Review of supercritical fluids in inorganic materials science

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This review paper highlights how supercritical fluid technology applied to materials processing can play a great role in materials science. It is shown that this way of materials processing offers the possibility of controlling the synthesis by varying operating parameters. Understanding how each parameter influences the synthesis process allows one to control the characteristics of the material, in terms of size, morphology, structure and composition. It is equally shown how these operating parameters influence the properties of the material, and therefore their applications in numerous technologically important fields such as energy, chemistry, electronics, optics and pharmacology.

Keywords: Materials science; Supercritical fluids; Size; Morphology; Structure; Composition

1. Introduction

Materials science can be defined as the study of the relation between the organization of matter at the atomic level and the microstructure and the properties of materials [1]. Thus the aim of materials science is to understand matter to be able to tune its properties. The potential value of a material can be evaluated using four guidelines, as shown in Fig. 1:

- synthesis and processing (axis 1, Fig. 1),
- chemical and physical characteristics (size, morphology, composition and structure) (axis 2, Fig. 1),
- specific properties (axis 3, Fig. 1),
- marketability and market (axis 4, Fig. 1).

The performance of a particular material can be represented by the surface marked with the grey lines. Thus in this representation, a large area corresponds to a more useful material.

Not only must methods of material synthesis and processing have a high degree of reproducibility and control, but it is also necessary for such methods to be viable in real world applications. For example, methods must therefore be environmentally friendly and practical when employed at a large scale. Tailoring methods of materials synthesis and processing to these needs is now the challenge of the field of materials science. In this context, the synthesis of materials by methods involving supercritical fluids demonstrated great promise.

Supercritical fluids exhibit unique properties, which offer the opportunity to manipulate the reaction environment such as density, viscosity, diffusivity or surface tension, through the control of pressure and temperature, continuously from gas-like to liquid-like properties as desired. These specific properties are then exploited for application in materials processing. For example, the ability to control mass transfer properties of a supercritical fluid is particularly useful for the nucleation and growth of crystals or films.

Design of inorganic materials using methods involving supercritical fluids is achieved through two distinct processes. Particle formation can thus be based on either a physical transformation or a chemical reaction. Papers exist which present a good overview of state of the art concerning the first kind of processes (RESS, SAS, PGSS, DELOS, ...) [2–4], in which the driving force of particle nucleation and growth is a physical transformation (rapid depressurisation, antisolvent effect, ...).

Over the past decade, the second family of processes has received considerable attention [5]. In such methods, supercritical fluids are used as reaction media to synthesize a number of materials (metals, semiconductors, nitrides, oxides, etc.) from micrometer down to nanometer scale. This paper will be devoted to this kind of processes of materials synthesis. Different chemical reactions, which take their inspiration from solution chemistry, are performed in supercritical fluids for materials synthesis:

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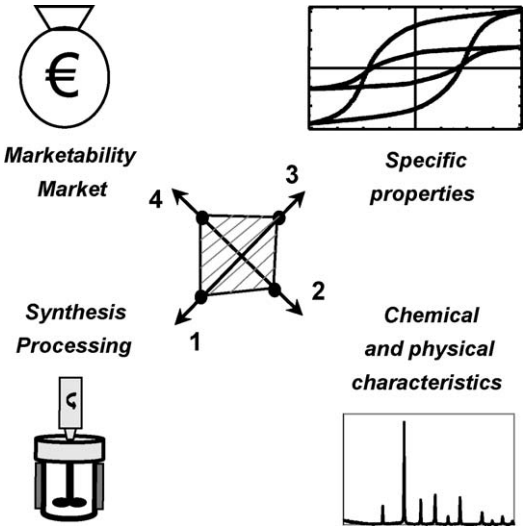


Fig. 1. Schematic description of materials science.

- *Hydrothermal reactions in supercritical water* with a two steps mechanism [4,6]: hydrolysis and dehydration of metal nitrates and metal-organic precursors,
- *Thermal decomposition* of metal-organic precursors [7],
- *Red/ox reactions* of metal salts or metal-organic precursors, generally, in presence of hydrogen [8],
- *Sol–gel reactions* with the well-known two steps mechanism [9]: hydrolysis and condensation.

These four chemical reactions are mainly used to synthesize materials, especially nanomaterials, in supercritical fluids and are carried out using batch or continuous reactor technology.

In this paper, we review the different kinds of inorganic materials which have already been synthesized in supercritical fluids, by way of chemical reactions. The influence of operating parameters on material's characteristics is discussed, in terms of size, morphology, chemical composition and structure. Finally, the role played by this technology in the field of materials science is explored by showing the correlation between the synthesized materials and their applications.

2. Size control in supercritical fluids

At the beginning of the 21st century, nanotechnology and nanosciences represent an area with great potential for the future. In the field of inorganic or hybrid nanomaterials, size is a key parameter explaining the unexpected and interesting properties of nanomaterials. Two size-dependent phenomena arise: quantum confinement effects and effects deriving from the surface/volume ratio. These phenomena can give rise to unique and useful optical, electronic and catalytic properties.

For these applications to become a commercial reality, many improvements in materials synthesis and processing methods are still required. To overcome the drawbacks of solution chemistry approaches, supercritical fluid technology for materials synthesis has been developed in the last 15 years.

The synthesis of size controlled functional nanomaterials in supercritical fluids can be achieved by three general approaches: (1) "growth controlled by thermodynamic fluid properties and chemical reaction kinetics", (2) arrested precipitation and (3) compartmentalized growth. The second and third approaches are widely used in solution chemistry. Concerning the third approach, only the synthesis of nanoparticles in water-in-CO_2 microemulsions will be discussed, as the compartmentalized growth of nanoparticles in inorganic nanoreactors such as carbon or silica aerogels is covered in another article of this issue.

