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Preparation of thin porous silica foam on alumina disk substrate

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This work reports how a novel macro-porous silica foam thin layer, applicable as a new catalyst support with high porosity, can be produced via spheres templating method. Three-dimensional close-packed crystals of polystyrene (PS) spheres were assembled on a porous alumina disk via vacuum filtration. The PS templates were filled with a silica colloidal solution, after annealing and adsorption of a surfactant, to generate interconnected macropores after calcination.

KEY WORDS: polystyrene; template; filtration; macro-porous; silica; foam; alumina disk.

1. Introduction

Fast reactions over solid catalysts in liquid phase can easily cause concentration gradients in reactors and catalysts because of relatively slow diffusion as well as low concentrations of reactants, e.g. dissolved gasses. Mass-transfer induced concentration gradients will influence both reaction rates as well as selectivity. Conventional strategies for gas–liquid–solid phase catalytic reactions comprise slurry reactors and trickle bed reactors. In trickle bed reactors, diffusion limitation occurs very frequently because catalyst particle are relatively large (typically 1 cm) because of hydrodynamic constraints. In slurry reactors, catalyst particles are usually much smaller (typically 20–100 μm) and mass transfer limitation is less likely, although fast kinetics will still induce significant concentration gradients, e.g. in hydrogenation of nitrate [1–4]. The disadvantage of slurry operation is the high cost of removal of the catalysts from the products. Therefore, development of structured catalysts is an active research area aiming to combine the advantages of slurry reactors and trickle bed reactors. Most work was done based on monoliths [5–7], but also corrugated plates, structured packing and glass fibers have been used, as reviewed by Centi *et al.* [8,9]. Our laboratory recently contributed to this field by preparing a new type of thin, highly porous carbon-nanofibres layers on monoliths and metal foams [10–12].

Porous materials are essential for applications including catalysis, sorption and separations. High surface area materials with limited control over pore size distribution without any control over the arrangement of pores are still the working horses in this area, e.g. activated carbon, alumina and silica. The development of synthetic zeolites has made available crystalline materials with superior control over pores sized approximately up to 2 nm [13]. Later, mesoporous MCM-type of materials were discovered [14], templating with surfactant assemblies results in well-defined pore size (up to 33 nm) and shape despite the fact that the silica skeleton is amorphous [15].

Colloidal crystals of latex spheres in two and three-dimensional arrays are well known [16–20], which have been used as organic templates to control the pore structure of inorganic solids with pore sizes ranging up to micrometers [21–24]. Templating techniques thus have been studied intensively recently to prepare macro-porous (> 50 nm) materials [25]. The template can be formed by gravitational sedimentation, centrifugation, filtration and the convective assembly method [26,27]. Photonic crystals with three-dimensional ordered pores in the order of 100 nm are prepared using this method. The key problem for application of such materials as catalyst support is mechanical stability and control over the size of the particles. To circumvent this problem this work focuses on the preparation of thin templated layers on structured materials mentioned above. On the other hand, long order ordering and very narrow particles size distribution is key for photonic crystals. Fortunately, this is much less so for catalysts supports, so that cheaper latexes can be used. Preparation of thin layers of macro-porous solids has been reviewed recently by Guilants *et al.* [28]. Limited work has been done on the preparation of macro-porous thin layers of silica.

This work presents a general procedure for preparing three-dimensional interconnected macropores in a thin silica layer on porous alumina disk substrates via filtration. The method is explored using one single pore size as a demonstration. The resulting ordered micro-foam provides significant surface area, useful as catalyst supports, combined with excellent accessibility of active sites that can be attached on the walls of the foam.

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2. Experimental

2.1. Materials

Alumina disks (Small Parts, Inc., USA) were used as substrate. The monodisperse polystyrene (PS) suspensions (Polysciences, Inc., Germany) were used to form template on alumina disks. Tetraethoxysilane (TEOS, Aldrich) were used to prepare silica colloidal. The surfactant hexdecyltrimethylammonium bromide (HTAB) was obtained from Aldrich.

2.2. Methods

The mono-disperse PS suspensions (750 nm) were filtered through 29 mm diameter 7 mm thick alumina disk with pore size of 500 nm. Prior to use, the surface of alumina disk substrate was polished and rinsed with pure water. The concentration of PS in the suspension was between 0.05 and 0.5% by volume.

The PS arrays obtained are not suitable for direct use as template for the formation of porous silica due to the lack of initiators of the solidification process. The surface of the PS microspheres is polar and does not display any reactivity with the silica colloidal solution [29]. Therefore, after the PS arrays were deposited it needed to be washed with HTAB solution for 10 min.

