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(54) **Title**: CARBONACEOUS MATERIALS, THEIR MANUFACTURING PROCESS AND THEIR USE IN SUPERCAPACITORS

(57) **Abstract**: Resorcinol-formaldehyde carbon xerogels with improved porosity characteristics are provided. Their manufacturing method by using a microwave-assisted process, and $Ca(OH)_2$ as catalyst is also disclosed, as well as their use for storing energy in supercapacitors.

Carbonaceous materials, their manufacturing process and their use in supercapacitors

Field of the Invention

The present invention relates to carbonaceous materials, their manufacturing process and their use in supercapacitors. More specifically, it relates to resorcinol-formaldehyde xerogels, to their manufacturing process using microwave technology and to the use of said xerogels for storing energy in supercapacitors.

Background of the Invention

An organic gel is a solid nanostructure comprised of nano-sized pores and interlinked primary particles obtained by means of polymerization reactions between hydroxylated benzenes (such as resorcinol, phenol, etc.) and aldehydes (such as formaldehyde, furfural, etc.) and then subjected to a drying process.

The formation of organic gels involves the following stages:

(i) formation of a three-dimensional polymer in a solvent, known as gelation step,

(ii) curing period where the crosslinking of previously formed polymer clusters (particles) takes place and, finally,

(iii) drying step, that can be performed under subcritical, supercritical or freezing conditions, resulting in xerogels, aerogels and cryogels, respectively (N. Job et al., *"Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials"*, Carbon 43, 2481-2494 (2005)).

Subsequently to the drying step, organic gels are subject to carbonization in order to obtain carbon gels. During carbonization any remaining oxygen and hydrogen groups are removed, yielding a thermally stable nanostructure mainly composed of carbon.

In the case of aerogels, supercritical drying involves eliminating the solvent in supercritical conditions (high pressures and temperatures). It is the best way to preserve the porous texture and structural properties created during the synthesis of the gels although it is very expensive and time consuming and it need exchange solvent which can affect the purity of the material.

In the case of cryogels, the solvent is frozen and then removed by sublimation. This procedure can lead to dramatic changes in the density of the cryogels after freezing and also to the formation of megalopores or voids as a result of the creation of crystals inside the structure of the gels (Kocklenberg et al., "*Texture control of freeze-dried resorcinol-formaldehyde gels*", Journal of Non-Crystalline Solids, 225, 8-13 (1998)). To prevent the formation of crystals which may deform the designed nanostructure of the polymer, the solvent is replaced before drying the gel which may lead to more impurities in the material and also increase the cost.

When the gels are dried by simple evaporation of the solvent (at ambient pressure and temperatures of around 100-150 °C), organic xerogels, to which the present invention is directed, are obtained.

The synthesis of organic xerogels is carried out, as previously indicated, by sol-gel reaction, where the polymer crosslinks and gelation and curing takes place and drying under subcritical conditions. Carbon xerogels, are obtained by carbonization of the dried organic xerogel (N. Job et al. *"Porous carbon xerogels with texture tailored by pH control during sol-gel process",* Carbon 42, 619-628 (2004)).

In all these steps, parameters like pH of the precursor solution, nature and molar ratio of reactants, have a great influence on the properties of the carbon xerogel, in such a way that small variations of them lead to significant changes in the structure and properties of the carbon xerogels. In this respect, the carbonization step plays an important role, since during this step the porous texture of the gel is modified and the microporosity is developed.

To increase the porosity or to enrich their chemical structure, carbon xerogels can be subjected to various activation, oxidation and doping processes, which can be performed during or after the carbonization step and the properties of the final carbonaceous material will be greatly influenced by the sequence used.

In addition to their highly developed porosity, tunable structural and textural characteristics depending on the operating conditions, carbon xerogels also present good conductive properties, and can be obtained in different morphologies such as powder,

monoliths, spheres, films or composite materials which make them suitable for a great variety of applications such as supercapacitors, fuel cells, desalination sytems, catalyst supports, liquid and gas-phase adsorbents, etc. (Calvo et al., "*Exploring new routes in the synthesis of carbon xerogels for their applications in electric double.layer capacitors"*Energy & Fuels, Vol. 24, 3334-3339, (2008); Zheivot et al., "*Carbon xerogels: Nano and adsorption textures, chemical nature of the surface and gas chromatography properties"* Microporous and Mesoporous materials, Vol. 130, 7-13, (2010); Zubizarreta et al., "*Ni-dopped carbon xerogels for H_2 storage*" Carbon, Vol. 48, 2722-2733 (2010)). For these reasons, carbon xerogels have acquired an increasing popularity in the last three decades.

Traditionally, the synthesis of carbon xerogels was a long and tedious process, which led to materials more expensive than the commercial activated carbons obtained from various types of residues, since it involved several heating steps, which required about 3-4 days. Therefore, the research in this field was addressed to the development of faster and cheaper methods of synthesizing carbon xerogels in order to make them more attractive and competitive than the activated carbons. In this respect, the most relevant results are shown in ES 2354 782 B1, where it is disclosed that the use of microwave radiation allows to carry out the process in one faster and simple step.

As previously indicated, there are also a number of variables (such as, for example, pH, and molar ratio of the reactants) which have an important influence on the porosity and structure of the xerogels (Rey-Raap et al.; *"Simultaneous adjustment of the main chemical variables to fine-tune the porosity of carbon xerogels",* Carbon 78, 490-499 (2014); N. Job et al. *"Porous carbon xerogels with texture tailored by pH control during sol-gel process"*Carbon 42, 619-628 (2004)). Of these variables, the pH of the resorcinol-formaldehyde mixture is the one that most affects the porosity of the final materials. Several bases can be used to adjust the pH, being sodium hydroxide the most used, although others basic catalysts such as ammonium carbonate, ammonium acetate, ammonium hydroxide or combinations thereof can also be used.

Also, the presence of impurities, such as alkali metals, halogens and other contaminants, play an important role in the properties of the synthesized carbon xerogels. Impurities have a negative effect because their presence may be relevant for some applications in

which a high degree of purity is required, such as, for example, the use in electrodes for supercapacitors. Impurities decrease the breakdown voltage of the electrolyte in which the electrolytes are immersed and therefore, they must be operated at lower voltages and have shorter lives than those not containing impurities.

The use of carbon xerogels in electrodes for supercapacitors have acquired over the last few years an increasingly popularity not only due to the porosity of the carbon xerogels and its high surface area but also to its capacity to withstand an increased number of charge and discharge cycles in comparison with the traditional activated carbons.

In order to get carbon materials suitable for supercapacitors which give adequate power and energy density, it is known that the presence of abundant micropores increases total surface area and energy density, while absence of mesopores limits ion diffusion, degrading power density so it is necessary to find the balance between micropores and mesopores. On the other hand, large pores will contribute little to the specific surface area and therefore will have little effect on capacitance so it is necessary to have high volume of micropores and volumes of small mesopores in order to get materials which allow high power density and high energy density supercapacitors.

In spite of the big efforts that are being made in order to obtain these porous carbonaceous materials which are able to substitute the traditional activated carbons in electrodes for supercapacitors, no material which, in addition to the above mentioned properties (mainly those related to porosity), is industrially reproducible and economically viable, has been found hitherto.

The pH value plays a crucial role in the reaction mechanism and in determining the porosity of resorcinol-formaldehyde xerogels. However, the type of catalyst used is also relevant. The nature of the catalyst exerts a double influence, since both, the cation and the anion of the catalyst has an impact on the volume and size of the porosity created which means that the catalyst not only has effect on the structure of the xerogel because of its anion but also because of the type of cation.

