

AN IMPROVED SOL-GEL ROUTE ASSISTED BY SUPERCRITICAL CO₂ FOR THE SYNTHESIS OF NANOPHASE CERAMIC OXIDES YSZ/PMMA CORE-SHELL NANOCOMPOSITE PREPARATION

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ABSTRACT

Material synthesis in supercritical carbon dioxide (SC-CO₂) is now of growing interest at international level. In our group, we experiment more specifically the synthesis of nanophase conductive ceramic powders by a SC-CO₂ assisted sol-gel process. High oxygen conductivity has been recently evidenced on the sintered materials, especially for gadolinium-doped ceria (CGO). On the other hand, the prepared yttria stabilised zirconia (YSZ) powders were less reactive to conventional sintering and suffered undesirable structural transformations. Therefore, our current work focuses on both a better understanding and an improvement of the synthesis method, namely through the development of a two-steps process. The first step corresponds to the synthesis of the ceramic oxide powder (YSZ powders) by the SC-CO₂-assisted sol-gel route. For this step, particular attention has been paid to the reproducibility of the powder characteristics, by studying and optimizing the key parameters and mechanisms of the synthesis process in order to control the mean particle size and size distribution. Both the selection of the co-solvent and the control of the heating rate revealed to be decisive parameters. The second step of the process deals with encapsulation of the ceramic powder through a subsequent SC-CO₂ polymerisation process. Polymethylmethacrylate (PMMA) was chosen as the suitable polymer because of its protective properties against air-moisture and its binding properties in ceramic processing. The polymer-shell thickness was controlled by the composition of precursors and a surfactant was necessary for ensuring a successful encapsulation. The derived YSZ/PMMA core-shell nanocomposite particles are easy to handle and we expect better compaction and densification rates for these powders. Indeed the ionic conductivity of conducting ceramics is directly related to the quality and homogeneity of their microstructure, in which connected porosity is prohibited and nanosized grains are recommended.

INTRODUCTION

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 the interest of supercritical carbon dioxide (SC-CO₂) for the synthesis of ceramic materials as SiO₂ fibers [1], TiO₂ powders [2], and various nanophase conductive ceramics [3-5]. The ceramic powders synthesized by this method do not need any

drying step, and their crystallization temperature is generally much lower compared to usual processes (e.g. conventional sol-gel process) [2].

Worldwide current research efforts are focused on lowering the operating temperature of solid oxide fuel cells (SOFC) down to 700°C (IT-SOFC). In previous works, we have shown the interest of SC-CO₂ derived gadolinium-doped ceria (CGO) and partially or totally stabilized zirconia (TZP or YSZ) powders for this application [3,4]. The oxygen conductivity of sintered pellets derived from CGO powders prepared in SC-CO₂ was measured by impedance spectroscopy and was evidenced to be higher than doped ceria prepared by other methods like conventional sol-gel process or hydrothermal synthesis [4]. For doped zirconia, the high residual pellets porosity was found to generate an important blocking effect. The tetragonal to monoclinic phase transition (t-m) occurring on the sintering treatment led to the degradation of conductivity properties. Works from the literature showed that structural parameters such as grain size, grain size distribution, porosity [6] and yttria distribution [7] are supposed to control the tetragonal transformation. So a better understanding of the synthesis mechanisms and of their influence on structural parameters is necessary to control the powder characteristics and their sintering behaviour.

In this work, we focused on the dissolution capacity of the used supercritical solvent and co-solvent and more precisely on the binary mixture CO₂/solvent behaviour. A transitory phase occurs when temperature and pressure are raised in order to crystallize the zirconia powder, thus leading to reproducibility problems. In this study a new two-steps process was developed enabling to control the powder characteristic. In the second step, the recovered crystallized 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, in order to improve the final material ionic conduction properties [5].

I. MATERIALS AND METHODS

Chemicals

Precursors used for the oxide powder synthesis were zirconium hydroxyacetate and yttrium acetate. Either pentane or 2-propanol were used as solvent medium for acetate precursors and nitric acid as dissolution additive. PDMS-g-PA and Pluronic PE8100 were used as surfactants in the encapsulation process. Methylmethacrylate (MMA) was the selected monomer and 2,2'-Azobis(2-methylpro-pioramidine) dihydrochloride was the initiator used for the polymerization.

