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Review

Novel supports in chiral stationary phase development for liquid chromatography. Preparation, characterization and application of ordered mesoporous silica particles

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ABSTRACT

Recent advances in the development of new materials are having a major impact on analytical chemistry. For example, the unique properties of ordered mesoporous silicas (OMSs) have been shown to enhance the analytical performance of many existing techniques or allow new, exciting ones to be developed. Likewise, the introduction of organo-functional groups makes OMSs highly versatile and enables them to perform specialized tasks, such as the separation of chiral compounds. This review provides an overview with the most relevant achievements in the preparation of OMS particles functionalized with chiral selectors. In addition, some examples from the last fifteen years regarding the analytical applications of functionalized OMS for chiral separations by high-performance liquid chromatography, ultra-high pressure high-performance liquid chromatography and capillary electrochromatography have been reviewed.

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1. Introduction

The discovery of ordered mesoporous silica-based materials (OMSs) in the early nineties marked the beginning of research in the development of high surface area porous materials with controlled porosity [1,2]. This discovery has aroused very interest in several research communities and has also favored numerous collaborations between scientific of different areas such as chemistry, physics, biology, materials, medicine, etc. All research concerning these materials has been driven with different targets related to fundamental aspects for their preparation or their potential applications [3]. Choice structuring agents and experimental conditions has quickly been identified as key factors for controlling pore size and particle geometry of OMSs. Subsequent chemical modification of these materials with organo-functional groups allows functionalized OMSs, which are potentially useful in those processes where the specific and selective physisorption of different kinds of compounds is required, to be obtained [4]. As a result, functionalized OMSs have emerged as being particularly important in diverse aspects of human activity and can be used for environmental, analytical and biomedical applications, amongst others, by incorporating specific organo-functional groups depending on the desired application requirements. On the other hand, organic functions

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can be introduced directly in the material backbone as pendant or main chain groups by co-condensation with mono- and/or bisilylated organosilane precursors. Periodic mesoporous organosilicas (PMOs) with organic groups integrated in the framework have offered a new family of OMSs with very interesting surface and mechanical properties and improved hydrothermal stability.

Functionalized OMSs have been studied in our research group for numerous applications as catalysis [5,6], drug release [7,8], electroanalysis [9–11] and environmental remediation [11]. Some advantages of such OMSs over non-template homologues (amorphous silica) have been reported: (1) better accessibility to binding sites due to open framework and regular structure, (2) high adsorption capacities because of its numerous functional groups, (3) better selectivity and (4) faster adsorption rates [11]. On the other hand, OMS particles have garnered increasing interest in separation technologies due to their high surface area, high porosity, controllable macro-morphologies and tailorable nanostructures. The dramatically higher surface area of OMSs in comparison to commercially available chromatographic grade silica enhances resolution of molecules by increasing capacity factors to allow effective separations of analytes. Up to date, a variety of OMSs have been proposed as stationary phases (SPs) or supports to prepare SPs for solid phase extraction [12,13], gas chromatography [14], size-exclusion chromatography [15] and HPLC [16,17]. The use of OMSs for chiral stationary phases (CSPs) preparation could improve enantioselectivity and resolution with respect to the use of conventional silica grafted with the same chiral selector. For these reason, the applicability of OMSs in chiral chromatography and electrophoresis has been explored in some works. Fig. 1 shows some chiral selectors used to prepare CSPs for this purpose.

In this review, a brief introduction to the most relevant achievements in the preparation of OMS particles functionalized with chiral selectors is presented. In addition, some recent examples from the last fifteen years regarding the analytical applications of such functionalized OMSs for their use in chiral high-performance liquid chromatography (HPLC), ultra-high pressure high-performance liquid chromatography (UHPLC) and capillary electrochromatography (CEC) are reported.

2. Preparation and characterization of chiral ordered mesoporous silicas

The exceptional OMSs characteristics and the growing number of its potential application drive to the continuous development of new and more attractive synthetic routes. These new materials have opened the door to interesting analytical applications for example in chiral chromatography and electrophoresis [18–20]. The new applications of these materials are limited to a good control of particle size and morphology, so the ability to produce particles with defined shapes and monodispersed sizes would increase the spectrum of chromatographic analytical applications for OMSs.

