Influence of alkaline compounds on the porosity of resorcinol-formaldehyde xerogels

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Abstract

Carbon xerogels (CX) were prepared by means of the sol-gel polymerization of resorcinol with formaldehyde using the following alkaline additives: NaOH, Ca(OH)₂, Na₂CO₃, NaHCO₃ and Li₂CO₃. Their porous and chemical structures were studied in depth using several characterization techniques. It was found that anion has a greater influence on the porous structure than cation since, in most of the cases studied, carbonate-based carbon xerogels have a larger pore size than their sodium and calcium hydroxide-based counterparts (i.e., a pore size of around 95 nm for carbon xerogels based on OH⁻ vs. ca. 1000 nm in the case of carbonate-based xerogels, for a specific value of pH, dilution and resorcinol/formaldehyde molar ratio). In addition, it was possible to remove the source of the sodium of the synthesis process, a highly corrosive element that damages the devices and equipment used in post-treatments. Both types of hydroxide lead to carbon xerogels with identical porous and chemical properties, except in their impurity content, which is smaller in the case of the sample produced from Ca(OH)₂.

Keywords: Resorcinol-formaldehyde xerogel; Alkaline compounds; Impurities; Porosity

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1. Introduction

Research papers published in recent years have underlined the versatility of resorcinol-formaldehyde xerogels (RF xerogels), high value-added polymers due to their excellent properties and simple manufacture by microwave technology [1, 2]. Characteristics such as porosity, density and structure can be easily modified depending on the operation variables [1-8]. For example, it is possible to produce a very light RF gel with a high macropore volume, suitable properties that allow it to be applied as thermal insulating material [9-11], or likewise a RF gel with well-developed microporosity, property that makes it an excellent material for storing energy in supercapacitors [12-14].

The influence of variables such as pH, R/F molar ratio, dilution ratio (D) and, even, the presence

of methanol in commercial formaldehyde solutions, on the porosity and structure of RF xerogels has been extensively investigated by the scientist community working in the field of these polymeric materials [1-8]. Of these variables, the pH of the resorcinol-formaldehyde mixture is the one that most affects the porosity of the final materials. The pH of the reaction medium regulates the polymerization mechanism between the monomers, a mechanism that occurs in two stages: (i) the base deprotonates the OH groups of resorcinol to O⁻, which facilitates the reaction between the aromatic rings and formaldehyde molecules to produce hydroxymethyl derivatives (addition reaction), and, (ii) these hydroxymethyl derivatives condense, causing colloidal particles to crosslink and form a 3D-network (condensation reaction) [1-6]. The rate of these two reactions is regulated by the value of the pH. According to the polymerization mechanism, high pH values favor the first reaction and, therefore, highly branched and unstable aggregates are formed, leading to smaller more interconnected particles and, hence, to materials of smaller pore size.

Most of the carbon xerogels mentioned in the literature are obtained by basic catalysis, mainly from alkaline carbonates and hydroxides (NaOH and Na₂CO₃, in most cases) [1-8, 15-17]. However, others agents such as K₂CO₃, Li₂CO₃, Ca(OH)₂, CH₃COOH or organic acids, have also been used by some authors to set the pH of aqueous resorcinol-formaldehyde mixtures [18-22]. The pH value plays a crucial role in the reaction mechanism and in determining the porosity of RF xerogels. However, the type of alkaline additive used is also relevant. The nature of the base exerts a double influence, since it has an impact both on the volume and size of the porosity created and on the amount of impurities in the final material, as a consequence of the different ions present in the mixture.

The presence of impurities, such as alkali metals like potassium (K) and sodium (Na), halogens such as chlorine (Cl) and other contaminants, has a negative effect because they cause corrosion and slagging of steel reactors operating at high temperatures [21, 22]. The economic impact caused by the corrosion of these reactors is very high, especially in processes developed on an industrial scale. Particularly, in the production of RF xerogels, steel reactors operating at high temperatures (1000 °C, for example), are used during post-treatment and, more specifically, during activation processes to increase their microporosity.