Silica solution was prepared by adding 26.9 g ethanol, 31.2 g TEOS, 4.8 g demi-water and 4.4 g hydrochloric acid in a conical flask under 333 K, stirred, reacted for 3 h and filtered [30]. It was diluted to 0.5 M by adding ethanol. The sample was soaked in the silica colloidal solution, and the liquid penetrated the interstitial spaces by capillary force. The excess solution on top was removed with the aid of vacuum filtration so as to avoid forming a dense layer on the top of the PS template. The PS/silica composite was firstly dried under room temperature and then under vacuum at 333 K for 1 h and finally calcined at 843 K in air. The temperature program used will be discussed in the result section. A TGA/SDTA 851 thermo-balance was used to follow the calcination process. The typical amount of sample studied in a single TGA experiment was 12 mg. After removal of the PS spheres from the composite, an ordered three-dimensional silica porous structure was obtained and characterized.

The morphology of the PS template, the composite of PS/silica and the final macro-porous silica foam-layer on the alumina substrate was studied with scanning electron microscopy (SEM) (LEO 1550 FEG SEM, Germany).

3. Results and discussion

A schematic presentation of the preparation method is given in figure 1. The PS arrays were prepared using the filtration method, as this allows easy washing and subsequent infusion with different media, as well as easy control of the thickness of the three dimensional crystalline layer. The PS suspensions were diluted to 0.1–0.2 vol% and slowly filtered through a smooth porous alumina disk substrate. The PS particles accumulated on the alumina disk surface in 5–8 h, building closely packed three-dimensional ordered layers of thickness 4–10 μm. The thickness of the template can be controlled by changing the concentration and the amount of the PS.

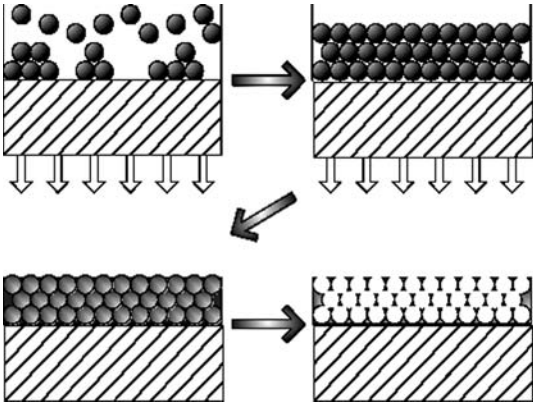

Figure 1. Schematic illustration of the preparation of macro-porous silica foam.

Figure 2 shows monodisperse PS latex spheres well ordered in close packed domains. This is in agreement with the fact that three-dimensional crystallization of colloidal particles results in microspheres crystallization in a random stacking of domains with different packing: hexagonally close-packed planes (rhcp) or face-centered cubic (fcc) lattices [16,17,31]. Close packed structure makes the PS particles effectively occupy the space and be likely to array closely so as to improve the stability. The result of such close packed structure is that each of the particles is tangent to six particles that is adjacent to it in the same layer.

The sample was soaked in silica colloidal solution and the excess solution on top was removed with the aid of vacuum filtration so as to avoid forming a dense layer

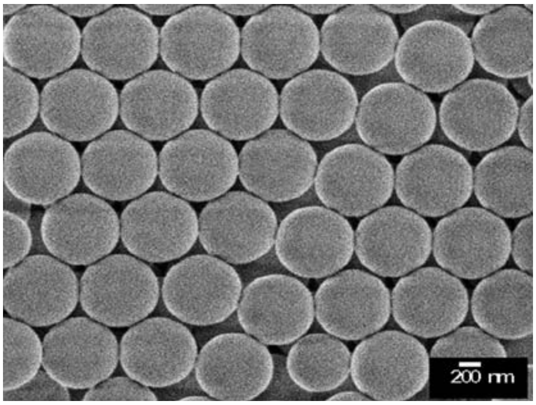

Figure 2. SEM micrographs of the PS sphere array.

