DEVELOPING AND CHARACTERISING NEW OXIDE NANOMATERIALS IN SUPERCRITICAL CO_2 PHASE: FROM LAB SCALE TO PRE-INDUSTRIAL APPLICATIONS

S. Sarrade[1,4*], B. Fournel[1,4], JC Ruiz[1,4], A. Hertz[1], C. Guizard[2,4], A. Julbe[3,4]

1: French Atomic Energy Commission (CEA) - Marcoule Research Centre DTCD/SPDE
BP 17171 – F-30207 Bagnols sur Cèze cedex : Fax : +334 66 7914 93
2 : SAINT GOBAIN CREE, 550 Avenue Alphonse Jauffret – BP 224
F-84306 Cavaillon cedex
3 : Institut Européen des Membranes (UMR CNRS 5635) - UM II – CC047
2, place Eugène Bataillon – F-34095 Montpellier cedex 5
4 : Supercritical Fluid Innovation - http://www.supercriticalfluid.org/
stephane.sarrade@cea.fr

Abstract
Research into the development of ceramic oxides in supercritical CO_2 phase (SC CO_2) is carried out since 1995 at the CEA in Marcoule, in association with the Institut Européen des Membranes in Montpellier. Thanks to its thermal properties, SC CO_2 (above 74 bars and 31°C) can be used as a synthesis and/or heat treatment medium to obtain nano-phased ceramics with original, adjustable morphology and characteristics.

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, TiO_2 powders, as well as doped ceria, lanthanum gallates and more recently zirconia. 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). In a previous work, we have shown the interest of SC-CO_2/co-solvent reaction media for the preparation of very pure and nanosized gadolinium-doped ceria (CGO) powders. The oxygen conductivity of the sintered pellets derived from these CGO powders and measured by impedance spectroscopy was evidenced to be higher than for doped ceria prepared by other methods like conventional sol-gel process or hydrothermal synthesis.

Recently we showed that encapsulation of the YSZ particles with a polymer in order to solve the problems of handling and aggregation of nanophase powders has been successfully carried out by using a MMA polymerization process in SC-CO_2.

The major step that we achieved was to suggest possible mechanisms occurring during reactions in order to develop semi-continuous reactors from lab scale to pre-industrial scale. The project of the MATCOS platform will be presented, a 1.4 M€ investment project for new inorganic materials produced in supercritical media.

Introduction

Over the past decade supercritical (SC) fluids have received considerable attention as solvent 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. Consequently, 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 formation 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 metal organics) in SC-CO_2 media, was controlled by tuning the operating parameters such as precursor concentration, temperature, reaction time in SC conditions and pressure release. The ceramic powders synthesized by this method does not need any drying step, and their crystallization temperature is generally much lower compared to traditional processes (e.g. classical sol-gel process). This "green chemistry" synthesis method considerably decreases the required solvent quantity but also improves reaction kinetics and allows the control of the morphology and size of particles. However, when nanophase ceramic powders are prepared, they often tend to aggregate when the reactor is opened to atmosphere [4].

So, the Idea was to find a solution for maintaining the nanophase structure of the powders in the final sintered materials. This objective has been reconsidered here for YSZ, with the aim to obtain after sintering a fully dense ceramic with mean grain sizes under 100 nm. Moreover, the problems often encountered with nanosize powders, e.g. handling and aggregation, have been solved by the encapsulation of the YSZ nanoparticules with polymethylmethacrylate (PPMA), using SC-CO_2 as polymerization solvent. In addition the polymer layer formed at the surface of the particles could serve as a shaping additive for ceramic material processing. Then the final step is to design specific devices in order to approach the scale up these processes.

