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Review article

Free silanols and ionic liquids as their suppressors in liquid chromatography

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ABSTRACT

In this review, we will firstly discuss the types and the general properties of silica, focusing on the silica support used in chromatography and capillary electrophoresis. Additionally, the characterization of functional groups (silanols and siloxanes) will be considered in terms of activity of the stationary phases. We will then discuss physical chemistry of the stationary phases applied in liquid chromatography and capillary electrophoresis. The use of ionic liquids as a silanols' suppressors will be presented in the next parts of the study, along with the examples of specific applications. The review is completed with conclusions and an outlook for the future developments in the area of analytical applications of ionic liquids.

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1. Silica materials for liquid chromatography and capillary electrophoresis

Silica and its derivatives are widely used as major stationary phase material in capillary electrophoresis and in all types of liquid chromatography, like normal phase liquid chromatography (NP-HPLC), reversed phase liquid chromatography (RP-LC) or hydrophilic interaction liquid chromatography (HILIC) [1–3]. Silica is commonly used as initial material to obtain bonded stationary phases, where different chemical groups are introduced, because of its potential to be easily modified, especially by silanization, in order to obtain solid support with desirable physicochemical properties [4].

Silica is an amorphous, non-crystalline material, widely applied in analytical chemistry due to the specific physical properties. The main advantage of silica is its chemical and mechanical stability, rapid mass transfer and a good load capacity, what is strictly connected with silica porous structure and morphology [2,3,5,6]. The porous morphology of silica maximizes the surface area, which provides an increased sorption capacity of stationary phase [3]. High mechanical stability makes use of silica convenient, especially in liquid chromatography, where the analysis is carried out at high pressure. Due to porous morphology of silica, the surface area is maximized, what provides an increased sorption capacity of stationary phase. On the other hand, the size and shape of the pores, limit surface penetration by the analytes. Heterogeneity and activity of silica support can be described by both, surface and structure heterogeneity. Structural heterogeneity is well characterized by amount of pores and both their type and shape, what directly determines the skeleton of the silica. The pore volume, surface area and pore size distribution are found as major property determining factors. The pore shape is associated with the ratio of the siloxanes and silanols and strictly related to the SiO₂ skeleton [3]. Surface heterogeneity is modified by different functionalities bound to siloxanes and silanols and well characterized by amount, type and shape of pores, which directly determines the skeleton of the silica.

In reference to the modern polymeric materials, silica is still more advantageous due to its mechanical stability and compatibility with a wide spectra of solvents. Stationary phases with pore size of 10 nm are recommended for the analysis of small molecules. For this kind of material, the specific surface area is 200–400 m² g⁻¹. In case of high molecular mass compounds' analysis, the silica support with pore size of 30 nm and specific surface area 100 m² g⁻¹ is recommended. For the choice of stationary phases, a fundamental rule is: with the increase of pore size, the specific area is decreased [7]. An important advantage of the silica support is the possibility to modify and reduce the size of particles, what results in improving column's efficiency and finally may lead to reduce the limit of detection (LOD) and the limit of quantification (LOQ) values [7–9].

Mechanical resistance of silica results in a maintenance of very thick pore walls. Its proper modification allows for a good penetration of alkyl chains, what can be provided by the larger pore diameter and pore volume, defined by the specific surface area. Also, from the retention coefficient point of view, pore size distribution and specific surface area are crucial.

Pore size distribution is described by both specific pore volume and its distribution in silica sol matrix [10]. In practice, the optimal retention and mass exchange is obtained [11]. Porous silica can be also characterized by the high degree of solvolysis, which is an affinity to be covered by the solvents [3]. The main disadvantage of silica-based stationary phase materials is a narrow range of pH (2.5–9), in which separation of analytes can be carried out. The remedy against this disadvantage was proposed by the introduction of hybrid stationary phases, which have an improved support's stability. Hybrid stationary phases are formulated by the coupling the best properties of silica and organic polymers. Their synthesis

is very similar to silica phase formulation and is based on agglomeration into the spherical organic-inorganic hybrid particles.

One of the parameters factor strongly influencing stability of stationary phase at high pH is presence of the bridges. Wyndham et al. reported that in case of hybrid stationary phases, the chemical stability is excellent and much improved in reference to unbonded hybrid materials [12]. Preparation of bridges results in increased resistance to hydrolysis.

By the use of two types of components: raw silica and several types of organic polymers, the stability increases up to pH 12 [3,12–14]. For that reason hybrid phases, composed of organic and inorganic material, are recommended to be used at high operation pH [15,16]. Hoffmann and Fröba [17] presented detailed, full of examples description of hybrid silica particles in their tutorially instructive review. Characterization of Organic-Inorganic Nanocomposite Materials (OINM) is also given in the paper published by Sayari and Hamoudi [18]. This type of material is commercialized in the XTerra[®] and XBridge[®] columns.

Silica can be obtained in several ways. The well-defined synthesis can be done when characteristic features, like: the size of particles, pore sizes, load ability and surface area, can be well controlled [3,19]. The major problem connected with the use of silica as a stationary phase has been its purity. Nowadays, widely used silica gel is of a very high quality, where contamination is extremely reduced. As was reported by Stella et al. [8], this parameter strongly affects retention reproducibility, accuracy and repeatability of the chromatographic parameters. On the other hand, the contamination of silica may naturally occur or be purposely introduced through the synthesis of desired stationary phases [2].

Although silica has a lot of advantages, there is still a lack of detailed knowledge on the mechanism of retention of individual analytes by this material. Peak tailing phenomena are often observed, even if amine quenchers are used as modifiers of the mobile phases [19].

1.1. Preparation of porous silica

Nowadays several methods for silica preparation can be used. Three of them are the most important: sol gel methodology, reverse microemulsion and high temperature flame decomposition [1,3,16,17]. The choice of preparation method is strictly connected with the type of silica which is to be obtained. Briefly, silica can be divided into porous and nonporous subtypes. According to this division, three types of the particles can be highlighted, namely spherical, irregular and pellicular. However, irregular particles are no longer used.

For the porous silica, spherical and irregular particles are typical. Nonporous silica surface is composed of the pellicular particles and the monolithic ones [8].

Reverse microemulsion method is used for nanosilica preparation. In this case, nanoparticles are grown inside the cavities. The silica is synthesized from silicon alkoxides with a catalyst present. The base catalyzed hydrolysis reaction is carried out in reverse microemulsions, what influences new silica nuclei formation. The disadvantage of this reaction is its high cost and problematic removal of the catalyst [22]. Polyethoxysilane method, as well as the sol gel method, is recommended for rods, spherical or irregular particles' preparation. Silica obtained with this method is slightly contaminated with trace metals and is characterized by a low resistance to hydrolysis.

High temperature flame hydrolysis is carried out in order to obtain the silica powder with required properties. The method is based on the hydrolysis of silica tetrachloride [23].

The sol gel polymerization reaction is found as safe, benign and convenient one [23]. Its two-step protocol is based on two types of reaction: hydrolysis and condensation, and it results in Si-O-Si

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