In light of the problems mentioned above, the aim of this paper is twofold: on the one hand, to evaluate the influence of different bases on the porosity and chemistry of RF xerogels and, secondly, to identify the pH modifier that produces materials with the least amount of impurities. To this end, two types of bases were used, hydroxides and carbonates: NaOH, Ca(OH)₂, Na₂CO₃, NaHCO₃ and Li₂CO₃. All of these were used in solid state, unlike other authors who used these bases in aqueous solutions, slightly altering the dilution ratio of the

precursor mixture, variable which also influences on the porosity of the RF xerogels [2, 4, 6, 7, 8, 20]. Although the main goal of this work was to avoid the presence of residual Na in the final carbon xerogels, three sodium bases were selected because they are the agents most commonly found in the literature (especially NaOH and Na₂CO₃). In addition, since they are all formed by the same cation, it will be possible to see whether the use of different anions results in materials with different properties.

2. Materials and Methods

2.1. Synthesis of RF xerogels

In order to analyze the influence of the alkaline additives on the porous and chemical properties of the RF xerogels, three different synthesis conditions (combinations of pH, dilution, i.e. the total solvent/reactant molar ratio, and R/F molar ratio) and five alkaline agents (NaOH, Ca(OH)₂, Na₂CO₃, NaHCO₃, Li₂CO₃) were selected, yielding 15 carbon xerogels (see *Table 1*). These values of pH, D and R/F were selected on the basis of the results of previous studies carried out by our research group with the aim of obtaining a series of carbon xerogels with very different pore volumes and sizes. Thus, whereas some samples were composed of narrow mesopores, others exhibited a high volume of large-size macropores. Although four variables (pH, dilution, R/F molar ratio and pH modifier) were modified, each of the series 1, 2 and 3 (see *Table 1*) has identical operation conditions, except the nature of the pH modifier used, so it is possible investigate the influence of this variable independently in three different types of carbon xerogel structures (i.e. with narrow mesopores, wide mesopores and macropores).

The 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), using deionized water as solvent and different alkaline salts to modify the pH. It is important to mention that the alkaline bases were applied in solid state, so as not to modify the dilution ratio (D). The procedure consists in the addition of small amounts of alkaline agent and subsequent measurement of the solution pH. This operation was repeated until the pH value desired was achieved. The amount of base added depended on the final pH desired as on its strength. Briefly, the microwave-assisted process involved the following stages: (i) heating at 85 °C for ca. 3 hours to perform the gelation and ageing 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.

Once the fabrication of the organic xerogels was completed, they were thermally stabilized by a pyrolysis in a tubular horizontal furnace (*Carbolite MTF 12/38/400*) under a nitrogen

atmosphere (150 mL min^{-1}), up to $700 \text{ }^{\circ}\text{C}$ ($50 \text{ }^{\circ}\text{C min}^{-1}$) with a soaking time of 2 hours. The final carbon xerogels are designated in this paper as X-y, where X is Na, Ca, Na_2 , NaH or Li_2 , depending on the base used, and y corresponds to a numerical value, between 1 and 3, depending on the experimental conditions used for their synthesis.

Table 1. Summary of the synthesis conditions of the RF xerogels studied in this work.

Base	pH	D	R/F	Nomenclature
NaOH	6.5	5.7	0.5	Na-1
	6.2	4.7	0.2	Na-2
	5.3	7.7	0.7	Na-3
$\text{Ca}(\text{OH})_2$	6.5	5.7	0.5	Ca-1
	6.2	4.7	0.2	Ca-2
	5.3	7.7	0.7	Ca-3
Na_2CO_3	6.5	5.7	0.5	Na_2 -1
	6.2	4.7	0.2	Na_2 -2
	5.3	7.7	0.7	Na_2 -3
NaHCO_3	6.5	5.7	0.5	NaH-1
	6.2	4.7	0.2	NaH-2
	5.3	7.7	0.7	NaH-3
Li_2CO_3	6.5	5.7	0.5	Li_2 -1
	6.2	4.7	0.2	Li_2 -2
	5.3	7.7	0.7	Li_2 -3

2.2 Physico-chemical characterization of the RF xerogels

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

The nitrogen adsorption-desorption isotherms were performed at $-196 \text{ }^{\circ}\text{C}$ in an adsorption analyzer (*Micromeritics Tristar 3020*), after the samples had been degassed at $120 \text{ }^{\circ}\text{C}$ 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 $p/p^{\circ} = 0.99$ and; pore size distribution (PSD), determined by applying the DFT method to the nitrogen adsorption branch.