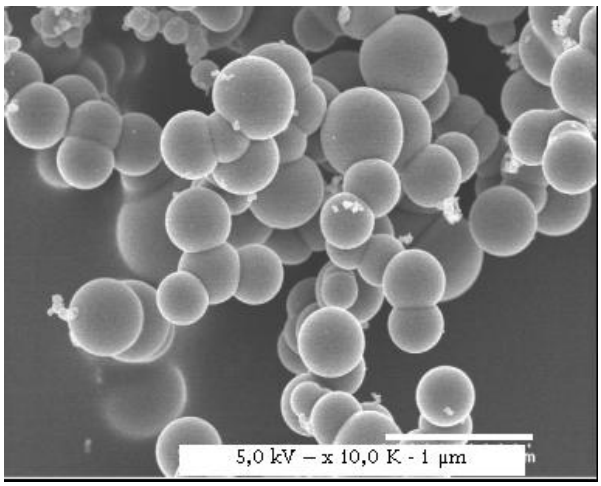

Figure 1: View of TiO_2 particles prepared in the SC CO_2 phase [2].

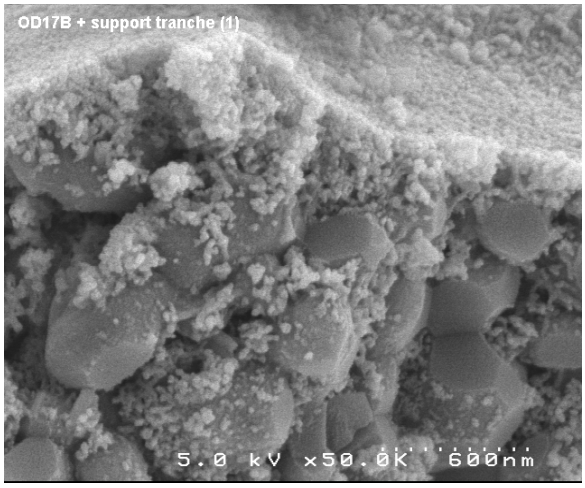

Figure 2: View of $LaGaO_3$ particles deposited and filtered into a porous substrate of the alumina type in the SC CO_2 phase [3].

Materials and methods

The precursors used for the oxide powder synthesis were alkoxide, hydroxyacetate or acetate Y provided by Aldrich. Pentane or Isopropanol (99% -PROLABO) were used as the solvent medium for precursors and nitric acid (65% HNO_3-FLUKA) as dissolution additive.

A schematic representation of the experimental set-up used in this study is shown in figure 3.

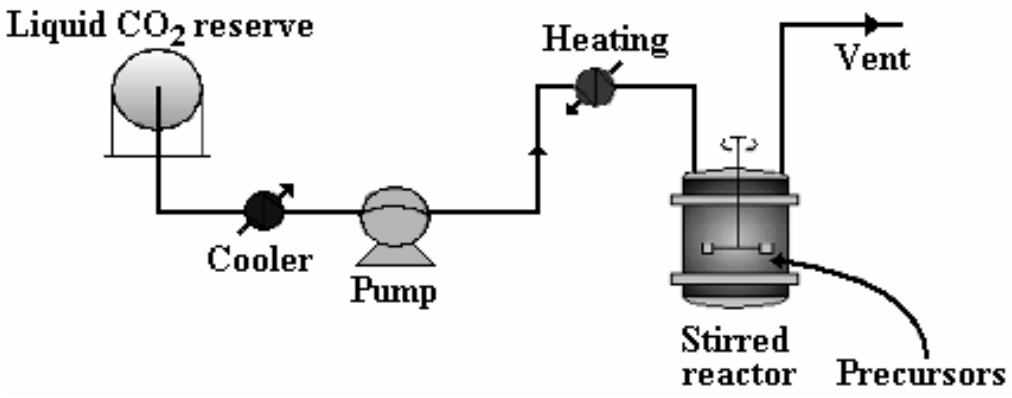

Figure 3: Schematic representation of the reactor used for the synthesis of ceramic oxide powders in SC-CO_2.

