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Chapter 5

Nanoporous Carbons with Tuned Porosity

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5.1. Introduction

Nanoporous carbons (*aka* activated carbons) are unique materials that have been extensively used in many specialized applications from gas adsorption and separation, environmental remediation, catalysis and energy storage [1-3]. Such variety of applications is mostly due to the flexible coordination chemistry of carbon atoms, that allows almost infinite possibilities of 3-dimensional structures, and to their ability to react with other heteroatoms (e.g., oxygen, nitrogen, boron) to incorporate specific functionalities. From a structural point of view, nanoporous carbons are composed of distorted graphene-like layers of sp^2 domains of carbon atoms also rich in defects (free edge sites), heteroatoms located at the edges (predominantly) or inserted in the basal-planes, and carbon atoms in sp^3 configurations [1,4]. The distorted graphene layers are stacked by weak Van der Waals forces either in an ordered or turbostratic structure with different degrees of planarity depending on the graphitization extent of the materials. The free sites are associated to armchair (carbyne-like) and zig-zag (carbene type) configuration carbon atoms (rather than H-terminated or free radicals as generally assumed for a long time), and account for the surface reactivity of carbons in gasification reactions or to chemisorb heteroatoms and create stable surface functionalities [5].

Nanoporous carbons can display a hierarchical pore structure and exist in 3D architectures reaching specific surface areas (SSA) over 1000 m²/g [1,2], and displaying a high fraction of pores of nanometric dimensions. The versatile surface chemistry of carbons also provides a useful tool to material's design, since small amounts of heteroatoms may control the

physicochemical properties of the final carbons (e.g., self-organization, chemical stability, reactivity) [3]. The combination of an structural arrangement of graphene layers in varied architectures and surface chemistry is responsible for the physicochemical properties of nanoporous carbons that make them to succeed when directly compared to direct competitor materials in many areas of adsorption, catalysis and so on [6].

There are numerous studies in the literature on the preparation of nanoporous carbons with varied textural and chemical features [1,2]. Hence, it is important to place this in the context of applications for gas storage. Indeed, the performance of an adsorbent in a specific application must (should) be modulated by selecting an adequate precursor and synthetic approach to control various characteristics such as structure, porosity, chemical composition and morphology.

Among the large spectrum of materials with potential ability to selectively adsorb specific molecules of a gas mixture, activated carbons play an important role due to the versatility of forms, morphologies and pore architectures. Indeed, numerous works in the literature describe that properly designed nanoporous carbons can achieve the target values for high-pressure gas storage of supercritical gases, when compared to other MOFs, zeolites and so forth [7-9]. They do not only provide excellent adsorption capacities and selectivity for mixtures, but also better mechanical stability under pressure (upon conforming), which is required for practical applications.

For practical gas-phase applications, an appropriate adsorbent must fit the requirements of high adsorption capacity at the operating conditions, fast adsorption kinetics, high selectivity towards the target gas molecule in a mixture of gases, easy regeneration and high working or delivered capacity. These aspects should be achieved and controlled by tuning the porosity (i.e., high pore volume and uniform distribution of pore sizes, high density and minimum interparticle space) and/or the surface chemistry, to promote specific gas-adsorbent interactions. Hence, knowledge of the optimum the pore dimensions for high-pressure gas storage becomes critical.

Adsorption of supercritical gases takes place predominantly in pores that are less than two or three molecular diameters in width [9-11], where the adsorption potential is larger; on increasing the pore width, the forces responsible for the adsorption decrease rapidly. Thus, pores larger than 2 nm are typically not useful for the enhancement of gas storage, although they may be necessary for transport into and out of the micropores. The density of the adsorbed gas in large pores is low and similar to that of compressed gas, whereas it increases inside nanopores of adequate dimensions. Indeed,

nanoporous carbons with extremely large SSAs usually have low packing densities.

For instance, for high-pressure hydrogen storage on nanoporous carbons, most experimental and theoretical studies fairly agree in the fact that the optimum pore size corresponds to pores that can hold two layers of adsorbed hydrogen (ca. 0.6-0.7 nm), whereas those larger than 1.5 nm contribute little to the storage and may be considered underused (Fig. 1) [10]. The volumetric storage capacity is also important; wide pores do not only adsorb H_2 less effectively, but contribute to reducing the packing density of the adsorbent. Concerning CO_2 storage, the optimal adsorption capacity and packing density have been reported for carbons with pores of ca. $\sim 0.65\text{--}0.8$ nm [11,12]; on the other hand, selectivity towards the separation of CO_2 (kinetic diameter of 0.33 nm) from gases of similar dimensions such as CH_4 (0.39 nm) and N_2 (0.36 nm) requires pores around $\sim 0.4\text{--}0.5$ nm. Pores below these limits must be minimized to avoid kinetic restrictions [11,12]. It has also been proposed CO_2 capture under post-combustion conditions (1 bar and $25^\circ C$) involves exclusively the micropores below 0.6 nm, whereas for pre-combustion conditions (20 bar and $25^\circ C$) the entire microporosity plays a role with optimal performances in the 1.5–2 nm range. Thus, the design of the porosity of the carbon material should be conducted differently depending on their application [13]. For methane storage, an optimum pore size of ca. 0.76 nm has been reported to maximize the deliverability at ambient pressures [9,14]. Other authors have indicated that the maximum methane storage at $25^\circ C$ and high pressure can be obtained in monolithic carbons with pore widths of 1.14 or 1.12 nm [15]. Another approach for methane storage is the adsorption of methane in the form of a gas hydrate (e.g., on activated carbons preloaded with water). As the methane hydrate is bulkier than the gas, the requirements of the adsorbent in terms of pore widths are different, and good performances have been reported for nanoporous carbons with micropores ca. 2-2.6 nm [16].

Besides dimensions, the shape of the pores is also important, due to its impact in the packing density of the adsorbed molecules. The microporous structure of activated carbons is dominated by slit-shaped pores, which favor a high packing density of adsorbed gas molecules, compared to cylindrical or spherical pores. This makes activated carbon most suitable adsorbents for the storage of small gases than zeolites or metal organic frameworks (MOFs) [7].

Fig.1 . Correlation of the micropore volume of nanoporous carbons and the adsorption capacity of (a) H₂ at -196 °C and 20 bar (squares, data from [17,18]) and at 25 °C and 200 bar (circles, data from [19]); (b) CO₂ at 25 °C and 1.5MPa. Data reproduced from [12]. Copyright 2014, with permission from Elsevier; (c) CH₄. Data reproduced with permission from [9]. Copyright 2017 American Chemical Society.

Most studies also agree on the best performance of monolithic or pelletized forms of carbon compared to granular or powdered adsorbents in order to comply with up-to-date requirements to achieve reasonable levels of gas storage [20-22].

The thermal management during cyclic operation in storage systems based on porous materials has to be considered as they may have a significant impact on their performance. Compared to other adsorbents, AC usually have low heats of adsorption that prevent excessive heating or cooling of the storage vessel during the adsorption-desorption cycles [8-10].

Considering all this, it is clear that the understanding of the pore size/shape requirements of nanoporous carbons is essential for a rational design of carbon materials with increased gas-storage capacity. While many theoretical studies may suggest optimal pore structures to maximize methane, hydrogen or carbon dioxide storage, they give no indication or suggestion on how such materials might be produced. Thus, the aim of this chapter is to provide an overview on the synthetic approach for the preparation of activated carbons with adequate porosity and surface chemistry for the storage and separation of small gases of strategic interest (e.g., H₂, CO₂ and CH₄). Even though numerous works exist on exploring approaches for the synthesis of mesoporous and macropores carbons with hierarchical and controlled architectures, we limit the discussion here to the control of the microporosity in carbons, since they exhibit the best performance in terms of gas storage, separation and packing densities.

5.2. Conventional activation methods

Activated carbons are produced at industrial scale by so-called conventional activation methods (i.e., physical and chemical activation). Most

processes start with a carbonization (pyrolysis) or an oxidation step of the precursor, followed by the exposure of the carbonized material to a reactive atmosphere in the presence of an activating agent that allows the development of a porous structure. The preparation of activated carbons from charcoals is an ancient artwork, and extensive work has been done to enhance the porosity of the resulting carbon adsorbents by the use of different activating agents, the choice of precursors, the optimization of the activation conditions (temperature, heating rate, gas flow), and the usage of various impregnation methods (soaking, stirring) [1]. The purpose of this chapter is to summarize the main differences of the conventional activation methods, considering both thermal (pyrolysis and gasification) and chemical activation.

5.2.1 Carbonization

Carbonization or pyrolysis involves the thermal transformation of a material to moderate/high temperatures in an inert atmosphere, with the purpose of eliminating most of the volatiles of the precursor. The residual solid obtained is a carbonaceous char, which is composed of carbon atoms arrangement in a cross-linked condensed aromatic structure in a random manner. The disorganized structure of the carbon atoms leaves interstices between the aromatic layers (incipient porosity, eventually filled with the tars formed during the carbonization). A subsequent activation of the char enlarges the incipient porosity and creates new pores.

Carbon chars are among the first synthetic materials manufactured by men, thus knowledge of their production has been accumulated over a long time [23]. The use of pyrolysis as a thermal process to produce solids (chars), liquid fuels and gaseous products that can be suitable for application in several fields (adsorbents, fertilizers, biofuels) has been largely investigated, as the yields of the gas/liquid/solid fractions depend on the thermal conditions (temperature, residence time, heating rate, atmosphere). For instance, carbonization at elevated pressure improves the yield of charcoal production and reduces the reaction time of the synthesis. This allows to extend the activation of the char over time, and thus to obtain larger burn-offs while maintaining reasonable yields and densities [24]. Slow pyrolysis at low temperatures, heating rates and long residence times favors the production of chars [23], as opposed to fast and flash pyrolysis (ca. moderate temperatures and short residence time) that favor the production of a liquid fraction [25].