In Job et al. "*Effect of the counter-ion of the basification agent on the pore texture of organic and carbon xerogels*" Journal of Non-Crystalline Solids 354, 4698-4701 (2008)

different resorcinol-formaldehyde carbon xerogels are prepared using different catalysts, such as Na (OH), $Ca(OH)_2$, $Ba(OH)_2$ and $Sr(OH)_2$. The gels are obtained by drying under vacuum and the carbon materials are obtained by pyrolysis. The materials so obtained exhibits low surface area and the pore diameter of the obtained carbon xerogel is such that it is not suitable for being used in supercapacitors. In addition, the pore size of the carbon materials greatly depends on the catalyst that has been used.

In Mei-Fang Yan et al. "*Synthesis and characterization of carbon aerogels with different catalysts*" Journal of Porous Materials, 22, 699-703 (2015) carbon aerogels were obtained by a sol-gel process by polycondensation of phloroglucinol, resorcinol and formaldehyde using different catalysts. When using $Ca(OH)_2$ the surface area and the pore volume is very low, and also the material has pores higher than 30nm so obtained carbon aerogel is such that it is not suitable for being used in supercapacitors. In addition, the pore size depends on the catalyst that has been used. Regarding the process for obtaining the carbon aerogels, it has to be noted that is a long and tedious process which takes about 6 days and solvent exchange is needed

In Barral, K. "*Low density organic aerogels by double-catalysed synthesis*" Journal of Non-Crystalline Solid 225, 46-50 (1998) different phloroglucinol-formaldehyde carbon aerogels are prepared using different catalysts, such as for example Na_2CO_3, NaOH, $Ca(OH)_2$, KOH and $CaCO_3$, in order to examine the lowest density of the material that can be achieved. The materials so obtained exhibit very low density (lower than 0.10 g/cm^3) due to the fact that the pore size ranges from 10nm to hundreds of nm, which makes them not suitable for supercapacitors.

From the above, it is clear that it would be desirable to find a material having the required surface and porosity properties which would allow its use as electrode in supercapacitors, while being possible to manufacture them via an economically viable process and in such a way that it is industrially reproducible.

Summary

Therefore, the problem to be solved by the present invention is to provide a material that overcomes the above mentioned disadvantages, in particular to provide a material with enhanced surface and porosity properties over the existing materials, which make

them suitable for being used in supercapacitors' electrodes, while being easily and economically obtainable.

The solution is based on that the present inventors have found that carbon xerogels wherein resorcinol and formaldehyde are used as precursors and $Ca(OH)_2$ is used as catalyst, and wherein microwave technology is used for carrying out all the steps of the synthesis, have less impurities than those obtained with traditional catalysts, such as for example NaOH, and exhibit higher SBET.

In a first aspect, the invention is directed to a carbon xerogel with a calcium content in the range of 500 to 800 ppm, a SBET higher than 1900 m^2/g having a pore size distribution such that at least 95% of the mesopores in relation to the total mesoporosity are comprised in the range from 2 to 15 nm and that and that the macropore volume is less than 0.01 cm^3/g.

In a second aspect, the invention is directed to a process for obtaining the above mentioned xerogel, which comprises the following steps:

a) mixing a polymerizable hydroxybenzene and a polymerizable aldehyde in water and in the presence of $Ca(OH)_2$ in the amount necessary to impart to the solution a pH in the range from 4 to 8,

b) subjecting the mixture of step a) to microwaving at a power such that the mixture reaches a temperature in the range of 40°C to 100°C so that the mixture is polymerized, and then maintaining the microwaving until the polymerized mixture has a moisture content lower than 40%;

c) subjecting the polymerized product obtained in step b) to a carbonization and/or activation step at a temperature of between 900 and 1200°C in CO_2 steam for 1 to 6 hours.

In the carbonization and/or activation step, the carbonization and the activation processes can take place simultaneously in a single step, or in the form of two

consecutive or sequential sub-steps: an carbonization step followed by an activation step.

In a third aspect, the invention is directed to the use of the above mentioned xerogels in electrodes of supercapacitors.

Brief Description of the drawings

Figure 1- SBET values for carbonized resorcinol-formaldehyde xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.5, D=5.7, R/F=0.5 (Ex. 1 and Comp. Ex. 1); and pH= 6.2, D=4.7, R/F=0.2 (Ex. 2 and Comp. Ex. 2).

Figure 2- Mesoporosity characteristics for carbonized resorcinol/formaldehyde xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.5, D=5.7, R/F=0.5 (Ex. 1 and Comp. Ex. 1). V_{meso} is shown in Figure 2a) and d_{pore} in Figure 2b).

Figure 3- Pore size distributions obtained from N_2 isotherms for carbonized resorcinol/formaldehyde xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.2, D=4.7, R/F=0.2 (Ex. 2 and Comp. Ex. 2).

Figure 4- Pore size distributions obtained from N_2 isotherms for activated resorcinol/formaldehyde carbon xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: a) pH= 6.5, D=5.7, R/F=0.5 (Ex. 1 and Comp. Ex. 1), b) pH= 6.2, D=4.7, R/F=0.2 (Ex. 2 and Comp. Ex. 2), c) pH= 6.8, D=5.7, R/F=0.5 (Ex. 3 and Comp. Ex. 3)

Figure 5- Thermogravimetry in CO_2 of resorcinol/formaldehyde xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.5, D=5.7, R/F=0.5 (Ex. 1 and Comp. Ex. 1).

Definitions

Prior to a discussion of the detailed description of the invention, a definition of specific terms related to the main aspects of the invention is provided.

The expression "carbonaceous material" denotes herein a material comprised substantially of carbon. Carbonaceous materials include both amorphous and crystalline carbonaceous materials.

The term "amorphous" denotes herein a material whose constituent atoms, molecules or ions are arranged randomly without a regular repeating pattern.

The term "impurity" denotes herein an external substance within a material which differs from the atoms that constitute the molecular formula of the raw material used as precursors (C, O, H) and from the atoms that constitute the molecular formula of the used catalyst. Examples of impurities in the present invention are alkali metals such as K, and halogens such as Cl, Fe, Ni, among others.

The expression "ash content" denotes herein non-volatile inorganic matter which remains after subjecting a material to a high decomposition temperature.

The term "organic xerogel" denotes herein a gel which has been dried by simple evaporation of the solvent, preferably at ambient pressure and temperatures up to 150 ^{o}C, more preferable up to 300°C.

The term "Activated xerogel" denotes herein a carbon xerogel which has been obtained by the activation of an organic xerogel.

The term "activation" denotes herein a heating treatment of a material in the presence of an oxidizing atmosphere, such, for example CO_2, at temperatures of about 900-1200°C, to produce the activated material.

The terms "carbonization" and "pyrolysis" denote herein a process wherein a carbon-containing material is heated in an inert atmosphere or in vacuum such that the obtained material is mainly carbon.

The expression "carbonization and/or activation" denotes herein a process of carbonization and activation where a heating treatment of an organic gel in the presence of an oxidizing atmosphere, such as, for example CO_2, at temperatures of about 900-1200°C, to produce the activated material. These two processes can take place simultaneously in a single step, or in two sequential carbonization and activation sub-steps.

The expression "carbonized xerogel" denotes herein a xerogel that has been subjected to carbonization, but it has not been activated.

The term "macropore" denotes herein pores having a diameter above 50 nm.

The term "mesopore" denotes herein pores having a diameter in the range of 2 to 50 nm.

The term "micropore" denotes herein pores having a diameter below 2 nm.

The term "polymer" denotes herein a macromolecule which comprise two or more structural repeating units.

The term "polymerization" denotes herein the process whereby two or more structural repeating units form a polymer.

The term "gelation" denotes herein a process whereby a gel is formed, the gel being defined as a solid polymer network that is synthesised by a sol-gel method. The sol-gel method consists in a conversion of monomers into a colloidal solution (sol) that acts as the precursor so, as the polymerization proceeds, the viscosity of the solution increases forming an integrated network (or gel) of either discrete particles or network polymers, which continues polymerizing to form a solid polymer network.