The stainless steel autoclave (supplied by Autoclave-France) is mechanically stirred and works in a batch mode. The internal volume of the reactor is 1 liter, and the maximal working conditions are 600°C and 400 bar. For each experiment, the reactor was operated according to the following protocol: after introducing the solution of reactants, the reactor was closed and CO_2 was injected at room temperature up to a value of 50 to 60 bar, 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. Final temperature and pressure were maintained from several minutes to a few hours (residence time) in order to allow the formation of ceramic powder. Finally, temperature was decreased and CO_2 was vented. The reactor was then opened and the reaction products were recovered.

Ceramic powder synthesis

The synthesis of the YSZ powder can be described as a SC-CO_2 aided sol-gel process. In a first step, a solution of acetate precursors was prepared directly in the reactor, or in a Beaker when the sol was aged before introduction in the reactor. Yttrium and zirconium acetates were mixed with pentane and nitric acid was added drop wise until a transparent sol was obtained. Then CO_2 was injected in the reactor and both temperature and pressure were increased up to 250°C and 300 bar respectively. The temperature was selected in order to obtain a crystallized YSZ powder. After the reaction was completed, CO_2 was vented and temperature was slowly decreased down to 100-150°C in order to avoid the condensation of pentane in the reactor. The reactor was opened in order to evacuate the residual pentane vapors. The ceramic oxide particles were recovered in ambient conditions. A large range of yttrium proportion (3.8-17%) towards zirconium was studied in order to obtain partially or fully stabilized zirconia.

Characterization methods

The morphology and homogeneity of the produced powders (encapsulated or not) were studied using scanning electron microscopy (Hitachi S4500). Crystalline phases were determined by X-ray diffraction studies on powders (Brucker D800) and crystallite sizes determined by the Scherrer formula from diffraction lines (101) for tetragonal structure, (111) for fluorine one and ($\bar{1}$11) for monoclinic one. The specific surface area of powders was determined by applying the BET equation to the adsorption branch of the N_2 adsorption-desorption isotherms (Micromeritics-Asap 2010).

RESULTS

Nanosize YSZ powder synthesis

The synthesis of the nanosize YSZ powder has been carried out by the SC-CO_2-assisted sol-gel route. In this process, different mechanisms are involved in crystalline powder formation, based on the hydrolysis and condensation reactions of the precursors as well as nucleation and particle growth due to the anti-solvent effect of SC-CO_2. Both the co-solvent selection and the control of the heating rate revealed to be decisive parameters for producing pure and fully crystallized YSZ phase from the two precursor mixtures in CO_2/pentane and CO_2/isopropanol. Making use of these results enabled the preparation of tetragonal stabilized, nanosize and monodisperse particles, 40-80 nm in size, and exhibiting specific surface area up to 200 m^2. Typical powder morphology is shown in figure 4a..

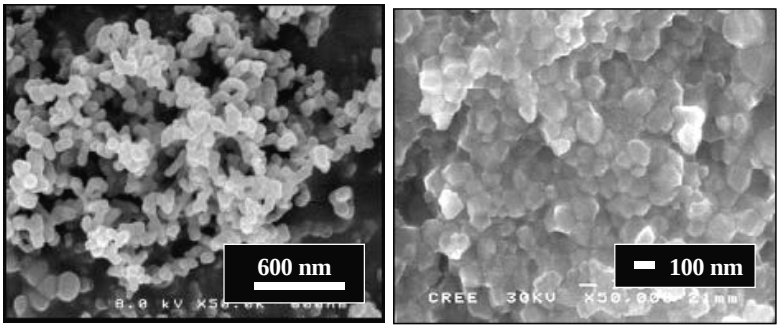

Figure 4: FESEM observation of – a) YSZ powder with controlled characteristics and –b) SPS sintered YSZ with a 97% densification rate.