2.1. Size control with thermodynamic fluid properties and chemical reaction kinetics

Batch processing is a useful technique for the synthesis of highly crystalline products and large single crystals can be obtained with a long reaction time. However, to obtain submicron- and nano-sized particles, continuous processing systems are very promising. Fig. 2 shows a schematic representation of a continuous facility of materials processing in supercritical fluids. The control of the aforementioned chemical reactions, and thus of materials characteristics (size, morphology, structure, and composition) is achieved by choosing specific operating parameters: solvent nature, pressure, temperature, reagent nature and concentration, reactor technology, residence time in the reactor, additive agents (co-solvent, catalyst, surfactants, ...). The control of these parameters is performed as follow:

- pressure (p): a back pressure regulator,
- temperature in the reactor (T_4): the pre-heaters (T_1, T_2 and T_3), a reactor heating system and the heat of the chemical reaction,
- residence time in the reactor (t_s): the pump mass flow rates (Q_{m1}, Q_{m2} and Q_{m3}), the reactor volume and the temperature,
- concentrations of reagents: the pump mass flow rates (Q_{m1}, Q_{m2} and Q_{m3}) and the initial concentration of feed solutions.

The control of T_5 is equally very important to recover the powder with the desired characteristics.

Numerous submicron- and nano-sized inorganic particles have been produced, mainly by way of the hydrothermal reactions in supercritical water or the thermal decomposition reactions in different solvents ($scCO_2$, scEtOH, $scNH_3$ or a mixture of these). Arai et al. have extensively studied the hydrolysis of metal salts in scH_2O to crystallize hydroxide or oxide particles (AlOOH, Fe_2O_3, Fe_3O_4, Co_3O_4, NiO, TiO_2, $BaFe_{12}O_{19}$, ZrO_2, CeO_2, $LiCoO_2$, $BaTiO_3$) in the size range of 10 nm to 1 μm [10,11]. The syntheses were mainly performed between 400 and 490 °C, using continuous reactors pressurized to 30–40 MPa. The residence time of the starting salt solutions was about 2 min in most of the experiments. Hydrolysis of metal acetates in sub or supercritical water was studied by Poliakoff et al. [6,12,13]. According to these authors, the acetate hydrolysis reaction followed by the hydroxide dehydration of metal acetates without the addition of bases is the simplest route for synthesizing metal oxides and solid solutions. Oxides as CeO_2, ZrO_2, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $Ni_xCo_{1-x}Fe_2O_4$, $ZnFe_2O_4$, La_2CuO_4, $Ce_{1-x}Zr_xO_2$, $Zr_{1-x}In_xO_2$, $Ce_{0.1}Y_xZr_{0.9-x}O_2$ were produced in the size range of 3–105 nm. The syntheses were car-

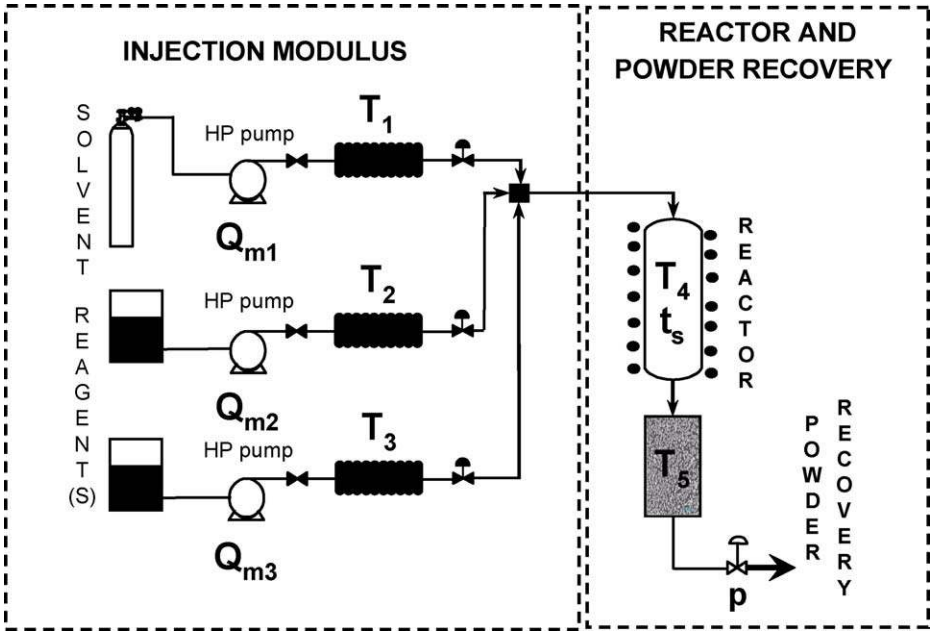


Fig. 2. Experimental setup of continuous reactor method of material processing using supercritical fluids.

ried out in the temperature range of 200–400 °C and at 25 MPa using continuous reactors.

Continuous decomposition of metal precursors in supercritical carbon dioxide/ethanol and ammonia/methanol, or mixtures of these solvents, has been carried out by Cansell et al. in order to produce nitrides (Ni_3N, Cu_3N, Co_2N, Cr_2N, Fe_4N), metal (Cu) and oxides (CuO_2, Ga_2O_3, TiO_2, Al_2O_3) [14,15]. These synthesis methods, performed between 170 and 290 °C at 16–19 MPa, allow a control of the particle size in the range of micrometers down to few nanometers, simply by adjusting the operating parameters.