The expression "BET surface"(SBET) denotes herein the total specific surface measured using the Brunauer/Emmett/Teller (BET) technique according which, an inert gas is used to measure the amount of gas adsorbed on a material.

The term "electrode" denotes herein a conductor through which an electric current enters or leaves a medium.

The term "supercapacitor" denotes herein an electric double-layer capacitors (EDLC) which are electrochemical capacitors which energy storage predominant is achieved by Double-layer capacitance.

Detailed description of the invention

As previously indicated, a first aspect of the invention refers to carbon xerogel with a calcium content in the range of 500 to 800 ppm, a SBET higher than 1900 m^2/g having a pore size distribution such that at least 95% of the mesopores in relation to the total mesoporosity are comprised in the range from 2 to 15nm and that and that the macropore volume is less than 0.01 cm^3/g.

The xerogel is synthesized in two steps. In general terms, in the first step, an organic xerogel with controlled mesoporosity is obtained, and in the second step, where the microporosity is developed, the organic xerogel is converted into a carbon xerogel. The manufacturing method is disclosed in detail hereinbelow.

In a first step, resorcinol, formaldehyde, water and $Ca(OH)_2$ are mixed for 10-30 minutes at 10-30ºC in order to ensure an homogenous precursor solution.

The resorcinol is dissolved with stirring in deionized water. Then, an aqueous solution of formaldehyde in methanol is added. The molar ratio of the precursor monomers, referred herein below R/F (resorcinol/formaldehyde), should be such that the polymerization is ensured. Such proportion ranges from 0.1 to 1, preferably from 0.2 to 0.5. The dilution D, which is the molar ratio of precursor monomers /solvent, being the solvent water, is in the range from 4.7 to 5.7. The $Ca(OH)_2$ is added in solid state, until a pH in the range of 4 to 8 is achieved. Below 4, the materials properties are not suitable for their use in supercapacitors, due to the presence of pores of hundreds of nm, and above 8, the porosity developed in the material is too low. More preferably the pH ranges from 5 to 7, and even more preferably from 6.2 to 6.8.

This mixture is carried out in a reactor able to withstand temperatures at which polymerization takes place, which are in the range of 60 to 90ºC. Preferably, the

material of the reactor is transparent to microwaves. Preferred materials are glass, quartz, teflon, polypropylene, polyethylene or, in general, any plastic material transparent to microwave radiation.

Then, the precursor mixture is subjected to a microwave-assisted process which is accomplished in air at a power such that the mixture reaches a temperature in the range of 40 to 100ºC, more preferably from 60 to 90ºC. This power lies preferably in the range of 100 to 600 W/L, more preferably from 200 to 400 W/L and most preferably around 250 W/L. Initially, the mixture is subjected to microwaving at a temperature of about 85ºC. After a few minutes, when the gel is formed, the crosslink takes place and a stable polymer is obtained. When using conventional heating methods these processes take several days. Therefore, the microwave process leads to savings in time and energy.

Once the gelation has finished, the temperature is maintained or it can be raised progressively.

It is not required to complete the drying of the organic xerogel. In fact, the inventors have found that organic xerogels with moisture in the range of 20 to 40 wt %, preferably with a moisture of 30 wt%, lead to easily obtainable carbon xerogels.

In a second step, the obtained organic xerogel is subjected to a carbonization and/or activation process at 900-1200ºC in CO_2 steam for 1-6 hours, more preferably at 1000ºC during 2 hours. During this step the following processes take place:

-Thermal stabilization of the material, which leads to a material with a C composition higher than 95wt %;

-Carbonization and/or activation of the material. The CO_2 partially gasifies the carbonaceous material, micropores are formed while maintaining the mesopores size previously formed in the organic xerogel in the first step, and the specific surface greatly increase in comparison with that of the organic xerogel, as will be explained in detail in the accompanying examples.

As previously indicated, the carbonization and/or activation step can be carried out simultaneously or in two sequential sub-steps: one carbonization step followed by an activation step.

As it will be shown herein below, the materials so obtained are amorphous carbon materials that have less impurities than those materials obtained when other catalysts, such as NaOH, are used, while maintaining pore sizes which make these materials optimally suitable for being used as electrodes for supercapacitors. In addition, they exhibit BET surfaces higher than the values obtained when using other catalysts, such as, for example, NaOH. Namely, the carbon xerogels obtained under the method disclosed above exhibit a mean micropore size which ranges from 0.5 to 1.9 nm, more preferably from 0.9 to 1.6 nm, and a micropore volume which ranges from 0.2 to 1.5 cm^3/g, more preferably from 0.8 to 1.0 cm^3/g. The mean mesopore size ranges from 2 to 15 more preferably from 8 to 11 nm, and the mesopore volume ranges from 0.5 to 2, more preferably from 1.0 to 1.3. The SBET ranges from 1000 to 2700 m^2/g, more preferably it is higher than 1900 m^2/g.

Any combination of any of these features is envisaged.

The carbon xerogel obtained under these conditions has a pore size distribution such that at least 95% of the mesopores in relation to the total mesoporosity are comprised in the range from 2 to 15 nm, more preferably at least 98%. This material, when used as electrode in a supercapacitor, shows a capacity higher than 120 F/g and can deliver energy densities higher than 18 Wh/kg and power densities in the range of 20,000 W/kg.

It should be noted that the above-cited experimental conditions lead to a material with optimal technical features for the purpose sought. Any departure from the above-disclosed experimental conditions (different catalyst, different drying step, different solvent, etc…) may lead to a different material with less optimal properties.

The present invention is further illustrated by the following Examples. However, it should be understood that the invention is not limited to the specific details of these examples.

Examples

a) Synthesis of organic xerogels

Organic xerogels were synthesized by the polymerization of resorcinol (Indspec, 99.6 wt. %) and formaldehyde (Química SAU, aqueous solution with 37 wt. % formaldehyde and 0.6 wt. % of methanol). First the resorcinol was dissolved with magnetic stirring using deionized water. Then, the formaldehyde solution was added until a homogeneous solution was obtained. Different alkaline salts were used as catalysts. Namely, solid NaOH (comparative examples) or $Ca(OH)_2$ were added until reaching the desired pH, which ranges from 5 to 7, and more preferably from 6.2 to 6.8 The purity of NaOH is 99% and the purity of the $Ca(OH)_2$ is 95%. The proportions of resorcinol and formaldehyde were such that the resorcinol/formaldehyde molar ratios (R/F) were in the range from 0.2 and 0.5 and the dilution molar ratio (D, molar ratio of precursor monomers/solvent) was in the range from 4.7 to 5.7.

Briefly, the microwave-assisted process involved the following stages: (i) heating at 85 °C for about 3 hours to perform the gelation and ageing (i.e. polymerization) stages and, (ii) heating to a temperature above 100 °C to evaporate the water used as solvent. This stage ends when a mass loss of 50 wt. % is reached. The synthesis takes about 5 h and it brings materials with a residual moisture of about 30 wt%.

The synthesis conditions are summarized in Table 1 below. R/M denotes the molar ratio of resorcinol to the base used (NaOH or $Ca(OH)_2$).

Catalyst	pH	D	R/F	R/M	Example
NaOH	6.5	5.7	0.5	174	Comp. Ex. 1
	6.2	4.7	0.2	260	Comp. Ex. 2
	6.8	5.7	0.5	104	Comp. Ex 3
$Ca(OH)_2$	6.5	5.7	0.5	417	Ex. 1
	6.2	4.7	0.2	650	Ex. 2
	6.8	5.7	0.5	174	Ex. 3

Table 1- Summary of the synthesis conditions of the organic xerogels

b) Carbonization of the organic xerogels obtained in Section a) and physico-chemical characterization of the same.