Forming and sintering of YSZ electrolyte membrane for SOFC

Ion conductive ceramic membranes can be considered with regard to their impact in SOFC technologies for electricity supply but also for applications in many other domains such as gas sensors, gas separation, catalytic membrane reactors or high temperature electrolysis of steam. Either porous or dense ion conductive materials can be used depending on the expected application. Current industrial developments are centered on dense ion (oxygen) or mixed ion-electron conductive ceramics among which yttria-stabilized zirconia (YSZ) is still the standard electrolyte materials in SOFCs.

Due to the high specific surface area of the initial YSZ powders almost dense ceramic pellets (> 97 % d_{th}) were readily obtained by SPS at quite low temperature (1200°C) and pressure (100 MPa) compared to usual conditions for YSZ ceramic sintering. Interestingly, the mean grain size in these pellets is about 100 nm as shown in figure 4b. The sintering procedure is currently under investigation in order to further improve and adapt to special shapes the sintering parameters of these YSZ electrolyte membranes.

Powder particle encapsulation

Encapsulation was carried out by performing a SC-CO_2 assisted polymerisation process (figure 5) on the recovered YSZ powders. In a first step, the CO_2-phobic part of a surfactant self-organizes at the surface the particles, resulting in the formation of a CO_2-philic shell. Then steric interactions between surfactant shells help the dispersion of particles in SC-CO_2. Finally, the monomer adsorbs on the CO_2-phobic part of the surfactant, and its polymerization is promoted by the presence of a free radical initiator. The surface accessibility of the powder to MMA molecules dissolved in SC-CO_2 governs the quantity of adsorbed monomer and then the quantity of formed polymer in the porous structure of the powder. This quantity can be controlled by the ratio of the monomer concentration to the total powder surface introduced in the reactor.

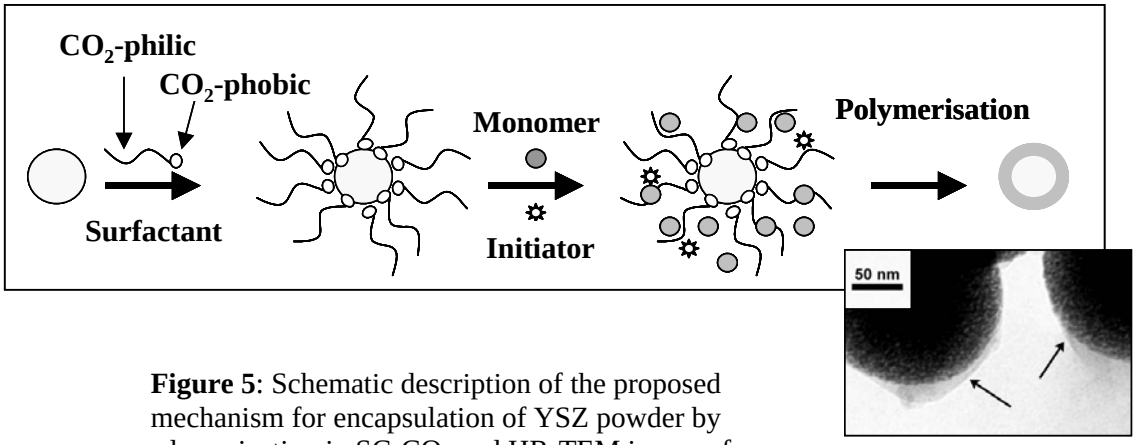

Figure 5: Schematic description of the proposed mechanism for encapsulation of YSZ powder by polymerization in SC-CO_2 and HR-TEM image of the encapsulated aggregate.

From Labscale to pre-industriel scale: The MATCOS platform

The major step that we achieved was to suggest possible mechanisms occurring during reactions in order to develop semi-continuous reactors from lab scale to pre-industrial scale.

We then designed 5 experimental devices.

The two first one will be created in 2008 and devoted to the synthesis of single and mixed ceramic oxides. Their capacities will allow us to obtain significant amounts (0.1 to 1 kg) of powders. Then it will be possible to investigate the properties of such compounds in pre-industrial conditions.

