PREPARATION AND CHARACTERIZATION OF CERAMIC BEADS WITH HIERARCHICAL POROSITY FABRICATED BY A PHASE INVERSION TEMPLATING METHOD

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SUMMARY

In this study we report the synthesis and characterization of ceramic beads of hierarchical porosity in the meso and macro pore range. The materials preparation is based on the combination of polymer templating and phase inversion methods. Three different kind of ceramic powders: α-alumina (α-Al_2O_3), yttria stabilized zirconia (YSZ) and apatite type lanthanum silicate oxide (LFSO) were used for the formation of mm monomodal sized beads. High total porosity values were found (40%-75%) depending on the material sintering properties and the preparation method. The pore size distribution revealed graded pores in the range of large meso and macro pore range depending on the thermal treatment of the materials.

INTRODUCTION

In the recent past several synthetic strategies for tailoring spherical particles in terms of meso and macroscale ordering. Most of them use colloidal chemistry based methods some times in combination with engineering methods. Particles with a wide range of composition, morphology, and pore microstructure have been reported [1, 2]. In cases spray drying achieves agglomeration in the μm range introducing hierarchical mesoporosity [3].

However for the preparation of mm or even cm sized functional beads only a fraction of the published studies report on the existence of a hierarchical porous structure [1, 4]. In such cases structures are reported as polymer or polymer matrix composites with methods originating from polymer membranes fabrication including phase inversion [4]. However mesostructured but not hierarchical ceramic spheres are known using templating techniques [5].

In this work we report the preparation and characterization of mm sized YSZ, α-Al_2O_3 and LFSO beads of radial hierarchical porosity. This was achieved by combining a polymer templating and a polymer/solvent/ non-solvent induced phase inversion method.

METHODS AND RESULTS

In a polyethersulfone (PESf)/methyl-2-pyrrolidone (NMP) solution, a proper amount of polyvinylpyrrolidone (PVP) was added followed by the addition of ceramic powder [6, 7]. The as prepared slurry was dropwise added into an aqueous bath, forming beads of uniform size. Each drop readily forms a bead due to the non-solvent induced phase inversion method. During phase inversion the PESf/ceramic powder slurry is transformed into a two phase system in which a solidified polymer/ceramic phase forms a porous structure, while a liquid phase, poor in polymer, fills the pores [8]. Thermal treatment removes the polymer matrix, forming inorganic beads of porous ceramic structure. The features of the as formed porous macrostructure of the beads can be largely determined by adjusting parameters controlling the phase inversion process.

Beads (Figure 1) were calcined under air at various temperatures up to 1500ºC.

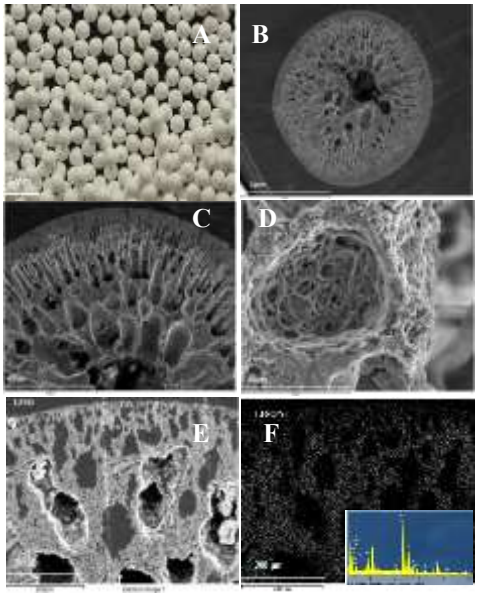

Figure 1. SEM images of the as prepared (A), calcined (B, C, D, E, F) YSZ beads as well as LFSO and Ni impregnated LFSO beads (E, F: Ni EDX)

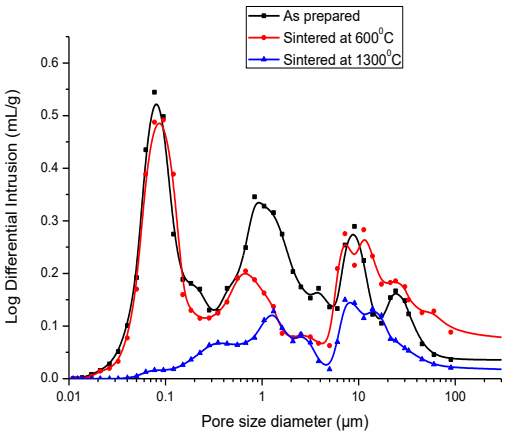

Figure 2. Hg intrusion results for the as prepared YSZ beads and sintered at 600ºC and 1300ºC respectively.

The as prepared polymer/ceramic composite beads samples were studied for their thermal properties by Thermal Gravimetry (TGA) [9] and Differential Scanning Calorimetry (DSC). The porosity features of the prepared beads were measured by Hg intrusion and Archimedes method. Samples morphology and microstructure was observed by means of optical and Scanning Electron Microscopy (SEM).

Typical pore size distribution results are shown in Figure 2. Ceramic beads of α-Al_2O_3, YSZ and LFSO [10-13], show high porosity even after sintering at high temperatures e.g 40% to 75% at 1500ºC. SEM reveals a microstructure of hierarchical porosity radially graded. The core of the particle is hollow. Beads exhibit finger like macropores from the core to the outer cell. Outer cell has a sponge like structure i.e. in YSZ this cell has pores of 70 nm (Figure 2) together with finger-like larger pores ranging from few to several μm (Figure 1, 2).

CONCLUSIONS

Highly porous beads of radial hierarchical multimodal porosity were prepared. Typical sponge like and finger like pore structure is fabricated with size ranging in 3 orders of magnitude from large mesopores to large macropores. The as formed porosity, microstructure and shape are maintained even after sintering at elevated temperature i.e. 1500ºC. These structures may be beneficial for the development of various surface processes including catalysis (supports, membrane microreactors etc), adsorption and separation.

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