Synthesis, characterization, and evaluation of a superficially porous particle with unique, elongated pore channels normal to the surface☆

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ABSTRACT

In recent years, superficially porous particles (SPPs) have drawn great interest because of their special particle characteristics and improvement in separation efficiency. Superficially porous particles are currently manufactured by adding silica nanoparticles onto solid cores using either a multistep multilayer process or one-step coacervation process. The pore size is mainly controlled by the size of the silica nanoparticles and the tortuous pore channel geometry is determined by how those nanoparticles randomly aggregate. Such tortuous pore structure is also similar to that of all totally porous particles used in HPLC today. In this article, we report on the development of a next generation superficially porous particle with a unique pore structure that includes a thinner shell thickness and ordered pore channels oriented normal to the particle surface.

The method of making the new superficially porous particles is a process called pseudomorphic transformation (PMT), which is a form of micelle templating. Porosity is no longer controlled by randomly aggregated nanoparticles but rather by micelles that have an ordered liquid crystal structure. The new particle possesses many advantages such as a narrower particle size distribution, thinner porous layer with high surface area and, most importantly, highly ordered, non-tortuous pore channels oriented normal to the particle surface. This PMT process has been applied to make 1.8–5.1 μm SPPs with pore size controlled around 75 Å and surface area around 100 m^2/g. All particles with different sizes show the same unique pore structure with tunable pore size and shell thickness. The impact of the novel pore structure on the performance of these particles is characterized by measuring van Deemter curves and constructing kinetic plots. Reduced plate heights as low as 1.0 have been achieved on conventional LC instruments. This indicates higher efficiency of such particles compared to conventional totally porous and superficially porous particles.

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1. Introduction

In the history of HPLC column development, two main routes have been used to increase column efficiency and achieve faster separation. One is making totally porous particles (TPPs) with smaller diameter to reduce the intra-particle diffusion distance and shorten the analysis time as predicted by Knox and Saleem [1].

Another route is making superficially porous particles (SPPs) that have a solid core with an outer porous shell [2]. The thin porous shell provides faster mass transfer for analytes, especially macro-molecules [3]. A second generation of superficially porous particles has drawn great interest since 2007 because of their unique particle structure, and most importantly their high efficiency with fairly low backpressure for both small and large molecule separations. Many papers have been reported on the synthesis, fundamentals, and applications of SPPs in HPLC [4–10]. The advantages of using SPPs as packing materials include less eddy dispersion due to a more homogeneous packed bed and less longitudinal diffusion due to their lower particle porosity, resulting in smaller A and B terms in the van Deemter equation, respectively. In addition, the shorter diffusion distance may lead to a smaller C term because of the faster

mass transfer. To further improve the performance of SPPs, we need to revisit how SPP particles are made.

In general, two processes have been employed in the synthesis of SPPs. One is called "multilayer technology" in which solid silica cores are repeatedly coated with layers of colloidal nanoparticles by alternating layers of oppositely charged nanoparticles and polymers containing amino-functional groups, until the particles reach the desired sizes [11]. The process can be labor-intensive and generates different types of aggregated particles, resulting in low particle yield. Another method involves one-step coacervation, where solid silica spheres are suspended in a coacervation reaction mixture including urea, formaldehyde, and colloidal silica sol under acidic conditions. A coacervate of urea-formaldehyde polymer and ultrapure silica sol is thus formed and coats the solid cores [12]. The urea-formaldehyde polymer is then removed by burning at c.a. 600 °C, and the particles are then strengthened by sintering at elevated temperatures.

The conventional methods of preparing SPPs use silica nanoparticles as the building blocks to build the outer porous shell. As a result, the porous shell has randomly distributed pores with wide pore size distribution. This is similar to all totally porous particles currently used in HPLC, which have randomly distributed tortuous pore structures. In addition, these conventional methods may lead to rough external particle surfaces that may limit the performance of columns containing such particles, especially at high mobile phase velocities, by generating an unusually high film mass-transfer resistance [13].

