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Synthesis and encapsulation of yttria stabilized zirconia particles in supercritical carbon dioxide

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Abstract

Nanocrystalline oxide powders synthesized in supercritical CO_2 (SC-CO_2) generally consist in nanoparticle agglomerates, which are difficult to handle. In this work a particle encapsulation method in SC-CO_2 was developed to overcome this problem. By performing both the synthesis and encapsulation steps in the supercritical fluid, the agglomeration of particles can be limited, their handling can be improved and the powder behavior can be modified depending on the selected encapsulation agent. Poly(dimethylsiloxane)-graft-polyacrylate (PDMS-g-PA) phase separation method and methylmethacrylate (MMA) polymerization on particle surface are typical encapsulation processes usable in batch mode, with SC-CO_2 as a solvent, for ceramic powder encapsulation. This paper describes preliminary results concerning the synthesis of yttrium stabilized zirconia (YSZ) in SC-CO_2 and its encapsulation with PDMS-g-PA or PMMA in SC-CO_2. It has been shown that both phase separation and polymerization allow coating of the oxide particles, and clearly modify their properties. On the other hand, the use of a surfactant like PDMS-g-PA allows anchoring of MMA monomer and promotes polymerization on the particle surface. The choice of the surfactant is considered as a key parameter for a successful encapsulation process. This preliminary work offers new perspectives for synthesis and encapsulation of ceramic powders in SC-CO_2.

Keywords: Sol–gel processes; Nanocomposites; ZrO_2; CO_2; SC-CO_2

1. Introduction

Over the past decade, supercritical (SC) fluids have received considerable attention as solvents or reaction media for the synthesis of a number of ceramic and closely related oxide materials. Above its critical parameters, temperature and pressure, a SC fluid exists as a single phase. Moreover, SC fluids offer a novel combination of gas like (viscosity, diffusion coefficient) and liquid like (density) properties, which make them unique as solvent and drying media for ceramic forming and processing. In the ceramic area, production of fine, uniform, crystalline or amorphous powders suitable for subsequent compact forming and sintering is certainly the most promising development for supercritical methods. Processing of ceramic precursors by a supercritical CO_2 assisted sol–gel method was already investigated in our group as a suitable synthesis pathway yielding SiO_2 fibers,[1] TiO_2 powders,[2] as well as doped ceria, lanthanum gallates and zirconia.[3] In particular, the size and morphology of oxide nano-particles obtained by reacting the precursors (salts or metallo-organics) in SC-CO_2 media, was controlled by tuning the operating parameters such as precursor concentration, temperature, reaction time in SC con-

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ditions and pressure release. The ceramic powders synthesized by this method do not need any drying step, and their crystallization temperature is generally much lower compared to traditional processes (e.g. classical sol–gel process). However, when nanophase ceramic powders are prepared, they often tend to aggregate when the reactor is opened.

Encapsulated liquid or solid particles are designed for several applications, such as drug-controlled delivery in the pharmacy, sector pigment stabilization for paint in the chemistry sector, protection of active ingredients in the cosmetic industry or ingredient and aroma addition in powder form in the food industry. Several encapsulation processes exist,[4] which can be classified in two categories: physical methods (vibrating nozzle, rotating disk, pan coating, fluidized bed, spray drying, etc.) and chemical methods (coacervation, phase separation, interfacial polymerization, in situ polymerization, sol–gel methods, etc.). Actually, encapsulation with a polymer is one of the processes used for preventing aggregation of ceramic powders. The encapsulation of TiO_2 particles modified with titanium alkoxide through MMA emulsion polymerization in an aqueous solution of sodium dodecylsulphate (SDS) surfactant can be quoted as a relevant example reported by Caris et al.[5]

Regarding SC fluids, different methods have been described for the encapsulation of powders,[4,6] in particular those based on the rapid expansion of supercritical solutions (RESS)[7] and its derived processes[8] obtained by coupling with a non-solvent (RESS-N)[9,10] or with a fluidized bed.[11,12] Anti-solvent processes (GAS or SAS)[13,14] or phase separation[15,16] are also used for this purpose. Another encapsulation method, well adapted for batch operation, involves polymerization on the particle surface in SC-CO_2. This method is equivalent to the aforementioned emulsion polymerization route in aqueous media,[5] except that SC-CO_2 is used as the polymerization solvent.[17] SC-CO_2 is now a classical solvent used for polymerization reactions in dispersed media,[18,19] and MMA polymerization is often studied in SC fluids.[20–22] More recently encapsulation in SC-CO_2 has been found to be of particular interest for recovering and processing metal oxide nanoparticles.[23,24]

In this work, a synthesis and encapsulation process in SC-CO_2 was applied to yttrium stabilized zirconia (YSZ) powders. In a first step, sol–gel synthesis combined with an anti-solvent process (GAS or SAS) was used for YSZ powder production. In a second step, the recovered ceramic particles were coated in SC-CO_2, by a phase separation method or by polymerization of a monomer in presence of amphiphilic compounds such as poly(dimethylsiloxane)-grafted-polyacrylate (PDMS-g-PA) or FOMBLIN. PDMS-g-PA was also the encapsulation polymer used in the phase separation method for comparison with the polymethylmethacrylate (PMMA) formed in the second method by methylmethacrylate MMA polymerization.

