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► To cite this version:

François Cansell, Cyril Aymonier, Anne Loppinet-Serani. Review of materials science and supercritical fluids. *Current Opinion in Solid State and Materials Science*, 2003, 7 (4-5), pp.331-340. 10.1016/j.cossms.2004.01.003 . hal-00165780

HAL Id: hal-00165780

<https://hal.science/hal-00165780>

Submitted on 8 Jun 2021

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Review on materials science and supercritical fluids

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Abstract

Some supercritical fluids are able to replace toxic industrial solvents. So, from an industrial point of view, supercritical fluids are widely used in many fields such as pharmacy, food industry and environment. From a scientific point of view, the main interest of supercritical fluids is connected to the possibility to adjust continuously the physicochemical properties of these reactive media, such as selectivity, solvation, solubility or reactivity. In this paper, we present recent work on processes using supercritical media for processing materials related to fine particle synthesis, porous materials synthesis, polymer synthesis and surface modifications.

Keywords: Material; Supercritical fluid; Nanomaterial; Particle; Polymer; Cleaning; Surface modification; Porous material

1. Introduction

Both the capability of some supercritical fluids to replace toxic solvents and the ability of tuning solvent characteristics for highly specific separations or reactions have led to the current scientific and industrial interest in supercritical fluids. These fluids possess physicochemical properties, such as density, viscosity and diffusivity, which are intermediate between those of liquids and gases and which are continuously adjustable from gas to liquid with small pressure and temperature variations. Processes using these fluids are particularly attractive in many fields such as analytical and preparative separations, organic and inorganic synthesis, waste management, material processing (nanomaterials, nanostructured materials, thin films, coating), porous materials and earth science (volcanism, geothermal energy, hydrothermal synthesis) [*1,*2,*3].

A fluid is said to be “supercritical” when its temperature and pressure exceed the critical temperature (T_c) and pressure (P_c). Fig. 1 shows a schematic representation of density and organization of molecules of a pure fluid in solid state, gas state, liquid state and supercrit-

ical domain. At the critical point, the density of the gas phase becomes equal to that of the liquid phase and the interface between gas and liquid disappears. The macroscopic behaviour of these fluids is characterized by mechanical and thermal instabilities. These instabilities result from the singular behaviour of some properties such as the isothermal compressibility ($K_T = -1/V(dV/dP)$ where V is the molar volume), which tends to infinity. The value of this isothermal compressibility remains important in the current conditions of using supercritical fluids ($1 < \frac{T}{T_c} < 2$ and $1 < \frac{P}{P_c} < 3$). From a microscopic point of view, this behaviour has been interpreted by local fluctuations of the local density leading to the critical opalescence phenomenon due to the fact that the correlation length is of the same order of magnitude that of visible light. As reported in Fig. 2a, the local organization includes simultaneously regions of both gas and liquid local densities. This local organization is dynamic (with a life time of approximately 100 ps) and these local fluctuations of density allow us to explain the increase of the fluid compressibility. In order to discuss this point, we will study the case of a high-pressure vessel with a volume V and filled with n molecules at T temperature.

In this high-pressure vessel, the fluid can be described as a system consisting of microdomains with localized densities of both gaseous and liquid levels which are in dynamic equilibrium. If one reduces the volume V (with T and n constant) with a mechanical action, the system

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Fig. 1. Schematic representation of microscopic behaviour of a pure fluid in the $P-T$ plane phase diagram.

Fig. 2. Schematic representation of the molecule distribution simulation in a supercritical pure fluid (a) and solvent and solute molecules in a supercritical solution (b).

will react and particles in a microdomain with a local density like a gas will go to a microdomain with a local density like a liquid. So this reaction of the system leads to a very weak increasing of pressure and explains the high value of the fluid compressibility.

Regarding the classical description of solvation, this takes into account interactions at small distances whereas interactions at long distances, due to the critical behaviour of the fluid, are considered by the evolution of the solute partial molar volume, which is a macroscopic data. The large volume contraction is interpreted according to the solvent structure and the intermolecular forces. In the case of an attractive mixture, the addition of a solute causes a change in the solvent organization and generates the aggregation of solvent molecules close to the solute (Fig. 2b). This phenomenon (which means the aggregation of solvent molecules around the solute) cannot be independent of local fluctuations of density.