Once the fabrication of the organic xerogels was completed, they were thermally stabilized by pyrolysis in a tubular horizontal furnace (*Carbolite MTF 12/38/400*) under a nitrogen atmosphere (150 ml min^{-1}), up to 700 ºC (50 ºC min^{-1}) with a soaking time of 2 hours.

The porous and chemical properties of the samples were evaluated by means of the following techniques: mercury porosimetry, N_2 adsorption-desorption isotherms, elemental analysis and inductively coupled plasma mass spectrometry (ICP-MS).

Mercury porosimetry (AutoPore IV 9500 from Micromeritics) was used for the characterization of macroporosity. Samples were degasses at 120ºC and 0.1 mbar for 8 hours using a *Micromeritics VacPrep 0.61* device before analysis. The intrusion was performed between atmospheric pressure and 228 MPa. The surface tension and contact angle were taken to be 485mNm−1 and 130°, respectively, and the stem volume was between 45–58% in all the analysis performed. Initially, in the low pressure step, the samples were evacuated to 6.7 Pa and the equilibration time used was 10 s. Subsequently, the pressure was gradually increased to the maximum value and the subsequent mercury intrusion evaluated.

The nitrogen adsorption-desorption isotherms were performed at -196 ºC in an adsorption analyzer (*Micromeritics Tristar 3020*), after the samples had been degassed at 120 ºC and 0.1 mbar for 8 hours using a *Micromeritics VacPrep 0.61* device. With this technique, the following parameters were obtained: S_{BET} and V_{micro}, which were calculated by applying the Brunauer-Emmett-Teller (BET) and Dubinin-Raduskevich (DR) equations, respectively; total pore volume (V_p) estimated from the amount of nitrogen adsorbed at p/p^o = 0.99 and pore size distribution (PSD), determined by applying the DFT method to the nitrogen adsorption branch.

The elemental analysis results were obtained using two different devices, a LECO-CHNS-932 microanalyzer, to determine the C, N and H content and a LECO-TF-900 furnace coupled to an IR spectrometer, to measure directly the oxygen content.

The amount of residual elements resulting from the use of the diverse alkaline catalysts was measured by ICP-MS, on an *Agilent 7700x* device. Before this analysis, the carbon xerogels were subjected to microwave-assisted digestion using nitric, hydrochloric and hydrofluoric acids.

b.1) Characterization of the pore structures of carbonized xerogels

The specific surface area (S_{BET}) values of some of the carbonized xerogels obtained in Section b) are presented in Figure 1. Namely, carbonized xerogels of Ex.1 and 2, and Comp. Ex. 1 and 2 (see table 1) are shown. In this figure, it can be observed that S_{BET} values obtained for xerogels in which $Ca(OH)_2$ has been used as catalyst (Ex. 1 and 2) are higher than those obtained when NaOH is used as catalyst (Comp. Ex. 1 and 2).

The characteristics of the mesoporosity of the carbonized xerogels, with regard to volume and average mesopore diameter, has also been studied, and is summarized in Figures 2a) and 2b) respectively. In these figures, the results obtained for carbonized xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.5, D=5.7, R/F=0.5 (Ex. 1 and Comp. Ex. 1) are shown. From this results, it can be seen that the V_{meso} is slightly higher in the case of the carbonized xerogels using $Ca(OH)_2$ while the pore sizes are very similar (about 10 nm).

In addition, the pore size distributions (obtained from N_2 isotherms) of the carbonized xerogels obtained using NaOH and $Ca(OH)_2$ as catalysts, under the following synthesis conditions: pH= 6.2, D=4.7, R/F=0.2 (Ex. 2 and Comp. Ex. 2) are shown in figure 3. This figure highlights the fact that using NaOH or $Ca(OH)_2$ under the indicated synthesis conditions of pH, dilution and resorcinol-formaldehyde proportions, leads to materials having similar porosity.

Furthermore, according to the ICP-MS analysis, it has been found that in the carbonized materials under Ex. 2 and Comp. Ex. 2, the residual Na content is reduced from ~800 ppm in the case of Comp. Ex. 2 (NaOH used) to 180 ppm in the case of Ex. 2 ($Ca(OH)_2$ used). Therefore, replacing the sodium cation by calcium cation, under the above mentioned conditions, leads to carbonized xerogels with a higher degree of purity and a similar porosity, even though NaOH has a higher purity than $Ca(OH)_2$.

Macropore volume is less than 0.01 cm^3/g which is considered to be within the measurement error values, and therefore it can be considered that no macropores are substantially present.

This result is confirmed by the elemental analysis performed under ICP-MS. As can be seen in table 2, the carbonized xerogels are predominantly composed of C (≥ 95 wt. %) and the ash content, which is the solid residue directly obtained after the combustion of the material, is lower in the case of the calcium-based catalyst, and so is the one that results in a carbonaceous material of greatest purity.

	pH= 6.2, D=4.7, R/F=0.2	
	Comp. Ex. 2 (NaOH)	Ex. 2 ($Ca(OH)_2$)
C / wt. %	96.3	96.7
H / wt. %	1.4	1.5
O / wt. %	2.1	1.7
Ash content / wt. %	0.20	0.14

Table 2- Elemental analysis of carbonized xerogels using NaOH (Comp. Ex. 2) and $Ca(OH)_2$ (Ex. 2) as catalysts.

c) Carbonization and activation of the organic xerogels obtained in Section a) and physico-chemical characterization of the same

The organic xerogels obtained as described in Section a) where subjected to heating at 1000ºC in CO_2 for 2 hours.

As previously indicated, during this step the following processes take place:

-Thermal stabilization of the material, which leads to a material with a C composition higher than 95wt %;

-Activation of the material. The CO_2 partially gasifies the carbonaceous material, micropores are formed and the specific surface greatly increase in comparison with that of the organic xerogel, while maintaining the size of the mesopores previously formed when synthesizing the organic xerogel.

Mercury porosimetry (AutoPore IV 9500 from Micromeritics) was used for the characterization of macroporosity. Samples were degasses at 120ºC and 0.1 mbar for 8 hours using a *Micromeritics VacPrep 0.61* device before analysis. The intrusion was performed between atmospheric pressure and 228 MPa. The surface tension and contact angle were taken to be 485mNm−1 and 130°, respectively, and the stem volume was between 45–58% in all the analysis performed. Initially, in the low pressure step, the samples were evacuated to 6.7 Pa and the equilibration time used was 10 s. Subsequently, the pressure was gradually increased to the maximum value and the subsequent mercury intrusion evaluated.

The nitrogen adsorption-desorption isotherms were performed at -196 ºC in an adsorption analyzer (*Micromeritics Tristar 3020*), after the samples had been degassed at 120 ºC and 0.1 mbar for 8 hours using a *Micromeritics VacPrep 0.61* device. With this technique, the following parameters were obtained: S_{BET} and V_{micro}, which were calculated by applying the Brunauer-Emmett-Teller (BET) and Dubinin-Raduskevich (DR) equations, respectively; mesopore volume (V_{meso}) estimated from the amount of nitrogen adsorbed at p/p^o = 0.99 and pore size distribution (PSD), determined by applying the DFT method to the nitrogen adsorption branch.

The elemental analysis results were obtained usinga LECO-CHNS-932 microanalyzer, to determine the C.

The amount of residual elements resulting from the use of the diverse alkaline catalysts was measured by ICP-MS, on an *Agilent 7700x* device. Before this analysis, the carbon xerogels were subjected to microwave-assisted digestion using nitric, hydrochloric and hydrofluoric acids.

True density was evaluated by helium picnometry in AccuPyc II 1340 from Micromeritics after the samples had been degassed at 120 ºC and 0.1 mbar for 8 hours using a *Micromeritics VacPrep 0.61* device. Helium displacement method was used to measure accurately the true volume of a known amount of sample, and therefore obtain a reliable value of the true density (referred herein He).

