

The enhancement of porosity of carbon xerogels by using additives

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ABSTRACT

Resorcinol-formaldehyde carbon xerogels were synthesized by means of microwave heating by using precursor solutions with pH values ranging from 3 to 7 and adding various amounts of sodium sulfate, hexadecyltrimethylammonium bromide and Span80. It was found that the amount of additive that can be introduced depends to a large extent on the final pH of the precursor solution. Characterization of the porous structure of the carbon xerogels thus synthesized demonstrated that their porosity was modified by interactions between the additives and the polymeric structure of the xerogels. It is worth noting that carbonaceous materials with a pore size that could not be obtained by merely modifying the pH could be synthesized by adding different types of additive, with the result that a significant improvement of the porous properties of the carbon xerogels was achieved. The addition of sodium sulfate increased the size of the clusters and pores due to repulsive forces created between the additive and resorcinol anions. Hexadecyltrimethylammonium bromide gave rise to a dense branched structure with pores of a small size attributable to forces of attraction between the cations of the additive and resorcinol anions. In contrast, the presence of Span80 in the precursor solution produced a condensation reaction between the resorcinol and the additive, as a result of which the amount of resorcinol available for the sol-gel reaction was reduced.

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1. Introduction

Carbon gels are porous materials that are obtained by drying and carbonizing organic polymer-based gels [1]. The most common process for synthesizing this organic gel is by the polymerization of resorcinol with formaldehyde in the presence of a solvent following Pekala's method [2]. The great advantage of these materials is that their final properties can be controlled and tailored to fit specific applications by modifying the process conditions.

From a chemical point of view, the pH of the precursor solution is the variable that has the greatest influence, though the concentrations of water, resorcinol and formaldehyde are also key variables that determine the final porous structure of the carbon gels [1, 3-5]. In terms of the process conditions, the drying method also plays a very important role in determining the final properties [1]. Resorcinol-formaldehyde gels can be dried under supercritical conditions, giving rise to materials known as aerogels [2, 6, 7] or by the sublimation of water from the pores by a lyophilization process, resulting in the formation of cryogels [8]. In both of these processes, the surface tension forces are small and hence the gel structure shrinks only slightly, leading to materials with well-developed porous structures. Although these drying methods yield highly porous materials, they involve cumbersome solvent exchange processes and complex drying stages.

The solvent can be also removed by direct evaporation, which is a simpler and quicker drying process that yields more competitive materials, known as xerogels [9-11]. However, evaporative drying causes greater shrinkage than supercritical and freezing drying, resulting in materials with less developed porous structures. It is therefore necessary to modify the

synthesis process in order to avoid or reduce the effect of collapse of the polymeric structure. As a solution to this problem, some authors have proposed the addition of additives to the precursor solutions of carbon gels to prevent shrinkage during drying and to obtain well developed mesoporous materials [12, 13].

The most widely used additives for synthesizing carbon gels are surfactants, which can be anionic, cationic or non-ionic. Of the possible anionic and cationic surfactants, probably the most commonly used for synthesizing RF gels are sodium dodecylbenzenesulfonate (SDBS) [6, 9, 12, 14] and hexadecyltrimethylammonium bromide (CTAB) [7, 9, 13-16], respectively. Alternatively, the non-ionic surfactants Span and Pluronic are frequently used [9, 14]. However, it is difficult to assess the effectiveness of each of these surfactants as researchers use different experimental conditions that influence the effect of these additives. Most studies on the synthesis of carbon gels by the addition of surfactants employ the emulsion technique [6, 7, 9, 15] which requires the surfactants to be added after gelation has taken place, while other authors dissolve the surfactant in a solution of resorcinol prior to the sol-gel reaction [14, 16]. Furthermore, to the best of our knowledge, all these carbon xerogels were conventionally synthesized and, there is no evidence in the literature as to what effect these additives would have on the synthesis of carbon xerogels if another heating source, such as microwave radiation, is used.

Accordingly, the aim of this work is to elucidate the effect of different additives on the formation of the polymeric structure of carbon xerogels synthesized by means of microwave heating and establish whether they can be used to tailor porous properties. All of the synthesized carbon xerogels were subjected to characterization of their porous

structure to establish the effect of these additives when modifying both the initial pH of the precursor solution and the amount of additive. Moreover, possible chemical interactions between the additives and the polymeric structure were also investigated.

2. Experimental

2.1. Materials

The resorcinol was purchased from Indspec (99 %). Formaldehyde (37 wt. % in water, stabilized by 10-15 wt. % of methanol), hexadecyltrimethylammonium bromide (CTAB, 98%) and Span 80 were supplied by Merck. Sodium sulfate (Na_2SO_4 , 99%) was purchased from VWR International. Other chemicals used included deionized water and 5M sodium hydroxide (Analar Normapur, VWR International) solution.

Sodium sulfate, instead of sodium dodecylbenzenesulfonate (the most common anionic surfactant used to synthesize carbon gels), was used in order to investigate whether the formation of micelles, a phenomenon typical of surfactants, plays a role in the modification of the pore structure of carbon xerogels or whether the repulsive forces produced by sulfate anions are sufficient to prevent the collapse of the polymeric structure during the drying of RF xerogels.

2.2. Preparation of pure RF precursor solutions

Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. After dissolution formaldehyde was added and the resulting mixture was stirred until a homogeneous solution was obtained. Five different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide.

All the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7. The dilution ratio parameter is defined as the molar ratio between the total amount of solvent and the total amount of reactants. The term total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst the term reactant refers to the resorcinol and formaldehyde.

2.3. Preparation of Na₂SO₄-RF precursor solutions

Resorcinol and sodium sulfate were first dissolved in deionized water in separate unsealed glass beakers under magnetic stirring. After dissolution, both solutions were mixed together and then formaldehyde was added. The resulting mixture was stirred until a homogeneous solution was obtained. Twenty different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide and with four different concentrations of sodium sulfate (0.5, 2, 4 and 8 wt. %). All the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7.

2.4. Preparation of CTAB-RF precursor solutions

Precursor solutions containing hexadecyltrimethylammonium bromide (CTAB) were prepared following the same methodology as that described above for the preparation of Na₂SO₄-RF precursor solutions (section 2.3) but dissolving CTAB instead of sodium sulfate in an unsealed glass with deionized water.