2. Materials and methods

2.1. Chemicals

The precursors used for the oxide powder synthesis (yttrium doped ZrO_2) were zirconium hydroxyacetate ($Zr(acetate)_x(OH)_y,zH_2O$ ($x+y=4$)) and yttrium acetate ($Y(acetate)_3\cdot xH_2O$) both provided by Aldrich. Pentane (99% -PROLABO) was used as the solvent medium for acetate precursors and nitric acid (65% HNO_3-FLUKA) as dissolution additive. CO_2 (Carboxyque-France) was used as an anti-solvent for polymer encapsulation and as a solvent for monomer polymerization. All the chemicals for encapsulation and polymerization methods were supplied by ALDRICH. PDMS-g-PA was used as encapsulation polymer (*phase separation method*) or surfactant (*polymerization method*). MMA was the selected monomer and 2-2′-Azobis (2-methylpro-pioramidine) dihydrochloride was the initiator used for its polymerization. FOMBLIN (ALDRICH) was also used as a surfactant instead of PDMS-g-PA.

2.2. Apparatus

A schematic representation of the experimental set-up used in this study is shown in Fig. 1. A stainless steel autoclave is mechanically stirred and works in a batch mode. The internal volume of the reactor is 1 l, and the maximal working conditions are 600 °C and 40 MPa. For each experiment, the reactor was operated according to the following procedure: after introducing a solution of reactants, the reactor was closed and CO_2 was injected at room temperature up to 5 to 6 MPa, depending on the required final pressure and temperature. Then stirring and heating (external electric heater) were started. The increase of temperature induces an increase of pressure following an isodensity curve. The final temperature and pressure were maintained from several minutes to a few hours (residence time) in order to allow the formation of ceramic powder or polymer-coated particles. Finally, temperature was decreased and CO_2 was vented. The reactor was then opened and the reaction products were collected.

2.3. Ceramic powder synthesis

The synthesis of the YSZ powder can be described as a SC-CO_2 aided sol–gel process. Yttrium and zirconium ac-

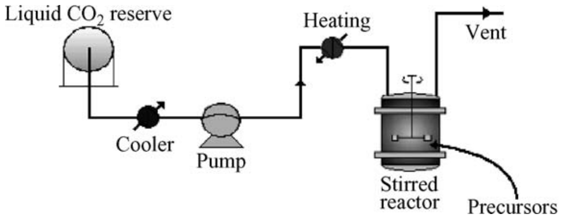

Fig. 1. Schematic representation of the reactor used for the synthesis and encapsulation of ceramic oxide powders in SC-CO_2.

Table 1
Experimental conditions used for the synthesis of the YSZ ceramic oxide in SC-CO_2

Sample ref.	Synthesis method	Sol (aging time, h)	T (°C)	P (MPa)	Acid content (wt.%)	Y_2O_3 content (mol %)
A	a	–	250	30	10	<8
B	b	20	250	30	10	<8
C	b	40	250	30	10	<8
D	b	112	250	30	10	<8
E	b	40	250	20	10	<8
F	b	40	250	10	10	<8
G	c	–	250	30	10	>8
H	c	–	200	30	10	>8
I	c	–	200	30	25	>8
J	d	64	200	30	25	>8

etates were mixed with pentane and nitric acid was added drop wise until a transparent sol was obtained. The solution of acetate precursors was prepared either directly in the reactor without sol aging (methods a and c, Table 1), or in a beaker (methods b and d, Table 1) when sol aging was carried out prior to its introduction into the reactor. The yttrium proportion was calculated in order to obtain partially (methods a and b, Table 1, $Y_2O_3 < 8\%$ with respect to ZrO_2) or fully stabilized zirconia (methods c and d, Table 1 – $Y_2O_3 > 8\%$ with respect to ZrO_2). Each solution composition was tested with and without sol aging. Then, CO_2 was injected in the reactor and both temperature and pressure were increased up to 250 °C and 30 MPa respectively. The temperature was selected in order to obtain a crystallized YSZ powder. After completion of the reaction, CO_2 was vented and temperature slowly decreased down to 100–150 °C in order to avoid condensation of pentane in the reactor. The reactor was opened in order to evacuate the residual pentane vapor and the ceramic oxide powder was recovered in ambient conditions.

2.4. Powder encapsulation methods

Two encapsulation methods were tested on several powder samples synthesized according to the previously described method. For each method, the powder was synthesized first, then the reactor was opened and the different reagents for encapsulation were introduced in the reactor.

Before encapsulation experiments, the solubility in SC-CO_2 of the amphiphilic compounds used as surfactants, was studied in a sapphire cell having a volume of 38 ml and able to work at 300 °C and 50 MPa. The cell was put in an oven in order to control the temperature. The concentration of surfactants was chosen higher than for the encapsulation test and the dissolution was studied at 30 MPa for various temperatures (60; 90; 110 and 150 °C). 10 wt.% of PDMS-g-PA was introduced into the sapphire cell and the CO_2 pressure was increased up to 30 MPa. Dissolution of PDMS-g-PA started when the temperature reached 90 °C. At 150 °C, about 75% of the product was dissolved in SC-CO_2. In comparison, for the encapsulation experiments, the concentration of polymer introduced in the reactor was $\leq$0.05 wt.% in CO_2 at 30 MPa and 150 °C. In the same way, FOMBLIN was introduced with a concentration of 30 wt.% in CO_2 and was totally dissolved at 90 °C and 30 MPa.