Models have been proposed to explain the variation of particle size using thermodynamic fluid properties and chemical reaction kinetics without the use of surfactants or templates [11,15–17]. Arai et al. and Adschiri et al. have developed a tool to estimate the size distribution of particles produced in supercritical water. The simulation of the supercritical hydrothermal synthesis process is based on fluid dynamics, kinetics of hydrothermal reactions, metal oxide solubility, nucleation and particle growth and kinetics of hydrothermal reactions [11,17]. They use the conventional nucleation and precipitation theories developed for crystallization reactors in chemical engineering. The local concentration of the considered chemical species is calculated from kinetics and transport equations and the degree of supersaturation from solubility and local concentration. Solubility of metal oxide is estimated using a simplified HFK model and kinetic data (reaction order, reaction rate constant and activation energy) are determined experimentally by following the progression of a reaction in time. Another approach was developed by Cansell et al. [15,16]. They propose a model of particle growth in supercritical fluids based on a two steps mechanism of coalescence and aggregation with variables linked to the crystalline structure of synthesized materials. The numerical model is based on the influence of the diffusion coefficient on the particle size (relation of Stockes–Einstein), assuming that particles are animated by Brownian movement. Using this model, one is able to calculate the predicted growth of particles based on the residence time in the reactor, the precursor concentration and the viscosity of the solvent (pressure, temperature, and solvent nature).

In summary, the data of Table 1 demonstrates how a wide range of materials have been produced using the continuous reactor method in supercritical fluids, with particle sizes ranging between 3 nm and 1 μm. Many desirable material properties can be obtained using supercritical methods, and these properties can be tailored to specific applications by controlling the size of the particles. For example, ceramics synthesized by this method can be preferable to those created by the sol–gel process, since the resulting nano-sized powder can be used without post-treatments such as washing or, drying [18,19]. However, if the desired application depends on properties of single nanoparticles (properties rising from quantum confinement or surface to volume ratio effects), nanoparticles must be functionalized. Up to now, most research on the synthesis of functional nanoparticles in supercritical fluids have been performed using batch reactor processes with size control achieved through the concepts of arrested precipitation and compartmentalized growth.

2.2. Size control by arrested precipitation and compartmentalized growth

Due to thermodynamic considerations, synthesis of non aggregated nanoparticles is only possible if nanoparticles are protected with a layer which provides an electrostatic or steric barrier to aggregation (arrested precipitation method) or if nanoparticles are synthesized in confined media or in nanoreactors (compartmentalized growth method).

The arrested precipitation method in supercritical fluids is developed with two approaches depending on the solvent nature,

Table 1
Summary of inorganic materials synthesized in supercritical fluids and their applications

Materials	Property studied	Applications	References
Ag	Size (2–70 nm), morphology (nanowire, nanobanner), architecture (film)	Nanoscale optical and electronic devices	[51,69]
Pd	Size (2–10 nm)	Catalysis	[23,25,27,32]
Ni @ Cu, $SmCo_5$ @ Cu	Architecture (core-shell)	Magnetic storage	[66,67]
Ge, Si, GaAs, GaP, CdS, ZnS	Size (1–60 nm), morphology (nanowire)	Nanoscale optical and electronic devices, sensors	[34,35,44–47]
Carbon	Morphology (nanotube)	Superconductors, single-molecular transistors, magnetic storage	[52–54]
ZnO	Size (15–100 nm), morphology (nanorod, nanobar, whisker)	Nanoscale optical and electronic devices, sensors, catalysis	[48,49]
$K_2O{\cdot}6TiO_2$	Size (10 nm), morphology (nanowire)	Insulation, photocatalysis	[50]
$BaTiO_3$ @ Al_2O_3	Architecture (core-shell)	Electronic devices	[68]
SiO_2	Architecture (three-dimensional mesoporous)	Insulation, catalysis, high surface-area adsorbents, pharmaceutical and cosmetic products	[9,71]
TiO_2, $Ti(OH)_4$	Size (20–50 nm), architecture (mesoporous fibers)	Sensors, photoelectrochemical cells, catalysis, pigments, mineral membranes	[11,37,56,70]
CeO_2	Size (20–300 nm)	Refractory materials, solid oxide fuel cell, sensor, polishing materials	[10]
$LiCoO_2$, $LiFePO_4$	Size (40 nm–2 μm), crystallinity (high)	Li ion battery cathode materials	[10,65]
$M(Fe_2O_4)$, $BaFe_{12}O_{19}$	Size (30–110 nm), composition (M = Fe, Co, Ni, Zn), crystallinity	Magnetic pigments/fluids, magnetic storage	[10,60]
$KNbO_3$, $K_4Nb_6O_{17}$, $NaNbO_3$	Size (10–500 nm), composition, crystallinity (high)	Electro and non-linear optical devices, photocatalysis, photorefractive materials	[61–64]
$Ba_{1-x}Sr_xTiO_3$	Size (10–100 nm), crystallinity (low OH lattice defects), composition ($0<x<1$)	Electronic devices	[18,57–59]
$Ce_{1-x}Zr_xO_2$	Size (3–7 nm), composition ($0<x<1$)	Catalysis, glass polishing, solid oxide fuel cell, UV absorbers	[6,12]
M_xN	Size (5 nm–10 μm), composition (M = Ni, Cu, Co, Cr, Fe)	Refractory materials, magnetic materials, catalysis	[14]

For size, when referring to nanowires, nanotubes, nanobanners, etc., the quoted size represents the diameter of the particle.

