

NaOH AND KOH FOR PREPARING ACTIVATED CARBONS USED IN ENERGY AND ENVIRONMENTAL APPLICATIONS

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Abstract

Alkaline hydroxides, especially sodium and potassium hydroxides, are multi-million-ton per annum commodities and strong chemical bases that have large scale applications. Some of them are related with their consequent ability to degrade most materials, depending on the temperature used. As an example, these chemicals are involved in the manufacture of pulp and paper, textiles, biodiesels, soaps and detergents, acid gases removal (e.g., SO₂) and others, as well as in many organic synthesis processes. Sodium and potassium hydroxides are strong and corrosive bases, but they are also very stable chemicals that can melt without decomposition, NaOH at 318°C, and KOH at 360°C. Hence, they can react with most materials, even with relatively inert ones such as carbon materials. Thus, at temperatures higher than 360°C these melted hydroxides easily react with most types of carbon-containing raw materials (coals, lignocellulosic materials, pitches, etc.), as well as with most pure carbon materials (carbon fibers, carbon nanofibers and carbon nanotubes). This reaction occurs via a solid-liquid redox reaction in which both hydroxides (NaOH or KOH) are converted to the following main products: hydrogen, alkaline metals and alkaline carbonates, as a result of the carbon precursor oxidation. By controlling this reaction, and after a suitable washing process, good quality activated carbons (ACs), a classical type of porous materials, can be prepared.

Such carbon activation by hydroxides, known since long time ago, continues to be under research due to the unique properties of the resulting activated carbons. They have promising high porosity developments and interesting pore size distributions. These two properties are important for new applications such as gas storage (e.g., natural gas or hydrogen), capture, storage and transport of carbon dioxide, electricity storage demands (EDLC-supercapacitors-) or pollution control. Because these applications require new and superior quality activated carbons, there is no doubt that among the different existing activating processes, the one based on the chemical reaction between the carbon precursor and the alkaline hydroxide (NaOH or KOH) gives the best activation results.

The present article covers different aspects of the activation by hydroxides, including the characteristics of the resulting activated carbons and their performance in some environmental-related applications. The following topics are discussed: i) variables of the preparation method, such as the nature of the hydroxide, the type of carbon precursor, the hydroxide/carbon precursor ratio, the mixing procedure of carbon precursor and hydroxide (impregnation of the precursor with a hydroxide solution or mixing both, hydroxide and

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carbon precursor, as solids), or the temperature and time of the reaction are discussed, analyzing their effect on the resulting porosity; ii) analysis of the main reactions occurring during the activation process, iii) comparative analysis of the porosity development obtained from different activation processes (e.g., CO₂, steam, phosphoric acid and hydroxides activation); and iv) performance of the prepared activated carbon materials on a few applications, such as VOCs removal, electricity and gas storages.

1. Introduction

Alkaline hydroxides, especially those from sodium and potassium, are multi-million-ton per annum commodity chemicals that have great ability to degrade many materials [1,2]. Both are strong caustic metallic bases that are widely used in many different topics, for example organic synthesis processes (acting as catalysts or as nucleophilic reagents), demineralization of coals and other carbon materials, disaggregating agents in analytical chemistry, as well as in large scale applications such as the manufacture of pulp and paper, textiles, tissue digestion, biodiesels, soaps and detergents, acid gases removal (e.g., SO₂), drinking water treatment and others [1-5]. Although KOH and NaOH can be used interchangeably in a large number of applications, NaOH is preferred by the industry because of its lower cost. Hence the worldwide production of NaOH is about one hundred times higher than for KOH (e.g., for 2005, the production of NaOH was 70 million tonnes, whereas it was approximately 700,000 tonnes for KOH) [1, 2, 6, 7].

Although these two hydroxides are strong and corrosive bases, NaOH and KOH are interestingly stable chemicals that melt without decomposition at 318°C and at 360°C, respectively [7]. However, at these temperatures both melted hydroxides are even stronger caustic bases, as a result of which they react with most materials and even start reacting with the quite inert carbon materials. At temperatures about their melting points, these melted hydroxides strongly react with most types of carbon containing raw materials (coals, lignocellulosic materials, pitches, etc.), as well as with most pure carbon materials (carbon fibers, carbon nanofibers and carbon nanotubes) [8-10]. The reaction between the carbon precursor and the hydroxide can be controlled by means of many experimental variables (e.g., the nature of the precursor and the hydroxide, the reaction temperature and time, or the hydroxide carbon ratio, among others). The resulting solid products of the reaction are mixtures formed by the remaining carbon, alkaline carbonates and, depending on the reaction conditions, unreacted hydroxides. If such residue is washed, filtered and dried, the remaining carbon material results to be a super activated carbon (AC) [10].

Such activation reaction occurs via a solid-liquid redox reaction in which the hydroxides (both NaOH and KOH) are converted to the following main products: hydrogen, alkaline metals and alkaline carbonates, as a result of the carbon precursor oxidation [8-10], and some remaining carbon reactant. This remaining carbon is the objective of such type of reaction in which the number of pores of the carbon precursor used has increased considerably, as well as the size of the existing ones. Hence, by this hydroxide-carbon reaction we can prepare superior class activated carbons having high adsorption capacities. Therefore, under these experimental conditions, sodium and potassium hydroxides become very useful chemical agents for the carbon activation process and hence for preparing superior quality super-activated carbons [10-13].

Since the pioneer patent of Wennerberg et al. [14] a considerable work has been done over the years related to chemical activation with hydroxides [11-13, 15-39]. In this large number of papers, we can see that most of the variables affecting this activation process have been analyzed, specially the precursor and the hydroxide/carbon ratio. From all these papers it can be stated that carbon activation by alkaline hydroxides is a promising process. This statement is confirmed by industrial production of very high surface area activated carbons (e.g., Maxsorb series, commercialized by Kansai Coke and Chemical Company, Japan [13]).

The present article shows and discusses the reaction of two strong caustic chemicals (i.e., NaOH and KOH) with a large variety of carbon precursors, in order to highlight their specific use for preparing good quality “super-activated” carbons. Considering the increasing interest in the use of alkaline hydroxides as activating agents, and the large number of published papers related to the variables affecting this activation process, this article reviews and updates the most important aspects of this activation process. This article, covering the most important aspects of the hydroxide-carbon reaction, will be useful for the reader to understand such activation process and the unique properties of the resulting ACs. These properties and their performance in some environment-related applications will be analyzed, discussing the following topics: i) variables of the preparation method (e.g., the nature of the hydroxide, the carbon precursor, the hydroxide/carbon precursor ratio, the mixing procedure (impregnation or mixing of solids), the reaction temperature and time), analyzing their effect on the resulting porosity, ii) analysis of the main reactions occurring during the activation process, iii) comparative analysis of the porosity development obtained from different activation processes (e.g., CO₂, steam, phosphoric acid and hydroxides activation), and iv) performance of the prepared activated carbon materials on a few applications which are related to energy and environment, such as VOCs removal, electricity and gas storages.

2. Activated Carbons

The term activated carbon (AC) corresponds to a large group of carbonaceous adsorbents which are mainly formed by carbon atoms and have the peculiarity of possessing valuable, and tunable properties such as: adsorption capacities, apparent surface areas and porosities (from low to very high) and porous textures with tunable pore size distributions. All these characteristics, including their different morphologies (powder, granular, pellet, fiber, monoliths, cloth and others) can be tailored and developed according to their final applications. As a result of these tunable properties, ACs are the adsorbents which are mostly used in a large number of industrial applications and their world consumption is steadily increasing, being estimated this consumption around 650,000 tons in 2007 [40]. Furthermore, they are among the best candidates for emerging applications, particularly related to the environmental pollution remediation [41]. However, since ACs are not present in nature, they have to be prepared artificially, especially considering the consumption increase expected in the next five years [40].

2.1. Characterization

Considering the variety of fields in which activated carbons are used, their porous textures require a suitable characterization. Such complex characterization needs a combination of techniques, allowing to control and to optimize the performance of an AC for a given application. Amongst others, the following techniques should be underlined: physical adsorption of gases, mercury porosimetry, small angle neutron and X-ray or neutron scattering, transmission and scanning electron microscopy, scanning tunnel microscopy or immersion calorimetry. From them, undoubtedly physical adsorption of gases (e.g., N₂, CO₂ and many others) is the main technique and N₂ (at 77 K) the gas most widely used. Its main advantage is that it easily covers a wide relative pressure range (from 10⁻⁸ to 1). However, it has the disadvantage of having possible problems of N₂ diffusion inside the narrow porosity (size < 0.7 nm). To overcome this problem, the use of other adsorptives has been proposed, CO₂ adsorption at 273 K being an easy alternative to N₂ for the assessment of such narrow microporosity [42-45]. When the micropore volumes, deduced from both N₂ (77 K) and CO₂ (273 K) adsorption isotherms, are compared by applying a suitable equation (e.g., the DR equation) three cases can be found; i) a CO₂ micropore volume (V_{DR}(CO₂)) higher than the N₂ micropore volume (V_{DR}(N₂)), ii) a similar value (V_{DR}(N₂) ≈ V_{DR}(CO₂)) and iii) a lower V_{DR}(CO₂) value than V_{DR}(N₂). The first case indicates that the porosity of the carbon sample is very narrow (micropore size < 0.7 nm), causing diffusion problems to the N₂ molecules to reach it. Case ii) indicates that the carbon sample has an homogeneous, and narrow micropore size distribution (with a size of about 0.7 nm), and in case iii) the higher the difference between these two values, the wider (and heterogeneous) the carbon samples' porosity, with well developed supermicroporosity and mesoporosity [25,46-55].