The first encapsulation method, based on phase separation (Fig. 2), was performed according to the following procedure. The synthesized YSZ powder and the SC-CO_2 soluble polymer PDMS-g-PA (4–8 wt.% with respect to the oxide quantity) were introduced and mixed in the reactor before filling with CO_2. Complete dissolution of PDMS-g-PA was obtained by increasing the temperature up to 150 °C, and keeping the pressure in the reactor at 30 MPa during 30 min under stirring (test #3, Table 3). Then, pressure and temperature were decreased leading to polymer precipitation and coating of the ceramic particles. Pressure release was carried out at 45 °C and 10 MPa in order

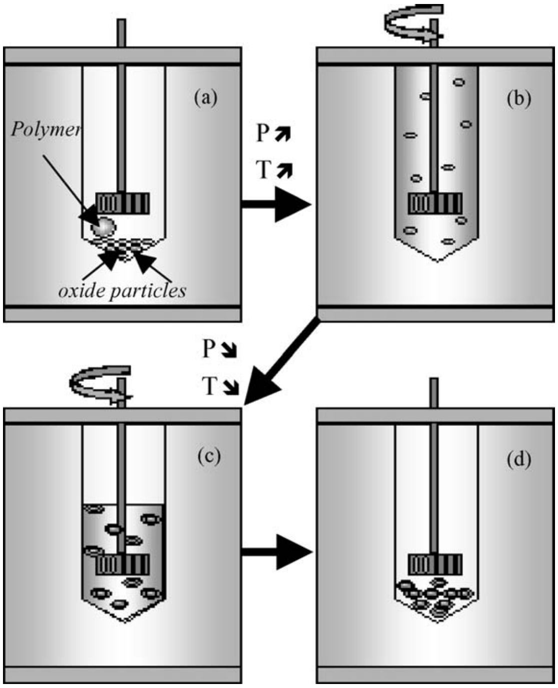

Fig. 2. Schematic representation of the encapsulation method by phase separation: (a) introduction of YSZ particles and PDMS-g-PA in the reactor; (b) dissolution of PDMS-g-PA in SC-CO_2 by increasing P & T; dispersion of insoluble YSZ particles in the mixture; (c) PDMS-g-PA precipitation and encapsulation of particles by decreasing T & P; (d) recovering of encapsulated particles (adapted from [15]).

to recover the encapsulated powder at atmospheric pressure.

The second investigated encapsulation method is based on an in situ polymerization process at the surface of ceramic particles. The YSZ powder, the MMA monomer, the surfactant (PDMS-g-PA or FOMBLIN) and the initiator were introduced in the reactor containing pentane. The reactor was closed and the mixture stirred. Contrary to Caris' case,[5] it was not necessary to modify the oxide surface. Indeed, CO_2 is non-polar whereas the oxide surface is polar. Therefore, the surfactant molecules tend to assemble spontaneously at the surface of the particles with the polar or CO_2-phobe part anchored on the particles, and the non-polar or CO_2-phile part dissolved in SC-CO_2 under specific conditions.[25–28] In all cases, polymerization was carried out in SC-CO_2 during 4 h at 30 MPa and 150 °C. The concentrations of used products were typically the followings: monomer 4 wt.%, initiator and surfactant respectively 4 wt.%, 0.04–0.12 wt.% and 0.2 wt.% with respect to the oxide.

2.5. Characterization methods

The morphology and the particle sizes of the produced powders (encapsulated or not) were studied using scanning electron microscopy (Hitachi S4500).

Crystalline phases were determined by X-ray diffraction (Brucker D800) on powders and crystallite sizes were determined by the Scherrer formula from diffraction lines $(\underline{1}\,0\,1)$ for the tetragonal structure, (1 1 1) for the cubic one and (1 1 1) for the monoclinic one. The fractions of monoclinic phase (f_M) in YSZ powders were determined from intensities (I) of monoclinic (M) and tetragonal (T) lines according to the following relationship:

$$f_M = \frac{1.311 \times X_M}{1 + 0.311 \times X_M} \quad \text{with} \quad X_M = \frac{I_M(\bar{1}11) + I_M(111)}{I_M(\bar{1}11) + I_M(111) + I_T(101)}$$

The specific surface area of powder samples was determined using the BET equation and the adsorption curve of the N_2 adsorption–desorption isotherms (Micromeritics-Asap 2010).

Thickness of the polymer shell was assessed using the specific surface area S_{BET} (m^2/g) of YSZ powders and results of thermogravimetric analyses performed on coated and uncoated powders in order to determine the weight of polymer M_p (g) per gram of powder: $M_p = m_C - m_{UNC}$, where m_C (g) represents the weight loss for 1 g of coated powder and m_{UNC} the weight loss for 1 g of uncoated powder. We can then calculate S (m^2), the surface accessible by the polymer for 1 g of coated powder:

$$S = S_{BET}(1 - M_p)$$

The quantity of polymer deposited on 1 m^2 of YSZ, M_p/S, and its density ρ (g/m^3) allow the calculation of the thickness of polymer shell.

$$e = \frac{M_p}{S} \times \frac{1}{\rho} = \frac{m_C - m_{UNC}}{\rho \times S_{BET} \times (1 - (m_C - m_{UNC}))}$$

The presence of the polymer on the oxide surface was also checked by a simple visual floating test carried out by preparing suspensions of the powder samples in water. Typically, 0.1 g of powder was introduced in 50 ml of water contained in a beaker, under magnetic stirring. Both PMMA and PDMS-g-PA are hydrophobic, therefore, initial powders and their encapsulated counterparts should behave differently. Indeed, whereas the initial powders first disperse and then settle on the bottom of the beaker when stirring is stopped, the encapsulated powder remains at the water/air interface because of the polymer shell.