Slow pyrolysis is typically carried out in an inert atmosphere, although the presence of oxidant agents such as steam can improve the SSA of the resulting chars [26-28]. This has been attributed to the ability of steam to penetrate more efficiently on the solid precursor during the slow pyrolysis,

enhancing devolatilization [29], and gasification reactions -if the temperature is high enough- [30]. The effect of steam also varies with the nature of the feedstock; SSA values ranging from 405 to 940 m²/g have been reported under steam-assisted slow pyrolysis of various biomass feedstocks [26-28]. Giudicianni et al. [27] found that the content in cellulose of the feedstock is determinant for the development of a microporous structure, with higher SSAs obtained for biomass precursors with cellulose content of 55 wt.%.

The temperature of the pyrolysis has an important effect in the development of the porosity. At low heating rates, the internal surface area development is strictly correlated to the degree of devolatilization and to the formation of cracks inside the matrix. Mild thermal conditions of ca. 400 °C favor the development of a macroporous structure due to the removal of large amounts of volatile matter. At about 500 °C, micropores and mesopores are created, leading to an increase in surface area and porosity; and at T>800 °C, the structure and micropore coalescence lead to low values of SSA [26,31]. For certain precursors (e.g., high rank coals), a preoxidation step in air is needed for boosting the incipient porosity of the char [32].

It is important to highlight that carbon chars usually display a constricted pore network comprised of nanopores of small dimensions accessible through pore mouths or necks of narrow dimensions [1]. Thus, the low surface areas of these materials seen by N₂ at -196 °C, might not be an indication of the lack of a microporous structure, but rather due to the restricted diffusion of N₂ at cryogenic temperatures into pores smaller than 0.5 nm [33]. Following IUPAC recommendations [34], the analysis of the narrow microporosity of carbon materials with pore constrictions should be performed by CO₂ adsorption at 0 °C.

5.2.2 Physical activation

The term thermal or physical activation refers to the development of porosity in the gas phase, usually by reaction of a char with oxygen air, CO₂, steam or their mixtures. The reaction is generally at elevated temperatures (between 750-1100 °C) and proceeds through the formation of surface oxygen complexes. A detailed review on the understanding of the chemical reactions, thermodynamics and kinetics of the physical activation with these gases can be found in [1]. We herein provide a comprehensive summary of the effect of various activation parameters on the development of a microporous network useful for gas storage applications.

The objective of the activation process is to enlarge and to open the incipient porosity developed during the carbonization. This is carried out under a

reactive atmosphere in the presence of oxidants such as oxygen (or air), steam, and carbon dioxide, according to:

The gasification of chars under CO_2 and steam (and their mixtures) is preferred over the use of oxygen (air) due to the high exothermic enthalpy of the latter, which makes the reaction temperature difficult to control. As a result, oxygen does not penetrate inside the particles of the char, and a fast gasification occurs in the external surface, leading to the complete burn-out of the carbon material rather than to the formation of pores. In the case of CO_2 or steam the reactions are endothermic, thus an external heat supply is required, allowing an accurate control of the experimental conditions.

Physical activation is commonly carried out as a two-stage process, starting by the carbonization of the precursor and further activation of the obtained char. The use of a single-stage process is also possible, and it does not seem to have a significant impact in the porous features of the activated carbon in terms of micropore volume (V_{micro}) and SSA [35].

Many experimental conditions can influence the final textural features of an activated carbon: the precursor origin and reactivity, the heating rate, the gas flow rate, the temperature and dwelling time of the activation, the activating agent, and so forth.

The choice of the gasification temperature is not arbitrary and depends on the reactivity of the precursor under CO_2 and steam. It is important to keep a moderate reactivity to assure a diffuse regime control of the reaction and prevent the fast gasification of the external surface of the materials (leading to a non-porous material). A simple approach to measure the gasification rate consists in carrying out a thermal profile of the char under CO_2 or steam atmosphere, and evaluating the rate of mass loss with the temperature. This test provides an idea of the onset temperature of the reactivity for the oxidizing gas chosen, and allows comparing the reactivity rate of different precursors. Additionally, for certain precursors (e.g., coals) a pre-oxidation step is recommended to favor the formation of an incipient porosity in the char [36], as well as a well-developed microporosity after the gasification.

Among other parameters, the effect of the flow rate of the activating agent is also important. Slow rates (ca. below 10 ml/min) favor the development of microporosity due to a more uniform gasification through the whole

carbon particle network [37]. At high CO₂ or steam flow rates, the gas does not penetrate deeper in the material, and the burn-off on the external surface of the carbon particle becomes more important than the generation of internal porosity. As a result, the carbon yield decreases and the activated carbons display low total pore volumes, and the porosity is mainly composed by macropores. This is an important difference with chemical activation, where fast rates favor the development of microporosity, as it will be addressed below. The particle size is also important, with smaller particle sizes leading to denser carbon materials and much more developed SSAs and narrow micropores.

Regarding the evolution of the porous features with the activation extent, as a general rule burn-off degrees lower than ca. 50 wt.% render microporous activated carbons, with total pore volume and SSAs increasing with the burn-off, regardless the nature of the precursor (Fig. 2) [37-39]. The initial increase in the V_{micro} (particularly the narrow microporosity determined by CO₂ adsorption at 0 °C) during the gasification of the char becomes gradually smaller as the burn-off increases. Above 40-50 wt.% burn-off, a fall in the V_{micro} may be observed due to the widening of the pores, accompanied by the development of mesopores. Additionally, at high levels of burn-off the ablation of the carbon particles becomes important, thus the industrial gasification of chars rarely goes beyond 40-50 wt.% [1].

The activation under CO₂ and H₂O renders materials with different porosity. Comparison is not straightforward since the chars present different reactivity to the oxidizing gases. Based on studies performed on the same precursor using CO₂ and steam at similar gasification rates, it may be concluded that CO₂ activation produces activated carbons with a narrow distribution of micropores, whereas steam activation generates carbons with wider micropore size distributions, a slightly larger development of mesopores [39]. Both gases produce activated carbons with a low functionalization due to the high temperatures of gasification, although CO₂ activation creates a slightly larger number of more stable oxygen groups than steam [41].

Fig. 2. (a) Nitrogen adsorption isotherms at -196 °C and (b) differential pore size distribution for a series of activated carbons prepared by CO₂ gasification of polyethylene-terephthalate wastes at various burn-off degrees. Reprinted from [40], Copyright 2015, with permission from Elsevier; (c,d) Evolution of the total micropore (V_{micro}) and mesopores volumes (V_{meso}) with the burn-off for activated carbons obtained from CO₂ gasification of almond shells (c, squares), olive stones (c, circles) and polyethylene-terephthalate waste (d, triangles); (c) redrawn from [1], Copyright 2006, with permission from Elsevier; (e) Evolution of total micropore (V_{micro}), mesopores volumes (V_{meso}) and (f) narrow microporosity as a function of burn-off for CO₂ (full symbols) and steam (empty symbols) gasification of olive stones. (e,f) redrawn from [39], Copyright 1995, with permission from Elsevier.

Gasification using water at supercritical conditions has also been studied for the preparation of activated carbons [42]. The gasification reaction using supercritical water is about 10 times faster than steam, favoring activated carbons with large V_{micro} and higher mechanical strength. As in the

case of steam activation, increasing the activation temperature and time increases the SSA of the activated carbons, whereas the water flow rate favors the microporosity but has a subtle effect on the mesoporosity.

5.2.3 Chemical activation

In general terms, chemical activation is considered as a reaction between a solid precursor and a chemical activating agent during the heating of the mixture in an inert atmosphere. The most studied precursors are lignocellulosic materials, coals and chars; as activating agents the most used are ZnCl_2 , H_3PO_4 and alkali hydroxides (e.g., KOH and NaOH).

Chemical activation has recognized advantages for the production of activated carbons with high developed porosity, as it leads to higher yields and allows the use of lower temperatures than physical activation. Additionally, the activation mechanisms are different in both processes, and so it is the porosity of the resulting activated carbons. A detailed review on the mechanism of the different chemical activation reactions for various activating agents can be found in [1]. It has been reported that differences on activation mechanisms when using ZnCl_2 , H_3PO_4 , KOH are clear when using lignocellulosic materials as precursors [43]. Although the three chemicals react with the precursor, some clear differences can be observed at the end of the impregnation step. ZnCl_2 and H_3PO_4 produce a dehydration of the precursor components yielding in a reduction in the dimensions of the particle. During the thermal treatment, the reactants remain inside the particles acting as a template for the creation of microporosity. The small size of the ZnCl_2 molecule or its hydrates drives to the creation of small and uniform size micropores whereas the mixture of molecules produced during thermal treatment in H_3PO_4 (e.g., H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_5$ or $\text{H}_{13}\text{P}_{11}\text{O}_{34}$) leads to an heterogeneous microporosity. Therefore, ZnCl_2 would acts at temperatures below 500°C and H_3PO_4 below 450°C .

KOH does not act as a dehydrating agent on the precursor, and starts to react above 700°C , after the formation of the char. In such a case activation initially consists of a redox reaction, where carbon is oxidized to CO or CO_2 , thus, incidentally, creating some porosity and K_2CO_3 as a by-product. As a result, KOH is reduced to metallic potassium. Potassium can be intercalated between the graphene layers of the carbon particles favouring the process by separating the layers, which generates micropores or even new high energy sites for the redox reactions [44-46]. As K can be intercalated into graphite-like structures, whereas Na can be only intercalated/inserted in more disordered carbons [46], the development of porosity for precursors with low structural order (e.g., lignocellulosic and low rank coals), is better with NaOH , whereas KOH produce better results for highly ordered ones (e.g., high range coals) [47]. As a consequence of such differences on

activation mechanism, zinc chloride and phosphoric acid are activating agents usually used for the activation of raw lignocellulosic materials and alkaline metal hydroxides are mainly used for coal precursors or chars.

