



Spherical mesoporous silica particles by spray drying: Doubling the retention factor of HPLC columns

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ABSTRACT

Micrometer sized spherical mesoporous MCM-41 particles were synthesized to use as a packing material for High Performance Liquid Chromatography. Spray drying was used for the synthesis of the particles and this enables easy up scaling. The entire synthetic procedure was optimized to ensure optimum particle morphology while preserving a high surface area and acceptable yields. The resulting material, with an average particle size of 1.8 μm , a narrow size distribution and a large porosity was subsequently grafted with C18 groups, packed into column assemblies and evaluated by reversed phase HPLC. The packing remained stable during the entire series of HPLC analysis, which were performed (>300 runs). Moreover the high accessible surface area leads to superior retention factors (doubling the best performing commercial columns) opening prospects for, e.g., the analysis of difficult mixtures of highly polar components.

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1. Introduction

Since they first saw the light in 1992, MCM-41 silica materials and analogues are now widely available through various chemical suppliers [1]. Nevertheless, thus far the number of applications thereof has been relatively limited. Mesoporous materials show unique properties which can be beneficial for a wide range of applications. They are fairly easy to functionalize to yield heterogeneous catalysts or adsorbents for gas and liquid waste stream clean ups. An emerging field is the application of mesoporous thin films as low- k insulators, in superconductors and as solar-cells [2–6]. Although these benefits are mentioned in almost every contribution making use of these materials, still very few of them prove that they are in fact a better or a useful alternative to the commercially available materials they are to replace. In this work we demonstrate that mesoporous materials possess distinct benefits as packing materials for high end separations in HPLC (High Performance Liquid Chromatography). The use of particles with a highly uniform spherical morphology is important in a packed column as this results in a more regular flow profile and in minimal chromatographic peak broadening. The specific goal in this work is to create uniform spheres with a controlled and ordered mesoporosity together with a high surface area.

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The classical method to generate uniform spherical silica particles is the Stöber-method, which employs a water/alcohol/ammonia/tetraalkoxysilane system. Herein alcohol plays the role of a dispersing agent. In this way the silica condensation cores can grow in a freely dispersed way to generate disjointed spheres contrary to the cauliflower structures which are otherwise obtained [7]. This is still the most abundantly used methodology to produce silica spheres for HPLC columns. The original Stöber method, which introduces no ordered porosity in the particles, has also been modified, making use of surfactants, to generate mesoporous templated nanoparticles in this way. The only problem with this method is that the surfactant counter effects the dispersing role of the alcohol affecting the reliability of the approach [8–10].

Secondly an emulsion technique can be used to make silica spheres. Herein a non-ionic surfactant is used as an emulsifier to disperse the silica condensation cores, preventing them from inter-growing. However, most of these materials either have a poorly ordered pore system or no pores at all. Additionally most of the emulsion approaches generate spheres in the nanometer range, which is too small for chromatographic applications [11–13].

Thirdly a morphosynthesis route can be used to produce spheres with an ordered porosity. Herein preformed uniform silica spheres are added to a solution of surfactant and acid. After a certain reaction time the surfactant has templated an ordered pore system inside the spheres without destroying the spherical morphology. Although this seems an interesting approach it

actually leads to an additional step in the production of ordered mesoporous silica spheres [14].

A fourth method to induce spherical particle morphology is an aerosol assisted synthesis, during which the precursor solution is atomized inside a hot air stream.

MCM-41 was the first ordered mesoporous material to be successfully spray dried [15–21]. However, this is the first contribution in which the synthesis of MCM-41 analogues by spray drying is performed through a systematic approach which proves independent from the used machinery. Two different spray driers, with different nozzle types were used, both yielding the same results. The materials are not MCM-41 *stricto sensu*, as spray drying was not covered in the original patent [22,23], but we will show that our materials are structurally identical to MCM-41 and we will refer to them as spherical mesoporous ordered silica or spherical hexagonally ordered mesoporous silica or other variations. The analysis of the physical parameters that determine the morphology and the porosity of the materials leads to an independent optimization of these parameters. Mesoporous materials synthesized via spray drying follow an aerosol assisted evaporation induced self-assembly process (EISA) in which the solvent evaporation occurs within a matter of seconds. The speed of this process strains the reaction conditions.

First a systematic approach was used to investigate the influence of various relevant aspects on the synthesis of hexagonally ordered mesoporous silica spheres. After this preliminary approach these factors were subjected to an in-depth analysis to optimize the synthesis to obtain uniform spherical mesoporous particles. Hereafter the surface silanol groups were functionalized with a C-18 chain and subsequently packed in a narrow bore column and tested by reversed phase HPLC. They have proven to be at least as effective to obtain a very stable column packing for liquid chromatography and their retention is much larger when compared with commercial columns.