Specific properties of supercritical fluids such as their low viscosity (matrix penetration as gas-like) and their

relatively high density (solute solubilization as liquid-like) allow, for example, easier mass transfer which leads to their development on an industrial scale for extraction process. Concerning hydrothermal oxidation for waste management, the main interest is connected to the specific properties of supercritical water regarding its chemical reactivity with a high solubility of organic compounds and oxygen (suppression of interface) and a high reactivity (total organic destruction) [4]. This paper is focused on recent work for materials processing in supercritical media related to fine particle synthesis, porous materials synthesis and modification, polymer synthesis and surface modifications.

2. Fine particle synthesis

Particle processing is today one of the major developments of supercritical fluid applications in industrial fields such as the chemistry, pharmaceutical, cosmetic and agro-food industries. Two main processes of fine particle synthesis in supercritical fluids have been developed. For the first one, particle formation is based on a physical transformation and for the second, particle formation is based on a chemical reaction. Two recent papers [5,6] present a good overview of the state of the art concerning the first kind of processes: (i) rapid expansion of supercritical solutions (RESS) characterized by a rapid depressurisation of a supercritical fluid solution containing the solute; the decompression being the driving force of particle nucleation and growth; (ii) supercritical anti-solvent (SAS) described by the dissolution of a supercritical fluid (generally CO_2) in an organic solution containing the solute, the very low solubility of the solute in the resulting fluid leads to the particle nucleation and growth; (iii) particles from gas-saturated solutions (PGSS) based on the depressurisation of a mixture consisting of a dense gas dissolved into a liquid, which can be either a solution (sometimes a suspension) of a compound or a melted solid; this depressurisation leads to the generation of particles. Numerous research studies are published and/or patented every year on these technologies; industrial applications are expected soon in many sectors, especially in the pharmaceutical industry.

Over the past decade, the second family of processes using supercritical fluids as reaction media to synthesize a number of finely divided materials has received considerable attention [7]. Beyond the environmental aspect, this new way of materials processing is developed to give a better control of particle synthesis in terms of size, size distribution, morphology, chemical composition and structure. The main processes of fine particle synthesis by chemical methods, especially fine metal, semiconductor, nitride and oxide particles are presented hereafter.

2.1. Fine metal and semiconductor particle synthesis

The thermal decomposition of bis(hexafluoroacetylacetonate)copper(II) hydrate in a supercritical CO_2 /ethanol (80/20 wt.%) mixture, at 19 MPa and 200 °C, leads to the synthesis of nanostructured copper particles [8,**9]. Different kinds of metal particles in terms of size, morphology and surface properties can be obtained (Fig. 3). The thermal decomposition of the metal precursor in a supercritical medium leads to a high nucleation rate, and thus, to the generation of metal clusters composed by few atoms. These clusters grow by binary contact and coalescence to give nanoparticles of a few nanometers (Fig. 3, step 1). As a function of the main process parameters (pressure, temperature, residence time, metal precursor concentration, ...), these nanoparticles can: (i) grow to larger crystalline particles (Fig. 3, step 2; Fig. 4); (ii) aggregate to produce nanostructured particles with sizes between a few nanometers and a few micrometers (Fig. 3, step 3); (iii) be stabilized by surfactants, dendrimers, hyperbranched molecules, in order to give stabilized metal nanoparticles of a few nanometers (Fig. 3, step 4); (iv) be deposited into porous materials such as aerogels or membranes (Fig. 3, step 5). So, this process based on the thermal decomposition of metal precursors in supercritical media allows the synthesis of metal particles with control of the size (from few nanometers to few micrometers), the morphology

and the surface properties, and recovery of the particles as dry powders without any trace of solvent.

Another approach inspired by solution chemistry concerns the use of reverse micelles in supercritical fluids as “nanoreactors” to synthesize metal and semiconductor nanoparticles [*10]. Production of silver and copper nanoparticles with water in sc-alkane microemulsions has been investigated. To replace flammable and expensive alkane solvents, reverse micelles in supercritical CO_2 (sc- CO_2) were studied to synthesize metal (Ag, Cu) or semiconductor (CdS) nanoparticles [11,**12,13]. Although the size and morphology of nanoparticles can be readily controlled by the reverse micelle properties, it is nevertheless difficult to collect the as-prepared nanoparticles owing to their aggregation and coalescence upon removal of the supercritical fluid. So, the reduction of metal precursors in sc- CO_2 in the presence of fluorinated surfactants to synthesize stabilized Ag, Ir, Pt, Pd nanoparticles has been performed [14,*15]. In the same way, stabilized copper nanoparticles were produced in sc- H_2O [16].