The main parameters of the preparation method affecting the porous texture characteristics of activated carbons (SSA, pore size and pore size distribution) are impregnation ratio, activation temperature, activation time and activating atmosphere. The impregnation ratio is the correlation between the weights of chemical agent and the precursor. The activating agent is generally in solution where concentration can be varied but in some cases, as for NaOH, a direct mixing of the solid chemical and the precursor results more efficient for developing high SSA [48]. The impregnation ratio is a variable that highly affects not only the SSA but also the pore size distribution of the resulting activated carbon. A general trend is that increasing the impregnation ratio also increases the SSA of the activated carbon up to a maximum value. Regarding the pores size and volume (Fig. 3) there is a strong development of porosity when increasing the impregnation ratio shows, whatever the activating agent. For low impregnation ratios the increase in the SSA is related to the generation of micropores without an appreciable contribution of mesoporosity. For the particular example of KOH, the V_{micro} deduced from CO_2 adsorption at 0°C are quite similar to those deduced from N_2 adsorption at -196°C , indicating the development of only narrow micropores. At higher impregnation ratios, there is a less pronounced increase in the porosity and the pore size distribution becomes more heterogeneous, the differences among the effect of the chemicals becoming more clearly shown. ZnCl_2 develops both wide micropores and small mesopores whereas H_3PO_4 also develops large mesopores and even macropores; KOH mostly produces the widening of the microporosity [43,49,50]. As a general rule, activation in NaOH renders similar results than KOH for a variety of carbon precursors [47,48,51].

Hence, the decrease in SSA generally observed at high impregnation ratios is due to the collapse of micropores due to weakness of pore walls after intensive dehydration for ZnCl_2 and H_3PO_4 and to an extensive gasification of pore walls for KOH or NaOH activation. Therefore, the differences in the activation mechanism of each activated agent drives to marked differences in the development of porosity when increasing the concentration of the chemical agent.

Fig. 3. Evolution of different sets of pore volume along activation with (a) zinc chloride at 500°C, (b) phosphoric acid at 450°C of olive stones either in monolith (filled symbols) or powder (open symbols) (Reprinted from [49], Copyright 2007, with permission from Elsevier); and with (c) KOH at 700°C of an anthracite (data redrawn from [50]). Symbols: V_{N_2} (circles); V_{CO_2} (triangles); V_{meso} (squares).

As a general trend, for a given impregnation ratio, an increase in the activation temperature leads to an increase in surface area due to the volatilization process, and to a decrease in the carbon yield. Such effect cannot be dissociated from the effect of the activation time (i.e., the time that the sample is maintained at the fixed activation temperature), as for a given activation temperature this should be long enough to allow the evolution of volatiles from the precursor in order to enable the pore development. However, too long activation times usually bring about the enlargement of the pores, causing a decrease in the SSA.

The combined effect of temperature and time for the activation of a lignocellulosic material (e.g., corncob) using $ZnCl_2$ at a constant impregnation ratio of 1 is shown in Fig. 4a [52]. In the temperature range studied (400–800°C), the SSA and the total pore volume increased with the pyrolysis temperature, reaching a maximum at about 500°C. Rising the temperature from 500 to 800°C resulted in a reduction in the SSA pore volume, likely due to a shrinkage of the carbon structure. The soaking time seems to play a less important role in the production of activated carbons (Fig. 4a); by increasing the soaking time from 0.5 to 1.0 hour, the SSA and pore volume of the samples increased; longer soaking times reduced both textural parameters, which is most likely attributed to the further gasification of the micropore walls [52]. For temperatures higher than 500°C, the carbon yield strongly decreases. Therefore in order to develop carbons with high SSA and V_{micro} with an acceptable carbon yield, by means of $ZnCl_2$ activation of a variety of precursors and carbonization conditions, a temperature of 500°C is recommended by several authors [53,54].

Fig. 4. Effect of selected activation conditions on the texture of the activated carbons. (a) Effect of temperature and time on the total pore volume (V_T) upon $ZnCl_2$ activation of corn cob at an impregnation ratio of 1 (data from [52]). Response surface (temperature and time) for (b) mesopore and (c) micropore volume upon H_3PO_4 activation of almond shell at an impregnation ratio of 1.1 (data from [55], Copyright 2011, with permission from Elsevier). (d) Effect of temperature and time on total (V_{DRN_2}) and narrow micropore volume (V_{DRCO_2}) upon KOH activation of an anthracite using an impregnation ratio of 2 (data from [50]). (e) Effect of the gas flow on V_{DRN_2} , V_{DRCO_2} and surface area (S_{BET}) upon KOH activation at 700 °C of an anthracite using an impregnation ratio of 2 (data from [50]).

Izquierdo et al. [55] applied a response surface to study the combined effect of activation temperature and time over the carbon porous texture characteristics when using H_3PO_4 as activating agent and a lignocellulosic precursor. The authors found optimal activation temperatures in the range 400-550°C and activation times between 85-120 min for obtaining carbons with high SSA. Fig. 4b,c depict the dependence of V_{micro} and mesopore volumes for an impregnation ratio of 1.1. The higher mesopore volume is obtained in similar range of activation temperature and time than that obtained for the higher values of SSA. However, maximum V_{micro} is obtained at higher activation temperatures in the same range of activation time. Thus, in order to obtain an activated carbon with high SSA the response surface methodology indicates a wide temperature range of 400-550 °C and an a wide activation time range between 90-120 min. However, for obtaining a microporous carbon, the range of temperature shifts to higher temperatures and the range of activation time becomes narrower (600-800 °C, 112-120 min). However in such conditions, the carbon yield is too

low.

In activation with alkali hydroxides, for temperatures below 700 °C the initial redox reactions between the hydroxide and the carbon (starting at 375-475 °C for NaOH and at 250-375 °C for KOH, depending on the structural order of the precursor) [45] drive to a gasification of the carbon producing gases as CO, CO₂ and H₂ and to a moderate development of porosity [56]. At temperatures above 700 °C, metallic potassium or sodium are produced and intercalate to the carbon matrix increasing the pore volume. Therefore temperatures lower than 700 °C are not adapted for obtaining carbons with well-developed SSAs when using alkali hydroxides as activation agents. For temperatures above 700 °C it has been reported that increasing the activation temperature results in higher SSAs and V_{micro} but also in a decrease in the carbon yield. Fig. 4 shows for the same impregnation ratio and time of pyrolysis, increasing activation temperature from 700 to 800 °C results in a chemically activated carbon with higher total V_{micro} (calculated from the N₂ adsorption data) [50]. Nevertheless, as in the case of the effect of the KOH/carbon ratio, the higher temperature of pyrolysis produce a wider micropore size distribution as differences between the V_{micro} calculated from CO₂ and N₂ adsorption became larger. Moreover, an activation temperature higher than 800 °C is not recommended when narrow micropore size distributions are desired. This is attributed to the additional gasification due to the CO₂ formed upon the decomposition of the alkaline carbonate, causing the widening of the pores and a decrease in the overall reaction yield [57].

Little attention has been paid to the flow rate of the gas used during the heat treatment process. Lozano-Castello et al. showed the great impact of the gas flow on the porosity development of an anthracite coal activated with KOH [50]. During the hydroxide-carbon reaction gases as CO, CO₂ and H₂ are evolved, hence an increase in the gas flow improves the system purge, shifting the reaction towards the products and influencing the porous texture of the ACs. Fig. 4 shows that changing the N₂ flow rate from 80 to 800 ml/min increases the microporosity development. Thereby, the V_{micro} and SSAs of the produced ACs are doubled; however, and interestingly, the micropore size distribution is not changed. It should be pointed out that the effect of the flow rate in the porous development using chemical activation is opposed to that of physical activation, as discussed above.

Regarding the nature of the inert gas, nitrogen, argon and helium have been studied as purging atmospheres, using similar flow rates [57]. The main observation is that the sample porosity development increases with the efficiency of these three gases to remove the reaction products (i.e., their molecular weight), following the order He < N₂ < Ar, which confirms their role as purging gases.

5.3. Novel Approaches for Control of Microporosity

Conventional activation methods for the synthesis of nanoporous carbons do not allow a precise control of the pore size and volume. Furthermore, the formation of pores is usually accompanied by significant mass loss (hence low overall yield) and high energy consumption. Thus, introducing a rational design and new approaches that allow to control the porosity at a nanometric scale has received much attention. In the following sections, we will summarize most relevant methodologies to control the porosity in the synthesis of carbons, emphasizing on the generation of microporous carbons.

5.3. 1 Hydrothermal Carbonization

Just like natural renewable resources and sustainable chemical agents seem to be the key for the production environment-friendly nanoporous carbons with high SSA and controlled properties, alternative carbonization approaches are explored for lower energy consumption in the preparation of nanoporous carbons. A hydrothermal carbonization (HTC) is a thermochemical process in subcritical water for the conversion of wet/dry biomass to carbon materials. Typically, the yield of the solid fraction in HTC is higher than in hydrothermal gasification (e.g., above the supercritical temperature, with the gas fraction as primary product) and ‘hydrothermal liquefaction’ (e.g., close to 400 °C, with the predominant production of liquid hydrocarbons). Thus, it has proven to be a powerful technique for the synthesis of carbons from biomass. The first studies reporting the hydrothermal transformation of biomass sources into coal-like materials were reported long ago, but the interest for the use of this technique as a simple method to obtain carbon materials (hydrochars) at mild conditions has growth much just in the last 20 years [58,59].

During hydrothermal carbonization, water acts as a solvent and a catalyst, facilitating hydrolysis reactions and accelerating the decomposition of the biomass oligomers and monomers in smaller fragments, leading to the formation of a carbonaceous solid [60]. The choice of the hydrothermal carbonization conditions (temperature, residence time, pressure and so forth) depends on the nature of the precursor and its thermal stability [61-63]. As a general rule, increasing the temperature and pressure of the hydrothermal conditions results in an increase in the conversion of the biomass feedstock into carbon particles. Both high-temperature and low-temperature HTC processes can be applied for the preparation of carbon materials. The first one, typically between 300-800 °C is beyond the stability of biomass components and other natural or organic precursors, and it

has been mainly described for the synthesis of carbon filaments and graphitic carbons [64]. The low-temperature HTC process performs below 300 °C, and is commonly used for the preparation of hydrochars and activated carbon derivatives, either based on direct solid conversion of biomass feedstocks [65] or the polymerization of the monomers generated upon the decomposition of biomass (carbohydrates/cellulose) [66].