2. Experimental

2.1. Materials

Hexadecyltrimethylammonium bromide (99%) (CTAB), tetraethyl orthosilicate (98% reagent grade) (TEOS), dichloromethane (99.8%), hexane (99.9%), 2-propanol (99.9%, chromasolv), acetonitrile (HPLC grade), H₂O (LCMS grade) the HPLC testing solutes (uracil, caffeine, phenol, toluene, 1-phenyl-1-ethanone, 1-phenyl-1-butanone, 1-phenyl-1-pentanone, 1-phenyl-1-hexanone, 1-phenyl-1-heptanone, 1-phenyl-1-octanone, 1-phenyl-1-decanone, 1-phenyl-1-dodecanone, benzene, naphthalene, anthracene, fluoranthene, benzo[k]fluoranthene, methyl-4-hydroxybenzoate, ethyl-4-hydroxybenzoate, propyl-4-hydroxybenzoate, butyl-4-hydroxybenzoate) were of the highest purity and obtained from Sigma–Aldrich. Fuming hydrochloric acid 37 m/m% was purchased from Roth, anhydrous toluene (>99.9%) for the grafting was obtained from Acros. n-Octadecyldimethylchlorosilane (97%) was supplied by ABCR. All chemicals were used without further purification. Empty HPLC column assemblies (5 cm length, 2.1 mm internal diameter and with 0.5 μm mesh frits) were purchased from Restek.

2.2. Synthesis

The experimental setup comprises a mixing and a spray drying step. Spray drying was performed on a Buchi B290 with a two-fluid nebulizer connected to pressurized air. The heater inlet temperature was held constant at 493 K and the outlet temperature stayed constant at 398 K. The aspirator ran at a maximum air velocity of 40 m³/h. The nozzle gas flow and the solution feeding speed were

Table 1

The various reaction conditions.

	Solution flow rate (pump%)	H ₂ O ratio ^a	Stirring time (h)	Gas flow rate (L/min)	CTAB ratio ^a
Low	10	700	0.5	6	0.12
High	17	1400	1.5	8	0.24

^a Molar ratio compared to a TEOS:CTAB:H₂O:PrOH/BuOH:HCl (1:0.12/0.24:700/1400:10:5) solution.

variable factors during the scouting experiments. During the first step a solution of CTAB, H₂O, TEOS, HCl is mixed with 1-butanol at room temperature for a certain amount of time (see Table 1). Subsequently this clear mixture is fed to the spray dryer, resulting in MCM-41 powders which are collected by a cyclone separator. The particles are calcined under air at a heating rate of 1.5 K per minute from room temperature to 823 K and kept at this temperature for 6 h. After this the samples were analyzed with XRD, N₂-adsorption and SEM to obtain information about the porosity and the morphology.

2.2.1. Varying the surfactant/TEOS ratio

Only the surfactant/TEOS ratio was varied while the rest was kept constant. The composition of the mixture was TEOS:CTAB:H₂O:BuOH:HCl = 1:x:1400:10:5 where x equals 0.12, 0.21 and 0.24. The feeding speed and the gas flow were held constant at 3 mL/min and 8 L/min respectively.

2.2.2. Varying the H₂O/TEOS ratio

Here only the water/TEOS ratio was varied while the rest was kept constant. The composition of the mixture was TEOS:CTAB:H₂O:BuOH:HCl = 1:0.21:x:10:5 with x equal to 700, 1400, 2800, 5200 or 8400. The feeding speed and the gas flow were held constant at 3 mL/min and 8 L/min respectively.

2.2.3. Varying the gas flow

During this section only the gas flow was varied while the rest was kept constant. The composition of the mixture was TEOS:CTAB:H₂O:BuOH:HCl = 1:0.21:1400:10:5. The feeding speed was held constant at 3 mL/min and the gas flow was varied between 6, 8 and 10 L/min.

2.2.4. Up scaling to the synthesis of gram levels

The final step involved up scaling the approach and to test the robustness of the synthesis procedure. The molar composition of the solution was thereby: 1:0.21:8400:10:5 for TEOS:CTAB:H₂O:BuOH:HCl, which was also the final composition used for the manufacturing of the particles that were eventually functionalized and packed. The largest batch was spray dried from a 7.5 L solution, while the batches used during the development as described in the previous paragraphs varied between 63 and 793 mL. With this increased solution volume a larger type of spray drier was used, i.e. Mobil Minor from GEA Niro A/S with a rotary nozzle. The nozzle pressure was held constant at 4.5 bar, connected to the pressurized air. The solution pump was Watson Marlow 520U which was pumping at 6 rpm, corresponding to a flow rate of 27 mL/min for this solution. The inlet temperature of the spray chamber was kept constant at 473 K and the outlet temperature at 362 K.

2.2.5. C-18 functionalisation

n-Octadecyldimethylchlorosilane was used to functionalize the silanol groups on the surface of the spray dried mesoporous spheres according to a previously described procedure [24,25]. For every gram of silica, 1.2 g of n-octadecyldimethylchlorosilane

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