3. Results and discussion

3.1. Synthesis of the YSZ ceramic powder

The experimental conditions for YSZ powder synthesis are summarized in Table 1. The tetragonal phase was obtained from methods a and b, and the cubic phase from methods c and d. Typical X-ray diffraction patterns of samples prepared by the methods a, b and d are shown in Fig. 3. In the case of method a, a significant percentage of monoclinic zirconia is present with the partially stabilized tetragonal phase whereas only traces of monoclinic zirconia were detected from method b. Although the aging time of the sol and the quantity of yttrium seem to have a major influence on the crystallization of the YSZ phases, the other synthesis parameters listed in Table 1 have an influence too. The characteristics of the synthesized powders are summarized in Table 2 and the relation to the synthesis parameters is discussed below.

The quantity of acid introduced in the sol has first an influence on the stabilization of single-phase compounds. For instance, sample H was prepared with only 10% acid concentration and the reaction of the precursors was incomplete. Indeed, SEM observations (Fig. 4) revealed the presence of residual unreacted product attributed to acetate precursors, present as amorphous spheres. These spheres transformed to monoclinic zirconia after a thermal treatment at 1150 °C in air. Conversely, sample I prepared with a higher quantity of acid (25%) did not show any presence of unreacted precursors. In this case, although the crystallites cannot be detected by XRD before any thermal post-treatment, the cubic phase was observed after calcination at 1150 °C. Moreover, a comparison of samples H and I with sample G, revealed that 200 °C was sufficient to perform the reaction of precursors and the crystallization of the YSZ cubic phase. In other respects, at low acid content, the crystallite size was decreased to values close to 10 nm (samples G and H, Tables 1 and 2).

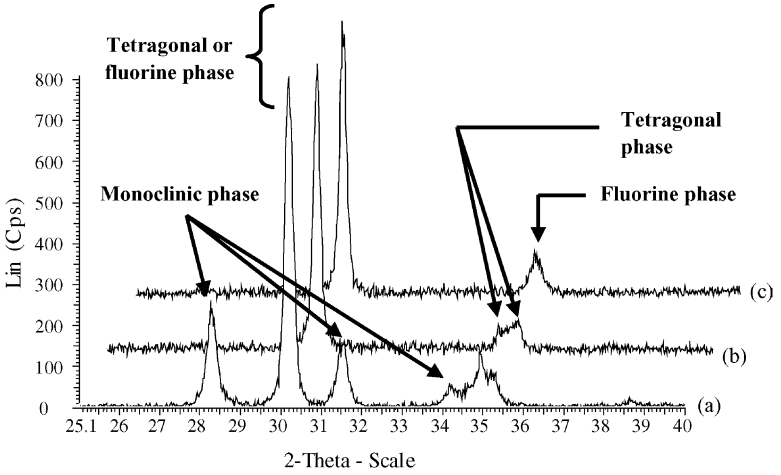

Fig. 3. XRD patterns of Y-doped zirconia powder obtained from different synthesis methods: (a) monoclinic and tetragonal structure (sample A with 1150 °C thermal treatment); (b) tetragonal structure (sample D with 1150 °C thermal treatment); (c) cubic structure (sample J with 1150 °C thermal treatment).

Fig. 4. FESEM micrograph of the YSZ powder synthesized with 10% nitric acid, revealing the presence of unreacted zirconium hydroxyacetate precursor.

Aging of the starting sol, prior to its introduction in the reactor, was favorable for stabilizing tetragonal or cubic phases, with a minimum quantity of monoclinic phase (samples B and J, Table 2). Increasing the aging time significantly affects the size and the size distribution of the ceramic oxide particles (Fig. 5). Indeed, a long aging time (112 h in sample D) leads to a monodispersed size distribution centered on 100 nm, whereas shorter aging times (f.i. 20 h for sample B) yielded a bimodal size distribution, typically at 30 and 300 nm. On the other hand, a similar effect was observed when the reaction pressure was decreased for samples C, E, F. Indeed, decreasing the pressure from 30 to 10 MPa led to a homogenization of particle size and a decrease of particle mean diameter from 100 nm to about 40 nm. The analyses of XRD patterns also showed a decrease of crystallite size from 23 nm at 30 MPa to 17 nm at 10 MPa.

3.2. *Post-synthesis encapsulation of the YSZ powder*

3.2.1. *Encapsulation by phase separation*

The phase separation method was implemented in the same reactor just after the powder synthesis step. The encapsulation was performed with PDMS-g-PA on a YSZ powder synthesized according to method b for which a 64-h sol aging was used. Only very slight evolution in texture and color was noticed from the initial to encapsulated powder (tests #1 and 2, Table 3). The aqueous floating test showed that the encapsulated powder behaves differently than the initial powder. The treated powder floated on water after stirring was stopped, and stronger stirring led to the formation of aggregates at the water/air interface. This shows that the separation phase method can be quite efficient for covering ce-

Table 2
Characteristics of YSZ powders prepared by SC-CO_2 assisted sol–gel process

Sample ref.	Synthesis method	Particle size (nm)	S_{BET} (m^2/g)	Crystallite size (nm)	Crystalline phase after thermal treatment at 1150 °C
A	a	–	–	–	Tetragonal + monoclinic 57%
B	b	30/300	–	23	Tetragonal
C	b	50/230	36	25	Tetragonal + monoclinic 5%
D	b	100	–	29	Tetragonal
E	b	40	39	19	Tetragonal + monoclinic 13%
F	b	40	33	17	Tetragonal
G	c	60	71	9	Cubic + monoclinic 20%
H	c	50	–	12	Cubic + monoclinic 11%
I	c	50	106	N	Cubic + monoclinic <5%
J	d	40	–	N	Cubic

N: non-measurable; XRD: limit of detection.