on the top of the PS template. The appearance of the surface of the resulting composite structure after drying is shown in figure 3. It shows that some PS particles appear in ellipsoidal shape. The reason may be the function of expansibility during the solidification process. Furthermore, it is obvious that the interstitial volume of the PS layer is indeed filled with silica. On the other hand, the shape of the PS spheres in the top layer is very well recognizable after adding silica. This proofs that vacuum filtration is indeed able to remove the excess of silica sol above the sample without emptying most of the interstitial spaces. It may well be that the capillary force is sufficient to prevent emptying of the pores, although we do not know the surface tension and wetting in this system. Alternatively, it is possible that the excess of liquid is drained via a few preferential large pore pathways such as cracks. These cracks may be emptied due to the vacuum below the sample, relieving the pressure drop over the disc, thus leaving the small pores filled with silica sol. It should be stressed that the occurrence of such cracks would be detrimental if the layers were to be used as filters or photonic crystals. However, for the application as catalyst support the occurrence of crack is less important because the layer is designed to act as support material only and does not have any separation function as in a membrane. Cracks will only decrease the support surface area available to insignificant extent.

Figure 4 shows the result of thermogravimetric analysis (TGA) of calcination of the PS/silica composite. Even after the vacuum drying, the composites contained some residual water, which desorbed below about 453 K. The PS/silica composites loses weight rapidly above 500 K, as a result of the thermal degradation and oxidation of the PS particles. The sudden decrease in weight is indicative for an ignited process. The PS/silica composites had lost approximately 40% of its original weight, and the additional loss up to 843 K was about 6%. This slow weight loss at high temperature is due to dehydroxylation of the surface of the silica formed. The remaining weight of 54% may be attributed to the silica in the porous sample. The porosity of the final material was 63 vol%, as estimated [32] based on the weight and density of both PS and silica in the composite before calcination. This value is a little smaller than that which may be expected for a material with close-packed ordered spherical pores [16]. The reason may be that the array of the PS template is not completely close-packed. On the other hand, we do not consider the presence of the surfactant, which could lead to errors in the estimation of porosity.

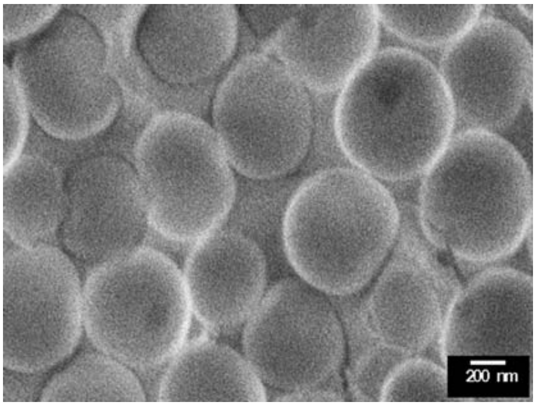

Figure 3. SEM micrographs of the PS sphere array filled with silica.

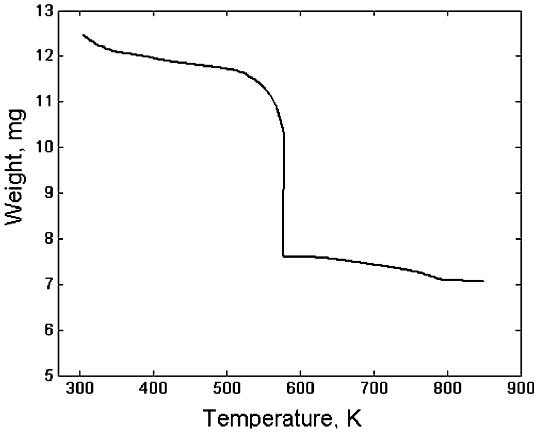

Figure 4. TGA plot obtained during calcination of PS/silica composites.

Based on these results, the calcination of the samples were preformed on two steps; first at 573 K for 5 h with a ramp of 1.5 K min^{-1} and second at 843 K for 5.5 h with a ramp of 1.5 K min^{-1}. Figure 5a, b show the surface morphology of the resulting silica layers. The pore diameters are about 30% smaller than the original latex spheres due to shrinkage during calcination. This effect is well known [24,33] and is due to further densification via dehydroxylation of the silica.

The SEM image in figure 5b shows that the porous silica is two dimensional: a regular arrangement of single cavities can be observed without any connection to lower layers. The PS layer had been treated at 353 K for 60 min before HATB treatment in this case. Interconnectivity of pores can be obtained by varying the thermal treatment of the PS layer. Figure 6 shows the final structure of the silica layer after thermal treatment of the PS layer at 383 K for 18 min, just above the glass transition temperature. It is clear from figure 6 that interconnectivity is now obtained thanks to partial sintering of the PS spheres. The number of the connections to pores below seems to vary. In part of the sample every pore is connected to four pores below, implying a square structure of the PS lattice, with the layer on top positioned in the hollow sites (figure 6a). On the other hand, figure 6a show mostly only one connection per pore, indicative for an on-top arrangement in the PS lattice.