Since 1992, another method called micelle templating has been explored to create totally porous materials with highly ordered pore structures, mostly for the catalysis industry [14,15]. In contrast to the conventional sol-aggregated techniques where pore channels are tortuous, the ordered mesostructured materials provide a very different, unique, well-organized pore arrangement. The ordered porous inorganic materials are formed via self-assembly of surfactants and metal oxide clusters. The size of uniform channels can be tuned from 20 to 300 Å by the choice of the templating surfactant molecule. This was first discovered by Mobil Oil researchers when amphiphilic ionic surfactants were used to produce an ordered hexagonal pore framework involving preformed micellar structures via a liquid crystal templating mechanism [14,15]. Zhao et al. also found that amphiphilic triblock copolymers can be used as the structure-directing agents to form well-ordered uniform pore sizes up to 300 Å with thicker silica wall and greater hydrothermal stability [16,17]. Despite the highly ordered pore structure, most of the end materials are irregularly shaped porous powders, and this limits their use in other areas such as HPLC. Yang and others then tried to tune the material morphology into spherical particles [18–20]. They focused on optimizing the one-pot reaction through adjustments of pH, stirring rate, adding cosolvent, using spray drying, etc., to control the particle size, particle size distribution, pore size, and pore size distribution simultaneously. However, it is extremely difficult to control both silica-surfactant mesophase and form monodisperse particles in one reaction. The synthesized materials usually have either a broad particle size distribution or small pore sizes.

The concept of micelle templating has also been used to synthesize superficially porous particles. Two processes have been reported, as shown in Fig. 1. One was very similar to the conventional multilayer method, where a thin porous silica shell was grown on nonporous particles multiple times with the presence of a surfactant. At least seven layers were required to form a final particle with a surface area of 100 m^2/g. Also, the pore channels seemed to be in parallel to the particle surface [21].

Different from bottom–up methods, such as coacervation and multilayer, a top–down method called "pseudomorphic transformation" (PMT) was used to form monodisperse micelle-templated

Synthesis of conventional SPPs (sol aggregation)
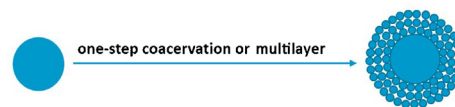
Synthesis of micelle-templated SPPs (Direct Synthesis or PMT)
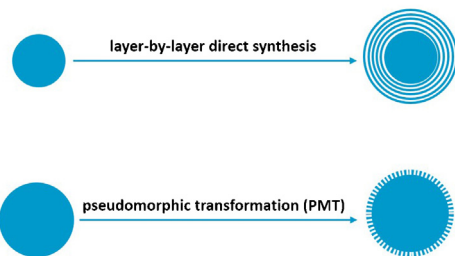

Fig. 1. Synthetic process of sol-aggregated SPPs and micelle-templated SPPs.

SPPs in one step [22–24]. In the PMT process, nonporous silica particles are dispersed in an alkaline solution with the presence of surfactant. When the temperature increases, the silica on the particle surface first dissolves and the silicic acid subsequently precipitates around ordered, positively charged micelles on the silica particles without changing the overall particle morphology. The process was first reported to transform amorphous preshaped totally porous particles to micelle-templated totally porous particles with the same particle morphology [25–28]. The advantage of this process is that we can independently optimize the properties of the particles and the properties of the pore structure. The particle size and size distribution are determined by the starting materials and the intra-particle pore structure is controlled by the PMT variables such as surfactant, swelling agent, pH, and reaction time.

The micelle-templated SPPs have a thin-walled silica skeleton and ordered pore arrangement that result in high surface area with a thin porous shell. The shortened diffusion distance and unique pore structure are expected to improve the mass transfer kinetics and provide better separation efficiency. For 2.1 × 50 mm id columns, Omamogho et al. [21] reported a reduced HETP of 1.9–2.5 on 1.75 μm micelle-templated SPPs with shell thickness from 0.15 to 0.35 μm. Min et al. [24] reported a reduced HETP of 2.47 on a 1.90 μm micelle-templated SPP with a shell thickness of about 0.20 μm. When compared to a reduced HETP of 2.0 from the same dimension of conventional SPP columns [29], performance improvement has not been observed. It is interesting to note that both studies applied a pore-etching step after the particles were formed by the micelle-templating process. It is possible that the pore structure was modified during the etching step. This might have a negative impact on column efficiency.

In this article, micelle-templated SPPs were synthesized via one-step pseudomorphic transformation (PMT). The effect of a post-synthesis etching process on the pore structure was investigated. Various types and amounts of swelling agents were studied to optimize the pore structure and particle morphology. The optimized process was then applied to make SPPs with particle sizes from 1.8 to 5.1 μm, followed by various material characterizations as well as chromatographic evaluations, such as van Deemter flow studies and kinetic plots. For simplicity, we refer to this material as PMT-SPPs.