

SYNTHESIS AND ENCAPSULATION WITH A POLYMER, OF NANOPHASE YSZ PARTICLES IN SUPERCRITICAL CO₂

A. Hertz¹, S. Sarrade², C. Guizard³, A. Julbe⁴, J-C. Ruiz¹ and B. Fournel¹

¹CEA VRH/ DEN/DTCD/SPDE/LFSM - BP 111 – 26702 Pierrelatte Cedex, France

²CEA VRH/DEN/DTCD/SPDE – BP 17171 – 30207 Bagnols sur Ceze, France

³Laboratoire de Synthèse et Fonctionnalisation des Céramiques, FRE 2770 CNRS SAINT-GOBAIN C.R.E.E.,
550 Avenue Alphonse Jauffret, 84306 Cavaillon, France

⁴IEM, UMR 5635 CNRS-UMII-ENSCM, UM2-CC047-Place Eugene Bataillon, 34095 Montpellier, Cedex 5,
France

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Abstract. Supercritical fluids exhibit a large range of unusual properties that can be exploited for preparing new materials, which are qualitatively different from those derived from classical methods. We have already shown in previous works the interest of supercritical carbon dioxide (SC-CO₂) for the synthesis of ceramic materials, in particular nanophased conductive ceramics. This work reports specifically the strategy for limiting the aggregation and improving both the handling and sinterability of SC-CO₂ derived Yttria Stabilised Zirconia (YSZ) powders. A two steps synthesis method has been developed, leading to an encapsulation of the YSZ grains with a polymer in SC-CO₂. The selected encapsulation method is based on the dispersion-polymerisation of MMA in SC-CO₂. Surfactants were used as coupling agents between the ceramic oxide surface and the polymer. The choice of the surfactant revealed to be a decisive parameter.

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. Processing of ceramic precursors by a SC CO₂ assisted sol-gel method was already investigated in our group [1,2] as a suitable synthesis pathway yielding SiO₂ fibers [1,2], TiO₂ powders [3], as well

as doped ceria, lanthanum gallates and zirconia [4]. 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) [2]. In a previous work, the oxygen conductivity of sintered pellets derived from ceria powders prepared in SC CO₂ was measured by impedance spectroscopy and was evidenced to be higher than doped ceria prepared by other methods like classical sol-gel process or hydrothermal synthesis [5]. For doped zirconia, the high residual pellets porosity was found to generate an important blocking effect [4].

In the present work, a two-steps synthesis and encapsulation process in SC-CO₂ was applied for

Corresponding author: A. Hertz, e-mail: audrey.hertz@cea.fr

the preparation of yttrium stabilized zirconia (YSZ) nanophase powders with improved properties. In a first step, the YSZ powder was prepared by sol-gel synthesis in SC-CO₂ medium. In a second step, the recovered ceramic particles were coated in SC-CO₂, by polymerization of a MMA monomer in the presence of amphiphilic compounds. Such an encapsulation with PMMA should prevent particle agglomeration, protect the powder from air moisture and facilitate its compaction and densification.

2. MATERIALS AND METHODS

Chemicals. The precursors used for the YSZ powder synthesis were zirconium hydroxyacetate and yttrium acetate. Either pentane, 2-propanol or ethanol was used as a solvent and nitric acid (65% HNO₃) as a dissolution additive. Methyl MethAcrylate (MMA) was the selected monomer, Poly(DiMethyl-Siloxane)-*greffed*-PolyAcrylate (PDMS-g-PA) was the tested surfactant, and 2-2'Azobis(2-methylpropionamide) dihydrochloride, was the polymerization initiator.

Apparatus. A schematic representation of the experimental set-up is shown in Fig. 1. It consists in a stainless steel autoclave, mechanically stirred and working in a batch mode. The internal volume of the reactor is 1 liter, and the maximal operating conditions are 600 °C and 40 MPa. A second reactor was also used, its internal volume is 0.5 liter, and its maximal operating conditions are 350 °C and 30 MPa.

