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Use of gel-casting to prepare HPLC monolithic silica columns with uniform mesopores and tunable macrochannels

Chengdu Liang,[ab] Sheng Dai*[a] and Georges Guiochon*[ab]

[a] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120, USA. E-mail: dais@ornl.gov; Fax: +(865)576-5235; Tel: +(865)576-7307

[b] Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600, USA

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Monolithic silica columns with defined mesopore and a tunable macropore structure were fabricated by the gel-casting of ordered mesoporous silica precursors.

Since the time the researchers at Mobile Research and Development Corporation published a breakthrough report on the synthesis of surfactant-templated ordered mesoporous silica,[1] a variety of mesoporous silica with uniform pore sizes have been synthesized through the sophisticated selection of surfactants and reaction conditions. This versatile methodology initiated an era of investigations of mesoporous silica materials. A number of silica materials, such as M41S,[1] FSM-16,[2] HMS,[3] MSU-x,[4] and SBA-x,[5] have been successfully used as supports for catalyst and separations, as well as templating hosts for the synthesis of nano-scale particles, wires and ordered nonsiliceous porous materials. For example, the use of MCM-41 and FSM-16 as the stationary phase for high-performance liquid chromatography (HPLC) has been reported. The critical problem associated with the HPLC applications of the above-named mesoporous materials is the limited mechanical strength of the very thin wall structures which makes it difficult for them to sustain the high pressures involved in HPLC systems.[6] Recently, several successful applications have been reported when such porous materials are prepared with a spherical morphology, posessing a narrow size distribution. Unger *et al.* prepared spherical MCM-41, MCM-48, and HMS types particles by a modified Stober synthesis.[7] Acid-prepared mesoporous spheres (APMS) and their HPLC applications were first reported by Landry *et al.*[8] Zhao and Stucky and their coworkers synthesized SBA-15 spheres, using cetyltrimethylammonium bromide (CTAB) as cosolvent[9] while Boissiere *et al.* developed a two-step procedure to control the particle size of the MSU-1 spheres by simply adjusting the ratio of the fluoride catalyst to silica.[10] All these applications demonstrated that uniform mesoporous silicas are superior HPLC supports.

In spite of these successes achieved by preparing spherical mesoporous beads for HPLC packing, the efficiency of the particle-packed HPLC column is limited by a necessary compromise between particle size and pressure drop. Due to the high hydraulic resistance of the fine-particles packed column, the silica beads are required to have a strong mechanical strength. However, because of their high porosity, mesoporous silica spheres are usually not strong enough for fine-particle packing. Hence, the HPLC application of mesoporous silica spheres is still limited. The latest studies in HPLC columns showed that a monolithic column could overcome the pressure drop of particle packed columns. Knox first recognized the intriguing advantage of monolithic columns early in 1972.[11] The monolithic columns could provide nearly the same efficiency as the conventional particle-packed column with a hydraulic resistance an order of magnitude lower. Recently, our group proposed a theoretical model of the structure of monolithic stationary phases that allows the derivation of relationships between the characteristics of the mass transfer kinetics inside the networks of macro- and mesopores and the first two moments of low concentration bands obtained with monolithic columns.[12] Silica-based monolithic columns were first reported by Nakanishi and Soga in 1991[13] and then commercialized by Merck KGaA. Monolithic silica columns have a bimodal pore structure including networks of macropores and mesopores. The properties of the mesopores are critical for achieving separations. The development of specific mesopore morphologies for monolithic silica columns has not yet been reported. We describe a general procedure for preparing monolithic silica columns with various mesopore morphologies.

Generally, mesoporous silica is obtained as a precipitate from a mixture of surfactant and silicon-source solutions. The resulting product is in the form of fine particles. Although several groups of researchers have attempted to produce monolithic mesoporous silica,[14] the synthesis of large size crack-free mesoporous silica particles with ordered structure is still a challenge. Moreover, mesoporous silica of solely mesoporous structure is not suitable for HPLC. An additional macropore or channel network is required for allowing a stream of mobile phase to percolate with a low hydraulic resistance. Monolithic silica columns with a bimodal pore structure (*i.e.*, mesopores and macropores) demonstrated that a hierarchical porous structure is a good solution for resolving problems involving pore size and mass transfer kinetics. Though the phase-separation method developed by Nakanishi *et al.*[13] can synthesize bimodal monolithic columns with narrow size distributions of mesopores, this method is not suitable for the synthesis of monolithic columns with well-defined mesopore structure, such as those of hexagonal-structured MCM-41 and SBA-15 and cubic-structured MCM-48 and SBA-16. In this communication, we describe a simple procedure that uses gel-casting to prepare monolithic columns of large dimensions (3.8 mm i.d. with lengths ranging from 5 to 25 cm) that have a well-defined mesopore structure.

Gel-casting originated with the ceramic-forming technique. It has recently been used to create hierarchical zeolite structures with designed shape.[15] Silica particles were entrapped in a cross-linked polyacrylamide maromolecular network. The elastic polymer/particle composition faithfully replicates the shape of the model. Mesoporous particles of MCM-41, MCM-48, SBA-15, SBA-16, and HMS were synthesized according to the original reports. As-synthesized silica powder was suspended in a solution of monomer acrylamide, cross-linker *N*,*N*′-methylene-bisacrylamide, and the initiator [ammonium persulfate $(NH_4)_2S_2O_8$]. The weight ratio of monomer, cross-linker, initiator, and water was 5 : 0.5 : 0.05 : 100. The suspension was sonicated for 10 min to ensure a homogeneous mixture. The mixture was transferred into a 4.0 mm i.d. glass tube, and centrifugated at 1000 to 2000 rpm for 5 min. The silica particles were packed at the bottom of the tube by the centrifugal force. By replacing the upper layer of solution with the suspension and repeating the centrifugation several times, a column of desired length was easily achieved. The silica-packed glass tube was then capped, put into an oven, and cured at 50 °C for 1 h. The monomer and cross-linker were polymerized into an elastic hydrogel. The polymer network holds the silica particles as an intact cylinder. The hydrogel was hardened by removing the cap from the tube and retaining the tube in the oven at 50 °C overnight. The hard column was dried thoroughly in a vacuum oven at 60 °C for 2 d. Sintering the column at 700 °C for 10 h

