

MATERIALS PROCESSING USING SUPERCRITICAL FLUIDS

One of the most interesting areas of supercritical fluids applications is the processing of novel materials. These new materials are designed to meet specific requirements and to make possible new applications in: pharmaceuticals design, heterogeneous catalysis, micro- and nano-particles with unique structures, special insulating materials, super capacitors and other special technical materials.

Two distinct possibilities to apply supercritical fluids in processing of materials: synthesis of materials in supercritical fluid environment and/or further processing of already obtained materials with the help of supercritical fluids. By adjusting synthesis parameters the properties of supercritical fluids can be significantly altered which further results in the materials with different structures. Unique materials can be also obtained by conducting synthesis in quite specific environments like reversed micelles.

This paper is mainly devoted to processing of previously synthesized materials which are further processed using supercritical fluids. Several new methods have been developed to produce micro- and nano-particles with the use of supercritical fluids. The following methods: rapid expansion of supercritical solutions (RESS), supercritical anti-solvent (SAS), materials synthesis under supercritical conditions and encapsulation and coating using supercritical fluids were recently developed.

The particle design is a major development of supercritical fluids applications, with potential applications in the pharmaceutical, food, cosmetic and specialty chemicals industries. This text presents a concise survey of the published material classified according to the different processing concepts currently used to manufacture particles or other dispersed material.

RESS – Rapid Expansion of Supercritical Solutions

Rapid Expansion of Supercritical Solutions (or RESS) is the method in which a pressurized solution is rapidly expanded through an adequate nozzle, causing an extremely fast nucleation of the solid solute in a micronized form. This process is attractive due to the absence of organic solvent during processing, but its application is restricted to products reasonably soluble in supercritical fluids (commonly used fluid is carbon dioxide). The basic concept of RESS was first described more than a hundred years ago [1], while modern development started after the pioneering works of Krukonic [1] and especially the Battelle Institute research team [2,3].

As presented in Figure 1, a supercritical fluid saturated with the substrate(s) is expanded through a heated nozzle into a low pressure chamber in order to cause an extremely rapid nucleation of the substrate(s) in a micronized form.

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Author address: Aleksandar Orlović, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, PO Box 3503, 11120 Belgrade, Serbia and Montenegro
E-mail: orlovic@tmf.bg.ac.yu
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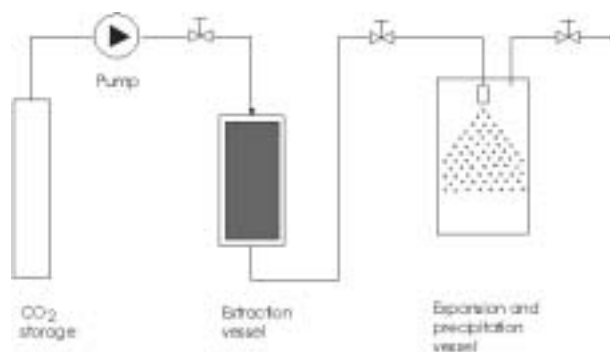


Figure 1. The RESS process

The pure carbon dioxide is pumped to the desired pressure and preheated to extraction temperature through a heat exchanger. The supercritical fluid is then percolated through the extraction unit packed with one or more substrate(s). In the precipitation unit, the supercritical solution is expanded through a nozzle that needs to be heated in order to avoid plugging by substrate(s) precipitation. Typically used expansion nozzles are capillaries of diameter <100 μm or laser drilled nozzles of 20–60 μm diameter. The process allows control over several parameters affecting the expansion: the solute concentration, the pre-expansion temperature and pressure, the nozzle dimensions and background expansion conditions. Application of an expansion nozzle defines the path of the expanding solution, which allows manipulation of the solvent density at various stages of the expansion and permits some degree of control over the solute nucleation characteristics. The rate of nucleation is [4].

$$J = \Theta \alpha_c V_{2,\text{mol}} v_2^2 \sqrt{\frac{2\sigma_G}{\pi m_{2,\text{mol}}}} \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T}\right) \quad (1)$$

$$\frac{\Delta G_{\text{crit}}}{k_B T} = -16 \frac{\pi}{3} \left(\frac{\sigma_G V_{2,\text{mol}}^{2/3}}{k_B T} \right)^3 \frac{1}{\left[\ln S - V_{2,\text{mol}}(p_2 - p_{2,S}) \left(\frac{1}{k_B T} \right)^2 \right]^2} \quad (2)$$

where Θ is the non-isothermal factor, α_C is the condensation factor, $V_{2,\text{mol}}$ is the solute molecular volume, $m_{2,\text{mol}}$ the solute molecular mass, α_G the interfacial tension, v_2 the solute concentration in vapor phase, p_2 the partial pressure of the solid, $p_{2,S}$ the saturation vapor pressure of the solid, S the saturation ratio, k_B Boltzmann's constant and T is the absolute temperature.

The morphology of the resulting solid particles has been observed to vary with changes in RESS processing conditions. Products obtained using RESS have included uniform sub-micrometer scale particles, thin films and fine fibers. If dissolved species of a low vapor pressure solid exist in sufficient concentration in the supercritical fluid prior to expansion, they nucleate and grow rapidly in the expansion jet as the fluid solvating capacity drops, which results in the generation of fine powders. Particle size, agglomeration, and other characteristics can be affected by the chemical properties of the solute, its concentration in the solution prior to expansion, temperature, pressure drop, distance of impact of the jet against the surface, dimensions of the expansion vessel, nozzle geometry and the phase behavior of the solvent in the expansion jet [1,4,5]. For example, micronization of Ibuprofen by RESS using carbon dioxide indicated decrease in crystallinity of the obtained material when compared to the original one [6]. No clear dependence of the particle size on the extraction pressure was observed, while an increase in the spraying distance increased the particle size. However, an increase in the pre-expansion temperature, capillary length, and collision angle, were found to have reducing effect on the average size of Ibuprofen particles.

It should be noticed that the initial investigations of RESS were focused on micronization of pure substrates in order to obtain very fine particles with narrow size distribution [5,7], while the recent publications are related to mixture processing in order to obtain microcapsules of a substrate inside a carrier [8] or to bioavailability improvement of pharmaceutical agents [9].

The RESS process can be implemented in relatively simple equipment, it can produce very fine particles and it is solvent free, although particle collection from the gaseous stream is difficult. Other disadvantages of the process are: high gas/substrate ratios due to the low solubility of the typical substrates, high pressures and temperatures, and large volumes of pressurized equipment.

SAS – Supercritical Anti-Solvent precipitation and related processes

Supercritical fluid anti-solvent processes have been recently proposed as alternatives to liquid anti-sol-

vent processes commonly employed in the industry. The key advantage of the supercritical processes over liquid ones is the possibility to completely remove the anti-solvent by pressure reduction. This step of the process is problematic in case of liquid anti-solvents since they require complex post-processing treatments for the complete elimination of liquid residues. Furthermore, the supercritical anti-solvent is characterized by diffusivity that can be up to two orders of magnitude higher than those of liquids. Therefore, it's very fast diffusion into the liquid solvent produces the supersaturation of the solute and its precipitation in micronized particles with diameters that are not possible to obtain using liquid anti-solvents or other methods.