(mainly water, hexane, octanol and carbon dioxide) [20–27]. Supercritical water has specific properties inducing low solubility of inorganics due to its low dielectric constant, which makes it well suited for the synthesis of hybrid nanoparticles. Nanocrystal formation is favoured and standard organic hydrocarbon capping ligands are fully miscible and can react with the surface of nanoparticles. Ziegler et al. have synthesized copper nanoparticles (3–15 nm) stabilized with alkane-thiol ligands (1-hexanethiol) in supercritical water [20]. Adschiri et al. have also developed techniques for in situ surface modification of nanoparticles with alkenes, aldehydes or carboxylic acids during crystallization in continuous reactors [21]. The use of other supercritical fluids at high temperature (350–600 °C to crystallize highly covalent nanoparticles) has offered the possibility to synthesize materials such as silicon (1.5–4 nm) and germanium (2–70 nm) nanoparticles in supercritical hexane and octanol, where octanol is employed as a capping ligand [22,23].

The other approach concerns the arrested precipitation method in supercritical CO_2. One of the challenges of this process of nanocrystal synthesis is the development of specific CO_2-philic capping ligands, mainly fluorous- and siloxane-based molecules and macromolecules. Shah et al. reported the first synthesis of fluorocarbon-coated silver, iridium and platinum nanocrystals ranging in size from 2 to 12 nm (reduction of soluble organic-metal precursors with H_2 in $scCO_2$ between 60 and 100 °C) [24]. Silver (3–12 nm), palladium (3–6 nm) and silver–palladium with a core-shell structure (4–5 nm) nanoparticles have equally been prepared by reduction of organic-metal precursors with dimethylamine–borane in the presence of a fluorinated surfactant [25]. Nanocrystal dispersibility was studied in CO_2 with various capping ligands [26]. It was shown that increasing density leads to greater steric repulsion and dispersibility.

With the aim of developing a CO_2-based process for continuous production of metal nanoparticles, McLeod et al. have explored the concept of spraying a CO_2 carrier solution containing CO_2-soluble metal precursors into a CO_2 receiving solution containing a reducing agent ($NaBH(OAc)_3$ or H_2) and fluorocarbon thiol stabilizing ligands [27]. Metallic nanoparticles of palladium and silver (1–15 nm) were synthesized with this approach.

The final way of preparing such size controlled nanoparticles is using water-in-CO_2 (W/C) microemulsions, which have been studied extensively in the last 10 years [26,28–41]. W/C microemulsions are characterized by surfactant-stabilized aqueous cores dispersed in a continuous CO_2 phase. The nanometer-sized aqueous cores serve primarily as a carrier solution containing reagents (metal salts, reducing agents, . . .) and secondly as a system of nanoreactors that compartmentalize nanoparticle growth. Metal and semiconductor nanoparticles have been prepared with this approach, such as silver (5–15 nm) [28–31],

copper (5–15 nm) [29], palladium [32], silver halide (3–10 nm) [31,33], cadmium sulfide (1–2 nm) [34,35], zinc sulfide (1.6 nm) [35] and copper sulfide (4–6 nm) [36]. W/C microemulsions have also been used as nanoreactors for preparation of TiO_2 [37]. Similar to the W/C microemulsion method, sc-alkane-based microemulsions have also been used to synthesize silver and copper nanoparticles (<15 nm) [38–41]. By controlling the $[H_2O]$/[surfactants] ratio, the size of the aqueous nano-droplets and thus the size of the nanoparticles can be adjusted between 1 and 15 nm. Even though the size of nanoparticles formed within these microemulsion systems can readily be controlled, it is still difficult to collect the as-prepared nanoparticles, due to their aggregation and coalescence upon removal of the supercritical fluid. The further development of W/C microemulsions technology is therefore strongly linked with the synthesis of new surfactant systems [42,43].

3. Morphology control in supercritical fluids

In addition to their size, the morphology of a given material's constituent particles strongly affects its characteristics. Morphologies such as nanowires and nanotubes attract significant interest due to their potential applications in microelectronics, interconnections, optoelectronics, and as nanoscale electronic devices. However, such applications can only be realized if the nanostructures can be manipulated and organized in a controlled fashion. This section discusses the synthesis of semiconductors, carbons, metals and oxides with the above mentioned one-dimensional morphologies.

3.1. Nanowires and nanorods

3.1.1. Semiconductor nanowires

Semiconductor nanowires are receiving increasing attention for applications in technologies ranging from connecting integrated circuits to electronic and optical devices. Classical synthesis methods rely on metal particles (such as gold nanocrystals) to induce nanowire growth above the semiconductor/metal eutectic temperature. Such reaction can be carried out either in the gas phase (called vapor–liquid–solid or VLS method) or in the liquid phase (called solution–liquid–solid or SLS method). Korgel et al. have developed a new synthesis method for producing nanowires less than 10 nm in diameter using supercritical fluids [44]. This process has been called fluid–liquid–solid or FLS method and involves thermally degrading a precursor such as diphenylsilane in a supercritical fluid rather than in a gas or liquid (VLS and SLS methods, respectively). Silicon nanowires with diameters between 4 and 5 nm and lengths of several micrometers have been grown with this method on 2.5 nm alkanethiol-coated gold nanocrystals. Chemical vapor deposition combined with sized-selected Au particles have also been used for the controlled synthesis of silicon and gallium arsenide nanowires. Supercritical fluids such as hexane and cyclohexane were used to disperse a greater quantity of metal nanocrystals and 1000 times more precursor, while studying the effects of temperature and precursor concentration. The nanowire morphology can be controlled with great flexibility using the FLS method. Moreover, the use of a continuous rather than a batch reactor system provided straight silicon nanowires while inhibiting the formation of other particles. For this reason, the FLS process was also used to produce germanium nanowires [45], gallium arsenide nanowires, [46] gallium phosphide nanowires [47]. In each case, the FLS process proves to be a great method of synthesizing single-crystal semiconductor nanowires. Compared to VLS synthesis, this process offers more flexibility in designing the characteristics of a given material, results in higher yields and provides a wide range possibilities for in situ doping and chemical surface derivatization.