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eventually caused the silica particles to form a hard structure. The polymer network was totally burned up during the sintering procedure. The monolithic column was chemically bonded by refluxing in a toluene solution of octadecyldimethylchlorosilane and equivalent pyridine for 10 h. The bonded-phase column was end-capped by adding 1 ml of trimethylchlorosilane to the toluene solution for 2 h of additional reflux. After having been copiously washed with ethanol, the modified column was dried overnight in a vacuum oven at 60 °C.

The configuration of the monolithic column is illustrated in Fig. 1. In brief, a silica rod was clad in an oven at 340 °C by using a piece of heat-shrinkable Teflon tubing. The encapsulated silica rod was then glued into a precut 4.6 mm i.d. stainless steel tube using epoxy glue. After being equipped with a pair of end fittings, the monolithic column was tested on a HP 1100 (Agilent Technologies, Palo Alto, CA) HPLC liquid chromatograph.

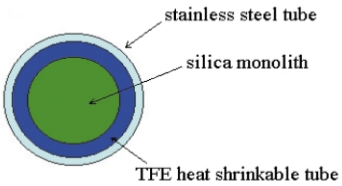

Fig. 1 Configuration of the monolithic column.

This column showed good resolution with extremely low hydraulic resistance and affords rapid separations. Fig. 2 shows an application for the separation of phenol–toluene at flow rates of 0.5, 1.0, and 5.0 ml min^{-1}. When the column was operated at a flow rate of 5 ml min^{-1} with a mobile phase of acetonitrile–water (7 : 3), phenol and toluene were totally resolved within 0.4 minute. The pressure drop corresponding to the flow rate of 5 ml min^{-1} was only 87 bars.

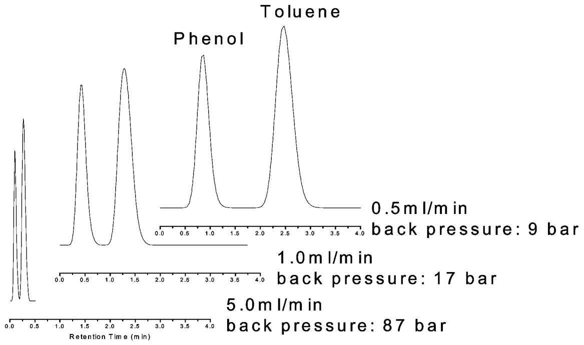

Fig. 2 Separation of phenol and toluene by using C-18 gel-cast monolithic column at different flow rates.

Obviously, the high porosity (80.7% measured by chromatography) of the column contributes to its low hydraulic resistance. The porosity of the column is attributed to its combination of macropores and mesopores. Fig. 3 shows a SEM image of a cross-section of the monolithic column. The macrochannel was formed by the void space among the sintered particles. The channel size depended on the particle size of the silica precursors, which were ground and sieved to different sizes. The hydraulic resistances of the monolithic columns were related to the sizes of the silica colloid precursors and to their macropore structure. Typically, sintering of 10 μm SBA-15 particles results in a monolithic column with an average macrochannel size of 5 μm. The mesopore structure and pore size distribution of the column are tailored by using various mesoporous silica colloid precursors such as MCM-41, SBA-16, and HMS. These precursors are calcined at 550 °C before grinding and sieving. The BET nitrogen adsorption–desorption test showed that the mesopore diameter undergoes only slight shrinkage during the gel-casting treatment. TEM images show that the gel-casting treatment does not change the morphology of the mesopores.

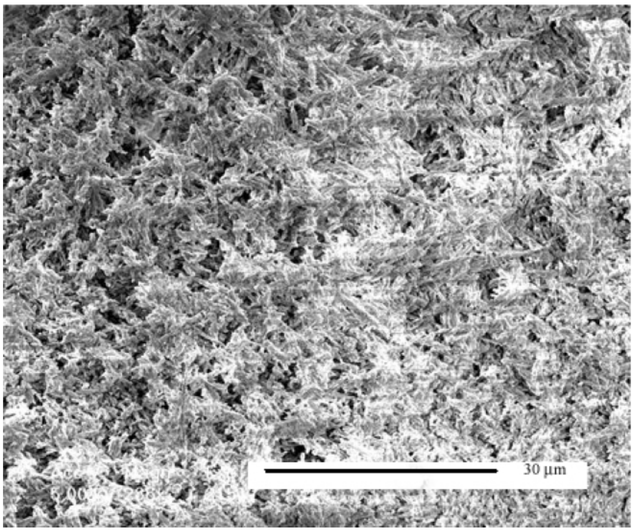

Fig. 3 SEM image of monolithic column cross-section.

In conclusion, we report here a general procedure for the synthesis of monolithic silica columns with a bimodal pore structure. Both the macropores and the mesopore modes are adjustable. Monolithic columns with a large diversity of mesopore morphology were readily prepared by using various silica precursors. The total porosity and hydraulic resistance of the column were easily tailored by gel-casting of silica colloids of various sizes. Our procedure also demonstrated that gel-casting is a convenient method for the synthesis of hierarchically structured silica with designed shape. Gel-casting of various silica precursors made it possible to fine-tune the design of monolithic silica columns.

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