The electrochemical behaviour of the activated xerogels was evaluated on disc-shaped electrodes prepared by mixing the activated xerogels (90 wt%) and polytetrafluoroethylene (PTFE) binder (10 wt%). A homogeneous mixture of both

compounds was obtained and rolled out in order to obtain a homogeneous thin film. Electrodes were manufactured by punching pellets from this film. Subsequently, the electrodes were pressed and dried. The electrodes were 100-200 μm thick, 1 cm wide and weighed around 3-5 mg.

The electric conductivity of the activated xerogels was obtained by evaluating their sheet resistivity of the disc-shaped electrodes mentioned above using the four-point probe technique (FPP) (model SR-4-6L, Everbeing) based on the Van der Pauw equation.

The electrochemical measurements were performed using a two-electrode testing cell (Teflon Swagelok®) using stainless steel as current collector, a fibre glass separator (400 μm) and two electrodes of the materials studied. The equipment used was a potentiostat/galvanostat VMP Biologic and H_2SO_4 1M as electrolyte. Galvanostatic charge/discharge measurements at 0.2 A g^{-1} with U=1.0 V in a voltage window from 0.6 to 1.2 V, were performed.

c.1) Characterization of activated carbon xerogels

In tables 2 to 4, the specific surface area (S_{BET}), micropore volume (Vmicro), mesopore volume (Vmeso) and size pore as measured from the nitrogen adsorption-desorption isotherms, of organic xerogels obtained in Section a) (see Table 1) and their corresponding activated carbon xerogels obtained in Section c) are shown. It has to be noted that the macropore volume is less than 0.01 cm^3/g which is considered to be within the measurement error values, and therefore it can be considered that no macropores are substantially present in any of the Exemplified xerogels.

	pH=6.5; D=5.7; R/F=0.5			
	Comp. Ex.1 (NaOH) R/Na=174		Ex.1 ($Ca(OH)_2$) R/Ca=417	
	Organic Xerogel	Activated carbon xerogel	Organic Xerogel	Activated carbon xerogel
SBET (m^2/g)	434	1400	477	1900
Vmicro (cm^3/g)	0.2	0.6	0.2	0.8

Mean micropore size (nm)	1.5	1.5	1.5	1.6
Vmeso (cm^3/g)	0.8	0.9	0.9	1.0
Mean mesopore size (nm)	11	10	10	10
He (g/cm^3)	1.3	2.2	1.4	2.1

Table 3- Characterization of pore structure of the organic xerogel and its corresponding activated carbon xerogel under the indicated synthesis conditions.

	pH=6.2; D=4.7; R/F=0.2			
	Comp. Ex.2 (NaOH) R/Na=260		Ex.2 ($Ca(OH)_2$) R/Ca=650	
	Organic Xerogel	Activated carbon xerogel	Organic Xerogel	Activated carbon xerogel
SBET (m^2/g)	443	1600	464	2000
Vmicro (cm^3/g)	0.2	0.7	0.2	1.0
Mean micropore size (nm)	1.0	0.9	1.0	1.0
Vmeso (cm^3/g)	1.0	0.7	0.8	1.3
Mean mesopore size (nm)	13	13	12	11
He (g/cm^3)	1.4	2.2	1.3	2.2

Table 4- Characterization of pore structure of the organic xerogel and its corresponding activated carbon xerogel under the indicated synthesis conditions.

	pH=6.8; D=5.7; R/F=0.5			
	Comp. Ex.3 (NaOH) R/Na=104		Ex.3 ($Ca(OH)_2$) R/Ca= 174	
	Organic Xerogel	Activated carbon xerogel	Organic Xerogel	Activated carbon xerogel
SBET (m^2/g)	438	1500	425	2200
Vmicro (cm^3/g)	0.2	0.6	0.2	1.0
Mean micropore size (nm)	1.0	1.0	1.0	0.9

Vmeso (cm^3/g)	0.8	0.7	0.9	1.0
Mean mesopore size (nm)	9	9	9	8
He (g/cm^3)	1.4	2.2	1.3	2.1

Table 5- Characterization of pore structure of the organic xerogel and its corresponding activated carbon xerogel under the indicated synthesis conditions.

The samples "Ex. 1" and "Comp. Ex. 1" described in Table 3 above were subjected to electrochemical characterization using the above-described experimental conditions, obtaining and the following results:

	pH=6.5; D=5.7; R/F=0.5	
	Comp. Ex.1 (NaOH) R/Na=174	Ex.1 ($Ca(OH)_2$) R/Ca= 417
	Activated carbon xerogel	Activated carbon xerogel
Electric conductivity (S/cm)	1	1
Capacity (F/g)	120	140
Energy density (Wh/kg)	18	20
Power density (W/kg)	20,000	20,000

Table 5- Electrochemical characterization of the activated carbon xerogels of Table 3 (example 1).

The results of Table 5 show that, under the same testing conditions, Ca-xerogels show high electric conductivity despite its very high SBET area (usually they are opposed properties). The good combination of electric conductivity and high surface area leads to higher capacitance and energy density values for the supercapacitor built with Ca-xerogels. The power density is very similar to the Na-xerogels because of their similar pore structure (i.e. pore size) and conductivity.

From these tables it can be seen that activated xerogels containing Ca in its structure lead to materials with a mesoporosity similar to that obtained when using NaOH instead of $Ca(OH)_2$. The size of the mesopores is similar in both cases, but materials having a higher porosity are obtained when $Ca(OH)_2$ is used as can be seen from the higher

mesopore volumes (V_{meso}). This trend can be seen in figures 4a) to 4c), where the pore size distributions of the activated carbon xerogels are shown. These data highlight the fact that the use of NaOH or $Ca(OH)_2$ leads to materials having similar mesopore sizes as it had been previously shown for non-activated carbon xerogels (see Figure 3).

From these figures, the distribution of mesopore sizes has been obtained. The results are shown in Table 6.

	Comp. Ex. 1	Ex.1	Comp. Ex. 2	Ex.2	Comp. Ex.3	Ex. 3
% of mesopores between 2-15 nm (in relation to the total porosity)	51	54	37	61	54	52
% of mesopores between 2-15nm (in relation to the total mesoporosity)	95	98	88	95	98	98
% of micropores (in relation to the total porosity)	40	44	50	43.47	46.15	50
% of mesopores between 2-50nm (in relation to the total porosity)	60	66	50	56.53	53.85	50

Table 6- Mesopore and micropore size distribution of activated carbon xerogels.

Regarding the microporosity, the micropore volume (Vmicro) is higher when using $Ca(OH)_2$ instead of NaOH, and surprisingly it has been found that the BET area is higher when $Ca(OH)_2$ is used and, in addition the obtained BET areas are considerably higher than those of the carbonized materials (see Figure 1) .

In figure 5, the reactivity of the organic xerogels, as measured using termogravimetry of Ex.1 and Comp. Ex.1 is shown. In this figure, in the temperature range of 200 to 850ºC the weight loss is parallel in both cases which involves that the reactions taking place are analogous. However, at temperatures of about 850ºC and higher temperatures the material obtained using $Ca(OH)_2$ shows a higher loss weight velocity which is an evidence of a more efficient activation. Therefore, these materials can be obtained in a more economical way.

Regarding macroporosity, it has to be noted that the macropore volume is less than 0.01 cm^3/g, which is considered to be within the measurement error values, and therefore it can be considered that no macropores are substantially present.

Furthermore, the total content of impurities of the activated carbon xerogels was measured using ICP-MS as well as the content of Carbon, Sodium and Calcium. The results are shown in Table 7 below.

