J Mater Sci (2009) 44:6583–6590
DOI 10.1007/s10853-009-3918-5

Studying chemical activation in carbon xerogels

Leire Zubizarreta · Ana Arenillas · José Juan Pis · Jean-Paul Pirard · Nathalie Job

Received: 21 November 2008 / Accepted: 19 September 2009 / Published online: 8 October 2009

Abstract Chemical activation of carbon xerogels synthesized with different resorcinol/sodium carbonate molar ratios (*R*/*C*) was performed using alkaline hydroxides (KOH and NaOH). The effect of *R*/*C* and the type and amount of alkaline hydroxide on the final properties of the activated carbon xerogels were evaluated. It was found that, in general, both hydroxides produce an increase in microporosity regardless of the *R*/*C* value chosen, without altering the meso/macroporosity developed during the synthesis. KOH develops the microporosity of micro-mesoporous carbon xerogels more efficiently than NaOH, and for samples of large pore size (micro-macroporous samples), a similar textural development was observed for both hydroxides. However, when NaOH is used as activating agent, it is more difficult to eliminate residual Na from the activated carbon xerogels.

Introduction

Carbon gels display very interesting structural and performance characteristics. The resultant nanostructure is very sensitive to the synthesis and processing conditions [1, 2]. This offers the possibility of designing and tailoring the materials to fit specific applications. The effects of various synthesis conditions have been tested, and it has been shown that it is possible to tailor the mesopore and macropore structure of carbon gels [2, 3]. However, microporosity, which is developed during the carbonization step, is restricted by constant and rather low volumes ($\sim 0.25\ \mathrm{cm}^3\ \mathrm{g}^{-1}$). For some applications, such as hydrogen storage or supercapacitors, it would be useful to be able to increase and control microporosity development.

Chemical activation with alkaline hydroxides has been established as a good method for many carbon materials [4–7]. However, several works have shown that the nature of the chemical activating agent may influence the development of microporosity [8–12] and that the selection of alkaline hydroxide is highly dependent on the type of carbon material used. In some cases, KOH is more active in the production of microporosity than NaOH (i.e. anthracite coals [4], carbon nanotubes [9]), or vice versa (i.e. isotropic carbon fibers [8]). Consequently, in order to optimize the development of microporosity by chemical activation of carbon materials, the effect that the different alkaline hydroxides have on these materials needs to be studied.

In this work, the chemical activation of carbon xerogels employing two different alkaline hydroxides (KOH and NaOH) was performed. The effect of the nature and amount of activating agent used on two carbon xerogels with different textural properties was studied. The aim of this work was to determine the most suitable conditions and procedures for increasing the micropore volume of carbon xerogels.

Experimental

Synthesis of carbon xerogels

Aqueous organic gels were synthesized by polycondensation of resorcinol (*R*) with formaldehyde (*F*) in water (*W*)

L. Zubizarreta · A. Arenillas · J. J. Pis
Instituto Nacional del Carbon, CSIC, Apartado 73,
33080 Oviedo, Spain

J.-P. Pirard · N. Job (✉)
Laboratoire de Génie Chimique, Université de Liège,
Institut de Chimie B6a, Sart-Tilman, 4000 Liège, Belgium
e-mail: Nathalie.Job@ulg.ac.be

following a method already applied elsewhere [2]. Sodium carbonate (*C*) was used as basification agent. All the gels were synthesized in the following conditions: the *R*/*F* molar ratio was chosen to be equal to the stoichiometric value (0.5) and the dilution ratio, *D* (i.e., the total solvent/reactant molar ratio), was fixed at 5.7. Note that "total solvent" includes added deionized water, and the water and methanol contained in formaldehyde solution, while the "reactant" refers to resorcinol and formaldehyde. Methanol is a stabilizer that prevents the formaldehyde molecules from undergoing polymerization during storage. Two distinct organic gels were synthesized using different *R*/*C* molar ratios: 300 and 1000, which correspond to mesoporous and macroporous carbon xerogels, respectively [2].

Resorcinol (VWR International, 99 wt%) and sodium carbonate (UCB, 99.5 wt%) were first solubilized in deionized water in a sealed flask under magnetic stirring. After dissolution, formaldehyde (Aldrich, 37 wt% in water, stabilized by 10–15 wt% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. The solution was then placed in an oven at 85 °C for 72 h to undergo gelation (after 30 min to 2 h) and ageing.

