



Monolithic zirconia foams synthesis from emulsion stabilized by colloidal clusters



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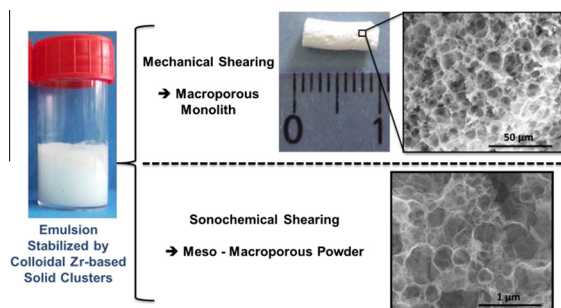
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HIGHLIGHTS

- Emulsions stabilized by colloidal clusters lead to the synthesis of porous ZrO₂.
- The material porosity can be easily tuned using different emulsification modes.
- For an appropriate porous network, monolithic zirconia foam is obtained.
- Zirconia monolith is interesting for Sr removal in column separation process.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel procedure for the build-up of monolithic zirconia foams and macro-mesoporous zirconia powders has been developed. A Zr-based colloidal sol is used as emulsifier in an emulsion free of surfactant in molecular form and where stability is given by the presence of colloidal clusters at oil/water interface. The accurate control of the sol-gel transition of these clusters made of Zr-based nanoparticles leads to the elaboration of porous materials in a two-in-one step method. Different parameters have been studied to allow a good control of the porosity of the material. This latter, characterized by SEM and nitrogen adsorption-desorption, is easily tuned (from 15 nm to 20 μm) by varying the emulsion shearing rate and mode. In appropriate conditions, the emulsified system can either lead to the formation of macroporous zirconia monoliths or macro-mesoporous zirconia powders. The monoliths were identified by X-ray diffraction as two pure crystalline phases depending on the thermal treatment: tetragonal and monoclinic at 400 and 1000 °C, respectively. The mechanical properties of the monoliths as well as an example of using these materials for solid phase extraction process are finally discussed.

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1. Introduction

Since two decades we can observe a growing interest in the development of new routes for producing porous ceramics. Indeed, materials (SiO₂, ZrO₂, TiO₂ or Al₂O₃ [1–3]) with tailored porous structures exhibit some specific properties in a wide range of areas

such as catalysis [4], tissue engineering [5], separation techniques [3] or chromatography [6]. Coupled with sol-gel processes, different methods have been described in the literature among them phase separation [3,7], gel casting [8] or hard templating [9]. In particular, strategies based on the use of soft templates [10–12] represent attractive methods of manufacturing ceramic foams with different associated porous architectures. By controlling the synthesis conditions, especially the nature of the template (e.g. polymers, surfactants or emulsions), the material porosity can be tuned, as a function of the application, in a wide range of mean

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pore sizes [13]. Furthermore, a monolithic shape can be required owing to its ability to handling as well as its mechanical strength and an adequate macroporosity has to be well defined in order to facilitate the fluid transport through the monolith. However, unlike a material such as silica, obtaining a mechanically stable monolithic zirconia is not so trivial and the development of a simple synthesis route is still an exciting challenge. Indeed, due to the high reactivity of the zirconium to hydrolysis, the control of the gelation reaction can be problematic. Furthermore, thermal treatments could significantly affect the mechanical strength of the final material due to some shrinkage effects [7].

Recently, two techniques of monolithic zirconia synthesis have been reported. Phase separation is one of them [3,6,7]. Polymerization reactions of a Zr-based solution are realized in presence of a precipitated polymer phase, acting as a template. Then, after the gelation of the system, this precipitated polymer phase is removed to open the macroporosity. Pore size is then controlled by adjusting the amount of polymer. This technique can be combined with the addition of surfactants, allowing the formation of mesoporosity and thus hierarchically porous materials [3], or with a solvothermal process which can improve the mechanical strength of the final monolith [7]. The second technique is based on the formation of either a liquid foam or an emulsion both stabilized by surfactants [14,15]. Therefore, in this case, the template is either air bubbles or oil droplets. The aqueous phase is once again a Zr-based sol and its gelation around the template leads to the formation of monolithic zirconia foams after an adjusted thermal treatment. Droplet or bubble size respectively combined with the amount of oil or surfactant determines the final pore characteristics as well as the mechanical strength of the material.