The carbon xerogels with large mesoporosity or macroporosity were also evaluated by means of

mercury porosimetry on an *AutoPore IV 9500, Micromeritics*, a device able to operate in a pressure range from atmospheric pressure to 228 MPa. The surface tension value and contact angle selected were 485 mN m⁻¹ and 130°, respectively. Mercury porosimetry analysis based on the Washburn intrusion theory yielded the pore size distributions, bulk densities and mesopore/macropore volumes. The device is not able to detect pores smaller than 5.5 nm, therefore the V_{meso} comprises pores ranging from 5.5 to 50 nm.

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 bases 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.

3. Results and Discussion

3.1. Characterization of the pore structures of the RF xerogels

The specific surface area (S_{BET}) values of all the carbon xerogels synthesized in this work are presented in Figure 1. At first glance, there is no outstanding difference between the samples: the S_{BET} is around 650 m² g⁻¹, except in the case of the three xerogels synthesized from NaHCO₃, whose S_{BET} values range from 500 to 600 m² g⁻¹. This behavior was to be expected since variables such as the pH or type of pH modifier mainly affect the meso-macroporosity of the xerogels. Microporosity usually remains unchanged, since this kind of porosity is developed during the carbonization processes [1, 2].

During the pyrolysis of organic xerogels, the removal of volatile matter takes place, causing an increase in microporosity. However, meso-macroporosity may also be affected to some extent, since there is a shrinkage of the xerogel structure, which can lead to a reduction in the pore size. For example, sample **Na₂-1** displays a V_{meso} value of 0.74 ± 0.04 cm³ g⁻¹ whereas after carbonization, this is reduced to 0.63 ± 0.04 cm³ g⁻¹, due to the compacting effect of the porous structure which causes some of the narrow mesopores to turn into micropores ($d < 2$ nm). When the xerogel comprises large macropores (e.g. Na₂-3 xerogel) this phenomenon does not occur because, although the pore size is slightly reduced, they are still very large and belong to the macropore range. Therefore, the macropore volume remains almost invariable after the pyrolysis stage (V_{macro} of 1.73 and 1.79 ± 0.04 cm³ g⁻¹ for the organic and carbon xerogel Na₂-3, respectively).

With the exception of the NaHCO_3 -based xerogels, it seems that the trend in surface area values is $S_{\text{BET-R1}} > S_{\text{BET-R2}} > S_{\text{BET-R3}}$, and this can be attributed to their porous characteristics. The samples synthesized from experimental conditions R1 have a porosity that is composed of small-to-medium size mesopores, with the five RF xerogels displaying a mesopore diameter of between 8-13 nm (see *Figure 2*). Conversely, recipes 2 and 3 yield meso and macroporous samples, respectively. It is well known that the BET surface area is also influenced by narrow mesoporosity and accordingly in this case, samples with narrower mesopores (xerogels R1) are those with the highest values of S_{BET} . This phenomenon also serves to explain the lower S_{BET} values of samples NaH-1 and NaH-2 (523 and $552 \pm 5 \text{ m}^2 \text{ g}^{-1}$, respectively), since these two xerogels have a lower narrow mesopore content. The samples obtained from NaOH and $\text{Ca}(\text{OH})_2$ also cater to this argument. The differences between S_{BET} values for recipes 2 and 3 are almost negligible, while the carbonates-based additives produce materials with more marked differences in their surface area. Carbonates yield carbon xerogels with larger pore size (see *Figure 3* and *4*), pores that not contribute to increase its specific surface area.

