Toward more sustainable chemical activation strategies for the production of porous carbons

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Abstract

The preparation of porous carbons attracts a great deal of attention given the importance of these materials in many emerging applications such as hydrogen storage, CO₂ capture, and energy storage in supercapacitors, batteries, *etc.* In particular, porous carbons produced by applying chemical activation methods are preferred because of the high pore development achieved. However, given the environmental risks associated with conventional activating agents (*e.g.,* KOH), the development of greener chemical activation methodologies is an important objective. Herein, we review recent progress in the production of porous carbons by using more sustainable strategies based on chemical activation. The use of less-corrosive chemical agents as an alternative to KOH is thoroughly reviewed. In addition, we look in detail at the progress achieved so far using emerging self-activation methodologies applied to organic salts and biomass products.

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Introduction

Basically, a porous carbon can be described as a material made up of randomly arranged defective graphene layers that enclose numerous interconnected nanocavities (pores). Due to the presence of these small cavities, porous carbons can achieve high internal pore volumes (> 1 cm³ g⁻¹) and surface areas that can exceed 3500 m² g⁻¹. Apart from pore development, porous carbons have other important properties that are crucial in many applications. They have good electrical conductivity and chemical inertness, and can be easily functionalized by the insertion of a variety of heteroatoms such as N, O, S, B, etc.^[1] The importance of porous carbons lies in the fact that they are very useful in a wide range of applications, such as: a) removal of pollutants in liquid (usually water)^[2] or gas (usually air)^[3] phases, b) separation of gas mixtures (carbon molecular sieves),^[4,5] c) storage of gases such as methane ^[6] or hydrogen,^[7,8] d) CO₂ adsorption, ^[9,10] e) as catalysts or catalytic support, *etc*.^[11] In the last twenty years, there has been renewed interest in the fabrication of porous carbons due to their key role in electrochemical energy storage systems such supercapacitors, batteries (Li, Li-S, Na, K, etc.) and hybrid ion capacitors.^[8,12–15]

There are two requirements for the raw organic materials to be used as precursors of porous carbons: a) they must be able to produce significant carbon residue after heat treatment under an inert atmosphere, and ii) they must give rise to carbons with a disordered microstructure (non-graphitizable carbon). The materials that meet both characteristics include biomass or biomass-derived products (*e.g.*, saccharides and bio-polymers), coal/petroleum and certain types of polymers. Nowadays, biomass is the preferred precursor due to its Earth abundance, sustainability and low cost. Usually, the production of porous carbon (activation) is based on the reaction between the carbonaceous precursor and certain substances (activating agents) that induce a controlled removal of a number of carbon atoms, which causes the formation of numerous internal pores. When the activating agents are reactive gases such as carbon dioxide or steam, the activation process is called *physical activation*, which usually requires long reaction times at temperatures > 800 °C.^[16,17] An alternative route for producing porous carbons is known as the chemical activation process, which involves the co-carbonization of the carbonaceous matter with certain chemical substances (KOH, NaOH, ZnCl₂ or H₃PO₄) that, at high temperatures, act as oxidizing agents promoting the creation of numerous pores.^[18-21] Compared to physical activation, chemical activation processes yield porous carbons that have higher pore development (pore volumes > 1 cm^3 g^{-1} and BET surface areas > 2000 m² g⁻¹) and a pore network that usually combines micro- and mesopores. Owing to these superior textural characteristics, this methodology has been the subject of great interest for the production of highly porous carbons that are ideal for several emergent applications such as H₂ storage,^[8,22,23] CO₂ capture,^[24–26] and as electrodes in electrochemical applications such as supercapacitors,^[8,15,27] Li-S batteries,^[28] and hybrid-ion capacitors.^[29] However, the chemical activation agents noted above, and in particular the most frequently used KOH, are highly corrosive substances categorized as "Extreme Danger" as shown in Figure 1. This severely limits their use at an industrial level and, consequently, most of the commercially available porous carbons for electrochemical applications

(Kuraray, Norit) are produced by means of *physical activation*. Accordingly, it is imperative to introduce more benign activating chemical agents as well as implementing greener activation techniques in order to scale-up chemical activation from its current laboratory scale to an industrial level.



Figure 1. NFPA 704 hazard labels of different chemical activating agents.

Unlike other recent reviews focused on the production of porous carbons for specific applications or from a specific precursor such as biomass,^[13,27,30–32] this review is exclusively focused on the preparation of porous carbons using more environmentally friendly chemical activation strategies. First, we discuss recent advances in the synthesis of porous carbons by means of chemical activation using less-corrosive chemical agents. We place particular emphasis on understanding the operating reaction mechanisms and on the evaluation of textural properties. Subsequently, we look in detail at the progress achieved through emerging strategies to produce porous carbon by using self-activation techniques. We perform thorough review of different types of organic salts of K, Na, Ca, Fe and Zn that are able to generate porous carbons by means of a simple one-step carbonization. In addition, bearing in mind the great practical importance of using biomass as a carbon precursor, we analyze the selfactivation processes applied to biomass products in depth.

2. Harmless chemical activating agents

2.1. Alkali metal carbonates and bicarbonates

Given that KOH is one of the most powerful activating agents, researchers have analyzed the efficiency of other potassium salts. One of the oldest, which is in fact one of the reaction products during potassium hydroxide activation, is potassium carbonate. Compared to KOH, K_2CO_3 is a milder basic compound, less toxic and corrosive, as can be seen in its corresponding NFPA 704 hazard label (see Figure 1). The porogenic action of K_2CO_3 , schematically illustrated in Figure 2, is based on a redox reaction with carbon, according to:^[33,34]

$$K_2CO_3 + 2 C \rightarrow 2 K + 3 CO$$

in which potassium carbonate oxidizes the carbonaceous matter to CO yielding porosity in the carbon residue. In addition, potassium vapors may intercalate between the graphene layers to cause swelling and the disruption of the carbon microstructure, which thereby generates additional porosity.^[35,36] Also, for temperatures higher than 850 °C, K₂CO₃ slowly decomposes following the reaction:^[37]

$$K_2CO_3 \rightarrow K_2O + CO_2$$

Both activation products can lead to further activation of the carbon. Thus, the CO_2 reacts with carbon creating new pores or enlarging the existing ones, according to the Boudouard reaction:

$$C + CO_2 \rightarrow 2 CO$$

On the other hand, the K_2O can be reduced by carbon to K, etching additional carbon atoms in the following manner:

$$K_2O + C \rightarrow 2 K + CO$$



As a result, the materials obtained by K_2CO_3 activation are normally rich in micropores with a limited amount of small mesopores. On the other hand, the inorganic matter remaining in the solid product after the activation process is un-reacted K_2CO_3 (or a hydrated phase owing to the contact with ambient air), which is normally removed by washing with diluted acid. The emitted gases are

(1)

(2)

(4)

(3)



similar to those of a carbonization process (*i.e.*, CO₂, CO, H₂O, H₂, CH₄, *etc.*), although in different proportions.^[38] It is important to note that reaction (1) takes place at temperatures higher than 600-700 °C,^[34,37] whereas the redox reaction with KOH starts at lower temperatures (~ 400 °C),^[36,39] which explains the lower pore development achieved with K₂CO₃ compared to KOH (see Table 1).^[40–44] Besides, as mentioned above, K₂CO₃ is one of the products during KOH activation, so that for T > 600-700 °C, reactions (1) to (4) also take place during KOH activation, yielding additional pore development. However, K₂CO₃ has two important additional advantages over KOH. Firstly, it allows the preservation of the morphology of the precursor (see Figures 3a-b).^[37,40] Secondly, it has a catalytic action on the carbonization of biomass products, promoting the hydrolysis and de-polymerization reactions of cellulose and hemicellulose components ^[34] and the dehydration and polymerization reactions of monosaccharides,^[45] which increases the carbon yield, similarly to other more toxic chemical activating agents, such as ZnCl₂ ^[46] and H₃PO₄.^[47] This is very important from the industrial production point of view.



Figure 3. SEM pictures of a) KOH-activated and b) K₂CO₃-activated hydrochar (Reproduced from ref. [40] with permission from the Royal Society of

Chemistry). c) Illustration of the synthesis procedure of porous carbons by using a mixture of K_2CO_3 and KCI. SEM pictures of (d) glucose and (e) tannic acidderived porous carbons prepared by a salt template-assisted chemical activation process (Reproduced from refs.[45,48] with permission from the Royal Society of Chemistry and Wiley-VCH).

Among all the examples available in the literature, we would like to highlight the work by Mestre et al., who compared the chemical activation of hydrothermally carbonized biomass, *i.e.* hydrochar, at 800 °C with K₂CO₃ and KOH (activating agent/hydrochar weight ratio = 4).^[40] A microporous carbon with a surface area of ~ 1400 m² g⁻¹ and a pore volume of 0.63 cm³ g⁻¹ was obtained with K_2CO_3 (Table 1), compared to values of 2430 m² g⁻¹ and 1.14 cm³ g⁻¹ for the porous carbon fabricated with KOH. However, the typical spherical morphology of sucrose-derived hydrochar was preserved when K₂CO₃ was used, whereas KOH completely destroyed the particle morphology (see Figures 3a-b). This is important since a spherical morphology leads to better packing properties and reduced ion diffusion distances. Thus, the packing density of the materials was determined to be 0.79 and 0.36 g cm⁻³ for the K_2CO_3 - and the KOH-derived ACs, respectively. This much higher packing density of the K₂CO₃-derived AC is not only explained by its lower pore development, but also by the particle morphology, since the particle density of the materials is 0.89 and 0.61 g cm⁻³ for the K_2CO_3 - and the KOH-derived ACs, respectively.

