



Thermal pretreatments of superficially porous silica particles for high-performance liquid chromatography: Surface control, structural characterization and chromatographic evaluation[☆]



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ABSTRACT

This study reports the impact of thermal pretreatment between 400 and 1100 °C on superficially porous silica particles (e.g. core-shell, fused-core; here abbreviated as SPP silica). The different thermally pretreated SPP silica (400 °C, 900 °C and 1100 °C) were chemically bonded with an octadecyl chain under microwave irradiation.

The bare SPP silica, thermally untreated and pretreated, as well as the chemically bonded phases (CBPs) were fully characterized by elemental analysis, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and solid state cross polarization magic angle spinning (CP-MAS) ²⁹Si NMR. The chromatographic properties of the overall set of C₁₈-thermally pretreated SPP silica stationary phases were determined using the Tanaka test. Complementary, the simplified Veuthey test was used to deeply study the silanol activity, considering a set of 7 basic solutes with various physicochemical properties. Both tests were also performed on different commercial SPP silica columns and different types of bonding chemistry (C18, Phenyl-hexyl, RP-amide, C30, aQ). Multivariate data analyses (hierarchical cluster analysis and principal component analysis) were carried out to define groups of stationary phases with similar chromatographic properties and situate them in relation to those commercially available. These different C₁₈-thermally pretreated SPP silicas represented a wide range of stationary phases as they were spread out along the score plot. Moreover, this study highlighted that the thermal pretreatment improved the chemical stability of the SPP silica compare to untreated SPP silica and untreated porous silica. Consequently, higher thermal pretreatment can be applied (up to 900 °C) before functionalization without destruction of the silica matrix. Indeed, a significantly lower dissolution of the thermally pretreated SPP silica under aggressive conditions could allow the use of the corresponding functionalized stationary phases at high temperature (60 °C) with good lifetime of the columns.

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1. Introduction

Silica is largely used as a support of the stationary phase in High-Performance Liquid Chromatography (HPLC) because of its numerous advantages, including its large specific surface area and its mechanical stability. The particles can be manufactured as small

spheres with a narrow size distribution and a controlled pore size, which makes a good starting material for preparing efficient HPLC stationary phases.

To increase the chromatographic efficiency and improve the productivity, several methods are currently used such as Ultra-High-Performance Liquid Chromatography (UHPLC) with fully porous sub-2 μm particles, which may or may not be coupled with High-Temperature Liquid Chromatography (HTLC), or the use of monolithic stationary phases. Among these methods, the use of superficially porous silica particles (SPP silica) is another alternative requiring neither specific apparatus nor complicated transfer

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methods [1]. Moreover, various chemistries of superficially porous silica particles are commercially available, which is not currently the case for the monolithic stationary phases.

Generally, the analysis of basic molecules is still a challenge in HPLC because of the peak tailing resulting from the strong interactions between these molecules and the different residual silanols present onto the silica surface (hydrogen bonding, ion interactions). Because the ligands (e.g., commonly: C₈, C₁₈), generate steric hindrance, the functionalization is not complete. As a result, some silanols are still accessible, leading to a non-univocal molecular mechanism of retention, which affects the efficiency by peak tailing. Many strategies were developed to hinder the silanol accessibility of the porous stationary phases, such as vertical and horizontal polymerization [2–6], applying a polymer coating [7–11], and the use of lateral bulky chains [12–14] or propylene bridges for bidentate phases [15,16]. The silanols can also be blocked by the addition of a polar embedded group (PEG phases), such as an amide, carbamate, urea, sulfonamide, quaternary ammonium, or an ether group, to the alkyl structure [17–21]. Recently, a new generation of mixed octadecylsilane (ODS) bonded phase called Charge Surface Hybrid (CSH) was developed to improve the peak symmetry in a low ionic strength mobile phase by realizing a first coating with charged compounds [22]. Alternatively, Pesek and coworkers modified the silica structure before the final bonding step by forming a monolayer of SiH groups on the surface [23].

In addition, a second treatment of the silica surface is commonly used to reduce the number of residual silanols after the first attachment of the main ligand [24]. This end-capping involves the bonding of a smaller organosilane such as hexamethyl-disilazane, trimethylsilyl-imidazole or trimethyl-chlorosilane. Another strategy based on the blockage of the remaining silanol groups during the chromatographic analyses was proposed by Reta and Carr [25], who added divalent metals and amines in the mobile phase as silanol blocking agents. Alternatively, Hill [26] and Vervoort et al. [27] used triethylamine and longer hydrocarbon tertiary amines to block the activity of the silanols.