The effect of the various operating parameters of HTC on the quality and yield of the products (solid char, liquid and gas) has been extensively investigated [61,62,67]. It would seem that once the composition of the precursor is known, the hydrothermal conditions could be adapted in order to obtain carbon materials with optimized features.

Most hydrochars obtained from HTC using water as dispersion medium display poor textural parameters (e.g., SSAs seldom exceeding ca. 50 m²/g). A few examples are shown in Table 1. High surface areas hydrochars can be prepared by adjusting the salinity of the solution, as this modifies the cross-linking and growth of the primary carbon particles formed during the hydrothermal carbonization process. As an example, Fechner et al. [68] reported hydrochars with SSAs of 673 m²/g from the HTC of glucose under hypersaline conditions (Table 1). The nature of the salt system was found to be important, with high surface areas obtained for hygroscopic salt ions or eutectic salt melts (e.g., ZnCl₂, LiCl, NaCl, KCl). Iron nanoparticles have also been used to accelerate the dehydration, condensation and carbonization reactions occurring during HTC, thereby increasing the SSA of the resulting hydrochars [69].

Post-synthesis activation of the hydrochars is another alternative for producing activated carbons with high SSAs. In this regard, the reactivity of precursor and the oxygen content in the hydrochar are important indicators to predict the extent to which porosity will be developed in further chemical activation processes [61,82]. Various authors have reported the production of high surface area activated carbons (ca. up to 3362 m²/g) upon chemical and physical activation of hydrochars prepared from various precursors (e.g., furfural, glucose, rice husks, starch, cellulose, eucalyptus sawdust). A summary of the porous features of selected hydrochars-derived activated carbons is presented in Table 1. In general, the yields of physical and chemical activation of hydrochars are similar, although the latter activated carbons display higher porous features [76,80]. The temperature of the HTC step has a strong impact on the porosity of the activated carbons after post-synthesis activation. When the HTC is carried out from 180 to 240 °C, the higher density of carbonyl moieties and the low degree of aromatization, favor the development of porosity after KOH activation [82]. Raising the temperature of the HTC process up to 280 °C en-

hances the chemical stability and structural order of the hydrochars, thus activated carbons with lower porosity upon KOH activation are obtained.

Table 1. Specific surface areas of hydrochars and activated hydrochars obtained from different starting raw materials and activation conditions. Reprinted from [61], Copyright 2016, with permission from Elsevier.

Precursor	Synthesis parameters	S_{BET} [m ² /g]	Reference
Orange peels	Citric acid catalyst	0.2	[70]
Orange peels	CO ₂ activation	618	[71]
Oak Leaf	Citric acid catalyst	15.5	[70]
Pine cone	Citric acid catalyst	34	[70]
Glucose	LiCl/ZnCl ₂	673	[68]
Glucose	NaCl/ZnCl ₂	546	[68]
Glucose	KCl/ZnCl ₂	425	[68]
Glucose	NaCl	Not detected	[68]
Glucose	ZnCl ₂	477	[68]
Glucose	ZnCl ₂	small	[68]
Glucose	Borax	233	[72]
Glucose	Borax	427	[73]
Starch	Fe (NH ₄) ₂ (SO ₄) ₂	113	[69]
Starch	Fe ₂ O ₃	402	[69]
Hazelnut shell	--	45	[74]
Hazelnut shell	KOH activation	1700	[75]
Glucose	NaOH activation	2120	[76]
Glucose	KOH activation	3152	[76]
Sucrose	H ₃ PO ₄ activation	2120	[76]
Sucrose	CO ₂ activation	2555	[76]
Rice Husk	HTC at 200 and 300 °C	14-25	[77]
Rice Husk	KOH activation	3362	[78]
Rice Husk	H ₃ PO ₄ activation	1498	[79]
Rice Husk	CO ₂ activation	446	[80]
Coconut Shell	ZnCl ₂ activation	1421	[81]
Coconut Shell	ZnCl ₂ activation	1775	[81]
Coconut Shell	ZnCl ₂ activation	1530	[81]

The structural order of the carbon precursor it is also important [83]; as observed for the KOH activation of coals, a low porous development is ob-

tained upon activation of hydrochars with high degree of aromatization and structural order [82].

Less corrosive alternatives to KOH activation have proven to yield highly microporous materials when hydrochars are used as precursors, with textural properties matching those of optimized KOH-ACs. Activation using K_2CO_3 resulted in better yields than KOH, and in the retention morphology of the hydrochar [84]. Microporous materials with SSAs of ca. $3000\text{ m}^2/\text{g}$ have also been obtained upon activation of hydrochars with $KHCO_3$ and a mixture of potassium oxalate and melamine [85,86]. The materials also presented higher packing densities than superactivated carbons prepared upon KOH activation, due to a narrow distribution of micropores.

The incorporation of a catalyst (acid, oxidant, metallic salt) during the hydrothermal carbonization process also enhances the development of the pore structure in the subsequent activation step, due to the impact in the formation of hydrochars with higher content in oxygen groups. The resulting hydrochars display more efficient features for their use as precursor in a subsequent chemical activation step [61,69,81]. For instance, the hydrothermal carbonization of coconut shell in the presence of H_2O_2 and $ZnCl_2$ led to the preparation of hydrochars with SSA of about $1753\text{--}2440\text{ m}^2/\text{g}$, with a large fraction of mesopores [81]. It was attributed to the better dehydration of the biomass by $ZnCl_2$ at hydrothermal conditions.

5.3.2 Nanocasting techniques

Nanocasting techniques are classified into two categories depending on the template used: endo- and exo-templating routes, also called soft- and hard-templating, respectively. The concept soft-templating refers to the preparation of porous material using an organic template (e.g., surfactants) that is self-assembled in a solvent in the presence of a polymerizable carbon precursor. The carbon material is obtained after a carbonization process, where the template is either consumed becoming a carbon precursor or sacrificed generating the final porous carbon [87]. It has been mainly used for obtaining mesoporous carbons through the self-assembly of block copolymers and precursors such as phenolic resins or resorcinol. The exo-templating approach consists on using a porous solid as sacrificial scaffold, so that the porous material obtained is an inverse replica of the template used. Zeolites of varied topology, mesoporous silica/oxides and opals or colloidal silica templates have been used as scaffolds to obtain micro-, meso- and macroporous materials, respectively [88].

5.3.2.1 Hard-templating

Hard-template techniques consist in the use of an appropriate porous material as sacrificial scaffold to replicate its porosity and structure through the

infiltration of a carbon precursor followed by carbonization of the composite and removal of the template. The obtained carbon is a negative replica of the template, meaning that the carbon skeletal structure is related to the pores of the template, while the porosity of the carbon is related to the walls of the template after the chemical etching. Even though hard-templating has marked a milestone in controlling the pore structure of carbons, the process is quite challenging and complex, and still has to face a great disadvantage for scaling up applications due to the need to remove the template.

Pioneering research studies on preparing microporous carbons via nanocasting methods were performed by Kyotani and co-workers using zeolites and layered clay minerals as templates [89,90] and resulted to be particularly suitable for the synthesis of carbons with a desired structure of micropores of uniform sizes and shape. These materials are commonly referred to as zeolite templated carbons (ZTC), and due to the well-defined three-dimensional structure of most zeolites, very often present a periodic arrangement of micropores in the range of 1–2 nm (Fig. 5) [90–94].

Unlike the preparation of mesoporous carbons, the nanocasting technique for the synthesis of microporous carbons with a uniform pore structure has important limitations, typically related to the infiltration of the carbon precursor within the narrow channels of the zeolites, or the restricted polymerization in small pores that bring about a low carbon yields, and ultimately provokes the collapse of the carbon after the etching off the template [91].

The topology of the zeolite is important as it defines the size of the cavities and their connectivity; both parameters are critical to assure an efficient impregnation of the cavities to form robust carbon replica that retains the ordered structure of the zeolite after the removal of the scaffold. To obtain microporous carbons with high structural regularity, the pores in the zeolite template should be sufficiently large ($> 0.6\text{--}0.7$ nm) and three-dimensionally interconnected. As an example, zeolites Y (X), b, L, EMT and mordenite have been successfully used for this purpose. Whereas zeolites EMT and Y render porous ZTC with a high structural regularity, zeolites L and mordenite produce randomly oriented (non-porous in the case of zeolite L) carbons with no periodic order after dissolution of the template. This is due to the disconnected 1D or 2D pore system of the zeolite template [92,96,97].

The acidity of the zeolite also plays a role, as it affects the formation of the carbon layer when the infiltration is made by chemical vapor deposition (CVD), as the catalytic decomposition of a hydrocarbon gas is catalyzed by the acidic sites of the zeolite pores, avoiding the deposit of pyrolyzed carbon outside the zeolite particles. Thus, zeolites with poor acidic activity

(such as silicalite-1) are not recommended as scaffolds. Similarly, zeolites with Si/Al ratio below 20 are preferred as they display higher acidity and greater heat stability [91,98].

Regarding the carbon precursor, CVD of small hydrocarbon gases, polymer carbonization of organic monomers, and the combination of both have been mainly explored. The polymer carbonization consists in loading an organic monomer (e.g., furfuryl alcohol, acrylonitrile) inside the zeolite pores, and then polymerize and carbonize. Although the method allows uniform carbon coverage of the pores, the obtained carbon replica usually do not present very high SSAs nor retains the ordered structure of the zeolite. This is due to the large fraction of volatiles decomposed ruining the carbonization of the polymerized monomer. On the other hand, the CVD method allows the incorporation of larger amounts of carbon inside the pores of the zeolites, thus the carbons usually present a robust and ordered structure. Different hydrocarbons have been explored (acetylene, propylene, benzene) to obtain pure and doped ZTC. Better results in terms of higher surface area and micropores have been reported for acetylene due to its small size [97,99]. It is also important to maintain the temperature of the CVD process lower than the temperature of the self-decomposition of the hydrocarbon, to avoid carbon deposition outside the zeolite particles. Other factors such as the concentration of the hydrocarbon feedstock and a thermal annealing of the zeolite/carbon composite before the removal of the template also allow obtaining carbons with high surface areas and an ordered structure.