	C(%)	Na (ppm)	Ca (ppm)	Impurities (ppm)
Ex. 1 ($Ca(OH)_2$)	97	-	600	400
Comp. Ex. 1 (NaOH)	97	1000	-	1000
Ex. 2 ($Ca(OH)_2$)	97	-	500	500
Comp. Ex. 2 (NaOH)	97	1000	-	1000
Ex. 3($Ca(OH)_2$)	97	-	800	400
Comp. Ex. 3 (NaOH)	97	1300	-	1200

Table 7- Impurities and C, Na,Ca content of activated carbon xerogels

From this table, it can be seen that the impurities of the final materials is considerably lower when using $Ca(OH)_2$ instead of NaOH. Therefore, replacing the sodium cation by calcium cation, leads to activated xerogels with a higher degree of purity. This trend was also observed in carbonized xerogels materials obtained in section b) (see table 2).

From all the above results, it is evident that the materials obtained by the polymerization of resorcinol and formaldehyde, using $Ca(OH)_2$ as catalyst in a microwave-assisted process leads to carbonaceous materials that exhibit higher micropore and mesopore volume and SBET than those obtained with other catalysts typically used in the prior art, while also lead to a carbon xerogel having a macropore volume less than 0.01 cm^3/g. and with more than 95% of the total volume of mesopores in the range of 2nm to 15nm. Besides, the obtained carbon xerogels has about 50% to 67% less impurities than the one obtained by the same method using NaOH. As can be seen from the table, the impurities content is 500 ppm or less. These advantages make these materials suitable for being used in supercapacitors.

CLAIMS

1. Carbon xerogel with a calcium content in the range of 500 to 800 ppm, a SBET higher than 1900 m^2/g having a pore size distribution such that at least 95% of the mesopores in relation to the total mesoporosity are comprised in the range from 2 to 15 nm and that and that the macropore volume is less than 0.01 cm^3/g.

2. Carbon xerogel according to claim 1, wherein the micropore volume ranges from 0.2 to 1.5 cm^3/g.

3. Carbon xerogel according to claim 2, wherein the micropore volume ranges from 0.8 to 1.0 cm^3/g.

4. Carbon xerogel according to any one of claims 1 to 3, wherein the mean micropore size ranges from 0.5 to 1.9 nm.

5. Carbon xerogel according to claim 4, wherein the mean micropore size ranges from 0.9 to 1.6 nm.

6. Carbon xerogel according to any one of claims 1-5, having an impurities content of 500 ppm or less.

7. Carbon xerogel according to any one of claims 1-6, which is obtained by a process which comprises the following steps:

a) mixing a polymerizable hydroxybenzene and a polymerizable aldehyde in water and in the presence of $Ca(OH)_2$ in the amount necessary to impart to the solution a pH in the range from 4 to 8;

b) subjecting the mixture of step a) to microwaving at a power such that the mixture reaches a temperature in the range of 40°C to 100°C so that the mixture is polymerized, and then maintaining the microwaving until the polymerized product has a moisture content lower than 40%;

c) subjecting the polymerized product obtained in step b) to a carbonization and/or activation step at a temperature of between 900 and 1200°C in CO_2 steam for 1 to 6 hours.

8. Carbon xerogel according to claim 7, wherein the hydroxybenzene is resorcinol and the aldehyde is formaldehyde.

9. Carbon xerogel according to claim 8, wherein the molar ratio of resorcinol to formaldehyde ranges from 0.2 to 0.5.

10. Carbon xerogel according to any one of claims 7 to 9, wherein the pH ranges from 6.2 to 6.8.

11. Carbon xerogel according to any one of claims 8 to 10, wherein the molar ratio of resorcinol plus formaldehyde to water ranges from 4.7 to 5.7.

12. Carbon xerogel according to any one of claims 7 to 11, wherein the carbonization and/or activation step is carried out as two sub-steps: a carbonization step followed by an activation step.

13. Process for obtaining a carbon xerogel, which comprises the following steps:

a) mixing a polymerizable hydroxybenzene and a polymerizable aldehyde in water and in the presence of $Ca(OH)_2$ in the amount necessary to impart to the solution a pH in the range from 4 to 8;

b) subjecting the mixture of step a) to microwaving at a power such that the mixture reaches a temperature in the range of 40°C to 100°C so that the mixture is polymerized, and then maintaining the microwaving until the polymerized product has a moisture content lower than 40%;

c) subjecting the polymerized product obtained in step b) to a carbonization and/or activation step at a temperature of between 900 and 1200°C in CO_2 steam for 1 to 6 hours.

14. Process according to claim 13, wherein the hydroxybenzene is resorcinol and the aldehyde is formaldehyde.

15. Process according to claim 14, wherein the molar ratio of resorcinol to formaldehyde ranges from 0.2 to 0.5.

16. Process according to claim 13 to 15, wherein the pH ranges from 6.2 to 6.8.

17. Process according to any one of claims 13 to 16, wherein the molar ratio of resorcinol plus formaldehyde to water ranges from 4.7 to 5.7.

18. Process according to any one of claims 13 to 17, wherein the carbonization and/or activation step is carried out as two sub-steps: one carbonization step followed by an activation step.

19. Use of the material according to any one of claims 1 to 12 in electrodes of supercapacitors.

20. Electrode for supercapacitor comprising the xerogel of any one of previous claims 1 to 12.

21. Electrode for supercapacitor according to claim 20, wherein the energy density delivered by the electrode, when measured in galvanostatic charge/discharge cycles at 0.2 A g^{-1} with U=1.0 V in a voltage window from 0.6 to 1.2 V, is higher than 18 Wh/kg.

22. Electrode for supercapacitor according to claim 20, wherein the power density delivered by the electrode, when measured in galvanostatic charge/discharge cycles at 0.2 A g^{-1} with U=1.0 V in a voltage window from 0.6 to 1.2 V, is at least 20000 W/kg.

23. Electrode for supercapacitor according to claim 20, wherein the capacity of the electrode, when measured in galvanostatic charge/discharge cycles at 0.2 A g^{-1} with U=1.0 V in a voltage window from 0.6 to 1.2 V, is higher than 120 F/g.

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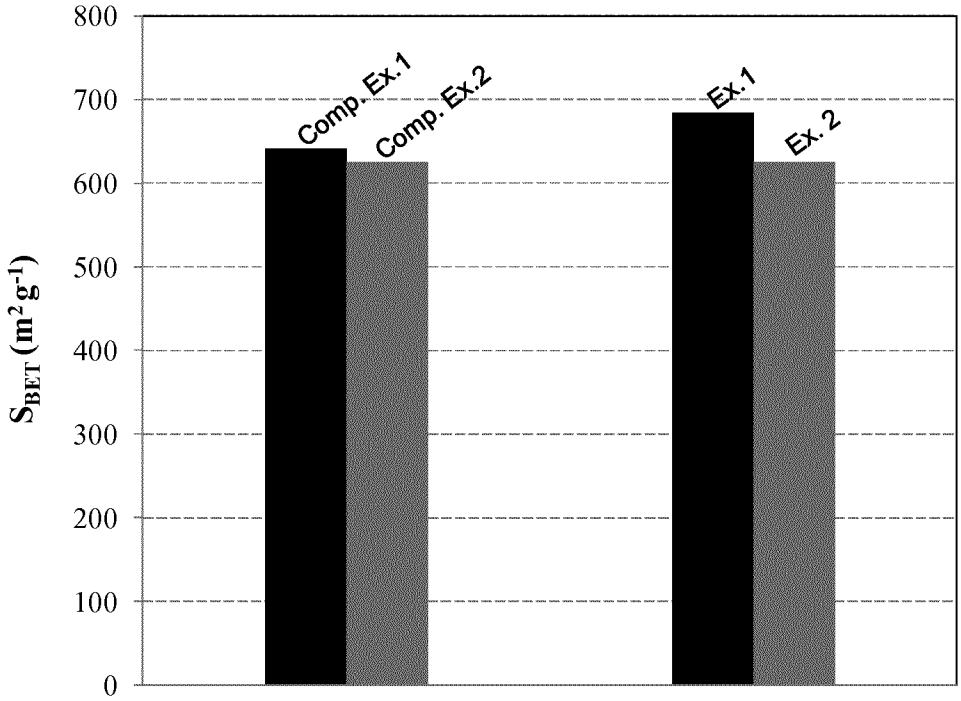
800
700
600
500
400
300
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100
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S_{BET} ($m^2 g^{-1}$)
Comp. Ex.1
Comp. Ex.2
Ex.1
Ex. 2