Apparatus

A schematic representation of the experimental set-up is shown in figure 1. It consists in a stainless steel autoclave, mechanically stirred and working in a batch mode. The internal volume of the reactor is 0.5 liter, and the maximal operating conditions 350 °C and 30 MPa.

Processing principles

A detailed description of the methods used for powder synthesis and encapsulation is given in [5]. The synthesis of the YSZ powder can be briefly described as a SC-CO₂ aided sol-gel process. First the zirconium and yttrium acetates solutions were prepared in either pentane or 2-propanol. The effect of solution ageing time (maturation) before supercritical treatment was studied. Then, the reaction was carried out in SC-CO₂ during 1 hour at 30 MPa and 250 °C for

pentane solutions or 350°C for 2-propanol solutions. The proposed encapsulation method is based on the polymerization of MMA at the surface of ceramic particles. The MMA monomer, the surfactant, the initiator and the solvent used for polymerization were introduced in the reactor containing the YSZ powder. In all cases, polymerization was carried out in SC-CO₂ during 4 hours at 30 MPa and 100-150 °C.

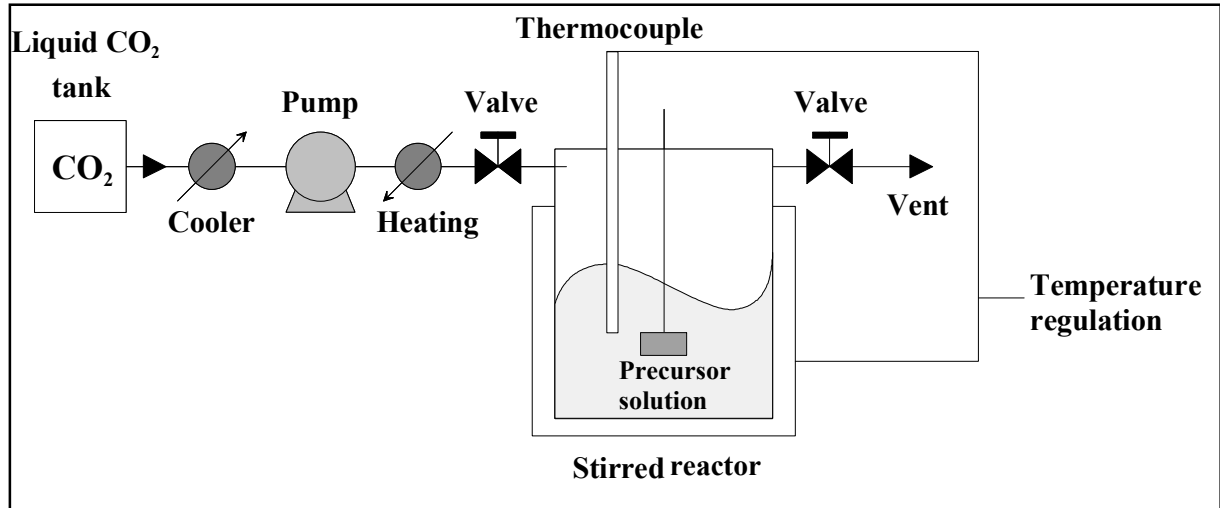


Figure 1: Schematic representation of the reactor used for the synthesis and encapsulation of ceramic oxide powders in SC-CO₂.

Characterization methods

Morphology and particle sizes of the produced powders (encapsulated or not) were studied using scanning electron microscopy (FESEM-Hitachi S4500). The specific surface area of the powders was determined using the BET equation (Micromeritics-Asap 2010). The polymer shell thickness was assessed using both the specific surface area S_{BET} (m²/g) of YSZ powders and the results of thermogravimetric analyses of both coated and uncoated powders (Universal V3.1E - T.A. Instruments). The presence of the polymer on the oxide surface was checked by a simple visual floating test carried out by preparing suspensions. High resolution transmission electron microscopy observations (HR-TEM -JEOL – JEM-200FX) allowed to complete the characterization of the encapsulated YSZ powders.

