text{-}4\times10^{-3}$	$0.2\text{-}2\times10^{-5}$	$1\text{-}4\times10^{-1}$	D_m (cm^2/sec)	Diffusivity
$1\text{-}3\times10^{-4}$	$0.2\text{-}3\times10^{-2}$	$1\text{-}3\times10^{-4}$	μ (gr/cm.s)	Viscosity

NANOPARTICLE GENERATION

A possible general classification of SCF based nanoparticles generation techniques can be proposed according to the role played by the SCF in the process. Indeed, SCFs have been proposed as solvents, solutes, anti-solvents and reaction media. As particle design is presently a major development of supercritical fluids applications, mainly in the pharmaceutical, nutraceutical, cosmetic and specialty chemistry industries, number of publications are issued and numerous patents filed every year (Chattopadhyay and Gupta, 2000). This document presents a survey (that cannot pretend to be exhaustive!) of published knowledge classified according to the different concepts currently used to manufacture particles, microspheres or microcapsules, liposomes or other dispersed materials (like microfibers) (Cote, *et al.,* 2002):

RESS: This acronym refers to ‘Rapid Expansion of Supercritical Solutions’; this process consists in solvating the product in the fluid and rapidly depressurizing this solution through an adequate nozzle, causing an extremely rapid nucleation of the product into a highly dispersed material. Known for long, this process is attractive due to the absence of organic solvent use; unfortunately, its application is restricted to products that present a reasonable solubility in supercritical carbon dioxide (low polarity compounds).

GAS or SAS: These acronyms refer to Gas (or Supercritical fluid) Anti-Solvent, one specific implementation being SEDS (Solution Enhanced Dispersion by Supercritical Fluids); this general concept consists in decreasing the solvent power of a polar liquid solvent in which the substrate is dissolved, by saturating it with carbon dioxide in supercritical conditions, causing the substrate precipitation or recrystallization. According to the solid morphology that is wished, various ways of implementation are available.

GAS or SAS recrystallization: This process is mostly used for recrystallization of solid dissolved in a solvent with the aim of obtaining either small size particles or large crystals, depending on the growth rate controlled by the anti-solvent pressure variation rate.

ASES: This name is rather used when micro- or nano-particles are expected; the process consists in pulverizing a solution of the substrate(s) in an organic solvent into a vessel swept by a supercritical fluid.

SEDS: A specific implementation of ASES consists in co-pulverizing the substrate(s) solution and a stream of supercritical carbon dioxide through appropriate nozzles.

PGSS: This acronym refers to 'Particles from Gas-Saturated Solutions (or Suspensions)': This process consists in dissolving a supercritical fluid into a liquid substrate, or a solution of the substrate(s) in a solvent, or a suspension of the substrate(s) in a solvent followed by a rapid depressurization of this mixture through a nozzle causing the formation of solid particles or liquid droplets according to the system.

The use of supercritical fluids as chemical reaction media for material synthesis, two processes are described: thermal decomposition in supercritical fluids and hydrothermal synthesis. We will successively detail the literature and patents for these four main process concepts, and related applications that have been claimed (Li, *et al.,* 2002). Moreover, as we believe it is important to take into account the user's point-of-view, we will also present this survey in classifying the documents according three product objectives: particles (micro- or nano-) of a single component, microspheres and microcapsules of mixtures of active and carrier (or excipient) components, and particle coating (Hu, *et al.,* 1999).

SYNTHESIS IN SUPERCRITICAL FLUIDS

Powder synthesis in gas phase can be carried out by reaction of precursor gases. Powders produced by the gas to particles route can have a sharp particle size distribution and are formed by non-porous primary particles. In analogy with the classical methods, nanoparticles can also be the product of a reaction in which a SCF is used as the reaction medium (Hakuta, *et al.,* 1998).

SOL-GEL DRYING

The use of SCFs is well established in gels drying since it allows the drying process with zero surface tension, avoiding the gel collapse. In this process, the SCF is only used to recover the produced nanoparticles (Table 2). Hu et al (1999) proposed the preparation of gels in aqueous solution, the replacement of water in the precipitate with a mixture of *n*-propanol and benzene and, then, the elimination of the organic solution using SC-CO_2. In this case the process was finalized to the production of copper borate nanoparticles. (Hu, *et al.,* 1999) proposed the formation of TiO_2 nanoparticles by sol preparation and the replacement of water in the precipitate with n-butanol and subsequent supercritical drying. Particle sizes ranging between 10 and 20 nm and surface areas up to 166.8 m^2/g were obtained. The same research group (Ji, *et al.,* 1999) also performed the supercritical drying of a beryllium borate aerogel to produce nanoparticles. In this case the replacement of water in the precipitate was obtained with a mixture of n-butanol and ligroin; then, supercritical drying was obtained using CO_2. In a subsequent work they used supercritical ethanol as the drying medium to recover magnesium borate nanoparticles.