The two-step method combines the advantages of both of them, allowing the uniform carbon deposition of the polymer carbonization and the formation of a robust carbon framework with an ordered structure and high SSA of the CVD method [17,90,92,100]. As a result, ZTC with extremely high SSAs between 3600- 4100 m²/g, and micropore volumes of up to 1.5 cm³/g without detectable mesopores have been reported after an annealing treatment at high temperature before removing the template (Fig. 5) [90,93].

Although the SSA of some KOH activated carbons is over 3000 m²/g, these carbons always suffer from the presence of some mesoporosity and have a broad pore distribution. Furthermore, ZTC prepared by a two-step method can also present high mechanical stability upon compaction, which is a desirable feature for gas storage applications [17].

Sample	Synthesis parameters	S_{BET} [m ² /g]	V_{micro} [cm ³ /g]	V_{meso} [cm ³ /g]
b-P8(2)	Zeolite b, propylene CVD 800 °C, 2 h	1970	0.8	0.4
b-P8(4)	Zeolite b, propylene CVD 800 °C, 4 h	2050	0.9	0.4
b-PFA-P7(4)	Zeolite b, PFA carbonization, propylene CVD 700 °C, 4 h	1420	0.6	0.5
b-PFA-P8(2)	Zeolite b, PFA carbonization, propylene CVD 800 °C, 2 h	1640	0.6	0.5
b-PFA-P8(4)	Zeolite b, PFA carbonization, propylene CVD 800 °C, 4 h	1400	0.5	0.4
b-PFA-P7(4)-H	Zeolite b, PFA carbonization, propylene CVD 700 °C, 2 h	1270	0.8	0.4
b-PFA-P8(2)-H	Zeolite b, PFA carbonization, propylene CVD 800 °C, 2 h, heat treatment at 900 °C	2010	0.8	0.5
ZSM5-P8(4)	Zeolite ZSM-5, PFA carbonization, propylene CVD 800 °C, 4 h	110	0.0	0.1
M-P8(2)	Zeolite Mordenite, PFA carbonization, propylene CVD 800 °C, 2 h	180	0.1	0.3
L-P7(4)	Zeolite L, PFA carbonization, propylene CVD 700 °C, 2 h	570	0.2	0.4
L-P8(2)	Zeolite L, PFA carbonization, propylene CVD 800 °C, 2 h	360	0.1	0.6
d Y-PFA-P7(4)-H	Zeolite Y, PFA carbonization, propylene CVD 700 °C, 4 h, heat treatment at 900 °C	2750	1.5	0.0

Fig. 5. (scheme) Synthesis procedure of the ZTC. (a) Crystal structure of the zeolite Y template, (b) illustration of zeolite/carbon composite. Impregnated carbon is shown by a black framework and (c) framework structure of the liberated ZTC after HF washing. Reprinted from [95], Copyright 2009, with permission from Elsevier. (table) Selected textural parameters of ZTC prepared from various zeolites. Adapted from [96], Copyright 2003, with permission from Elsevier.

Besides zeolites, the research has been extended to a wide variety of hard templates such as multilayered clays, colloid crystals, mesoporous silica and several MOFs [101-103]. As an example, highly microporous carbons

with large pore volumes (ca. $2.06 \text{ cm}^3/\text{g}$) and SSA of up to $2872 \text{ m}^2/\text{g}$ have been obtained using various MOFs as templates (Liu 2008). The MOFs have a dual role providing the metal and carbon sources and acting as the sacrificial template [104]. Yang et al. [102] reported the synthesis of ultra-microporous MOF-derived carbons with hierarchical pore structures and high SSAs and total pore volumes. Due to the exceptional porosity, they exhibited better reversible H_2 storage capacity than those previously reported for other carbons and MOFs.

5.3.2.2 Soft templating

Soft-templating approaches are based on the formation of supramolecular arrangements of precursor molecules (e.g., carbon precursor) with a template (e.g., surfactants), stabilization of the carbon matrix by polymerization and the removal of the template. The microphase separation induced by the usually well-ordered phases of the templates is responsible for the ultimate structure of the resulting materials. One of the advantages of this approach is that the template is either destroyed or consumed as carbon precursor during the carbonization process, avoiding the need of a chemical etching off. However the scaling-up is still economically and environmentally questionable, due to the synthetic origin of most of the templates. The interest of soft-templating approaches has been mostly directed towards the preparation of carbon materials with hierarchical meso- and macroporosity [87] but it can also be extended to microporous carbons with high pore volumes and/or molecular sieving effects (thus of interest for gas storage applications) (Fig. 6). In this regard, the preparation of carbon materials with pores of different sizes is intimately related to the nature of the template. For instance, polyethylene oxide (PEO) blocks in block copolymeric surfactants tend to produce microporosity, ionic surfactants produce micropores and small mesopores (2-4 nm), whereas non-ionic surfactants (e.g., Brij and Pluronics) generate mesopores of up to 10 nm [105]. The morphology of the carbon materials can also be modulated by adjusting the concentration of the surfactant or block copolymer, the pH of the solution or the temperature of the reaction [106].

Precursor molecules typically employed in the resin formation that precedes the synthesis of soft-templated carbons are hydroxylated aromatic molecules (e.g., phenol, resorcinol, phloroglucinol, resol) or functionalized compounds (e.g., melamine, pyrrol) if doped-carbons are targeted. The chemical cross-linking of these molecules is often carried out in the presence of an aldehyde (formaldehyde, glyoxal) acting as a linker, to form the oligomer that co-assemble with the template micelles. The chemical composition of the polymeric carbon precursor controls the interaction strength with the template polymer, and thus the degree of cross-linking that will

define the porosity of the soft-templated carbon.

Fig. 6. (a) Schematic illustration of the soft-templating synthesis of porous carbons with a hierarchical macro-, meso-, and microporous structure. (b) N_2 adsorption isotherms at -196 °C and cumulative pore volumes of selected carbons, where the solid and broken lines represent the results from the CO_2 (0 °C) and N_2 (-196 °C) adsorption isotherms, respectively. Reprinted from [107], Copyright 2016, American Chemical Society.

For instance, Liang et al. reported that phloroglucinol interacts more strongly than phenol-formaldehyde or resorcinol-formaldehyde complexes with Pluronic templates due to the formation of triple hydrogen bonds. As a result, soft-templated carbons prepared with phloroglucinol possessed a highly ordered 2-D hexagonal system, whereas those prepared using resorcinol and phenol rendered in poorly structured microporous carbons [108]. Since soft-templating routes are most often used for the preparation of mesoporous carbons, post-synthetic activation has been much explored to obtain microporous carbons [109-111]. In this regard, it is important to

consider the stability of the material before the thermal activation. The pH conditions for polymerization of the carbon precursors and self-assembly strongly influence the thickness of the pore walls of the template carbon, which is determinant for its structural stability during the activation, particularly when using harsh activating agents such as KOH [112]. As a general rule, carbons synthesized under acidic conditions are more resistant to post-activation steps [109] than those obtained by using a basic synthesis route [109,110,113]. Another alternative for creating microporosity in mesoporous carbons involves the incorporation of TEOS during the soft-templating synthesis [114]; the dissolution of the silica precursor homogeneously distributed in the composite materials leads to the creation of micropores in the mesopore walls.

5.3.3. Sol-Gel Approaches

Sol-gel techniques are bottom-up approaches that enable a precise control over the synthesis parameters, and thus over the final characteristics of the porous material. In 1989, Pekala et al. [115] reported the preparation of organic sol-gel based materials through the polycondensation of resorcinol-formaldehyde (RF) mixtures in the presence of acid or base catalysts in aqueous media. The resulting materials contain abundant oxygen functionalities and thus are commonly referred to as organic gels or resins. A final carbonization step would convert them into carbon gels (Fig. 7).

The sol-gel process starts with the polymerization and condensation of the precursors (typically R and F), initially through an addition reaction to form hydroxymethyl derivatives that subsequently condensate to form methylene and methylene ether bridged-compound. When the reaction starts, polymer chains grow into aggregated clusters of a few nanometers in diameter; the cross-linking of these colloidal particles lead to the stiffening of an organic gel with an interconnected structure. To prepare the polymerization of the reactants, these are mixed with the catalyst and the solvent, stirred for form a homogenous mixture and allowed to gelate and polymerize at moderate temperatures in sealed vessels to minimize the solvent evaporation. Dynamic viscosity measurements have shown that the initial cluster formation and particle growth takes about 1 h [116], at this stage, the mixture constitutes a colloidal solution of clusters of monomeric particles. This general mechanism depends on the solution pH, the components molar ratios and the temperature, among others [117]. The next stage is the covalent crosslinking of the clusters until they become unstable and undergo spinodal decomposition leading to the solidification of the gel. The sol-gel polycondensation of R-F mixtures in the presence of a catalyst is endothermic, and then heating is required to provide the necessary energy for this reaction. The typical temperature for this reaction in aqueous

medium is ca. 80 °C [117], although it may be decreased when longer gelation times [118] or alternative solvents to water are used [119]. The curing step is also important since it allows the polymeric clusters to crosslinking and form the final shape of the gel. This is usually carried out at 80-90 °C for about a week to prevent the swelling during the drying stage [117,120].

Fig. 7. Steps and principles of the sol-gel approach for the preparation of nanoporous carbons.

After the pioneering work of Pekala [115] much of the effort has focused on how different synthetic parameters affect the final organic gels and carbons, optimizing the porosity within the full nanometric scale. The nature of the catalyst and its concentration also affect the porosity of the carbon gel. The most widely used catalyst is Na₂CO₃; as a general trend, low R/C molar ratio favor the formation of predominantly microporous carbon gels with low SSAs and poor mechanical properties. In contrast, for high R/C ratios, the resulting gels possess larger surface areas, a predominantly mesoporous structure and good mechanical strength [117,121].

