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Preparation and characterization – including in situ Small Angle X-Ray Scattering – of gas chromatographic capillary columns with mesoporous silica thin films as stationary phases

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ABSTRACT

In this study the preparation of various mesoporous silica thin films as new stationary phases for gas chromatography (GC) columns is presented. The synthesis was performed inside capillaries via a sol–gel process using a templating route. The as-obtained columns were found to be highly efficient for the fast separation of light n-alkanes (C1–C5) mixture; these columns exhibiting a normalized retention 30 times higher than that of a commercially available silica column used as standard. A particular effort was directed towards the characterization of the stationary phase physical features: thin film inspection by Scanning Electron Microscopy and, for the first time to our knowledge, in situ SAXS characterization using synchrotron radiation were used to study the impact of the pore-network structuration on the GC properties. Worm-like, cubic and hexagonal phases were observed for specific preparation conditions. Unexpectedly, the normalized retention relative to film thickness appeared higher with disordering of the pores network.

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1. Introduction

In the last decades, Gas Chromatography (GC) has become a key technique for the analysis of volatile compounds. Despite its central role, there is still a need for the development of new stationary phases in order to improve GC column performances, analysis throughput, column mass production and also the design of portable systems [1,2].

For the analysis of light alkanes and permanent gases, gas–solid chromatography, which uses solid adsorbents as stationary phase, is often preferred to liquid film stationary phase columns that fail to separate very volatile compounds. Traditionally, the solid stationary phase is packed into the columns and made of various adsorbing materials such as porous polymers, molecular sieves, carbonaceous materials, silica and alumina gel [3]. However efficiencies of such packed columns are poor. Alternatively monolithic columns, which were initially developed for high-performance electrochromatography or liquid chromatography, have recently been investigated for GC [4–7]. For example Korolev et al. have thoroughly studied them, successfully preparing monoliths made of silica, polydivinylbenzene or acrylate polymers. They demonstrated fast separation of light hydrocarbons and permanent gases but at the cost of relatively high back pressure.

PLOT (Porous Layer Open Tubular) columns are thus the most commonly used GC columns for permanent gases and light alkanes separation. PLOT columns use same adsorbent materials as those present in packed columns but they benefit from all the advantages of open tubular columns, i.e. greater efficiencies and faster separations with fewer instrument requirements (lower pressures). However developments are still required to improve columns performances, to produce shorter and thinner columns and to address new applications [8]. Indeed, in the case of silicon microcolumns, the development of stationary phases and deposition processes that can meet small section channel constraints is of huge interest [9–11]. The more common approach for coating solid adsorbents into capillary columns is similar to of liquid stationary phase, i.e. dispersion of the stationary phase in a solvent, insertion into the column and further solvent evaporation. However the as obtained stationary phase is quite thick (several μm) whereas faster

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analysis would benefit from thinner stationary films. Several alternative approaches, like sputtered silica or nanoparticles layer by layer deposition, were explored, but usually with limited chromatographic efficiency (low plate number) [12,13].

As suggested in literature precedents, the fine tuning of the stationary phase porosity (porous network structuration and pore size distribution) may influence the column performances by limiting, for instance, chromatographic peak broadening or asymmetry [14].

Indeed, since the 1990s, the versatility of the sol–gel process allowed the development of numerous mesostructured oxide based materials exhibiting a high degree of porous network organization and pore calibration [15]. Such materials are highly mesoporous (high surface area over $800 \, m^2/g$ and porous volume over 0.8 cm^3/g). Their pore sizes can be adjusted (from 2 nm to 30 nm) and the long range ordering of their porous network can be controlled. For instance, using different experimental conditions and structure directing agents (surfactants) during the sol–gel process, various pore structuration could be obtained: 2D hexagonal porous structures as in the famous MCM-41 mesoporous silica [16], but also various cubic phases (primitive, body centered or face centered) and 3D hexagonal phases [17]. These new materials were found to be very attractive for numerous applications such as catalysis, optic or separation [18].

In the field of gas chromatography, Malik and co-workers first reported on the use of sol–gel strategies for the development of stationary phases for open tubular capillary columns, with polydimethylsiloxane or polyethylene glycol based phases [19,20]. A sol–gel process using a templating route was then used by Patrushev et al. to develop mesoporous stationary phases [14,21]. Higher loading capacities of such columns with respect to disordered commercial silica gel homologues were found. This result was attributed to the higher surface area of the mesoporous stationary phase. However the high thickness of the as-obtained films (several μm) would prevent its use in microcolumns. Moreover, no detailed characterization of the porestructuration of such porous stationary phases was given in this study. Indeed, studies on flat surfaces have shown that the gelation process was strongly dependent on the evaporation rates of solvents (ethanol and water) and thus on the coating conditions (spin coating or deep coating, ambient temperature and humidity) [22,23]. Thus the porous structure obtained in capillary columns may be really different from that obtained on flat samples using the same conditions. But up to now, no direct characterization of the porosity in the silica film deposited in GC column was undertaken.