Supercritical anti-solvent micronization can be performed using different processing methods and equipment [10]. Different acronyms were used by the various authors to indicate the micronization process. It has been referred to as GAS (Gas Anti-Solvent), PCA (Precipitation by Compressed Anti-solvent), ASES (Aerosol Solvent Extraction System), SEDS (Solution Enhanced Dispersion by Supercritical fluids) and SAS (Supercritical Anti-Solvent) process [1,10]. Since the resulting solid material can be significantly influenced by the adopted process arrangement, a short description of the various methods is presented below.

In GAS or SAS, a batch of solution is expanded by mixing it with a supercritical fluid in a high pressure vessel (Figure). Due to the dissolution of the compressed gas, the expanded solvent exhibits a decrease of the solvent power. The mixture becomes supersaturated and solute precipitates in the form of microparticles. As shown in Figure 2, the precipitator is partially filled with the liquid solution of solid substance. The supercritical anti-solvent is then pumped up to desired pressure and introduced into the vessel, preferably from the bottom in order to achieve a better mixing of the solvent and anti-solvent. After a specified residence time, the expanded solution is drained under isobaric conditions in order to wash and clean the precipitated particles. In this mode of operation, the rate of supercritical anti-solvent addition can be an important parameter in controlling the morphology and the size of solid particles.

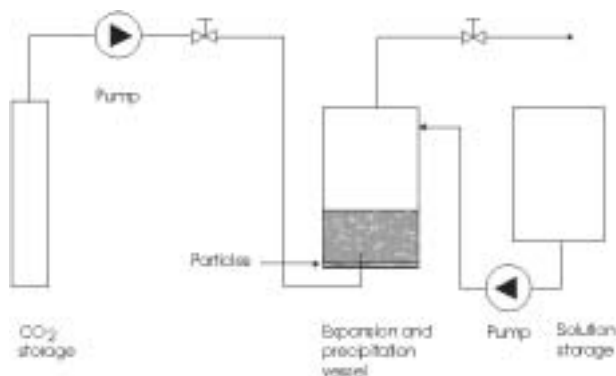


Figure 2. The GAS, PCA or SAS process

Another method (ASES) involves spraying of the liquid solution through an atomization nozzle as fine droplets into chamber filled with supercritical anti-solvent. The fast dissolution of the supercritical fluid into the liquid droplets is followed by a large volume expansion of droplets. This is followed by a reduction of the liquid solvent power, causing a sharp rise in the supersaturation within the liquid mixture. As a consequence, fine and uniform particles are being formed. The supercritical fluid is pumped to the top of the high pressure vessel by a high pressure pump. Once the system reaches steady state (temperature and pressure), the active substance solution is introduced into the high pressure vessel through a nozzle. Particles are collected on a filter at the bottom of the vessel. The fluid mixture (supercritical fluid plus solvent) exits the vessel and flows to a depressurization tank where the conditions (temperature and pressure) allow gas-liquid separation. After stopping the spraying of solution the pure supercritical fluid continues to flow through the vessel to remove residual solvent from the particles. As in the previous case (GAS, SAS and PCA) the performed operation is not at steady state and it is difficult to analyze the effect of the process parameters on the final characteristics of the powders. Beside that, batch operation is usually not suitable for industrial application.

In order to overcome the limitations of batch processing a continuous SAS process was developed and reported by Reverchon et al. [11]. In continuous operation, the liquid solution and the supercritical anti-solvent are continuously delivered to the precipitation chamber whether in co-current or counter-current mode. This mode of operation provides the possibility to investigate influence of different process variables on the evolution of micronized particles. The important process parameters which can be studied at steady state operation are: the flow rates, the solution/anti-solvent ratio and pressure. Beside those advantages, continuous steady state operation is also suitable for industrial application. A key role in the continuous operation as well as in the ASES process is played by the liquid solution injection device. The injector is designed to produce liquid jet break-up and to form small micronic droplets that expand in the precipitator. The solid solute is released when its local concentration exceeds the saturation limit. Various injection devices have been proposed in the literature. Some authors propose a nozzle of various diameters ranging from 5 to 50 μm [10]. Other authors have used small internal diameter capillaries [12], or vibrating orifices [13]. This last apparatus produces a spray by superimposing a high frequency vibration on the liquid jet that exits from an orifice. It is also possible to use a premixed injector in which the liquid solution is mixed into the flowing CO_2 before the entrance in the precipitator, or to use stirred autoclaves [14]. The type of injection device used can also strongly influence the precipitation process: the size of droplets, their coalescence, and mixing of the dif-

ferent fluids. In view of some authors the initial droplet size, formed at the nozzle, does not have an effect on final particle size [15]. The authors suggest that the particle size is probably more determined by the mass transfer effects.

The SEDS method was developed by the Bradford University [16,17] in order to achieve smaller droplet size and intensify mixing of supercritical fluid and solution for increased transfer rates. The supercritical fluid is used both for its chemical properties and as 'spray enhancer' by mechanical effect: a nozzle with two coaxial passages allows to introduce the supercritical fluid and a solution of active substance(s) into the particle formation vessel where pressure and temperature are controlled. The high velocity of the supercritical fluid (Reynolds number of the order of 10^5) allows to break up the solution into very small droplets. Furthermore, the conditions are set up so that the supercritical fluid can extract the solvent from the solution at the same time as it meets and disperses the solution.

A key role in the precipitation by supercritical anti-solvent is played by the volumetric expansion of the liquid solvent. This phenomenon is the result of massive dissolution of the supercritical anti-solvent into the liquid phase. Two methods have been used to obtain volumetric expansion data. The first is the direct observation of the expansion of the liquid solvent (solution) through a view window. At a fixed temperature, a given quantity of solvent is charged in the vessel and pressure is progressively increased by adding the anti-solvent. The expansion of the liquid phase is monitored by measuring the increase of the liquid level inside the vessel. The second method on the other hand, measures the variation of the density of the liquid solvent-supercritical anti-solvent mixture at increasing pressures. Using the known density of the liquid phase and its composition, the volume expansion is calculated by a modified Peng-Robinson equation of state [18]. As stated previously the liquid expansion reduces the solubility of the solute and precipitation takes place. The precipitation consists of initial nucleus formation and subsequent growth of the nucleus. The rate of initial nucleus formation is:

$$J = Z \exp\left(\frac{\Delta G_{\max}}{RT}\right) \quad (3)$$

where J is the rate of nucleus formation, Z the collision frequency (calculable from the classical kinetic theory) and ΔG_{\max} is the Gibbs free energy.

At low volume expansion, particles are being formed by precipitation from a liquid phase at the bottom of the precipitator. The liquid phase saturated with anti-solvent is formed as the result of vapor-liquid equilibrium at operating pressure and temperature. Under these conditions the precipitation of samarium acetate connected nanoparticles was observed by Reverchon et al. [11]. Our investigations indicated a similar structure

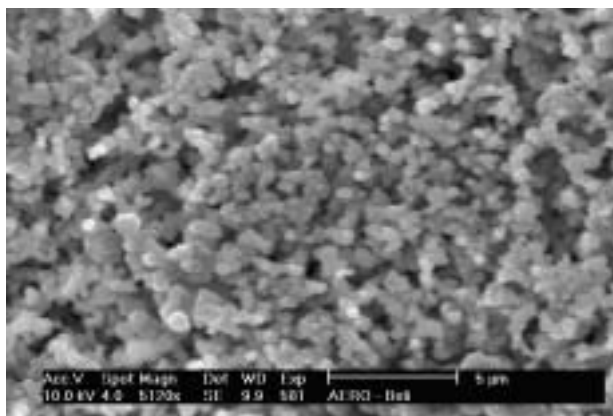


Figure 3. SEM image of the submicron sol-gel obtained aluminum oxo-chloride particles

of aluminum oxo-chloride submicron particles, which was observed after precipitation under similar conditions (100 bar, 313 K). These particles shown in Figure 3 were obtained by the non-hydrolytic sol-gel synthesis from aluminum trichloride and diethyl ether as precursors dissolved in carbon tetrachloride [19]. Supercritical anti-solvent precipitation was achieved from the solution of particles in carbon tetrachloride using supercritical carbon dioxide as an anti-solvent.