3.1.2. Oxide nanowires and nanorods

Due to its possible applications, the synthesis of the wide-band-gap semiconductor zinc oxide is highly desirable. For example, zinc oxide can be used in the fabrication of gas-sensors, varistors and pigments. The current challenge is to manufacture highly crystalline ZnO materials with controlled morphologies that cannot otherwise be obtained using classical techniques. Highly crystalline ZnO with a hexagonal wurtzite structure has successfully been produced using a flow-type reactor employing supercritical water [48]. Zinc nitrate was the starting material, and it was found that various morphologies were synthesized depending on its concentration in solution. For instance, with a concentration of 0.05 mol/L, a bar-like morphology was obtained, while a wisker structure formed at a lower concentration of 0.02 mol/L. Furthermore, the extremely short reaction times below 30 s are another advantage of this synthesis method. However, the mechanism which determines these changes in ZnO morphology is not yet understood. To improve the understanding of this synthesis method, Arai et al. have studied how heating the starting solution and varying the reactant concentration and flow-rate influence the aspect ratio of the resulting ZnO crystals [49]. ZnO nanorods were obtained with KOH and $Zn(NO_3)_2$ in aqueous solutions at 400 °C and 30 MPa. The pre-heating of the zinc nitrate starting solution has led to nanorods with an average length:width ratio of 230:38 nm. Potassium hexatitanate (KTO) was synthesized using a similar method, and was found to have a long and fibrous morphology and high photocatalytic activity [50]. This flow method allows the production of nano-scaled KTO particles in several seconds from titanium hydroxide and potassium hydroxide aqueous solutions, while the short heating time prevents the formation of crystalline TiO_2. Furthermore, since hydrothermal crystallization of KTO was completed in a short time, individual particles did not form, and nanowires were obtained with a high yield and efficiency.

Not only were semiconductor and oxide nanowires synthesized, but the self-organization of metal silver nanoparticles to form nanowires was also studied [51]. It has been shown that supercritical water can help to control the shape and organization of silver nanoparticles by decomposing Ag_2O to form Ag particles (27.5–49 MPa, 400–500 °C, 10–60 min). At 400 °C and 49 MPa, Ag nanoparticles formed first into well-stacked assemblies and then into crystallized into chain-like nanowires (diameters ranging between 50 and 70 nm with lengths of several micrometers).

3.2. Carbon nanotubes

Like semiconductor, metal and oxide nanowires, carbon nanotubes (CNTs) exhibit a variety of unique properties. Their potential applications such as use in superconductors and magnetic recording devices have led to widespread efforts to improve their synthesis. Gas phase synthesis results in low yields and poor crystallinity, while the high temperature required for the process limits the practicality for its use on a large scale. Recently, supercritical carbon dioxide has been used to prepare well-crystallized CNTs [52]. Carbon dioxide was used as the carbon source in a relatively low temperature process, and lithium metal was used as a reducing agent. Typical operating conditions were 550 °C and 70 MPa. Compared with CO_2 gas, supercritical CO_2 enhances the adsorption of carbon dioxide on the surface of lithium, and therefore facilitates and accelerates the electron transfer process. Large amounts of CNTs were produced which were 55 nm in diameter and more than one micrometer in length, without the use of a catalyst and in relatively mild and low cost reaction conditions. A similar approach was recently used to produce multiwalled carbon nanotubes (MWNTs) in supercritical toluene [53]. The concept was to take advantage of pressure effects to lower the high temperatures usually required to synthesize CNTs. In this process, supercritical toluene served both as the carbon source for nanotube growth, and also as the reaction media. Ferrocene, iron or platinum iron nanocrystals were used as catalysts in this process, and these catalyst particles were always observed at the tip of the MWNTs. The temperature and the seed particle size (iron particles) appear to be the most significant parameters in the product quality. For the reaction to proceed, it was necessary to reach temperatures needed to degrade toluene and thus to produce MWNTs. The optimum temperature was found to be 600 °C, while after this temperature neither filaments nor nanotubes were formed. These studies demonstrated that the size of the seed particle is a key parameter for the formation of CNTs. Fahlman et al. therefore used metal-encapsulated dendrimers since catalysts for nanotube growth, as the size of the entrained metal may easily be manipulated by changing the core/periphery structure of the dendrimer [54]. $ScCO_2$ permits the use of this fragile catalyst structure due to the low operating temperatures used. The average diameter of the as-produced CNTs in $scCO_2$ from the decomposition of carbon tetrachloride was 20–25 nm at 27.6 MPa and 175 °C. The role of $scCO_2$ for nanotube formation in this process is three-fold: it assists the decomposition of the precursor (CCl_4), it delivers the intermediate species to the encapsulated metal surface for nucleation and growth of CNTs and it also purges the reactor. Its critical role in CNT formation is demonstrated by the fact in the absence of supercritical CO_2 no nanotube growth was observed.