Afterwards, the obtained aqueous gels were dried by vacuum evaporation without any pre-treatment. The unsealed flasks were kept at 60 °C and the pressure was progressively reduced from 10^5 Pa to 1.2×10^3 Pa. The drying procedure was performed over a period of 20 h. The samples were then heated to 150 °C at 1200 Pa and kept at this temperature and pressure overnight.

After drying, the gels were pyrolyzed at 800 °C under nitrogen flow in a tubular oven; the procedure was the same as that used in previous works [2, 3]. The following heating program was employed: (i) ramp at 1.7 °C min^{-1} to 150 °C and hold for 15 min; (ii) ramp at 5 °C min^{-1} to 400 °C and hold for 60 min; (iii) ramp at 5 °C min^{-1} to 800 °C and hold for 120 min; and (iv) cool slowly to room temperature.

Activation of carbon xerogels

Carbon xerogels, which are the carbon precursors, were activated chemically with KOH or NaOH. In order to study the effect of the amount of the activating agent, four values of activating agent/carbon precursor mass ratio, *A*/*P*, were used: 1, 2, 3 and 4 g/g. The activating agent and carbon precursor were mixed by the wet impregnation method. Thus, 3.75 g of carbon precursor was mixed by magnetic stirring with a solution of 3.75, 7.5, 11.25 and 15 g of KOH or NaOH in 94 cm^3 of water in order to obtain the required *A*/*P* mass ratio (i.e. 1, 2, 3 and 4 g/g, respectively). The mixtures were stirred continually at 85 °C until the water was eliminated and then carbonized at 750 °C under nitrogen flow. The heating rate was 5 °C min^{-1} and the nitrogen flow rate was fixed at 0.6 mmol s^{-1}. The samples were maintained at the maximum temperature for 2 h and then were allowed to cool down slowly by natural convection.

The samples were then washed. First, the solid was immersed in HCl 5 M solution and the mixture was heated at 85 °C for 30 min. Then, the acid solution was removed by filtration, after which the solid remaining in the filter was rinsed with distilled water until the pH of the drained solution was 6. Finally the samples were dried at 110 °C overnight.

Sample designation

Throughout the text, the samples are denoted as follows: in the case of the activated samples, the first letter refers to the type of activating agent (K for KOH and Na for NaOH); this is followed by the value of the *R*/*C* molar ratio and finally the *A*/*P* ratio. For example, sample Na-300-1 corresponds to the following sequence: the chemical activation of carbon xerogel synthesized with *R*/*C* molar ratio of 300, using NaOH with $A/P = 1$. In the case of the unactivated samples, the carbon xerogels synthesized with an *R*/*C* molar ratio of 300 and 1000 are denoted as CX-300 and CX-1000, respectively.

Characterization of the carbon samples

Textural characterization of the samples was carried out by carbon dioxide adsorption–desorption at 0 °C in a TriStar 3000 from Micromeritics. The nitrogen adsorption–desorption isotherms were performed at −196 °C in a Sorptomatic Carlo Erba 1900 from Fisons Instruments. The use of carbon dioxide adsorption at 0 °C for the textural characterization of the narrow micropores has been established as an effective procedure [13, 14]. Carbon dioxide adsorption occurs in pores smaller than 0.7 nm, while nitrogen does not easily enter such small pores. A combination of nitrogen and carbon dioxide adsorption isotherm data provides interesting complementary information about the entire micropore range. The Dubinin–Radushkevich (DR) method [15] was applied to the carbon dioxide and nitrogen adsorption isotherms in order to obtain the narrow micropore volume, $V_{\mathrm{DUB-CO_2}}$, and the wide micropore volume, $V_{\mathrm{DUB-N_2}}$, respectively. The BET surface area, S_{BET}, was also evaluated from the nitrogen adsorption isotherms [16]. The maximum pore diameter, $d_{\mathrm{p,max}}$ (i.e., the pore diameter limit below which pores represent 95% of the total pore volume), was deduced from the pore size distribution by applying the Broekhoff-de-Boer method to the adsorption branch of the nitrogen isotherm [17]. The pore volume at saturation, V_{p}, was also calculated. In the case of the microporous and/or mesoporous materials,