Ceramic powder synthesis. The synthesis of the YSZ powder consists in a SC-CO₂ aided sol-gel process. Yttrium and zirconium acetates were mixed with a solvent (pentane or 2-propanol) and nitric acid. The solution of acetate precursors was prepared

either directly in the reactor (no aging time) or in a beaker (with a given aging time). The reaction was performed in SC-CO₂ at 300 bar and from 200 to 350 °C during 1 hour. Then the reactor was depressurized and the oxide powder was collected.

Powder encapsulation method. The 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 and the initiator were introduced in the reactor with a solvent (pentane or ethanol). In all cases, the polymerization was carried out in SC-CO₂ during 4 hours at 30 MPa and 150 °C. The monomer, initiator and surfactant concentrations were respectively 4 wt.%, 0.04-0.12 wt.%, and 0.2 wt.% with respect to the oxide.

Characterization methods. The morphology and particle sizes of the produced powders (encapsulated or not) were studied using scanning and transmission electron microscopy (FESEM & HR-TEM). The crystalline phases and crystallite sizes were determined by X-ray diffraction on powders. The specific surface area, S_{BET} , was determined by applying the BET equation to the adsorption branch of the N₂ adsorption-desorption isotherms. The thickness of the polymer shell was assessed by coupling the results of thermogravimetric analyses (TGA) on coated and uncoated powders, and the S_{BET} (m²/g) value of the YSZ powder. The presence of the polymer on the oxide surface was also checked by a simple visual floating test on powder suspensions dispersed in water.

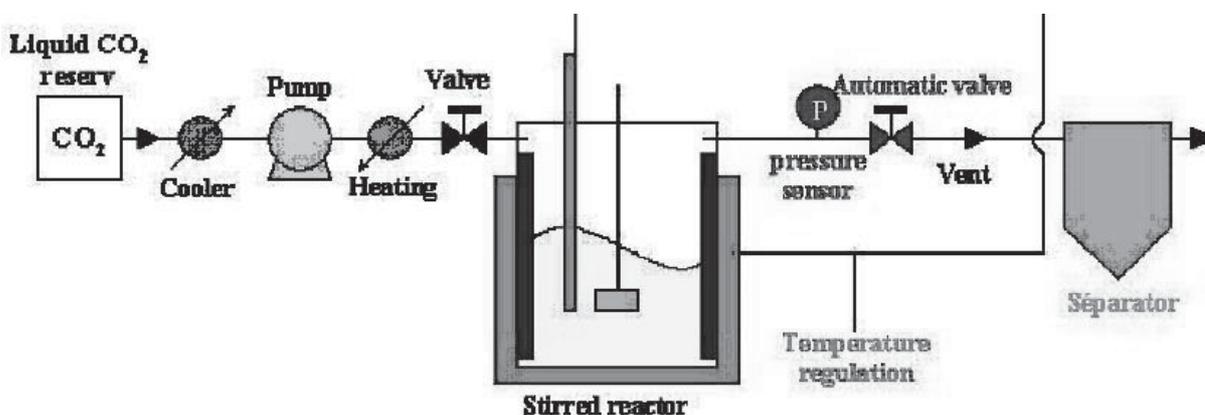


Fig. 1. Experimental set-up.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the YSZ ceramic powder

The influence of the synthesis parameters on the derived zirconia powder characteristics is typically evidenced in Table 1. The quantity of yttrium in the sol (Y_2O_3 mol.%) influences the type of crystalline phase which forms: mainly tetragonal for $[Y_2O_3] < 8$ mol.% and cubic for $[Y_2O_3] > 8$ mol.%. The quantity of added acid and the aging time used for sol preparation seem to have a major influence on the crystallization of the YSZ phases. For instance, Sample #C (Table 1) was prepared with only 10 wt.% of acid and the reaction of the precursors was incomplete: residual unreacted product, attributed to acetate precursors, transformed itself to monoclinic zirconia after a thermal treatment at 1150 °C in air. Sample #D (Table 1) prepared with a higher quantity of acid (25 wt.%) did not contain 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. Finally, aging of the starting sol, prior to its introduction in the reactor, was in favor of tetragonal or cubic phases stabilization (Samples #B & E, Table 1), containing a minimum quantity of monoclinic phase.