Table 2. Compounds produced in nanoparticles by SC-drying (Holmes, *et al.,* 2003).

Supercritical Fluid	**Particle dimensions (nm)**	**Material**
CO_2	10-20	$Cu_3B_2O_6$
CO_2	10-20	TiO_2
CO_2	7	$Be_2BO_3(OH)$

HYDROTHERMAL SYNTHESIS IN SUPERCRITICAL WATER

Hydrothermal synthesis (HTS) is used to produce synthetic materials imitating natural geothermal processes. The reaction equilibrium of metal salt aqueous solutions changes with temperature and results in the formation of metal hydroxides or metal oxides. Supercritical water (SCW) provides an excellent reaction medium for hydrothermal synthesis, since it allows varying the reaction rate and equilibrium by shifting the dielectric constant and solvent density with pressure and temperature. One of the expected benefits is higher reaction rates and smaller particles (Chattopadhyay and Gupta, 2000). The reaction products have to be not soluble in SCW. The HTS-SCW process is usually operated as follows: a metal salt aqueous solution is prepared, pressurized and heated. The pressurized metal salt solution and a supercritical water stream are combined in a mixing point, which leads to rapid heating and subsequent reaction. After the solution leaves the reactor, it is rapidly quenched and in-line filters remove larger particles. Cooling water is directly fed to the reactor to quench the reaction (Fig. 2). Two different process modes have been proposed: the first uses a batch reactor and is characterized by a long reaction time; the second uses a flow reactor that assures continuous operation (Viswanatha and Gupta, 2003).

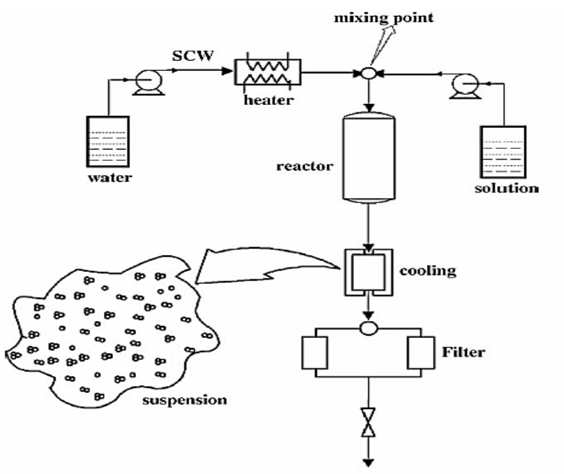

Fig. 2. A schematic representation of the HTS-SCW process (Viswanatha and Gupta, 2003).

HTS-SCW process has been extensively explored by (Adshiri, *et al.,* 2003, Hakuta, *et al.,* 1998, Li, *et al.,* 2002) in various works to produce nanometric particles of several single and complex metal oxides. This research group used several types of flow apparatus to perform HTS-SCW experiments. They evidenced several parameters of the process that can control dimension and morphology of the produced nanoparticles. First of all, solubility of metallic oxides in SCW has to be considered and its dependence on temperature and pH. Also the initial concentration of the feed and the heating rate can play a relevant role in this process. (Cabanas, *et al.,* 2001) used a small continuous reactor to produce $Ce1\text{-}xZn_xO_2$ by HTS-SCW starting from mixtures of cerium ammonium nitrate and zirconium acetate. According to these authors, the continuous reactor allows a better control of the experimental conditions when compared to the batch process. Very small nanoparticles have been obtained. After calcination at 1000 ºC for 1 h the material sintered up to 145 nm. In a subsequent work they used continuous HTSSCW to obtain nanoparticles of Fe_3O_4 and various Fe-Ni-Zn mixtures. In all cases, crystalline particles with mean diameters lower than 100 nm were obtained. (Cote, *et al.,* 2002) produced nanocrystals of Fe_2O_3 and Co_3O_4 using two variations of the continuous hydrothermal technique: cold mixing and hot mixing of the reactants. Compressed water (sub-critical) was used in the experiments. In a subsequent work they also obtained $CoFe_2O_4$ nanocrystals using the same process variations. Viswanathan and Gupta (2003) obtained ZnO nanoparticles in a continuous tubular reactor starting from zinc acetate and using various flow rates and feed concentrations. Spherical nanoparticles with a mean size down to 39 nm were identified by laser scattering and down to 120 nm by TEM analysis. HTS-SCW can produce very small nanometric particles; however, this process requires challenging operative conditions since supercritical point for water is located at 374 ºC and 220 bar. To operate in SCW, stainless steel with special characteristics is required due to the simultaneous application of high pressures and high temperatures. Moreover, SCW is a strong oxidizing agent not only for processed materials, but also for the elements of the plant which it is in contact with. HTS-SCW can be used only for compounds that are stable at high temperatures.