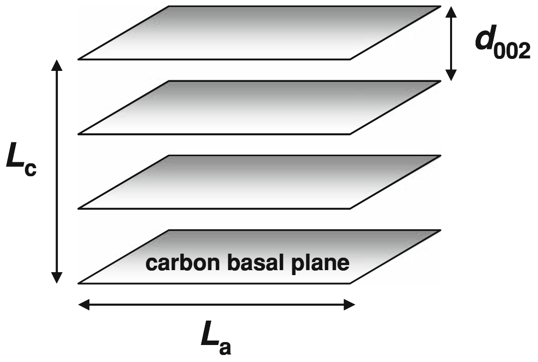

Fig. 1 Crystallographic parameters d_{002}, L_a and L_c of a carbon crystallite

V_p corresponds to the total void volume of the material, V_v. However, in the case of the macroporous samples, nitrogen adsorption is not accurate enough to obtain the real total pore volume, due to the large error margin at $p/p_0 = 1$. In this case, mercury porosimetry was used to determine the total void volume, and the maximum pore size was deduced from Washburn's equation [18]. The measurements were performed in a Carlo Erba Porosimeter 2000 after outgassing at 10^{-3} Pa for 2 h. However, Hg measurements are limited to pores larger than 7.5 nm. Since the volume of pore sizes ranging from 2 to 7.5 nm was quite low in all macroporous samples (<0.1 cm^3/g), the total pore volume, V_v, was taken to be equal to the sum of V_{Hg} and V_{DUB-N_2}.

The morphology and structure of the samples was evaluated by X-ray diffraction. The X-ray diffractograms were collected by a Bruker D8 Advance diffractometer equipped with a Göbel mirror and a Cu Kα radiation tube ($\lambda = 0.15406$ nm). Scherrer's equation [19] was used to calculate the different crystallographic parameters (i.e. L_c, d_{002} and L_a, see Fig. 1). L_c, the layer dimension in the direction perpendicular to the carbon basal planes, and d_{002}, the interlayer distance, were obtained from the (002) diffraction peak. L_a, the layer dimension in the direction parallel to the basal planes, was calculated from the (101) diffraction peak.

The chemical composition of the samples was measured by elemental analysis using combustion/pyrolysis processes and element detection by infrared. The ash content of the carbons was obtained by weighting after complete combustion in air.

Results

Table 1 shows the textural properties of the carbon xerogels activated by means of NaOH and KOH. In general, chemical activation of carbon xerogels by means of alkali hydroxides leads to development of microporosity: S_{BET} and the micropore volume, V_{DUB-N_2}, increase, as does V_{DUB-CO_2}. However, Table 1 shows that when low amounts of activating agent are used ($A/P \leq 2$) the values of S_{BET} decrease for some activated carbon xerogels. This was only observed in carbon xerogels with a mesopore size of around 10 nm (i.e. K-300-2, Na-300-1 and Na-300-2), their surface areas decreasing from 640 (CX-300) to 450, 470 and 300 $m^2\ g^{-1}$ respectively. In addition, the increase in S_{BET} with the A/P ratio is limited: in some cases, a slight decrease in S_{BET} is observed when the A/P increases from 3 to 4 (K-300-3 and K-300-4: 1540 and 1390 $m^2\ g^{-1}$; Na-1000-3 and K-1000-4: 1720 and 1430 $m^2\ g^{-1}$).

Figure 2 shows the N_2 adsorption–desorption isotherms of activated carbon xerogels synthesized with $R/C = 300$ and 1000, and activated with NaOH or KOH at $A/P = 3$. As discussed above with reference to Table 1, the isotherms show that, when activated by these hydroxides, the micropore volume increases, as the volume of N_2 adsorbed at low relative pressure increases. However, the mesoporosity developed during the synthesis step, and present in the material after drying and pyrolysis, remains intact. This is confirmed by the shape of the N_2 isotherms which remains unaltered: type IV isotherm with hysteresis [20] in the case of the carbon xerogels synthesized with $R/C = 300$ corresponding to the mesoporous materials (see Na-300-3 and K-300-3 in Fig. 2a) and type II isotherms [20] in the case of the carbon xerogels synthesized with $R/C = 1000$ corresponding to the macroporous materials (see Na-1000-3 and K-1000-3 in Fig. 2b). However, in order to confirm whether the macroporosity remains intact, the use of N_2 adsorption is not enough and characterization by Hg porosimetry should also be applied. Table 1 shows the macropore sizes evaluated from the Hg porosimetry curves for samples activated with NaOH and KOH. The macropore size remains quite similar for $A/P = 0$, 1, 2 and 3 for both activating agents. However, increasing A/P up to 4 leads to an increase of the macropore size and size range (120–400 nm), indicating that too high amounts of activating agent lead to a degradation of the carbon 3D network.

