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Studies on the porosity of SiO_2-aerogel inverse opals synthesised in supercritical CO_2

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Abstract

A new technique to produce highly porous SiO_2-aerogels inverse opals in supercritical carbon dioxide ($scCO_2$) is being developed at our laboratory. Polystyrene latex particles decorated with methacrylic acid or a mixture of methacrylic and itaconic acid groups are organized in three-dimensional 3D-latex arrays and used as templates. The polymeric template is reacted with tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) dissolved in $scCO_2$ at 40 °C and 85 bar. The reaction is catalysed by organic acids attached to the latex particle surface. SEM and TEM images show that, upon calcination of the template, highly porous materials replicating the structure of the original template are obtained. N_2-adsorption isotherms reveal the presence of a large porosity located in the macropore wall. In all the cases, the maxima in the pore size distribution appear in the mesopore range. In this paper we investigate ways of controlling the porosity of the material by changing the precursors, the catalyst and/or its concentration. SEM, TEM and N_2-adsorption data show that, at the reaction conditions, reactivity of TEOS and TMOS on the templates is similar, yielding materials of comparable surface area. In the same way, the porosity of the aerogels obtained with templates impregnated using benzosulfonic (BSA) acid and *p*-toluene sulfonic acid is the same. Lower yields were obtained using monochloroacetic acid. The effect of the catalyst concentration is more important; as the concentration of BSA in the template increases, lower values are obtained for the maximum in the pore size distribution.

Keywords: Inverse opals; Supercritical fluids; SiO_2-aerogels; Porous materials; Gas adsorption

1. Introduction

Porous materials have many applications in catalysis, chromatography, separation, biomaterials, microelectronics and photonic materials [1,2]. Most of these applications require a uniform pore size as well as a regular ordering of the pores. In order to achieve a structured pore system, different methods have been applied in the literature [3]. The templating technique is one of the most popular due to the variety of pores sizes and structures which can be achieved by changing the template, thus pore size can be tuned from the micropore to the macropore range. We are interested in the synthesis of structured macroporous materials to be used as separation membranes, supports for catalysts and photonic band gap materials. These materials can be easily produced using colloidal crystal templates such as monodisperse polymer latex or SiO_2 spheres.

A new method to produce structured macroporous materials using supercritical fluids has been recently developed at our laboratory [4,5]. The method involves the impregnation and reaction of inorganic precursors dissolved in supercritical CO_2 ($scCO_2$) on the surface of well-ordered colloidal crystal templates. Monodisperse polystyrene (PS) spheres decorated with different hydrophilic groups on their surface are mixed with small amounts of organic acids and are organized in 3D-ordered

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arrays by solvent evaporation, membrane filtration, or centrifugation [6,7]. The arrays are then used as templates and ceramic precursors are infused and reacted into the voids created by the polymer particles. After the reaction, the template is removed by calcination or dissolution. Infusion of reactants into the template in the liquid-phase has been previously carried out in the literature [8–10]. The novelty of our method consists in carrying out the infusion and reaction process in a supercritical fluid. Reactions are performed in supercritical CO_2 since it is cheap, non-toxic and has relatively low critical temperature and pressure ($T_c = 31$ °C, $P_c = 73.8$ bar) [11]. Furthermore many metal alkoxides (ceramic precursor) dissolve in $scCO_2$ at moderate pressure and temperature [12]. The low viscosity, high diffusivity relative to liquids and very low surface tension of $scCO_2$ promote infiltration in complex geometries and mitigate mass transfer limitations common to liquid-phase processes. CO_2 is a gas at ambient pressure and it is eliminated completely upon depressurization. When using polymeric templates, attention should be paid to the stability of the template, as CO_2 is quite soluble in many polymers, thus decreasing the glass transition temperature (T_g) of the polymer [13]. This effect can produce aggregation and even coalescence of the polymer particles [14].

Up to date we have shown the synthesis of SiO_2-aerogel inverse opals in $scCO_2$ using tetraethylorthosilicate (TEOS) [4,5]. Because of the good transport properties of the supercritical fluids, materials with exceptional porosity were obtained. The effect of the latex composition on the porosity of the material was further studied. In this paper we investigate ways of controlling the porosity of the material by changing the precursors, the catalyst and/or its concentration.