2.2. Fine nitride particle synthesis

Fine nitride particles exhibit interesting properties in many fields such as chemistry, physics, mechanics and optics. Whereas the standard solid-state chemistry methods of nitride processing use very high pressures

Fig. 3. Schematic representation of particles processing in supercritical media by thermal decomposition of metal precursors.

Fig. 4. SEM pictures of different shapes of crystalline particles of copper obtained by thermal decomposition of bis(hexafluoroacetylacetonate)copper in a mixture of CO_2 /ethanol (80/20) at 200 °C and 19 MPa [**9].

11 μm

Fig. 5. SEM picture of cubic copper nitride monocrystals obtained by thermal decomposition of bis(hexafluoroacetylacetonate)copper in a mixture of NH_3 /methanol (70/30) at 200 °C and 16 MPa [*17].

and/or temperatures, the process based on the thermal decomposition of metal precursors allows synthesis of nitride particles in supercritical ammonia at low temperature and low pressure [*17]. Ni_3N , Cu_3N , Co_2N , Cr_2N , Fe_4N particles were obtained by decomposition of the corresponding metal precursors in sc- NH_3 /methanol (70/30) in a range of temperatures between 170 and 290 °C at 16 MPa. The nitride particle characteristics (size, size distribution, morphology, structure, surface properties) can be tuned with the process operating parameters. Fig. 5 presents, as example, SEM picture of cubic copper nitride monocrystals obtained by thermal decomposition of bis(hexafluoroacetylacetonate)copper in a mixture of NH_3 /methanol (70/30) at 200 °C and 16 MPa [*17].

2.3. Fine oxide particle synthesis

Since the beginning of the 1990s, supercritical fluids are widely used as reaction media for the synthesis of ceramics and closely related oxide materials, in order to improve the physicochemical properties of the powders. The process based on the thermal decomposition of a metal precursor is also very interesting to produce fine oxide particle with a control of the size, the size distribution, the morphology and the structure by tuning the process operating parameters [**7,8,**9,*17,18]. Different kinds of fine oxide particles, nanocrystalline or amorphous, were obtained including Fe_2O_3 , Cu_2O , Cr_2O_3 , Al_2O_3 or Ga_2O_3 from the thermal decomposition of the corresponding metal precursors in sc- $(\text{CO}_2/\text{ethanol})$ in a range of temperatures between 180 and 260 °C at about 16 MPa (Fig. 6).

Different research teams using supercritical media to synthesize fine crystalline oxide particles have adapted

2 μm

Fig. 6. SEM picture of alumina oxide particles obtained by thermal decomposition of bis(hexafluoroacetylacetonate)alumina in a mixture of CO_2 /ethanol (80/20) at 230 °C and 16 MPa [*17].

the standard sol gel chemistry. Synthesis of TiO_2 (anatase structure) or bimetallic oxides such as MgAl_2O_4 (spinel structure) and BaTiO_3 (cubic structure) in sc-alcohol or sc- $(\text{CO}_2/\text{alcohol})$ has been investigated [19]. As in a previous process, a dry powder can be recovered by removal of the supercritical solution.

Reverse micelles in supercritical fluids as “nanoreactors” to produce oxides in a controlled way were also studied. For example, fine TiO_2 particles were obtained with water in sc- CO_2 reverse micelles [20].

Finally, hydrothermal synthesis is also a route to produce fine oxide particles in sub- and supercritical water. For example, hydrolysis followed by a dehydration reaction in sc-water of metal nitrates leads to a wide variety of metal oxide crystals [21]. In the same way, metal-organic precursors lead to metal oxide nanoparticles [22].

The synthesis of materials in supercritical fluids by a chemical process can be governed by high nucleation rate and low crystal growth as a function of the process operating parameters. So nanocrystals of a few nanometers are easily obtained. This process is very efficient to control the size, the morphology and the structure but also to synthesize fine metal, nitride and oxide particles at relatively low temperatures.

The research efforts are more and more focused on the stabilization of nanomaterials due to their very interesting properties, which can be different of those of bulk materials.

3. Porous materials synthesis and modification

Porous materials have attractive physicochemical properties due to their high surface areas and their

porous structures. They have found a wide variety of applications in some areas such as catalysis, optics, phonic and thermal insulator. For example, porous materials with well-defined pore geometry are very interesting as catalysts and adsorbents for selective reactions. So, many investigations have been conducted to synthesize ordered porous materials and also to change porous structures by coating or loading them with functional molecules. As supercritical fluids have a high diffusivity, a low viscosity and a controllable solubility, they are good candidates for synthesizing porous structures and for coating on porous substrates.