At intermediate expansion levels expanded droplets (balloons) have been observed by Reverchon et al. [11]. Spherical balloons were also observed by Dixon et al. [20] during the processing of polystyrene. Different nucleation structures can appear and different kinds of balloons have been observed. For example, during the precipitation of samarium acetate empty shells of solute with a continuous surface were also observed [11]. This is explained by the solute precipitation which starts at the supercritical fluid-liquid interface and then propagates inside the liquid attracting the solute towards the separation surface. This mechanism results in the formation of hollow spherical structures [10].

At very large expansion levels (asymptotic expansion) nanoparticles are produced by balloons disintegration. An example of yttrium acetate nanoparticles is reported in Figure 4. These particles are very small (100–200 nm) and have a very narrow particle size distribution [11].

Other additional growth mechanisms have also been observed and they can superimpose on the one described above. These mechanisms can produce more complex particle geometries. The first one is the coalescence of nanoparticles. The physical coalescence is characterized by a particle to particle interaction, for example, by impact during the precipitation process. These particles can be separated by sonication. Chemical coalescence mechanism is the result of interaction between particles and solvent which can lead to the fusion of nanoparticles in groups where the single particle has no more a distinct identity. It is possible to take the

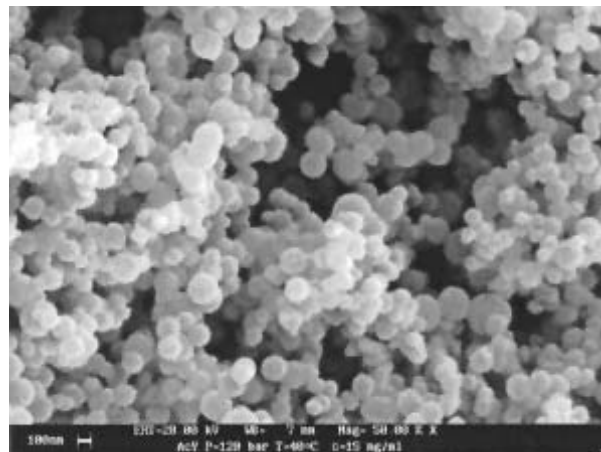


Figure 4. SEM image of yttrium acetate nanoparticles precipitated from DMSO (15 mg/ml) at 120 bar and 313 K, with mean diameters of about 150 nm. Reprinted from *The Journal of Supercritical Fluids*, Vol. 15, Reverchon et al, Pages 1–21.

advantage of coalescence and to produce larger or smaller particle aggregates.

The further growth of the solid particles in the solution inside the precipitation chamber is another mechanism that can strongly modify the morphology of particles. Although slow, this mechanism is responsible for the formation of more complex morphologies. A pronounced effect of co-solvent can lead to specific morphologies as well. This effect is well known in supercritical extraction processing and has been used to improve the solubility of poorly soluble compounds. The formed complex (a result of solvent-solute interaction) is a loosely bound aggregate but this fact does not necessarily imply that it is destroyed when the anti-solvent is added. As a result of co-solvent action, no solute or small quantities of solute are found (when compared with the injected quantity) in the precipitator since the solute is dissolved in the liquid-supercritical fluid mixture. Therefore, the solute is recovered in the liquid solvent collection chamber [21]. Another possible problem is the formation of a liquid phase at the bottom of the precipitation chamber even when asymptotic expansion of the liquid solvent should have been obtained, based on pure solvent curves. This problem can be the result of the modification of the solvent-anti-solvent phase equilibrium induced by the solute.

The influence of different methods and process parameters

The above described process modes can be divided into two large groups: precipitation from a liquid rich phase and from a supercritical fluid rich phase. The resulting particles obtained using these different process modes are usually quite different. Typically smaller and amorphous particles are obtained using the precipitation from the supercritical fluid rich phase. This fact could be explained by the faster expansion of the liquid phase

(due to high anti-solvent/solvent ratio) and to the larger liquid to supercritical fluid contact surface area produced by the formation of fine droplets. In liquid batch precipitation, the precipitation vessel has to be pressurized from atmospheric pressure up to the final pressure and this procedure results in the unsteady operation of the system and unsteady precipitating conditions. In general, when larger particles or crystalline materials are required liquid batch processing should be adopted which can lead to more ordered crystal structures than the original material [22]; if smaller and amorphous particles are required, anti-solvent rich precipitation is the best choice.

Contradicting results have been obtained by different authors about the influence of pressure on the particle size during gas batch and continuous operation [10,12-14,23]. Concerning reduction of the precipitation pressure some authors found a particle size decrease [12,23], others found the process insensitive to this parameter [14] and others observed a particle size increase [10]. Similarly, the temperature reduction produced a particle size decrease according to certain authors [12,14], had no influence according to the others [10] and produced larger particles according to another group [23].

Particle size was relatively insensitive to solute concentration in the liquid according to some authors [10,12], while others observed that backing away from saturation conditions may be a better choice to prepare more uniform particles [14]. A marked particle size increase and PSD enlargement with increasing concentration was observed by Reverchon et al. [11] in the SAS precipitation of yttrium, samarium and neodymium acetates.

Very different behaviors can be obtained by changing the liquid solvent. For example, in the case of amoxicillin and tetracycline precipitated from DMSO and NMP, the SAS processing using the first solvent was completely unsuccessful since both antibiotics were extracted from the precipitation chamber, whereas, precipitation from NMP was successful and antibiotic nanoparticles were produced [10]. Similarly, the micronization of salbutamol was successful with dimethylsulfoxide (DMSO) while methanol and ethanol-water mixture resulted in failed micronization [24]. Hong et al. have studied the influence of different solvents, the pressure, temperature and the flow rate of solution on the SAS processing of organic pigments (Bronze red) [25]. Their results indicate that the size and morphology of the particles were influenced by the temperature, pressure and flow rate when ethanol was used as the solvent. On the other hand, the application of acetone as solvent resulted in low sensitivity to temperature and pressure but the influence of the flow rate was significant. Chemical structure of the solute can play an important role as well since compounds having a relatively simple molecular structure can form only primary particles, while com-

pounds having a more complex chemical structure can exhibit further growth processes thus producing complex morphologies. Solubility, phase behavior of the system and SAS processing of the solute can also be influenced by the presence of another solute [26].

