Synthesis of hydrophobic resorcinol–formaldehyde xerogels by grafting with silanes

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ABSTRACT

Hydrophilic organic xerogels were transformed into hydrophobic materials by treating them with hexamethyldisilazane. This transformation was performed by a simple one-pot process without modifying the previously designed porosity of the xerogel, at very soft operating conditions (80 °C and atmospheric pressure) in the absence of catalyst or any other additional compound. Hexamethyldisilazane reacts with dangling hydroxyl surface groups, blocks the oxygen with methylsilane groups, and prevents the formation of hydrogen bonds with water molecules. The reaction proposed was corroborated chemically by X-ray photoelectron spectroscopy and thermogravimetric analysis coupled with a mass spectrometer. The porous structure of the organic xerogel determines the minimum time for the surface modification due to steric hindrance. Therefore, the former hydrophilic surface of the organic xerogel may be transformed into a hydrophobic one by a simple process, thus leading to the possibility of designing not only the porous structure but also the surface chemistry of the resorcinol–formaldehyde xerogels to fit the requirements of an application.

1. Introduction

Resorcinol–formaldehyde (RF) organic xerogels with a predetermined and purpose-designed pore texture can be obtained by selecting suitable physical and chemical variables during the synthesis process [1–3]. The use of microwave radiation as a heating source as an alternative to conventional synthesis offers the possibility of obtaining a tailored porous structure by a simple, fast, and cost-effective method suitable for producing RF xerogels on a large scale and has led to an increase in interest in these polymers [4].

Although the physical conditions used during the synthesis process may affect the porosity of the RF xerogels [5,6], the size and volume of their pores are mainly determined by the following chemical variables: (i) the pH of the precursor solution [7]; (ii) the dilution ratio [8], i.e., the reactant/solvent ratio; (ii) the R/F molar ratio [9]; and (iv) the percentage of methanol used as stabilizer in the formaldehyde solution [10]. RF xerogels are usually thermally treated in an inert or reactive atmosphere to produce carbon materials called carbon xerogels or activated carbon xerogels [11,12], which are useful for many applications because of their thermal and chemical stability. Under adequate synthesis conditions, these carbon materials preserve the porous structure of the RF precursors. The combination of these variables offers a wide range of possible porosities, thereby enabling the RF and carbon xerogels to be used in several very different applications (e.g., hydrogen

storage, thermal insulation, as electrodes in supercapacitors, and as catalytic supports) [13–16].

RF xerogels not only have the advantage of a purpose-designed porosity but also of a very rich surface chemistry (i.e., a large oxygen surface group content) [17], making them suitable for a wide range of applications [18,19]. Moreover, high-temperature posttreatments are not required for RF xerogels, thus leading to a notable reduction in the manufacturing costs. Furthermore, the high concentration of hydroxyl groups, which covers the surface of RF xerogels, provides them with a high hydrophilicity, which attracts moisture from the air, while their large pores improve their water sorption capacity, making them suitable for use as desiccant materials [17]. RF xerogels could also be used as thermal insulators because by tailoring their pore size and volume, it is possible to minimize their convective and conductive heat transfer capacities [20]. In this case, a hydrophilic surface in RF xerogels would be a disadvantage because the adsorbed water increases the conductivity of the material considerably; therefore, it would be mandatory to modify the original surface chemistry of RF xerogels to be used in this particular application. A hydrophobic surface is also clearly preferable when RF xerogels are used in applications such as adsorption or absorption of organic liquids and oils, transportation of nonpolar liquids in the nanoscale range in chemical and biotechnological applications, and adsorption of some toxic substances [21–22]. In these cases, the reversibility of the process itself would be even promoted by a

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reversibility of the surface chemistry of the materials.

In short, the possibility of tailoring the porosity (i.e., pore size and volume) of RF xerogels for a specific application is the main advantage of these synthetic materials. Nevertheless, the surface chemistry of RF xerogels may also play an important role, and the possibility of controlling their hydrophilic or hydrophobic nature will also be a determinant of their optimal performance in a specific application.

Several reports on a wide range of procedures for modifying hydrophilic surfaces into hydrophobic ones are already available in the literature. Some authors [23,24] performed such surface modifications by using colloidal silica particles and fluoroalkylsilane as a silylating precursor in sol–gel processes. Another option reported in a previous study [25] is the preparation of a two-tier roughness surface using silicon, followed by the fluorination of the silicon surface. Other authors used dopamine to perform this in imitation of the technique of mussel coating [26], while few others used the chemical vapor deposition techniques [27] or plasma etching treatments [28]. Such hydrophobic polymeric surfaces can be produced by several techniques (i.e., layer-by-layer deposition, electrodeposition, electropolymerization, plasma and laser treatments, electrospining, etc. [29]), most of which are quite complex and tedious processes. Therefore, although it is possible to modify the surface nature of materials, this modification usually results in a considerable decrease in the cost-effectiveness of the materials.