The pH of the initial solution also plays an important role on the properties of the final gel. Job et al reported that it is possible to tailor the morphology and porosity of carbon gels by varying the initial pH of the precursor solution. Resorcinol–formaldehyde gels prepared using a constant molar ratio of reactants and adjusting the pH. On average, increasing the pH decreased the pore size. Furthermore, the carbon gels were macroporous at pH between 2-4, micro–macroporous at pH 5.00–5.45, micro–mesoporous at pH 5.80–6.50, and quasi non-porous carbons at pH 7.35 [122]. Rasines et al. [123] observed that both the pH and a prepolymerization step were determinant for the preparation of carbon aerogels using melamine (M) as precursor. Attempts of preparing mechanically stable hydrogels at solution pH below 6 failed, regardless the M/R ratio used. Aerogels prepared at pH 8 and M/R = 0.5 ratio displayed low SSAs determined by N₂ at -196 °C (ca. 70-90 m²/g), but the analysis of the textural features by means of CO₂ adsorption isotherms at 0 °C revealed the presence of a non-negligible narrow microporosity. This was attributed to the low cross-linking degree of the monomers at high pH values, yielding hydrogels that do not stand the supercritical drying and carbonization steps. The formation of the mi-

porosity was favored at higher M/R ratio, with samples showing 700 m²/g and the micropores accounting for ca. 90 % of total pore volume [123].

The molar ratio of the monomers defines the micro- to mesopore ratio. Usually, microporous gels are obtained at low R/C ratios; an increase in the R/C and R/W molar ratios provoke an enlargement of the mesopores, with a small impact on the microporosity [124,125]. The temperature of the gelation/aging step mainly affects the mesopore network, whereas the microporosity is determined by the composition of the precursor's mixture [126].

The drying procedure of the organic gel defines the mechanical properties of the final carbon gel. Subcritical (solvent evaporation at atmospheric conditions), supercritical (the solvent is replaced by a fluid that is later removed at supercritical conditions) or freeze (the solvent is frozen and removed by sublimation) drying are most commonly used methods, giving rise to xerogel, aerogels or cryogels, respectively.

Subcritical drying is economically advantageous but produces carbon gels with rather low microporous structure, compared to supercritical drying. This is due to the surface tensions during the removal of the solvent. In contrast, supercritical drying minimizes the surface tensions and shrinkage giving rise to materials with higher pore volumes, although the pore size cannot be easily controlled [117,120,127,128].

Carbonization of the organic gels under an inert atmosphere provokes the removal of the volatiles and the densification of the carbon gel. The carbonization of xerogels typically provokes a partial collapse of the mesoporosity, but it favors the formation of a microporous structure. This effect is generally more remarkable in gels prepared using low R/C ratio [117].

The carbonized gels can be further activated to enhance the porosity, in a similar pathway as that of any other carbon precursor. Carbon gels with SSA of 1800-1900 m²/g and micropore volumes of 0.6-0.7 cm³/g, with no contributions of mesopores have been reported by activation using KOH at 800 °C (Fig. 8) [130]. Furthermore, chemical activation using wet-impregnation techniques can avoid the destruction of the mesoporosity, while increasing the SSA and micropore volumes [130].

Other monomers have been used as alternative precursors to resorcinol, including catechol, hydroquinone, phloroglucinol, phenol and other substituted phenolic rings, as well as heteroatom-containing monomers (e.g., urea, melamine, 3-hydroxypyridine) for the preparation of doped-carbons [87,123,124]. The differences in the polycondensation reaction kinetics of these molecules define the features of the carbon gels. In this regard, phloroglucinol, being a more reactive molecule towards polycondensation reactions than resorcinol promotes the formation of highly crosslinked

polymers with a microporous structure. On the other hand, the presence of only one hydroxyl group in phenol makes its reactivity slower in compare to both phloroglucinol and resorcinol [87].

Fig. 8. N₂ adsorption isotherms at -196 °C of carbon gels prepared by (a) photoassisted polycondensation of various organic molecules (reprinted from [129], Copyright 2017, with permission from Elsevier 2017) and (b) melamine-resorcinol-formaldehyde mixtures using a pre-polymerization step (reprinted from [123], Copyright 2015, with permission from Elsevier 2015); (c) Correlation between the main textural parameters (SSA, micropore and mesopore volumes) of activated xerogels as a function of activation temperature with (a) potassium carbonate and (b) potassium hydroxide for wet and powder impregnation. Reprinted from [130], with kind permission from Springer Science+Business Media Copyright 2017.

Low cost precursors (e.g., biomass, furfuryl alcohol) have also been explored as an economic alternative to the RF sol-gel process [128]. Antonietti and coworkers reported that the general principles of sol-gel chemistry can be transferred to a sustainable preparation of carbon materials following a hydrothermal approach of low cost and available precursors such as carbohydrates, saccharides or biowastes [131,132].

Sol-gel routes carried out under controlled illumination conditions offer several advantages for the preparation of nanoporous carbons. The first one is much shorter time scale, since the aging time needed to induce the cross-linking of the polymeric precursor is significantly reduced due to the energy provided by light [129]. Other advantages are the versatility of organic precursors; by changing the chemistry of the organic precursor, carbons of varied morphology and with SSAs ranging between 10 to 720 m²/g and showing molecular sieving effects have been prepared. The degree of cross-linking, and thus the porosity of the final carbons is defined by the structure and the number of reactive positions in the organic precursor. Linear dihydroxylated precursors formed dense porous carbon matrices mainly composed of narrow micropores, whereas trihydroxylated molecules assembled in large cross-linked clusters combining micro- and mesopores [129].

Another advantage of sol-gel routes is that they enable to produce carbon materials in the form of a monolith, which offers important advantages compared to powder or pellets (e.g., better diffusion and mass transfer rates of fluids, resistance to compression). Carbon monoliths are mostly hierarchical porous carbons, since their porosity is composed of interconnected pore networks of different sizes [133,134]. Del Monte et al. have reported the synthesis of hierarchical carbon monoliths through a synthetic route based on using deep eutectic solvents (DES) composed of a phenol derivative as H-bond donor and an ammonium salt as H-bond acceptor as low cost and sustainable precursors [22,135,136]. Depending on the initial DES composition, the pore structure and chemical composition of the carbon monoliths can be modified. For instance, 4-hexylresorcinol favors the formation of hierarchical microporous carbon monoliths with enhanced molecular sieve features, while the presence of urea favors the formation of large mesopores [22,135].

5.3.4 Self-activation

Self-activation is the name that is generally given to a single-step pyrolysis of a carbon precursor resulting in porosity development without adding any activating agent. In this sense, self-activation of polymer based precursors or biomass carbons have been reported if an alkali-rich precursor is

carbonized under an inert gas flow or if the own gas products of the pyrolysis of the precursor are used as activating agents. For some particular precursors, the method is very efficient for producing highly microporous carbons for being used as gas adsorbents.

The carbonization of organic salts has recently considering a facile synthesis strategy towards the preparation of highly microporous carbons using more sustainable approaches compared to chemical activation with harsh KOH. Highly porous carbons with different textural properties have been obtained by direct carbonization of organic polymers and their salts (i.e., gluconates, alginates, citrates, sulfonates, maleic acid) as precursors. These compounds combine a carbon precursor (i.e., the organic moiety) and certain elements that during the heat-treatment generate species capable of operating as activating agents. Sevilla et al. [137] reported the preparation of nanoporous carbons with SSAs ranging between 650-1960 m²/g and pore volumes of up to 2.6 cm³/g. The pore characteristics of the synthesized carbons can be modulated by selecting the appropriate organic salt, enabling the preparation of carbons which porosity would be exclusively made of micropores or mesopores. The high diapason of the inorganic elements acting as activating agents (e.g., Ca, K, Na) allowed to have high SSAs despite the low inorganic species content [137,138]. The pore characteristics were tuned from a microporous to a mesoporous carbon by simply choosing the appropriate organic salt. For instance, the alkali K and Na salts favored the development of micropores, as it is well-known for other alkali-based activating agents, while calcium compounds gave rise to mesopores.

Following the same principle, Nakagawa et al. [139] and Bando et al. [140,141] reported dynamic carbonization templating of a metal-loaded organic polymer (e.g., polystyrene sulfonic acid co-maleic acid derived salts or polystyrene sulfonic acid co-divinylbenzene derived salts), giving rise to polymer-derived carbons with a predominantly microporous structure due to the expansion of the matrix during carbonization in the presence of the metals undergoing reduction and oxidation reactions. The porosity of the material was deepening on the nature of the cation exchanged, with Na and Ni favoring the formation of microporous carbons, and Cu, Fe and Co mesoporous materials.

The direct pyrolysis of biomass materials containing naturally embedded alkaline or alkali earth elements at a molecular level (e.g., carbohydrates), has recently been demonstrated as a promising route to produce high surface area carbon without introducing extra activation agents. In particular, it has been shown that the pyrolysis of seaweeds rich in carrageenan (a potassium-rich biopolymer) or in sodium alginate results in carbon materials with high SSAs [142]. Due to the presence of Na or K polymers, which

play the same role as additives in chemical-activation processes, porosity can be developed without an additional activation step. A pyrolysis at temperature between 600-900°C drives to carbon materials with SSAs up to 1400 m²/g. It has been also reported that one-step carbonization of other biomass materials including dead leaves [143], amaranthus waste [144], eggplant [145] or chicken eggshell membranes [146] can produce porous carbons with SSAs over 1000 m²/g.

Recently, Zhang et al. [147] reported the importance of physiologic function of plant organs in the microstructure and porosity of formed carbon nanomaterials from one step pyrolysis of biomass. A disparity on porosity generation when pyrolyzing stems or leaves from lotus, asparagus lettuce or celery has been shown. As an example, the lotus stem pyrolyzed carbon at 800°C presents a SSA of 1610 m²/g, about 55% higher than the porous carbon from the leaves. Such results indicate that not only the alkali rich polymer salts included in the biomass composition act as activating agents but also the inorganic salts contained in the plant have an important role. The higher metal ion content in the stems, which plays the role of ion transportation for plants, would be on the origin of the extra porosity. Also, it has been shown that celery stem pyrolysis renders carbons with SSAs as high as 2194 m²/g without any extra activation process.