With respect to the nature of the activating agent, it can be seen that the development of porosity is similar when NaOH or KOH is used. In general, when mesoporous carbon xerogels (series with $R/C = 300$) are activated with KOH, samples with larger specific surface areas (i.e. more developed microporosity) are produced. In contrast, in the case of macroporous carbon xerogels, activation with NaOH produces in some cases activated carbon xerogels with a more highly developed microporosity than that of KOH (i.e. Na-1000-2, Na-1000-3).

Several studies have compared NaOH and KOH as activating agents for a wide range of different carbon

Table 1 Textural characterization of different carbon xerogels

Sample	S_{BET} (m^2 g^{-1}) ±10	V_{DUB-N_2} (cm^3 g^{-1}) ±0.01	V_v (cm^3 g^{-1}) ±0.05	$d_{p,max}$ (nm) ±1	V_{DUB-CO_2} (cm^3 g^{-1}) ±0.01
CX-300	640	0.26	0.58	10	0.26
CX-1000	660	0.27	2.2[a]	150[b]	0.28
K-300-1	680	0.29	0.65	10	0.29
K-300-2	450	0.23	0.75	9	0.40
K-300-3	1540	0.69	0.94	11	0.45
K-300-4	1390	0.58	0.87	10	0.43
K-1000-1	660	0.26	2.20[a]	150[b]	0.50
K-1000-2	1170	0.48	2.50[a]	150[b]	0.41
K-1000-3	1400	0.57	3.20[a]	150[b]	0.46
K-1000-4	1650	0.65	3.70[a]	370[c]	0.51
Na-300-1	470	0.19	0.49	9	0.24
Na-300-2	300	0.12	0.48	10	0.19
Na-300-3	1200	0.53	0.91	10	0.32
Na-300-4	1450	0.63	1.16	10	0.35
Na-1000-1	610	0.25	2.12[a]	150[b]	0.30
Na-1000-2	1360	0.56	2.80[a]	150[b]	0.42
Na-1000-3	1720	0.68	3.08[a]	150[b]	0.44
Na-1000-4	1430	0.57	2.92[a]	370[c]	0.49

S_{BET} specific surface area, V_{DUB-N_2} micropore volume calculated applying Dubinin–Raduskevich equation to N_2 adsorption isotherm, V_v total pore volume, $d_{p,max}$ maximum meso/macropore size, V_{DUB-CO_2} micropore volume calculated applying Dubinin–Raduskevich equation to CO_2 adsorption isotherm

[a] Macroporous sample: $V_v = V_{Hg} + V_{DUB-N_2}$ (±0.1 cm^3 g^{-1})

[b] Calculated from mercury porosimetry: ±10 nm

[c] Large pore size distribution (120–400 nm)

