



Desiccant capability of organic xerogels: Surface chemistry vs porous texture



Isabel D. Alonso-Buenaposada^a, Esther G. Calvo^a, M.A. Montes-Morán^a, J. Narciso^b,
J. Angel Menéndez^a, Ana Arenillas^{a,*}

^a Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

^b University of Alicante, Department of Inorganic Chemistry, Apartado 99, 03080, Spain

ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form

31 May 2016

Accepted 3 June 2016

Available online 7 June 2016

Keywords:

Water sorption

Desiccant materials

Xerogels

Hydrophilic materials

ABSTRACT

Resorcinol-Formaldehyde xerogels are organic polymers that can be easily tailored to have specific properties. These materials are composed of carbon, hydrogen and oxygen, and have a surface that is very rich in oxygen functionalities, and is therefore very hydrophilic. Their most interesting feature is that they may have the same chemical composition but a different porous texture. Consequently, the influence of porous characteristics, such as pore volume, surface area or pore size can be easily assessed. In this work, a commonly used desiccant, silica gel, is compared with organic xerogels to determine their rate and capacity of water adsorption, and to evaluate the role of surface chemistry versus porous texture. It was found that organic xerogels showed a higher rate of moisture adsorption than silica gel. Pore structure also seems to play an important role in water adsorption capacity. The OX-10 sample, whose porosity was mainly composed of micro-mesoporosity displayed a water adsorption capacity two times greater than that of the silica gel, and three times higher than that of the totally macroporous xerogel OX-2100. The presence of feeder pores (mesopores) that facilitate the access to the hydrophilic surface was observed to be the key factor for a good desiccant behaviour. Neither the total pore volume nor the high surface area (i.e. high microporosity) of the desiccant sample, is as important as the mesopore structure.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Organic gels are nanoporous materials that are obtained by the polymerization of hydroxylated benzenes and aldehydes in the presence of a solvent following Pekala's method [1]. Most organic gels presented in literature are synthesized using resorcinol (R) and formaldehyde (F) as precursors and water as solvent [2–5], although other precursors and reaction media can be used [6–9], to produce materials with different properties. In general, three main steps are involved in the formation of the organic gel: gelation, curing and the drying step. Depending on the drying method applied to remove the solvent, gels are classified into three main categories: aerogels, cryogels and xerogels where supercritical drying, freeze-drying and evaporative drying are employed, respectively [5,10–15]. In this study, microwave radiation was used as heating source throughout the entire synthesis process to

produce RF xerogels by means of a simple, fast and cost-effective methodology [16,17].

Over the last few years, organic and carbon xerogels have been demonstrated to be materials of great added value owing to the fact that their porosity can be controlled and designed by adjusting the synthesis variables, both physical (i.e. temperature, time of synthesis, etc.) [2,16] and chemical (pH, dilution, R/F ratio and percentage of stabilizer contained in the formaldehyde solutions) [17–22]. In addition to the large number of variables that need to be controlled, it has been shown that there exists a synergy between them. For this reason, statistical programs have been applied to allow the simultaneous study of all of these variables, allowing to designed porous properties for specific applications [18,21].

Not only is an appropriate porosity necessary for obtaining an optimum material for a specific application, but the surface chemistry also plays an important role. Most of the applications of RF xerogels are based on its carbonized form, for example: electrode material for supercapacitors, hydrogen storage, catalysis, heavy metal adsorbents, etc. [3,23–28]. As the structure of carbon xerogel is mainly made up of carbon colloidal chains (with a C

* Corresponding author.

E-mail address: aapunte@incar.csic.es (A. Arenillas).

content of up to 95%), sometimes the material is doped with heteroatoms, or chemically treated to change the surface chemistry and improve its behaviour for a specific application [29–32].

The surface chemistry of organic xerogels is different to that of their carbonized counterparts [20]. When polycondensation between resorcinol and formaldehyde takes place, a high concentration of hydroxyl groups remains on their surfaces. Thus, the chemical composition of a generic RF organic xerogel could be 65% wt. C, 5% wt. H and 30% wt. O. However, heat treatment of organic xerogels to obtain a thermally stable material (i.e. carbon xerogel) causes these labile oxygen surface groups to be released, leading to a more condensed carbonaceous structure consisting of about 95% wt. C, the remaining being divided between H and O [23]. Therefore the surface chemistries of organic and carbon xerogels are totally different, even though their designed porosities may be similar [33,34].

Desiccant materials are hygroscopic solids that induce or sustain a state of dryness in the surrounding air [35]. In order to be considered a good desiccant porous material, it not only needs to be hydrophilic but also highly adsorbent, which are two different concepts [35]. Its hydrophilicity refers to its affinity to water, while its adsorption capacity depends mainly on its porosity. For example, some carbon-based materials, though considered as hydrophobic, nevertheless have a high water sorption capacity due to their high porosity, but their rate of adsorption is low because their surface chemistry is not appropriate for attracting moisture.

