



Highly stable high performance liquid chromatography stationary phase based on direct chemical modification of organic bridges in hybrid silica

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ABSTRACT

Highly monodisperse 1,4-dimethoxybenzene-bridged organic/inorganic hybrid mesoporous spheres were synthesized by condensation of 1,4-dimethoxy-2,5-bis(triethoxysilyl)benzene using dodecylamine (DDA) and cetyltrimethylammonium bromide (CTAB) as co-templates. The spherical hybrid particles, which have specific surface area of 509 m²/g, pore volume of 0.8 cm³/g and average pore size of 63 Å, were characterized by elemental analysis, SEM, TEM, small angle X-ray scattering, Raman, FT-IR and nitrogen adsorption-desorption analysis. The hybrid material was further chemically modified with C12 chain group via formation of C–O–R bond, which is believed to be far more stable than traditional Si–O–Si bonding type at low pH condition. At the same time, the hybrid silica substrate has been proved to possess the improved chemical stability at high pH. In this way, combination of the hybrid silica substrate and this advanced modification method enable the stationary phase to be used in extended pH range. The chemical stability of this surface modified 1,4-dimethoxybenzene-bridged hybrid stationary phase was evaluated both at low pH (pH=0.95) and high pH (pH=11.0). Some acidic and alkaline pH chromatographic evaluations were performed to illustrate the advantages of the improved chemical stability of this packing material.

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1. Introduction

By far, silica-based materials are still the most commonly useful HPLC packing materials owing to their high chromatographic efficiency and excellent mechanical stability. In recent years, numerous improvements have been made on silica-based HPLC packing materials to deal with problems caused by either the silica supports or the bonded phases. However, contemporary silica-based reversed-phase (RP) HPLC packings still have two major limits. First, basic compounds always suffer from peak tailing and poor efficiency due to detrimental ionic interactions with acidic silanol groups [1–3]; second, the mobile phases are only allowed within the pH range of 2–8 due to the poor chemical stability of silica-based packings [4–8]. Peak tailing problem of basic solutes can be reduced by increasing the mobile phase pH above the analyte pK_a, where the analyte molecules will perform under ion suppression conditions [9–12], the same is true for the analyses of anionic analytes performed under low pH condition [12]. Nevertheless, when mobile phases are used with pH < 2 [4,13], the covalently bonded Si–O–Si organic ligands are susceptible to hydrolysis, and

with pH > 8, dissolution of silica substrate is substantially accelerated, which results in a loss of column efficiency and an increase in column back pressure [7,14]. While improving the chemical stability of silica particles is significant for extended pH chromatographic application, it is also a challenging task.

During the last decades, many chromatographers have put lots of efforts into improving the chemical stability of silica-based stationary phases [15]. Polymer-coated [16], horizontally polymerized [17,18], bidentate [5,13] and polar embedded stationary phases are typical examples. In recent years, a unique class of organic/inorganic hybrid silica materials have been developed, which is normally prepared by condensing alkoxyloxanes with monosubstituted XSi(OR)₃ or organic-bridged (R'O)₃SiRSi(OR')₃ [19–22]. Compared with inorganic silica materials, the columns packed with hybrid materials have increased chemical stability toward a broader pH range [15,19,22]. The most widely applied hybrid silica substrates are monomethyl-substituted [22] (condensation of MeSi(OEt)₃ and TEOS) and ethylene-bridged [15,19] (condensation of (EtO)₃SiCH₂CH₂Si(OEt)₃ and TEOS) series developed in recent decades. It was claimed that they could be used under mobile phase with pH value up to 10–11. Also, we have reported the phenylene-bridged hybrid organosilica spheres (PHS) [23,24], which is able to endure mobile phase with pH value up to 10. However, all of the surface modifications for hybrid particles were based on traditional surface bonding technology in the

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reported literatures. The organic ligands of all these stationary phases existed as Si–O–Si bonding type, which had already been proved to be susceptible to hydrolysis in the chemical environment of low pH. For examples, Kirkland et al. provided evidence that in acidic eluents the loss of bonded phase from a silica surface would occur by hydrolyzing and subsequently breaking the Si–O–Si bond [13]. This phenomenon was also observed in organic/inorganic hybrid packings. The XTerra C18 column which was packed with monomethyl-substituted hybrid silica particles lost about 20% of its initial retention after purging at pH 1.2 for 5 days, although it worked better than pure silica-based packings [22].

In organic/inorganic hybrid silica materials, the organic bridges are part of their porous framework. Surface modification can be carried out through modifying the organic moieties in bridged hybrid materials. For examples, sulfonation [25], amination [26] and formation of arenetricarbonyl complexes ($-\text{C}_6\text{H}_4\text{M}(\text{CO})_3-$, M = Cr, Mo) [27], have already been successfully achieved on phenylene bridged hybrid materials and applied as catalysts [28]. It should be noted that this kind of surface modification is totally different from the Si–O–Si–R bonding method, which widely adopted in the preparation of stationary phases. Compared with pure silica, organic/inorganic hybrid materials can be modified through a stable chemical bond derived from the organic-bridged groups. Loss of modified groups will not occur unless the whole structure of the porous material collapse. This surface modification method will be highly attractive for chromatographer, since it can lead to improvement of the chemical stability of RP stationary phase in extended pH range, particularly in low pH value conditions.