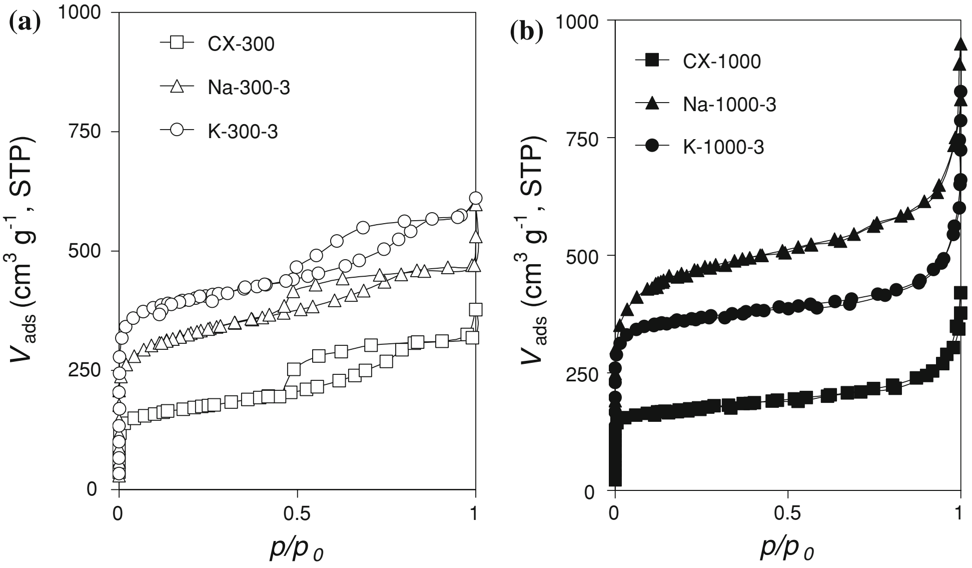

Fig. 2 N_2 adsorption–desorption isotherms of activated carbon xerogels synthesized (**a**) with $R/C = 300$ and (**b**) with $R/C = 1000$ and activated with NaOH or KOH at $A/P = 3$

materials and it has been concluded that the differences between these two activating agents are related to the structural order of the carbon materials [8, 9, 12]. This is determined by the dimensions of the layer in the direction perpendicular to the carbon basal plane (L_c), the interlayer distance (d_{002}) and the dimensions of the layer in the direction parallel to the basal plane of carbon materials (L_a). Table 2 shows the crystallographic parameters of the unactivated carbon xerogels used in this work. It can be seen that the values obtained are very similar for both carbon xerogels independently of the R/C molar ratio used during the synthesis and do not correspond to highly ordered carbon materials (i.e. graphite: $d_{002} = 3.35$–3.37 Å, $L_c = 91$–398 Å and $L_a = 55$–690 Å) [21].

Table 2 Crystallographic parameters of carbon xerogels

Sample	d_{002} (Å)	L_c (Å)	L_a (Å)
CX-300	3.89	10.84	40.66
CX-1000	3.87	10.04	47.43

d_{002} interlayer distance, L_c layer dimension perpendicular to the basal plane, L_a layer dimension parallel to the basal plane

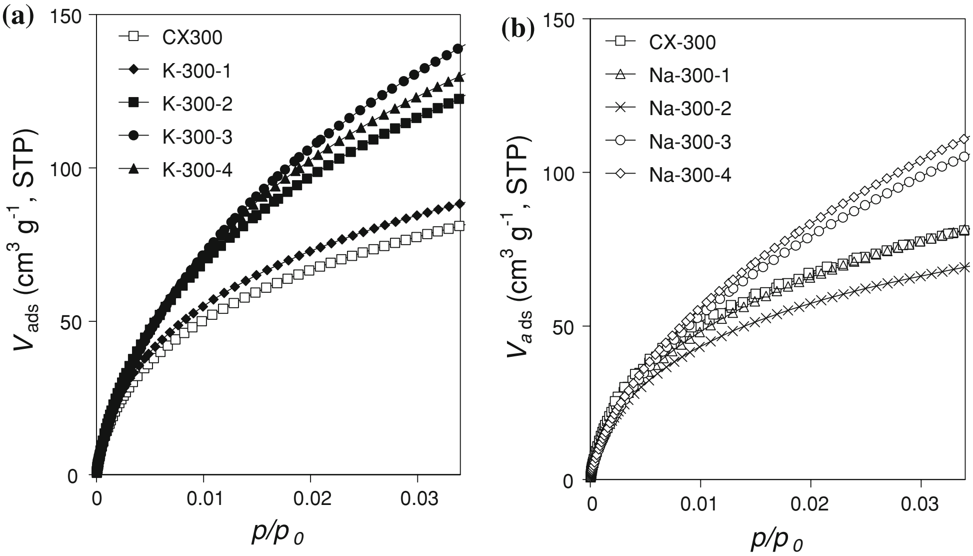

Fig. 3 CO_2 adsorption isotherms of activated carbon xerogels synthesized with $R/C = 300$ and activated with (**a**) KOH and (**b**) NaOH