Silica gels have hydroxyl groups covering their surface, which makes them a suitable and very commonly used desiccant material. The surface modification of silica gels has also been studied. The most common way of obtaining hydrophobic silica gels is to introduce methylsilane groups into the wet gel covering the surface, although other procedures such as postsynthesis treatments in liquid or gas phase can also be used [30,31]. The aims of such surface modifications are to prevent the collapse of pores during the drying step [32,33], improve the diffusion of certain solvents [34,35], and increase the durability of the material [36], among others. However, it is worth to be noted that these modifications usually modify the structure of the silica gel along with their surface chemistry. The compounds most commonly used to modify the surface of silica gels so that they become hydrophobic materials are trimethylchlorosilane (TMCS) [26,37], trimethyl-methoxylated (TMMS) [28,38], and hexamethyldisilazane (HMDZ) [32,39]. Moreover, these silanes are also commonly used for the protection of alcohols in organic chemistry synthesis [40]. The ideal protecting group for an active hydrogen moiety such as alcohol would be one that could be introduced in a high yield and remain stable in certain conditions but could be selectively removed in a high yield in other conditions without modifying other functional groups present in the organic molecule. However, this kind of treatment with silanes always needs special operating conditions and the use of catalyst to promote the protection reaction.

The aim of the present work is to modify the hydrophilic surface of RF xerogels without (i) using complex processes that may affect the cost-effectiveness of the RF xerogels, (ii) without changing the controlled structure of the designed RF xerogels, and (iii) without using any other additive or catalysts that may affect the purity of the RF xerogels. These aims, to the best of our knowledge, have not been achieved before. To this end, RF xerogels were treated with silanes. To evaluate the possible effect of the pore size of the xerogel on the grafting process, two RF xerogels with very different porosities were evaluated and compared depending on the effectiveness (hydrophobic strength), time of treatment required, and treatment durability over time.

2. Experimental section

2.1. Synthesis of RF xerogels

Two RF xerogels with average pore sizes of ca. 60 and 6000 nm (i.e., OX-60 and OX-6000, respectively) were evaluated for grafting with silanes.

To obtain xerogel OX-60, 16.33 g of resorcinol (Indspec, 99%) was dissolved in 83.36 mL of deionized water until complete dissolution under magnetic stirring. Subsequently, 100.31 mL of formaldehyde (37 wt% in water, stabilized by the addition of 12.5 wt% of methanol, supplied by Merck) was added. The pH of this solution was 3.25, and the proportions selected corresponded to a dilution ratio of 5.7 (i.e., the molar ratio of the total solvent to the reactants) and an R/F molar ratio of 0.12. In the case of OX-6000, 43.71 g of resorcinol (Indspec, 99%) was dissolved in 110.38 mL of deionized water until complete dissolution under magnetic stirring. Subsequently, 45.90 mL of formaldehyde (37 wt% in water, stabilized by adding 0.7 wt% of methanol, supplied by Química S.A.U) was added. To this precursor solution, drops of a 5-M NaOH solution (prepared from AnalaR Normapur, 99.9%) were added until a pH of 5 was obtained. The proportions selected corresponded to a dilution ratio of 8 and R/F molar ratio of 0.7.

Each precursor solution was placed in a microwave oven (in-lab designed and constructed [4]) at 85 °C for 3 h to allow gelation and curing to occur. After the formation of the polymeric structure, all excess water was eliminated by heating the gel in the same device continuously until a mass loss of 50 wt% was attained. This drying step lasted ca. 2 h. Each material was kept in the oven at 100 °C overnight to remove any traces of moisture and unreacted compounds to obtain a completely stable material.

The final material was ground and sieved to < 212 μm to obtain a homogeneous powder suitable for the treatments.

2.2. Grafting with silanes

The following silanes were used for the RF xerogel grafting process: TMCS (Merck, > 99%), TMMS (Merck, > 98%), and HMDZ VLSI selectipur (BASF). All the silanes were used in the treatments as received. Suspensions of 8 g of each RF xerogel in 100 mL of each silane compound were stirred at 80 °C and atmospheric pressure. Aliquots of the resulting material were extracted at different reaction times to measure the progression of the reaction. To remove any residual or nonreacted compounds from the porous structure of the samples, all the samples were degasified at 120 °C and vacuum overnight before any characterization. Furthermore, the samples were washed with hexane prior to the degasification procedure, to improve the elimination of physisorbed compounds; however, no differences were observed between washed and unwashed samples.

2.3. Sample characterization

2.3.1. Porous properties characterization

Before characterization, the samples were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and 120 °C overnight to remove any humidity and other physisorbed gases. The textural properties were characterized by nitrogen adsorption–desorption isotherms, mercury porosimetry, and density analysis.

The nitrogen adsorption–desorption isotherms were measured at − 196 °C using a *Tristar 3020* (*Micromeritics*) device. The pore volume and mean pore size were determined by mercury porosimetry, using an *AutoPore IV 9500* (*Micromeritics*) from atmospheric pressure up to 228 MPa. The range of pore sizes was from 5.5 to 2000 nm. The surface tension and contact angle were 485 mN m^{-1} and 130°, respectively, and the stem volume was between 45% and 60% in all the analyses. In the low-pressure step, the samples were evacuated up to 6.7 Pa, and the equilibration time used was 10 s. To determine the bulk density and the percentage of porosity of the samples, a *Geopyc 1360* (*Micromeritics*) device was set to a Dryflow of 0.8 g and a sample volume of around 50% of the total volume. A chamber with an internal diameter of 12.7 mm and a strength of 28 N for 20 cycles with a conversion factor of 0.1284 (cm^3 mm^{-1}) was used.