Recently, our group showed that the rational design of the activation procedure with K₂CO₃ can lead to materials with a pore development similar to that of benchmark KOH-derived ACs.^[45,48] The synthesis procedure is illustrated in Figure 3c. By adding KCI as a reaction medium, the reactivity between the carbon and K₂CO₃ is greatly enhanced as a consequence of the presence of a melted phase of KCl+K₂CO₃ for T > 631 °C. In this way, materials with BET surface areas of up to ca. 2800 m² g¹ and pore volumes of up to 1.42 cm³ g¹ are obtained from a variety of biomass-based products (*i.e.* tannic acid, glucose and soybean meal) (see Table 1). At the same time, the carbon yield is increased owing to the confined space provided by the melted KCI-K₂CO₃ mixture. This increase is, for example, 2 % in the case of glucose and soybean meal compared to the sole use of K_2CO_3 (for an increase in the pore volume of 40 %), and as high as 10 % in the case of tannic acid compared to its simple carbonization. Additionally, KCI plays a second role as a template, leading to materials with a 3D sponge-like morphology (see Figures 3d-e). It must be highlighted that, in contrast to the use of solely K_2CO_3 or KOH, in this synthesis strategy KCI and un-reacted K_2CO_3 can be removed by simply using water, which is an additional environmental benefit.

It is also worth highlighting the effect on pore development of adding an N-rich compound, such as urea or melamine, to the mixture of K_2CO_3 and carbon precursor (besides causing N-doping). In this regard, Tsubouchi *et al.* showed that the pyrolysis at 800 - 900 °C of a mixture of carbon precursor (lignin), urea and K_2CO_3 leads to materials with ultrahigh pore development and increased mesopore volume, with BET surface areas as high as 3300-3400 m² g⁻¹ and pore volumes of 2.2-2.3 cm³ g⁻¹.^[49] In contrast, activation of lignin with K_2CO_3 produces a material with BET surface area below 600 m² g⁻¹ and pore volume up to ~ 0.3 cm³ g⁻¹. Similar results were previously reported by our group by using mixtures of hydrochar, melamine and KOH,^[50,51] and more

recently by Schneidermann *et al.* using mixtures of biomass/biomass derivatives, urea/melamine and K_2CO_3 .^[52,53] Tsubouchi *et al.* provided mechanistic insights for those results. They observed that when the lignin+urea+ K_2CO_3 mixture is pyrolyzed, potassium cyanate (KOCN) is already present at 200 °C. It may be formed through the following reactions: CH₄N₂O + 0.5 K₂CO₃ \rightarrow KOCN + 0.5(CH₈N₂O₃) (5)

$$K_2CO_3 + C - N \rightarrow KOCN + -CO_2K$$
(6)

$$-CO_2K + C - N \rightarrow KOCN + CO$$

(7)

(8)

where C-N sites correspond to nitrogen bonded to carbon in the char (formed as a consequence of secondary reactions between radical species generated in the decomposition of urea and edge carbons in the char). For temperatures higher than 700 °C, KOCN completely disappears and potassium cyanide (KCN) appears, which suggests the oxidation of carbon by potassium cyanate according to the reaction:

 $\mathsf{KOCN} + \mathsf{C} \to \mathsf{KCN} + \mathsf{CO}$

It can therefore be assumed that this redox reaction along with the cleavage of C-N bonds within the carbon matrix by K-species produces a disorderly arrangement of microcrystals with larger gaps between them, which increases the specific surface area.^[49] This also explains the production of porous carbons with outstanding pore development and a micro-/mesoporous pore network when carbon precursors with a high nitrogen content (*i.e.*, polypyrrole) are chemically activated with KOH.^[22,54,55] Likewise, it explains the preferential removal of nitrogen species contained in the carbon precursor/char during chemical activation with K-based salts. At this point, it must be noted that potassium cyanide is highly toxic and this speaks against the suitability of these pore generation strategies based on N-rich foreign additives and K-based salts. When an N-rich carbon precursor is used, KCN is also formed, but in a much lower amount. In this kind of activations mediated by N-rich compounds, the emitted gases contain toxic N-species such as NH₃. However, the amount generated is smaller than during the carbonization of biomass and the N-rich additive, since most nitrogen is retained in the solid product (i.e., N-doped carbon and KCN).^[49]

As evidenced by Figure 1, an even milder potassium salt than potassium carbonate -and then appealing from the environmental point of view- is potassium bicarbonate. In a pioneering study, Deng *et al.* showed that the chemical activation of a variety of biomass products (*e.g.*, cellulose, chitin and bamboo) with KHCO₃ leads to carbon materials with a 3D hierarchical pore structure, comprising micropores, mesopores and macropores (see Figure 4a).^[56] To produce such a structure, they were inspired by the bread-making process and selected a gas-producing chemical substance such as KHCO₃. KHCO₃ decomposes at around 200 °C, according to:

$$2 \text{ KHCO}_3 \rightarrow \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \tag{9}$$

The CO₂ thus generated dilated and produced the macropores (see Figure 4b), while the micro- and mesopores were generated by the reaction between K_2CO_3 and the carbonaceous matter according to reactions (1) to (4). These materials exhibited BET surface areas up to *ca.* 1900 m² g⁻¹ depending on the carbon precursor and activation conditions (see Table 1) and a bulk density as

low as 0.043 g cm⁻³ (porosity of 85 %). By increasing the KHCO₃/cellulose weight ratio from 2 to 6, it was possible to increase the specific surface area from 1693 m² g⁻¹ to 1893 m² g⁻¹. However, at a higher ratio of 8 the surface area decreased to 1709 m² g⁻¹, which may be due to some pore collapse as a consequence of excessive activation. It should be noted that the carbon yield of the process is not very high, of around 6-10 % for a KHCO₃/precursor weight ratio = 4 (see Table 1). Since this study, KHCO₃ activation has been applied to a variety of precursors, including not only biomass,^[57–66] but also biochar ^[43,67–69] and hydrochar,^[37,70–72] for use in a variety of applications, as compiled in Table 1.



Figure 4. a) Schematic diagram of the formation of porous carbons by using $KHCO_3$ as activating agent, b) SEM pictures of the porous carbons derived from cellulose (C_{cel-LE}), chitin (C_{chi-LE}) and bamboo (C_{bam-LE}) (Reproduced from ref. [56] with permission from the Royal Society of Chemistry).

Similarly to K₂CO₃, our group has shown that KHCO₃ also allows the preservation of the morphology of hydrochar precursors, whose consolidated structure is not affected by the CO₂ evolved in the decomposition of KHCO₃.^[37] In this way, porous carbons made up of microspheres with surface areas in the 2000-2300 m² g⁻¹ range were obtained (Table 1). Similar to the case of cellulose above described, an increase of the KHCO₃/hydrochar ratio from 4 to 6 enhances the pore development (S_{BET} increases from 1996 to 2230 m² g⁻¹ and V_p from 0.87 to 1.05 cm³ g⁻¹) and causes certain rise in mesoporosity (the % of pore volume corresponding to mesopores rises from 13 to 20 %). However, further increase of the KHCO₃/hydrochar ratio to 8 causes some pore collapse, the pore volume decreasing to 0.89 cm^3 g⁻¹. The materials were mainly microporous, although some small mesopores could be introduced by lengthening the residence time at 850 °C, as a consequence of reactions (2) to (4) taking place. To further enhance mesopore development in the $KHCO_3$ -ACs, melamine was added to the HKCO₃/hydrochar mixture used in the activation process. In this way, a porous carbon with an ultra-large BET surface area and

pore volume was obtained (see Table 1), with a pore size distribution exhibiting maxima at ~ 0.9 and 2.3 nm and a V_{microp}/V_{mesop} ~0.84. In addition, a nitrogen content of ~ 4.2 wt % was measured. Importantly, a 10 % increase in the carbon yield of the final product was registered when using KHCO₃ instead of KOH.

In contrast to potassium-based carbonates and bicarbonates, their sodium-based counterparts have hardly been used as activating agents, as they are less effective (Table 1).^[64,73–78] This may be explained by the lower catalytic activity of the sodium carbonates for carbon gasification.^[74,79] The porogenic action of Na₂CO₃ (or any alkali metal carbonate) is based on the same redox reaction as in the case of K₂CO₃:

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO$$

which can be inferred by the presence of metallic sodium in the cool parts of the reactor. However, Na₂CO₃ decomposes only at temperatures higher than 1000°C,^[80] so that reactions equivalent to (2) to (4) but based on Na do not take place in the case of Na₂CO₃. As an example, Fujiki and Yogo analyzed the activation of chitosan by using a variety of alkali metal carbonates (*i.e.*, Na₂CO₃, K₂CO₃, Rb₂CO₃ or Cs₂CO₃) in the temperature range from 500 to 700 °C.^[74] The highest pore development was achieved at 700 °C for all the carbonates except for Cs₂CO₃, which showed the largest values of surface area and pore volume (respectively, 1530 m² g⁻¹ and 0.78 cm³ g⁻¹) at 600 °C. This work clearly demonstrates the lesser effectiveness of Na₂CO₃ as an activating agent, which leads to a maximum surface area value of 1328 m² g⁻¹ *vs.* 2045 and 2145 m² g⁻¹ for K₂CO₃ and Rb₂CO₃ at 700 °C, respectively (Table 1).