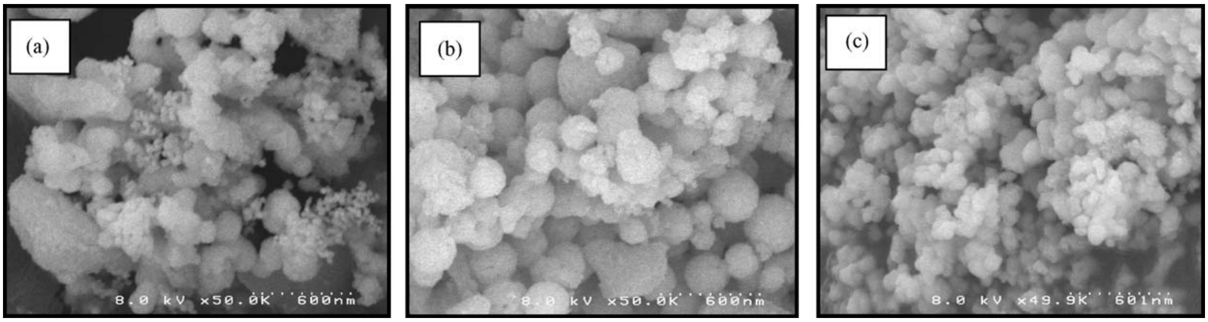

Fig. 5. FESEM micrographs showing the morphology of YSZ particles synthesized at different aging times: (a) sample B: 20 h; (b) sample C: 40 h; (c) sample D: 112 h.

Table 3
Quantities of polymer, monomer and surfactant used for the encapsulation experiments

Encapsulation method	Test #	MMA (wt.% with respect to oxide)	PDMS-g-PA (wt.% with respect to oxide)	Initiator (wt.% with respect to oxide)
Method 1: phase separation				
	1	–	4	–
	2	–	8	–
Method 2: polymerization in situ				
	3	330	0.2	0.04
	4	4	0.2	0.12
	5	4	–	0.12
	6	10	–	0.12
	7	–	0.2	0.12
	8	–	0.2	–
	9	4	0.2	–
	10	4	0.2 (FOMBLIN)[a]	0.12

[a] For this test, PDMS-g-PA was replaced by FOMBLIN.

ramic particles with the hydrophobic polymer. However, a small portion of the powder was apparently not encapsulated and remained as fine aggregated particles at the bottom of the beaker.

3.2.2. *Encapsulation by polymerization*

In these experiments, MMA and PDMS-g-PA were used respectively as monomer and surfactant according to the experimental procedure described in Section 2.4. Different tests were performed with the aim to adjust experimental conditions to a uniform particle covering by the polymer. The aforementioned characterization methods were combined in order to show the presence of the polymer on the ceramic particles.

In test #3, Table 3, an excess of monomer (10 g) compared to the quantity of oxide (3 g) was used in order to easily visualize the effect of encapsulation by SEM. After a reaction time of 4 h, the non-reacted monomer was evacuated with the CO_2 during pressure release. The treated powder showed a marked different aspect after reaction. The white original powder became gray and FESEM observations (Fig. 6) showed a slight increase in particle sizes after

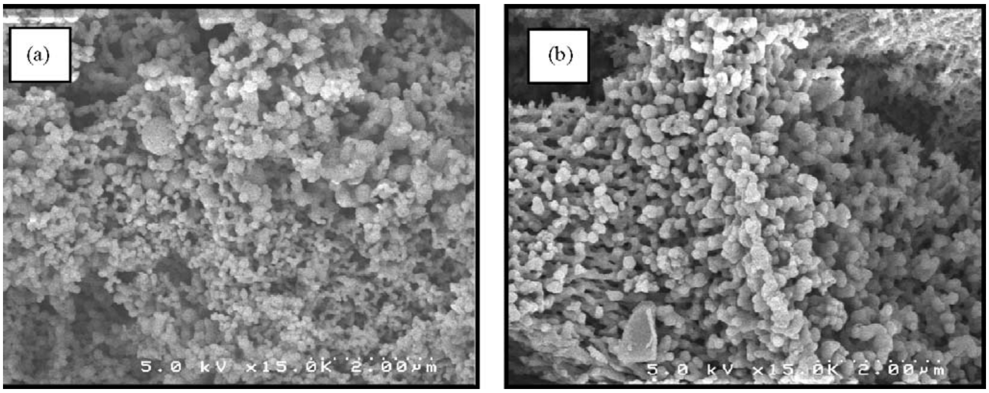

Fig. 6. FESEM micrographs of the ceramic oxide particles after synthesis and encapsulation in SC CO_2: (a) sample C: agglomerated particles after synthesis, no encapsulation; (b) sample 3: particles from sample C, after the in situ polymerization stage.

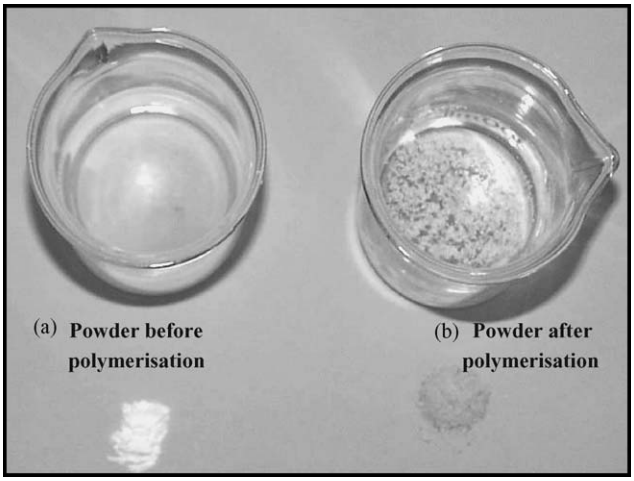

Fig. 7. Images showing the aqueous floating test evidencing the effect of encapsulation on the powder color and on the particle behavior in aqueous suspension: (a) zirconia powder before encapsulating polymerization; (b) zirconia powder after encapsulating polymerization (test #3, Table 2).

