



On the desiccant capacity of the mesoporous RF-xerogels



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ABSTRACT

Resorcinol-formaldehyde xerogels are ideal desiccant materials since the high concentration of hydroxyl groups on their surfaces confers on them a high hydrophilicity, which adsorbs moisture from their surroundings and their large porosity provides them with a high water sorption capacity. In this study, the porosity of organic xerogels was tailored by adjusting the proportion of methanol in the precursor solution in order to optimize their desiccant capability. It was found that, although an increase in microporosity improves the performance of the desiccant, mesoporosity is a more important property for this application. Organic xerogels are excellent desiccants which are able to adsorb more than 80% of their own weight in moisture and function efficiently for more than 3000 h, when their porosity is optimized. This is a great improvement on the commonly used silica gels that become saturated after only 150 h and can only adsorb a maximum of 40 wt % of their own weight in moisture. Moreover, RF xerogels have the advantage that they are organic materials resistant to acid attack and this allows them to be used in processes where conventional inorganic desiccants would rapidly deteriorate.

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1. Introduction

Resorcinol-formaldehyde (RF) gels have been the most widely studied nanoporous organic gels in recent years [1–3]. However, other precursors can be used to produce materials with similar properties [4–9]. The synthesis process of these polymers consists of three steps: gelation, curing and drying. Depending on the type of drying method used in the synthesis process, (i.e., supercritical drying, freeze-drying or evaporative drying), they are classified as aerogels, cryogels or xerogels, respectively [10,11]. In this study, microwave radiation was used as heating source to synthesize the xerogels described, as it is a simple, fast and cost-effective method to fabricate RF-xerogels in just one step using only one device [12].

The widely recognized advantage of RF xerogels is that it is possible to obtain materials whose porosity can be designed for a specific application by adjusting the variables used during the synthesis process (i.e., the pH of the precursor solution, dilution ratio, RF molar ratio, etc.) [13–16]. This versatility, in combination with the fact that they are light and cheap to produce, makes them suitable for a wide range of applications [17–21].

As already pointed out in a previous study, organic xerogels can be used as desiccant materials [22]. Any desiccant material, whose

behaviour is determined by surface interactions and not by chemical reactions [23–25], requires two main properties to ensure its effectiveness [26]: i) hydrophilicity, i.e., its high affinity towards water and ii) a good sorption capacity, i.e., an ability to retain a large volume of water. In the case of RF xerogels, the high concentration of hydroxyl groups on their surfaces provides them with a high hydrophilicity that attracts surrounding moisture through hydrogen bonding, and their large porosity gives them their high water sorption capacity. Their hydrophilicity and suitability for use as desiccant materials have been demonstrated in a previous work [22]. However, in that study only two samples were evaluated and compared with a silica gel, a mesoporous xerogel and a macroporous RF xerogel with pore sizes of 10 and 2100 nm, respectively. There is a huge difference in pore size between 10 and 2100 nm, and although pore size would seem to be the determinant factor for the performance of a desiccant, mesopores being more effective than others, there is still a need for pore-size optimization. Therefore, further studies on the influence of mesopore size on the desiccant behaviour of RF xerogels are required, as optimization of the mesopores is essential in light of the increasing use of desiccant materials for different applications in recent years [25,27–29]. Moreover, the optimization of desiccant performance in combination with the chemical resistance of these RF xerogels (i.e. in acid or basic media), their light weight and their production in just one-step (without the need for any post-treatment or a large number

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of steps in the production line), make these materials highly cost-effective and competitive for scaling up.

Accordingly, in this work the influence of porous properties, in the mesopore range, on the water adsorption capacity of RF xerogels is studied in order to optimize their effectiveness as light-weight organic desiccants.

2. Experimental

2.1. Synthesis of organic xerogels

Organic xerogels were obtained by a process described in detail elsewhere [22]. Briefly, resorcinol (R), and formaldehyde (F) were mixed at a R/F molar ratio of 0.3. Water was added at a dilution ratio of 5, and the pH of the precursor solutions was adjusted to 5 using a 0.1 M NaOH solution (Titripac, Merck). As previously reported, the methanol (MeOH) content of formaldehyde solutions plays a determinant role in the formation of the porosity [14]. For this reason, formaldehyde solutions with: 2, 4, 13, 20, 30 and 40% of MeOH were used in order to obtain different porosities. As the MeOH content is the only difference between the samples, the percentage of methanol is used in the nomenclature proceeded by OX in reference to the organic xerogel.

2.2. Sample characterization

Before characterization, the samples were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and 120 °C overnight in order to remove any humidity and other physisorbed gases.

2.2.1. Porous properties

The porosity of the samples was characterized by means of nitrogen adsorption-desorption isotherms and mercury porosimetry.