With regards to the use of NaHCO₃ as activating agent, Tian *et al.* explored the activation of a mixture of glucose and thiourea.^[76] Thiourea not only caused N- and S-codoping of the carbon materials obtained (see Table 1), but also some pore generation and enhancement of the BET surface area (the mechanism for pore generation is presumably similar to that of K-based salts with urea, as Na also readily reacts with N-containing compounds generating NaOCN).^[81] Similarly to the case of KHCO₃, materials with a hierarchical micro/meso/macroporous structure were obtained, albeit with a lower pore development (see Table 1).

2.2. Alkali metal organic salts

Organic salts comprising an alkali metal, such as sodium or potassium, and an organic part can be used as self-activators when the carbon yield is satisfactory (see Section 3 for a deeper discussion) or as activating agents when the organic part is completely decomposed during the pyrolysis process. In this latter case, only the corresponding carbonate remains, this being the actual activating agent. This is the case of potassium oxalate, whose toxicity is similar to that of K_2CO_3 and lower than that of traditional activating agents (Figure 1). When potassium oxalate is pyrolyzed, it decomposes in the temperature range of 500-600 °C according to:

 $\mathsf{K}_2\mathsf{C}_2\mathsf{O}_4\to\mathsf{K}_2\mathsf{CO}_3+\mathsf{CO}$

yielding no carbon residue.^[82,83] The K_2CO_3 thus generated can then react with the carbonaceous matter at T > 700 °C following reaction (1) (see Section 2.1), causing the partial etching of carbon atoms under controlled activation

(10)

conditions. For higher temperatures, reactions (2) to (4) can also proceed (see Section 2.1), creating additional porosity or enlarging the existing pores. The textural properties of the materials derived from potassium oxalate are therefore similar to those of potassium carbonates/bicarbonates, *i.e.* highly microporous carbons with some small mesopores and BET surface areas normally of up to around 2000 m² g⁻¹ (Table 1).^[83–87] It is worth noting that potassium oxalate melts at a low temperature of 390 °C, inducing a sheet-like morphology in carbons derived from melting precursors such as glucose or sucrose (Figure 5a).^[83,87] However, when non-melting precursors are used, such as hydrochar (Figure 5b) ^[82,83,88] or seeds (Figure 5c),^[85] the morphology is preserved in the same way as with carbonates/bicarbonates. In addition, it has been shown that the yield of the activation process in the case of saccharides is as high as 23-30 % (*i.e.*, 30-50 % higher than their simple carbonization). This is due to the fact that potassium oxalate catalyzes the dehydration and polymerization reactions that take place during the initial stages of the carbonization process.^[83]



Figure 5. SEM images of the ACs produced by $K_2C_2O_4$ activation using as precursor a) glucose (Reproduced with permission from ref. [87]. Copyright 2019, Elsevier, Ltd), b) glucose-derived hydrochar (Reproduced with permission from ref. [83]. Copyright 2018, American Chemical Society) and c) seeds (Reproduced from ref. [85] with permission from the Royal Society of Chemistry). Pore size distributions of the ($K_2C_2O_4$ +melamine)-derived ACs produced from d) hydrochar and e) glucose (Reproduced with permission from ref. [83]. Copyright 2018, American Chemical Society).

Interestingly, our group has shown that, when hydrochar is used as a carbon precursor, the mixture of potassium oxalate and melamine allows the production of highly microporous carbons with textural properties that mimic those of superactivated carbons prepared by KOH activation, *i.e.* BET surface areas of 2600-3000 m² g⁻¹, pore volumes of ~1.3-1.6 cm³ g⁻¹ and pore size distributions in the supermicropore-small mesopore (< 3 nm) region (see Figure 5d). Importantly, the carbon yield is almost twice that of KOH activation (see Table 1).^[82] We studied the mechanism of porous carbon formation by TGA, FTIR, XRD and N₂ physisorption, and showed that (besides the formation of KOCN/KCN as in the case of urea) a poorly polymerized carbon nitride is formed from melamine, its decomposition already causing substantial pore development at 500 °C. A further increase in temperature to 750 °C, the temperature at which reactions (1) and (8) take place (see Section 2.1), promoted the development of a high porosity and an increase in pore size. Although this type of procedure may initially seem benign, the generation of KCN as a by-product must always be examined and taken into consideration. On the other hand, we showed that when saccharides are used as a carbon precursor instead of hydrochar, the mixture of potassium oxalate and melamine leads to highly micro-mesoporous carbons with BET surface areas as large as $3500 \text{ m}^2 \text{ g}^{-1}$ and pore volumes up to 2.72 cm³ g⁻¹, the ratio of micropore to mesopore volume being of ~0.6 - 0.9 (Figure 5e).^[83] These results are similar to those of mixtures of carbon precursor, urea/melamine and KOH, K2CO3 or KHCO₃ (see Section 2.1). In addition, the materials are N-doped, with N content ranging from 1 to 20 wt% depending on the synthesis conditions (Table 1). In the case of using lignocellulosic biomass such as eucalyptus sawdust, an intermediate situation between that of saccharides and hydrochar was observed, which was attributed to a higher resistance (lower reactivity) of lignin (and hydrochar) to the activating mixture potassium oxalate + melamine owing to its higher degree of aromatization compared to saccharides.

Taking one step forward, we combined the use of potassium oxalate as an activating agent and calcium carbonate nanoparticles as a hard template to produce, in a one-pot scheme, hierarchical porous carbons from biomass.^[89] We found that, during carbonization, double carbonates $(K_2Ca(CO_3)_2)$ and $K_2Ca_2(CO_3)_3$) were formed in situ, which resulted in modifications in the morphology and size of the template nanoparticles. This gave rise to a carbon material with an open macroporous foam-like structure rich in micro-/mesopores (see Figures 6a,b), the latter developing via reaction (1) described in Section 2.1 and also as a result of the reaction between the carbon and the CO_2 evolved in various reactions. The final inorganic impurities present in the porous carbon are CaO and K₂CO₃, which can be easily removed by washing with diluted HCI. The pore structure of the materials produced could be tailored by selecting an appropriate carbon precursor. Thus, a direct relationship was observed between the amount of nitrogen present in the precursor and mesopore development (Figure 6c). Hence, the addition of urea to the mixture of glucose and potassium oxalate and CaCO3 nanoparticles also yielded micro-/meso-/macroporous carbons (Figure 6d). These results further confirm the essential role that nitrogen heteroatoms have on porosity development, regardless of whether they come from a foreign additive (e.g., melamine or urea) or they form part of the carbon precursor. The materials synthesized at 750 °C from N-rich biomass or glucose+urea combined ultra-large surface areas of $2400-3200 \text{ m}^2 \text{ g}^{-1}$ and notable N-doping (2-3 wt % N) (see Table 1). Very recently, Li et al. followed this same strategy, also producing hierarchical porous carbons from cornstalk without pith (Table 1).^[86]



Figure 6. SEM images of the hierarchical porous carbons produced by $K_2C_2O_4$ activation in the presence of CaCO₃ nanoparticles using as carbon precursor a) microalgae and b) soya flour. Pore size distributions of the hierarchical porous carbons produced from c) a variety of carbon precursors and d) with and without the addition of urea to glucose (Adapted with permission from ref.^[89]. Copyright 2017, American Chemical Society).

Another frequently used organic salt, with lower health hazards than potassium carbonate and oxalate (Figure 1), is potassium acetate. In this case, the materials produced are also microporous carbons with BET surface areas up to ~ 1900 m² g⁻¹ and pore volumes up to ~ 0.9 cm³ g⁻¹, depending on the activation conditions and the carbon precursor (Table 1).^[90–93]

Although sodium and potassium citrates (Na₃C₆H₅O₇ and K₃C₆H₅O₇, respectively) yield substantial carbon residue and therefore can be used as selfactivators as will be described in detail in Section 3, some researchers have also used them as activating agents, employing another main carbon source. The carbon materials thus produced are micro-macroporous with BET surface areas below 2000 m² g⁻¹ and pore volumes up to around 1 cm³ g⁻¹ (see Table 1).^[94–98] In addition, potassium/sodium citrates have frequently been incorporated during the synthesis of resorcinol-formaldehyde resins, thus yielding porous carbons (see Table 1).^[99–101]

2.3. Alkali metal sulfates and thiosulfates

Similarly to carbonates, sulfates are able to oxidize carbon at temperatures > 342 °C according to:

$$M_2SO_4 + 2 C \rightarrow M_2S + 2 CO_2 \qquad M = Na, K \qquad (12)$$

And, at temperatures higher than 520 °C, the following reaction is also feasible:

$$M_2SO_4 + 4 C \rightarrow M_2S + 4 CO$$

When thiosulfates are used instead, they decompose at temperatures above 250 °C according to the reaction:

$$4 M_2 S_2 O_3 \to 3 M_2 S O_4 + M_2 S_5 \tag{14}$$

In this way, the sulfate generated becomes the only oxidizing agent able to react with the carbonaceous matter generating porosity according to reactions (12) and (13). As a result, the solid residue will be made up of porous carbon and M_2SO_4 and sodium/potassium unreacted sulfide/polysulfides, which can be easily eliminated by water washing. These sulfide/polysulfides can be easily re-oxidized by a simple O₂ bubbling, giving rise to a solution containing the ingredient used for the synthesis of the carbon (*i.e.*, $M_2S_2O_3$), which could then be recirculated to the activation system.^[102,103] Besides, vapors of elemental sulfur are also generated by the disproportionation of the polysulfides ($M_2S_5 \rightarrow M_2S + 4S$) and condense in the cold parts of the reactor; from an industrial production standpoint, it could be collected and recovered from downstream cooled filters.