2. Experimental

For the synthesis of the polymeric templates, styrene, methacrylic acid and itaconic acid (reagent grade) from Sigma–Aldrich and distilled water were used. Tetraethylorthosilicate (99+%), tetramethylorthosilicate (99+%), benzosufonic acid (99+%) and *p*-toluenesulfonic acid monohydrate (98.5+%) were obtained from Aldrich. Monochloroacetic acid was supplied by Probus (purum). CO_2 (purity >99.99%) was supplied by Air Liquide. All chemicals were used as received.

Monosized polystyrene (PS) latex particles microspheres decorated with methacrylic acid (MA) groups or a mixture of MA and itaconic acid (IA) groups were copolymerised in a surfactant free emulsion in water following a procedure previously described [7,9,10]. The molar ratio of styrene (S) to the monomers MA and IA was 17:1 (PS-MA), and 50:1:2 (PS-IA-MA) . Suspensions were dialysed for four weeks against water to eliminate residual products. A small amount of monochloroacetic acid (ClAcH), benzosulfonic acid (BSA) or *p*-toluenesulfonic acid (pTSA) was added to the suspensions in varying concentrations and 3D-latex arrays were prepared by centrifugation or evaporation. Templates were dried in air at room temperature and at 45 °C in an oven. 3D-latex arrays formed by particles ⩾200 nm appeared iridescent to the visible light reflecting the 3D ordering of the templates. The degree of ordering in the template was also characterized using N_2-adsorption [7].

3D-latex arrays were infused and reacted with silicon alkoxide precursors such as TEOS or tetramethylorthosilicate (TMOS) dissolved in $scCO_2$. The experiments were carried out in a *ca.* 70 mL custom-made stainless-steel high-pressure reactor in the batch mode following a procedure previously described [5]. A diagram showing the experimental set-up is shown in Fig. 1. The reactor was loaded with three vials containing: (1) Pieces of 3D-latex arrays (1–5 mm thick), (2) TEOS or TMOS in large excess and (3) excess H_2O. The reactor was placed into a thermostatic bath (PolyScience) and was filled with CO_2 using a high-pressure syringe pump at the reaction temperature (Isco, Inc. Model 260D). The pressure was measured using a pressure transducer (Druck Ltd.). A safety valve (Swagelok) was fitted to the reactor. All experiments were performed at 40 °C and 85 bar. At these conditions, the morphology of the polymeric template was not altered. After 0.5–4 h, depending on the experiment, the reactor was depressurised through a needle valve in 0.5–2 h. TEOS or TMOS reacted on the template, which was removed by calcination in air at 500 °C for 3 h. The weight percentage remaining after calcination was determined by weight difference.

Materials were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N_2-adsorption experiments. SEM images were taken on a JEOL-6400 electron microscope working at 20 kV and a JEOL JSM-6330 F electron microscope working at 15 kV. Samples were gold coated prior to analysis. TEM images were obtained on a JEOL 2000FX electron microscope operating at 200 kV equipped with a double tilting (±45°) sample holder. Samples were dispersed in water or 1-butanol over copper grids and dried in air. N_2-adsorption–desorption isotherms at −196 °C were obtained using an ASAP-2020 equipment from Micromeritics. Prior to

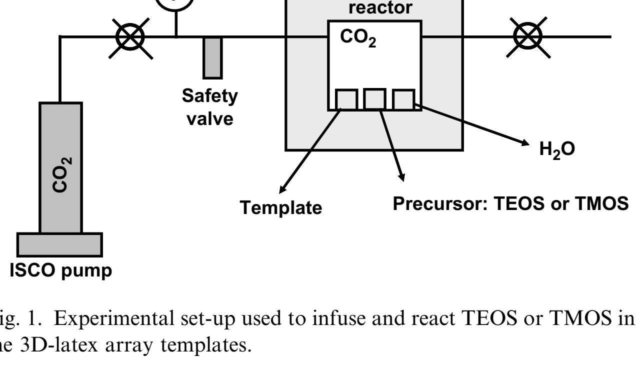

Fig. 1. Experimental set-up used to infuse and react TEOS or TMOS into the 3D-latex array templates.