



Preparation of high-purity monodisperse silica microspheres by the sol–gel method coupled with polymerization-induced colloid aggregation



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ABSTRACT

Ultra-pure mesoporous silica microspheres with good monodispersity were synthesized in two steps: nanometer-sized silica sol was produced by the sol–gel process, then micrometer-sized silica microspheres were synthesized by polymerization-induced colloid aggregation of the silica sol. The total metal content of the microspheres was extremely low, which eliminated the tailing of chromatographic peaks by chelating reagents. The pore structure of the silica microspheres could be controlled by altering the sol–gel conditions. The silica microsphere particle size could be adjusted by using different polymerization-induced colloid aggregation conditions.

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Introduction

Silica-containing organized mesoporous structures have potential applications in catalysis, separation, absorption, and drug delivery (Qiu, Liang, Sun, & Jiang, 2011). The properties of silica allow for effective and reproducible separation, so it is widely used in high-performance liquid chromatography (HPLC) packing materials (Unger, Skudas, & Schulte, 2008).

Mesoporous silica particles (MSPs) prepared by polymerization-induced colloid aggregation (PICA) exhibit good monodispersity and regular morphologies (Lee, Lee, Lee, Chang, & Hahn, 2003). The particle pore structure generally results from accumulation of the silica sol, so can be adjusted using sols of different sizes (Zhao, Yu, Guo, & Cheng, 2005). MSPs and bonded MSPs reportedly exhibit good chromatographic performance (Danielson & Kirkland, 1987). Commercial silica sols typically contain high total metal contents, and MSPs prepared from such sols generally contain many metal species. Thus, it is difficult to obtain high-purity MSPs from commercially available silica sols. Metals on the surface of silica-bonded

stationary phases cause peak tailing by chelating reagents during HPLC analysis. Undesirable physical and chemical reactions may also occur if impure MSPs are used as catalyst supports.

In the current study, a sol–gel process coupled with PICA was developed to produce high-purity MSPs. A nanometer-sized silica gel was first produced by the sol–gel process, and MSPs were then synthesized by PICA. The pore structure of the MSPs could be controlled by altering the sol–gel reaction conditions, and the MSP particle size could be adjusted using different PICA conditions. The MSPs were subsequently functionalized with dimethyloctadecylchlorosilane (C18) containing an eighteen-carbon aliphatic chain, by surface modification under hydrothermal conditions. The final materials were used as stationary phases in reverse phase-HPLC columns, and their separation performances were determined.

Materials and methods

Materials

Reagent grade ammonia, ethanol, tetraethyl orthosilicate (TEOS), acetone, toluene, diethyl ether, isopropanol, methanol, urea, formaldehyde (37%), HCl (Sinopharm, Shanghai, China) were

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Table 1
Specifications of the commercially available silica sol.

Brand	Diameter (nm)	Silica (wt%)	Stabilizer	Manufacturer
SW-25	10–20	25–26	Na ₂ O	Qingdao Haiyang Chemical Co., Ltd.

used to prepare the silica particles. The commercially available silica sol specifications are shown in Table 1. Particle silylation reactions were carried out with dimethyloctadecylchlorosilane (C18) (Fluka, Shanghai, China), in anhydrous toluene (Sinopharm) containing pyridine (Fluka) as the catalyst or acid acceptor. The HPLC mobile phase was prepared from HPLC grade methanol, acetonitrile (Sinopharm) and ultra-pure water (18.2 MΩ cm). Reagent grade uracil, nitrobenzene, naphthalene, fluorine, toluene, ethylbenzene, quinizarin, and amitriptyline (Kermel, Tianjin, China) were used as standard materials.

Synthesis

The silica sol was prepared by the sol–gel process. A given amount of ammonia, ethanol, and H₂O were added into a 250-mL round-bottomed glass reactor containing a magnetic stirrer at a temperature of 25 °C. 22.5 mL of tetraethyl orthosilicate (TEOS) was added. The hydrolysis/condensation of TEOS was monitored with a conductivity meter, eventually reaching an equilibrium value within 30 min. The suspension was stirred for another 12 h, to complete reaction. The solvent and catalyst were separated by vacuum distillation, and the silica sol was obtained.