In order to combine highly stable hybrid silica matrix and acid-resistant bonding phase, we presented the preparation monodisperse 1,4-dimethoxybenzene-bridged hybrid organosilica spheres (MeO-PHS), whose embedded dimethoxybenzene moieties were able to be further modified by introducing C–O–R bond on the surface. In the first step, the –OMe group was converted to –OH. In the second step, the –OH group on the silica surface was modified through the formation of C–O–R ($R = \text{C}_{12}\text{H}_{25}-$) bond to generate a novel RP stationary phase. Combination of high stable hybrid silica matrix and this advanced chemical modification method results in both high acidic and alkaline stability of the RP stationary phase.

2. Experimental

2.1. Chemicals and materials

1,4-Dibromo-2,5-dimethoxybenzene, *N,N*-dimethyldecylamine (DMDA), was purchased from TCI (Shanghai) Development Co., Ltd. Chlorotriethoxysilane was purchased from Aldrich. Dodecylamine (DDA), cetyltrimethylammonium bromide (CTAB) and tetraethylorthosilicate (TEOS) were purchased from ShangHai Chemical Reagent Inc. of Chinese Medicine Group. Boron tribromide and 1-bromododecane were purchased from Aladdin Reagent Co. Ltd. (China). 2,5-Bis(triethoxysilyl)-1,4-dimethoxybenzene was synthesized according to the literature [29]. Spherical silica (particle size: 5 μm ; pore size: 10 nm; surface area: 270 m^2/g^{-1}) was purchased from Fuji Silysia Chemical Ltd. (Japan).

2.2. Synthesis and pore size expansion of monodisperse 1,4-dimethoxybenzene-bridged mesoporous spheres

DDA (7.90 g, 42.7 mmol) and CTAB (0.79 g, 2.2 mmol) were dissolved in co-solvent of ethanol (690 mL) and water (460 mL). To this solution, 0.90 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 wt.% solution) was added. Then, the silica source of 2,5-bis(triethoxysilyl)-1,4-dimethoxybenzene (10 g, 21.6 mmol) was added to the solution with vigorously stirring

for 30 min at 25 °C. After aging for 12 h in static conditions at 25 °C, the white precipitate was filtered out and washed with acetone and methanol successively, and then dried in air. Pore expansion of the as-synthesized material was performed by swelling agent in corporation method (the SWE method) reported previously [24]. 3 g of as-prepared dry solid was suspended in water (60 mL) emulsion of DDA (0.6 g), DMDA (3 g) in a Teflon-coated autoclave. After hydrothermal treatment at 135 °C for 24 h and removal of templates, the product was obtained and denoted as MeO-PHS.

2.3. Modification of 1,4-dimethoxyphenylene-bridged mesoporous spheres

Removal of the protecting group of MeO-PHS. MeO-PHS (2.0 g) was taken in dried CH_2Cl_2 (20 mL) and cooled with an ice bath. Boron tribromide (2.2 mL, 24 mmol, 1 mmol/L solution in CH_2Cl_2) was added to the suspension dropwise with continuous stirring for 30 min, after which the reaction mixture was brought to room temperature, stirred for an additional 24 h. Saturated solution of NaHCO_3 was then added slowly to quench the reaction. The solid was filtered out washed successively with acetone, water, acetone, and CH_2Cl_2 , and finally dried at 50 °C under vacuum overnight. This material was denoted as OH-PHS.

Etherification of OH-PHS. Sodium hydride (1.6 g, 40 mmol, 60% dispersion in mineral oil) was suspended in 25 mL dry DMF. OH-PHS (1.8 g) was combined with 1-bromododecane (9.96 g, 40 mmol) and tetrabutylammonium iodide (10 mg) in 25 mL of dry DMF. The NaH suspension was added dropwise to the silica/1-bromododecane mixture over 20 min, and then the mixture was stirred at room temperature for 48 h under argon. The reaction was then quenched by slow addition of 1% acetic acid solution. The product was filtered out and washed thoroughly using 1% acetic acid solution, water, acetone, and methanol successively. This material was denoted as C12O-PHS.

2.4. End-capping of silanol groups

1.5 g C12O-PHS was added to a three-necked round bottom flask and dried in vacuum oven at 130 °C for 12 h. 20 mL dry toluene, 0.6 mL dry pyridine and 3 mL trimethylchlorosilane were added to the flask. The suspension was refluxed for 12 h under N_2 atmosphere and cooled to room temperature. After filtration, the products were washed by toluene, acetone and methanol. This material was denoted as C12O-PHS-TMS.

For comparison, a stationary phase of C8-bonded pure silica matrix was synthesized according to previous literature [24]. This material was denoted as C8-S.

2.5. Material characterization

Nitrogen sorption experiments were performed on a Micromeritics Tristar II 3020 apparatus. The samples were dried at 200 °C under vacuum overnight prior to measurements. Surface areas and pore-size distribution were measured using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Elemental analysis was measured on an elemental vario EL III (Germany). Scanning electron micrographs (SEMs) were obtained on a JSM-6360LV instrument. Raman microscope spectrum was obtained on Renishaw Invia Raman microscope. FT-IR was taken on a Spectrum Nicolet 6700 FT-IR spectrometer (Thermo, USA). Particle size distribution was obtained on BT-9300H laser particle size analyzer. Transmission electron microscopy (SEM) was collected using a JEM2100 (JEOL, Japan) at an acceleration voltage of 200 kV. The X-ray diffraction (XRD) patterns were recorded on Rigaku D/max 2550 VB/PC diffractometer using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) operating at

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