2.5. Preparation of Span80-RF precursor solutions

Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. After dissolution formaldehyde was added. Then Span80 was introduced and the resulting mixture was stirred until a homogeneous solution was obtained. The non-ionic surfactant was added to the resorcinol-formaldehyde solution rather than to the dissolved resorcinol due to its low solubility in water (HLB value of 4.3). Twenty different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide and with four different concentrations of Span80 (0.5, 2, 4 and 8 wt. %). All of the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7.

2.6. Synthesis of organic and carbon xerogels

Each precursor solution was placed in a microwave oven (in-lab design and construction) at 85 °C for 3 hours to allow gelation and curing to take place. After the formation of the polymeric structure, excess water was eliminated by continuing to heat the gel in the microwave oven until a mass loss of 50 wt. % was achieved. This drying step lasted 1-2 hours depending on the final pore structure of the material. After drying, the xerogels were carbonized at 700 °C under a nitrogen flow of 150 ml/min in a horizontal tubular furnace from Carbolite Ltd. The residence time was 2 hours and the heating rate was set at 50 °C/min. The carbon xerogels obtained were labelled CX followed by the pH value (from 3 to 7) and by the percentage of additive added (0.5, 2, 4 and 8 wt. %). An 'S', 'C' or 'NI' was appended to the name to indicate the type of additive added: sodium salt, cationic surfactant or non-ionic surfactant, respectively.

2.7. Sample characterization

Before being subjected to analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VacPrep 061. These degassing conditions had been previously optimized for outgassing this type of material. The porous properties of the carbon xerogels were characterized by nitrogen adsorption-desorption isotherm analysis performed at -196 °C using a Micromeritics Tristar 3020 instrument. It is well known that pore volume measurements by nitrogen adsorption are not precise enough in the case of samples with macropores or even large mesopores. For this reason, mercury porosimetry (Micromeritics AutoPore IV) was used as a complementary technique to determine the pore size distribution. Analysis by mercury porosimetry was based on Washburn's intrusion theory, following the methodology described elsewhere [17] (see Supporting Information for more details). The morphology of the carbon structure was observed using a Quanta FEG 650 scanning electron microscope. Thermogravimetric analysis was performed by means of a TA instrument DSC Q600 analyzer. The weight loss of each sample was monitored in the temperature range of 25-1000 °C by purging nitrogen at 20 ml/min and at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Na₂SO₄-RF carbon xerogels

The amount of sodium sulfate, Na₂SO₄, that can be added to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions depends on the final pH value of the precursor solution. The possible pH value and sodium sulfate addition combinations are shown in Figure 1 by the coloured region.

As illustrated in Figure 1, 0.5 wt. % of Na_2SO_4 can be added to the precursor solution when the pH value is set at a value of 4 or higher. The amount of additive can be increased as the pH value increases up to a maximum of 2 wt. % for a pH value fixed at 7. When concentrations of sodium sulfate above the levels specified in Figure 1 are used, the sol-gel reaction still occurs but in an uncontrolled manner since the precursor solution starts to boil. This phenomenon is due to the polymerization reaction between resorcinol and formaldehyde explained in detail elsewhere [3]. First, resorcinol anions are formed by the abstraction of hydroxylic hydrogen [1]. These anions are more reactive than resorcinol and promote the addition of formaldehyde to form hydroxymethyl derivatives, which are the monomers necessary for polymerization to occur [3]. These derivatives combine through methylene and ether bonds to form the polymer chains that produce an interconnected three-dimensional structure [9, 10]. Increasing the initial pH of the precursor solution (i.e. adding more catalyst) leads to the formation of more resorcinol anions, which favors the addition reaction and the formation of more clusters [3].

When no catalyst is introduced into the precursor solution (pH value of 3), the SO_4^- groups originating from the dissociation of the salt in solution contribute to the deprotonation of the resorcinol via the formation of HSO_4^- molecules (Reaction A, Figure 1). In this case, Na_2SO_4 acts as the catalyst of the reaction. Moreover, the great hygroscopic capacity of this additive leads to the hydration reaction shown in the Reaction B of Figure 1. Both reactions shown in Figure 1 are exothermic and, when there is an excess of additive, the synthesis temperature may increase to above $85\text{ }^\circ\text{C}$, causing the precursor solution to boil uncontrollably. When NaOH is introduced into the precursor solution it acts as the catalyst, i.e. it promotes the formation of resorcinol anions, preventing the deprotonation caused by

SO_4^- groups. An excessive increase in temperature during the reaction is thereby avoided and carbon xerogels can be synthesized under controlled conditions. Thus, the greater the concentration of catalyst used, the greater the amount of sodium sulfate that can be added without causing the precursor solution to boil.

When the catalyst concentration is large enough to prevent the deprotonation of the resorcinol by the SO_4^- groups, the Na_2SO_4 , which is in the solution, is in its dissociated form i.e. the solution contains SO_4^- anions and Na^+ cations. Repulsive forces are created among the SO_4^- anions and resorcinol anions generated during the addition reaction, and as a result, the formation of methylene and ether bonds is retarded. Thus, the structure of the xerogel forms more slowly and farther away from the additive anions, as shown in Figure 2.

It is clear that the addition of sodium sulfate alters the normal course of the sol-gel reaction, leading to changes in the formation of the polymeric structure and, in turn, in the final porous properties of carbon xerogels, as demonstrated in Figure 3, which shows the pore size distributions of carbon xerogels synthesized from precursor solutions with different pH values. Figure 3 also includes the pore size distribution of carbon xerogels synthesized from a precursor solution with a pH value of 7 and with different amounts of sodium sulfate. The average pore size increases from 6 nm (corresponding to sample CX-7 which does not appear in the figure due to its low pore size value) to 25 nm and 150 nm as the amount of sodium sulfate increases from 0.5 to 2 wt. % respectively. In other words, the addition of sodium sulfate to the precursor solution causes the samples to evolve from micro-mesoporous to micro-macroporous materials, as shown in the nitrogen adsorption-

desorption isotherm in Figure S2 (Supporting Information). The average pore size of sample CX-6 also increases from 16 nm to 86 nm as a result of the addition of 0.5 wt. % of sodium sulfate (Figure 3). The same trend was observed in the pore size distributions of the samples synthesized from a precursor solution with pH values of 4 and 5, which had an average pore size larger than 200 nm (the maximum value required for most applications) and, hence, they are not included in Figure 3 (more data related to porous properties are summarized in Table S1 in the Supporting Information). In short, the addition of just a small amount of sodium sulfate gives rise to materials with pore sizes that would be impossible to obtain by just modifying the pH value, facilitating the tailoring of the porosity of carbon xerogels.