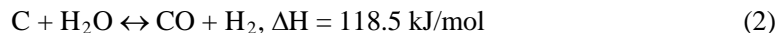
For a better understanding of the porosity results presented in the following sections of this article, all our activated carbons have always been characterized by both N₂ (77 K) and CO₂ (273 K) adsorption isotherms.

2.2. Preparation

For obtaining these ACs it is necessary to select the precursor and the method of preparation. Both have great importance, as they determine the final porous textures of the resulting ACs. In relation to the former, any carbonaceous precursor with high carbon atoms content in its composition can be used. Examples of the most used ones are the "classical precursors" such as wood, coconut shells and coals [56-58], while less used precursors include agricultural by-products, waste residues, pitches, polymers and so on [56-58]. Once a given precursor has been selected, the method of preparation to be used needs to be analyzed. In general, depending on the precursor used, different activation methods and activating agents will be chosen. The activation of a carbon precursor, with the objective of increasing the raw precursor's porosity and hence its adsorption capacity, can be carried out by any of the so-called "physical activation" and/or "chemical activation" processes [10,16,56-60].

The "physical activation" process is a controlled gasification in which the carbon precursor (previously carbonised or not) is activated at temperatures between 800-1000°C using carbon dioxide or steam. Both of these activating agents are commonly used and both

react endothermally with the carbon atoms of the precursor according to the following reactions:



In the course of the two reactions (1) and (2) shown before, carbon atoms from the precursor are oxidized and hence removed, starting with the less ordered and most reactive carbon atoms. For a suitable activation process (creation of micropores and/or size widening of the existing ones) such carbon atoms removal must take place predominantly inside the carbon particles, not in the external part, to allow a suitable porosity and adsorption capacity.

On the contrary, the “chemical activation” process consists of mixing a carbonaceous precursor with a chemical activating agent and heating the mixture in an inert atmosphere, similarly to a pyrolysis process. After such thermal treatment and after a subsequent washing process, the obtained carbon material is richer in carbon content and, ideally, has a well developed porous structure. Different compounds can be used for such type of activation; amongst others, H_3PO_4 , KOH, or NaOH have been reported in the literature [56-60].

In general, “chemical activation” presents advantages over “physical activation” that can be summarized as: i) it uses lower temperatures and pyrolysis times, ii) it usually consists of one stage and iii) it renders higher activation yields. Nevertheless, it also presents disadvantages as the need of a washing stage and the corrosiveness of some of the chemical agents used.

In both activation processes (“physical activation” and “chemical activation”) it is important to have a deep knowledge of different preparation variables (less numerous in the “physical” activation process than in the “chemical” one) that affect the porous texture development (surface area, pore size and pore size distribution). The knowledge of the effect of these preparation variables on the porous texture of the resulting activated carbons will allow to select them and, hence, the properties of the prepared ACs.

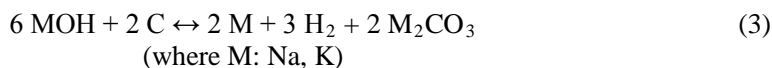
2.3. Carbon Activation by Alkaline Hydroxides

Carbon activation by alkaline hydroxides is known since long time ago (mainly restricted to KOH) and the research on such activation process increases continuously [11-13,15-39]. Nowadays, ACs obtained by this activation have started to be industrially used (about 100 tonnes per year). These ACs possess three unique characteristics that make them very attractive for new and potential applications. These are: i) their low ash content, even using precursors having high ash contents, ii) their very high adsorption capacity and iii) their controlled narrow porosity distribution (not possible to achieve using other activating agents). As a result, there is no doubt that among the different existing activation processes, chemical activation by NaOH or KOH is among the most powerful ones.

As it will be shown later on, new applications and/or potential ones, such as gas storage (e.g. natural gas and hydrogen), capture, storage and transport (e.g. of carbon dioxide), electricity storage (EDLC, supercapacitors) or pollution control require unique properties which are provided by superior quality activated carbons, prepared by alkaline hydroxides.

2.4. Understanding the Main Reactions of the Hydroxide-Carbon Reaction

The main reactions occurring during the carbon activation with hydroxides are of interest in order to understand the unique features of the resulting activated carbons, as it will be discussed on subsequent sections. By a combination of techniques (FTIR, “in situ” XRD and mass spectrometry), thermodynamic data and theoretical calculations (Gibbs Free Energy) we have analyzed the changes occurring in both chemical reactants (carbon and hydroxides), as well as the composition of the gaseous and solid reaction products [8-10,61]. From these results, and with a mass balance that accounts for more than 90 wt. % of the analyzed products, it has been shown that the hydroxide activation of carbon occurs via the following reaction:



It can be seen that this reaction is a solid-liquid redox reaction in which the hydroxides are converted to the following main products: hydrogen, alkaline metals and alkaline carbonates, as a result of the carbon precursor oxidation [8-10, 61].

Frequently, this reaction (3) is carried out in a temperature range of 700°C to 900°C and using lower hydroxide/carbon ratios than would be required for stoichiometry. Therefore, the hydroxide is the limiting reactant and, hence, some unreacted carbon will always remain. Much higher hydroxide/carbon weight ratios (about 10/1 for NaOH and 14/1 for KOH) would have to be used to avoid such hydroxide limitation.

2.5. Variables Affecting the Hydroxide-Carbon Reaction

Although many works have analyzed the variables of the hydroxide-carbon reaction [11,12,16,17,25-27,29,32,62], often the ACs obtained have not been similarly characterized. Thus, it is difficult, or even impossible, to compare results from different authors and hence to get conclusions. In a recent study [10], we reviewed the variables of the carbon activation by hydroxides in samples similarly prepared and characterized. In the present article, we summarize and update the fundamentals of the carbon activation by alkaline hydroxides and revisit it, adding new data obtained after this publication.

As it happens in most chemical reactions, the kinetics and extent of a reaction are generally affected by many variables, for example the reactants' concentrations, the reaction temperature and time. Contrarily to most chemical reactions, the key point regarding reaction (3) is the characteristics of the remaining carbon (i.e., its porosity development). Hence, it is important to know these variables and how they affect the porosity development of the remaining carbon material.

Amongst others, the most relevant variables for carbon activation by alkaline hydroxides affecting the final porous texture of the ACs are: i) the reactivity of the carbon precursor, ii) the way of mixing both reactants, iii) the nature of the hydroxide, iv) the hydroxide carbon ratio, v) the maximum reaction temperature and v) two additional parameters that have recently been reported as the flow and type of gas used during the heat-treatment [8, 10-12].

2.5.1. Reactivity of the Carbon Precursor

The importance of the carbon precursors' reactivity is summarized next, using some examples extracted from our study with 16 carbonaceous precursors. This study covers a large variety of different carbon precursors (coals, lignocellulosic materials and carbon materials) and their heat treatment previous to their activation by hydroxide. The main conclusion is that the reactivity of the carbon precursor itself (estimated by TG analysis in air) controls its reactivity in reaction (3), and hence the extent of the reaction and the degree of activation reached, as well as the subsequent properties of the prepared ACs [9,10]. Thus, Table 1 compiles some results related to the reactivity of the carbon-NaOH reaction (the same happens with KOH) such as: i) the air reactivity (estimated as the temperature at which 20 wt. % of the carbon precursor is burnt), ii) the temperature at which reaction (3) starts (estimated from coupled TG-MS) and iii) the wt. % of reacted carbon. These results show, as expected, that the reactivity decreases as the coal rank increases (lignite > subbituminous > anthracite) and that a heat treatment in the carbonaceous precursors previous to the activation reaction causes a decrease in their subsequent reactivity. Interestingly, the extent of the reaction (wt. % of carbon reacted) also depends on the reactivity of the starting carbon, decreasing from lignite to subbituminous coal to anthracite. The use of a pre-heat treatment step, prior to activation, provokes a more ordered carbon material and, hence, a less reactive one, as results of which the activation process becomes much more difficult [9, 10].

Table 1. Results related to the reactivity of the carbon precursor in relation to reaction (3)

Carbon Precursor	T (20% wt loss) (°C)	T (H ₂ appearance) (°C)	Reacted carbon (% wt)
L	266	250	9.0
SB	438	375	6.0
A	582	475	2.0
L850	445	450	5.2
A-1000	639	575	0.3

In addition to the reactivity of the precursor, other characteristics (especially its starting porosity) also affect the reaction. As stated above, the hydroxide-carbon activation depends very much on the reaction variables, as it will be shown later on.

Figure 1 presents the N₂ adsorption isotherms at 77 K of precursors which have different structures and textural properties. They are activated by KOH (Figure 1a) and by NaOH (Figure 1b), keeping constant the other variables (physical mixing; hydroxide/precursor ratio 2/1 (weight); heating rate 20°C/min up to 750°C; soaking time 1 h; N₂ flow rate during heat treatment 500 ml/min).

These N₂ adsorption isotherms clearly show that the precursor influences remarkably the resulting adsorption capacity, although in a different manner depending on the hydroxide used.

Thus, the observed adsorption capacity sequence of Figure 1 varies considerably depending on the nature of hydroxide used. It can be seen that, in general, when KOH is used, the structural order of the precursor favours the activation results (e.g., anthracite > subbituminous > lignite ≈ almond shell). However, when NaOH is used the low structural

order of the precursor favours the activation (e.g., lignite > almond shell > subbituminous > anthracite).