the polymerization stage. The visual floating test described in Section 2.5 was applied to this powder. As shown in Fig. 7a, the initial powder remained as a fine powder and settled at the bottom of the beaker, whereas the treated one totally remained at the air/water interface (Fig. 7b) forming agglomerates because of the hydrophobic character of the polymer. Apparently a more efficient powder encapsulation was obtained by this in situ polymerization method compared to the previous one based on phase separation. Accordingly, thermogravimetric analysis (Fig. 8) of the initial (sample C, Table 1) and the encapsulated YSZ powder led to a weight loss at 350 °C of respectively 4.4–18.96 wt.%. These results confirm the encapsulation process but do not give any information on the mean thickness of the polymer shell. The calculation of the shell thickness can be made according to the method mentioned in Section 2.5 starting from the specific surface area (33 m^2/g) of the YSZ powder and weight loss figures obtained from thermogravimetric analyses. It has been found that about 5 mg of PMMA were deposited on 1 m^2 of YSZ powder. Considering a PMMA density of 1.19 g/cm^3, and by supposing a homogeneous coverage of the YSZ particles, the calculated thickness for the polymer shell should be about 4.3 nm.

In order to evaluate the minimum quantity of monomer required for a homogeneous encapsulation of the ceramic powder particles with a very thin polymer film, a MMA polymerization test was carried out with only 4 wt.% of MMA related to the ceramic powder quantity (test #4, Table 3). In this case, the aqueous floating test showed that this quantity was sufficient to completely encapsulate the ceramic powder. Indeed no powder particles were present in suspension or at the bottom of the beaker after stirring and leaving at rest for a few minutes. Thermogravimetry analysis and specific surface area measurement led to a hypothetical shell thickness for the polymer of about 0.12 nm. Such polymer thickness being very improbable, it means that polymer coating probably occurs on small aggregates and not on individual nanoparticles. Complementary analysis is in progress to confirm this hypothesis.

3.2.3. *Role of the surfactant on monomer polymerization*

The role of the surfactant (PDMS-g-PA) for the encapsulation of ceramic particles by in situ MMA polymerization was investigated by comparing polymerization with and without surfactant, Table 2. The surfactant is supposed to favor polymer anchoring on the particle surface according to the polymerization pathway shown in Fig. 9. The aqueous floating test was used to check the efficiency of the encapsulation. Test #5, in which the polymerization was achieved without surfactant, yielded a powder sample behaving identically to the initial powder and settling on the bottom of the beaker. This confirms the absence of a continuous polymer shell on the ceramic particles. Even a higher quantity of monomer (test #6) did not lead to a homogeneous encapsulation of the particles. These results clearly demonstrate that the role of the surfactant is essential for a homogeneous encapsulation of the ceramic powder during MMA polymerization in SC-CO_2.

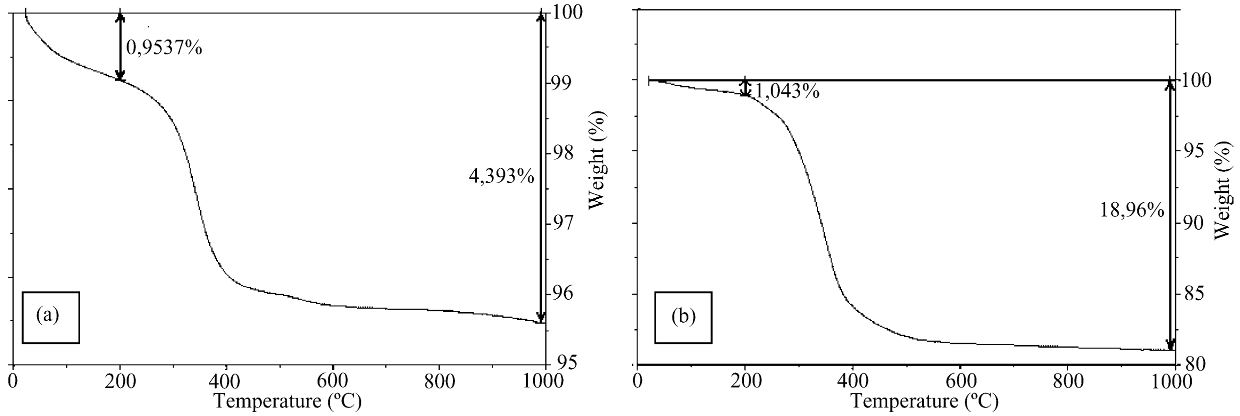

Fig. 8. Thermogravimetric analysis in air (5 °C/min) of YSZ powders: (a) before and (b) after encapsulation by MMA polymerization in SC-CO_2.

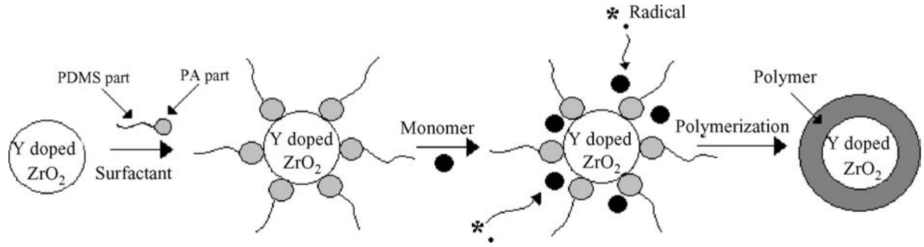

Fig. 9. Schematic description of the proposed mechanism for the encapsulation of YSZ powder by in situ polymerization in SC-CO$_2$ (adapted from[5]).