This paper describes an innovative and simple method to synthesize macroporous zirconia monoliths based on the formation of an oil-in-water emulsion stabilized by solid particles, also known as Pickering emulsions [16–18]. Unlike surfactants, particles irreversibly adsorbed at the oil–water interface, due to their high energy of attachment, have a shelf life of months and even years [19]. These types of emulsions are promising to act as templates for the manufacturing of macroporous ceramic foams and have been yet especially developed for silica-based materials [20–22]. In this paper, this process is adapted for the preparation of macroporous zirconia monoliths and macro-mesoporous zirconia powders. A colloidal sol is first obtained from a solution of zirconyl salts, which are much less sensitive to the air moisture than alkoxide precursors [23]. We also point out that sol–gel processes using alkoxide precursors release large amounts of alcohol which may alter emulsions due to its tendency to mix with both oil and water and to act as a co-surfactant. The use of a complexing agent leads to the formation of Zr-based nanoparticles clusters which then act as emulsifiers for the formation of a free surfactant solid-stabilized emulsion [24].

In this study, we demonstrate that the ceramic foam microstructure can be easily tuned by fine adjustment of the emulsion characteristics. The emulsion is stabilized by Zr-based colloidal clusters and no surfactant is used in this process. Then, the variation of the emulsion shearing rate and mode allows the control of the porous properties of the material. We thus have the flexibility to synthesize either macroporous monolithic materials with interesting mechanical properties or macro-mesoporous powders with a significant specific surface area. These materials, obtained through a unique and simple two-in-one step method, present different properties which are interesting as a function of the target application. The porous structure is studied and discussed using Scanning Electronic Microscopy (SEM) observations and nitrogen adsorption–desorption measurements. The zirconia monolith crystalline phases, driven by the final thermal treatment, are characterized by X-ray diffraction and some nanoindentation measurements

are performed to probe the mechanical properties. Finally, the adsorption properties of the porous zirconia for removal Sr^{2+} are compared. Strontium has been chosen as an example of radioactive pollutant from nuclear aqueous effluents. Due to their irradiation resistance and chemical and thermal stability, such materials are mainly used for the decontamination of liquid radioactive waste and particularly in ^{90}Sr [25,26]. ^{90}Sr is known to be a very hazardous element produced in nuclear industry and its removal is an important issue as a part of environmental (water, soil, air ...) or nuclear plant decontamination. Among the different inorganic materials reported in the literature [27–29], zirconia has a good adsorption capacity and a shaping under a monolithic form could allow a development in column separation process and better final waste management.

2. Experimental section

2.1. ZrO_2 synthesis

The different operations and reactions were performed at room temperature under an ambient atmosphere.

The procedure of synthesis of the emulsion containing Zr-based nanoparticles has been recently reported [24]. Zirconium precursor, $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (from Sigma–Aldrich), was dissolved into deionized water. The zirconyl nitrate concentration was set at 0.15 M. A complexing agent, acetylacetone (acacH) (from Sigma–Aldrich) was added with a defined ratio $K = [\text{acacH}]/[\text{Zr}]$ set at 0.5. Then pH was increased, using ammonia 3 M, to create a sol of $\text{ZrO}_{2-x}(\text{OH})_{2x}$ stabilized by the complexing agent and which becomes a gel after a maximum of a few hours (pH at approximately 5–5.5 [23]).

The drop wise addition of an organic solvent, dodecane 99% (from Acros), was then performed and the system was simultaneously sheared to create an emulsion stabilized by colloidal clusters using either an Ultra-Turrax (from IKA) homogenizer (simply named Ultra-Turrax) using a single rotor (S25N-10G, from IKA) at different rotation speeds (10.000, 13.000 and 20.000 rpm) or a Sonifier150 homogenizer (from Branson, $\approx 1 \text{ W cm}^{-3}$) (simply named Sonifier). Due to the relatively high pH value of the sol, the sol–gel transition quickly happened, creating a Zr-based network around the oil droplets. A 24 h waiting time at room temperature was then observed to completely achieve the sol–gel reaction. The final thermal treatment included two steps, with the drying of the emulsion and the calcination of the dried gel at different temperatures between 400 and 1000 °C for 6 h.

2.2. Sorption experiments

All the sorption experiments were performed by batch process at room temperature. Solutions of 30 mL were prepared at fixed concentrations of strontium nitrate (100 ppm of strontium) by dissolution of strontium nitrate, purchased from VWR, into deionized water. The pH of each solution was adjusted at 11 with NaOH 1 M. 0.12 g of sorbent was added to these solutions. Solutions were shaken for different times (between 5 min and 24 h). Then, the supernatants were removed and filtered with a 0.45 μm pore filter. The final strontium concentrations were determined by ICP-OES. The percentages of adsorption (%Ads) are calculated using the Eq. (1):

$$\% \text{Ads} = \frac{(C_0 - C)}{C} \times 100 \quad (1)$$

where C_0 and C are respectively the initial and final concentrations of strontium in solution (mg L^{-1}).

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