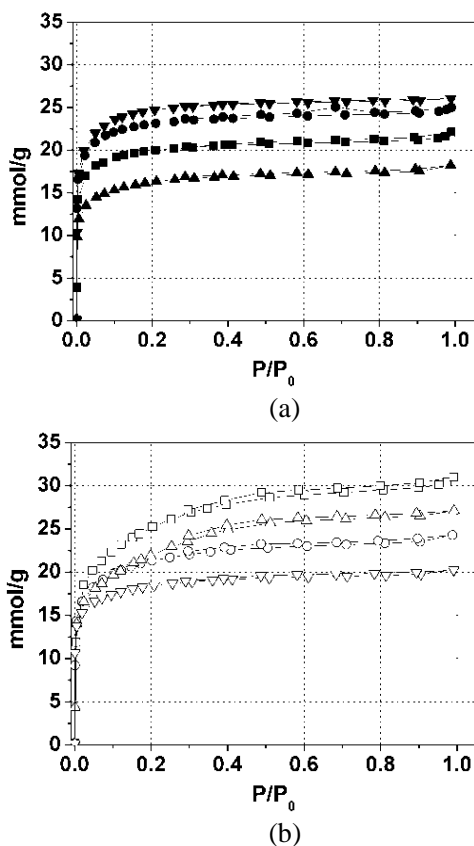


Figure 1. N_2 adsorption isotherms at 77 K for precursors activated similarly by (a) KOH ((!) Lignite, (.) Sub-bituminous, (B) Anthracite and (7) almond shell) and by (b) NaOH (empty symbols).

2.5.2. Way of Mixing the Hydroxide and the Carbon Precursor

The way of mixing the carbonaceous precursor with the alkaline hydroxide influences the properties of the prepared activated carbons. Most studies related to activation with alkaline hydroxides are based on the impregnation method and on the exclusive use of KOH. Impregnation consists of mixing by stirring, at a given temperature, the precursor with different volumes of a hydroxide solution [10,11].

After the impregnation process, the samples are heat-treated for activation. In contrast to this method, our research group has deeply investigated an alternative and more efficient method: the direct mixing, at room temperature, of the hydroxide and the carbonaceous precursor (i.e., in absence of water) [10,12]. Such method has shown to be very effective in all the carbon precursors used [10,12].

Additionally, and of special interest, is the observation that the mixing of NaOH with the carbon precursor can render comparable or even better results than with KOH (contrarily to what was assumed initially), with the advantage of its lower cost in comparison with KOH.

2.5.3. The Nature of the Hydroxide

Figure 2 presents the N_2 adsorption isotherms of two precursors (anthracite and almond shell) similarly activated with KOH (Figure 2a) and NaOH (Figure 2b).

The importance of the nature of the carbon precursor can be well observed; their activation behaviour and hence their adsorption capacities are different, due to their remarkable different reactivity and structural order. Additionally, these activation results depend on the nature of the hydroxide. This is shown in Figure 3, where the results of Figure 2 are presented, keeping constant the precursor used (Figure 3a for the anthracite and Figure 3b for almond shell).

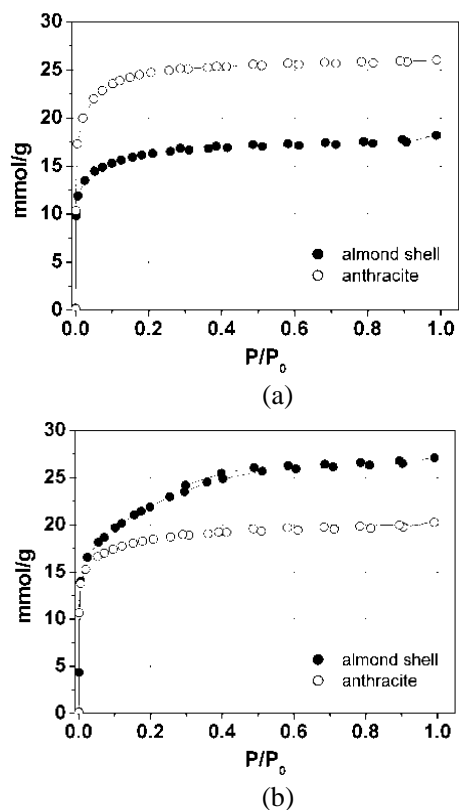


Figure 2. N_2 adsorption isotherms at 77 K for an anthracite and for an almond shell, both activated using the same experimental conditions by (a) KOH and (b) NaOH.

It can be seen that the results are different depending on the nature of the activating agent used. KOH is much more effective than NaOH for activating ordered precursors (e.g., an anthracite), but the contrarily happens for less ordered lignocellulosic materials (e.g., almond shell), for which NaOH gives much better results.

The conclusion that could be obtained from Figure 3a is that KOH is a better activating agent than NaOH, as it is usually done in the literature. However, this cannot be generalized, as shown in Figure 3b and in Figure 1.

During many years, and without explanation, it has been stated that KOH is the best hydroxide activating agent for carbon activation and that NaOH was not a suitable one. The

results of Figures 1 to 3, in line with many other results from our research group [10,33,53], show that the relative effectiveness of both hydroxides depends on the precursor used and that for some of them better activation results are obtained with NaOH than with KOH. The erroneous observation that confused the scientific community during many years is due to the importance of the structural order of the precursor that was not previously considered, and allows us to conclude that NaOH is better for carbons with poor structural order, whereas KOH produces better results for those having some structural order.

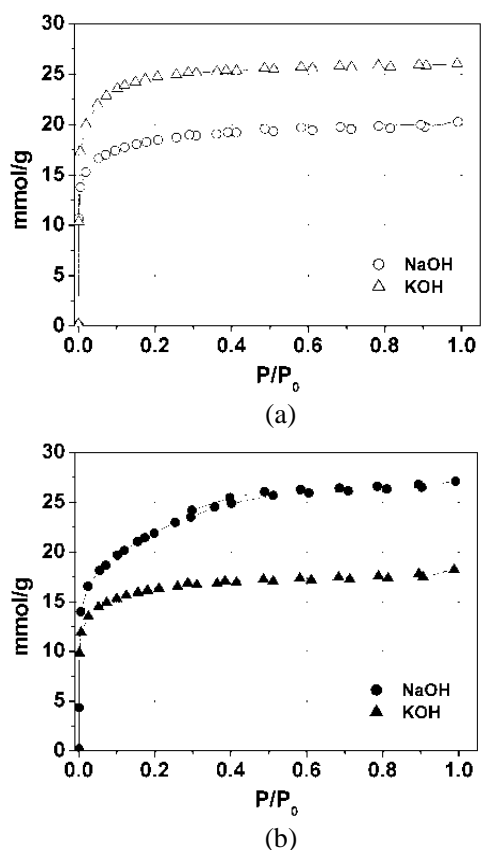


Figure 3. N₂ adsorption isotherms at 77 K showing the effect of the precursor used; (a) an anthracite and (b) an almond shell, both similarly activated by KOH or NaOH.

2.5.4. The Hydroxide/Carbon Ratio

The effect that the hydroxide/carbon ratio plays on the porosity development is analyzed next, taking as example a given carbon fiber (Donacarbono SL-242, provided by Osaka Gas, Japan). Such carbon fiber (CF) was activated at 750°C using NaOH or KOH at different ratios. Figures 4a and 4b show the effect that this variable has on the N₂ adsorption isotherms (77 K) and on their corresponding apparent BET surface areas. Table 2 (limited, as an example, only to KOH activation) also shows the important effect that the hydroxide/CF ratio has on the resulting ACFs properties.

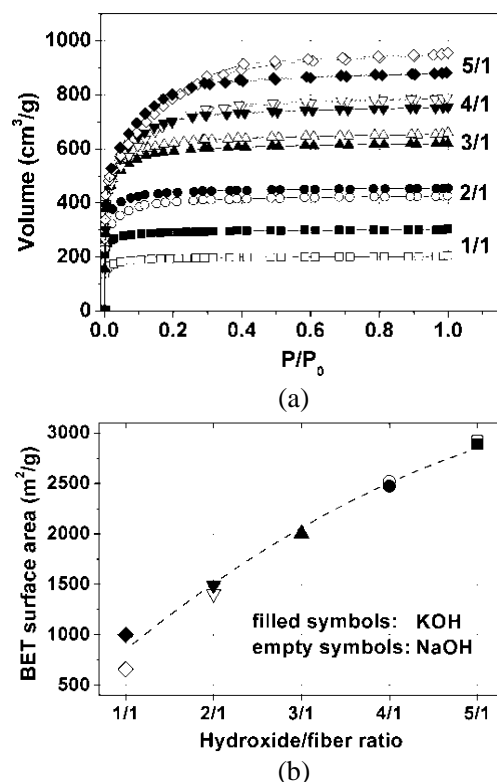


Figure 4. Effect of the hydroxide/CF ratio on: (a) the N₂ adsorption isotherms and (b) the BET surface area (empty symbols for NaOH and filled symbols for KOH) (redrawn from [63]).

The isotherms in Figure 4a are typical of microporous solids (type I) having most of the pores sizes below 2 nm. For the two lowest hydroxide/CF ratios (1/1 and 2/1) porosity is mainly due to narrow micropores (<0.7 nm), which implies that their micropore size distributions are quite narrow.

As the ratio increases, the knee of the adsorption isotherms widen, which indicates the presence of supermicroporosity (0.7 - 2 nm), and hence the widening of their pore size distributions.