Figure 1. S_{BET} values for the carbonized RF xerogels.

Since the variables pH, dilution and R/F molar ratio have already been exhaustively explored by our research group [2, 3, 5], and because the main purpose of this study is to elucidate the effect of alkaline additives on the final properties of RF xerogels, the remaining results are grouped according to the recipe used.

The RF xerogels obtained from recipe 1 (6.5-5.7-0.5) are micro-mesoporous materials composed of small-size mesopores, in agreement with the results reported by other publications on RF xerogels synthesized under identical operation conditions [2, 5]. The characteristics of their mesoporosity, with regard to volume and average mesopore diameter, are summarized in

Figure 2. General speaking, there are no major differences in mesoporosity depending on the type of the pH modifier. Leaving aside sample NaH-1, the other four xerogels have mesopore volumes between 0.4-0.6 $\text{cm}^3 \text{g}^{-1}$ with pore sizes ranging from 10 to 13 nm. Under these operation conditions, it is not easy to see any clear difference between the use of hydroxides and carbonates, and this may be due to the rapid kinetics of the polymerization reactions. Under the three experimental conditions selected, R1 results in shorter gelation times (about 10 minutes with microwave heating), and therefore, the possible effect of the catalytic species on the porous texture could be partially mitigated in this case.

If Figure 2 is examined closely, it can be seen that the base that leads to the sample with the greatest mesopore volume is sodium carbonate (i.e. V_{meso} of $0.63 \pm 0.04 \text{ cm}^3 \text{g}^{-1}$ with a mean pore size of ca. $13.6 \pm 1 \text{ nm}$). This result deserves a more detailed explanation since the same trend is repeated under the other two experimental conditions studied.

Figure 2. Mesoporosity characteristics (V_{pore} and d_{pore}) for the carbon xerogels obtained from experimental conditions R1.

Carbon xerogels obtained from the experimental conditions assigned as R2 contain a micro-mesoporous structure. The pore size distributions (PSD) of the five samples synthesized are shown in Figure 3: (a) PSD obtained from mercury porosimetry measurements and, (b) PSD of samples prepared using the alkaline hydroxides, obtained from N_2 isotherms, since in the case of micro-mesoporous samples based on narrow mesopores, the similarities/differences are more easily identified by the N_2 adsorption technique.

As can be seen, porosity differs heavily depending on whether hydroxides or carbonates were used to accelerate the polymerization process. The samples prepared from alkaline carbonates

show a more abundant and wider mesoporosity. In addition to the differences in pore size, the larger mesopore volume is worth noting since the carbon xerogels obtained from the carbonates display mesopore volumes that are around three times greater than those fabricated from NaOH and Ca(OH)₂: V_{meso} of 0.37, 0.29, 1.28, 0.92 and $0.99 \pm 0.04 \text{ cm}^3 \text{ g}^{-1}$ for carbon xerogels Na-2, Ca-2, Na₂-2, NaH-2 and Li₂-2, respectively. One possible hypothesis for the wider porosity yielded by the carbonate compounds might be related to the different size of the OH⁻ and CO₃²⁻ anions. Carbonate ions are larger and have a trigonal planar molecular geometry that may cause some steric hindrance and, as a result, the condensation of the intermediates derivatives will generate larger pores. As occurs with carbon xerogels-R1, in this case, also Na₂CO₃ yields a final material with higher volume and larger pores.

Figure 3. Pore size distributions obtained from Hg porosimetry (a) and N₂ isotherms (b) for samples derived from R2.

Figure 3 highlights the possibility of replacing sodium by calcium, without its having a serious impact on the porosity of the resulting material. Furthermore, according to the ICP-MS analysis,

the residual Na content is reduced (~800 vs. 180 ppm for Na-2 and Ca-2 xerogels, respectively). This proves that, when the OH⁻ anion is maintained, it is possible to replace the sodium cation by calcium cation in order to obtain a carbon xerogel without sodium and with similar porosity.

