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Functionalized SBA-15 mesoporous silica in ion chromatography of alkali, alkaline earths, ammonium and transition metal ions

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ABSTRACT

The retention properties of a SBA-15 mesoporous silica functionalized with $-(CH_2)_3COOH$ groups, synthesized by a co-condensation route, were investigated for the ion chromatography of different cationic species. A systematic study on the effect of different eluent compositions containing non-complexing (methanesulfonic acid) or complexing (oxalic or pyridine-2,6-dicarboxylic acids) eluents, in the presence of organic modifiers (CH_3CN, CH_3OH, CH_3NH_2) on the retention of cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, NH_4^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}) chosen as model analytes and for their environmental importance, allowed us to elucidate the mechanisms (cation-exchange or complexation) involved in the retention on the SBA-15 phase. For the first time separations of cations on SBA-15 based stationary phases are investigated, providing the basis for further development of mesoporous silica chemistry for in-flow ion-exchange applications.

1. Introduction

Ordered mesoporous silicas, templated by supramolecular aggregates, are characterized by high specific surface areas and ordered arrays of uniform mesopores [1]. They are widely investigated for applications in, for instance, catalysis, drug delivery, and nanocomposites [2]. In the last decade, several studies dealing with the adsorption and separation capabilities of mesoporous silica have been published. Some of the advantages of the use of mesoporous structured materials in separation methods, mainly liquid chromatography, are their high surface area, high pore volume, and adjustable pore size. These features improve column permeability, molecular selectivity [3] and hence make mesoporous materials promising supports for chromatographic stationary phases. Notwithstanding, the synthesis of mesoporous silica with homogeneous size and shape of the particles, which are required properties in determining column efficiency and separation performance, is still a challenge [4,5]. Mesoporous silicas were studied as chromatographic support only for HPLC reversed phase applications and, for instance, phenyl-functionalized ethane–silica [6] was tailored for the chromatographic separation of neutral organic compounds (*e.g.* benzene, naphthalene). Octyl modified mesoporous silicas were used and compared with commercial silicas carrying on similar functionalization, for the separation of uracil, benzene, naphthalene and biphenyl [4,7].

Among mesoporous materials, SBA-15 silica-based materials have larger pore size which allows for an even better control of adsorption/desorption processes [8,9]. Moreover, SBA-15 materials have a rich population of silanol groups [10] which allows the loading of functional groups, *e.g.* alkyl groups, for a surface modification. SBA-15 silica-based materials functionalized with C18 moieties, received attention as chromatographic stationary phase for proteins [2], while, recently, when functionalized with immobilized aminoalcohol, SBA-15 have found application as potential chiral stationary phase for chiral ligand exchange chromatography [11].

As far as ion-exchange interactions with mesoporous materials are concerned, SBA-15 functionalized by 2-diethylamino-ethanol was used as weak anion exchange matrix for chromatography to purify Der f2 allergen [12], but to the best of our knowledge, applications of properly functionalized mesoporous silica as cation-exchanger for chromatographic and separative purposes are lacking, with the unique applications being only adsorption measurements in batch conditions for a wide variety of transition metal ions [13,14] and more recently for Na^+, K^+, Cu^{2+}, Ca^{2+} [15] through sulfonic acid functional groups.

In parallel, the evolution of chemistry for column technology in cation-exchange chromatography is currently oriented towards selective weak exchangers with carboxylic or phosphonic groups

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that can avoid the use of relatively concentrated acidic eluents, and long analysis run, typical of sulfonic cation-exchangers.

In a previous paper we synthesized a SBA-15 sample functionalized with $-(CH_2)_3COOH$ groups by co-condensation from tetraethylorthosilicate and 4-(trethoxysilyl)butyronitrile [16] which exhibited different recoveries for metal ions (*i.e.* Ag^+, Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}) in batch experiments. The different recoveries were interpreted as differences in selectivity of the material towards metal ions; this property is particularly desired if the material must be used as stationary phase for chromatographic separations. The aim of this work is the evaluation of the performance of the –COOH functionalized SBA-15 material as a stationary phase for the retention and/or separation of different classes of cationic analytes. Therefore, alkali (Li^+, Na^+, K^+), alkaline earths (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}), ammonium and transition metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}) were selected as model cations for their importance in different environmental compartments. Systematic studies on the effect of different eluent compositions on the retention factors of analytes were performed, evaluating the different mechanisms involved during the separation. According to the results obtained, separations for the selected classes of cations are shown.

This is the first application of mesoporous materials, and in particular of SBA-15 based mesoporous silica, as cation-exchanger support in ion chromatography.

2. Experimental

2.1. SBA-15-COOH synthesis and characterization

The synthesis was carried out as described in [16], using Pluronic P123 triblock copolymer as surfactant, tetraethylorthosilicate (TEOS) and 4-(triethoxysilyl)butyronitrile, $(EtO_3)Si\text{-}BuCN$, acting as $-(CH_3)_2COOH$ precursor. The final molar composition is: 0.9 TEOS:0.017 P123:2.9 HCl:202.6 H_2O:0.1 $(EtO_3)Si\text{-}BuCN$. To remove the template and to hydrolyse the –CN groups to carboxylic groups, the procedure reported by Schüth et al. [17] was followed: 1.0 g dried sample was re-dispersed in 120 mL of 48% H_2SO_4 solution, and the mixture was heated to 368 K for 1 day. The product was washed with water until the eluent became neutral, then washed with acetone.

