



Short communication

A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels



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ARTICLE INFO

Article history:

Received 5 February 2015

Received in revised form

26 October 2015

Accepted 28 October 2015

Available online 6 November 2015

Keywords:

Carbon xerogels

Microwave heating

Tailored porosity

Scanning electron microscope

ABSTRACT

The hypothesis about the formation of the porous structure of carbon xerogels when the pH and the dilution ratio of the precursor solution are simultaneously modified has been validated by means of scanning electron microscope analysis. The morphology of the carbon xerogels showed that the size and number of the clusters produced during the sol–gel reaction is not only influenced by the pH but also by the dilution ratio. As with a decrease in the pH value, an increase in the dilution ratio caused the formation of a small number of large clusters, leading to materials with large pores. However, depending on the values selected the effect of the pH and dilution ratio was enhanced or diminished by the effect of the other. Hence, an appropriate adjustment of these two variables allowed microporous, micro-mesoporous and micro-macroporous materials to be obtained with pore volumes that could not be achieved by modifying the pH or the dilution ratio separately.

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1. Introduction

Carbon xerogels are porous materials obtained by the carbonization of an organic gel [1]. The most frequent organic gel found in the literature is obtained by means of polymerization between resorcinol and formaldehyde in the presence of a solvent [2,3]. The porous structure and, hence, the final properties of carbon xerogels depends on a large number of variables such as the pH [1,2,4–9], type and amount of solvent [6,10,11], concentration of reactants [5,10–12], type of catalyst [1,13,14], temperature and time of synthesis [10,14,15], carbonization conditions [1,16], etc. The fact that so many variables modify the properties of these materials is a great advantage since it allows their properties to be tailored to meet the requirements of a specific application.

In the literature, a large number of studies dealing with the effect of different variables (both chemical and physical) on the porous properties of carbon xerogels can be found [1,6,8,10,11,15,17]. However, it is generally accepted that it is the chemical variables that have the greatest influence and, in particular, the concentrations of the reactants (resorcinol, formaldehyde, solvent and catalyst) [3,5,6,11,18]. The pH, which is determined by the concentration of the catalyst, has been one of the most widely

studied variables as it has a great effect upon the porosity of carbon xerogels [1,2,4–8,11]. In general, it can be said that an increase in the pH value favors the addition of formaldehyde to resorcinol anions, leading to the formation of a small number of clusters of reduced size and hence to smaller pores [4,7]. On the other hand, the dilution ratio (D), which is commonly defined as the molar ratio between the total solvent and reactants, has an influence on the mechanical strength of carbon xerogels and, accordingly, on the shrinkage that takes place during the drying stage [6,11,19]. An increase in the amount of water results in a structure with low mechanical strength which during drying shrinks, leading to a material with small pores [3,6]. The effects of these two chemical variables are not isolated and the synergy between them must be taken into account when tailoring the porous properties of carbon xerogels [6,11]. However, despite the importance of the simultaneous modification of these variables on porosity, few studies in the literature focus on the effect of this synergy. Rey-Raap et al. have highlighted the importance of the synergy between pH and the dilution ratio on organic RF xerogels synthesized by microwave heating [6]. These authors provided a graphic illustration of how the pH and dilution ratio determined the size of the clusters and pores before and after the drying process. Although most studies based on carbon gels indicate that the mesoporosity and macroporosity generated during the synthesis of the organic gel is maintained during carbonization [8], some changes in the size of the clusters and pores can occur due to bonds and individual

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micropore walls breaking [7,11] and to the condensation produced during the carbonization process which may cause a slight shrinkage of the polymeric structure [7,11].

Therefore, in order to achieve total control of the tailoring of the porous structure of carbon xerogels, is worthwhile verifying whether the graphic hypothesis proposed by Rey-Raap et al. [6] for organic xerogels is also applicable to carbon xerogels. Accordingly, the aim of this study is to analyze the morphology of the structure of carbon xerogels synthesized by microwave heating through the simultaneous modification of pH and dilution ratio in the precursor solution.

2. Experimental

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent and sodium hydroxide as catalyst, following the method described in detail elsewhere [6]. Briefly, resorcinol (Indspec, 99%) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Merck, 37wt. % in water, stabilized by 10–15% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. Twelve different precursor solutions were prepared with four different initial pHs ranging from 5.0 to 7.0 and three different dilution ratio values (D) ranging from 5.7 to 11.7. All the xerogels were synthesized from 200 ml of precursor solution using the stoichiometric R/F molar ratio (i.e., 0.5).