It should be noted that the use of sodium/potassium sulfate/thiosulfate has hardly been described in the scientific literature despite being benign salts (see Figure 1), which may be because they normally produce materials with surface areas below ~1000-1500 m² g^{-1 [102-104]} However, Liu and Antonietti,^[104,105] and our group ^[102,103] have developed novel approaches for the area efficient production of high surface porous carbons from sulfates/thiosulfates. Liu and Antonietti introduced a molten salt activation approach, in which K_2SO_4 is able to produce a microporous carbon from glucose with a BET surface area of 1520 $m^2 g^{-1}$ in a high carbon yield of 55 % by using an eutectic mixture of LiCl and KCl (melting point = 353 °C) as reaction medium (T = 900 °C) (Table 1).^[105] This molten salt activation approach is not only efficient in producing porous carbons, but also allows the controllable production of S-doped 2D carbon nanosheets (Figure 7a). Later on, these authors extended the approach to $Na_2S_2O_3$ in order to increase S-doping. By doing so, a porous material composed of nanosheets with surface area of 3250 $m^2 g^{-1}$ and S content of ~ 4.8 wt% was synthesized at 900 °C (carbon yield > 25 %, Table 1).^[104] According to the authors, the high porosity of the carbons seemed to be the result of the cooperative interaction of the inert chloride salts and the reactive salts. More recently, our group has shown that materials with similar characteristics can be produced by simply mixing Na₂S₂O₃ and KCI.^[102,103] This is due to the fact that the Na₂S formed according to reactions (12) and (13) forms a liquid phase at T > 740 °C with the unreacted Na₂SO₄ (*i.e.*, eutectic point at 28% mol Na₂S) and KCl also melts at ~ 770 °C. Under these conditions, the melted KCI acts as a confinement medium which reinforces the contact between the solid carbonaceous matter and the Na₂SO₄-Na₂S liquid system, enhancing the reactivity (see Figure 7b). Thereby, highly

(13)

porous carbons with BET surface areas up to ~ 2700 $m^2 g^{-1}$ were produced from biomass and biomass-derivatives (Table 1). It is worth highlighting that these porous carbons were obtained by using considerably lower ratios of activating agent to precursor (< 1.5) than those used in KOH activation (usually \sim 4) and, in contrast to KOH, there is no need for an acid to remove the inorganic salts. Furthermore, high carbon yields in the 11-20 wt% can be obtained by the confinement effect of KCI, while direct KOH activation of biomass leads to considerably lower carbon yields and sometimes even to its complete consumption. In this case, depending on whether the carbon precursor melts (e.g., tannic acid or glucose) or not (e.g., eucalyptus sawdust), the porous carbon particles present a foam-like structure as a result of the templating effect of KCI and Na₂SO₄ solid particles at low temperatures (Figure 7c) or retain the typical structure of the precursor (Figure 7d). Besides that, the materials are basically composed of narrow micropores for Na₂S₂O₃/precursor weight ratios \leq 1, while there is a notable increase in the proportion of large micropores (1 - 2 nm) and also of small mesopores (~ 2 - 5 nm) for weight ratios above 1. The general applicability of this strategy for the production of highly porous carbons has also been demonstrated by using a polymer such as polypyrrole (S_{BET} up to ~ 2500 m² g⁻¹, see Table 1).^[106,107] Moreover, the polysulfides/sulfides generated during the activation step can be used for the insitu synthesis of sulfur nanoparticles confined within the porosity of the porous carbon and, in this way, the synthesis of sulfur/carbon composites for Li-S batteries.[106-108]



Figure 7. SEM image of the porous carbon produced in a $K_2SO_4@LiCl/KCl$ system (carbon precursor: glucose) (Reproduced with permission from ref. [105]. Copyright 2014, Elsevier, Ltd). b) Schematic illustration of the synthesis procedure of porous carbons by using a $Na_2S_2SO_3/KCl$ system (Reproduced with permission from ref. [102], Copyright 2019, Elsevier, Ltd). SEM images of the porous carbons produced in a $Na_2S_2SO_3/KCl$ system using as carbon precursor c) glucose (Reproduced with permission from ref. [103]. Copyright 2018, American Chemical Society) and d) sawdust (Reproduced with permission from ref. [102], Copyright 2019, Elsevier, Ltd).

Table 1. Summary of porous carbons produced by chemical activation with a variety of benign alkali metal salts.

Activating agent	Carbon precursor	Mixing procedure	Additives	Doping (%) ^[a]	T _{pyrolysis} (°C)	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^[b]	Pore structure ^[c]	Carbon yield (%) ^[d]	Application	Reference
	Nutshells	Solution	-	-	500- 900	~300-1800	~0.1-0.85	Mi	n.d.	-	[34]
	Hydrochar	Solution	-	-	700- 800	~700-1400	0.3-0.6	Mi	13-15 ^[e]	CH ₄ storage and landfill gas/biogas upgrade	[40]
	Agave	Hand- grinding	-	-	800	~600-1900	0.3-1.0	Mi	20-50	Pharmaceuticals removal	[41]
	sisalaria	Solution	-	-	800	~1400	0.7-0.9	Mi+Me			
	Lignocellulosic residues	Hand- grinding		N – 1.3- 1.5	900	~1500-1700	0.6-0.7	Mi	n.d.	Biogas purification	[42]
Potassium	Chitosan+ glutaraldehyde	Solution	-	N – ~4.12	800	1013	0.58	Mi+Me+Ma	n.d.	Supercap	[44]
carbonate	Glucose, soybean meal	Solution+ freeze	KCI	N – 0.4- 0.5	800- 850	2000-2600	0.8-1.2	Mi+Me+Ma	14-16	Supercap	[45]
	Tannic acid	drying		-	750- 900	~2300-2700	0-2700 ~1-1.4 Mi+Me+Ma 32-38		[48]		
	Lignin	Ball milling	Urea	N – ~6-9	800	<i>ca</i> . 2000- 3000	~1.2-2.1	Mi+Me	13	Supercap	[52]
	Biomass	Ball milling	Melamine and/or urea	N – ~4- 12	800	1200-3200	0.7-2.1	Mi+Me		Li-S batteries	[53]
	Biochar	Hand- grinding	Urea	N – 1.2	850	~1000-1600	0.5-0.8	Mi	n.d.	Supercap	[43]
	Biomass	Hand- grinding	-	-	600- 900	600-1900	0.3-1.4	Mi+Me+Ma	4-16	Supercap	[56]
	Hydrochar	Solution	-	-	850	2000-2300	0.9-1.4	Mi+Me	1.4-4	Supercap	[37]
	Biochar	Hand- grinding	Urea	N – 4.2 N – 0.6	850	~800-1500	0.4-0.6	Mi	n.d.	Supercap	[43]
	Histidine	Solution	-	N – <i>ca.</i> 4-15	700- 900	700-1600	0.9-2.0	Mi+Me+Ma	n.d.	Supercap and carbon capture	[57]
Potassium	Chestnut shell	Solution	-	-	850	~1850-2300	1.0-1.5	Mi+Me+Ma	n.d.	Supercap	[58]
bicarbonate	Eggplant	Solution+ freeze drying	-	N – 2.7	600- 900	111-1226	0.07-0.7	Mi+Me+Ma	n.d.	Capacitive desalination and ORR/OER	[59]
	Corn stalks	Hand- grinding	Ferric chloride	-	800	1313	0.80	Mi+Me+Ma	n.d.	Extraction of carbamates	[60]
	Eucalyptus leaves	Hand- grinding	-	N – 1.7	750- 950	1183-2133	~0.8-1.3	Mi+Me	n.d.	Supercap and Li-ion battery	[61]
	Chitin	Solution	-	N – 2.5	800	n.d.	n.d.	n.d.	n.d.	Li-O ₂ battery	[62]
	Cattail fibers	Hand-	Melamine	N - 6.4	900	2345	1.42	Mi+Me	n.d	ORR	ودما

		grinding									
	Shiitake mushroom	Hand- grinding	-	N – 1.3	900	1790	1.12	Mi+Me	15.1	Supercap and Na-ion battery	[64]
	Pomelo peel	Solution	$NH_4H_2PO_4$	N – 0.7 P – 0.12	800	2726	1.73	Mi+Me	n.d	Capacitive deionization	[65]
	Sophora flowers	Hand- grinding	MgO	N – n.s.	800	1800-2500	n.d.	Mi+Me	n.d.	Water remediation	[66]
	Biochar	Ball milling	-	N – 0.8- 4.5	800	~1600-2100	1.0-1.1	Mi	15-17 ^[f]	Supercap and ORR	[67]
	Biochar	Ball milling	Melamine	N – 11.6	800	1676	1.03	Mi+Me	n.d.	ORR	[68]
	Biochar	Solutiob	-	-	600- 800	1430-2360	0.6-1.3	Mi+Me	n.d.	Capacitive deionization	[69]
	Hydrochar	Hand- grinding	-	-	850	~1100-1300	0.55-0.72	Mi+Me	n.d.	Water remediation	[70]
	Hydrochar	Hand- grinding	-	-	850	1057	0.64	Mi+Me+Ma	n.d.	Supercap	[71]
	Hydrochar	Hand- grinding	-	N – 0.6- 1.1	800	2200-2400	0.9-1.1	Mi+Me	n.d.	Supercap and carbon capture	[72]
	Chitosan	Solution	-	N – 2.4- 6.5	600- 900	440-1150	0.2-0.7	Mi	n.d.	-	[73]
Sodium carbonate	Chitosan	Solution	-	N – 3-8	500- 700	~10-1330	0.04-0.78	Mi+Me	n.d.	Carbon capture	[74]
	Cork	Hand- grinding	-	N – 1.9	700	386	0.16	Mi	21	-	[75]
	Shiitake mushroom	Hand- grinding	-	-	900	1110	0.83	Mi+Me	15.0	Supercap and Na-ion battery	[64]
	Glucose	Solution	Thiourea	N - 3.4- 9.6 S - 0.2- 0.4	700	1044-1608	0.7-1.0	Mi+Me+Ma	n.d.	Pharmaceuticals removal	[76]
Sodium	Flour	Solution	-	N – 0.41	1000	1376	0.99	Mi+Me+Ma	n.d.	Supercap	[77]
bicarbonate	Microalgae	Hand- grinding	-	N – 2-10	600- 800	~280-1500	~0.2-0.9	Mi+Me+Ma	n.d.	Supercap	[78]
	W/boot flour	Solution	Na ₂ CO ₃ / K ₂ CO ₃	N – 1.07	700	1278	0.68	MitMotMo	nd	Carbon capture and water	[109]
	Wheat hour	Solution	Na ₂ CO ₃ / K ₂ CO ₃ / dicyandiamide	N – 7.3- 12.2	600- 900	~650-3040	0.4-1.9	wii+ivie+ivia	n.u.	remediation	
	Phenolic resin	During synthesis	-	-	800	760-2130	~0.3-0.8	Mi	n.d.	Carbon capture	[84]
Potassium	Semen cassiae	Solution	-	N – 0.5- 0.9	600- 800	655-1100	~0.5-0.6	Mi+meso	60-70	Supercap	[85]
CAURIE	Glucose	Hand- grinding	-	-	850	2575	~1.5	Mi+me	n.d.	Catalyst (Rh) for H ₂ production	[87]
	Hydrochar	Hand-	-	-	800	~1700-2500	~0.9-1.5	Mi+me	n.d.		[88]