Other processes

Reverse microemulsions are systems in which fine aqueous droplets are uniformly dispersed in a continuous low-polarity fluid phase by the presence of surfactant shells [2]. Individual aqueous phase droplets are typically of 3-20 nm in diameter, and their size is strongly dependent on the molar water/surfactant ratio. Although they are thermodynamically stable and able to exist in optically clear solutions for extended periods of time, these droplets are very dynamic at the molecular level. Surfactant molecules associated with aqueous droplets exchange rapidly with monomers dissolved in the continuous phase. Also, collisions between droplets lead to rapid restructuring and repartitioning of surfactant molecules and aqueous core contents on a short time scale. Reverse microemulsions offer a unique environment for chemical reactions. The dispersed aqueous droplets behave as miniature chemical reactors accommodating hydrophilic species in an otherwise hydrophobic environment. Low values of water/surfactant ratio result in highly ordered water molecules in the droplets due to association with the surfactant polar head groups. At higher values of water/surfactant ratio droplet core usually resembles bulk water making it possible to dissolve various water soluble compounds. Supercritical fluids offer specific characteristics which could be beneficial for reverse microemulsion systems. For example, diffusion of reacting species through the supercritical continuous phase is considerably improved, thereby improving the kinetics of diffusion limited reactions. Additionally, the stabilities of supercritical fluid microemulsions are highly pressure sensitive, with the single-phase microemulsions separating into two or more distinct phases at some pressure boundary. This characteristic offers a possibility to shift equilibrium of certain reactions by manipulating the pressure of the system. The silver nanoparticles were obtained by the reduction of silver nitrate in bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles in compressed propane [27]. Salaniwal et al. have studied reverse micelles in supercritical carbon dioxide using molecular dynamics simulation [28].

The supercritical fluids have received considerable attention as solvents for the synthesis of a number of ceramic, metal and other materials. These new applications have been developed in order to improve the characteristics of the obtained powders, such as chemical homogeneity or unique structural properties. Unlike previously described processes (RESS, SAS and PGSS) which are principally physical transformation, the chemi-

cal transformation of materials in supercritical fluid is the principle of different reactive processes.

Particles can be produced by thermal decomposition with a supercritical solvent where precursors are thermally decomposed in a supercritical media. At the end of the reaction supercritical solvent is depressurized and the solvent, turned to gas phase, separates from the particles which remain in a highly divided state. The advantage of processing in a supercritical media is that high nucleation rate and low crystal-growth rate can be achieved, leading to the formation of very fine particles. Furthermore, the high density of the supercritical fluid avoids aggregation problems encountered in liquid-solid separation steps of conventional wet chemistry processes [29,30]. When the thermal stability of the precursor does not allow dissolution in the supercritical fluid, a variant process can be used: a sol-gel reaction is conducted at high pressure and high temperature, followed by supercritical drying. Fine powders (diameter: 50 nm) can be obtained using this process [1]. The hydrothermal processes typically designate processes conducted at relatively high temperatures and pressures in the presence of water. Under the supercritical hydrothermal conditions very fine crystalline oxide powders can be produced. Simple oxides, as well as more complex compositions, can be generated. The produced powders are commonly pure, crystalline and with highly uniform particle size distributions.

Materials synthesis under supercritical conditions

The supercritical fluid can be used as a solvent and a reactant. The processes of this type described in the literature commonly use supercritical water. Hydrothermal synthesis has been used for microparticles or large crystals processing. In order to prepare oxide powders, low-cost precursors (oxides, hydroxides or salts) are first dissolved in water and the solution is introduced into a reactor operated at supercritical conditions. This process has a potential to manipulate the direction of crystal growth, morphology, particle size and size distribution, due to the controllability of thermodynamics and transport properties by pressure and temperature [31]. Moreover, high reaction rate leads to ultra fine powder formation while crushing and calcination steps used in conventional processes are avoided. It is also possible to apply reducing or oxidizing atmosphere by the introduction of oxygen, hydrogen or other gases. On the other hand, filtration, washing and drying are still necessary, and corrosion problems associated with supercritical water is serious disadvantage of the process.

Specific physicochemical properties of the supercritical fluids offer flexible alternatives to established processes like chemical vapour deposition (CVD) which is used in the preparation of high-quality metal and semiconductor thin films on solid surfaces. Watkins et al. [32] reported a method (named chemical fluid deposition or CFD) for the deposition of CVD-quality platinum

metal films on silicon wafers and polymer substrates. Process proceeds *via* hydrogenolysis of dimethyl-(cyclooctadiene)platinum(II) at 353 K and 155 bar.

Inorganic particles obtained using supercritical fluids

The application of RESS in the processing of inorganic particles is relatively limited since the solubility of inorganic solids in most of the supercritical fluids is very low. For example, solubility of SiO₂ in supercritical water at 773 K and 100 MPa is 2600 ppm and solubility of Al₂O₃ in supercritical water at the same conditions is only 1.8 ppm [2]. Therefore, RESS is considered for application only in the case of special inorganic materials. The literature data of processing of the inorganic material using RESS are shown in Table 1 [33–36].

Table 1. Inorganic solids obtained by the RESS.

Substrate	SC Fluid	Results	Ref.
SiO ₂	water	>1.0 μm thick film and 0.1–0.5 μm diameter spheres	33
GeO ₂	water	5 μm agglomerates or 0.3–0.5 μm diameter spheres	33
AgI	acetone	Ag film after reaction at 873 K	34
Ag triflate	Et ₂ O	Ag film after reaction at 873 K	34
Al(hfa) ₃	pentane	Al film after reaction at 953 K	34
Al(hfa) ₃	N ₂ O	Al ₂ O ₃ film after reaction at 373 K	34
Cr(acac) ₃	acetone	Cr film after reaction at 1073 K	34
Cr(hfa) ₃	N ₂ O	Cr ₂ O ₃ film after reaction at 373 K	34
Cu(oleate) ₂	pentane	Cu film after reaction at 1013 K	34
Cu(thd) ₂	N ₂ O	Cu film after reaction at 973 K	34
Cu(thd) ₂	N ₂ O	CuO film after reaction at 373 K	34
In(acac) ₃	CO ₂	In film after reaction at 873 K	34
Ni(thd) ₂	pentane	Ni film after reaction at 873 K	34
Pd(tod) ₂	pentane	Pd film after reaction at 873 K	34,35
Si(OC ₂ H ₅) ₄	N ₂ O	SiO ₂ film after reaction at 373 K	34
SiO ₂ , KI	water	20 μm agglomerates	33
Y(thd) ₃	N ₂ O	Y film after reaction at 960 K	34
ZrO(NO ₃) ₂	ethanol	Particles 0.1 μm	33
Zr(tfa) ₄	Et ₂ O	Zr film after reaction at 873 K	34
Pb(NO ₃) ₂	NH ₃ , EtOH, MeOH	PbS nanoparticles 4 nm diameter	36

Abbreviations used: MeOH, methyl alcohol; EtOH, ethyl alcohol; thd, *bis*(2,2,6,6-tetramethyl-3,5-heptanedionato); acac, *tris*(2,4-pentanedionato); hfa, *tris*(1,1,1,5,5,5-haexafluoro-2,4-pentanedionato); tfa, *tetrakis*(1,1,1-trifluoro-2,4-heptanedionato); tod, *bis*(2,2,7-trimethyl-3,5-octanedionato).

As it can be seen from Table 2 [37–41], processing of inorganic material using SAS and related processes is dominantly applied to obtain organic compounds which serve as precursors for synthesis of inorganic solids. An interesting route to synthesize ceramic material was proposed by Moner-Girona et al. [41]. Spherical silica aerogel particles were obtained by the hydrolytic sol-gel

Table 2. Inorganic solids obtained by the SAS, and related processes.