REVERSE MICELLES

Water-in-oil (w/o) microemulsions are thermodynamically stable aggregates formed by a nanometric sized water core in a polar continuous phase. They are generated by amphiphilic surfactants with a hydrophilic head group surrounding the water core and a hydrophobic tail that extends into a polar continuous phase (Viswanatha and Gupta*,* 2003). The oil-surfactant interactions form a large variety of structures to avoid the direct water/oil contact. Micelles are the simplest structure: they are spherical or cylindrical objects formed by surfactant molecules separating oil and water. Drops of oil in water are called micelles, reverse micelles are drops of water in oil (Cote, *et al.,* 2002). Reverse micelles are widely used as nanoreactors to synthesize organic and inorganic nanoparticles. A reactant is, as a rule, contained in the aqueous core and the other in the continuous organic phase. As the reaction is confined in the water core, whose dimensions are controlled by thermodynamic conditions, the diameter of the produced nanoparticles can be controlled by the core size (Zhang, *et al.,* 2001). Traditional recovery methods have a relevant effect on the increase of particle size and particle size distribution, due to aggregation phenomena. A large amount of the surfactant remains on the nanoparticles. Supercritical CO_2 has a large affinity with many organic solvents; therefore, it can be used in the recovery step as an anti-solvent, or solvent-catcher, to extract all the liquid solvent (and most of surfactant) producing dry non-coalescing nanoparticles in a single process step. Using selected surfactants that can stabilize water droplets in near critical or supercritical CO_2, an elegant process, is also possible in which water-in-CO_2 (w/c) microemulsions are formed. In this case no organic solvents are required for the continuous phase and particles collection can be performed by simple decompression (Cabbanas, *et al.,* 2001). Zhang and coworkers (2001) synthesized Ag nanoparticles in water-in-isooctane continuous phase using w/o reverse micelles and sodium bis (2-ethylhexil) succinate (AOT) as surfactant. Chattopadhyay and Gupta (2000) used w/o microemulsions in a different process. They injected the w/o microemulsion into a batch reactor containing SC-CO_2 that acted either as the solvent-catcher eliminating the organic solvent and either as a reactant. They tested this process in the precipitation of silica nanoparticles obtaining nanoparticles with narrow particle size distributions, changing pressure, surfactant (AOT) concentration and water/surfactant ratio. The formation of w/c reverse micelles was explored by (Holmes, *et al.,* 2003) using as surfactant ammonium perfluoropolyether (PFPE-NH_4) for the synthesis of CdS nanoparticles. Particles with mean diameters ranging between 0.9 and 1.8 nm were obtained. (Ji, *et al.,* 1999) used w/c reverse micelles to synthesize Ag nanoparticles with average sizes ranging between 5 and 15 nm. Surfactants with fluorinated tails were used by these authors.

CONCLUSIONS

A large quantity of SCF based processes that were successful in producing nanomaterials has been found in the literature at laboratory scale. They can be divided in new processes and (more commonly) adaptation of existing processes to the use of SCFs. In all cases, using SCFs, more flexible and/or simplified processes have produced and with a reduction of the environmental impact. The final result is that nanomaterials with potentially better performances have been obtained using improved processes. Probably not all the SCF based processes that have been proposed will find an application; a “natural” selection is expected among them and only some will be used. The application to a large variety of nanomaterials has been proposed and we can expect that different materials will be tested in the future. However, extensive scientific research is still required on the large majority of the process proposed to evaluate: the extent of their applicability and their scalability outside the scientific laboratories. Moreover, a problem shared by all nanomaterials processed is the nanomaterial collection after its generation. Among all the processes reviewed, at the best of our knowledge, only SAS has been successfully proposed on the pilot scale yet, and some efforts are in progress to develop it on the industrial scale. We expect that this development stage will be reached in the next future by several other SCF based processes.

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