Figure 3 shows the CO_2 adsorption isotherms of the carbon xerogels synthesized with $R/C = 300$ and activated with different types and amounts of hydroxide. In the case of KOH (Fig. 3a), the CO_2 adsorption capacity of the samples at $p/p_0 < 0.03$ increases as the (A/P) mass ratio increases, indicating that the narrow micropores develop as the amount of activating agent increases up to $A/P = 3$. However, when NaOH is used (Fig. 3b), as in the case of S_{BET}, the use of low amounts of NaOH leads to a decrease in CO_2 adsorption and therefore the volume of the narrow micropores decreases. When higher amounts of activating agent are used, the narrow micropore volume starts to increase (i.e. $A/P = 3$). As can be seen from Fig. 3, the CO_2 adsorption capacity at $p/p_0 < 0.03$, and therefore the narrow micropore volume, is always lower when NaOH is used for activated samples synthesized with $R/C = 300$. In the case of samples with $R/C = 1000$, a similar volume of narrow micropores is obtained with both activating agents. If the samples activated with the same hydroxide are compared, it can be seen that carbon xerogels with $R/C = 1000$ always display a higher narrow microporosity development (Table 2).

With respect to the chemical composition of the samples, Table 3 shows that the activated carbon xerogels obtained display a high carbon content (>90 wt%). The oxygen content of the samples increases during the activation process, from 2.2 wt% (CX-300) to around 5–6 wt% (K-300-1, K-300-4, Na-300-1 and Na-300-4), in the case of the carbon xerogel synthesized with $R/C = 300$, and from 3.2 (CX-1000) up to 7–7.7 wt% (K-1000-1, K-1000-4, Na-1000-1 and Na-1000-4) in the case of the carbon xerogel synthesized with $R/C = 1000$. However, the most significant difference between the composition of the carbon xerogels activated with KOH and NaOH is the ash content (Table 3). The carbon xerogels activated with KOH present low ash content (i.e., from 0 to 1.4 wt%). In contrast, the ash content of the samples activated with NaOH, are systematically higher (from 1.8 to 9.4 wt%). Since the washing conditions were the same in all cases, these results indicate that the residual products generated during chemical activation with NaOH are more difficult to eliminate than those generated by KOH activation.

Table 3 Chemical characterization of carbon xerogels

Sample	Ultimate analysis (wt%, on dry basis)			
	C	H	O	Ash
CX-300	96.9	0.8	2.2	0.3
CX-1000	95.6	0.4	3.2	0.3
K-300-1	94.1	0.5	5.2	0.7
K-300-4	93.8	0.4	5.3	0.0
K-1000-1	90.6	0.5	7.5	1.4
K-1000-4	92.8	0.4	7.1	0.0
Na-300-1	90.6	0.5	5.9	2.3
Na-300-4	92.5	0.3	5.8	1.8
Na-1000-1	90.5	0.4	7.7	2.8
Na-1000-4	83.8	0.6	7.4	9.4

Note that the reproducibility of the activation method was tested by repeating the activation/washing process for several fractions of the same carbon precursors. The repeatability was found to be quite good, differences in specific surface areas and ash content being lower than 5%, whatever the carbon chosen and the activation conditions.

Discussion

The initial carbon xerogel prior to activation is composed of interconnected near-spherical nodules forming a three-dimensional network; the mesopores or macropores correspond to the voids between the nodules, while the micropores correspond to the voids inside the nodules [2]. After chemical activation, this structure remains intact, independent on the amount of activating agent or type of hydroxide used. The activation process does not alter the characteristic interconnected structure of carbon gels. The reactivity of alkaline hydroxides with carbon xerogels is not high enough to alter significantly the mesoporosity (except for macroporous samples at high A/P values) but it is sufficient to increase the microporosity inside the nodules. The activation process may also increase the roughness of the nodules by removing the carbon, thereby contributing to an increase in microporosity.

Table 1 shows that in activated carbon xerogels synthesized with $R/C = 300$ (i.e. micro–mesoporous materials), the values of S_{BET} are higher for KOH than for NaOH. However, when carbon xerogels synthesized with $R/C = 1000$ (i.e. micro–macroporous materials) are activated, NaOH is generally more effective in developing the microporosity.