		grinding	[Γ	[
	Glucoso		CaCO ₃	-		1813		Mi+Ma	9		
	Glucose		CaCO ₃ , urea	N – 0.9-2		3200-3300	~ 2.0	Mi+me+Ma	10		
	Glucosamine, microalgae, deffated soya flour	Hand- grinding	CaCO ₃	N – 0.5- 2.8	750- 800	~2400-3100	1.3-2.8	Mi+Me+Ma	5-12	-	[89]
	Cornstalk w/o pith	Hand- grinding	CaCO ₃	N – 0.5- 0.8	800	1200-2050	~0.4-1.4	Mi+Me+Ma	n.d.	Supercap and carbon capture	[86]
	Hydrochar	Solution	Melamine	N – 0.5- 0.9	800	~1800-3000	~0.8-1.5	Mi+Me	40-53	Supercap	[82]
	Glucose	Hand-	-	-	800- 850	~1300-170	0.5-0.7	Mi	16-21 ^[g]		[83]
	Olucosc	grinding	Melamine	N – 1-21	800	<i>ca.</i> 900- 3500	0.6-2.7	Mi+Me	8-37	Carbon capture	
	Potassium humate	Solution	-	-	800	~1200-1300	~0.6	Mi	33-34	Supercap	[90]
Potassium	Bean curd	Solution+ freeze drying	-	N – <i>ca.</i> 3	750	90-2200	0.05-1.2	Mi+Me+Ma	6-11	Supercap	[91]
acetate	Resin	Solution	-	N – 1.8- 6.4	700- 900	800-1950	0.4-1.0	Mi	n.d.	Supercap	[92]
	Glucose	Hand- grinding	-	-	600- 800	~900–1900	0.68-0.85	Mi	n.d.	Carbon capture	[93]
	Bacterial cellulose pellicles	Hand- grinding	-		850	1037	1.04	Mi+Ma	n.d.	Supercap	[98]
	Agar	Solution	Urea	N – 2.4	700	1300	~ 0.6	Mi+Ma	n.d.	Supercap	[94]
	Polyacrilamide	Solution	-	N – 1.5	600- 800	~560-1900	0.23-0.91	Mi+Ma	n.d.	Supercap	[95]
Potassium citrate	Asphalt	Hand- grinding	-	N – 0.5- 0.9	800	~800-1400	0.4-0.6	Mi	5-11	Supercap	[96]
	Glucose	Hand- grinding	-	-	750- 900	~1300-2100	~0.8-1.2	Mi	n.d.	Carbon capture	[97]
	Resin	During synthesis	Melamine	N – 1.5- 3.6	850	~700-1800	~0.5-0.8	Mi+Me+Ma	n.d.	Supercap	[99]
	Resin	During synthesis	-	-	850	~900-1400	~0.5-0.9	Mi+Me+Ma	n.d.	Supercap	[100]
	Resol resin	During synthesis	-	N – ~2-4	700	350-1050	0.2-0.5	Mi	n.d.	Carbon capture	[101]
Sodium citrate	Resin	During synthesis	hexamethylenetetramine	N – 1.6- 6.2	650- 850	~900-1300	~0.4-1.1	Mi+Me+Ma	n.d.	Supercap	[110]
Potassium	Glucose	Ball milling	LiCI/KCI	-	900	1520	0.92	Mi+Me	55	-	[105]

sulfate				S – 5-18	500- 1000	300-1500	~0.2-1.1	Mi+Me	n.d.	-	[104]
	Glucose	Ball milling	LiCI/KCI	S – 5 - 28	500- 1100	~400-3250	~0.2-2.3	Mi+Me	n.d.	ORR	[104]
Sodium thiosulfate	Saccharides, gelatin	Hand- grinding	KCI	N – ~2-3 S – 1.5- 3.6	800	1900-2400	~1.0-2.4	Mi+Me	11-19	-	[103]
	Tannic acid, sawdust	Hand- grinding	KCI	S – ~2-6	800	~2400-2700	~1.1-2.0	Mi+Me	14-21	Supercap	[102]
	Polypyrrole	Hand- grinding	KCI	N – 1.8- 2.0 S – 5.6- 6.1	800	~2100-2500	1.6-2.4	Mi+Me	5-12	Li-S battery	[106]
	Polypyrrole nanoparticles	Hand- grinding	KCI	N – 2-2.7 S – 4.2- 7.7	800	1380-1690	1.3-2.2	Mi+Me+Ma	~2.5-10	Li-S battery	[107]

^[a] Depending on the work, the values are provided in at % or wt %. ^[b] Total pore volume determined by N₂ physisorption. ^[C] Mi - microporous, Me – mesoporous and Ma – macroporous pore network.^[d] Carbon yield is defined as g of porous carbon/100 g of raw carbon precursor. ^[e] A yield of 30 % is assumed for the hydrothermal carbonization step. ^[f] A yield of 40 % is assumed for the hydrothermal carbonization step.

3. Self-Activation Methods

The self-activation technique involves the production of porous carbons without the use of any foreign activating compounds, the porogenic action being exclusively performed by substances that are part of the carbon precursor. In this way, carbon materials with notable pore development are produced, comparable to that produced by means of conventional activating techniques. This methodology has two important and obvious advantages: a) it avoids the use of activating agents that are in many cases harmful and corrosive, and b) it is easy and cheap given that the carbon precursors are low-cost, readily-available products. Raw materials appropriate to be carbon precursors need to include one of the following elements in their composition: alkali metals (K, Na), alkali earth metals (Ca, Mg) or other elements such as Fe or Zn. A variety of simple organic salts (*i.e.* citrates, acetates, gluconates, tartrates, alginates, *etc.*) or polymeric salts (*i.e.* polystyrene-based, *etc.*) meet this requirement. Importantly, this technique can also be applied to certain biomass materials which contain appreciable amounts of alkali elements (*i.e.* K, Na).

3.1. Self-Activation Mechanisms

The self-activation of the organic or polymeric salts involves three pore generation mechanisms: i) chemical activation (oxidation of carbon by carbonates or oxides), ii) physical activation (gasification of carbon by the CO_2 produced *in situ*), and iii) removal of inorganic nanoparticles embedded in the carbon matrix (endo-template processes). Figure 8 schematically illustrates the self-activation process.



Figure 8. Schematic illustration of the self-activation process of an organic salt: (1) partial decomposition of the organic salt that includes the salt melting and the formation of the initial inorganic phase (T < 400°C), (2) carbonization and activation (T > 400 °C), and (3) removal of the inorganic products.

During the first steps of the thermal treatment (<300 °C) of an organic salt, three important processes occur: i) melting of the raw salt (most of the organic salts melt at temperatures below 300°C), ii) dehydration and decarboxylation reactions ^[111,112] and iii) formation of the inorganic species (*i.e.* carbonates, sulfates or oxides). At this point, the melted semi-carbonized mass is covering the inorganic nanoparticles, which ensures very close contact between the carbonaceous matter and the inorganic particles that act as activation agents. Furthermore, the melting phenomenon has another significant effect since the final morphology of the carbon particles is pre-shaped in this stage. In some cases, the pyrolysis of organic salts leads to free or interconnected porous carbon nanosheets that have a thickness < 100 nm.^[113–118] This is an important achievement since this kind of morphology provides short diffusional paths, which is extremely important for many applications that require fast adsorption-desorption rates (*e.g.* supercapacitors, sodium-ion batteries, hybrid-ion capacitors, *etc.*).^[119]

The potassium organic salts are especially interesting since they normally lead to carbon materials with a high pore development. During decomposition of potassium organic salts, K_2CO_3 appears at around 300°C.^[120] At higher temperatures (> 600-700 °C), K_2CO_3 oxidizes the carbon according to reactions (1) to (4) described in Section 2, leading to the formation of an extensive pore network made up mainly of micropores and small mesopores, as previously discussed.