Process	Substrate/solvent	SC Fluid	Results	Ref.
SAS	NH ₄ Cl / DMSO	CO ₂	Particles 1 – 5 μm	37
SAS	BaCl ₂ / DMSO	CO ₂	Particles 1 – 7 μm cubic or needle like	37
SAS/ASES	SmAc / DMSO	CO ₂	Particles 0.1 – 0.3 μm	10,11
SAS/ASES	YAc / DMSO	CO ₂	Balloons; Particles 0.08 – 2 μm	10,11
SAS/ASES	NdAc / DMSO	CO ₂	Particles 0.1 μm	10,11
SAS/ASES	GdAc / DMSO	CO ₂	Particles 0.2 – 0.4 μm	38
SAS/ASES	EuAc / DMSO	CO ₂	Particles 0.2 – 0.4 μm	38
SAS/ASES	ZnAc / DMSO	CO ₂	Particles 50 – 150 nm	39
SAS	VOHPO ₄ .0.5H ₂ O / isopropanol	CO ₂	Catalyst spheres 50 – 700 nm	40
SAS	SiO ₂ / acetone	CO ₂	1.2 – 2.2 μm, fibers	41

Abbreviations used: DMSO, dimethylsulfoxide; TTIP, titanium tetraisopropoxide; Ac, acetate.

method in acetone followed by the particles precipitation in supercritical carbon dioxide.

Supercritical fluids have received considerable attention as solvents for the synthesis of ceramic or similar materials. One method applies thermal decomposition of precursors in a supercritical fluid, which is at the end of the reaction depressurized and removed from the system. After removal of the solvent, obtained inorganic material is typically in the form of micron or sub-micron particles. The second method uses supercritical fluid as a solvent and a reactant. In this case the typical supercritical fluid is water, and the process is called hydrothermal synthesis. Inorganic solids obtained by the decomposition in the supercritical fluid, or by the synthesis using supercritical reactant, are listed in Tables 3 [22,23,35–38] and 4 [31,41,46–48] respectively. As it can be seen from the presented data different morphologies can be obtained on the micrometer or nanometer scale.

Polymer solid particles obtained using supercritical fluid processing

Polymer processing with supercritical fluids can result in the formation of very fine powders, fine fibers, microspheres, micro balloons and thin films. As indicated in Table 5 [33,49–56] very fine particles with submicron diameters and ultra-thin films (6 nm) were obtained using RESS. Although different polymers were processed with RESS as indicated in Table 5, its application is relatively limited due to the low solubility of polymers in supercritical solvents.

Table 3. Inorganic solids obtained by the decomposition in supercritical fluid.

Substrate / precursor	SC Fluid	Results	Ref.
MgAl ₂ O ₄ / MgAlTBSB	ethanol	Spheres 0.5–2 μm	22,23
MgO / MgChe, MgAc	CO ₂ + ethanol	Particles 0.5–2 μm	35
TiO ₂ / TTIP	ethanol	Spheres 0.5–2 μm	22,23
TiO ₂ / TTIP	CO ₂ + isopropanol		36
TiO ₂ / TTIP	CO ₂ + aq, surf	Spheres 0.1–2 μm	37
TiO ₂ / TTE	ethanol + water + Et ₂ O	Particles 60–400 nm	38

Abbreviations used: AlTBSB, aluminum tri-sec butoxide; TTIP, titanium tetraisopropoxide; TTE, titanium tetraethoxide; Et₂O, diethyl ether; MgChe, magnesium chelate; MgAc, magnesium acetate; aq, surf, aqueous solution of surfactant.

Table 4. Inorganic solids obtained by the synthesis with supercritical reactant.

Substrate / precursor	SC Fluid	Results	Ref.
AlOOH / Al(NO ₃) ₃	water	Hexagonal, rhombic or needle like particles; size 100–600 nm	46,47
Co ₃ O ₄ / Co(NO ₃) ₂	water	Octahedral particles 50 nm	46,47
Ti(OH) ₄ / TTIP	CO ₂ /H ₂ O	Spheres 70 – 110 nm	48
SiO ₂ / TEOS	CO ₂	Particles < 1 μm	41
Fe ₂ O ₃ / Fe(NO ₃) ₃ , FeCl ₂ , Fe ₂ (SO ₄) ₃	water	Spheres 50 nm	46,47
Fe ₃ O ₄ / Fe(NH ₄) ₂	water	Spheres 50 nm	46,47
TiO ₂ / TiCl ₄	water	Spheres 20 nm	46,47
LiCoO ₂ / LiOH, Co(NO ₃) ₂	water + O ₂	Particles 700 nm	31

Abbreviation used: TTIP, titanium tetraisopropoxide.

Table 5. Polymers obtained by the RESS.

Substrate	SC Fluid	Results	Ref.
Polystyrene	pentane	1 μm diameter fibers or 20 μm diameter spheres	49
Poly(carbo-silane)	pentane	Particles < 0.1 μm diameter, or 1 μm diameter fibers	33, 49
Poly(ε-caprolactone)	chlorodifluoromethane	Powder or fibers	50
L-PLA	carbon dioxide	Particles 10–90 μm	51
PGA	carbon dioxide	Particles 10–20 μm	52
D-PLA	carbon dioxide	Particles 10–20 μm	52
PMMA	CCl ₂ F ₂	Particles 200–600 nm	53
PEMA	CCl ₂ F ₂	Particles 200–600 nm	53
PDMS	carbon dioxide	Particles 2–3 μm	54
Teflon AF2400 (Du Pont)	carbon dioxide	Thin films approx. 6 nm thick	55
PEHA	carbon dioxide	Particles 270–340 nm	56

Abbreviations used: L-PLA, Poly-L-lactic acid; PGA, Poly-glycolic acid; D-PLA, Poly-D-lactic acid; PMMA, Poly-methyl methacrylate; PEMA, Poly-ethyl methacrylate; PDMS, Poly(dimethyl-siloxane); PEHA, Poly(2-ethylhexyl acrylate).

Table 6. Polymers obtained by the SAS, and related processes.

Process	Substrate/ solvent	SC Fluid	Results	Ref.
ASES	L-PLA / acetone	carbon dioxide	Particles 1 – 10 μm	21
ASES	Polystyrene / toluene	carbon dioxide	Particles 0.1 – 20 μm	13
SAS	PLGA / CH_2Cl_2	carbon dioxide	Particles 40 – 60 μm	57
SAS	L-PLA / CH_2Cl_2	carbon dioxide	Particles 0.5 – 5 μm	12
SAS	Polyamide / DMSO	carbon dioxide	Particles 2 – 10 μm , fibers	58
SAS	Polyamide / DMF	carbon dioxide	Fibers	58
SAS	L-PLA / DMSO	carbon dioxide	Particles 1.25 – 1.75 μm	59
SAS	Dextran / DMSO	carbon dioxide	Particles 130 – 150 nm	59
SAS	HPMA / DMSO	carbon dioxide	Particles 150 nm	59
SAS	L-PLA / chloroform	carbon dioxide	Particles > 200 nm	60
SAS	PC+SAN / THF	carbon dioxide	Particles < 10 μm	61
SAS	Polyamide / DMAc+LiCl	carbon dioxide	Fibers	62
SAS	Polystyrene / toluene	carbon dioxide	Spheres 1 – 20 μm	20
ASES	PLCG / methy- lenechloride	carbon dioxide	Microparticles	63

Abbreviations used: L-PLA, Poly-L-lactic acid; DMSO, dimethylsulfoxide; DMF, N,N-dimethylformamide; poly-(hydroxypropylmethacrylamide); PC, polycarbonate; SAN, poly(styrene-co-acrylonitrile); THF, tetrahydrofuran; DMAc, N,N-dimethylacetamide; PLCG, poly lactide-co-glycolide.

Different polymers (and applied solvents) micronized using SAS and related processes are shown in Table 6 [12,13,20,21,57–62]. As it can be seen different morphologies were obtained, including particles, fibers and microspheres.