Self-activation of some polymers or biomass can be also performed by using the pyrolysis gases to prepare microporous activated carbons without any physical or chemical agent. Bommier et al. [148] synthesized high surface-area nanoporous carbon from cellulose by using a very low Ar flow for increasing the residence time of evolving gases (e.g H₂O, CO₂) in the reaction chamber. As a result, in-situ activation reactions between the resulting carbon and the gases that are evolved during pyrolysis of cellulose are allowed to take place over a wide range of temperatures. A linear relationship was obtained between the flow rate of Argon during the reaction and several key properties of the nanoporous carbons, including SSA, pore volume and short-range degree order. For a pyrolysis temperature of 1100°C using a low flow rate of 10 mL/min, a SSA as high as 2600 m²/g and a pore volume of 2.1 cm³/g were obtained, as opposed to 98 m²/g and 0.06 cm³/g when a high flow rate of 200 mL/min was used.

Jeong et al. [149] also reported the synthesis of lignin-derived microporous carbons through direct carbonization in a tight closed reactor previously purged with Ar. The high amount of oxygen present in the lignin extracts (e.g., between 21-29 wt.%) is in the origin of a large amount of oxygen containing gases during carbonization. It has been observed that the molecular weight of the lignin precursor plays an important role, where low-molecular-weight lignin precursors produce less defective and high SSA carbons. The highest surface area development was obtained when using

Kraft lignin as precursor with a value of $1092 \text{ m}^2/\text{g}$.

Self-activation has been also reported when biomass is pyrolyzed in a closed reactor in the presence of air. In such a case, air and moisture in the furnace are the responsible of the self-activation process of the materials. The oxygen may react with biomass-converted carbon to form CO_2 and together to the moisture and carbon dioxide in the air may serve as activating agents, under an auto generated pressure, to directly to activate the converted carbon.

The effect of the precursor and the pyrolysis conditions on the texture of the activated carbons when pyrolysis is carried out in a closed reactor without inert gas flowing has been described by Xia and Shi [150]. Regarding the precursor, the SSA reported for different biomass pyrolyzed at 1100°C for 2 hours were: kenaf bast fibre $1280 \text{ m}^2/\text{g}$; kenaf core $1148 \text{ m}^2/\text{g}$, sugarcane bagasse $910 \text{ m}^2/\text{g}$, sugarcane leaf $591 \text{ m}^2/\text{g}$, coconut fibre $1413 \text{ m}^2/\text{g}$, peanut shell $722 \text{ m}^2/\text{g}$, and sawdust $1199 \text{ m}^2/\text{g}$. The pyrolysis yield, the SSA, the pore volume and the pore size distribution will depend on the pyrolysis temperature and the dwelling time as shown in Fig. 9 for the particular example of kenaf fibers as feedstock.

Fig. 9. Pyrolysis of Kenaf fibers in a closed reactor. (a) Temperature-dependent yield (pyrolysis time: 10 hours); (b) Temperature-dependent surface area and pore volumes (pyrolysis time: 10 hours); (c) Dwelling time-dependent surface area and pore volumes (pyrolysis temperature: 1000°C) (reproduced from [150] by permission of The Royal Society of Chemistry).

As the activation is produced by the reaction of CO_2 and H_2O gas with the char, the development of porosity as a function of the temperature and the time follows the same tendencies than those shown in section 2 for physical activation of lignocellulosic materials.

Sun et al. [151] selected other biomass feedstocks as coconut shell, almond stone, walnut shell and slash pine sawdust to verify the effectiveness of the self-activation with pyrolysis gases in a non-purged reactor for generating microporous carbons. The carbons prepared at temperatures ranging be-

tween 800-1000 °C presented SSAs from 700 to 1150 m²/g and pore volumes up to 0.61 cm³/g with around 80% micropores.

5.3.5 Carbon molecular sieves

Carbon molecular sieves (CMS) are carbonaceous materials with a narrow pore size distribution, with pores having several angstroms in diameter. Such unique pore structure of CMS can discriminate molecules on the basis of size, shape or on a difference in adsorption equilibrium or, even, in adsorption rate. Thus, microporous CMS require the presence of a specific porous network containing pore mouths of molecular dimensions, together with a relatively high micropore volume. These features will confer them with a high adsorption capacity and selectivity into a given application. Hence, a proper molecular sieve must exhibit high adsorption capacity and fast adsorption kinetics of certain components of a gas mixture which leads to high selectivity [152,153].

Although some porous carbon obtained by standard processes as carbonization and activation can present molecular sieve properties by carefully selecting the precursors and conditions [154,155], numerous procedures for specifically preparing CMS have been proposed. There are three major approaches to prepare CMS (Fig. 10): i) the modification of existing porosity of a suitable porous carbon, mainly by CVD; ii) the synthesis of CMS by the one-step pyrolysis of a carbon precursor, and iii) the pyrolysis of polymer blends. The last two approaches are related to the direct pyrolysis of polymers or polymer blends, thus could be considered as self-activation methods. However, as they have been identified in the literature as procedures for specifically designing CMS, they will be described in the present section. Some other methods reported for preparing CMS, such as the pyrolysis of ion exchange resins containing different types of cations, have been already described in section 3.4.

The most extended method for modifying the existent porosity of a porous carbon is CVD, which is based on the deposition of pyrolytic carbon at the mouth of the pores to reduce the pore entrance. This method is particularly effective if performed over microporous carbons [156,157]. CMS can be prepared from a wide variety of porous carbons e.g. lignocellulosic biomass [158], coal [159] or porous activated carbon fibres [156,160]. However, CVD conditions as temperature, duration of deposition, vapour flow rate and composition must be accurately optimized for avoiding the excess of carbon deposition driving to a complete pore blocking.

Although pyrolytic carbon or pyrocarbon can be obtained from thermal decomposition of a number of volatile unsaturated hydrocarbons as benzene [156,157], methylpentane [161] or methane [160], considerable attention has been paid to benzene, as it does not generate intermediate com-

pounds during the cracking process, making the deposition process controllable.

It has been reported that the deposition mechanism of carbon from benzene depends mainly on the temperature. At temperatures up to 700 °C, the benzene diffusion through the pores is faster than reaction, there are no diffusion limitations and carbon will deposit uniformly over the entire pore surface, reducing the pore size but also the pore volume. At temperatures in the range 700-800°C, reaction is faster than diffusion and there will be strong pore diffusion limitations, thus the reactant will not reach the interior pore surfaces and carbon deposition will occur mainly at the pore entrances, reducing the accessible pore size but do not decreasing pore volume. Finally, at temperatures above 800°C, the kinetics are controlled by mass transfer (external diffusion) and carbon deposition will occur on the external surface of the adsorbent particles blocking all the pores. Thus, in order to reach the desired effect for a CMS, carbon deposition must be carried out in the kinetic regime corresponding to strong pore diffusion limitations (Fig. 10). Such conditions must be determined in each case, since they depend on the type of hydrocarbon and on the texture of the pristine activated carbon [157].

Other approach for modulating the porosity of a porous carbon for conferring molecular sieve properties consists in pyrolyzing a mixture of coal and organic additives such as pitch, phenol and formaldehyde [164-166]. Miura et al. [164] reported the possibility of control the micropore diameter with accuracy at a sub-angstrom level. They found that the pore size of the resultant carbons were controllable with changing the relative amount of the additives. It has been shown that with increasing the amount of a coal tar pitch over a coal, the pore diameter shifts from 0.43 to 0.37 nm, without modifying the total micropore volume.

The synthesis of CMS has been also reported by direct pyrolysis of organic precursors as polymers or resins. The use of organic compounds with well-known structure might open up the possibility for the design of MSC formation at molecular level [152]. In practice, commercial microporous CMS are mainly produced by CVD, but it has been reported that some commercial MSC from polymer precursors (e.g., C-1012 from Supelco Corp.), can be purely microporous (pore diameter below 0.56 nm) with high specific surface areas and micropore volumes (2000 m²/g and 0.73 cm³/g, respectively) [153]. Such materials are on a granular (spherical) form but the main research effort during the last years on synthesis of CMS from polymers has been done to obtain materials with a filmy shape for being applied as membranes for gas separation/adsorption.

Fig. 10. Schemes for CMS synthesis by different methodologies; (a) CVD (Adapted with the permission from [156]. Copyright 1996 American Chemical Society); (b) Polymer pyrolysis (adapted from [162]. Copyright 2017, with permission from Elsevier); (c) Polymer blend pyrolysis (Adapted from [163], Copyright 2017, with permission from Elsevier).

Koresh and Soffer [167] first shown that carbon molecular sieve membranes can be easily obtained by pyrolysis of thermosetting polymer membranes such as polyacrylonitrile (PAN), poly(vinylidene chloride) (PVDC), PFA, cellulose or saran copolymer, able to keep the morphology of the parent materials. They described that the pore dimensions of carbon were dependent on the morphology of the organic precursor and on the pyrolysis conditions. According to their results, by appropriately choosing a sequence of thermal treatments, membrane pore size can be continuously tuned. Research development after that initial work has shown that the choice of the polymeric precursor is important because pyrolysis of different precursors may yield different kinds of carbon membranes having completely different porous textures from microporous to macroporous, and adsorption/separation behaviors [168]. Mainly microporous carbon membranes have been synthesized from several precursors, including polyimides [169,170], coal tar pitch [171], furfuryl alcohol [172], PVDC copolymer [173], or phenolic resin [174].

The pyrolysis of polyimides is one of the most investigated methods, as it allows to prepare either amorphous or graphitic carbons, and nanoporous or dense (non-porous) materials, by simply selecting the molecular structure of the precursor and the pyrolysis conditions. As an example, Ohta et al. [170] reported the use of polyimides with repeating units containing pendant groups of $-\text{CH}_3$ and $-\text{CF}_3$. The authors found that varying the amount of F content in repeating unit from 5 to 31 wt.%, the microporous surface area after a pyrolysis at 600°C went from 856 to 1342 m²/g, and

the micropore volume from 0.28 to 0.44 cm³/g. In both conditions the average micropore diameter was around 0.55 nm.