3.1. Aerogels

A sol gel method is often used to synthesize porous materials. Classically, during the solvent vaporization step, the collapse of the three-dimensional network leads to a xerogel (Fig. 7). This collapse leads to the emergence of cracks or to the destruction of the material. In order to avoid this collapse, supercritical drying has been performed (Fig. 7) in numerous studies [23–25]. Recently, an organic aerogel of 2,3-didecyloxyanthracene (DDOA) was synthesized and dried using sc-CO₂ as a solvent [26]. The formation of DDOA aerogel requires both higher pressure and temperature than for a classical supercritical drying process in order to obtain the CO₂ solvation properties. But aerogels formed with this entire supercritical procedure looked like cotton material with a very low density of $2 \times 10^{-3} \text{ g cm}^{-3}$. Silica aerogel microparticles were also easily obtained by a one

step and versatile method with supercritical acetone as the solvent [27]. This method reduces the number of steps of traditional sol gel processes. Fiber-like structures and spherical morphologies were obtained. The properties of the resulting materials widely depend on the experimental parameters.

3.2. Three-dimensional devices

Mesoporous materials, such as silicates or aluminosilicates, have a great specific surface, a perfectly controlled porosity and unidirectional pores. They are distinguished from zeolites by pores which are definitely larger (from 1.8 to 15 nm as compared with a maximum of 1.3 nm for zeolites). These materials allow widening of the field of heterogeneous catalysis or separation of bulky molecules. Mesoporous materials can also act as nanoreactors. Coating with silica in supercritical fluid and in liquid ethanol onto nanoporous structures such as micro- and mesoporous silica and activated carbon has been investigated [28]. The silica precursor (tetraethylorthosilicate) dissolved in the liquid solvent does not enter into the pores due to the low diffusivity, the high velocity, the disturbance of the wettability and of the surface tension of the liquid solvent. On the other hand, a high diffusivity, a low viscosity and a non-cohesiveness of supercritical fluids facilitate the introduction of the precursor more deeply into the pores than for the liquid solvent. Using the same idea, dimensionally ordered semiconductor nanowires of silicon were synthesized with the supercritical fluid inclusion-phase

Fig. 7. Schematic representation of gel drying to produce xerogel and aerogel in a diphasic medium (gas liquid) and monophasic medium (supercritical fluid), respectively.

technique [**12]. Metal and semiconductor nanowires were prepared within the pores of mesoporous silica hosts. This procedure is reproducible, extremely fast (15–30 min against days usually), efficient and cost effective. This inclusion technique is easily applied to other semiconductor and metal nanowires such as germanium, copper, cobalt, iron oxide and nickel. Another application of these interesting properties of supercritical fluids deals with the impregnation of polymeric substrates with antimicrobial substances such as silver, zinc and/or copper or metal-complexes or metal salts [29]. In this case, in addition to their interesting properties of diffusivity, viscosity and non-cohesiveness, supercritical fluids were chosen for their innocuousness compared with potentially toxic organic liquids.

Silica aerogels are also very porous materials with a large surface area. The pore size (1–100 nm) and porosity can be controlled by the preparation conditions. This large surface area enables the aerogel to retain a large number of nanoparticles. The key point is to fix them firmly on the silica structure. Incorporation of metal nanoparticles in silica aerogel was performed [30]. Dodecanethiol-passivated gold nanoparticles were prepared and a wet gel was then immersed in the particle solution leading to the formation of an ultra-fine metal particle/wet gel composite. The gel was then dried in sc-CO₂ in order to avoid shrinkage of the gel.

3.3. Membrane

Al₂O₃ membranes were directly modified by TiO₂ deposition on ceramic substrates by hydrolytic decomposition of titanium tetraisopropoxide in supercritical propan-2-ol [31]. Depending on the experimental conditions, different thickness (1–3 µm), infiltration depths (15–30 µm) and pore sizes (micro- or mesopores) were obtained. Another recent procedure for ceramic membrane synthesis was a sol gel process carried out directly in supercritical carbon dioxide [**32]. This method was applied to the preparation of titania membranes on a macroporous Al₂O₃ support. The modification of experimental parameters allows control of the structure and the morphology of the membranes. In particular, both pressure and residence time strongly influence particle sizes and related surface areas. Mixed oxides were also obtained in sc-CO₂. The synthesis of crystalline Ce_{1-x}Gd_xO_{2-x/2} membranes was carried out in sc-CO₂ from cerium and gadolinium acetates as precursors [33].