The above description is appropriate for potassium salts, but it is not entirely applicable to sodium salts. As noted in Section 2.1, Na_2CO_3 is less effective than K_2CO_3 and its role as an activating agent is limited to reaction (10) since it decomposes above 1000 °C, *i.e.* beyond the typical carbonization temperatures, so that most of the sodium carbonate remains unaltered. Then, the unreacted Na_2CO_3 nanoparticles operate as an endo-template leading in many cases to the formation of macroporous carbon sponges once they are removed.^[115,121]

In the case of the thermal decomposition of alkali earth metal organic salts (*i.e.* Ca, Mg), the corresponding carbonates cannot oxidize the matter and they simply decompose, carbonaceous generating oxide nanoparticles and CO_2 [MCO₃ \rightarrow MO + CO₂]. In the case of calcium carbonate, since the decomposition occurs at high temperatures (> 750 °C), it can be assumed that the emitted CO_2 will react with carbon according to Equation (3) generating a certain number of micropores. However, in the case of MgCO₃, the decomposition occurs at T < 600 °C ^[122] and, accordingly, the reaction between the released CO₂ and the carbonaceous matter is irrelevant. Furthermore, considering the fact that the oxide nanoparticles generated by the decomposition of the carbonates (*i.e.*, CaO or MgO with sizes below 50 nm) are embedded within the carbon matrix, they play an important role because they will act as endo-templates leading to large mesopores once the carbonized sample is washed with an acid. In the case of the pyrolysis of organic salts of Fe or Zn, the formation of the corresponding oxides (Fe_2O_3 or ZnO) takes place firstly at T < 400 °C.^[123] At higher temperatures (> 600°C in the case of Fe₂O₃ or > 850°C in the case of ZnO), these oxides are reduced by the carbonaceous matter to the corresponding metals [MO + C \rightarrow M +CO]. This reaction causes the creation of a certain number of pores, and the subsequent acid etching of the embedded metal nanoparticles will create an additional mesoporous network. In the case of organic zinc salts, it is important to note that, because zinc vaporizes at ~ 910 °C, carbonization above 950 °C produces an inorganicfree porous carbon and no additional acid leaching is needed.^[124]

Table 2 summarizes the main characteristics and applications of the porous carbons produced by self-activation of organic salts. This table includes the type of organic salt, the additives employed and degree of heteroatom doping, the textural properties, the type of morphology, and the carbon yield.

3.2. Porous carbons from alkali metal organic salts

Since it has been proven that the carbonization of organic salts leads to carbons with high pore development, a wide variety of these types of substances have been investigated as precursors of porous carbons. To this end, special attention has been paid to organic salts of potassium and sodium because of the well-proven capacity of the alkali compounds as activating agents.

In 2004, Hines et al. demonstrated for the first time that a porous carbon could be obtained without the use of an external activating agent.^[125] They reported that the carbonization of the sodium salt of poly(styrene sulfonic acidco-maleic acid) yields a microporous carbon with a sponge-like structure exhibiting a high BET surface area of 1380 m² g⁻¹. Subsequently, our group showed that a variety of porous carbons could be easily synthesized by means of the pyrolysis of simple organic salts that combine an organic moiety with appropriate cations (K, Na, Ca, Fe or Zn).^[35] In this respect, we discovered that the pyrolysis of potassium citrate or sodium gluconate leads to carbon nanosheets. In particular, porous carbon particles with a (rose-dessert)-like morphology built up of interconnected carbon nanosheets (Figure 9a) were prepared by the pyrolysis of potassium citrate.^[35,113] These nanosheets have a thickness of around 50 nm, a high surface area up to 2220 m² g⁻¹, porosity made up of narrow micropores and small mesopores, and good electrical conductivity (Figures 9b-d). In the case of sodium gluconate, the pyrolysis of this salt leads to a porous carbon that has a unique morphology consisting of individual carbon nanosheets with a very large aspect ratio (length > 100 μ m and thickness < 200 nm), as illustrated in Figure 9e.^[116] These carbon nanosheets exhibit a BET surface area up to 1390 m² g⁻¹ and a hierarchical porosity made up of large cage-like spherical mesopores (~ 10-20 nm) interconnected by narrow micropores (Figures 9f-i). Yang et al. studied the pyrolysis of sodium citrate and found that, whereas at low temperatures (400-500 °C) the formation of carbon dots takes place, higher temperatures (> 600°C) produce a sponge-like structure built up of thin carbon sheets that have an area of around 200 m² g⁻¹.^[115] The self-activation occurs not only with simple organic salts, but certain polymeric salts are also able to produce porous carbons.^[125–128] In a typical example, Roberts et al. reported the self-activation of sodium poly(4-styrenesulfonate).^[128] During the thermal treatment of this salt, the pyrolysis of the polymeric moiety occurs and then the generated carbonaceous matter is chemically activated by the Na₂SO₄ generated in situ (Reactions 12 and 13 in Section 2.3).



Figure 9. Interconnected porous carbon nanosheets produced by self-activation of potassium citrate: a) SEM and b) TEM images, and c) N_2 adsorption isotherms and d) pore size distributions (Reproduced with permission from ref. [113]. Copyright 2014, American Chemical Society). Carbon nanosheets synthesized by self-activation of sodium gluconate: e) SEM and f) TEM images, and g) N_2 adsorption isotherms and h,i) pore size distributions (Reproduced with permission from ref. [116]. Copyright 2015, American Chemical Society).

Sometimes, in order to provide the porous carbon with specific properties, certain substances (additives) have been used simultaneously. These additives are not a source of carbon, but cause the incorporation of certain types of heteroatoms in the carbon framework ^[114,129,130] or promote pore development.^[120] Gao *et al.* pyrolyzed sodium citrate together with cysteine, producing a N, S-doped porous carbon with a sponge-like structure.^[130] In another approach, our group recently demonstrated that the addition of urea to potassium citrate leads to a porous carbon with ultra-high pore development (BET surface area of 3350 m² g⁻¹), which is considerably superior to that obtained using potassium citrate alone (1970 m² g⁻¹) (Figure 10).^[120]



Figure 10. Schematic illustration of the synthesis of porous carbons with ultrahigh surface area by self-activation of potassium citrate in presence of urea (Reproduced with permission from ref. [120]. Copyright 2018, Elsevier Ltd).

3.3. Porous carbons derived from organic salts of Ca, Mg, Fe and Zn

For the non-alkali metal organic salts, as already explained in Section 3.1, most of the porosity originates once the remaining inorganic nanoparticles (templates) are removed by acid leaching. As a clarifying example, our group observed that the pyrolysis of calcium citrate leads to a CaO/C composite with a BET surface area of only 112 m² g⁻¹, but once the CaO nanoparticles are removed by acid etching, a carbon with a BET surface area of 1610 m² g⁻¹, a large pore volume of 2.6 cm³ g⁻¹ and a porosity made up almost exclusively of mesopores of around 10 nm is obtained ^[123,131,132] (Figures 11a-c). In a recent work, Wang *et al.* reported that the carbonization of calcium gluconate at > 800°C leads to a sponge-like cellular structure where the CaO nanoparticles formed are deposited on the carbon nanosheets.^[133] Tsumura *et al.* pyrolyzed magnesium acetate at temperatures of 900 °C obtaining a mesoporous carbon with a BET surface area of around 1800 m² g⁻¹ and a pore volume of > 2.5 cm³ g⁻¹.^[134]



Figure 11. Mesoporous carbon produced by self-activation of calcium citrate: a) synthesis scheme (Reproduced with permission from ref. [132]. Copyright 2019, Elsevier Ltd. b) N_2 sorption isotherm and PSD and c) TEM image showing the mesoporous structure (Reproduced with permission from ref. [123]. Copyright 2015, Elsevier Ltd.). Nitrogen sorption isotherm and TEM images of mesoporous carbons derived from: d) iron (III) citrate and e) zinc citrate (Reproduced with permission from ref. [123]. Copyright 2015, Elsevier Ltd.).

In the case of iron organic salts, our group showed that the carbonization of iron (III) citrate leads to a mesoporous carbon with a bimodal mesopore distribution (sizes centered around 9 and 20 nm) ^[123] (Figure 11d). Similarly to the iron salts, the pyrolysis of zinc organic salts also yields a mesoporous carbon, as we verified for Zn (II) citrate (Figure 11e).^[123,131]

The well-known capacity of Zn^{2+} ions to attach certain organic moieties has been used to synthesize Zn-organic coordinated compounds that are able to generate porous carbons by self-activation. Zhao *et al.* showed that the reaction between ethylene glycol and zinc acetate leads to zinc glycolate: (-Zn-OCH₂CH₂O-)_n, whose pyrolysis at 600 °C and subsequent acid leaching yields porous carbon nanofibers with a high aspect ratio (length of 30 µm and diameter of 240 nm) and high pore development (BET surface area of 1725 m² g⁻¹).^[135] Recently, Tong *et al.* reported a general route for producing hierarchically porous carbons by means of the carbonization of (organic-Zn) compounds synthesized by coordinating Zn²⁺ cations with deprotonated organic ligands that possess polytopic chelating sites.^[124] They showed that combining terephthalic acid with Zn(NO₃)₂ in an aqueous alkali medium, a non-porous Znorganic framework is easily synthesized (Figure 12a), which, once carbonized, gives rise to a carbon that exhibits notable pore development with a hierarchical





Figure 12. a) Synthesis scheme, b) N_2 sorption isotherm and c) pore size distribution of hierarchically porous carbon produced by self-activation of a Zn-terephthalic coordination polymer (Reproduced with permission from ref. [124]. Copyright 2020, American Chemical Society).