The polymer industry is a major user and emitter of volatile organic compounds (VOCs) which are toxic and cause harm to the environment. As a result of growing pressure to reduce emission, there has been considerable effort devoted to finding alternative non-polluting solvents. De Simone and others have shown the applicability of supercritical carbon dioxide as a viable medium for a number of polymerization reactions [64–66]. An example of application in processing of polymeric powders is continuous precipitation polymerization of vinylidene fluoride in supercritical carbon dioxide [67–69]. This polymer is produced commercially in batch reactors by either emulsion or suspension method, at monomer pressures from 10 to 200 bar and at tempera-

tures from 283 to 403 K. In the emulsion process, the latex is coagulated, thoroughly washed, and then spray dried to form powder. The suspension method requires thorough washing and drying as well. In both processes, large quantities of waste water are generated and large quantities of energy are required to dry the polymer. Continuous precipitation polymerization in supercritical carbon dioxide eliminates generation of waste water, reduces energy consumption and results in the formation of micrometer-scale particles of poly(vinylidene fluoride) [68].

Encapsulation and coating using supercritical fluids

Among the prospective applications of supercritical fluids are also the coating and encapsulation of: inorganic compounds, metal micro- and nano-particles, active pharmaceutical ingredients and other. Over the last decade polymer microcapsules of inorganic nanoparticles have been attracting much attention in the catalytic, cosmetics, printing and electronic industry [70]. Another potential field of application is in coating of metal powders with thin films [71], which are common components of the pyrotechnic and solid propellant compositions. Coating of metal powders reduces deterioration through corrosion and aggregation caused by moisture or other aggressive substances, and it also reduces flammability. The increasing trend in research and development of drug delivery systems will intensify in the pharmaceutical industry. The distribution of active substance directly to the target will enhance the treatment efficiency and reduce the doses and related side-effects, while many efficient drugs will have to be reformulated in order to allow control of delivery location and rate. This last criterion is of particular importance for long-term treatments like cancer or various chronic diseases. The microencapsulation could offer solutions by enhancing controlled delivery of active substances and material stability.

For microencapsulation of inorganic nanoparticles, preparation methods such as *in situ* polymerization may be used [72]. However, these methods often require toxic organic solvents and/or surfactants. Furthermore, the removal of residual surfactants and/or solvents is needed, since they cause faults on the product. An environmentally benign solvent like supercritical carbon dioxide can be used to encapsulate inorganic nanoparticles. But its use is limited because of the low solubility of most of the polymers and inorganic solids in supercritical carbon dioxide. A novel method, rapid expansion of supercritical solution with nonsolvent (RESS-N), has been reported by Mishima et al. [73,74]. The process differs from conventional RESS as it applies organic cosolvents. Since polymers are usually insoluble in the supercritical carbon dioxide at temperatures and pressures of interest, several cosolvents are used to enhance solubility of the polymer in supercritical media.

These solvents are nonsolvents for polymer at atmospheric pressure and they are only sparingly soluble in the polymer particles produced during expansion. As a result of RESS-N the polymer precipitates and coats the inorganic nanoparticles [75]. RESS-N method was used to coat TiO₂ nanoparticles which are of interest as cosmetic, printing and electronic materials. The obtained particles were of the order of 10 – 30 µm and not adhesive to each other.

Debenedetti et al. [76] obtained microparticles by the RESS co-precipitation of a drug (lovastatin) and a biodegradable polymer (poly(D, L-lactic acid)). The co-precipitation of the polymer and the drug led to a heterogeneous population of microparticles consisting of microspheres containing a single lovastatin needle, larger spheres containing several needles, microspheres without protruding needles and needles without any polymer coating.

Elvassore [1] described the formation of protein-polymer microcapsules by supercritical anti-solvent techniques. Homogeneous protein/polymer mixtures were contacted with supercritical carbon dioxide in order to produce microspheres with diameter ranging from 1 to 5 µm and containing around 80% of protein. Production of PLA microparticles containing insulin, lysozyme and chymotrypsin is claimed. Chou and Tomasko [1] studied SAS crystallization of a pharmaceutical (naproxen) and a biodegradable polymer (poly-lactic acid). The results from SAS studies showed very small spherical particles composed of a naproxen core surrounded by a polymer shell. Sze Tu et al. [1] used the ASES technique for the coprecipitation of a model drug, parahydroxybenzoic acid (p-HBA) with the biodegradable polymers, poly(lactide-co-glycolide) (PLGA) and poly(L-lactic acid) (PLA).

Supercritical fluid-soluble substrates can be easily impregnated inside porous media. Domingo et al. [1] used this process to prepare controlled drug delivery systems. In this work, zeolite, several amorphous mesoporous inorganic matrices (silica gel, alumina and florasil) and a polymeric matrix (amberlite) have been impregnated with various thermally unstable organic compounds (benzoic acid, salicylic acid, aspirin, triflusal, ketoprofen) by diffusion from saturated supercritical carbon dioxide solutions. Copper and iron chelate complexes were impregnated into a polyarylate matrix from the solution in supercritical carbon dioxide by Said-Galiev et al. [77].

The precipitation methods previously described (RESS, SAS, PGSS and thermal decomposition) can be used for particle coating while those currently used in the industry are the Wurster process [78] and fluidized bed coating [79]. The latter was also investigated for application at supercritical conditions [80]. It was found that operating parameters have influenced the morphologies of coated particles. Kobe Steel Ltd. patented a process related to the RESS concept for microparti-

cles formation and coating [1]. Primary microparticles are formed by rapid decompression of a supercritical solution of the core material. These particles are mixed with a supercritical solution of the coating agent and depressurized to form microcapsules. Coating with multiple layers can be achieved using this process. Sunol used a different process for coating polymeric thin films on particles [1]. The method involves a recirculation system that includes dissolution of the polymer into the supercritical solvent and coating the particles through a temperature swing operation in the fluidized bed. This system has been tested with hydroxyl-terminated polybutadiene (HTTB) as coating polymer and particles of salt (30–500 µm). The film thickness was as low as 0.2 µm. In the method patented by Mainelab [1] the coating agent is solubilized into supercritical carbon dioxide. In a stirred vessel, particles of an active substance are dispersed into the supercritical solution. By changing the pressure and the temperature, the solubility of the coating agent in the supercritical fluid can be reduced so that it can precipitate on the particles. Microcapsules of active substance are collected after depressurization, allowing a good control of the structure (composition, thickness) of the microcapsule without using organic solvents. This process was used to encapsulate substances such as: dyes, antibiotics, vitamins, proteins. Coating agents which have to be soluble in supercritical carbon dioxide were used, such as waxes, glycerides, alcohols, fatty acids and esters. Similar process was reported by Glebov et al. [81] used for coating of metal particles. In another method patented by Mainelab [1], a suspension of active substance in a solution of a slightly polar polymer (insoluble in liquid or supercritical carbon dioxide) in an organic solvent is used. This suspension is contacted with supercritical carbon dioxide so that the organic solvent is solubilized in such a manner that there is coacervation of the coating polymer onto the particles. Microcapsules are collected after decompression.

Beside the above treated processes, the synthesis of aerogels [82–84] and PGSS (particles from gas saturated solutions/suspensions) [85] are techniques used in materials processing.