4. Polymer synthesis

Since the late 1990s, chemical reactions performed in supercritical fluids and all subsequent related studies have increased exponentially [**34,**35]. This tremen-

dous growth relies on the physicochemical properties of these fluids, which make them extremely attractive as green solvents. Among the supercritical fluids, CO₂ is the most desirable for polymerization reactions. A large part of the studies revolve around homogeneous and heterogeneous radical polymerization techniques. Regarding ionic cationic and anionic and transition metal-catalyzed processes, recent results have shown these to be promising for the polymerization of vinylic, cyclic or olefinic monomers. Emulsion-templated polymers using a high internal phase CO₂-in-water emulsion have been developed [**36].

Regarding anionic polymerization, copolymerization of epoxides with CO₂ by species such as Zn(β-diimine)X (X = Et, OAc, N(SiMe₃)₂, OH, OMe, OⁱPr, Br, Cl) was further investigated [37]. A pseudo-anionic ring opening polymerization of ε-caprolactone initiated by M(OⁱPr)₃ (M = Al, Y, La) was reported and investigations of the CO₂/M(OⁱPr)₃-initiator interactions by in situ IR spectroscopy confirmed the reversible formation of carbonate type dormant species of the three metals, Al, Y, and La [38].

Regarding electrochemical synthesis, conducting polypyrrole films were obtained in sc-CO₂ (8.3–9.7 MPa; 38–43 °C). The characteristics of the polypyrrole films synthesized in sc-CO₂ are comparable to those prepared electrochemically in aqueous HCl and non-aqueous acetonitrile solutions [39].

A great number of studies have revolved around both the evaluation of the solubility of different species in various polymerization media [40–42] and the design and the use of surfactants and/or fluorinated species [**43]. Indeed, CO₂-soluble amphiphilic block copolymer surfactants, incorporating a CO₂-philic fluorinated or siloxane components and a CO₂-phobic hydrophilic or lipophilic components, as well as fluorinated substituted catalysts monomers or additives have been designed and appear as the key entities for successful polymerizations. Fluorocarbon solvents were used for synthesized cross-linked polymer microspheres by dispersion polymerization [44].

Finally, sc-CO₂ as a porogen solvent has attracted much interest for materials synthesis with macroporous polymer beads by suspension polymerization using supercritical fluid as a “pressure-adjustable” [**45] medium and with macroporous polymer monoliths [46].

5. Surface modifications

The specific properties of supercritical fluids can be used to improve or to modify surfaces by coating in a controlled way or by cleaning. These two aspects of surface modification in supercritical fluids are described hereafter.

5.1. Surface modification by coating

Beyond the production of fine particles, another application of the processes described in 2 concerns the surface modification by coating:

(i) *Surface modification by chemical processes in supercritical fluids*: over the past decade, numerous studies have involved the development of chemical fluid deposition (CFD) techniques and related technologies based on the reaction of a precursor in a supercritical solution. The thermal decomposition of metal precursors was applied to the coating of substrates by metal, oxide or nitride films, in particular the coating of fine particles, even with complex morphologies. New core-shell structures, as Ni/Cu and SmCo₅/Cu, were synthesized to exhibit interesting properties, more particularly in the magnetic recording field [47]. Fig. 8 presents the main steps of this process with two SEM pictures of a Ni particle before and after coating by a Cu shell. Another approach consists of the formation of metal, metal oxide or metal sulphide films onto substrate surfaces initiated by a reaction with a precursor in supercritical fluid (generally a reduction reaction with H₂). For example, this process succeeded in depositing continuous palladium films at controlled depths within porous alumina disk [48]. Beyond the CFD techniques, a supercritical fluid immersion deposition (SFID) method was recently developed for producing thin films of metals and alloys on substrates or into porous solids of silicon, germanium, and other “fluorine-philic” elemental semiconductors [49]. Pd, Cu, Ag and other metal films were deposited on Si-based substrates in sc-CO₂.

These methods for coating in supercritical fluids were developed to overcome the limitations of standard

chemical vapour deposition process (CVD), as for example volatile, toxic and expensive precursors.