Cation	Organic moiety	Aditives	Doping (%)	T _{pyrolysis} (°C)	S _{вет} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^[a]	Pore structure ^{[b}	Morphology	Carbon yield (%) ^{[c}	Application	Reference
K⁺	Citrate	-	-	700-900 850	1360-2220 1740	0.6-1.3	Mi+Me	Interconnected nanosheets	2-5	- Supercap Supercap	[35,113,118]
		Urea	N: 0.5- 4.5	700-900	2750-3350	1.56-2.65	Mi+Me	3D-irregular	2.2	Supercap	[120]
		NH ₄ citrate	-	800	940-1900	0.5-0.95	Mi	Interconnected nanosheets	24-34	Supercap	[114]
	Gluconate			800	1410	0.76	Mi+Me	3D-irregular	17	-	[35]
	Gluconate	Melamine	N: 6-17	800-900	730-1040	0.3-0.4	Mi	3D-irregular	30-40	Supercap	[129]
	Tartrate			600-900	400-1300	0.2-0.7	Mi+Me	3D-irregular	20	Supercap	[136]
	poly(acrylamide- co-acrylic acid)			1000	1330	-	Mi	sheets	-	Supercap	[127]
	phthalate		1	600-1000	500-2100	0.3-1.1	Mi	-	-	CO ₂ capture	[137]
Na ⁺	Poly(4- styrenesulfonic acid-co-maleic acid)	-		1000 800	1720 1400	- 0.93	Mi+Me Mi+Me	3D-irregular 3D-irregular	- 17	Supercap -	[126] [125]
	Citrate	-		400-1000 750 800 800	200 180 660 650	0.40	Mi+Me	Sponge-like	3-4 3-4	Na storage K-ion battery Supercap	[115] [121] [117] [35]
	Chloroacetates	-		300-1000	740 1020	0.5 0.4	Mi+Ma Mi+Ma	3D-irregular 3D-irregular	4 30	Supercap	[138] [139]
	Ascorbate	-		400-1000	500-1300	0.44-1.15	Mi+Me	Lamellar flakes	-	Na-ion battery	[140]
	EDTA disodium magnesium	-		500-900	100-1260	0.1-1.2	Mi+Me	3D-irregular	3-7	Supercap	[141]
	EDTA tetrasodium	-		600-900	410-1170	0.21-0.71	Mi+Me	3D-irregular	-	Supercap	[142]
	EDTA disodium zinc			600-900	590-1470	0.56-1.32	Mi+Me	3D-irregular	-	Supercap	[143]
	oxalate	-		600-900	450-1450	0.5-1.5	Me	3D-irregular	-	Supercap	[144]
	glutamate	NaCl	N: 2-8	700-900	400-1000	0.22-0.56	Mi	3D-irregular	-	Supercap	[145]
	poly(4-styrene sulfonate)	-		800	1051	0.43	Mi+Ma	3D-irregular	32	Li-S battery	[128]
	gluconate	-		700-900	280-1390	0.21-1	Mi+Me	nanosheets	8.5-22	Supercap	[116]
	alginate	-		800 600	1250 270	0.63	Mi Mi	3D-irregular	9 16	- Supercap	[35] [146]
	Citrate	Cysteine	N: 2, S:0.8	800	500	-	Mi+Me	Interconnected Nanosheets	-	Electro- oxidation	[130]

Table 2. Summary of porous carbon prepared by self-activation of organic salts.

	lignosulfonate	-	Τ	600-1000	250-1330	0.22-1.06	Mi+Me	3D-irregular	-	Supercap	[147]
	Poly(styrene sulfonic acid-co- maleic acid)	-		800	1380	0.93	Mi+Me	3D-irregular	-	-	[125]
	UF-PAAS polymer ^[d]	-		900	1960	1.1	Mi	3D-irregular		Supercap	[148]
Ca ²⁺	Citrate	- Melamine	- N: 9.2	800	1510 1350	2.6 1.79	Me Me	3D-irregular 3D-irregular	6 - -	- Supercap, ORR	[35] [123] [131]
	Gluconate	-	-	700 800	790 810	0.7 1.07	Ме	Nanosheets	17 -	- Catalyst	[35] [149]
	Alginate	-		700	830	0.54	Mi+Me		17	-	[35]
Mg ²⁺	Citrate	-	-	900 700	1800 2320	2.5 1.3	Me Me	3D-irregular	-	Li storage Supercap	[134] [150]
Fe ³⁺	Citrate	-		800	950	1.8	Me	3D-irregular	1.5	-	[123]
Zn ²⁺	Citrate	- Melamine	- N: 8.5	800	1380 1190	1.4 1.2	Me	3D-irregular	6 -	ORR	[123] [131]
	salicylate	Mg acetate	-	900	2010	3.4	Me	3D-irregular	-	Supercap	[151]
	glycolate			600	1725	2.7	Me	nanofibers	-	Supercap	[135]
	Organic framework	-	N: up to 5	1000	up to 2650	up to 2.35	Mi+Me+Ma	3D-irregular	-	ORR	[124]

^[a] Total pore volume determined by N₂ physisorption. ^[b] Mi - microporous, Me – mesoporous and Ma – macroporous pore network. ^[c] Carbon yield is defined as g of porous carbon/100 g of raw carbon precursor. ^[d] Urea-formaldehyde polymer interpenetrated with sodium polyacrylate.

3.4. Self-activation of biomass

Considering their low-cost, Earth abundance and sustainability, biomass products constitute the main feedstock for the production of porous carbons. Usually, the methods for producing porous carbons from biomass involve the use of foreign chemical compounds that act as activating agents following either physical or chemical activation routes. However, it has been demonstrated that the production of porous carbons from biomass products can also be carried out without the aid of any foreign substances. Self-activation strategies applied to biomass involve the use of certain substances as activating agents that are part of the biomass or are emitted during its pyrolysis. In general, two different routes can be distinguished in the self-activation of biomass: a) physical selfactivation consisting of the reaction between certain reactive gases emitted during pyrolysis (mainly CO₂ and H₂O) and the carbonaceous matter;^[152-156] and b) chemical self-activation, which is based on the activation power of alkali elements (K and Na) and alkali earth elements that are part of the biomass.^{[157-} ^{160]} Both processes are illustrated in Figure 13. It is important to point out that in the case of physical self-activation, the chemical activating action of alkali or alkali earth elements present in the biomass cannot be discarded and, in this case, it is reasonable to assume that both processes (physical and chemical self-activation) will operate together.



Figure 13. Schematic illustration of the physical and chemical self-activation routes of biomass products.

At this point, it should be noted that examples of carbons produced simply by pyrolysis of biomass that exhibit surprisingly high pore development can be found in the literature.^[161–166] In most cases, these apparently anomalous results can only be explained by assuming the occurrence of

physical or chemical self-activation processes. As an example, Gao *et al.* reported that just pyrolyzing amaranthus waste led to a carbon with a surprisingly high pore development (1010 m² g⁻¹, 0.80 cm³ g⁻¹ and a micro-mesoporous structure).^[161] These textural properties are only understandable by assuming the existence of a chemical self-activation process.

Table 3 summarizes numerous examples of physical and chemical selfactivation for a variety of biomass products.

3.4.1. Physical self-activation of biomass

The physical self-activation of biomass is based on the gasification reactions between the carbonaceous matter and the reactive gases evolved during pyrolysis, in particular CO₂ and H₂O [C + CO₂ \rightarrow 2CO and C + H₂O \rightarrow CO + H₂]. In order to achieve high pore development, the pyrolysis needs to take place under controlled conditions that favor the gasification reactions between the emitted gases and the carbonaceous matter. Specifically, it requires a reactor with special features that allow partial or complete restriction of the carrier gas flow. In this respect, Bommier et al. showed that simply by restricting the flow of argon during pyrolysis of cellulose from 200 to 10 mL min⁻¹, the BET surface area of the derived porous carbon increased from 98 to 2600 m² g⁻¹ (Figures 14a, b).^[152] In another approach, Xia and Shi carbonized kenaf fibers in a closed reactor (no carrier gas was used in this experiment) obtaining a porous carbon with a high BET surface area up to 2430 m² g⁻¹ and a pore volume up to 1.74 cm³ g⁻¹.^[153] Due to the low reaction rates of the gasification reactions, long reaction times are required and consequently in this case pore development is notably enhanced by long dwell times, as illustrated by the results in Figure 14c. This conclusion is confirmed by the results produced by Smith el al., who investigated the production of porous carbons by means of physical self-activation of ten hardwood species.^[156] The production of doped carbons by using this methodology has been investigated by Yang et al., who reported the preparation of N, O-doped porous carbons (N: 2.6 at %, O: 7.4 at %) with a BET surface area of up to 950 m^2 g⁻¹and a micro-mesoporous pore network by means of the physical self-activation of hollyhock leaves.^[155]



Figure 14. Physical activation of biomass: a,b) effect of the flow rate upon the pore development for the self-activation of cellulose (Reproduced with permission from ref. [152]. Copyright 2015, Elsevier, Ltd), c) effect of dwell time upon the textural development (Reproduced from ref. [153] with permission from the Royal Society of Chemistry). Chemical self-activation of biomass: d) structure of a lotus plant and concentration of K and Na in leaf and stem, and e) effect of temperature of self-activation upon surface area of the carbons obtained from stem and leaf of a lotus plant ^[157].