The results reported so far suggest that anions make a greater contribution to porosity than cations. Several studies in the literature focus on the effect of pH modifier (basic or acidic) on the porosity of resorcinol-formaldehyde gels. However, they are not easy to compare because specific operating conditions were employed in each study, and even further, if one considers that the carbon xerogels of this study were synthesized with microwave radiation. Despite the different experimental conditions used, some similarities can be found with the findings proposed by other authors. For example, T. Horikawa et al. [23] prepared RF aerogels using four different compounds: Na₂CO₃, K₂CO₃, NaHCO₃ and KHCO₃ and claimed that porous characteristics vary depending on the type of additive. The greatest discrepancies between the samples were in relation to mesopore volume and size and they are attributed to the gelation process varying depending on the base used. With none of the alkaline carbonates, did the fact of replacing sodium by potassium modify the porosity of the carbon aerogel, as in the case of the present study when NaOH/Ca(OH)₂ and NaHCO₃/Li₂CO₃ were used. However, contrary to the present findings, the use of sodium carbonate instead of bicarbonate caused a decrease in both the size and pore volume (V_{meso} of 0.53 and 0.79 cm³ g⁻¹ for Na₂CO₃ and NaHCO₃ with pore radius peaks located at 2.2 and 2.8 nm, respectively). D. Fairén-Jimenez and co-workers [18] also used two types of carbonates (Na₂CO₃ and K₂CO₃) for the manufacture of carbon aerogels. For a given set of synthesis conditions (R/F = 0.5, R/W = 0.08 and pH = 6.4), a large variation was observed when Na₂CO₃ was replaced by K₂CO₃ since, a micro-mesoporous material was obtained with a sodium bases, whereas the use of potassium carbonate led to a micro-macroporous aerogel with a PSD centered at 660 nm. These two examples reveal the complexity of this type of materials since different combinations of pH, dilution and R/F molar ratio, result in completely opposite trends. In another paper [20], alkali metal hydroxides (LiOH, NaOH and KOH) and alkaline earth metal hydroxides (Ca(OH)₂, Ba(OH)₂ and Sr(OH)₂) were used to catalyze the sol-gel reaction of resorcinol and formaldehyde monomers. The results indicated that carbon xerogels obtained from M²⁺ cations display a more developed porosity (a higher volume of larger pores) than those prepared by using M(OH). The explanation for this is still unclear, although at the time it was suggested that the different charge and concentration of cations may have been responsible for the changes in the porous structure. These three examples, together with the results reported in the present paper, have brought to light the discrepancies between the different works because, whereas some authors state that the ion that plays the major role is the anion, in agreement with this study, others hold the opposite view, i.e., it is the cation that mainly defines the porosity of the final material.

In order to complete the presentation of the porous properties of the carbon xerogels, Figure 4 illustrates the PSD, obtained by means of mercury porosimetry, of the carbon xerogels synthesized from the experimental conditions denoted as number 3. The five samples synthesized with the combination 5.3-7.7-0.7 have a micro-macroporous structure, as might be expected from their pH value, high dilution and R/F molar ratio greater than the stoichiometric value. From previous studies [2, 5], it is known that a high volume of macropores is obtained with a $\text{pH} \leq 5$ and $D > 7$. As the pH decreases, the addition reaction is slower and hence, a smaller number of resorcinol anions are formed. The polymeric particles have enough time to grow and produce large but weakly clusters. The consequent condensation of these lightly branched groups leads to a structure composed of large-size pores. In turn, as the dilution ratio increases, the number of resorcinol and formaldehyde monomers in the mixture decreases. Therefore, in this case also, sparsely cross-linked particles are formed.

Figure 4. PSD derived from porosimetry measurements for CX obtained using 5 alkaline additives and recipe number 3.