It should be pointed out that i) as shown in Table 2, the starting CF porosity has almost no adsorption of N₂ at 77 K, while contrarily its adsorption of CO₂ at 273 K is noticeable. This is due to the well known diffusion problem of the N₂ molecules at 77 K, which impedes them to get into the porosity at this low adsorption temperature [42,43] ii) the porosity of the starting CF develops very well upon activation with both hydroxides, reaching a comparable maximum high BET value (about 3000 m²/g) for both hydroxides at a ratio of 5/1, iii) with the increase in the hydroxide/CF ratio, the extent of the reaction increases and, hence, also the resulting adsorption capacity, and iv) contrarily to most carbon precursors, it can be observed that with this Donacarbono SL-242 precursor, the adsorption capacity developed by both hydroxides is similar.

Table 2. Porous texture data, yields and packing density of ACFs prepared at different KOH/CF ratios

Sample	S _{BET} (m ² /g)	V _{DR} (N ₂) (cm ³ /g)	V _{DR} (CO ₂) (cm ³ /g)	Yield (%)	*Packing ρ (g cm ⁻³)
CF	7**	0.003	0.11	---	0.99
KOH 1/1	999	0.46	0.47	83	0.74
KOH 2/1	1491	0.71	0.65	80	0.74
KOH 3/1	2004	0.94	0.79	74	0.67
KOH 4/1	2472	1.13	0.71	65	0.58
KOH 5/1	2888	1.23	0.80	55	0.56

*Data used later (Hydrogen storage application)

** Low value due to N₂ diffusion problems at 77 K.

Additionally, Table 2 confirms that for low ratios, the volumes of micropores deduced from CO₂ adsorption are quite similar to those deduced from N₂ adsorption; however, for higher ratios, the micropore volumes deduced from CO₂ and N₂ differ, being much lower for CO₂. Both observations indicate the widening of the pore size distributions due to the presence of larger pores (supermicropores, between 0.7 and 2 nm and mesopores, between 2 and 7 nm). Similar results were also obtained by NaOH activation for most of the carbon precursors analyzed [10,12,53].

Particularly important from an economic point of view is the activation yield. This parameter is compiled in Table 2 and, interestingly, high values are obtained, covering a range between 83 % and 55 %. It can be seen that with the increase in the KOH/precursor ratio the activation yield decreases. When NaOH is used, lower yields are reached [53].

2.5.5. Maximum Reaction Temperature (A Misleading Variable)

Literature shows that a large range of activation temperatures (from about 700°C to 1000°C) is being used for the carbon activation by hydroxides, without paying attention to its importance. However, the activation temperature is a very important parameter that merits much more attention. Of course, for higher activation temperatures, the extent of the reaction will be higher and hence the activation degree.

Nevertheless, according to reaction (3), one product of the reaction is the alkaline carbonate which, at temperatures higher than about 800°C, decomposes, evolving CO₂, following reaction (4). In presence of the remaining carbon, such CO₂ evolution causes an additional type of carbon activation, due to reaction (1).



In reaction (1) carbon activation takes place through a different mechanism (CO₂ gasification), as a result of which a much broader widening of the porosity is observed, as well as a decrease of the reaction yield. These two observations, which depend very much on the hydroxide and carbon precursor used, disturb two of the main advantages of the hydroxides activation as it will be commented later on: the reaction yield and the narrow pore

size distribution. Consequently, an activation temperature higher than 800°C is not at all recommended, especially when narrow micropore size distributions are desired.

2.5.6. Flow and Type of Gas Used During the Heat-Treatment

Little attention has been paid to the flow rate of the gas used during the heat treatment process. During the hydroxide-carbon reaction H_2 is evolved (see reaction (3)), 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. It has been shown [10,12] that changing the N_2 flow rate from 80 to 800 ml/min increases the microporosity development. Thereby, the micropore volumes and surface areas of the produced ACs are doubled; however, and interestingly, the micropore size distribution is not changed [10]. Nitrogen, argon and helium have been studied as purging atmospheres, using similar flow rates. 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 $He < N_2 < Ar$, which confirms that they act in the reaction only as purging gases [8].

2.5.7. Concluding Remarks

As it has been shown above, the carbon reaction with hydroxides depends on a large number of variables (much more variables than for physical activation).

By a suitable control of these variables, the characteristics of the resulting ACs can be selected, as it is summarized in Figure 5. The figure shows, for a fixed carbon precursor (anthracite), the large range of BET surface areas that can be obtained ($\approx 4000 \text{ m}^2/\text{g}$) changing the variables of the hydroxide-carbon reaction.

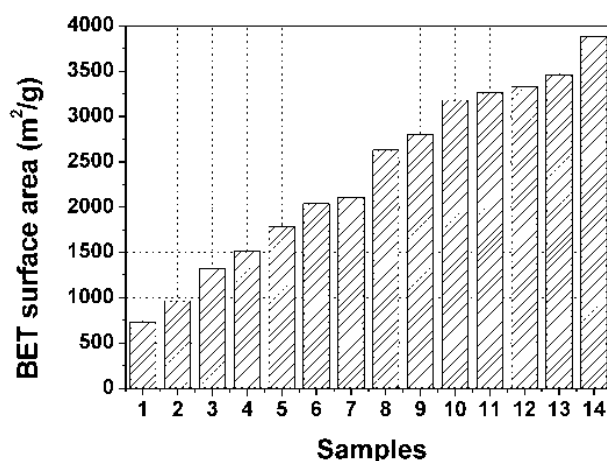


Figure 5. Apparent BET surface area development obtained varying experimental variables of the carbon-hydroxide activation. Numbers indicate different types of variables used.

3. Comparison of NaOH, KOH, Steam and Phosphoric Acid Activations

According to the above comments, the suitable selection of the experimental conditions of the hydroxide-carbon reaction allows to prepare ACs with well developed porosity. However, for some applications (as it is discussed later on) it is necessary not only to develop porosity (pore volume and surface area), but also to control the pore size distributions (PSD) of the prepared ACs. For a given precursor, it is difficult to control simultaneously porosity and pore size distribution for the activated carbons prepared either by physical activation (e.g., CO₂ or steam) or by chemical activation with conventional activating agents (e.g., phosphoric acid). In both cases, as the pore volume is developed, there is a subsequent widening of the PSD. Interestingly, with a suitable selection of the experimental preparation variables, carbon activation by hydroxides (HA) allows, simultaneously, to develop activated carbons with large porosity without a noticeable PSD widening. In the present section we compare the singularity of the porosity developed by hydroxides activation with the two most used activation procedures, first with physical activation (PA) and secondly with phosphoric acid activation (PAc).

3.1. General Features of the Physical Activation (PA)

Using N₂ (77 K) and CO₂ (273 K) adsorption data of a large series of ACs, the general features of the physical activation process (i.e., development of the micropore volume accompanied by widening of the PSD) are discussed. For it, ACs from different carbon precursors, such as lignocellulosic materials, coals, Saran polymer, carbon fibers, activated with steam or with CO₂ at different degrees of activation are used as examples. Figure 6 presents the obtained results, plotting their micropore volumes ($V_{DR}(N_2)$) and narrow micropore volumes ($V_{DR}(CO_2)$), both calculated from DR equation, versus their apparent BET surface area. High surface areas (with maximum BET values in the range of 2500-3000 m²/g) can easily be prepared by physical activation. As expected, a linear relation is found between the micropore volumes ($V_{DR}(N_2)$) and the BET values. This can be explained due to the fact that, although both equations differ on their fundamentals, they both analyze the same adsorption isotherm (N₂ at 77 K) and, hence, both give related results, as shown in Figure 6. Thus, as the activation degree increases (from a small percentage to 90 %) both the $V_{DR}(N_2)$ and the apparent BET surface area increase similarly and linearly.

However, this is not the case for $V_{DR}(CO_2)$, which only increases linearly up to a certain degree of activation or apparent BET (never above 1000 m²/g). The carbon precursor that gets the highest $V_{DR}(CO_2)$ is the Saran sample, as shown in Figure 6, for which that linearity extends up to ≈ 0.6 cm³/g.

The maximum $V_{DR}(CO_2)$ is much lower for the other carbon precursors used, decreasing from Saran in the following order: carbon fibers, lignocellulosic materials and, finally, coals.

These observations indicate that $V_{DR}(N_2)$ and $V_{DR}(CO_2)$ develop differently with the activation degree. $V_{DR}(CO_2)$ develops at low activation degrees, whereas at higher burn-offs wider micropores (supermicropores) appear. From these results we can conclude that, by physical activation, it is indeed difficult to prepare ACs with apparent surface areas higher

than $1000 \text{ m}^2/\text{g}$ having simultaneously similar $V_{\text{DR}}(\text{N}_2)$ and $V_{\text{DR}}(\text{CO}_2)$ values. Above $\approx 1000 \text{ m}^2/\text{g}$ physical activation produces an important widening of the porosity.

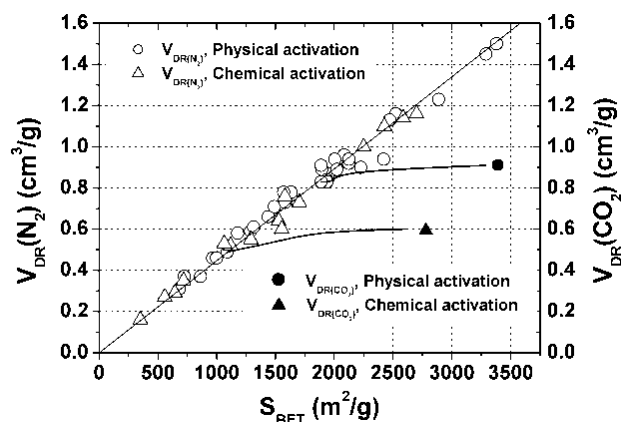


Figure 6. Comparative micropore volume ($V_{\text{DR}}(\text{N}_2)$) and narrow micropore volume ($V_{\text{DR}}(\text{CO}_2)$) evolutions vs apparent BET surface area for samples activated by physical and chemical activation.