The effect of PI film pyrolysis temperature and atmosphere of CMS porous texture has been shown by Lua and Su [175]. The authors reported that increasing the pyrolysis temperature simultaneously created new pores and narrowed the existing ones. The carbon membranes prepared at 1000°C under vacuum displayed the highest micropore volume (detected by CO₂ adsorption), whilst the membranes prepared at 800°C under vacuum had the highest characteristic adsorption energy.

As recently reviewed by Yang et al. [163], polymer blend technique is an efficient method for the preparation of microporous carbon materials having controlled structure and textures. The carbonization behaviour depends predominantly on the precursor (matrix-forming polymer), but pore structure of the final carbons can be controlled by the selection of blended polymers, which can be either vaporized or decomposed into gases to leave pore in the matrix (labile polymer). Various polymers have been employed as the matrix-forming ones, such as polyimides (PI), phenol resins (FR), polyacrylonitrile (PAN), poly(phenylene oxide) (PPO) and pitches, and as the labile ones, such as polyvinylpyrrolidone (PVP), polystyrene, polyethylene, poly(ethylene glycol) (PEG), polyurethane and polybenzimidazole. After blending two polymers either as solids or in a liquid, either membranes or fibres are formed by casting and spinning, respectively, followed by carbonization after stabilization if necessary (as depicted in Schema Xc). The pore formation in the resulting carbon membranes and fibres is mainly due to the decomposition or vaporization of the labile component; this process may be called sacrificial templating.

As an example, pore control in carbon membranes derived from polyimide is successfully performed by blending polyvinylpyrrolidone (PVP) with different molecular weights. As exposed above, the pyrolysis of PI membranes results in porous carbons but, Kim et al. [176] have shown that the micropore volume when blending with PVP increases with increasing the amount of PVP but also with increasing the M_w of PVP. Other blends that effectively work to increase micropores in the carbon films are PPO/PVP [177] or PF/PEG [178].

5.3.6 Carbide Derived Carbons

Carbide derived carbons, CDC, previously named « mineral carbons » [179] have caught increasing attention during the last decades due to the possibility of tuning their textural properties for applications in energy and gas storage [180-184]. CDCs are produced by selective etching of metals from crystalline metal carbides. In such a way the metal carbide lattice has the role of template as metal is extracted layer by layer. The transformation

is conformal and an atomic level control can be achieved at the same time that the carbide sample size and shape is maintained. Depending on the carbide used as precursor and the synthesis conditions, different carbon allotropes can be produced ranging from amorphous carbon to graphite or even nanocrystalline diamond [185].

Several methods have been reported for selective removal of metal or metalloid atoms from carbides as hydrothermal leaching, thermal decomposition, etching at high temperatures in molten salts, halogenation or electrochemical etching at room temperature. Hydrothermal leaching, thermal decomposition and electrochemical etching at high temperatures drives to non-porous or low porosity carbons whereas halogenation and electrochemical etching at room temperature are the most suitable routes for obtaining nanoporous carbons as it will be detailed below.

Electrochemical etching by oxidation of carbides has proven to be efficient for producing CDCs at room temperature from binary metal carbides as VC, V_2C [186] or MAX phase metal carbides (Ti_3AlC_2 , Ti_2AlC and Ti_3SiC_2) [187]. In particular, the CDC films obtained by electrochemical oxidation of Ti_3AlC_2 in HF present a very narrow pore size distribution with pores smaller than 2 nm diameter. Such a promising synthesis pathway of nanoporous CDC has been not much explored even if in a recent work Messner et al. [188] demonstrated that many metal carbides (NbC, Nb_2C , TaC, Ta_2C , VC, VCrC, TiC and TiCrC) having a cubic or hexagonal structure, can be oxidized electrochemically producing soluble metal ions in the solutions and carbon.

Halogenation is the most suitable for obtaining nanoporous carbons. The general reaction involved in the synthesis of carbon from metal carbides by halogenation can be written as: $Me_xCy(s) + (z/2) X_2(g) \rightarrow x MeXz(g) + y C(s)$ where Me represents metal and X the halogen

The most commonly used etching agent is Cl_2 but other halogens such as F_2 and XeF_2 can be used instead of Cl_2 [189]. The chlorination process for obtaining CDCs has been first reported by Hutchins in 1918 [190]. At that time, the carbon was considered just as a subproduct of the reaction of SiC with chlorine for obtaining $SiCl_4$. Some decades later, in 1959, Mohun et al. [191] showed that carbons obtained at various chlorination temperatures through a slightly modified method had interesting adsorption capacities of some vapours. However the first detailed study of the porous texture of the CDC carbons by N_2 and CO_2 adsorption was performed by Boehm et al. in 1975 [192] over carbons produced by chlorination of SiC and TaC. The factors controlling the porous textures of the carbons produced by chlorination of carbides are related to the initial carbide chemistry and porosity, some processing parameters as gas mixtures or chlorination temperature, and post-halogen treatment.

At low chlorination temperatures the crystal structure of the carbide templates the pore size distribution of the final CDC. As different carbides have different spatial distribution of carbon atoms in their lattice, halogenation for removing metals will lead to different carbon pore size distributions [193]. It has been reported that binary carbides with würtzite/zinc blend (hexagonal/cubic) structure as SiC or with NaCl (cubic) one as 3C-SiC, TiC, VC or ZrC yield small micropores with narrow pore size distribution as the first neighbour separation is uniform. Binary carbides with rhombohedral e.g. B₄C or orthorhombic e.g. Mo₂C and layered hexagonal ternary carbides with a MAX phase e.g. Ti₂AlC, Ti₃SiC₂ with a large non-uniform nearest neighbour separation show larger pores and a wide pore size distribution having a great contribution of mesoporosity (Fig. 11) [194-198].

Overall, increasing the chlorination temperature also increases the average micropore size of the CDC, regardless the carbide used as precursor (see Fig. 11a). As exposed above, at low chlorination temperatures, the parent carbide controls the initial pore size, but increasing the chlorination temperature from 400°C to 1200°C can result in a 10-fold increase in the pore width. Higher chlorine treatment temperatures increase the mobility of carbon atoms and facilitate the formation of larger-sized graphene fragments and graphene layers stacking, which results in the formation of larger pores [199]. Larger and straighter pores facilitate the removal of trapped metal chlorides produced during the chlorination reaction. In addition the chlorides rapidly produced at high temperatures may cause expansion of CDC particles, particularly those produced from layered carbides [196-198]. These phenomena contribute to increase the total pore volume and size in CDC. In general, at low chlorination temperatures, N₂ or Ar adsorption isotherms of the resultant carbons are of type I since they become of type IV when increasing temperature indicating the presence of mesopores [200]. At the same time, specific surface area was reported to have a bell-shaped temperature dependence independently of the parent carbide (see Fig. 11b).

In sum, limiting factors for the specific surface area include, at low temperature, clogging of pores with chlorides and chlorine residues and, at high temperature, graphitization and structure collapsing. Therefore, in order to obtain only micropores with pore sizes adapted to the adsorption of small gases as CO₂, CH₄ or H₂, a moderate chlorination temperature should be used. As an example, gas separation analysis shows that CDCs obtained at temperatures lower than 1000°C from binary carbides have an important specific surface area and a narrow pore size distribution being excellent materials for the complex CO₂ separation from N₂, i.e. nitrogen accessibility at room temperature and atmospheric pressure is inhibited compared to

larger molecules (e.g. CH_4) probably due to specific interactions at the pore mouth [183].

Fig. 11. (a) [11-20] Projection of Ti_3SiC_2 with removal of all Ti and Si atoms (Reprinted from [198], Copyright 2005, with permission from Elsevier) (b) [110] projection of 3C-SiC with removal of all Si atoms (Reprinted from [201], Copyright 2006, with permission from Elsevier). Effect of chlorination temperature over average pore size (c) and BET surface area (d) for porous carbons obtained from TIC (data depicted from [202]); VC (data depicted from [203]); B₄C (data depicted from [202,204]); Ti_2AlC (data depicted from [196,202]).

A strategy for obtaining microporous carbons with high micropore volume, narrow pore size distribution and high surface area would be to perform chlorination at low temperature and to add a post-treatment step. It has been reported from one side that a heat treatment under H_2 at temperatures around 200-600 $^\circ\text{C}$ is effective for opening the clogged pores and to increase the pore volume and from the other, a chemical or physical activation can be performed over the CDC for increasing the pore volume and specific surface area [182,184,205,206].

5.4. CONCLUSIONS

Among the large spectrum of materials with potential ability to selectively adsorb specific molecules of a gas mixture, nanoporous carbons play an important role due to the versatility of forms, morphologies and pore architectures. They do not only display excellent adsorption capacities and selectivity for gas mixtures, but also better mechanical stability under pressure, which is required for practical applications. The combination of these features makes them to succeed when compared to direct competitor materials such as zeolites and metal organic frameworks. For practical gas-phase applications, an appropriate adsorbent must present a high adsorption capacity at the operating conditions, which can be achieved and modulated by tuning the porosity, for which the preparation of carbon materials with optimum the textural features (in terms of specific surface area and adequate pore dimensions) becomes critical for gas storage. Nanopo-

rous carbons are traditionally manufactured by so-called conventional activation methods based on the thermal or chemical gasification of a carbon precursor under carbon dioxide or steam atmospheres. This process is used at industrial scale for over a century, and thus knowledge on the optimized operating conditions depending on the nature and reactivity of the precursor has been accumulated over the years. In the last years, these classical approaches are being revisited from new perspectives, trying to increase carbon yields, use renewable sources and wastes as precursors, to modulate the textural features of the resulting carbons by more sustainable and less energy demanding processes. However, a small control over the porous features is obtained with conventional activation methods, for which the design and development of new approaches that allow a precise control of the porosity (in terms of pore size and volume) of the carbon materials has received much attention in the last decades. The combination of hydrothermal carbonization of various precursors with post-synthesis activation, the use of nanocasting approaches with adequate templates, or microporous carbons obtained from carbides, are among most promising approaches to obtain porous carbons with adequate porosity for gas storage. The critical issue to be solved in a near future would be to demonstrate whether if the performance of such highly featured carbons with ad-hoc porous features can overcome the cost associated to the synthesis for a scale-up, hence granting their practical application.

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