Additional tests were performed in order to have a better understanding of the specific roles of surfactant, monomer and initiator. Tests #7 and #8 were operated only with PDMS-g-PA without any MMA. Despite an expected arrangement of the amphiphilic macromolecules at the surface of the ceramic particles, no change in the powder behavior was noted during the aqueous floating test. Obviously the amphiphilic polymer alone does not allow an efficient encapsulation process. These results are in agreement with those obtained in tests #1 and #2. Test #9 also demonstrated that in the absence of initiator, MMA did not polymerize and the powder was not encapsulated.

The PDMS-g-PA was selected as the amphiphilic polymer surfactant because the siloxane network is soluble in SC-CO$_2$[29,30] and favors particle dispersion. Moreover the polyacrylate part ensures the anchoring of the surfactant on the oxide surface and acts as the starting point for the polymerization. Therefore, this surfactant helps the polymer anchoring on the ceramic oxide particles. However, due to its chemical composition, it will release silicon atoms in the ceramic after sintering. Therefore, for those applications (e.g. ionic conductive ceramics) for which Si is an undesirable impurity, the PDMS-g-PA surfactant will have to be replaced by a completely organic surfactant. This was attempted in test #10 in which PDMS-g-PA was replaced by FOMBLIN, a perfluoropolyether surfactant soluble in SC-CO$_2$. The powder derived from this test did not satisfy the aqueous floating test showing that a homogeneously encapsulated powder was not achieved. In this case, FOMBLIN appeared as a non-adapted surfactant.

From these results, it appears that a homogeneous particle encapsulation effectively results from MMA polymerization and not only from surfactant or monomer adsorption on the particles. The choice of the adequate surfactant is important as far as it has to adsorb on the ceramic particle surface allowing the polymerization to start. In relation with the work of Caris et al.[5] we can summarize in Fig. 9 the followed pathway for the polymer encapsulation process of ceramic particles by polymerization in SC-CO$_2$. In a first step, the CO$_2$-phobic part of the surfactant self organizes around the particles with anchoring of the CO$_2$-philic part on the particle surface. Steric interactions between surfactant shells help the dispersion of the particles in SC-CO$_2$. In a second step, the monomer adsorbs on the CO$_2$-phobic part of the surfactant, and polymerization is promoted by the presence of free radical initiator.

4. Conclusion

Ceramic processing in SC-CO$_2$ is a very promising technique for creating nanocrystalline and homogeneous mixed oxide systems from metal organic compounds. The porous texture, morphology, crystalline structure and size distribution of the derived ceramic powders can be controlled by adjusting the synthesis parameters (sol composition, type and quantity of additives, aging time, temperature, pressure). In this work the method was applied for the synthesis of YSZ powders with particle diameters from 30 to 300 nm and crystallite sizes from 10 to 25 nm.

We investigated the encapsulation of the YSZ particles by phase separation and MMA polymerization in SC-CO$_2$. A number of attractive results arose from this preliminary study. The necessary role of the surfactant (PDMS-g-PA) for MMA polymerization was demonstrated. Because it is soluble in SC-CO$_2$ in the selected experimental conditions, the surfactant allows the dispersion of YSZ particles in the SC-CO$_2$ due to the PDMS part. The PA part, adsorbed on the YSZ particle surface, facilitates polymerization by fixing monomers in the core shell formed by the surfactant. Further work remains to be performed in order to better control the thickness of the polymer film on the YSZ particles, to increase the fraction of encapsulated particles, and to limit the fraction of free polymer out of the particles. In particular, the concentration of the different reagents (surfactant, initiator, monomer) has to be further optimized. Various types of surfactants (Si based or totally organic) have also to be considered according to envisioned applications.

Finally this encapsulation method in SC-CO$_2$ media can be extended to other ceramic oxides and with other encapsulating agents (organic or organometallic). The foreseen advantage of this technique is to avoid the contact of the nanophase oxide powder with air moisture, which is responsible for particle aggregation and for difficult powder handling. In addition, ceramic particle encapsulation with a polymer should facilitate further powder processing operation such as crushing, pelletizing, sintering and may also stabilize powder suspensions depending on the used encapsulating agent.