3.4.2. Chemical self-activation of biomass

Biomass products contain abundant amounts of alkali (K and Na) elements, as illustrated in Figure 14d.^[157] The presence of these elements is the cause of the chemical self-activation. Thus, during pyrolysis, the alkali elements are converted to the corresponding carbonates (K_2CO_3 and Na_2CO_3) that will act as activating agents, as previously described in Sections 2.1 and 3.1 (*vide supra*). In addition, calcium and magnesium are also transformed into carbonates that subsequently decompose to oxide nanoparticles (CaO and MgO), which can act as endo-templates, thus contributing to the generation of a certain number of pores.

The chemical self-activation of biomass has been investigated by using a wide variety of products such as kenaf stems,^[158] seaweeds,^[159,167] wild pokeweed,^[168] neem leaves,^[169] eggplant,^[170] tobacco stems,^[160] celery,^[171] pine needles,^[172] and lotus stems.^[157] In a pioneering work published in 2004, Inagaki et al. carbonized inner cores of kenaf (with a K content of around 2.7 %) at 1000 °C at a high heating rate (11 °C min⁻¹) and obtained a porous carbon with a notable surface area of 1400 m² g⁻¹, the carbon yield being 13 %.^[158] Subsequently, Raymundo-Piñero et al. showed that the pyrolysis of selected seaweeds leads to porous carbons with high surface areas up to 1300 m² g⁻ ¹.^[159] The key to this approach is the selection of certain types of seaweeds that are rich in carrageenan (a potassium-rich carbohydrate) and in sodium alginate, which ensure the presence of notable amounts of K and Na. Zhang et al. provided an illustrative example of the chemical self-activation approach.[157] These authors analyzed the chemical composition of lotus stems and leaves and found that the alkali content of K and Na in the stems is notably superior to that in the leaves (*i.e.*, K content is ~ 2.5 % in stems vs. ~ 1 % in leaves) (Figure 14d). This means that, although the porous carbon derived from lotus stems carbonized at 800 °C exhibits a high BET surface area of 1610 m² g⁻¹, the carbon sample derived from the leaves has a significantly lower surface area (1040 m² g⁻¹) (Figure 14e). Niu et al. proposed an alternative approach consisting of the use of the hydroxyapatite $[Ca_6(PO_4)_3(CO_3)(OH)]$ present in animal bones as an activating agent. In this case, the thermal treatment of cattle bones leads to the decomposition of hydroxyapatite (at T > 750 °C) giving rise to several products that act as activating agents (*i.e.*, CO₂, H₂O and also CaO nanoparticles). The carbon produced at 1100 °C has a high pore development with a BET surface area of 2100 m² g⁻¹ and a porosity made up almost exclusively of mesopores.^[173]

By selecting biomass products with a large content of heteroatoms (*i.e.,* N, S, *etc.*), doped porous carbons can be produced by self-activation as has been demonstrated by He *et al.*, who produced N-doped porous carbons (S_{BET} up to 1190 m² g⁻¹) by means of the chemical self-activation of N-rich biomass such as celery plants.^[171] On similar lines, Liu *et al.* prepared nitrogen-rich mesoporous carbons with up to 8 % N simply by pyrolyzing shrimp skin at temperatures in the 600–900 °C range^[162]

Biomass	T _{pyrolysis} (°C)	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^[a]	Pore structure ^[b]	Carbon yield (%) ^[c]	Application	Reference				
			Physical self-	activation		•					
Cellulose	1100	2600	2.1	Ме	1.6	Supercap	[152]				
Kenaf core	900-1100	500-2400	0.34-1.7	Me	16-2.8	-	[153]				
Rice husk	800	530	0.33	Mi+Me	-	Supercap	[154]				
Hollyhock (leaves)	850	950	0.6	Mi+Me	25	Supercap	[155]				
Wood (Afromosia)	1050	>2500	1.4	Me	-	-	[156]				
Chemical self-activation											
Kenaf core	1000	1400	-	Mi	13	-	[158]				
Seaweed	900	1300	0.53	Mi+Me	15	Supercap	[159]				
Lessonia nigrescens							[167]				
Pokeweed	900	720	0.56	Ме	20	Phenol removal	[168]				
Neem leaves	1000	1230	-	Mi+Me	-	Supercap	[169]				
Eggplant	1000	950	-	Mi+Me	-	Supercap	[170]				
Tobacco stems	800	1750	0.95	Mi	-	Supercap	[160]				
Amaranthus	900	1010	0.80	Mi+Me		ORR	[161]				
Lotus stem	800	1610	0.8	Mi	13	Supercap	[157]				
Letucce stem		1075	-			Supercap					
Celery stem		1230				Supercap					
Cattle bones	1100	2100	1.8	Me	-	Supercap, Li-ion	[173]				
						battery					
Shrimp skin	800	510	0.71	Ме	-	Na-ion battery	[163]				
Pine needles	1000	780	0.5	Mi+Me	-	Supercap	[172]				
Celery stem	900	1190	0.64	Ме	>30	Supercap	[171]				

Table 3. Porous carbons prepared by self-activation of biomass products.

^[a] Total pore volume determined by N₂ physisorption. ^[b] Mi - microporous, Me – mesoporous and Ma – macroporous pore network. ^[c] Carbon yield is defined as g of porous carbon/100 g of raw carbon precursor.

4. Summary and outlook

There is no doubt that porous carbons play a key role in many emergent applications, including electrochemical energy storage/production, carbon capture and gas storage (e.g., H₂ or CH₄), and still play a leading role in traditional applications such as catalysis and water/gas purification. Traditional activation processes, especially chemical activation procedures, are based on the use of (highly) corrosive, toxic substances. This not only poses significant restrictions on equipment and safety protocols, but also represents a serious environmental threat. This has spurred the search for greener chemical activating agents, as well as the development of novel activation procedures. However, it should be noted that potassium hydroxide is still massively used at the laboratory scale, as it allows the synthesis of high-performing activated carbons with advanced properties. It is the authors' opinion that future efforts are mandatory from the scientific community to replace potassium hydroxide, as its use is quite unrealistic from the industrial point of view.

In the search for greener activating agents, potassium-based carbonates, bicarbonates and organic salts have been explored. What they have in common is that the actual activating agent is potassium carbonate, which is also the main reaction product during potassium hydroxide activation. Even though the pore development achieved with these activating agents is normally lower than that achieved via KOH activation, they stand out for allowing higher activation yields and preserving the particle morphology of the precursor. Furthermore, it has been shown that the rational design of the activation procedure allows the production of materials with a pore development similar to that of benchmark KOH-derived ACs. Thus, confinement of the reactants in an inert medium such as KCI, which forms a eutectic mixture with K₂CO₃ below the temperature at which the redox reaction with carbon takes place, enhances the reactivity between the carbonaceous matter and K₂CO₃. An additional important advantage of this confined activation is the increase in the yield. In fact, the main disadvantage of conventional chemical and physical activation processes lies in the low carbon yields, especially for high pore developments. Therefore, future efforts must be targeted at developing strategies that enhance the yield of activation processes. In this regard, salt melt approaches are very promising. Contrary to potassium-based carbonates/bicarbonates/organic salts, their sodium-based counterparts have been little-used as activating agents, as they are less effective than potassium-based agents.

It is worth noting the role that nitrogen heteroatoms have on porosity development, no matter whether they come from a foreign additive (*e.g.*, melamine, urea, *etc.*) or they form part of the carbon precursor. Porous carbons with ultra-large BET surface areas in excess of $3000 \text{ m}^2 \text{ g}^{-1}$ and pore volumes above 2 cm³ g⁻¹ have been obtained. Additionally, these materials normally exhibit a bimodal micro-mesoporous structure with a large proportion of mesopores, in contrast to K₂CO₃ or KOH-derived ACs which have a predominantly microporous pore network. However, highly toxic potassium cyanide is obtained as a by-product in these activation processes, which speaks against the suitability of these activation strategies. Therefore, novel methodologies for tuning the pore size distribution of activated carbons must be

sought. Indeed, control over the pore size distribution of activated carbons is still a challenge to be overcome and a key aspect in many applications (*e.g.*, supercapacitors or gas storage).

Recently, potassium/sodium sulfates and especially thiosulfates have been shown to be powerful activating agents when the activation process is carefully engineered. Confinement of the activation reactions in eutectic mixtures of salts (*e.g.*, LiCl and KCl) or just in a salt melting below the synthesis temperature (*e.g.*, KCl melts at 770 °C), reinforces the contact between the solid carbonaceous matter and the Na₂SO₄-Na₂S liquid system, thereby enhancing the reactivity. Furthermore, this confinement substantially improves the carbon yield, enhancing the efficiency of the synthesis process.

As an alternative to the use of foreign activating compounds, there has been increasing interest in self-activation techniques, where the porogenic action is performed exclusively by substances that are part of the carbon precursor. They are not only greener, but also low-cost, simpler, less-time consuming, and generate less waste. Indeed, the production of the porous carbon can be performed in one step by a standard carbonization process. The raw materials appropriate as carbon precursors need to include one of the following elements in their composition: alkali metals (K, Na), alkali earth metals (Ca, Mg) or other elements such as Fe o Zn. They can be organic or polymeric salts or even better, biomass. The self-activation involves three pore generation mechanisms: i) chemical activation (oxidation of carbon by carbonates or oxides), ii) physical activation (gasification of carbon by CO₂) and iii) endotemplate processes (after removal of the inorganic phases embedded in the carbon matrix). Interestingly, one can envisage that an effective activation of biomass can be carried out by means of a methodology that combines the advantages of physical and chemical self-activation processes. For example, by selecting biomass products with high content of alkali and alkali earth elements and by performing the pyrolysis under restricted flow conditions, the easy, sustainable, low-cost production of highly porous carbons would be possible.

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Conflict of Interest

The authors declare no conflicts of interest.

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