The two following devices will be designed and set up in 2009. They will be devoted to cleaning, functionalisation or impregnation of porous media. For instance the treatment and impregnation of SiC honeycombs or foams with catalysts will be studied with scale one pieces.

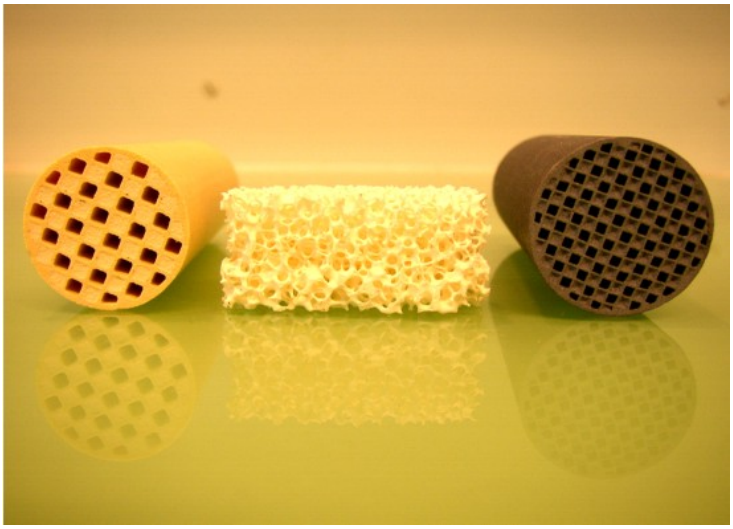

Figure 6: Porous substrates for catalyst impregnation.

Then, the last facility in 2010 will be a pre-industrial plant with a capacity of 1 to 20 kg of powder produced per batch

The MATCOS project represent a 1.4 M€ investment for new inorganic materials produced in supercritical media.

Conclusion

Ceramic processing in SC-CO_2 is now a relevant technique for creating nanocrystalline and homogeneous mixed oxide ceramic powders from metal organic compounds. Several reaction mechanisms can be assumed from the present results: gel formation and maturation time of the liquid phase are responsible for antisolvent or condensation mechanisms. Porous texture, morphology, crystalline structure and size distribution of these powders can be controlled by adjusting the synthesis parameters.

Furthermore, the encapsulation of the particles with a polymer in order to solve the problems of handling and aggregation of nanophase powders has been successfully carried out by using a MMA polymerization process in SC-CO_2.

First results on YSZ electrolyte membrane preparation lead to interesting densification rates (> 97% d_{th}) by SPS with ceramic grain sizes close to 100 nm. These materials are now suitable for electrochemical characterization and ionic conductivity evaluation. Further work is in progress to make use of these powders in other forming and sintering ceramic processes with the aim to produce YSZ electrolyte membranes with different shapes.

The major step that we achieved was to manage and monitor the possible mechanisms occurring during reactions in order to develop semi-continuous reactors from lab scale to pre-industrial scale. The project of the MATCOS platform is now under progress, with a 1.4 M€ investment project for new inorganic materials produced in supercritical media.

Acknowledgements

Authors would like to thank Didier COT, Abdeslam El MANSOURI, Nathalie MASQUELEZ from the Institut Européen des Membranes for powder characterization, and Guillaume BERNARD-GRANGER from Saint-Gobain for SPS experiments and TEM analysis.

References

[1] Sarrade S., Schrive L., Guizard C. and Julbe A., in *PCT Int,*. **1998**, WO9851613: France.

[2] Guizard C., Julbe A., Sarrade S., Robbe O. and Papet S., in *8th Meeting on Supercritical fluids*. **2002**, Bordeaux, France, n° ISBN 2-905267-34-8: p. 291-296.

[3] Guizard C., Julbe A., Robbe O.,and Sarrade S., Catalysis Today, **2005**, 104(2-4): p. 120-125.

[4] Hertz A., Sarrade S., Guizard C. and Julbe A., Journal of European Ceramic Society, **2006**, 26(7): p. 1195-1203.