These results are in good agreement with those reported by other studies where sodium dodecylbenzenesulfonate (anionic surfactant) was used. The authors of those studies demonstrated that the addition of anionic surfactant generates repulsive forces, preventing the formation of RF-surfactant composites [6, 9, 12, 14]. In this work, sodium sulfate also generated repulsive forces, preventing shrinkage during drying, despite the fact that no micelles were formed when Na_2SO_4 was dissolved in water. Thus, the effect of sodium sulfate seems to be similar to that of sodium dodecylsulfate since the materials obtained by means of the anionic surfactant displayed structures with a large pore size similar to those prepared in the present work. However, Jirglovà et al. [14] have published SEM images showing that the addition of sodium dodecylbenzenesulfonate leads to the formation of needle structures, whereas the use of sodium sulfate gives rise to more spherical and homogeneous clusters, as illustrated in Figure 4.

Repulsive forces created among the SO_4^- anions and resorcinol anions retard the development of crosslinkages. As a result, the structure forms more slowly, causing a gradual increase in the size of the clusters. In addition, the formation of clusters takes place farther away from the additive anions (Figure 2) leading to larger voids between the clusters (Figure 3).

3.2. CTAB-RF carbon xerogels

The amount of hexadecyltrimethylammonium bromide (CTAB) that can be added to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions also depends on the final pH value of the precursor solution. However, the behavior of CTAB is contrary to that observed with the addition of sodium sulfate, in that the lower the pH of the precursor solution, the greater the quantity of surfactant that can be added to synthesize CTAB-RF xerogels under controlled conditions, as shown in Figure 5. In contrast to these results, Matos et al. [9] obtained carbon xerogels prepared from precursor solutions with a pH value of 6.4 and concentrations of CTAB of up to 15 wt. % without the occurrence of precipitation. This may have been due to their method of preparation. In the present work the surfactant was added to the dissolved resorcinol prior to the addition of formaldehyde, whereas Matos et al.[9] added the CTAB to the resorcinol-formaldehyde solution.

The limits to the quantities added in Figure 5 are determined by the appearance of precipitates that modified the basicity of the solution. The resulting precipitates were analyzed by thermogravimetry together with the cationic surfactant and sample CX-6 with

and without surfactant in order to establish the composition of the precipitate. The results of this analysis are shown in Figure S3 (Supporting information). The precipitate obtained at high pH values is mostly the cationic surfactant impregnated with some RF gel. The cationic surfactant used in this study is a soluble compound in an acid media, so that as the pH increases, its solubility decreases, causing it to precipitate. However, it is necessary to point out that sample OX-6 and OX-6-0.5%C exhibit similar TGA profiles, indicating the possible formation of a CTAB-RF composite (Figure S3). The reason for this is that the dissolved CTAB forms micelles leaving the positive charges in contact with the reaction media and the carbon chain inside the micelle [13, 15]. Resorcinol anions are attracted to the cations of the surfactant, so that crosslinkages occur close to the cation, as shown in Figure 5, giving rise to chemical interaction between the polymeric structure and the surfactant.

CTAB behavior during the polymerization reaction has a direct effect on the final porous properties of carbon xerogels. In fact, the addition of CTAB to the precursor solutions leads to the formation of a large number of small clusters, as shown in Figure 6. Furthermore, the clusters are close to each other due to the effect of the surfactant, resulting in a very densely branched structure with pores of a small size (Figure 6b). When the concentration of CTAB is increased, carbon xerogels evolve from macroporous material to micro-mesoporous and even to exclusively microporous materials, as confirmed by the nitrogen adsorption-desorption isotherm shown in Figure S4 in the supporting information.

When CTAB is added, the N₂ adsorption-desorption isotherms of the carbon xerogels evolve from a combination of type I and II to a combination of type I and IV. From Figure

S4 in the supporting information it can be seen that an increase in the concentration of CTAB to above 0.5 wt. %, causes a narrowing of the hysteresis loop, which indicates a decrease in the volume adsorbed at high relative pressures, resulting in structures with a smaller volume of pores and of a smaller size. Jirglovà et al. [14] and Wu et al. [7] also observed a decrease in the clusters and pore sizes when CTAB was employed, whereas Matos et al. and Bruno et al. [15] obtained materials with a larger pore size [9]. Again, the differences in the effect of the surfactant could have been due to the method of preparation. Hence, the way in which CTAB is added to the precursor solutions will result in carbon gels with different porous properties.

3.3. Span80-RF carbon xerogels

When a non-ionic surfactant is used, the maximum amount that it can be added is determined by the initial pH of the precursor solution since the surfactant used in the study, Span80, alters the initial pH values, as shown in Figure 7a.

When no surfactant is added to the precursor solution, the initial pH value is around 3.0, whereas when 2 wt. % of Span80 is added, the initial pH value increased to 5.0. Therefore, it is not possible to synthesize Span80-RF xerogels over the whole range of pH values with the addition of Span80, unless acid catalysts are used. The use of acid catalysts for microwave-assisted synthesis was discarded for this study since the sol-gel reaction takes place via a different route and hence falls outside the scope of this work. It is worth noting that, although several works in the literature deal with the use of Span80 for the synthesis of carbon gels, to the best of our knowledge no evidence has been reported to suggest any modification of the initial pH value of the precursor solutions.