II. RESULTS AND DISCUSSIONS

Several mechanisms in competition for powder synthesis

Two successive mechanisms controlling the particle size and the tetragonal phase stabilization could be attributed to the role of ageing time (maturation) and supercritical parameters when synthesis is carried out with pentane solutions. The first one takes place during the maturation phase in which condensation of precursors and cluster growth give rise to gel formation. The second one occurs during the supercritical treatment, with first the dispersion of the gel phase in the pentane/CO₂ mixture and then particle growth due to the precipitating effect of both temperature and SC-CO₂ phase. As shown in figure 2, longer maturation steps lead to smaller rounded particles. Stabilization of the tetragonal phase could be explained in this case by an insertion of yttrium at the molecular level during gel formation.

Synthesis conditions were different with 2-propanol solutions. Actually, no gel formation was observed during the maturation step. It is likely that reaction of precursors, followed by

nucleation and particle growth, occur only into the reactor during the supercritical treatment. This is supported by the fact that both the powder morphology and the tetragonal phase stabilisation are not controlled by ageing time.

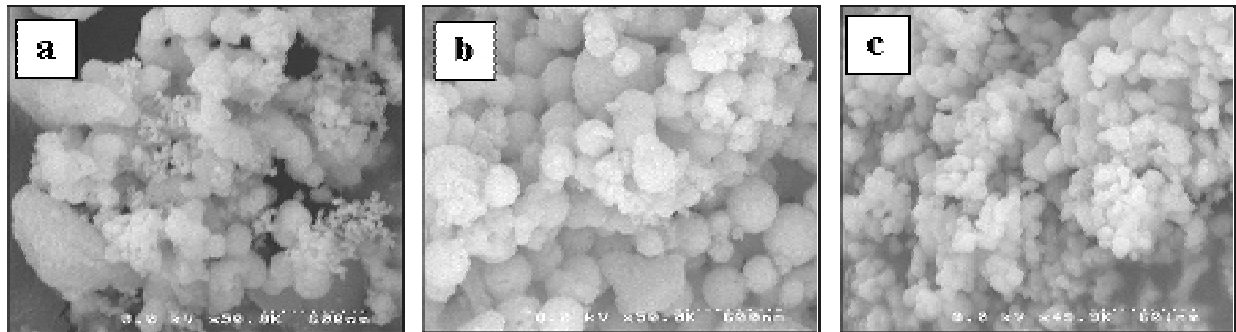


Figure 2: FESEM micrographs showing the morphology of YSZ powders ($S_{\text{BET}} \sim 70 \text{ m}^2/\text{g}$) prepared from pentane solutions with different ageing times: a) 17h – b) 41h – c) 120h.

Starting from the critical temperature and pressure data and from the classical liquid/gas equilibrium diagrams, it has been possible to construct the phase diagrams for the two mixtures at the used compositions, i.e. 0.92 mol fraction of CO_2 for the CO_2 /pentane mixture and 0.8 mol fraction of CO_2 for the CO_2 /2-propanol mixture. The location of the transitory phases areas versus temperature were compared in both diagrams. Two differences were noticed between the two mixtures. The first one concerns the latency period before entering the supercritical area and the second one is related to the transitory phases met when increasing temperature (mainly liquid for CO_2 /pentane and liquid/gas for CO_2 /2-propanol). These observations bring about to consider two different mechanisms for particle formation: principally due to a CO_2 antisolvent effect with pentane solutions and rather related to a continuous process involving precursor reaction, seed formation and particle growth, with 2-propanol solutions. Consequently, the latency period before entering the supercritical area appears as a very decisive parameter for the control of powder characteristics. Making use of these results enabled the preparation of nanosized (40-80 nm) and monodisperse powders which were relatively agglomerated (figure 3).

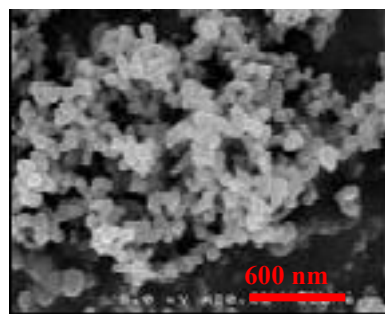


Figure 3: FESEM micrographs showing the optimized and controlled morphology of YSZ powders ($S_{\text{BET}} \sim 200 \text{ m}^2/\text{g}$).