Lastly, another method consists of controlling the silanol population before any derivatization or chromatographic analyses. Halfpenny et al. [28] proposed to use ultraviolet laser radiation to dehydroxylate the surface with controlled irradiance. This dehydroxylation can also be achieved by a thermal treatment of the silica surface [29,30]. Three types of silanols are present on the silica surface; the vicinal silanols that interact through hydrogen bonds, the geminal silanols for which two hydroxyl groups are linked to the same silicon atom and finally, the isolated single silanols. It is established that the type of silanol differs on the silica surface depending on the temperature. Indeed, temperature treatments transform silanols into more hydrophobic siloxane bridges by dehydroxylation [31]. Some authors used the thermal process to selectively rehydroxylate the silica surface for better homogeneity [32,33] and may include an acid treatment [34]; Boudreau and Cooper [35] described a dehydroxylation without rehydroxylation. Different stages can be distinguished during a thermal treatment. At a temperature lower than 400 °C, the dehydration occurs as multilayers of water physically adsorbed on the silica surface are removed. The siloxane bonds formed are unstable, and the silanols can be restored by exposure to water. However, above 400 °C, the siloxane bonds are much more stable, such that even after 2500 column volumes, no rehydroxylation was noticed by Sunseri et al. [36]. Van der Voort and Vansant [30] as well as Zhuravlev [37] also closely studied the surface chemistry of amorphous silica and noticed that between 190 and 400 °C, the first silanols to disappear were the vicinal silanols, favored by the hydrogen bond already created that facilitates the departure of the water molecules. This process is readily reversible upon the introduction of an excess of water, and the complete rehydroxylation takes place by splitting of the weakened

strained siloxane bridges. Then, geminal silanols are totally removed at 400 °C, and the amount of vicinal silanols decreases from 0.8 to 0.2 $\mu\text{mole m}^{-2}$ between 200 °C and 800 °C; finally, the isolated single silanol amount is maximized from 400 °C. Those remain at the surface at higher heating temperatures (1 $\mu\text{mole m}^{-2}$ at 800 °C) [30], where shrinkage and sintering of the silica matrix is noticed [37]. It is necessary to heat to 1200 °C to achieve the complete removal of all silanol groups (only siloxane bridges), but the surface fusion forms a solid network that is chromatographically unusable [36].

Different thermal treatments have already been applied to totally porous silica gels. Maws and Engelhardt showed the influence of the type of silanols on the selectivity of the stationary phase [38], and the ability to reduce the residual silanols was reported by Sunseri et al. [36]. El Rassi and Gonnet [39] found that the most convenient phase for the analysis of apolar solutes was the bonded 300–400 °C pretreated silicas, which presented the maximum coverage. On the contrary, the most suitable phase for the analysis of polar solutes was the bonded 600 °C pretreated silicas, which presented the minimum concentration of hydroxyl groups.

To our knowledge, the present study is the first detailed study of the effect of thermal pretreatments on superficially porous silica particles. Starting from the same superficially porous silica batch, the aim of this work is to control the type of silanol groups on the silica surface before applying the C₁₈ grafting under microwave irradiations, as previously described [40]. Each step was followed by DRIFT, and the degree of coverage was determined by elemental analysis. The type and relative abundance of silanol groups, as well as the covalent bonding of the C₁₈-chains to the different silicon atoms were determined by ²⁹Si CP/MAS and HPDEC solid state NMR, as well as ¹³C, ¹H solid state NMR. The general chromatographic properties of the columns packed with the C₁₈-thermally pretreated SPP silica were studied via the Tanaka test [41]. In addition, the modified [42] and simplified Veuthey test [43] was performed to study the residual silanol activity toward basic solutes in detail and to determine whether a thermal treatment is to be favored for a better base-deactivation of the final SPP silica stationary phases. Starting from the same SPP silica batch, functionalized with the same organosilane, the effect of thermal pretreatment on the final stationary phases was investigated in terms of selectivity and hydrophobicity.

2. Experimental

2.1. Chemicals

The SPP silica particles were provided by Interchim (Montluçon, France). Their specific surface area, nominal particle diameter and pore diameter were 126 m² g⁻¹, 2.6 μm and 90 Å, respectively. Bis(dimethylamino)(dimethyl)octadecylsilane (ODMAS), bis(dimethylamino)(trimethyl)silane (DATS) and bis(dimethylamino)dimethylsilane (BMMS) were obtained from ABCR (Karlsruhe, Germany). Toluene, benzylamine (B), phenol (P), caffeine (C) and uracil were supplied by Sigma–Aldrich (Saint-Quentin Fallavier, France). Butylbenzene (BB), triphenylene (T), o-terphenyl (O) were purchased from Alfa Aesar (Schiltigheim, France). Procainamide hydrochloride, pyridine, anhydrous quinine and L-nicotine were purchased from Acros Organics (Geel, Belgium) and penbutolol hydrochloride by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sodium nitrate was supplied by Carlo Erba (Val-de-Reuil, France). Chloroprocaine hydrochloride was supplied by BASF Orgamol Pharma (Saint-Vulbas, France). Carvedilol was supplied by TCI (Tokyo, Japan). Methanol, acetonitrile and pentylbenzene (PB) were purchased from VWR (Fontenay-sous-Bois, France). For the chromatographic tests, all solvents were of HPLC grade. The columns (4.6 mm × 50 mm × 2.6 μm) were

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