Once the reactants were selected and mixed in the appropriate proportions, each precursor solution was placed in a microwave oven at 85 °C and kept there for 3 h, which is sufficient time for gelation and curing to be accomplished. After the formation of the polymeric structure excess water was eliminated by continuing to heat the gel in the same microwave oven until a mass loss of over

50% was achieved. The drying step lasted from 1 to 2 h depending on the pore structure of the material. Carbonization was performed at 700 °C under a nitrogen flow of 150 ml/min in a horizontal tubular furnace. The residence time was 2 h and the heating rate was set at 50 °C/min. The carbon xerogels obtained were denominated CX followed by the pH value and the value of the dilution ratio.

The porous properties of the carbon xerogels were characterized by nitrogen adsorption–desorption isotherm analysis performed at –196 °C and by means of mercury porosimetry, using a Micromeritics Tristar 3020 instrument and a Micromeritics AutoPore IV, respectively. Before each analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VAcPrep 061. These degassing conditions were previously optimized for outgassing this type of material. BET surface area (S_{BET}) was determined by applying BET equation to the N_2 adsorption isotherm and microporosity (V_{DUB}) was estimated by the Dubinin-Raduskevich method. Parameters such as pore size (d_p) and mesopore/macropore volume (V_{meso} , V_{macro}), were determined by mercury porosimetry, while porosity was obtained by means of envelope density analyser, using a Micromeritics GeoPyc 1360.

The morphology of the carbonaceous structures was examined using a Quanta FEG 650 scanning electron microscope. Samples were previously attached to an aluminum tap using conductive double-sided adhesive tape. An accelerating voltage of 25 kV and a secondary electron detector EDT (Everhart-Thornley) were used in all analysis.

3. Results and discussion

The porous structure of the materials studied was determined by means of nitrogen adsorption–desorption analysis and the isotherm classification proposed by the IUPAC. The nitrogen

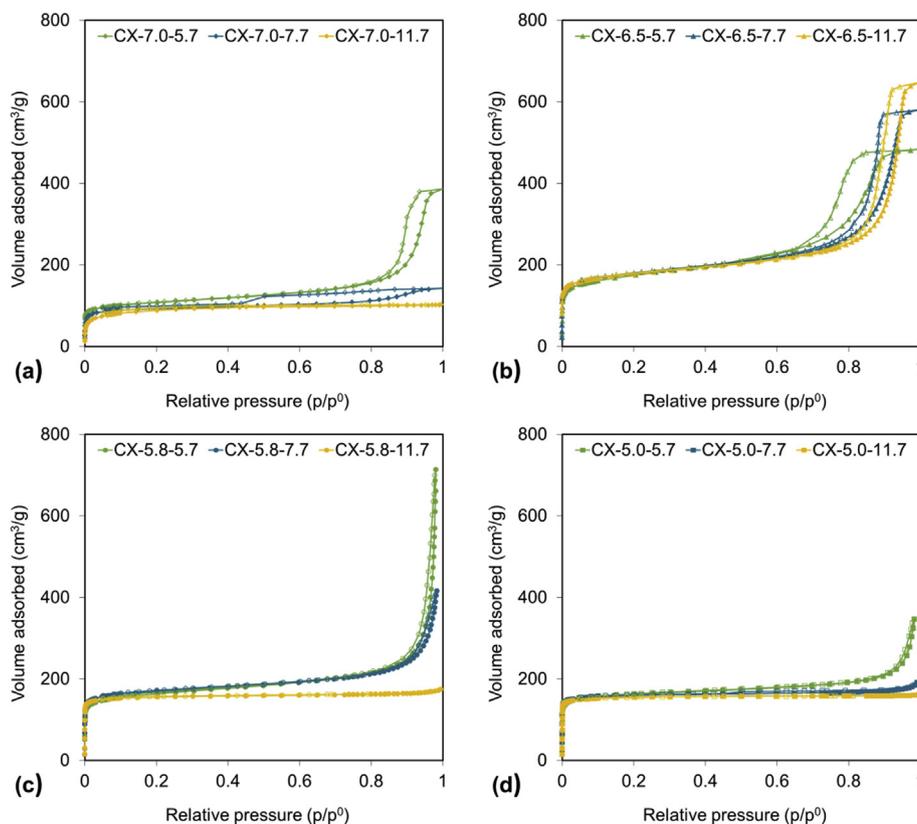


Fig. 1. N_2 adsorption–desorption isotherms of carbon xerogels.

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