During the polymerization reaction between resorcinol and formaldehyde, hydroxymethyl derivatives are formed [3] and combine to create methylene and ether bonds that lead to a polymeric structure [14, 16]. It has been conjectured that the presence of Span80 in the precursor solution produces a condensation reaction between the hydroxyl groups from the resorcinol and the alcohol groups from the surfactant, as shown in Figure 7b. This hypothesis is verified by the TGA profiles of the Span 80, OX-6 and OX-6-0.5%NI depicted in Figure S5 (Supporting information). Sample CX-6 follows the trend of the most common thermogravimetric profile for RF gels. According to the literature [10], the TGA profile for RF gels displays three major weight losses at temperatures ranging between i) 80 and 200°C when moisture is removed, ii) 300 and 400°C when volatile material is eliminated and C-O bond breakage occurs and iii) 500 and 600°C when the C-H bonds break. As Figure S5 shows, the mass loss in sample CX-6 is higher than in sample CX-6-0.5% Ni, which indicates that the non-ionic surfactant has interacted with the polymeric structure, modifying the formation of bonds.

The fact that a condensation reaction between the non-ionic surfactant and the hydroxyl groups in the resorcinol molecule occurs means that, for a given molar ratio between resorcinol and formaldehyde, the sol-gel reaction behaves as if the proportion of resorcinol were lower, since part of this compound is retained during the condensation reaction with the surfactant. A decrease in the amount of resorcinol, i.e., a decrease in the R/F molar ratio, promotes the addition reaction that takes place during the sol-gel stage, resulting in a faster formation and growth of clusters which leads to more interconnections between them and, hence, to a highly branched structure. The mechanical strength of organic xerogels

increases and therefore no shrinkage occurs during drying, giving rise to a structure with larger pore volume. This hypothesis is consistent with the SEM images in Figure 8a and 8b for samples with a pH value of 6 (the same trend was observed for samples with different pH values).

The materials obtained show an increase in the volume of pores and a variation in the sizes of the pores with increasing addition of Span80 to the precursor solution (Figure 9). As can be seen from Figure 9, an increase in the pH by just one unit, from 5 to 6, leads to a decrease in the average pore size from 75nm to 16 nm. By adding different amounts of Span 80 a whole range of average pore sizes between 75 and 16 can be achieved (more data related to porous properties are summarized in Table S3 in the Supporting Information). These values could not be obtained by just modifying the pH value of the precursor solution. In short, the addition of Span80 facilitates the tailoring of porous properties of carbon xerogels.

4 Conclusions

Carbon xerogels with different pH values and different types and concentrations of additives were synthesized by means of microwave heating. It was found that the amount of additive that can be added to the precursor solution depends to a large extent on the pH value of the solution and the nature of the additive. Furthermore, the use of these additives modifies the formation of the polymeric structure, and hence, its addition to the precursor solution can be considered a useful alternative for tailoring the porous properties of carbon xerogels.

It was also observed that the addition of sodium sulfate causes certain sluggishness in the development of crosslinkages due to the repulsive forces produced between the additive anions and resorcinol anions, resulting in the formation of larger clusters. The addition of a cationic surfactant (CTAB) gives rise to forces of attraction between the surfactant cations and resorcinol anions, leading to chemical interaction between the surfactant and the polymeric structure. When Span80 is added, a polycondensation reaction between this additive and the resorcinol takes place, reducing the amount of resorcinol available. Thus, the effect of adding this surfactant is similar to that of decreasing the molar ratio between the resorcinol and formaldehyde.

The addition of both sodium sulfate and Span80 give rise to materials with porous properties that could not be obtained by just modifying the pH value of the precursor solution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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FIGURE CAPTIONS

Figure 1. Combinations of pH values and amount of sodium sulfate that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the chemical behavior of sodium sulfate during the sol-gel reaction between resorcinol and formaldehyde.

Figure 2. Effect of Na_2SO_4 on the pore size of carbon xerogels synthesized by microwave heating.

Figure 3. Pore size distribution of carbon xerogels synthesized with and without sodium sulfate.

Figure 4. SEM images of sample CX-6 (a) and CX-6-0.5%S (b).

Figure 5. Combinations of pH values and amount of CTAB that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the effect of CTAB micelles on the formation of the polymeric structure.

Figure 6. SEM images of sample CX-6 (a) and CX-6-0.5%C.

Figure 7. Combinations of pH values and amount of Span80 that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions (a) and condensation reaction between resorcinol and Span80 (b).

Figure 8. SEM images of sample CX-6 (a) and CX-6-0.5%NI (b).

Figure 9. Pore size distribution of samples synthesized from precursor solutions with pH values of 5 and 6 and different amount of Span80.

FIGURES

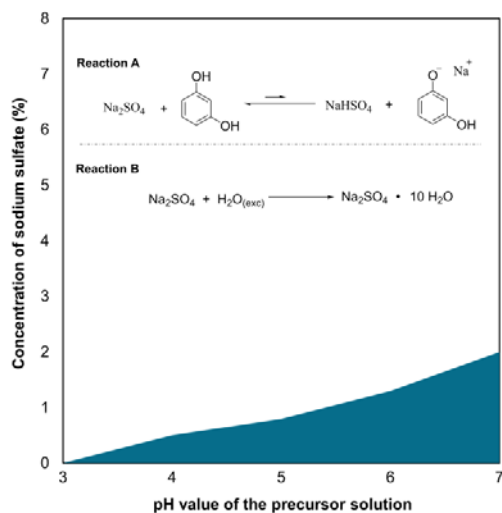


Figure 1. Combinations of pH values and the amount of sodium sulfate that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the chemical behavior of sodium sulfate during the sol-gel reaction between resorcinol and formaldehyde.