Different techniques are used to characterize functionalized OMSs in order to obtain information regarding their structural, morphological and textural properties and information about the functional groups attached to the silica. For example, the pore structure is traditionally measured by low-angle powder X-ray diffraction (XRD) and by transmission electron microscopy (TEM). Similarly, the pore volume, pore size distribution and specific surface area are usually measured by N_2 adsorption–desorption, which reveals type IV isotherms according to IUPAC classification that are characteristic of mesoporous materials with a high surface area and a narrow pore-size distribution. The wall thickness of the materials is usually determined by combining the XRD data and the average pore diameter obtained from N_2 adsorption–desorption analysis. The particle morphology and size is measured by scanning electron microscopy, SEM. NMR spectroscopy (especially ^{13}C and ^{29}Si MAS-NMR) and FTIR spectroscopy are powerful techniques for verifying the incorporation of functional groups by enabling the simultaneous identification of multiple functionalities as well as the different types of silanol groups and the effectiveness of the covalent bonding of the ligand to the silica framework. Other common measurements include elemental chemical analysis and thermogravimetric analysis (TGA), which is used to quantify the incorporation of organic groups and to estimate the thermal stability of the hybrid material.

Commercial HPLC and CEC columns are usually packed with silica particles with no ordered porosity. The packing materials exhibit low surface areas and large pore size distribution which are provided mainly by the inter-particle porosity. In the field of chromatographic separations, OMSs could have a promising application as SPs, in which crucial parameters are uniform particle-size, high surface area and well-defined pore size. The high surface area of OMSs can give rise to a high retention of some selected analytes to enhance the chromatographic efficiency for multi-component separations. In addition to the textural properties, the morphology of the packing materials also plays an important role, and as a result, many efforts have been devoted in order to improve this aspect. According to the previous reports, morphology can be tuned by altering the reaction parameters such as pH, surfactant concentration, the mixture of co-solvent, co-surfactant and electrolyte, etc. [21–23]. In this sense, the use of particles with uniform spherical morphology is important in a packed column, as this result in a more regular flow profile and in minimal chromatographic peak broadening.

The progress made recently in the synthesis of spherical silica micro/nanomaterials has been discussed in detail in several excellent review articles and will therefore not be discussed here in detail [24]. The classical method to generate uniform spherical silica particles that employs a water/alcohol/ammonia/tetraalkosysilane system is the Stöber's method. Herein the alcohol plays the role of a dispersing agent. This is still the most abundantly used methodology to produce silica spheres for chromatographic columns. The original Stöber-method, which introduces no ordered porosity in the particles, has also been modified, making use of surfactants, to generate mesoporous template nanoparticles in this way [25]. Secondly, morpho-synthesis route can be used to produce spheres with ordered porosity. Herein preformed uniform silica spheres are added to a solution of surfactant and acid. After a certain reaction time the surfactant has template an ordered pore system inside the spheres without destroying the spherical morphology [26]. A third method to induce spherical particle morphology is an aerosol assisted synthesis, during which the precursor solution is atomized inside a hot air stream [27].

One of the most advantageous properties of OMSs is the ease with which it can be functionalized with a variety of moieties in different regions of the particle. The introduction of functional groups makes OMSs highly versatile and enables them to perform specialized tasks. Two main approaches have been developed to chemically bind functional groups: (a) the post-synthesis, or "grafting", method and (b) the co-condensation, or "one-pot", method. The type and functionality of the silane employed for surface modification is very crucial. For example, modification of the mesoporous surface with alkyl chains provides the possibility: (i) tailor the accessible pore size or the mesoporous solids, (ii) to increase the surface hydrophobicity, (iii) to passivate the silanol groups, and (iv) to protect the framework against hydrolysis [16]. The high surface area of OMS is accompanied by a high amount of potential surface binding sites. Apart from attachment of the organic components at the outer particle surface, the large pore size gives access to binding sites at the pore interior. As a result, materials with high material loading can be obtained.