3.2. Physical Activation (PA) vs Hydroxide Activation (HA)

The comparison between these two activation processes can also be deduced from Figure 6, where the $V_{\text{DR}}(\text{N}_2)$ and $V_{\text{DR}}(\text{CO}_2)$ are plotted versus the apparent BET surface area for a large series of ACs prepared by KOH activation.

It can be observed that, contrarily to what happened by physical activation, the $V_{\text{DR}}(\text{CO}_2)$ can reach linearity for activated carbons having BET surface areas much higher than $1000 \text{ m}^2/\text{g}$, allowing to prepare ACs with more than $2000 \text{ m}^2/\text{g}$, having simultaneously $V_{\text{DR}}(\text{N}_2) \approx V_{\text{DR}}(\text{CO}_2)$. These results confirm that hydroxide activation develops porosity in a different way than physical activation, and shows an important advantage of the carbon activation by hydroxides.

To strengthen the comparison between physical and chemical activation processes, three ACFs prepared by KOH, NaOH, and CO_2 activation from milled coal tar pitch-derived carbon fibers (Donacarbon S-241 precursor, supplied by Osaka gas Co., Ltd) with similar apparent surface areas have been selected. Table 3 compiles the characterisation results of the three ACFs and Figure 7 presents their PSDs.

Table 3. ACFs prepared by CO_2 , NaOH and KOH

Sample	$S_{\text{BET}} (\text{m}^2/\text{g})$	Yield (%)
CF	---	---
CO_2	2487	6
NaOH	2541	40
KOH	2420	50

Two observations merit to be pointed out: i) the activation yield of the CO_2 activation is low, in comparison with the ones obtained for hydroxide activations, and ii) the PSD

results obtained from the three activation agents show a noticeable dependence on the activation method used, the narrowest one being obtained for KOH, followed by NaOH and, finally, by CO₂.

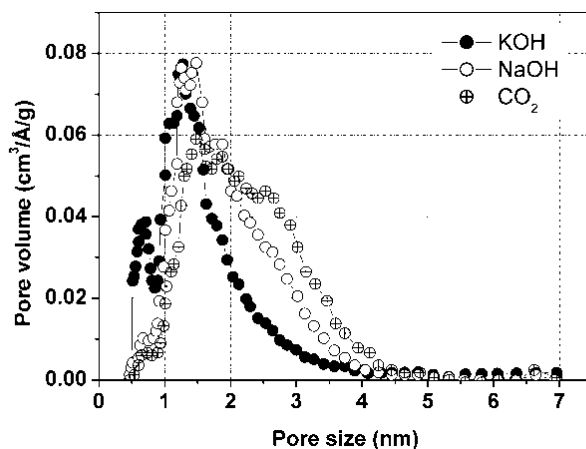


Figure 7. PSDs of these ACs (redrawn from [10]).

In summary, the previous examples show that carbon activation by hydroxides is advantageous over physical activation because, in addition to its higher activation yields, ACs with both high porosity development and narrow PSD can be prepared. These characteristics are very interesting for some specific applications, as it is discussed later on.

Table 4. Commercial ACs prepared from different activation processes

Sample	Activation	S_{BET} (m ² /g)	$V_{\text{DR}}(\text{N}_2)$ (cm ³ /g)	$V_{\text{DR}}(\text{CO}_2)$ (cm ³ /g)
A20, Osaka Gas	Physical act.	2206	0.79	0.43
Kynol ACF-25	Physical act.	1989	0.87	0.62
GF45, Norit	Chemical act. (H ₃ PO ₄)	1718	0.75	0.35
A1100, Westvaco	Chemical act. (H ₃ PO ₄)	1757	0.67	0.36
Maxsorb, Kensai Chemical	Chemical act. (KOH)	3178	1.20	0.69
AX21, Anderson Co.	Chemical act. (KOH)	2513	0.93	0.68
UA*	Chemical act. (KOH)	2122	0.92	0.89

* KOH activated anthracite prepared in the University of Alicante.

The advantage of the hydroxides activation in relation to other activation processes, in terms of porosity and pore size distributions, can also be inferred from Table 4, which compiles the adsorption characteristics of well-known commercial ACs prepared from different activation processes and precursors. These commercial ACs are: two ACFs prepared by physical activation (from Osaka Gas (A20) and from Kynol (ACF-25)), two phosphoric acid activated carbons (from Norit (GF45) and from Westvaco (A1100)), and two KOH activated carbons (Maxsorb3 and AX21). The table also includes a KOH-activated anthracite which was prepared in our laboratory. The selected commercial samples cover apparent BET

surface areas from about 2000 m²/g to 3000 m²/g. From these data, it can be concluded that commercial ACs or the one prepared in our laboratory by KOH activation possess much higher $V_{DR}(CO_2)$ than those obtained by phosphoric acid or by physical activation. For example, the sample prepared in our laboratory has a BET surface area above 2000 m²/g and, interestingly, similar $V_{DR}(N_2) \approx V_{DR}(CO_2)$.

3.3. General Features of the Phosphoric Acid Activation (PAC)

The main feature of the phosphoric acid activation is the development of ACs with a large volume of supermicropores and mesopores [64,65]. These features lead to special applications (e.g., in gasoline car canisters for gasoline evaporation control [66]). Using a series of ACs prepared by phosphoric acid or alkaline hydroxide (KOH or NaOH) activation, their N₂ (77 K) and CO₂ (273 K) adsorption data are compared, in terms of porosity development.

3.4. Phosphoric Acid Activation (PAC) vs Hydroxide Activation (HA)

Using a given precursor, its activation by H₃PO₄, NaOH and KOH is compared in the present section. The precursor is a coconut fiber matting (CFM) waste, generated in the commercial production of coconuts (*Cocos nucifera*) in Salvador. In phosphoric acid activation, the precursor has been impregnated drop by drop with a given H₃PO₄ solution to prepare different H₃PO₄/precursor ratios (1.7/1, 3.0/1, and 4.1/1) [67], whereas for NaOH and KOH activations three hydroxide/precursor ratios have been used (1/1, 1.5/1 and 2/1) and the physical mixing method has been employed [12].

Figure 8a presents the N₂ adsorption isotherms (77 K) for ACs activated with NaOH and KOH (ratios from 1/1 to 2/1) and Figure 8b shows the isotherms of the ACs prepared with H₃PO₄ at three ratios (from 1.7/1 to 4.1/1). As the activating agent/precursor ratio increases, the resulting adsorption capacity increases for the three activating agents. However, they develop differently the samples' porosity, as evidenced by the different isotherm shapes: type I for samples activated with hydroxides (microporous samples) and type I + IV for samples activated with H₃PO₄ (microporous and mesoporous samples).

Table 5 compiles the textural properties of activated carbons prepared by activation with NaOH, KOH or H₃PO₄. It can be seen that the three activating agents used are very effective for developing high porosity, especially NaOH. The achieved porosities are remarkable, considering the low activating agent/precursor ratios used.

Table 5. Characteristics of ACs obtained by chemical activation with NaOH, KOH and H₃PO₄

Activating agent	Sample CFM	S _{BET} (m ² /g)	V _{DR} (N ₂) (cm ³ /g)	V _{DR} (CO ₂) (cm ³ /g)	V _{Meso} (cm ³ /g)
NaOH	Na1/1	1437	0.62	0.45	0.12
NaOH	Na1.5/1	1927	0.82	0.54	0.17
NaOH	Na2/1	2622	0.97	0.57	0.41
KOH	K1/1	1178	0.58	0.46	0.04
KOH	K2/1	1888	0.91	0.76	0.05
KOH	K1.5/1	1570	0.78	0.62	0.04
H ₃ PO ₄	P1.7/1	2285	0.94	0.48	0.47
H ₃ PO ₄	P3.0/1	2320	0.89	0.46	0.67
H ₃ PO ₄	P4.1/1	2569	1.01	0.49	0.86

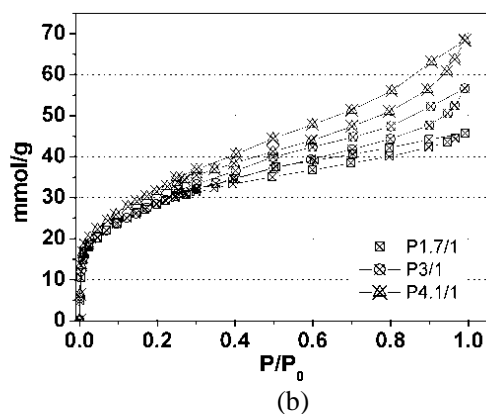
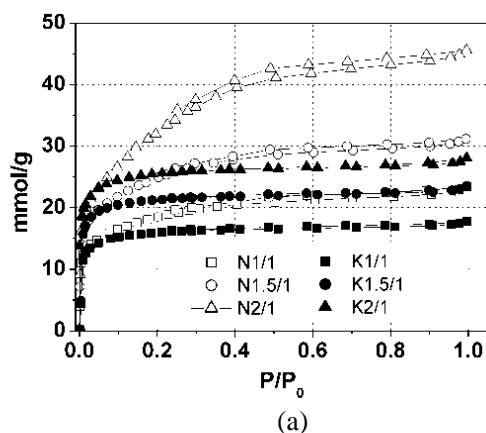


Figure 8. N₂ adsorption isotherms at 77 K for ACs prepared from coconut fiber matting (CFM) activated by (a) NaOH or KOH, and (b) H₃PO₄.