3.2. Encapsulation by polymerization

Different tests were performed in order to adjust the experimental conditions for obtaining a uniform coverage of YSZ particles by *in situ* polymerization. In these experiments, MMA and PDMS-g-PA were used respectively as the monomer and the surfactant. A polar and a non-polar solvent (ethanol and pentane) for polymerization, as well as YSZ powders prepared with either pentane or 2-propanol were studied. The corresponding experimental conditions and results of the floating test are reported on Table 2.

According to the floating test, samples #1&2 (Table 2) behaved as encapsulated oxide powders. Indeed, the initial YSZ powder remained as a fine powder and settled at the bottom of the beaker, whereas the polymer encapsulated one totally remained at the air/water interface forming agglomerates because of the hydrophobic character of the polymer.

The shell thickness calculated by coupling TGA and S_{BET} measurements, and assuming a homogeneous coverage of the YSZ particle surface, was about 4.3 nm for sample #1. The calculated polymer shell thickness was reduced down to 0.12 nm for sample #2, which was prepared with a smaller quantity of monomer (4 wt.%). Such an improbable thickness suggests that the polymer coats ceramic

Table 1. Experimental parameters used for the synthesis of the zirconia ceramic powders in SC-CO₂ and derived crystalline phases after a thermal treatment at 1150 °C.

Ref.	Aging	T (°C)	P (MPa)	Acid (wt.%)	Y ₂ O ₃ (mol.%)	Crystalline phase After treatment at 1150 °C
YSZ powders obtained from sols prepared with pentane						
A	No	250	30	10	< 8%	Tetragonal + Monoclinic 57%
B	Yes	250	30	10	< 8%	Tetragonal
C	No	250	30	10	> 8%	Cubic + Monoclinic 20%
D	No	200	30	25	> 8%	Cubic + Monoclinic <5%
E	Yes	200	30	25	> 8%	Cubic
YSZ powders obtained from sols prepared with 2-propanol						
F	No	350	30	10	< 8%	Tetragonal + Monoclinic 40%
G	yes	350	30	10	< 8%	Tetragonal

Table 2. Experimental parameters used for the encapsulation of the YSZ particles in SC-CO₂ and typical results.

Ref	MMA*	PDMS-g-PA*	Initiator*	Solvent used for the YSZ for synthesis	Solvent used for the encapsulation	Floating test results
1	330	0.2	0.04	Pentane	Pentane	Encapsulation
2	4	0.2	0.12	Pentane	Pentane	Encapsulation
3	4	-	0.12	Pentane	Pentane	No encapsulation
4	4	0.2 (FOMBLIN)**	0.12	Pentane	Pentane	No encapsulation
5	4	0.2	0.12	Pentane	Ethanol	No encapsulation
6	4	0.2	0.12	2-propanol	Pentane	No encapsulation
7	4	0.2	0.12	2-propanol	Ethanol	No encapsulation

* wt.% with respect to YSZ

** For this test, PDMS-g-PA was replaced by FOMBLIN

aggregates rather than individual nanoparticles. This hypothesis was confirmed by HR-TEM observations of the encapsulated YSZ powders.

3.3. Role of the surfactant on monomer polymerization

The PDMS-g-PA was selected as the amphiphilic polymer surfactant because the siloxane chain, which is soluble in SC-CO₂ [6,7], is supposed to favor particle dispersion, whereas 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.