It should be noted that the variation observed in the local structure is not detrimental for the purpose as catalyst support, as opposed to photonic crystals and

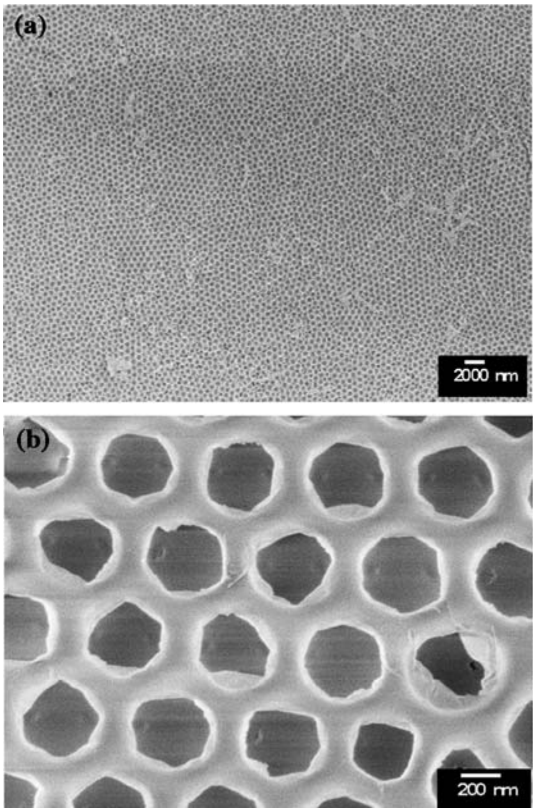

Figure 5. SEM micrographs of porous silica foam on alumina disk substrate.

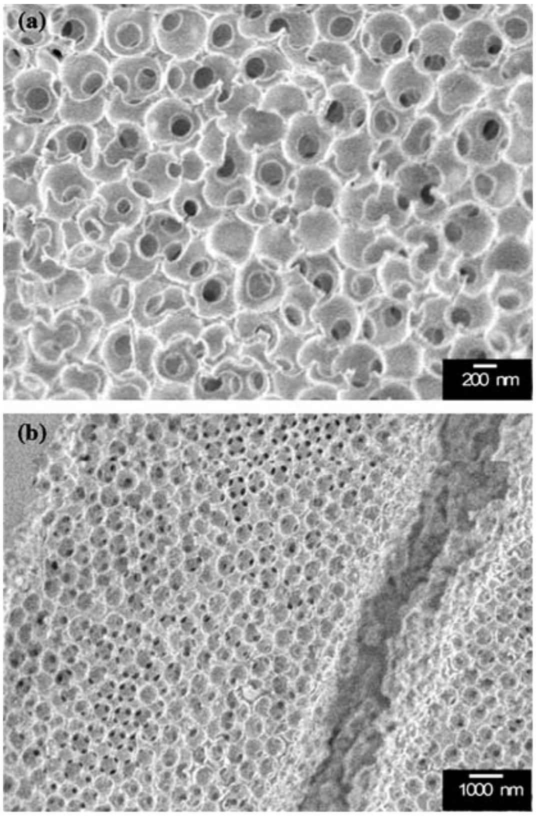

Figure 6. SEM micrographs of porous silica foam on alumina disk substrate (annealed at 383 K for 18 min).

membranes. This obtained porous silica foam will find potentially application as catalyst support. A macroporous thin layer is formed with extremely large pores and low tortuosity. The geometrical surface area estimated based on the pore sizes in figure 5 amounts 4 m^2/g, which can be easily increased by using smaller PS particles. As compared to conventional washcoats, this thin foam layer will allow far more efficient mass transfer of reactant and products when active sites are deposited on the surface of this new foam layer.

4. Conclusions

The method of preparation of a large area, thin macro-porous silica foam layer on alumina disk substrate is presented in this paper. The scheme is based on assembling PS particles into three-dimensional colloidal crystal, functionalized with HTAB and used as template for silica sol-gel solidification. Porous silica foam is obtained after removal of PS template. Filtration through the porous alumina support facilitates both the formation of the PS thin layer as well as the introduction of the colloidal silica. Furthermore, this appears an effective procedure to remove excess silica solution on top of the PS layer. The mechanical stability of the colloidal crystal template as well as the interconnectivity of the macropores can be controlled via a suitable sintering treatment of the PS thin-layer.

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