The research works presented in this section demonstrate how supercritical fluid technology for materials processing allows the efficient control of material morphology. Along with the ability of controlling particle size, the control of morphology allows the possibility of a wide range of material properties, and thus applications, to be realized, as detailed in Table 1.

4. Composition/structure control in supercritical fluids

Composition and structure are also key parameters in explaining and adjusting a material's property. This section summarizes recent works performed in the field of chemical synthesis of inorganic materials, emphasizing the degree of control that can be achieved over the composition and structure of particles formed using sub and supercritical fluids. The focus will be on works related to the synthesis of metal oxides.

Although water has been the most popular solvent and/or reagent used for synthesizing oxides in the past, other media such as alcohols, CO_2, ammonia or mixtures of these are increasingly being employed for producing metals, oxides and nitrides. Both synthesis methods, called hydrothermal and solvothermal synthesis, respectively, have been conducted for years in closed reactors and under autogeneous pressure (batch mode). Nowadays, from the point of view of facilities and operation costs, continuous reactors seem to be the most promising technology for synthesizing materials at an industrial scale (continuous mode).

4.1. Control of extent of oxidation in supercritical fluids

Using continuous processing, the extent of oxidation of oxides can easily be controlled, due to the enhancement of gas miscibility under supercritical conditions [10]. During synthesis, oxidizing or reducing media are obtained in introducing oxidizing (O_2, etc.) or reducing (H_2, CO, etc.) gases in the reactor. These gases can be also formed in situ when the decomposition of organic-like precursors takes place. Such is the case for Fe_3O_4 spherical nanoparticles (50 nm) prepared from $Fe(NH_4)_2H(C_6H_5O_7)_2$ solutions in supercritical water. The Fe^{3+} ions are reduced to Fe^{2+} by the CO produced during the thermal decomposition of the ammonium citrate precursor. The miscibility of CO in supercritical water allows the preparation of single-phase magnetite powders due to the homogeneity of the reaction medium. In order to synthesize Fe_2O_3, the reduction of Fe^{3+} must be avoided. Under identical pressure and temperature conditions (35 MPa and 400 °C), the decomposition of $Fe(NO_3)_3$ results in single-phase Fe_2O_3 nanoparticles having the same morphology and mean particle size as Fe_3O_4. The production of $LiCoO_2$ nanoparticles from $Co(NO_3)_3$ and LiOH is another example of how controlling the oxidizing/reducing environment affects the extent of oxide oxidation. For the production of this oxide, O_2 gas was introduced into the reactor for the purpose of oxidizing Co^{2+} ions during the hydrothermal reaction. The $LiCoO_2$ oxide (single-phase powder) was obtained at supercritical conditions, whereas Co_3O_4 was the main product obtained in near supercritical water. This behaviour is related to the formation of a homogeneous phase between O_2 and H_2O only under supercritical conditions.

4.2. Composition/crystallinity control in supercritical fluids

The crystallinity and nature of phases synthesized under sub and supercritical conditions can be also controlled by changing the temperature of the reactor [10,11]. After hydrothermal

reaction of $ZrOCl_2$ or $TiCl_4$ solutions, the products obtained at different temperatures were: (i) amorphous hydrous oxide gels (400 °C), (ii) anatase nanoparticles (TiO_2 of 20 nm at 450 °C) and (iii) cubic zirconia nanoparticles (ZrO_2 of 20 nm at 490 °C). In general, oxide crystallinity is enhanced by raising the reactor temperature. However, in the case of boehmite particles (AlOOH of 600 nm) synthesized by the hydrothermal treatment of $Al(NO_3)_3$ solutions, the thickness of XRD boehmite peaks diminished with a temperature increase, but even at 490 °C the oxide crystallization (Al_2O_3) was never reached.

The possibility to control the chemical composition of titanium compounds by changing the solvent nature and experimental conditions can be analyzed by comparing different studies. Papers exist that describe the decomposition of titanium (IV) isopropoxide in a continuous reactor, using supercritical isopropanol [55] or supercritical CO_2/H_2O mixtures [56] as reaction media. When the precursor is decomposed in supercritical isopropanol (350 °C, 10 MPa), crystalline TiO_2 was produced through a hydrolytic reaction (alcohol dehydration provides water molecules after 250 °C), whereas if the solution is directly hydrolyzed at lower temperatures in supercritical CO_2/H_2O mixtures (60 °C, 14 MPa), only amorphous $Ti(OH)_4$ powders are produced.

The effect of water density on the kind of $BaTiO_3$ polymorph synthesized in sub or supercritical water has recently been shown [57]. The crystallization of cubic or tetragonal phases depends not only on the reactor temperature, but also on the reactor pressure and thus the fluid density. For example, the tetragonal phase was obtained only under supercritical conditions for water densities below 0.5 g/cm^3. To explain this behaviour Arai et al. suggested that the dehydration step proceeds more rapidly in supercritical than in near supercritical water due to the enhanced diffusivity. Consequently, the residual OH ions present in the lattice (OH defects) are reduced and tetragonal phase is obtained. Moreover, the stoichiometry of $BaTiO_3$ varies from a Ba to Ti ratio of 0.85–1.05 depending on the experimental conditions chosen (300–420 °C, 30 MPa) [58].