Figure 1

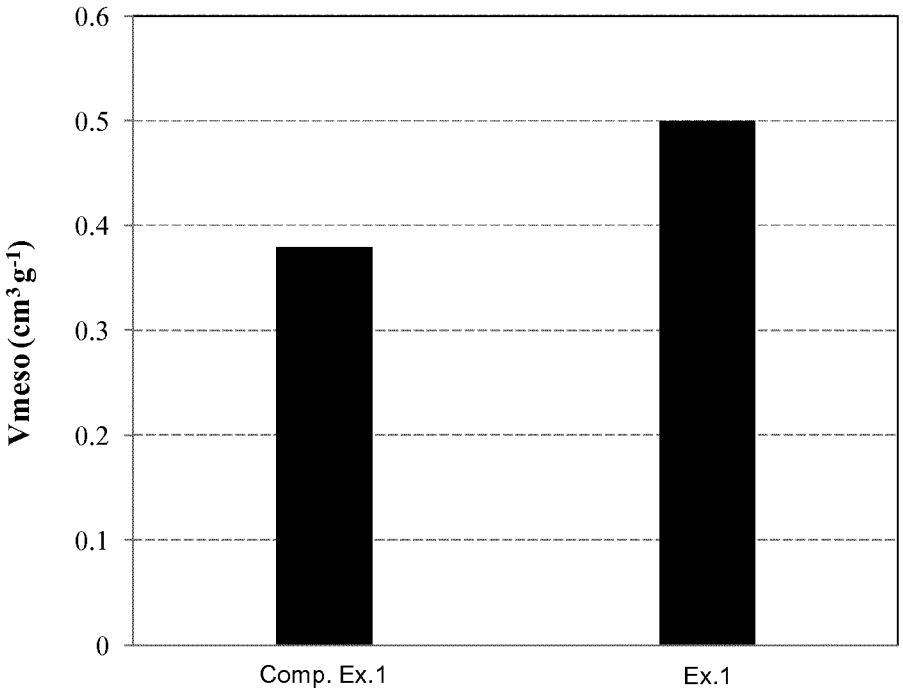

Figure 2a

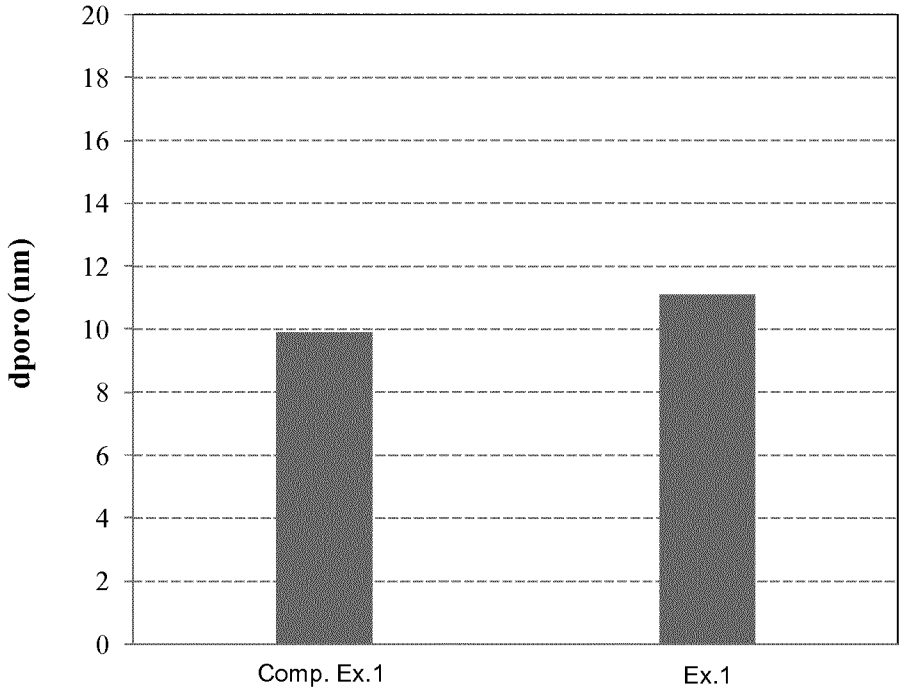

Figure 2b

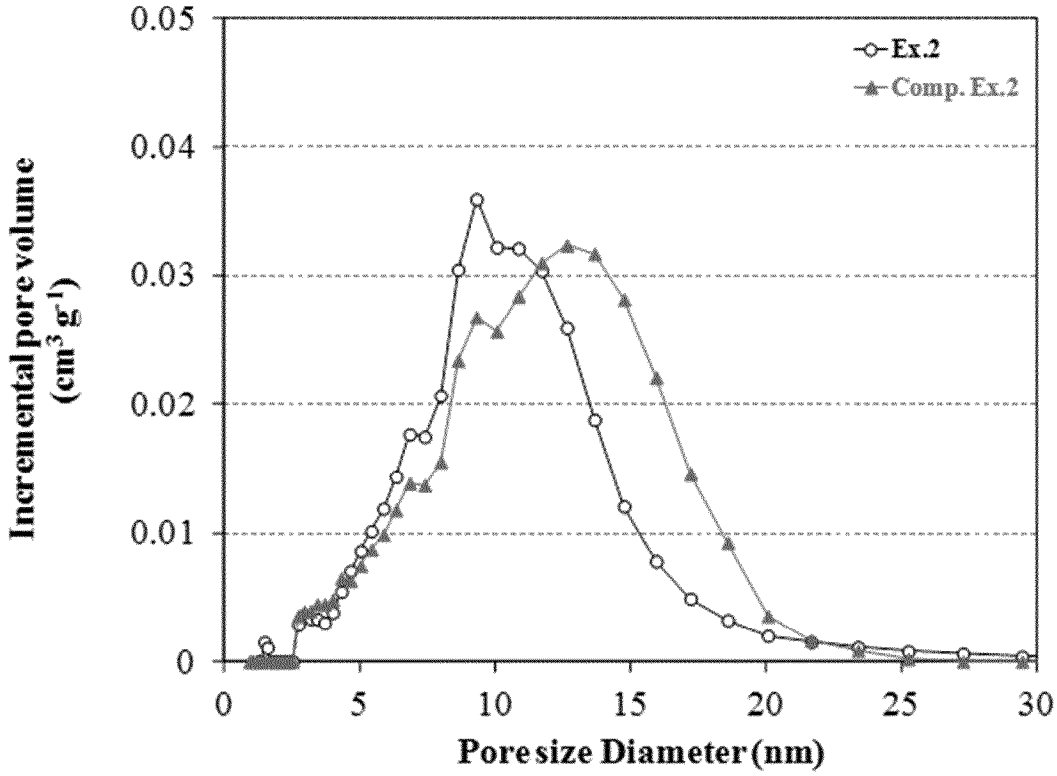
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
25
30
Ex.2
Comp. Ex.2
Incremental pore volume (cm3 g-1)
Pore size Diameter (nm)