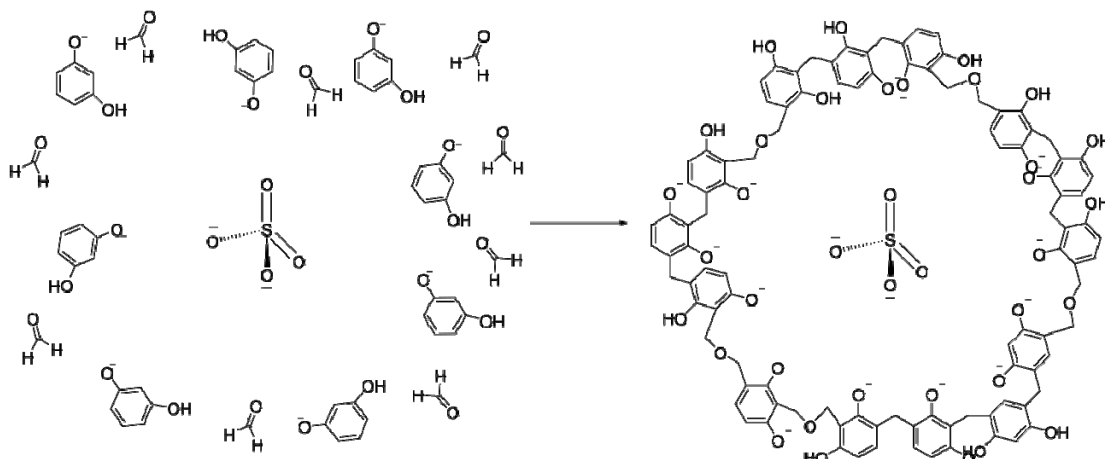


Figure 2. Effect of Na₂SO₄ on the pore size of carbon xerogels synthesized by microwave heating.

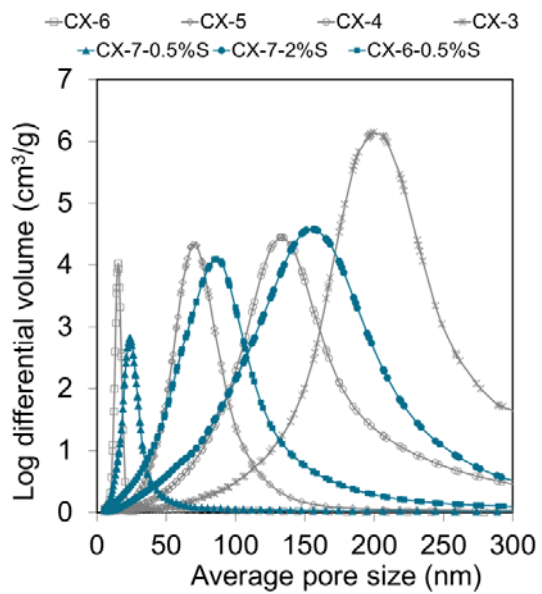


Figure 3. Pore size distribution of carbon xerogels synthesized with and without sodium sulfate.

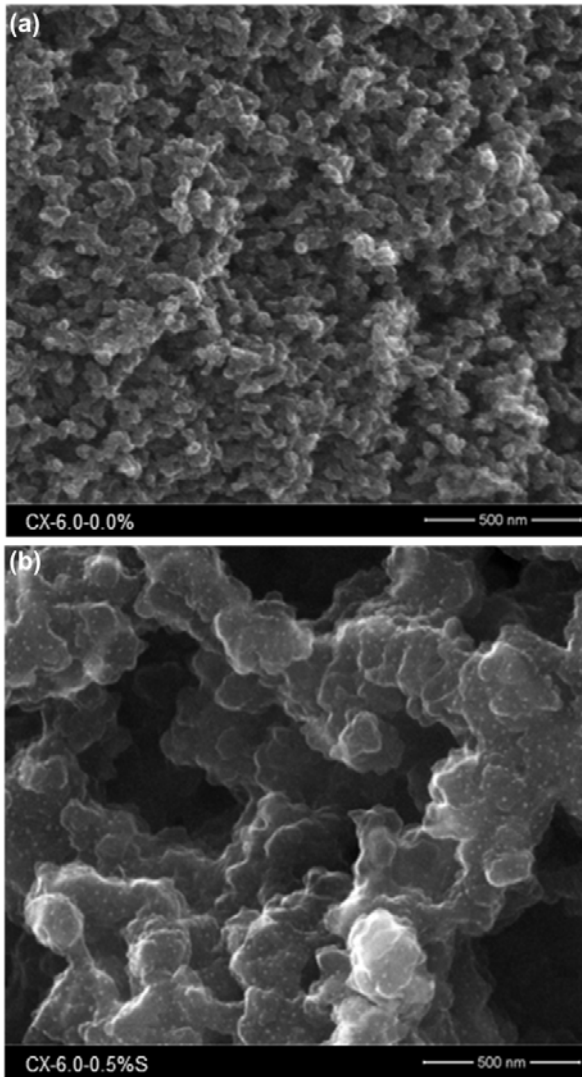


Figure 4. SEM images of sample CX-6 (a) and CX-6-0.5%S (b).

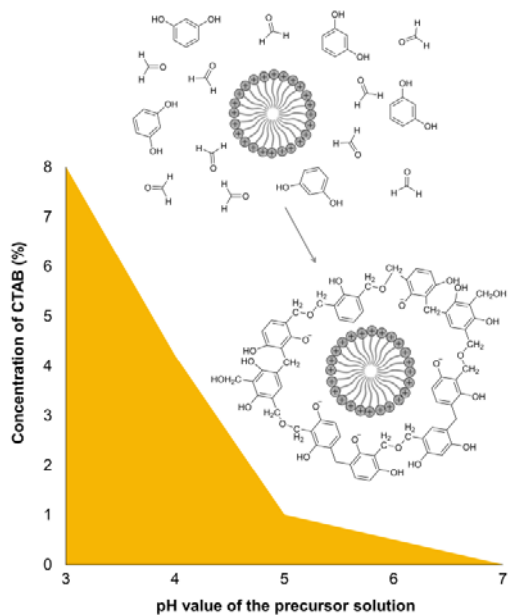


Figure 5. Combinations of pH values and amount of CTAB that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the effect of CTAB micelles on the formation of the polymeric structure.