Also, it can be observed that the development of narrow microporosity increases in the order: H₃PO₄ < NaOH < KOH, whereas the mesoporosity develops in the order: KOH < NaOH < H₃PO₄, being especially relevant for H₃PO₄ activation. For a better comparison of

these activation results, Figure 9 presents the PSDs of some selected ACs which have similar S_{BET} surface areas (K2/1, N1.5/1 and P1.7/1 samples). The PSDs clearly confirm the conclusions deduced from the N_2 adsorption isotherm shapes. Thus, the ACs prepared with H_3PO_4 have the widest pore size distributions, whereas the ACs obtained with NaOH and, especially, KOH have narrow pore size distributions.

From the previous results we can conclude that NaOH, KOH and H_3PO_4 are good activating agents which allow to obtain highly porous ACs. However, they develop different kinds of porosity. Thus, large mesopore volumes are obtained with H_3PO_4 activation, whereas narrow microporosity is obtained with KOH.

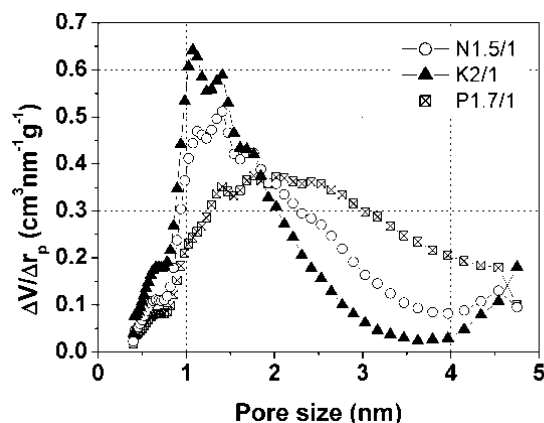


Figure 9. Pore size distributions of CFM samples prepared with KOH, NaOH and H_3PO_4 having similar BET surface area (around $2000 \text{ m}^2 \text{ g}^{-1}$).

In order to improve the ACs performance according to their application, it is necessary to develop a suitable porosity. For example, the development of narrow microporosity is important in applications such as volatiles organic compounds (VOCs) removal at low concentration [27,68,69] or gas storage [59,60] and high development of mesoporosity is interesting in gasoline vapour recovery [66].

4. The use of ACs Prepared by Hydroxide Activation for Selected Potential Applications

The narrow microporosity (pores $< 0.7 \text{ nm}$), which can be well developed with the activation by alkaline hydroxides (especially with KOH), is the controlling key for some specific applications of the ACs, as it will be commented in the following sections.

4.1. VOCs Removal at Low Concentration

As an example, Figure 10a plots the relationship between benzene adsorption capacity at 200 ppmv in helium (at 25°C) and the volume of narrow micropores for a series of ACs. These samples comprise a group of granular and powdered activated carbons, as well as activated carbon fibers. Most of them were prepared by chemical activation with hydroxides,

and the activated carbon fibers were prepared by steam or carbon dioxide activation [68,69]. From the results of this figure, it can be seen that the development of high narrow micropore volumes (pore size < 0.7 nm) is highly beneficial for VOCs removal.

Figure 10a seems to suggest, at a first glance, that those adsorbents with fibrous morphology present higher VOCs removal capacities than the others. However, the surface oxygen groups content of the materials have to be taken into account since, as discussed elsewhere, the presence of surface oxygen groups decreases VOCs removal [27,68,69].

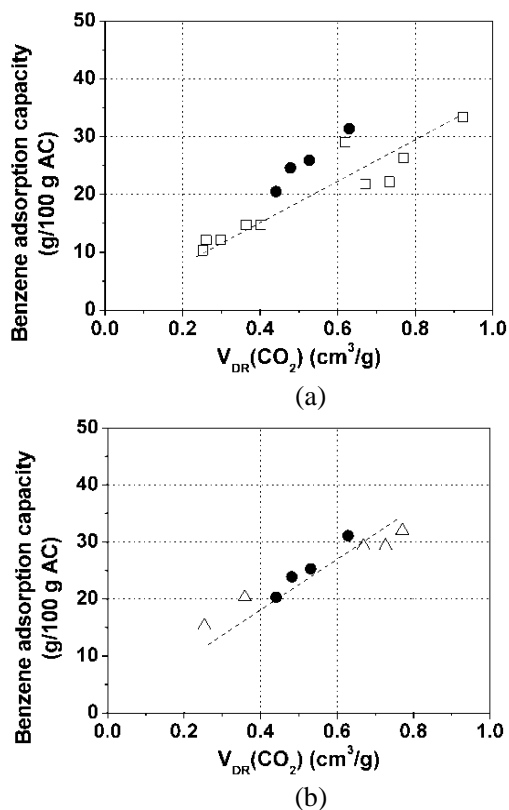


Figure 10. Relationship between benzene adsorption capacity, at 200 ppmv (and 25°C), and the volume of narrow micropores, redrawn from [68, 69], for: (a) ACFs (black circles) and pristine ACs (open squares) and (b) ACFs (black circles) and heat-treated ACs (open triangles).

Thus, results from Figure 10a can be understood considering that these ACFs, which present higher benzene adsorption, have lower oxygen surface groups than the other materials tested. This can be confirmed in Figure 10b, in which all the AC samples (except ACFs) have been heat-treated to reduce their surface oxygen content.

Because all the samples in Figure 10b have similar oxygen contents, benzene adsorption depends only on their corresponding narrow micropore volumes [68].

Therefore, it is necessary to further improve the development of larger narrow micropore volumes for getting even better adsorption capacities. These results also emphasize the importance of having a low content of surface oxygen groups in order to enhance low-polarity VOCs adsorption at low concentration.

4.2. Electricity Storage (EDLC-Supercapacitor-)

The electric double layer capacitor (EDLC) is an increasingly popular energy storage device. Due to its high energy and power densities, it bridges the gap between batteries and classical electric capacitors [70]. An example of the application of alkaline hydroxides to prepare suitable ACs as electrodes for supercapacitors will be presented using activated carbon nanofibers (ACNFs) [71].

These materials were prepared from polymer blend-based CNFs which were activated with potassium hydroxide at different KOH/precursor ratios (from 0.5/1 to 3/1), as shown in Figure 11.

Their use as supercapacitor electrodes has been studied in cells having different electrolytes. Figure 11b presents their specific capacitance versus their apparent BET surface area in two electrolyte solutions (aqueous KOH, and aqueous H₂SO₄) [71].

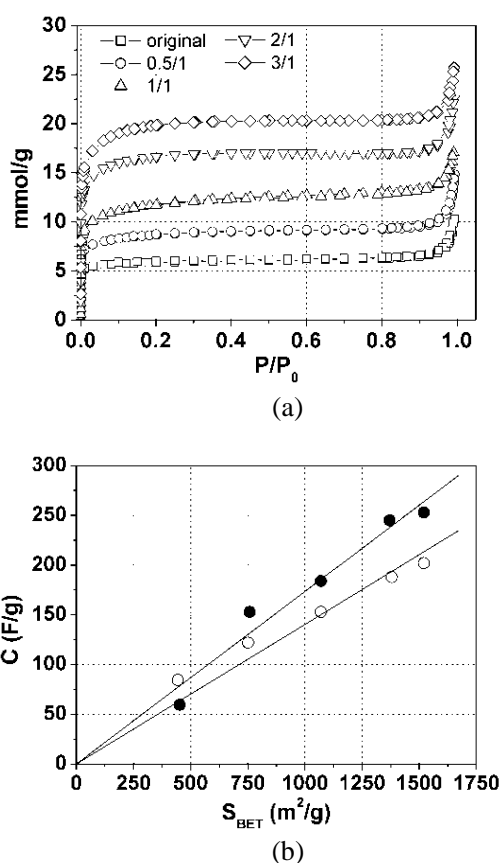


Figure 11. (a) N₂ adsorption isotherms, and (b) specific capacitance of ACNFs measured at 1mAc^{m-2} (C) vs. BET specific surface area (S_{BET}) in two electrolytes: H₂SO₄ (black circles) and KOH (open circles) (redrawn from [71]).

It can be seen that an increase in the KOH/CNFs ratio causes an enhancement of the adsorption capacity. Furthermore, a linear relationship exists between the apparent BET surface area and the specific capacitance, as it is shown in Figure 11b, which is also

confirmed by results in the literature [72]. Considering that the apparent surface areas of these samples are $< 1700 \text{ m}^2/\text{g}$, their capacitance results are high, presumably due to their relatively high conductivity. Thus, they present enhanced specific capacitances, in relation to conventional ACFs (fibers with diameters of about $10 \mu\text{m}$), because of their nanometric size diameters. Additionally, their capacitances are less dependent on the current density in comparison with conventional ACFs. These advantages, useful for EDLC application, were attributed to a faster adsorption-desorption rate in the micropores of the ACNFs, due to their smaller diameters [71, 73].

4.3. Gas Storage

The high pressure storage of gases such as hydrogen, methane, carbon dioxide and others has a special interest for their potential use as fuels (e.g., hydrogen) or in the case of carbon dioxide for its capture and truck transport to its final storage point, for example in a geological reservoir. The storage principle of these gases is the use of a high pressure adsorption process (or physisorption), as a supercritical gas (e.g., H_2) or as a subcritical one (e.g., CO_2). Such adsorption process has some advantages: a high storage capacity (very much depending on the surface area, porosity and pore size of the material), fast kinetics of storage and release (reversibility), a short refueling time, a low heat evolution and an efficient cyclability. As shown above, ACs prepared by hydroxides activation present interesting properties such as very high porosity, different morphologies and tunable characteristics (sizes and shapes). Additionally, they possess good chemical stability, a suitable packing density and have relatively low cost.