Most of the works that compare the effectiveness of NaOH and KOH as activating agents of carbon have concluded that KOH is a better activating agent for carbon materials with a high structural order, whereas NaOH is more effective for materials that have a low structural order [9]. As a first hypothesis, the different porosity development obtained by both hydroxides could be due to the differences in structural order of the carbon gels synthesized at different R/C. Carbon xerogels have a nanocrystalline structure which is closer to activated carbons than graphite. This means that this structure is less ordered than graphite, which displays a low d_{002} value and high L_c and L_a values ($d_{002} = 3.35$–3.37 Å, $L_c = 91$–398 Å and $L_a = 55$–690 Å). However, small ordered domains can be observed: these ordered domains are larger than in most activated carbons, which usually present lower values of crystallographic parameters L_c and L_a (i.e. $d_{002} = 3.7$–3.8 Å, $L_c = 8.9$–10.7 Å and $L_a = 31.3$–39.8 Å) [20]. Due to this characteristic structure of carbon xerogels, both hydroxides produce an increase in porosity in the carbon xerogels. However, as the interconnected structure of carbon gel is not altered during the activation, the reactivity of these hydroxides cannot be very high. The quantitative values of the interlayer distance (d_{002}), the dimensions of the layer in the direction perpendicular to the basal planes (L_c) and the dimensions of the layer in the direction parallel to the basal planes (L_a) are shown in Table 2: it can be seen that the crystallographic properties of the two carbon xerogels are very similar. Consequently, the structural order does not explain the different behavior of the two hydroxides.

Most studies that compare KOH and NaOH as activating agents of carbon materials use the activating agent/carbon precursor mass ratio (A/P) in order to compare the effect of the amount of activating agent used on the chemical activation reaction and the effectiveness of the alkaline hydroxide [8, 9, 12]. For the purpose of comparing our results with those published in the literature, we considered the same variable in this work. However, taking into account the fact that the chemical activation of carbon materials consists in a chemical reaction between KOH or NaOH and carbon, it would seem more appropriate to study the effect of the amount of activating agent in terms of the molar ratio. The molecular weight of K is higher than that of Na. Therefore, if the effectiveness of alkaline hydroxide in developing the porosity of carbon materials is compared at a constant (A/P) mass ratio, the amount of moles of KOH is lower than that of NaOH. The most useful variable to consider in the chemical activation of KOH and NaOH is the (A/P) molar ratio rather than the (A/P) mass ratio. So, in order to compare accurately the effectiveness of the two activating agents, the comparison needs to be based on the results obtained at a constant (A/P) molar ratio.

The relationship between the mass and molar (A/P) ratios is given by:

$$\frac{\left[\frac{A}{P}\right]_{\mathrm{mass}}^{\mathrm{KOH}}}{\left[\frac{A}{P}\right]_{\mathrm{mass}}^{\mathrm{NaOH}}} = \frac{M_{\mathrm{KOH}}}{M_{\mathrm{NaOH}}} \frac{\left[\frac{A}{P}\right]_{\mathrm{mol}}^{\mathrm{KOH}}}{\left[\frac{A}{P}\right]_{\mathrm{mol}}^{\mathrm{NaOH}}} \tag{1}$$

where M_{KOH} and M_{NaOH} are the molar mass of KOH and NaOH (i.e. 56 and 40 g mol^{-1} respectively). At a constant (A/P) molar ratio, the following relationship is obtained:

$$\left[\frac{A}{P}\right]_{\mathrm{mass}}^{\mathrm{NaOH}} = \frac{M_{\mathrm{NaOH}}}{M_{\mathrm{KOH}}} \left[\frac{A}{P}\right]_{\mathrm{mass}}^{\mathrm{KOH}} \cong \frac{2}{3} \left[\frac{A}{P}\right]_{\mathrm{mass}}^{\mathrm{KOH}} \tag{2}$$

This shows that when the comparisons are based on mass ratios, the differences in the surface areas of the samples activated with different hydroxides are overestimated. For this reason, the carbon xerogels activated with NaOH and a (A/P) mass ratio of 2 need to be compared with the samples activated with KOH and a (A/P) mass ratio of 3 (i.e. K-1000-3 and Na-1000-2). The specific surface areas, S_{BET}, of these two samples are very similar (1400 and 1360 m^2 g^{-1} respectively). However, for the same samples, if the same A/P mass ratio is used as a reference of comparison, NaOH seems to be more active: K-1000-2 and Na-1000-2 have a specific surface area of 1170 and 1360 m^2 g^{-1}, respectively, whereas the surface areas of K-1000-3 and Na-1000-3 are 1400 and 1720 m^2 g^{-1}, respectively. Another example is provided by the carbon xerogel activated with KOH and a (A/P) mass ratio of 4 (K-1000-4). In this case, the comparison in terms of molar ratio needs to be carried out using samples activated with NaOH and a (A/P) mass ratio between 2 and 3 (Na-1000-2 and