Generally speaking, there are two types of desiccant materials: (i) substances whose desiccant behaviour originates from a chemical hydration reaction, such as P_4O_{10} , $MgSO_4$, and (ii) substances whose desiccant behaviour is based on surface interactions like adsorption processes. The latter category includes molecular sieves, silica gels, clays and starches [35–37]. The water adsorption behaviour of a sorbent depends on many factors, such as the porous structure, chemical composition, surface functionality content, presence of charged species, etc. [32].

Desiccants have been used in recent times for a wide range of applications, with the aim of controlling the humidity in the air when a moisture-free ambient is necessary. Other examples include the use of desiccant materials for controlling the level of water in industrial gas streams, in air conditioner systems, for storing and protecting goods in shipping containers against moisture damage (e.g., electronic devices, foods, clothes, etc.) [38].

As mentioned above, silica gel is the most common desiccant as its chemical behaviour has been known since the XVII century and it has been used as a dehumidifier since the beginning of the XX century up to this day. Its good moisture adsorption capacity is due to its porous properties and the presence of hydroxyl groups on its surface which give it a hydrophilic nature. Water molecules are attracted by its surface chemistry which is rich in oxygen.

Due to the physical and chemical similarities between silica gels and RF organic gels, the aim of this work is to evaluate the desiccant behaviour of two bare RF xerogels with different porosities. The interest shown in these RF xerogels is due to a series of advantages that they offer, such as their light weight, the possibility of modifying their surface chemistry to enable them to adsorb (and eliminate) components other than moisture, their chemical resistance to acids that may be present in the fluids to be treated, and the fact that they do not require neither doping or post-treatment processes, such as carbonization or activation, which makes them more cost-effective.

2. Experimental section

2.1. Synthesis of organic xerogels

The organic xerogels used in this study were synthesized by the polymerization of resorcinol (R) and formaldehyde (F), using

deionized water as solvent and NaOH as catalyst. First of all, resorcinol (Indspec, 99.6%) was dissolved in deionized water in an unsealed glass beaker under magnetic stirring until completely dissolved. Then, a formaldehyde solution was added until a homogeneous solution was obtained. The R/F molar ratio used was 0.15 and 0.70 for the synthesis of the samples OX-10 and OX-2100, respectively. NaOH solution (0.1 M, Titripac, Merck) was added in each precursor solution dropwise until the desired pH was reached. In this case, a pH of 5.8 and 4.8 were selected for the preparation of samples OX-10 and OX-2100, respectively. The precursor solutions were placed in an open vessel inside a microwave oven at 85 °C for about 3 h in order for gelation and ageing to take place. The polymers were then dried also by microwave heating, in the initial vessel, until a mass loss of over 50% were recorded, the total time of synthesis being less than 5 h. As a result two different organic gels were obtained with a total yield in the whole process of 45 wt%.

2.2. Sample characterization

Before characterization, the xerogels 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} was determined from the N_2 adsorption branch and, in all cases; the number of points used to apply the BET equation was higher than 5. V_{micro} was estimated by the Dubinin-Raduskevich method [39]. This method only takes into account micropore surfaces. The external surface area (S_{EXT}) was determined by applying the *t-plot* method developed by Lecloux et al. [40], which measures the external surface of the meso-macropores but excludes the microporous surface area. These two techniques are therefore complementary. N_2 adsorption-desorption isotherms were only used to obtain information about microporosity (S_{BET} , V_{micro} and mean micropore size) and the S_{EXT} . Parameters, such as porosity (%), pore size distribution (PSD), bulk density and mesopore/macropore volumes (V_{meso} , V_{macro}), 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 detected by this apparatus was 5.5 nm, whereas V_{macro} referred to porosity ranging from 50 to 10000 nm. The surface tension and contact angle were 485 $mN m^{-1}$ and 130°, respectively, and the stem volume was between 45 and 58% in all the analyses performed. In the low pressure step, the samples were evacuated up to 6.7 Pa. The equilibration time used was 10 s.

2.2.2. Elemental analysis

Determination of C, H and N was carried out in a *LECO CHNS-932* analyzer. The oxygen content was determined using a *LECO VTF-900* analyzer.

2.2.3. TPD analysis

The typology of the surface oxygen groups contained in the RF xerogels was evaluated by temperature programmed desorption (TPD) using a Chemisorption *Autochem II 2920* device from *Micromeritics*. This equipment is a fully automated chemisorption analyzer, which includes a gas feeding system, a temperature-controlled reaction zone and a gas analyzer (mass spectrometer, OmniStar TM, Pfeiffer Vacuum). The amount of CO and CO₂ released was registered while the samples were subjected to heat treatment

Download English Version:

<https://daneshyari.com/en/article/6532615>

Download Persian Version:

<https://daneshyari.com/article/6532615>

[Daneshyari.com](https://daneshyari.com)