The nitrogen adsorption-desorption isotherms were measured at –196 °C in a Tristar 3020 (Micromeritics) device. S_{BET} , micropore volume and pore size distribution were determined from the N_2 adsorption branch, by applying the Brunauer-Emmett-Teller equation, Dubinin-Raduskevich equation and DFT method, respectively. Total pore volume was estimated from the amount of nitrogen adsorbed at $p/p^\circ = 0.99$.

Total pore volume and pore size were determined by means of mercury porosimetry, using an AutoPore IV 9500 (Micromeritics), which is able to measure from atmospheric pressure up to 228 MPa. In this study, the lowest limit of mesopores detectable by this apparatus was 5.5 nm. In accordance with the findings of previous studies [10], no alterations in the macro and mesoporosity were observed during the carbonization process (Fig. S1a). Therefore, the organic xerogels were thermally treated under an inert atmosphere (700 °C, 2 h) before mercury porosimetry characterization in order to avoid compression problems arising from the low mechanical resistance of these materials [30]. Fig. S1 in the supplementary material shows the problems of mercury porosimetry characterization of the organic samples due to their poor mechanical properties.

The bulk density and percentage of porosity of all the samples studied were determined by means of a Geopyc 1360 (Micromeritics) densitometer. A chamber with an internal diameter of 12.7 mm and a strength of 28 N over 20 cycles with conversion factor of 0.1284 ($\text{cm}^3 \text{mm}^{-1}$) was employed. The chamber was filled with 0.8 g of Dryflow and a sample volume of ca. 50% of the total volume.

2.2.2. Moisture adsorption capacity

For measuring the overall capacity of water vapour adsorption and kinetics, samples with a 2–3 mm particle size were kept in a

sealed vessel in conditions of 100% humidity at 25 °C. Weight changes were recorded until a constant value was obtained.

On the other hand, water vapour adsorption-desorption isotherms were also evaluated by a volumetric method at 25 °C using a Hydrosorb 1000 multigas instrument (Quantachrome). These isotherms were repeated five times for each sample in order to evaluate its regeneration capacity and the potential influence on moisture adsorption of the re-used desiccants. Samples were outgassed at 100 °C under vacuum for 3 h in the same analysis tube between subsequent water vapour isotherms.

2.2.3. Microscopy

A Zeiss DSM 942 scanning electron microscope was used to obtain micrographs of the RF xerogels. The samples were attached to an aluminium tap using conductive double-sided adhesive tape. An EDT Everhart-Thornley secondary electron detector, programmed to operate at an accelerating voltage of 25 kV, was employed for all the characterizations.

2.2.4. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) was applied to evaluate the surface chemistry of the RF xerogels. A Nicolet FTIR 8700 fitted with a DTGS detector was employed. The data were recorded between 4000 and 400 cm^{-1} , over 64 scans at a resolution of 4 cm^{-1} .

3. Results and discussion

In a previous work [22] it was observed that xerogels of large pore size (macropores of ca. 2100 nm) show a poorer water adsorption capacity than those with a narrow mesoporosity (ca. 10 nm). Nevertheless, there are many possible pore sizes between these two options, and given that optimal water adsorption capability seems to be in the mesopore range, the search for a good desiccant should be based on finding the optimal mesopore size.

Table 1 shows the porous properties of RF xerogels synthesized with formaldehyde solutions with different concentrations of methanol. It can be observed that just by varying the methanol content mesopore materials with pore sizes of 8, 22 and 51 nm for samples OX-20, OX-13 and OX-4, respectively, can be obtained as well as a macroporous sample with narrow macropores centred at 79 nm (OX-2). Thus, the lower the concentration of methanol used, the higher the total pore volume and pore size achieved with the result that the density of the materials is reduced and their porosity is increased. The role of the methanol in the formaldehyde solution is to serve as a stabilizer, i.e. to prevent the formaldehyde molecules from precipitating. However, the methanol also acts as a retardant of the polymerization reaction between formaldehyde and resorcinol, which delays the crosslinking step and causes an increase in the size of the nodules (Fig. 1a), generating wider pore inter-clusters and therefore less dense materials. As the methanol content increases, the nodules formed during the polymerization also decrease (Fig. 1b and c) together with the pore size, resulting in denser materials.

It should also be mentioned that an excess of methanol during the synthesis of RF xerogels may result in such a weak structure that it may collapse during the drying step. This is the case of sample OX-40, which shows no porous properties (see Table 1).

Previous studies suggest that the methanol concentration has an influence only on meso and/or macroporosity, but not on micropore volume [14]. However, the nitrogen adsorption-desorption isotherms in Fig. 2 show that the samples synthesized with very high concentrations of methanol experience an increase in volume adsorbed at low relative pressures, which indicates an increase in micropore volume and therefore, in the BET surface area (see

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