Specific surface area, pore size distribution, and pore volume have been evaluated by nitrogen adsorption/desorption isotherms (Quantachrome Autosorb1). Data are collected in Table 1.

The BET specific surface area has been calculated using a cross-section value for the nitrogen of 13.5 Å, as suggested in literature for hydrated silica surfaces [18]. The internal surface of the SBA-15-COOH sample, in fact, is expected to be highly hydrated because the material was not calcined (the surfactant was removed by extraction).

Pore size distribution has been calculated using NLDFT model for cylindrical pore. As far as particle size and shape are concerned, particles are elongated with size of a few microns. From particle size analysis (Particle Sizer Malvern 3600D) they appear to form aggregates of about 20 μm.

The acidic capacity is 0.98 mequiv./g (RSD% = 1.4), whereas the acidic dissociation constant (pK_a), measured according to Soldatov [19], is 4.74. The amount of –COOH groups measured by differential thermo gravimetric analysis (Mettler Toledo thermogravimetric analyzer with a heating speed of 10 K/min under air in a flow of 50 mL/min) was 1.1 mmol/g.

Table 1
Textural features of SBA-15-COOH.

Sample	$S_{BET}{}^{a}$ (m^2/g)	Pore volume (cm^3/g)	$D_{DFT}{}^{b}$ (nm)	$w_{1/2}{}^{c}$ (nm)
SBA-15-COOH	400	0.88	9.9	1.8

[a] Specific surface area.
[b] Pore diameter calculated according to Density Functional Theory model.
[c] Peak width at half-max of pore size distribution.

2.2. Column packing

The SBA-15-COOH was suspended in CH_3OH and stirred. A PEEK tube (50 mm × 4 mm i.d.) was slurry packed by a Minipuls 3 peristaltic pump (Gilson Inc., Middleton, WI, USA) set at 13 rpm. The column was subsequently equilibrated with H_2O at 0.5 mL/min under high pressure by connecting a peek tube of 2.6 m with an internal diameter of 0.08 mm (0.003 in., 1 μL/ft volume), generating a backpressure of about 2850 psi/m at 1 mL/min (Dionex Co., Sunnyvale, USA). The slurry packing and the equilibration were continued until the column was completely filled. The operating backpressure of the column at 0.5 mL/min ranged between 1130 and 1200 psi. The void volume of the column, evaluated as the water deep in the chromatogram, was 0.6 mL.

2.3. Instrumentation

For the study on alkali and alkaline earths, an ICS3000 (Dionex) chromatograph equipped with a 10 μL loop was used. Detection was performed with suppressed conductivity using a CSRS Ultra-II 2 mm suppressor in the external water mode. After preliminary experiments performed at 1 mM methanesulfonic acid, eluent flow rate was set at 0.1 mL/min; this value ensured the best efficiency for the analytes. According to the eluent concentration, the instrument automatically set the current for the suppression (the values ranged from 1 to 2 mA for 0.1 mL/min eluent flow rate).

The study on transition metal ions was performed on a 4000i model ion chromatograph (Dionex) equipped with a Rheodyne injector Model 7125 (100 μL loop) and with a VDM-II variable-wavelength UV–Vis detector. Eluent flow rate was set at 0.5 mL/min. Spectrophotometric detection was performed at 520 nm after a post-column reaction with 0.4 mM 4-(2-pyridylazo)-resorcinol (PAR) in 0.3 M $NaHCO_3$, 1 M 2-methylaminoethanol, and 0.5 M NH_4OH, 25% in water. The flow rate for the post-column reagent was set at 0.5 mL/min.

2.4. Reagents and solutions

Deionized water (18.2 MΩ cm resistivity at 25 °C) from a water purification system (Milli Q Academic, Millipore) was used for the preparation of the eluents and standards. Stock solutions (1000 mg/L) of analytes were prepared from Titrisol standard solutions (Merck, Darmstadt, Germany). Ammonium standard solution (10,000 mg/L) was prepared by dissolving the chloride salt in water. Methanesulfonic acid (MSA) 70% in water and $LiNO_3$ were from Aldrich (Missouri, USA), acetonitrile, methanol (HPLC grade), and pyridyne-2,6-dicarboxylic acid were from Fluka (Sigma–Aldrich, MO, USA). Oxalic acid was from Merck. Prior to use, all eluents were filtered through a 0.22 μm filter.

For the preparation of the post-column reagent, 4-(2-pyridylazo)-resorcinol (PAR) and 2-methylaminoethanol were from Fluka, $NaHCO_3$ from Riedel de Haen (Sigma–Aldrich), and NH_4OH from Acros Organic (Geel, Belgium).

2.5. Column washing protocol and column performance

Whenever the elution of the analytes was not observed, before changing the eluent composition, and after each day of measurements the column was washed with 7 mL of 0.1 M HNO_3 (Merck) at 0.5 mL/min. The re-equilibration of the column was performed with at least 10 mL eluent solution at the desired flow rate and until a stable baseline was obtained. This procedure ensured a good