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 or with another surfactant such as FOMBLIN. The results reported on Table 2 show that sample #3, for which the polymerization was achieved without any surfactant and sample #4 prepared with the FOMBLIN surfactant, behave identically to the initial powder during the floating test. This behavior confirms the absence of a continuous polymer shell on the ceramic particles and demonstrates that the role of the surfactant is essential for an homogeneous encapsulation of the ceramic powder during MMA polymerization in SC-CO₂.

Logically, the encapsulation process, Fig. 2, should happen as it follows. In a first step, the CO₂-

phobic acrylate part of the surfactant self-organizes around the YSZ particles, resulting in the formation of a CO₂-philic siloxane shell on the particle surface. Steric interactions between surfactant shells help the dispersion of the particles in SC-CO₂. In a second step, the monomer adsorbs on the CO₂-phobic part of the surfactant, and polymerization is promoted by the presence of free radical initiator.

However the nature of the solvent used either for powder synthesis or for MMA polymerization seems to have a strong effect on the encapsulation process. As reported in Table 2, when the YSZ oxide was prepared with 2-propanol (samples #6&7) instead of pentane (sample #2), encapsulation was unsuccessful. Moreover when ethanol was used as the solvent for polymerization the encapsulation also failed, even with sample 5 synthesized with pentane. A possible explanation could be a modification of the powder surface energy due the adsorption of polar (2-propanol and ethanol) or non-polar (pentane) solvents, depending on synthesis and polymerization conditions. In some cases, this surface modification would result in the inhibition of surfactant shell formation and by the way of the encapsulation process. Accordingly the way in which the surfactant assists polymerization and encapsulation is not straightforward and further work should be necessary for a better understanding of this process.

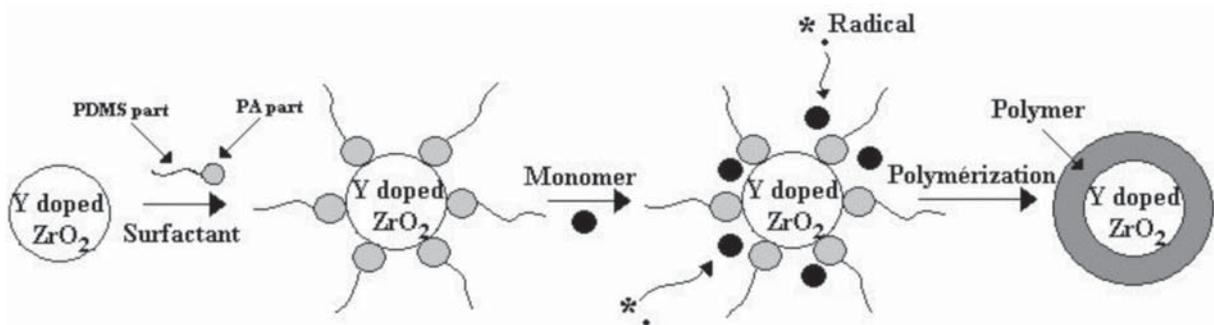


Fig. 2. Tentative schematization of the encapsulation mechanism.

4. CONCLUSION

Ceramic processing in SC-CO₂ is a very promising technique for producing nanocrystalline and homogeneous mixed oxide systems from metal organic compounds, as it has been shown with the synthesis of YSZ powders using a SC-CO₂ aided sol-gel method. The characteristics of the crystalline phases obtained for these ceramic powders can be controlled by adjusting the synthesis parameters. The encapsulation of the YSZ particles with a polymer in order to maintain the nanophase characteristics of the powder, has been successfully carried out by using a MMA polymerization process in SC-CO₂ with the presence of a surfactant. The results obtained from this preliminary study point out the role of the surfactant (PDMS-g-PA) and the importance of solvent choice for both the synthesis and encapsulation processes.

Further work is in progress 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. Other types of surfactants are also considered according to the envisioned applications of these encapsulated ceramic powders. Experiments are currently carried out with silicon-free hydrocarbonated surfactants able to fully decompose during the powder sintering step, without leaving any residual silica in the formed ceramic.

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