(ii) *Surface modification by physical processes in supercritical fluids*: RESS, SAS, and derivatives as well as PGSS are equally applied as microencapsulation and coating processes, in particular for microencapsulating active substance into a polymeric matrix. This includes the controlled drug release implicated in several industrial applications such as: pharmaceuticals, agrochemistry, cosmetics, inks, paints etc. Among the numerous works published and/or patented in this field, two examples are discussed in this review: the fluidized bed coating technology in supercritical fluids as an experimental and promising method and a process of microencapsulation of protein particles within lipids using a novel supercritical fluid coating approach, as a process in an industrial development state. The fluidized bed coating technology is based on the RESS process. The coating material is dissolved in sc-CO₂ and sprayed into the bulk of a fluidized bed containing the particles to coat. The first studies were applied for the coating of catalyst particles in a fluidized bed operating under atmospheric conditions. Recently, studies were performed on the coating of particles in a high-pressure fluidized bed [*50]. This coating process is very promising because it couples the advantages of two well-known processes, the RESS process and fluidized bed technology. But one of its limitations could be the coating of very fine particles and more precisely the stabilization in the fluidized bed of particle sizes lower than a few microns. The second example refers to a novel supercritical fluid way to process pharmaceutical products [51,**52]. It consists of the dissolution of one or more coating materials in sc-CO₂ and then adjusting

Fig. 8. Schematic representation of particle coating in supercritical media by thermal decomposition of metal precursors.

temperature and pressure working conditions in the reactor so that the coating material becomes insoluble and goes onto the surface of the dispersed particles. Today many efforts are provided in order to scale-up this process at the industrial scale under pharmaceutical conditions as good manufacturing practice (GMP).

5.2. Surface modification by cleaning

Supercritical carbon dioxide offers environmental and cost benefits to the semiconductor industry. Wet-chemical stripping processes are reaching their theoretical limits as circuit line architecture gets smaller [*53]. Compared to CO₂ pellet cleaning or CO₂ snow cleaning, sc-CO₂ rapidly penetrates crevices and boundary layers where snow cannot [**54]. Low viscosity, low surface tension and the relatively high density of supercritical fluids aid in penetrating materials and removing contaminants. Moreover, initial cleaning of wafers has been suggested since solubility of non-polar organic compounds from greases, oils, lubricants and fingerprints is high in sc-CO₂. More recently, new formulations and methods for removing unwanted materials from semiconductor wafers or other substrates have been proposed. These formulations may include co-solvent, surfactants, chelating agents and/or chemical reactants added to the supercritical fluid [55]. The efficiency of sc-CO₂ cleaning of Si wafers has been developed at an industrial scale and the efficiency reaches 99.7% in 5 min [56]. Sc-ozone was also used to clean semiconductor wafers [57]. The combination of supercritical fluid with megasonic acoustic wave was recently used for cleaning wafers, substrates and semiconductor work pieces [58]. Another application of materials cleaning has been developed for the extraction of gadolinium from a mixture of Gd₂O₃ and ZrO₂ selectively with sc-CO₂ containing TBH HNO₃ complex (TBH is tri-*n*-butyl phosphate) [59]. This method would be useful to the selective cleaning of materials contaminated with radioactive oxides such as UO₂/PuO₂. Even in the medical field, supercritical fluids have been used to clean implantable medical devices [60].

6. Conclusions and perspectives

Supercritical media present very attractive properties from a scientific point of view due to the possibility to modify continuously the properties of reaction media from a polar solvent to a non-polar solvent for water, for example, by adjustment of pressure and/or temperature. So, these media exhibit unique properties for well understanding kinetics and chemical pathways. The most promising developments of supercritical technologies, in the field of materials, will be processing of fine powders and core-shell particles, processing and/or

impregnation of aerogels, processing of polymers and surface modifications.

From an industrial point of view, the developments of processes using supercritical fluid as reactive media are connected with the synthesis of materials with unusual physicochemical properties, which cannot be obtained with standard processes. Supercritical carbon dioxide is the most widely used supercritical medium in the recent literature. It is often chosen because of its particular characteristics such as its innocuity, its low cost and its easy using conditions.

The main limiting factors are the mass and heat transfers, which are generally very low. The hydrodynamic and the heat transfers are well depicted with commercial calculation programs but a large amount of work is still needed on the development of programs to predict the solubility of solutes and to model their reactivity in supercritical media. Furthermore, financial, legislative and psychological aspects are determining factors from a socio-economic point of view.

The technological transfer from laboratory to industry is promoted in the Community Initiative Programme INTERREG III B with the network "Supercritical Fluids and Materials Network SUPERMAT" in which research and innovation are fundamental prerequisites to combine economic growth and sustainable development [61].

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* of special interest;

** of very special interest.

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