It has been shown by Cansell et al. that a continuous reactor method of synthesizing $BaTiO_3$ nanoparticles can be performed by hydrolyzing isopropoxide precursors in sub and supercritical water/ethanol mixtures (150–380 °C, 16 MPa) [18]. The crystallinity of the as-prepared nanopowders can easily be controlled by changing the water/ethanol ratio, achieving up to 90% when the ratio is equal to 1. It has been established that the hydrolysis reaction, which occurs rapidly in systems with a high water content, is an important step for producing well-crystallized oxides. The stoichiometry of the powder depends on the Ba/Ti molar ratio of the precursors. In addition to the control of the extent of crystallinity, more complex oxides can also be produced. For example, $BaTiO_3$–$SrTiO_3$ solid solution with an accurately control of its composition, for instance $Ba_{0.6}Sr_{0.4}TiO_3$, can be synthesized using the same continuous sol–gel supercritical chemical processing [59]. The composition of the solid-solution was easily controlled by varying the initial Ba/Sr ratio.

As described previously, the continuous decomposition of metal precursors in supercritical ammonia/methanol or carbon dioxide/ethanol mixtures has been carried out in order to produce nitrides (Ni_3N, Cu_3N, Co_2N, Cr_2N, Fe_4N), metal (Cu) and oxides (CuO_2, Ga_2O_3, TiO_2, Al_2O_3) particles [14,15]. It has been shown that the chemical composition of powders depends on the chemical nature of the solvents used. For example, metal copper particles were produced by the decomposition of copper precursors in a CO_2/ethanol supercritical mixture, whereas in a NH_3/methanol mixture, cubic copper nitride was obtained. This result is due to the fact that supercritical CO_2 acts as an inert solvent, while NH_3 reacts with metal atoms to produce nitrides (NH_3 plays the role of both solvent and reagent).

The stoichiometry and composition of magnetite (Fe_3O_4) and ferrites (MFe_2O_4 with M = Co, Ni, Zn) nanopowders (30–100 nm in size) also depend on the properties of the fluids used. Under continuous supercritical conditions, stoichiometric powders were never obtained due to M-cation deficiencies. It appears that powders become more stoichiometric (or completely stoichiometric) in subcritical rather than supercritical water [60].

Hydrothermal batch syntheses of potassium niobate powders with high crystallinities and large surface areas have recently been performed by many groups (Uchida et al., Goh et al., and Hayashi et al.). Crystalline Nb_2O_5 powder is employed as the starting material in different alkaline solutions [61–64]. Batch-type reactors are heated between 150 and 400 °C for periods ranging from 30 min to 143 h (autogeneous pressure). The phase formed in subcritical water conditions was potassium hexaniobate ($K_4Nb_6O_{17}$), while a mixture of phases was formed when supercritical water conditions were used ($K_4Nb_6O_{17}$ and $KNbO_3$). However, a single phase $KNbO_3$ powder can be obtained if the reaction time at supercritical conditions is increased above 24 h. The departure from stoichiometry observed in $KNbO_3$ powders (K/Nb = 0.96) corresponds to the compensation of hydroxyl lattice defects by cation vacancies. To control the chemical composition of the powder, Goh et al. used KOH or NaOH solutions as bases in order to produce $KNbO_3$ and $NaNbO_3$ powders.

The hydrothermal synthesis of $LiFePO_4$ particles has recently been performed by Teja et al. from $FeSO_4 \cdot 7H_2O$ and LiOH precursors in batch-type reactors (temperatures ranging from 121 to 388 °C at 33.5 MPa) [65]. The nature of the powder depends strongly on the pH of the system: (i) $LiFePO_4$ was obtained only over a narrow range of pH values in neutral or slightly basic conditions, (ii) a mixture of Fe_2O_4 and $LiFePO_4$ was obtained in strongly basic conditions and (iii) in moderately basic conditions $LiFePO_4$ and Li_3PO_4 were produced. In fact, in strongly basic conditions the sulphate precursor is partially hydrolyzed, resulting in $Fe(OH)_3$ which is then converted to Fe_3O_4.

The ability to control the structure, chemical composition, crystallinity, and the extent of oxidation of oxides permits the development of with very interesting and tunable properties, resulting in applications in various fields as shown in Table 1.

5. Control of architecture using supercritical fluids

The knowledge gained in the previous sections can be used to design more complex systems with controlled architectures employing supercritical fluids. For example, core-shell struc-

tures, particles organized on surfaces, or the development of three-dimensional devices can be pursued. This type of purposeful materials processing is achieved by controlling the architecture of systems.

5.1. Control of particle architecture

Even though the coating of particles with inorganic materials appears to be a very promising route for controlling and tuning nanoparticles properties, supercritical methods of synthesizing these core-shell structures remain relatively unexplored. A few years ago, Cansell et al. developed the first chemical fluid deposition process in order to achieve the deposition of metal (Cu) on particles (Ni and $SmCo_5$) particles [66,67]. The process consists of the thermal decomposition of bis-(hexafluoroacetylacetonate)copper(II) at 200 °C and 19 MPa in presence of Ni or $SmCo_5$ micrometer particles. The supercritical solvent is a mixture of carbon dioxide and ethanol (80/20 molar ratio). SEM images of copper-coated nickel particles demonstrate a significant modification of the initial particles. The coated particles are spherical in shape, but their surface is very smooth. Recently, this process has been applied at the nanometer scale. Nanoparticles of $BaTiO_3$ (50 nm) were coated with an amorphous alumina shell of about 3 nm [68]. After sintering the core-shell nanoparticles, the ceramic material exhibits very interesting and improved ferroelectric properties. In particular, amount of dielectric losses was lowered while maintaining a relatively high permittivity. This result opens the way to the production of new kinds of advanced ferroelectric materials.