4.3.1. Hydrogen Storage by High Pressure Adsorption

For a future energy sector, hydrogen is considered an ideal secondary energy carrier and a clean alternative to other fuels. For example, in fuel cells it can be used to provide electricity with high efficiency, emitting only water. However, its storage is one of the main drawbacks, due to its low density. In order to use hydrogen as a fuel in transportation, a number of different technologies are considered today [74-77]. Among them, the high pressure storage in adsorbent materials is a promising technology. Of course, the type of adsorbent plays the most relevant role, ACs being the most suitable candidates [75].

Two main alternatives can be used for storing hydrogen by high pressure adsorption; i) at room temperature and very high pressures (from 10 MPa to 70 MPa) and/or ii) at low temperatures (cryogenic temperatures) and moderate pressures ($< 4 \text{ MPa}$).

As an example of the performance of the ACs to store hydrogen, we have selected the results obtained with the Donacarbono SL-242 carbon fiber (CF), activated with KOH at different KOH/CF ratios that were commented before (see Table 2). Such series of KOH-activated carbon fibers cover a wide range of porosity, providing high volumes of narrow micropores ($< 0.7 \text{ nm}$), which are especially important to store hydrogen.

The hydrogen adsorption isotherms of the investigated materials, measured at 298 K, are shown in Figure 12a. The unactivated fiber precursor already adsorbs over 0.4 wt%. By chemical activation with KOH, the adsorption amount can be increased significantly. The hydrogen adsorption amount increases with the KOH/fiber ratio up to a ratio of 4/1, reaching

the maximum adsorption amount of 1.1 wt%. When the ratio is further increased to 5/1, no significant increase in hydrogen adsorption is observed. Probably, this is due to a destruction of the narrow microporosity which controls the hydrogen uptake at room temperature and 20 MPa.

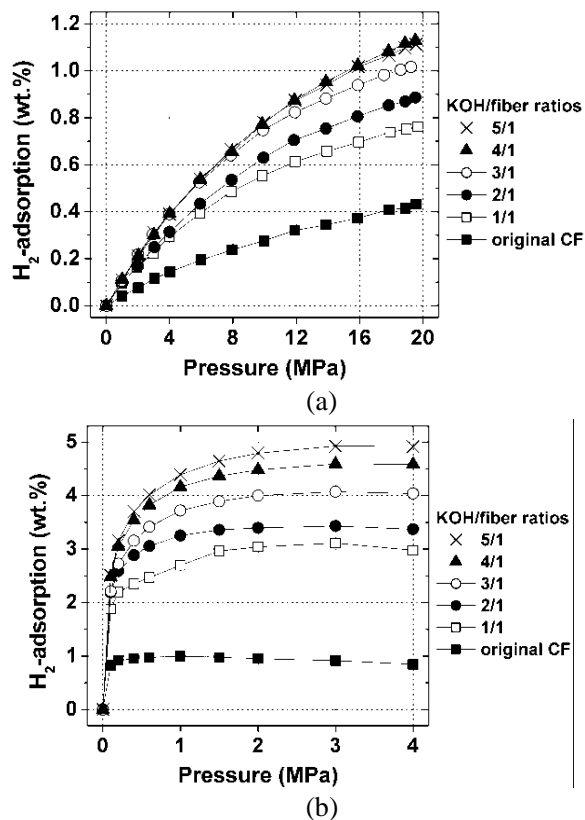


Figure 12. Gravimetric H₂ excess adsorption measured for an unactivated CF, and ACFs that were activated with KOH using KOH/fiber ratios between 1/1 and 5/1 (a) at 298 K, and (b) at 77 K (redrawn from [63]).

The hydrogen adsorption isotherms at 77 K and up to 4 MPa of the same samples are shown in Figure 12b. The unactivated carbon fiber already adsorbs 1 wt% of hydrogen at 77 K, due to a small amount of narrow microporosity. As expected, the adsorption increases significantly when the precursor is chemically activated with KOH. Thus, the adsorption capacities of the activated samples continuously increase with the KOH/fiber ratio. The highest adsorption amount of around 5 wt% is reached for a KOH/fiber ratio of 5/1.

It is a common practice to try to find correlations between porosity and hydrogen adsorption [63, 78-87]. In Figure 13a, the gravimetric H₂ adsorption values, obtained at 298 K and 20 MPa, are plotted versus the narrow micropore volume, $V_{DR}(\text{CO}_2)$. The hydrogen uptake values were taken from Figure 12, as well as from other ACF materials [72]. A linear relationship can be observed between $V_{DR}(\text{CO}_2)$ and the gravimetric hydrogen uptakes at room temperature. This is in agreement with findings from previous studies [63, 78-80, 87, 88].

In the case of hydrogen adsorption at 77 K and 4 MPa, previous studies found a better correlation with the total microporosity (< 2 nm) [63,78,79]. Accordingly, in Figure 13b, the maximum adsorption amounts at 77 K are plotted versus the total micropore volume, $V_{DR}(N_2)$. Also at 77 K the expected linear relationships with micropore volumes larger than $0.1 \text{ cm}^3/\text{g}$ can be observed, being in agreement with previously reported results [63,78-83,87].

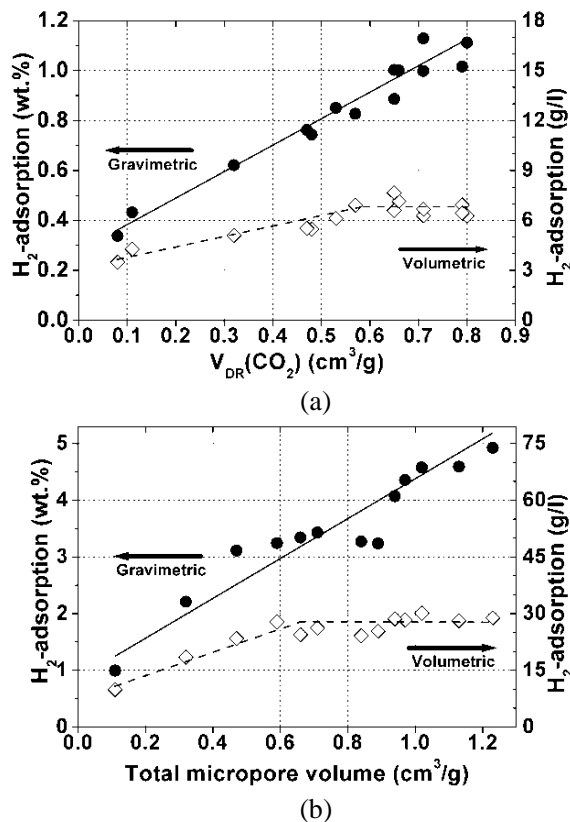


Figure 13. Maximum H_2 excess adsorption (redrawn from [63]) (a) at 298 K and up to 20 MPa vs the volume of narrow micropores ($V_{DR}(CO_2)$) and (b) at 77 K and up to 4 MPa vs the total micropore volume ($V_{DR}(N_2)$) for a large number ACFs. The H_2 excess adsorption is given on a gravimetric (left axis), as well as on a volumetric basis (right axis).

In addition to the gravimetric adsorption amounts, also the excess adsorption on a volumetric basis is correlated in Figures 13a and 13b. The volumetric adsorption amounts were calculated by multiplying the gravimetric values by the corresponding packing densities from Table 2. In contrast to what was found for the gravimetric values at both adsorption temperatures, no linear trend can be observed for the volumetric adsorption amounts. Interestingly, these results clearly indicate that also adsorbents with less developed porosity are able to obtain high volumetric adsorption values, if they have high densities. In volumetric terms, an optimum relation between developed porosity and packing density needs to be found.

Until now, only gravimetric and volumetric excess adsorption of H_2 has been discussed. However, for practical applications, it is of interest to determine the amount of hydrogen that can be stored inside a determined tank design. Real adsorbents always contain certain amount

of void space, and its contribution to the total storage needs to be taken into account in order to estimate the total storage capacity of a material. Therefore, the effort has to be made to reduce the void space as much as possible by increasing the packing density of the material. The void space can be estimated by means of the following formula: $V_{\text{Void}} = 1 - (\rho_{\text{Pack}}/\rho_{\text{Skel}})$ [63,78,79,87,89,90], where V_{Void} is the void space, ρ_{Pack} the packing density, and ρ_{Skel} the skeleton density of the material. When applied to the adsorption isotherms in Figure 12, high total hydrogen storage capacities are obtained: 17.1 g/l at 298 K, and 38.6 g/l at 77 K, respectively. Clearly, not only the porosity of the material, but also its packing density is of particular importance for the total amount of hydrogen stored. Following with this concept of total hydrogen storage, all the data shown in Figure 13 reaches considerably higher total hydrogen capacities than the plotted values. As an example, the two highest values obtained at 298 K (1.1 wt%) and at 77 K (4.9 wt%), give total hydrogen capacities of 2.8 wt% and 6.4 wt%, respectively. All these results indicate that interesting hydrogen storage materials can be synthesized by carbon fibers activation with hydroxides, although more work is required to further improve them.

4.3.2. Carbon Dioxide Storage by High Pressure Adsorption

According to the IPCC's report, there are unequivocal evidences which indicate that the climate-change is a reality attributable to the human activity [91].

Nowadays, carbon capture, storage and transport (for short-term CO₂ storage in CCS technologies) are some of the technological options that are being studied in order to control CO₂ emissions to the atmosphere and, hence, to reduce climatic change effects [91].