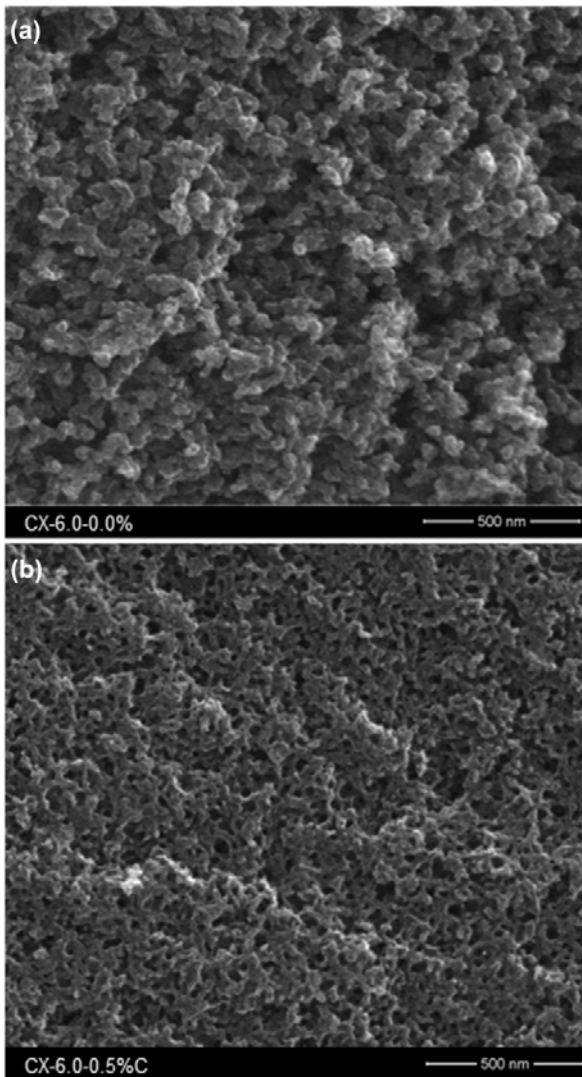
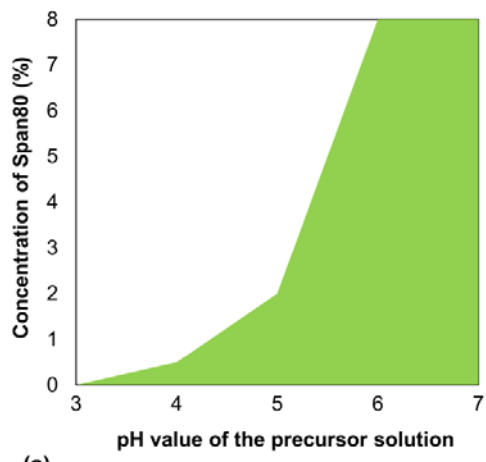
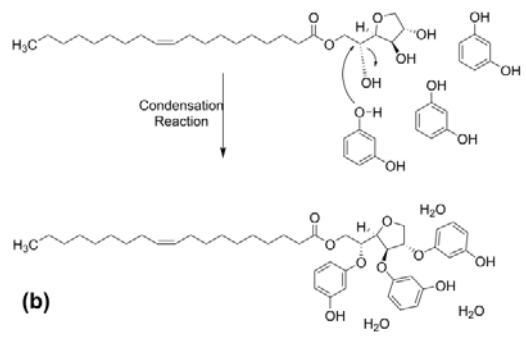


Figure 6. SEM images of sample CX-6 (a) and CX-6-0.5%C.



(a)



(b)

Figure 7. Combinations of pH values and amount of Span80 that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions

(a) and condensation reaction between resorcinol and Span80 (b).

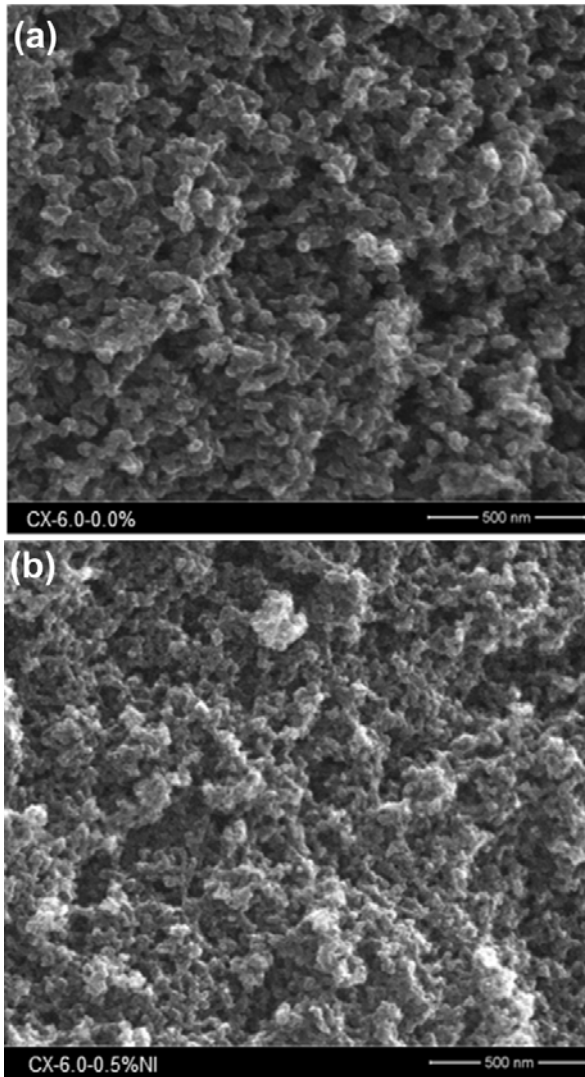


Figure 8. SEM images of sample CX-6 (a) and CX-6-0.5%NI (b).

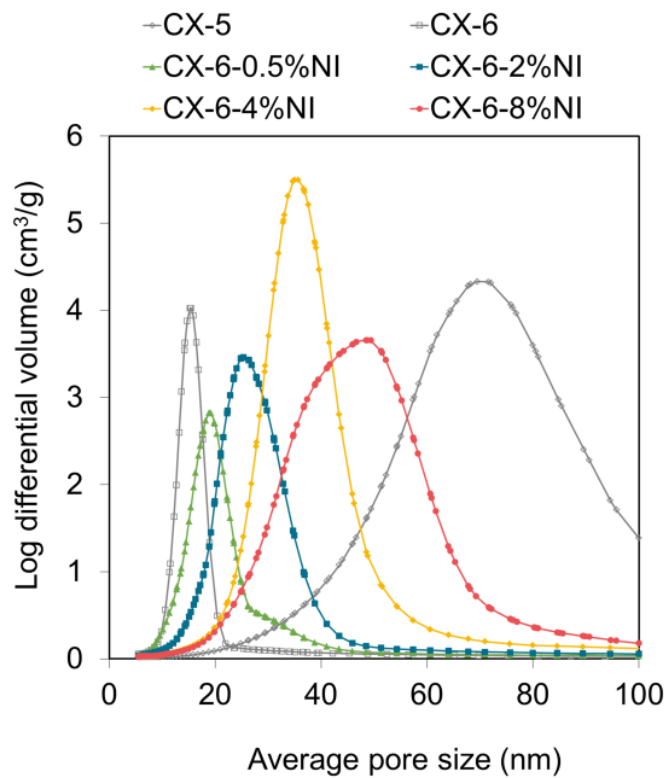


Figure 9. Pore size distribution of samples synthesized from precursor solutions with pH values of 5 and 6 and different amount of Span80.