In this context, we have developed here an original process based on the Evaporation Induced Self Assembly (EISA) approach [24] to deposit highly porous silica films into small inner diameter capillary columns. Different experimental conditions and structure-directing-agents (SDA), cationic surfactants and several non-ionic block co-polymers, were used to generate stationary phases. The as-obtained GC columns were tested for light alkanes separation and their performances were compared to classical commercially available PLOT columns. A particular effort was directed toward the characterization of the stationary phases into the columns in order to correlate the physical features of silica films (texture, pore organization, thickness...) to the GC performances.

2. Materials and methods

2.1. Reagents

Hydrochloric acid (HCl) standard solution (1 M), tetraethyl orthosilicate (TEOS), reagent grade, 98%, and absolute ethanol >99.8%, were purchased from Sigma–Aldrich.

Table 1
Summary of the different mesoporous stationary phase formulations that have used for the study; the retention factor and the number of theoretical plates per meter experimentally measured for propane at 30 °C are also given (values are the average of the results obtained for at least 2 columns); finally the averaged thickness measured from SEM inspection is also given.

SDA	SDA/Si	Propane retention factor	Plate number/m (m^{-1})	Averaged thin film thickness (nm)
CTAB	0.14	1.15 ± 0.02	3400	102 ± 34
	0.1	1.21 ± 0.01	3500	106 ± 24
	0.05	1.66 ± 0.01	2100	93 ± 28
F68	0.01	1.45 ± 0.19	3200	138 ± 73
	0.005	2.05 ± 0.05	3000	87 ± 28
	0.003	2.79 ± 0.04	2900	100 ± 13
	0.0017	2.81 ± 0.05	1700	77 ± 9
F127	0.005	1.78 ± 0.01	3300	81 ± 21
	0.0025	1.58 ± 0.03	3100	57 ± 19
P123	0.005	1.83 ± 0.01	3500	122 ± 14
	0.0025	1.30 ± 0.07	2400	60 ± 18

Cetyltrimethylammonium bromide (CTAB), Pluronic F68 (EO_{73}-PO_{28}-EO_{73}), Pluronic F127 (EO_{101}-PO_{56}-EO_{101}) Pluronic P123 (EO_{20}-PO_{70}-EO_{20}) from Sigma–Aldrich were used as SDA.

2.2. Sol preparation

The sol composition was prepared based on the work of J.P. Boilot and co-workers [25,26], following an EISA strategy as first used by C.J. Brinker et al. [24]. The pre-hydrolysis of the silica precursor, namely TEOS ($Si(OC_2H_5)_4$), was performed in acidic conditions. TEOS, water (adjusted at pH 1.25 using hydrochloric acid) and ethanol were mixed with a molar ratio of 1(TEOS):5 (H_2O):3.8 (Ethanol). The sol was slightly over-stoichiometric in water. Under these conditions, hydrolysis ends in a few seconds. The sol was then aged at 60 °C for 1 h, under constant steering.

SDA was dissolved in ethanol for at least 30 min in an ultrasonic bath. This ethanolic SDA solution was added to the sol just before the coating. The resulting dilution of the sol in ethanol has been adapted and fixed for all samples to a water:ethanol ratio of 3:1, as low dilution factors maximize the film thickness. Table 1 summarizes the final SDA/Si ratios of the different samples.

2.3. Film deposition process

Columns were prepared from fused silica capillaries purchased from Polymicro (100 μm inner diameter – 375 μm outer diameter). Prior to the coating, the internal surface of the capillaries was activated by flushing a solution of water, ethanol and sodium hydroxide (weight ratio 1:1.05:0.01). Then the capillaries were rinsed with distilled water and dried under nitrogen flow. 1.5 m-long segments were used during the coating process. 25 cm-long pieces were cut at both extremities before characterization and GC tests.

The deposition of the stationary phase into the CG columns was performed using dynamic coating process, where a solution plug is directly pushed inside the column by the drying gas under pressure, as described in [27]. A simple experimental set-up was used to inject the solution plug through the capillaries before pushing the solution excess with a dry nitrogen flux, with only a few handlings: a 2 mL glass vial partly filled with the sol solution was used. Two capillaries entered the vial through a septum. The first capillary was connected to the nitrogen gas line with a pressure regulator to control the pressure inside the vial. The second one was the capillary