Among them, high pressure adsorption on porous materials has a special interest and, hence, both the properties of the adsorbents (mainly surface area, micropore volume and narrow micropore volume) and the storage pressure used will control the final storage capacity. The use of solid adsorbents (porous materials) has been established as a potentially valid alternative for the CO₂ capture.

There is a large variety of available porous materials and, among them, activated carbon materials have emerged as promising adsorbents within CCS technologies [92-98]. This is due to their unique properties such as high pore volumes and surface areas, high stability and low chemical reactivity [56]. These properties make activated carbons attractive materials, not only in the CO₂ capture, but also in its transportation.

Capture and discontinuous transport of CO₂ have been investigated for years in our research group by using activated carbons obtained by different activation procedures (physical and chemical activation). Our results conclude that those ACs prepared by alkaline hydroxides show significant advantages for this application since their textural properties and porosity can be perfectly controlled and tailored, as it has been previously discussed.

In this section we illustrate the CO₂ uptake at room temperature (298 K) using a large number of activated carbons prepared from several precursors (i.e., lignocellulosic precursors and coals) and different activation variables (e.g., the use of NaOH or KOH as activating agents or the hydroxide/precursor ratios).

Consequently, these ACs have a wide variety of textural properties which allow to analyze the relationship between the amount of CO₂ adsorbed and their textural properties. Figure 14 presents their large range of adsorption capacities: (a) narrow micropore volume

($V_{DR}(CO_2)$), (b) total micropore volume ($V_{DR}(N_2)$), and (c) BET surface area (ranging from about $500 \text{ m}^2/\text{g}$ to more than $3000 \text{ m}^2/\text{g}$).

The high pressure device and the procedure used to store CO_2 on ACs are described elsewhere [78,99]. Figure 15 presents the storage results obtained in these ACs at different pressures (up to 4 MPa), showing the influence that the sample properties have on the results. Thus, Figure 15a relates the narrow micropore volume with the CO_2 uptake. It shows that the adsorption capacity controls the uptake and that a well defined linear relationship exists between these two parameters when the pressure range is limited to 0.1 and 1 MPa. Hence, at this pressure range the amount of CO_2 adsorbed is controlled by the narrow micropore volume ($< 0.7 \text{ nm}$).

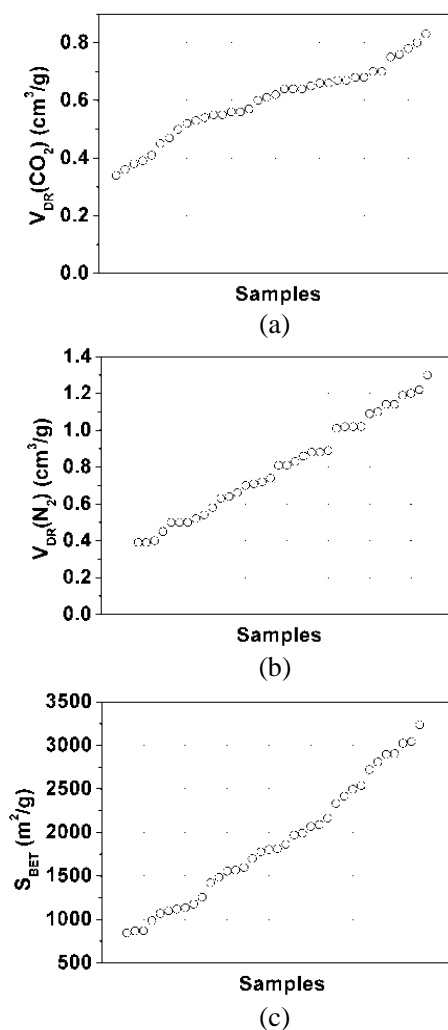


Figure 14. Textural properties obtained from the characterization of the chemically activated carbons. (a) narrow micropore volume, (b) total micropore volume, and (c) BET surface area.

For pressures higher than 1 MPa, such linear tendency is not observed anymore (see the bad defined correlation for 4 MPa). This indicates that, at higher pressures, the filling of

larger pores is taking place. This is confirmed in Figure 15b, where a linear relationship between the CO₂ uptake and the total micropore volume (or apparent BET surface area) is observed for the higher pressure range studied (from 1 to 4 MPa). In summary, these results show that CO₂ uptake at room temperature is sensitive to both, the pore size distribution and the storage pressure used. From an application point of view, the density of the ACs is needed to determine their CO₂ storage per unit volume. ACs prepared by hydroxide activation (as shown above) present interesting packing densities (i.e., density obtained by applying a certain pressure). An example is shown in Figure 16, where the total, the adsorbed and the compressed CO₂ are plotted per unit of volume (g CO₂/l).

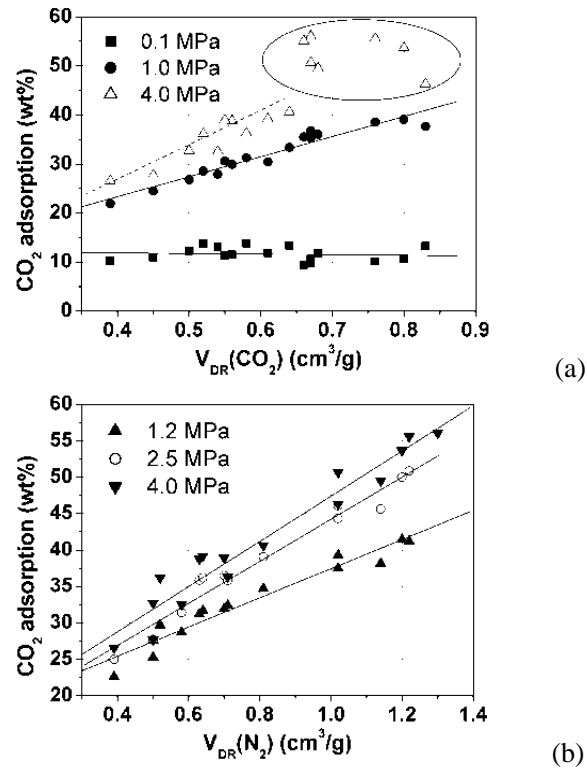


Figure 15. Influence of the different textural properties as a function of the pressure used for the adsorption process of CO₂ at 298 K versus (a) narrow micropore volume, $V_{DR}(CO_2)$, and (b) total micropore volume, $V_{DR}(N_2)$.

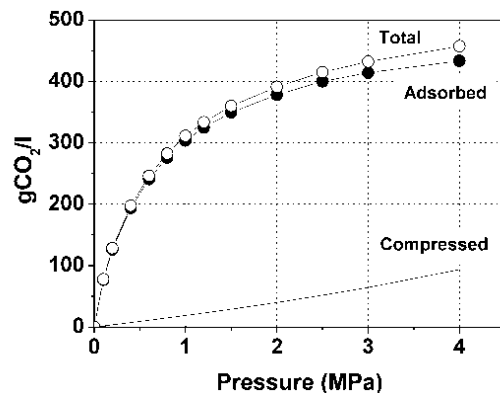


Figure 16. Comparison between CO₂ stored by compression and by adsorption on an activated carbon.

The amount of CO₂ stored per unit of volume in a tank vessel that contains activated carbon is higher than the CO₂ stored in the same tank by compression (empty vessel). For example, at 2 MPa, a tank filled with activated carbon could store almost 400 g/l, while the amount stored by compression would be only 40 g/l. Thus, the adsorption process can store more than 9 times the amount stored by compression, which is an important advantage for transport. At 4 MPa the CO₂ storage is indeed large, reaching for some monolithic samples 500 g/l.

5. Conclusion

In addition to the many large scale uses of alkaline hydroxides, this article analyzes and claims attention to a relatively new one: the hydroxide activation of carbon materials.

It is based on the strong reactivity of NaOH and KOH when they are mixed and heat-treated with carbon precursors. These strong chemical alkaline bases react with most carbon precursors, modifying their original porosities through a solid-liquid redox reaction. In this reaction, carbon is oxidized to carbonate and the hydroxide is mainly reduced to alkaline metal and hydrogen. Hence, both reactants are converted to hydrogen, alkaline metals, alkaline carbonates and to a reacted carbon product. Such remaining carbon product is due to the low hydroxide amount used, in relation to the stoichiometry of the carbon-hydroxide reaction.

After washing the reaction products, a super class activated carbon (AC) can be obtained from the resulting carbon material. The main features of the ACs obtained by this process are their high adsorption capacities and their narrow pore size distributions, which make them suitable for different applications. As it happens in most chemical reactions, the kinetics and the extent of the hydroxide-carbon reaction are generally affected by many variables.

However, contrarily to most chemical reactions, the key point of such reaction is the porosity characteristics of the remaining carbon. Hence, this article analyzes, in different sections, how the most relevant reaction variables affect the porosity of the prepared ACs.

The main conclusions which can be extracted from the analyzed variables (among others, the reactivity of the carbon precursor, the nature of the hydroxide and the hydroxide/carbon ratio) are: 1) all of them have important effects on the reaction extent and on the carbon activation degree, which determine the properties of the resulting activated carbons. 2) The

porosity development of the ACs prepared by such hydroxide activation process is quite singular in terms of porous texture and pore size distribution. 3) When compared with other activation processes, the characteristics of the resulting ACs can be controlled much more efficiently by the activation with hydroxides. 4) NaOH, as well as KOH, are among the most powerful known activating agents to prepare super high quality ACs and 5) the unique characteristics of the ACs prepared by hydroxide activation (high microporosity including a well developed narrow micropore volume) are very useful for most of the applications related to energy and environmental concerns which are discussed in this article (e.g., VOCs removal, supercapacitors, hydrogen storage, as well as capture, storage and transport of carbon dioxide).

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