Enhancing porous properties of carbon xerogels by using additives

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SUPPORTING INFORMATION

Analysis by mercury porosimetry

Three cases are usually encountered when analyzing mercury porosimetry data: i) simple intrusion of mercury in the pore network, ii) reversible shrinkage, and iii) shrinkage followed by intrusion [17]. In this work, the methodology described by Nathalie Jot et al. was applied to the samples studied. Mercury porosimetry data obtained for two different samples are displayed in Figure S1. The initial volume due to the densification by the isostatic pressure is almost negligible and mercury intrusion in the pore network suddenly occurs at a pressure of 10 MPa. It seems that the volume variation is not related to the material shrinkage and Washburn's equation can be used to analyze the data. In addition, the data obtained by mercury porosimetry is also consistent with the data obtained by all the others porous characterization techniques used in the present work.

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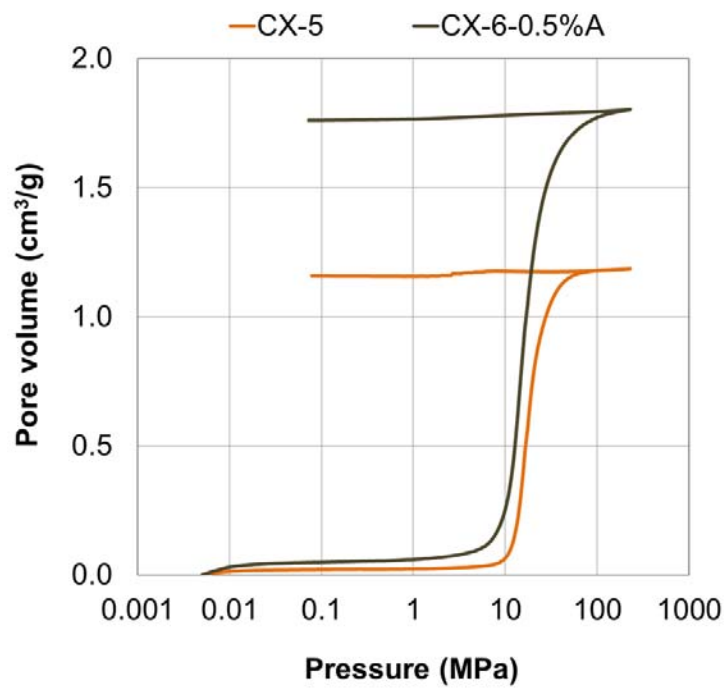


Figure S1. Mercury porosimetry data obtained for samples CX-5 and CX-6-0.5%A

Results

Na₂SO₄-RF carbon xerogels

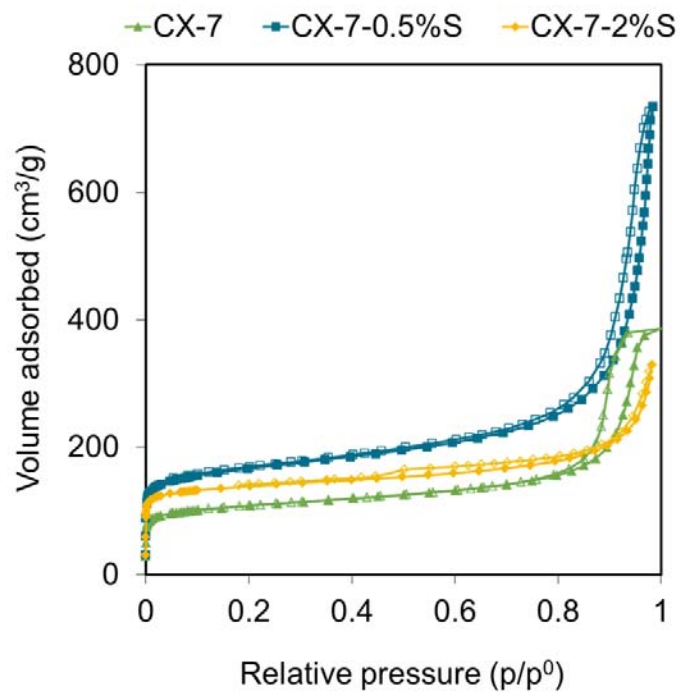


Figure S2. Nitrogen adsorption-desorption isotherm of samples synthesized from precursor solutions with pH 7 with different concentration of sodium sulfate.

Table S1. Porous properties of carbon xerogels synthesized from precursor solution with different pH values and different concentration of sodium sulfate.

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$V_{\text{DUB}}^{\text{a}}$ (cm^3/g)	V_{p}^{b} (cm^3/g)	D_{p}^{b} (nm)	Bulk density ^b (g/cm^3)
CX-7	666	0.26	0.02	6	1.22
CX-7-0.5%A	624	0.25	0.90	25	0.59
CX-7-2%A	538	0.21	1.87	150	0.38
CX-6	661	0.26	0.76	16	0.62
CX-6-0.5%A	623	0.25	1.74	86	0.39
CX-5	652	0.25	1.16	75	0.50
CX-5-0.5%A	580	0.22	1.19	1000	0.39
CX-4	623	0.25	1.50	135	0.42
CX-4-0.5%A	560	0.22	1.30	1100	0.36
CX-3	621	0.24	1.40	200	0.34

^a Measured by nitrogen adsorption-desorption isotherm.