Figure 3

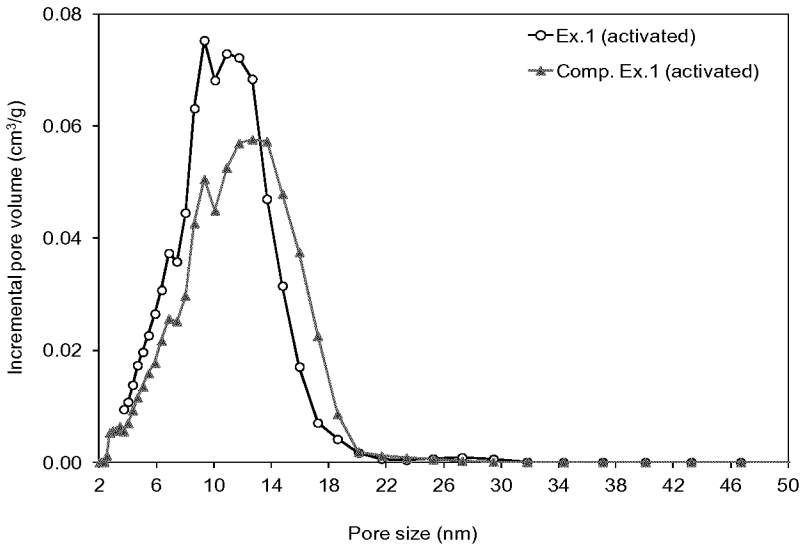

Figure 4a

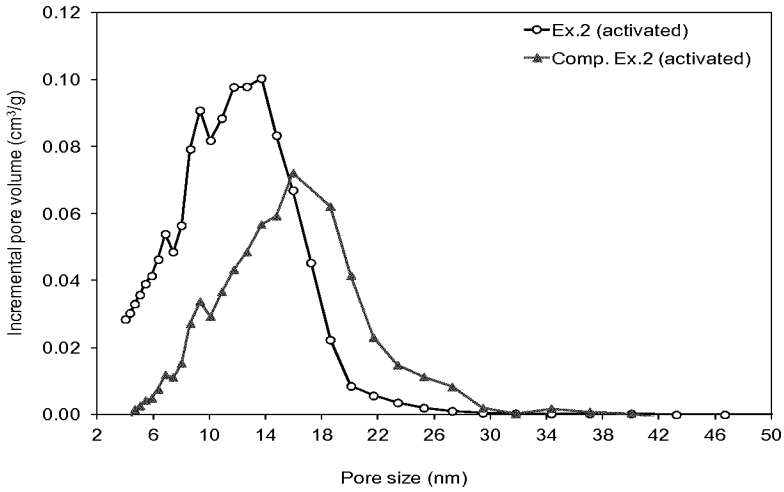

Figure 4b

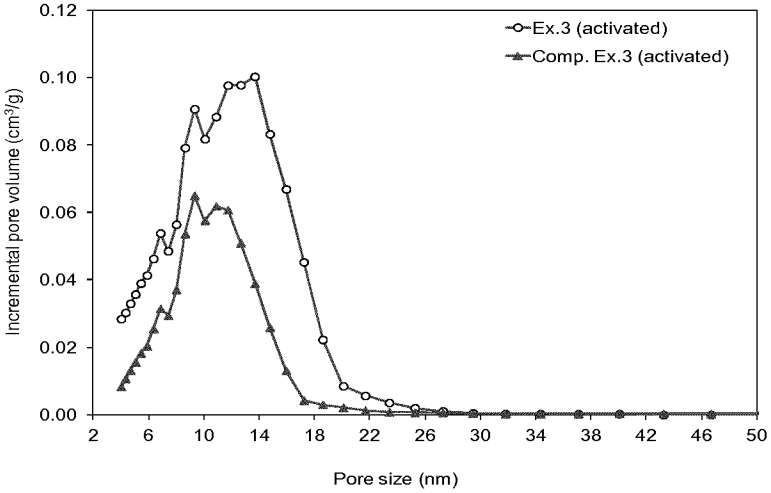

Figure 4c

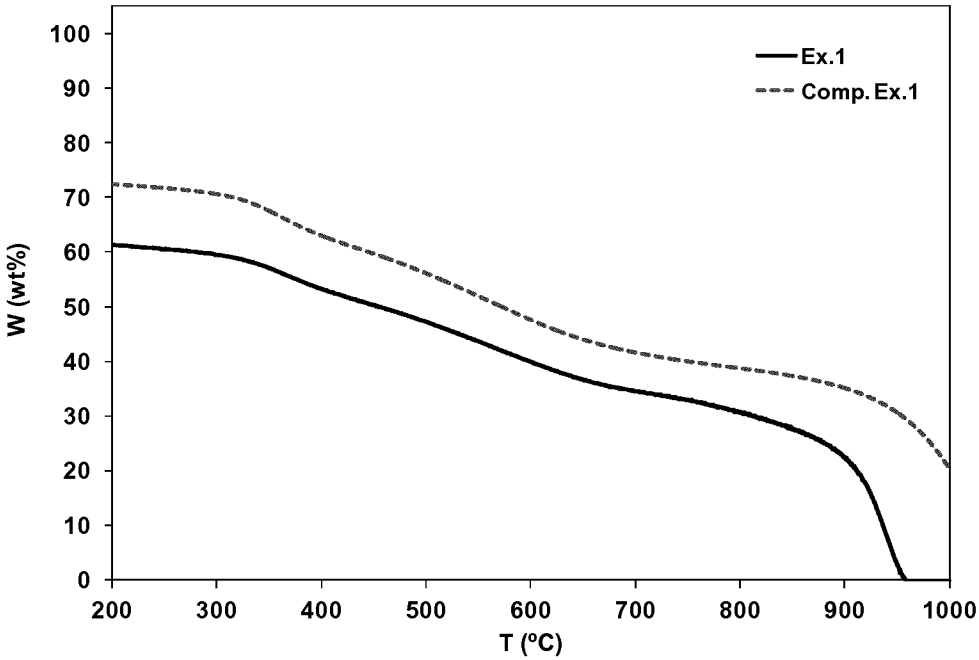
100
90
80
70
60
50
40
30
20
10
0
W (wt%)
200
300
400
500
600
700
800
900
1000
T (ºC)
Ex.1
Comp. Ex.1

Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/058704

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G8/10 H01G11/32 C01B32/00 C01B32/336
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B C08G H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CALVO E G ET AL: "Optimizing the electrochemical performance of aqueous symmetric supercapacitors based on an activated carbon xerogel", JOURNAL OF POWER SOURCES, vol. 241, 30 March 2013 (2013-03-30), pages 776-782, XP028675747, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2013.03.065	13-18
A	page 777	1-12, 19-23

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2017	19/06/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bomm, Jana

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CALVO E G ET AL: "Fast microwave-assisted synthesis of tailored mesoporous carbon xerogels", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS,INC, US, vol. 357, no. 2, 13 February 2011 (2011-02-13), pages 541-547, XP028370244, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2011.02.034 [retrieved on 2011-02-18] page 542	1-23
Y	JOB N ET AL: "Effect of the counter-ion of the basification agent on the pore texture of organic and carbon xerogels", JOURNAL OF NON-CRYSTALLINE SOLIDS, NORTH-HOLLAND PHYSICS PUBLISHING. AMSTERDAM, NL, vol. 354, no. 40-41, 15 October 2008 (2008-10-15), pages 4698-4701, XP025410035, ISSN: 0022-3093, DOI: 10.1016/J.JNONCRYSOL.2008.06.102 [retrieved on 2008-08-22]	13-18
A	page 4699	1-12, 19-23
A	WO 2015/042271 A1 (GEORGIA PACIFIC CHEMICALS LLC [US]) 26 March 2015 (2015-03-26) paragraph [0092] - paragraphs [0094], [0125]	1-23

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/058704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015042271 A1	26-03-2015	CN 105683259 A	15-06-2016
		EP 3046950 A1	27-07-2016
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		KR 20160058173 A	24-05-2016
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		WO 2015042271 A1	26-03-2015