REFERENCES

- [1] J. Jung, M. J. Perrut, *Supercrit. Fluids* **20** (2001) 179.
- [2] D.W. Matson, R.D. Smith, *J. Am. Ceram. Soc.* **72** (1989) 871.
- [3] R.C. Petersen, D.W. Matson, R.D. Smith, *J. Am. Chem. Soc.* **108** (1986) 2100.
- [4] B. Helfgen, M. Türk, K. Schaber, *J. Supercrit. Fluids* **26** (2003) 225.
- [5] R.S. Mohamed, P.G. Debenedetti, R.K. Prud'homme, *AIChE Journal* **35** (1989) 325.
- [6] D. Kayrak, U. Akman, Ö. Hortacsu, *J. Supercrit. Fluids* **26** (2003) 17.
- [7] S. Cihlar, M. Türk, K. Schaber, *J. Aerosol Sci.* **30** (1999) S355.
- [8]

- K. Matsuyama, K. Mishima, K. Hayashi, H. Matsuyama, *J. Nanoparticle Res.* **5** (2003) 87.
- [9] M. Türk, P. Hils, B. Helfgen, K. Schaber, H.-J. Martin, M.A. Wahl, *J. Supercrit. Fluids* **22** (2002) 75.
- [10] E. Reverchon, *J. Supercrit. Fluids* **15** (1999) 1.
- [11] E. Reverchon, G. Della Porta, A. Di Trolino, S. Pace, *Ind. Eng. Chem. Res.* **37** (1998) 952.
- [12] T.W. Randolph, A.D. Randolph, M. Mebes, S. Yeung, *Biotechnol. Progress* **9** (1993) 429.
- [13] D.J. Dixon, K.P. Johnston, R.A. Bodmeier, *AIChE J.* **39** (1993) 127.
- [14] W.J. Schmitt, M.C. Salada, G.G. Shook, S.M. Speaker III, *AIChE J.* **41** (1995) 2476.
- [15] M. Rantakylä, M. Jäntti, O. Aaltonen, M. Hurme, *J. Supercrit. Fluids* **24** (2002) 251.
- [16] B.Yu. Shekunov, M. Hanna, P. York, *J. Cryst. Growth* **198/199** (1999) 1345.
- [17] S. Bristow, T. Shekunov, B.Yu. Shekunov, P. York, *J. Supercrit. Fluids* **21** (2001) 257.
- [18] A. Kordikowski, A.P. Schenk, R.M. Van Nielen, C.J. Peters, *J. Supercrit. Fluids* **8** (1995) 205.
- [19] Dj. Janačković, A. Orlović, D. Skala, S. Drmanić, Lj. Kostić-Gvozdenović, V. Jokanović, D. Uskoković, *NanoStructured. Mater.* **12** (1999) 147.
- [20] D.J. Dixon, G. Luna-Barcenas, K.P. Johnston, *Polymer* **35** (1994) 3998.
- [21] J. Bleich, B.W. Muller, W. Wassmus, *Int. J. Pharm.* **97** (1993) 111.
- [22] S.-D. Yeo, M.-S. Kim, J.-C. Lee, *J. Supercrit. Fluids* **25** (2003) 143.
- [23] Y. Gao, T.K. Mulenda, Y.-F. Shi, W.-K. Yuan, *J. Supercrit. Fluids* **13** (1998) 369.
- [24] E. Reverchon, G. Della Porta, P. Pallado, *Powder Technol.* **114** (2001) 17.
- [25] L. Hong, J.Z. Guo, Y. Gao, W.-K. Yuan, *Ind. Eng. Chem. Res.* **39** (2000) 4882.
- [26] B. Warwick, F. Dehghani, N.R. Foster, J.R. Biffin, H.L. Regtop, *Ind. Eng. Chem. Res.* **39** (2000) 4571.
- [27] J.P. Cason, K. Khambaswadkar, C.B. Roberts, *Ind. Eng. Chem. Res.* **39** (2000) 4749.
- [28] S. Salaniwal, S. Cui, H.D. Cochran, P.T. Cummings, *Ind. Eng. Chem. Res.* **39** (2000) 4543.
- [29] M. Barj, J.F. Bocquet, K. Chhor, C. Pommier, *J. Mater. Sci.* **27** (1992) 2187.
- [30] K. Chhor, J.F. Bocquet, C. Pommier, *Mater. Chem. Phys.* **32** (1992) 249.
- [31] T. Adshiri, Y. Hakuta, K. Arai, *Ind. Eng. Chem. Res.* **39** (2000) 4901.
- [32] J.J. Watkins, J.M. Blackburn, T.J. McCarthy, *Chem. Mater.* **11** (1999) 213.
- [33] D.W. Matson, J.L. Fulton, R.C. Petersen, R.D. Smith, *Ind. Eng. Chem. Res.* **26** (1987) 2298.
- [34] B.N. Hansen, B.M. Hybertson, R.M. Barkley, R.E. Sievers, *Chem. Mater.* **4** (1992) 749.
- [35] B.M. Hybertson, B.N. Hansen, R.M. Barkley, R.E. Sievers, *Mater. Res. Bull.* **26** (1991) 1127.
- [36] Y.-P. Sun, R. Guduru, F. Lin, T. Whiteside, *Ind. Eng. Chem. Res.* **39** (2000) 4663.
- [37] S.-D. Yeo, J.-H. Choi, T.-J. Lee, *J. Supercrit. Fluids* **16** (2000) 235.
- [38] E. Reverchon, I. De Marco, G. Della Porta, *J. Supercrit. Fluids* **23** (2002) 81.
- [39] E. Reverchon, G. Della Porta, D. Sannino, P. Ciambelli, *Powder Technol.* **102** (1999) 127.
- [40] G.J. Hutchings, J.A. Lopez-Sanchez, J.K. Bartley, J.M. Webster, A. Burrows, J.C. Kiely, A.F. Carley, C. Rhodes, M. Hävecker, A. Knop-Gericke, R.W. Mayer, R. Schlögl, J.C. Volta, M. Poliakoff, *J. Catal.* **208** (2002) 197.
- [41] M. Moner-Girona, A. Roig, E. Molins, E. Llibre, *J. Sol-Gel. Sci. Technol.* **26** (2003) 645.
- [42] K. Chhor, J.F. Bocquet, C. Pommier, *Mater. Chem. Phys.* **40** (1995) 63.
- [43] V. Gourinchas-Courtecuisse, J.F. Bocquet, K. Chhor, C. Pommier, *J. Supercrit. Fluids* **9** (1996) 222.
- [44] M.E. Tadros, C.L.J. Adkins, E.M. Russick, M.P. Youngman, *J. Supercrit. Fluids* **9** (1996) 172.
- [45] T.-H. Kim, D.-Y. Lim, B.-S. Yu, J.-H. Lee, M. Goto, *Ind. Eng. Chem. Res.* **39** (2000) 4702.
- [46] T. Adshiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **75** (1992) 1019.
- [47] T. Adshiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **75** (1992) 2615.
- [48] E. Reverchon, G. Caputo, S. Corraera, P. Cesti, *J. Supercrit. Fluids* **26** (2003) 253.
- [49] D.W. Matson, R.C. Petersen, R.D. Smith, *J. Mater. Sci.* **22** (1987) 1919.
- [50] A.K. Lele, A.D. Shine, *AIChE J.* **38** (1992) 742.
- [51] J.-H. Kim, T.E. Paxton, D.L. Tomasko, *Biotechnology Progress* **12** (1996) 650.
- [52] J.W. Tom, P.G. Debenedetti, *Biotechnol. Prog.* **7** (1991) 403.
- [53] A.K. Lele, A.D. Shine, *Ind. Eng. Chem. Res.* **33** (1994) 1476.
- [54] G. Tepper, N. Levit, *Ind. Eng. Chem. Res.* **39** (2000) 4445.
- [55] M.O. Gallyamov, R.A. Vinokur, L.N. Nikitin, E.E. Said-Galiyev, A.R. Khokhlov, I.G. Yaminsky, K. Schaumburg, *Langmuir* **18** (2000) 6928.
- [56] J.-J. Shim, M.Z. Yates, K.P. Johnston, *Ind. Eng. Chem. Res.* **40** (2001) 536.
- [57] B. Subramaniam, R.A. Rajewski, K. Snavely, *J. Pharm. Sci.* **86** (1996) 885.
- [58] S.-D. Yeo, P.G. Debenedetti, M. Radosz, H.-W. Schmidt, *Macromolecules* **26** (1993) 6207.
- [59] E. Reverchon, G. Della Porta, I. De Rosa, P. Subra, D. Le-tourneur, *J. Supercrit. Fluids* **18** (2000) 239.
- [60] G.D. Bothun, K.L. White, B.L. Knutson, *Polymer* **43** (2002) 4445.
- [61] S. Mawson, S. Kanakia, K.P. Johnston, *Polymer* **38** (1997) 2957.
- [62] S.-D. Yeo, P.G. Debenedetti, M. Radosz, R. Giesa, H.W. Schmidt, *Macromolecules* **28** (1995) 1316.
- [63] A. Engwicht, U. Girreser, B.W. Müller, *Biomaterials* **21** (2000) 1587.
- [64] D.A. Canelas, J.M. DeSimone, *Adv. Polym. Sci.* **133** (1997) 103.
- [65] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, *Chem. Rev.* **543** (1999) 3.
- [66] M. Hagiwara, H. Mitsui, S. Machi, T. Kagiya, *J. Polym. Sci. Part A-1*, **6** (1968) 603.
- [67] P.A. Charpentier, K.A. Kennedy, J.M. DeSimone, G.W. Roberts, *Macromolecules* **32** (1999) 5972.
- [68] P.A. Charpentier, J.M. DeSimone, G.W. Roberts, *Ind. Eng. Chem. Res.* **39** (2000) 4588.
- [69] M.K. Saraf, S. Gerard, L.M. Wojcinski II, P.A. Charpentier, J.M. DeSimone, G.W. Roberts, *Macromolecules* **35** (2002) 7976.
- [70] S. Benita, *Microencapsulation: Method and Industrial Applications*, Marcel Dekker Inc., 1996, New York.
- [71] J.W. Tom, P.G. Debenedetti, R. Jerome, *J. Supercrit. Fluids* **7** (1994) 9.
- [72] T. Hirai, T. Saito, I. Komazawa, *J. Phys. Chem. B* **105** (2001) 9711.
- [73] K. Mishima, K. Matsuyama, D. Tanabe, S. Yamauchi, T.J. Young, K.P. Johnston, *AIChE J.* **46** (2000) 857.