^b Measured by mercury porosimetry

CTAB-RF carbon xerogels

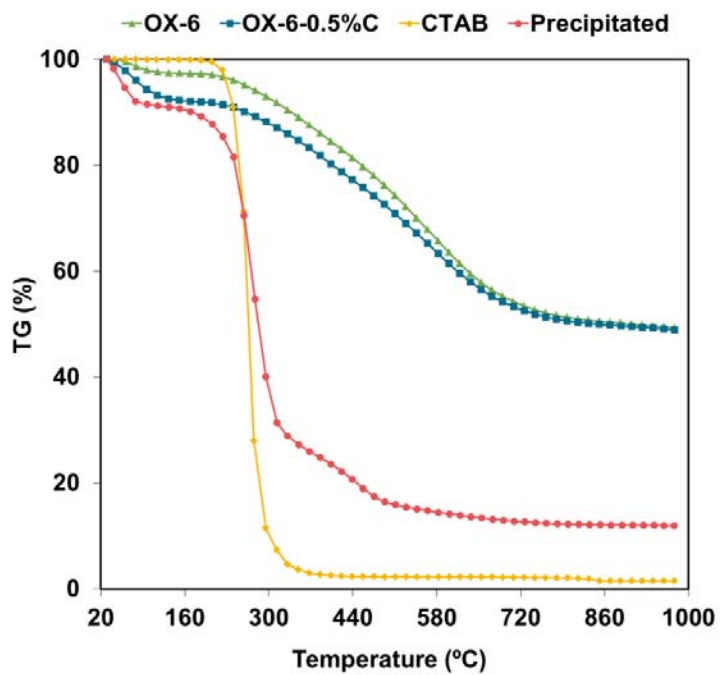


Figure S3. Thermal behavior of the precipitated sample, cationic surfactant, sample OX-6 and sample OX-6-0.5%C.

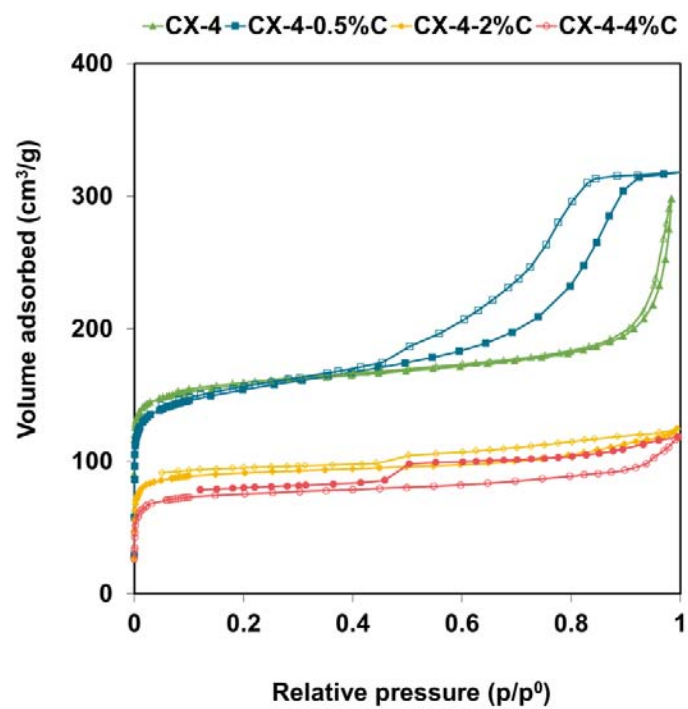


Figure S4. Nitrogen adsorption-desorption isotherm of samples synthesized from precursor solutions with pH 4 with different concentration of CTAB.

Span80-RF carbon xerogels

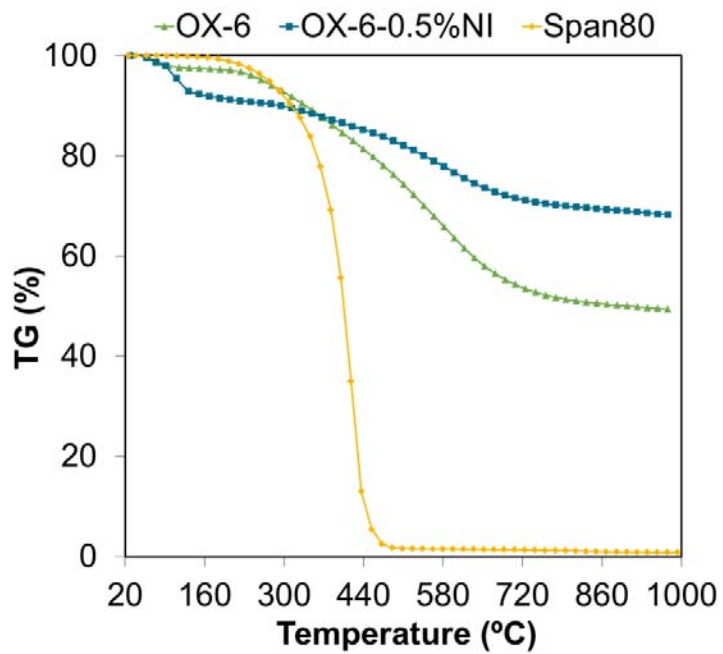


Figure S5. Thermal behavior of Span80, sample OX-6 and sample OX-6-0.5%NI.

Table S2. Porous properties of carbon xerogels synthesized from precursor solution with different pH values and different concentration of Span80.

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$V_{\text{DUB}}^{\text{a}}$ (cm^3/g)	V_{p}^{b} (cm^3/g)	D_{p}^{b} (nm)	Bulk density ^b (g/cm^3)
CX-6	661	0.26	0.76	16	0.62
CX-6-0.5%NI	655	0.26	0.78	19	0.60
CX-6-2%NI	636	0.25	1.23	28	0.53
CX-6-4%NI	635	0.25	1.27	35	0.48
CX-6-8%NI	570	0.22	1.30	47	0.47
CX-5	652	0.25	1.16	75	0.50
CX-5-0.5%NI	644	0.25	1.43	51	0.44
CX-5-2%NI	629	0.25	1.25	46	0.49
CX-4	623	0.25	1.50	135	0.42
CX-4-0.5%NI	615	0.25	1.52	75	0.43
CX-3	621	0.24	1.40	200	0.34

^a Measured by nitrogen adsorption-desorption isotherm.

^b Measured by mercury porosimetry