According to the PSD, the same trend as in the CX-R2 samples is observed. Hydroxide-based compounds produce carbon xerogels with an analogous porosity and, this porosity is also narrower than that derived from alkaline carbonates (pore size around 95 nm for CX-hydroxides as opposed to ~ 1000 nm for the samples prepared with NaHCO_3 and Li_2CO_3 , all of which with a macropore volume greater than $1 \text{ cm}^3 \text{ g}^{-1}$). As in the case above, for this combination of pH-D-r, sodium carbonate is also the agent that produces the material with the largest pores. The explanation for this phenomenon is not yet fully clear but it is undeniable that it is not by

chance, since under the three operating conditions studied, Na_2CO_3 produces RF xerogels with the greatest porous structure.

3.2. Chemistry characteristics of the RF xerogels

The results of the elemental analysis are presented in Table 2. The three recipes studied give rise to analogous results. Therefore, in order to avoid a too extensive table, only the data corresponding to the carbon xerogels obtained from experimental conditions R2 (6.2-4.7-0.2) have been included. As can be seen, the carbon xerogels are predominantly composed of C (≥ 95 wt. %) although there is also a slight oxygen content. If the data are analyzed in detail, it becomes clear that the samples fabricated from the bases Na_2CO_3 , NaHCO_3 and Li_2CO_3 contain a higher percentage of oxygen (> 3 wt. % in all the cases), probably due to the presence of three oxygen atoms in each molecule, instead of 1 and 2 in the case of the NaOH and $\text{Ca}(\text{OH})_2$ molecules, respectively. The ash content has also been included in Table 2, and although the five samples have low ash content, $\text{Ca}(\text{OH})_2$ is the one that results in a carbon material of greatest purity.

The ICP-MS results for the R2-carbon xerogels reveal that residual Na was dramatically reduced when free-sodium additives were used, with a reduction in the sodium content of one order of magnitude (i.e. from 800-1400 ppm in the case of sodium bases to ca. 200 ppm for $\text{Ca}(\text{OH})_2$ base). It may seem surprising that, even in the case of free-sodium bases, a small amount of sodium can be detected. However, these are almost negligible quantities and they might have resulted from the manipulation of samples during the synthesis or/and characterization of the RF xerogels.

Table 2. Elemental analysis of carbon xerogels synthesized from R2 conditions (pH: 6.2; D: 4.7 and R/F: 0.2). Values related to dry samples.

Sample	Na-2	Ca-2	Na_2 -2	NaH-2	Li_2 -2
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C (wt. %) ± 0.5	96.3	96.7	94.9	95.7	95.1
H (wt. %) ± 0.5	1.4	1.5	1.3	0.8	1.3
O (wt. %) ± 0.5	2.1	1.7	3.6	3.3	3.3
Ash (wt. %) ± 0.2	0.20	0.14	0.24	0.20	0.35

4. Conclusions

Five different alkaline species (NaOH, Ca(OH)₂, Na₂CO₃, NaHCO₃ and Li₂CO₃) were employed to promote the polymerization reactions between resorcinol and formaldehyde under microwave heating. The main conclusions drawn are the following:

- The alkaline compounds usually added to RF precursor solutions to adjust the desired pH cannot be considered as catalysts, as commonly can be found in the literature, as they take part of the reaction and define the final properties of the final material. Therefore, for the same pH value, it is possible to obtain two RF xerogels with different porosity by using two different compounds
- The three experimental conditions tested reveal that the additives based on hydroxides (NaOH and Ca(OH)₂) generate materials with a similar porosity and, in turn, this is narrower than the porosity created in carbon xerogels made by using the bases Na₂CO₃, NaHCO₃ and Li₂CO₃. In other words, it seems clear that the ion that plays the most important role in determining the final porous structure of RF xerogels is the anion.
- It is possible to reduce the sodium content of carbon xerogels and so avoid corrosion of the reactors by replacing NaOH by some other bases. However, the type of catalytic species used must be taken into account because the porous structure may be modified. If sodium is replaced by calcium hydroxide, the resultant synthesized materials show virtually identical porous and chemical properties, in addition to a reduction in sodium content. It is for that reason that this compound is highly appropriate for attaining the main objective pursued in this work.

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