- [74] K. Matsuyama, K. Mishima, H. Umemoto, S. Yamaguchi, Environ. Sci. Technol. **35** (2001) 4149.
- [75] K. Matsuyama, K. Mishima, K. Hayashi, H. Matsuyama, J. Nanopart. Res. **5** (2003) 87.
- [76] P. Debenedetti, J.W. Tom, S.D. Yeo, G.B. Lim, J. Controlled Release **24** (1993) 27.
- [77] E. Said-Galiev, L. Nikitin, R. Vinokur, M. Gallyamov, M. Kurykin, O. Petrova, B. Lokshin, I. Volkov, A. Khokhlov, K. Schaumburg, Ind. Eng. Chem. Res. **39** (2000) 4891.
- [78] S. Shelukar, J. Ho, J. Zega, E. Roland, N. Yeh, D. Quiram, A. Nole, A. Katdare, S. Reynolds, Powder Technol. **110** (2000) 29.
- [79] K. Sudsakorn, R. Turton, Powder Technol. **110** (2000) 37.
- [80] R. Schreiber, C. Vogt, J. Werther, G. Brunner, J. Supercrit. Fluids **24** (2002) 137.
- [81] E.M. Glebov, L. Yuan, L.G. Krishtopa, O.M. Usov, L.N. Krasnoperov, Ind. Eng. Chem. Res. **40** (2001) 4058.
- [82] A.M. Orlović, S. Petrović, D. Skala, J. Serb. Chem. Soc. **70**(1) (2005) 125.
- [83] A.M. Orlović, Dj. T. Janačković, S. Drmanić, Z. Marinković, D.U. Skala, J. Serb. Chem. Soc. **66**(10) (2001) 685.
- [84] A. Orlović, Dj. Janačković, D. Skala, Catal. Commun. **3** (2002) 119.
- [85] E. Weidner, Ž. Knez, R. Steiner, 3rd Int. Symp. On High Pressure Chem. Eng., Zürich, 1996, 223-228.

IZVOD

PROCESIRANJE ČVRSTIH MATERIJALA NATKRITIČNIM FLUIDIMA

(Pregledni rad)

Aleksandar Orlović, Dejan Skala

Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija i Crna Gora

Jedna od najinteresantnijih oblasti primene natkritičnih fluida je procesiranje novih tipova čvrstih materijala. Zahvaljujući svojim specifičnim karakteristikama, natkritični fluidi se mogu iskoristiti za dobijanje novih materijala sa osobinama znatno drugačijim nego kod konvencionalno dobijenih materijala. Ovi novi materijali su dizajnirani da zadovolje specifične zahteve i da omoguće nove primene u sledećim oblastima: farmaceutske hemikalije, heterogena kataliza, mikro i nano čestice za specijalne primene, novi izolacioni materijali, superkapacitatori kao i druge tehničke primene novih materijala.

Postoje dve osnovne mogućnosti primene natkritičnih fluida u procesiranju materijala: sinteza materijala pod natkritičnim uslovima i naknadno procesiranje dobijenih materijala uz pomoć natkritičnih fluida. Neke od sinteza materijala se odvijaju pod natkritičnim uslovima kao u slučaju poletilena niske gustine. Modifikacijom procesnih parametara moguće je modifikovati karakteristike natkritičnog fluida i na taj način promeniti karakteristike i strukturu dobijenog materijala. Materijali jedinstvenih struktura se mogu dobiti i u veoma specifičnim reakcionim uslovima kao što su na primer reverzne micelle. Ovaj rad je svojim većim delom posvećen materijalima koji se nakon sinteze procesiraju uz pomoć natkritičnih fluida. Poslednjih godina razvijeno je nekoliko novih metoda za dobijanje mikro i nano čestica uz pomoć natkritičnih fluida. Ove nove metode kombinuju karakteristike visoke gustine i moći rastvaranja natkritičnih fluida, sa mogućnošću njihove velike promene redukcijom pritiska. Metode kao što su: brza ekspanzija natkritičnih rastvora (RESS), natkritični anti solvent (SAS), sinteza pod natkritičnim uslovima i enkapsulacija, su poslednjih godina korišćene u procesiranju veoma različitih tipova i vrsta čvrstih materijala.

Ključne reči: Natkritični fluidi •
Procesiranje materijala • RESS •
SAS • Natkritična sinteza •
Enkapsulacija •

Key words: Supercritical fluids •
Materials processing • RESS •
SAS • Supercritical synthesis •
Encapsulation •