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References

1. Sarrade, S., Schrive, L., Guizard, C., and Julbe, A., Manufacture of single or mixed metal oxides or silicon oxide, *PCT Int*. 1998, WO9851613, France.
2. Guizard, C., Julbe, A., Sarrade, S., Robbe, O. and Papet, S., Chemical reaction of metal-organic precursors in supercritical CO_2. Application to ceramic oxides preparation. In *Proceedings of 8th Meeting on Supercritical Fluids*, 2002, pp. 291–296.
3. Robbe, O., Elaboration de poudres et de membranes céramiques conductrices par procédé sol–gel assisté par du CO_2 supercritique. PhD Thesis 2003. Université Montpellier II, Sciences et Techniques du Languedoc: Montpellier.
4. Richard, J., Benoït, J.-P., Microencapsulation. Ed. Techniques de l'ingénieur, France, 2000, J 2210.
5. Caris, C. H. M., van Elven, L. P. M., van Herk, A. M. and German, A. L., Polymerization of MMA at the surface of inorganic submicron particles. *Br. Polym. J.*, 1989, **21**, 133–140.
6. Jung, J. and Perrut, M., Particle design using supercritical fluids: literature and patent survey. *J. Supercrit. Fluids*, 2001, **20**, 179–219.
7. Kim, J-H., Paxton, T. E. and Tomasko, D. L., Microencapsulation of naproxen using rapid expansion of supercritical solutions. *Biotechnol. Prog.*, 1996, **12**, 650–661.
8. Wang, Y., Wei, D., Dave, R., Pfeffer, R., Sauceau, M., Letourneau, J. J. and Fages, J., Extraction and precipitation particle coating using supercritical CO_2. *Powder Technol.*, 2002, **127**, 32–44.
9. Matsuyama, K., Mishima, K., Hayashi, K.-I., Ishikawa, H., Matsuyama, H. and Harada, T., Formation of microcapsules of medicines by the rapid expansion of a supercritical solution with a nonsolvent. *J. Appl. Polym. Sci.*, 2003, **89**, 742–752.
10. Mishima, K., Matsuyama, K., Tanabe, D., Yamauchi, S., Young, T. J. and Johnston, K. P., Microencapsulation of proteins by rapid expansion of supercritical solution with a nonsolvent. *AIchE J.*, 2000, **46**(4), 857–865.
11. Tsutsumi, A., Nakamoto, S., Mineo, T. and Yoshida, K., A novel fluidized-bed coating of fine particles by rapid expansion of supercritical fluid solutions. *Powder Technol.*, 1995, **85**, 275–278.
12. Wang, T-J., Tsutsumi, A., Hasegawa, H. and Mineo, T., Mechanism of particle coating granulation with RESS process in fluidized bed. *Powder Technol.*, 2001, **118**, 229–235.
13. Bleich, J. and Müller, B. W., Production of drug loaded microparticles by the use of supercritical gases with the aerosol solvent extraction system (ASES) process. *J. Microencapsul.*, 1996, **13**(2), 131–139.
14. Elvassore, N., Bertucco, A. and Caliteci, P., Production of protein-loaded polymeric microcapsules by compressed CO_2 in a mixed solvent. *Ind. Eng. Chem. Res.*, 2001, **40**, 795–800.
15. Ribeiro dos santos, I., Richard, J., Pech, B., Thies, C. and Benoït, J.-P., Microencapsulation of protein particles within lipids using a novel supercritical fluid process. *Int. J. Pharm.*, 2002, **242**, 69–78.
16. Glebov, E. M., Yuan, L., Krishtopa, L. G., Usov, O. M. and Krasnoperov, L. N., Materials and interfaces—coating of metal powders with polymers in supercritical carbon dioxide. *Ind. Eng. Chem. Res.*, 2001, **40**, 4058–4068.
17. Cooper, A. I., Polymer synthesis and processing using supercritical carbon dioxide. *J. Mater. Chem.*, 2000, **10**, 207–234.
18. Wang, W., Griffiths, R. M. T., Naylor, A., Giles, M. R., Irvine, D. J. and Howdle, S. M., Preparation of cross-linked microparticles of poly(glycidyl methacrylate) by dispersion polymerization of glycidyl methacrylate using PDMS macromonomer as stabilizer in supercritical carbon dioxide. *Polymer*, 2002, **43**, 6653–6659.
19. Shiho, H. and DeSimone, J. M., Dispersion polymerization of acrylonitrile in supercritical carbon dioxide. *Macromolecules*, 2000, **33**, 1565–1569.
20. Giles, M. R., Hay, J. N., Howdle, S. M. and Winder, R. J., Macromonomer surfactants for the polymerisation of methyl methacrylate in supercritical CO_2. *Polymer*, 2000, **41**, 6715–6721.
21. Giles, M. R. and Howdle, S. M., New unsaturated surfactants for the dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide. *Eur. Polym. J.*, 2001, **37**, 1347–1351.
22. Wang, W., Griffiths, R. M. T., Giles, M. R., Williams, P. and Howdle, S. M., Monitoring dispersion polymerisations of methyl methacrylate in supercritical carbon dioxide. *Eur. Polym. J.*, 2003, **39**, 423–428.
23. Wang, Y., Dave, R. and Pfeffer, R., Polymer coating/encapsulation of nanoparticles using a supercritical anti-solvent process. *J. Supercrit. Fluids*, 2004, **28**, 85–99.
24. Liu, D., Zhang, J., Chen, J., Li, Z., Shen, D. and Yang, G., Recovery of TiO_2 nanoparticles synthesized in reverse micelles by antisolvent CO_2. *Colloids Surf. A: Physicochem. Eng. Aspects*, 2003, **227**, 45–48.
25. Calvo, L., Holmes, J. D., Yates, M. Z. and Johnston, K. P., Steric stabilization of inorganic suspensions in carbon dioxide. *J. Supercrit. Fluids*, 2000, **16**, 247–260.
26. DeSimone, J. M. and Keiper, J. S., Surfactants and self-assembly in carbon dioxide. *Curr. Opin. Colloid Interf. Sci.*, 2001, **5**, 333–341.
27. Johnston, K. P., Block copolymers as stabilizers in supercritical fluids. *Curr. Opin. Colloid Interf. Sci.*, 2000, **5**, 351–356.
28. Panza and Beckman, Surfactants in supercritical fluids. In *Supercritical Fluid Technology in Materials Science and Engineering: Syntheses, Properties and Applications*, ed. Ya-Ping Sun. Marcel Dekker, Inc, New York, Basel, 2002, pp. 274–284.
29. Fink, R. and Beckman, E. J., Phase behavior of siloxane-based amphiphiles in supercritical carbon dioxide. *J. Supercrit. Fluids*, 2000, **18**, 101–110.
30. Hill, R. M., Silicone surfactants—new developments. *Curr. Opin. Colloid Interf. Sci.*, 2002, **7**, 255–261.