Encapsulation by MMA polymerisation in supercritical CO_2

Encapsulation was carried out on the recovered YSZ powders using a SC- CO_2 polymerisation process. The use of a surfactant was evidenced as a key parameter in this process. Initially,

PDMS-g-PA was selected as an amphiphilic surfactant because the siloxane chain, soluble in SC-CO₂, is supposed to favor particle dispersion, whereas the polyacrylate part ensures surfactant anchoring on the oxide surface and acts as the starting point for polymerization. A second surfactant with a similar behavior was tested (Pluronic PE 8100). This silicon-free surfactant avoids the formation of silica during powder sintering, keeping in mind that residual silica could be detrimental to the ionic conductivity of the final material. The encapsulation process is summarized in figure 4. In a first step, the CO₂-phobic part of the surfactant self-organizes around the YSZ particles, resulting in the formation of a CO₂-philic 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 a free radical initiator.

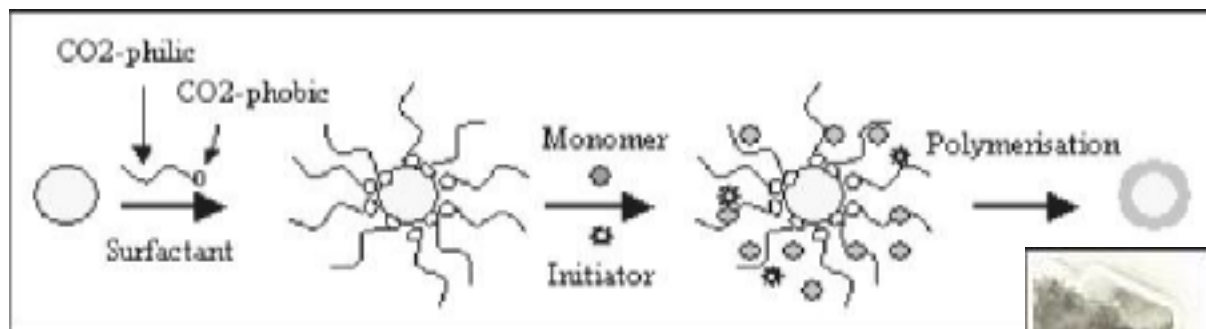


Figure 4: Schematic description of the proposed mechanism for encapsulation of YSZ powder by polymerization in SC-CO₂ and HR-TEM image of the encapsulated aggregate.

Different parameters were identified which can influence polymer shell quality (thickness, homogeneity). The polymerization rate was typically controlled by both the powder specific area and the surfactant quantity. Indeed, these two parameters control the number of favored polymerisation sites at the surface of particles. Then the polymer shell thickness can be controlled by the ratio of monomer (MMA) and powder amounts. As shown in figure 5, handling of encapsulated powders was facilitated by an increase of their apparent density. However, particle/polymer agglomeration was observed when too high MMA quantities were used.

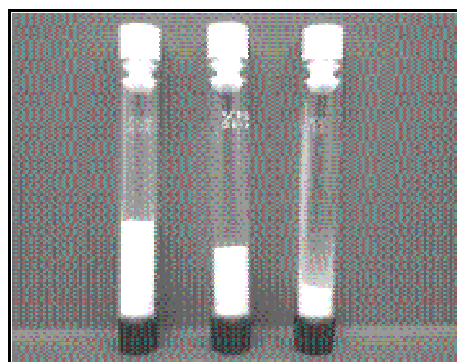


Figure 5: Apparent density changes for the same amount of YSZ powders. From left to right: without encapsulation, with 25 wt% of MMA and with 50 wt% of MMA.

CONCLUSION :

Ceramic processing in SC-CO₂ is a very promising technique for creating nanocrystalline and homogeneous mixed oxide ceramic powders from metal organic compounds. The porous texture, morphology, crystalline structure and size distribution of these powders can be controlled by adjusting the synthesis parameters. 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 whether pentane or isopropanol are used as co-solvent.

In a second step, the encapsulation of the YSZ particles with a polymer in order to maintain the powder nanophase characteristics of powders has been successfully carried out by using a MMA polymerization process in SC-CO₂. The key role of the surfactant was demonstrated. Powder specific area, surfactant and MMA quantity were proved to control the polymer shell thickness.

Foreseen advantages of this technique are to prevent particle aggregation and powder handling difficulties. In addition, ceramic particle encapsulation with a polymer should facilitate further powder processing operations such as crushing, pelletizing, and sintering; it may also stabilize powder suspensions depending on the used encapsulating agent. Studies making use of these properties are in progress.

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