The prepared silica sol, 15.7 mL of formaldehyde, 10 g of urea, and 135 mL of ultra-pure water were mixed in a 1-L Nalgene beaker. The pH was adjusted to 1.2 using HCl, and coacervation was initiated at 25 °C. The mixture became white and opaque within a few minutes, due to formation of particles of a silica-polymer complex. The solution was allowed to settle for 4 h, and the liquid was decanted off. The solid material was collected by filtration, washed with ultra-pure water and ethanol, and dried in a vacuum oven at 110 °C for 24 h. The solid product was then subjected to a staged heating process from 150 to 550 °C, to burn off the polymer. The particles were rehydroxylated by refluxing in 10% HCl for 24 h, and the final product MSPs was obtained.

MSPs were also synthesized from a commercially available silica sol, by a similar procedure. 23 mL of formaldehyde, 15 g of urea, 56 mL of SW-25 silica sol and 123 mL of ultra-pure water were added in a 1 L Nalgene beaker at 25 °C. PICA was initiated, the resulting mixture was treated, and the solid product (MSP-CS) was obtained as above.

Characterization

A droplet of the silica sol was deposited and allowed to dry on a copper grid, and observed by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). MSPs were observed by scanning electron microscopy (SEM, JSM-680LV, JEOL, Japan). The particle size and distribution were measured using a digimatic caliper (CD-15C, Mitutoyo, Japan). The monodispersity of the particles was described by the size distribution index (*U*), where a lower *U* indicates better monodispersity. Monodispersity is considered to be where *U* < 1.05. The average particle size (*D_n*) and the *U* of the silica particles were defined by statistics, according to:

$$D_n = \frac{\sum n_i D_i}{\sum n_i}, \quad D_w = \frac{\sum n_i D_i^4}{\sum n_i D_i^3}, \quad U = \frac{D_w}{D_n}.$$

N₂ adsorption–desorption isotherms were measured by a surface area and pore size analyzer (V-Sorb 2800P, App-one, China) at 87 K. Samples were first outgassed for 45 min at 423 K. Specific areas were calculated using Brunauer–Emmett–Teller (BET) theory, from the adsorption branches at relative pressure of 0.05–0.25. Total metal contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, Leeman, USA).

Modification

C18 was used to functionalize the MSPs, as previously described by Danielson and Kirkland (1987). 2.5 g calcined MSPs of diameter 5 μm were dried under vacuum at 120 °C for 5 h, and then dispersed in anhydrous toluene (120 mL) under N₂. 2.9 mL of anhydrous pyridine and 9.7 mL of C18 in 20 mL of anhydrous toluene were added. The mixture was refluxed for 12 h under N₂. The solid was collected by filtration, washed with toluene, acetone, acetone/H₂O, acetone, and diethyl ether. The C18-MSPs were obtained after drying at room temperature for 6 h, and then in an oven at 80 °C overnight.

Chromatographic tests

An HPLC system (P230 II, Dalian Elite, China) consisting of a quaternary pump, Valco injector with 20 μL sample loop, and variable-wavelength ultra violet detector was used for the test experiments. The original chromatographic column was substituted with a column packed with C18-MSPs. Packing was achieved using the slurry technique, with an HPLC slurry packer. The C18-MSPs were dispersed in isopropanol, and packed into a stainless steel column (4.6 mm internal diameter × 150 mm long) at 40 MPa. A standard mixture containing uracil, nitrobenzene, naphthalene, and fluorene was to be separated, using a mobile phase of methanol/water (85/15 v/v) at 0.9 mL/min, with detection at 254 nm.

The standard reference material 870 method (SRM870, 2002) was also used to characterize the chromatographic properties, including efficiency, void volume, retentiveness, and activity toward chelators and organic bases. The SRM870 method involves separating a methanol solution containing the organic compounds uracil, toluene, ethylbenzene, quinizarin, and amitriptyline. This mixture was separated in the column, using methanol/buffer (80/20 v/v) as the mobile phase at 1.0 mL/min, with detection at 254 nm and a column temperature at 23 °C. The buffer composition was 20 mmol/L potassium phosphate adjusted to pH 7.0.

Results and discussion

Physical characterization of MSPs

The influence of the catalyst used in the sol–gel process was examined, while all other conditions were held constant. Under acidic condition (S1, Table 2), linear oligomers initially formed, and the solution viscosity increased as the oligomer molecular chain length increased. A polymer film with a three-dimension network structure eventually formed, as shown in Fig. 1(a) (Titulaer, Jansen, & Geus, 1994). Under alkaline condition (S2, Table 2), TEOS was almost completely hydrolyzed to silicic acid before condensation started. The silicic acid concentration became supersaturated, upon which many primary silica nuclei formed and aggregated into stable particles (Wang et al., 2010). Fig. 1(b) shows that the silica sol prepared under base-catalyzed conditions consisted of uniform spherical particles of ~45 nm in diameter.

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