5.2. Control of surface architecture

In addition to studies focused on particle synthesis, the post-synthesis manipulation of particles is also a promising route of developing and tuning material properties. This approach demonstrates much promise, especially in the field of electrical and optical devices. A very interesting method for controlling architecture on surface has been recently studied by Roberts et al [69]. In addition to a gas antisolvent process, which induces the precipitation and deposition of nanoparticles dispersed onto large thin-films, a step involving supercritical fluids has been used to remove organic solvents. The extent of surface coverage is greater than that obtained when air-dried particles: 44% versus 17% covered. Moreover, using this supercritical fluid technique, the properties of such films can be tailored by varying pressurization rates of the fluid, or by using different particle ligands or size.

5.3. Control of the architecture of three-dimensional devices

Aerogels are interesting due to their extremely high porosity, having pore sizes ranging from 1 to 100 nm. The porosity is in excess of 90% and can be as high as 99.9%. Consequently, aerogels have a large amount of internal surface area and pore volume. Moreover, due to the interconnected structure of these open pores, this entire surface area is easily accessible for gases, liquids or fluids. For instance, silica aerogels contain primarily particles of 2–5 nm in diameter. This very small size provides an excellent surface-to-volume ratio and a corresponding high specific surface area. Consequently, the chemistry of the inner surface of aerogels plays a dominant role in its chemical and physical behavior. It is this property that makes aerogels well suited for use as catalysts, catalyst substrates and adsorbents.

Usually sol–gel reactions are carried out in two steps: the sol–gel reaction followed by the drying step. Nowadays this last step is carried out in a supercritical fluid medium in order to avoid the collapse of the as-formed network. However, an innovating synthesis of a silica aerogel was recently performed by Moner–Girona et al. in supercritical solvents [9]. The chemical reaction was carried out in supercritical acetone or CO_2 with organosilane as the reagent. The advantages of this method are that it reduces the number of necessary steps when compared to classical sol–gel syntheses, and also because it allows the fine control of aerogel morphology thanks to the tunability of supercritical media properties. Different morphologies were obtained in supercritical acetone depending on experimental parameters. Varying depressurization rates, for instance, leads to either spherical monodispersed particles or fiber-like structures, and the diameter of pores was found to be between 5 and 50 nm. With the supercritical carbon dioxide process, narrowly distributed and smaller particles were obtained at lower operating conditions.

Aerogel of titania nanoparticles have a wide variety of applications in areas such as chemical sensors and semiconductor electrodes [70]. A sol–gel route of the direct synthesis of mesoporous TiO_2 nanofibers has been performed in supercritical carbon dioxide, resulting in a low-density and brittle aerogel monolith. The fiber diameter was easily tuned by varying the precursor concentration (titanium(IV) isopropoxide in acetic acid), and the individual nanofibers had very uniform diameters and aspect ratios. Though the mechanism is not well understood, supercritical carbon dioxide combined with acetic acid seems to facilitate the formation of the nanostructures, while its low surface tension allows network structure to be maintained.

Recently, Holmes et al. have achieved the control of three-dimensional mesoporous silica and presented the engineering of the pore sizes [71]. During the hydrolysis of silica, supercritical CO_2 was used as a swelling agent, and its fluid pressure precisely regulated in order to achieve fine control of the hexagonal spacing of the pores of the mesoporous silica.

The properties of the aforementioned materials obtained by controlling the architecture of particles, surfaces or three-dimensional devices are described in Table 1.

6. Conclusions

Materials Science demands efficient methods of synthesizing materials with controlled sizes, morphologies, compositions and structures. By using supercritical fluids as a reaction media, material characteristics can be successfully tuned and improved, thus meeting these requirements.

This review paper describes how the unique properties of supercritical fluids have been exploited for material processing.

It is shown how the methods of material processing using supercritical fluids offers the possibility of controlling the synthesis of a material by varying different operating parameters. The roles of the relevant variables were discussed, such as the solvent and reagent nature and concentrations, the operating pressures, temperatures and residence times, the reactor technology employed and also the use of additive agents such as co-solvents, catalysts and surfactants. The knowledge of how these parameters influence the synthesis process allows the control of different material characteristics such as size, morphology, structure and composition.

The potential of supercritical fluids to be used in processing inorganic materials in a control way is presented for metals, semiconductors, oxides, nitrides and carbons, successively. Sizes from 1 nm up to 10 μm can be obtained through three main approaches: (1) growth controlled by thermodynamic fluid properties and chemical reaction kinetics, (2) arrested precipitation and finally (3) compartmentalized growth. Nanowires, nanorods and carbon nanotubes are examples of different morphologies that can be achieved using supercritical fluids. In terms of composition and structure, the synthesis of materials using supercritical fluids allows the control of the extent of oxidation and crystallinity of oxides, and also the structure and chemical composition obtained. This knowledge can then be applied to the design of more complex systems, such as core-shell structures, the organization of particles on surface, or development of three-dimensional devices.

Today, supercritical fluid technology allows the production of well designed materials with controlled properties for applications in many interesting fields, such as electronics, energy, optics and, pharmacology, . . .

Nevertheless, research works are still required on most of methods described in this paper from a fundamental and applied point of view. A first point concerns the development of multi-scale models from the understanding of interactions solute–solvent in complex chemical systems to the nucleation and growth of particles linked to kinetics and fluid dynamics. Secondly, the suitability of the methods described for used on a large scale must be evaluated. In addition, investigations on nanomaterial handling are necessary for technological and security considerations.

We expect that the transfer of supercritical fluid technology of material processing from laboratory to industry will be achieved in a near future in combining economical efficiency and sustainable development.

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