Na-1000-3, respectively). The specific surface area of K-1000-4 ($S_{\mathrm{BET}} = 1650\ \mathrm{m}^2\ \mathrm{g}^{-1}$) lies between the values obtained for Na-1000-2 and Na-1000-3 ($S_{\mathrm{BET}} = 1360$ and $1700\ \mathrm{m}^2\ \mathrm{g}^{-1}$, respectively). When the molar ratio is used, the differences between both activating agents are insignificant for $R/C = 1000$: the two alkaline hydroxides give rise to a very similar textural development. However, the comparison in terms of the (A/P) molar ratio shows that, in the case of mesoporous samples ($R/C = 300$), KOH is more efficient than NaOH: although fewer moles of KOH are used in the chemical activation reaction, KOH produces samples with a higher specific surface area than NaOH.

In the case of the mesoporous samples ($R/C = 300$), low amounts of activating agent lead to a decrease in porosity. When a low R/C (i.e. 300, mesoporous carbon xerogels) and low (A/P) ratios are used, both in the case of NaOH and KOH, the specific surface area increases slightly or decreases. In addition, the narrow microporosity is always higher in samples where $R/C = 1000$. This decrease in microporosity when $R/C = 300$ may be caused by the partial blockage of the micropores due to the fact that not all the alkaline compounds are removed. Carbon xerogels synthesized when $R/C = 300$ are micro–mesoporous materials with a mesopore size of about 10 nm. In contrast, the carbon xerogels synthesized with $R/C = 1000$ are micro–macroporous materials with a macropore size close to 150 nm. It can be inferred, therefore, that the porosity of the carbon precursor may have an influence on the removal of the residual Na and K species formed during activation.

Table 3 shows that the ash content decreases when a higher amount of alkaline hydroxide is used, from 0.7 wt% to zero in the case of samples K-300-1 and K-300-4, respectively, and from 2.3 to 1.8 wt% in the case of samples Na-300-1 and Na-300-4, respectively. This suggests that some of the residual alkaline compounds might be trapped when the pore size is not large enough, leading to the partial blockage of the final microporosity. However, when a higher amount of hydroxide is used, the micropore size increases and the residual K and Na compounds are probably more easily removed, leading to a good textural development. On the other hand, when carbon xerogels with $R/C = 1000$ are synthesized, the voids between the carbon nodules are larger, which facilitates the diffusion of residual metallic compounds. This may explain why the microporosity always increases with A/P in the case of macroporous carbon xerogels.

Finally, NaOH appears to be more difficult to remove from the samples, independently on the pore texture. This is confirmed by the ash content of the samples (see Table 3) and by the more pronounced decrease in specific surface area in the case of the mesoporous samples ($R/C = 300$) when NaOH is used: sample Na-300-2 has a specific surface area of $300\ \mathrm{m}^2\ \mathrm{g}^{-1}$ while the unactivated sample (CX-300) and the sample activated with KOH (K-300-2) have a specific surface area of 640 and $450\ \mathrm{m}^2\ \mathrm{g}^{-1}$, respectively. In addition, with low amounts of NaOH, the narrow microporosity either increases slightly or decreases. However, this does not occur for KOH, probably because sodium is smaller than potassium and can therefore diffuse more easily into the microporosity of the samples when the precursor is soaked in the hydroxide solution. This could also make it more difficult to eliminate the residual compounds during washing.

Conclusions

By chemically activating carbon xerogels with alkaline hydroxides it is possible to develop microporosity without altering the meso/macroporosity. The meso/macropore size can be tailored by modifying the resorcinol/sodium carbonate molar ratio (R/C), while chemical activation is being applied to increase the microporosity. Thus, by applying a combination of different synthesis and activation conditions, a wide range of activated carbon xerogels with different properties can be obtained. In order to compare the effectiveness of KOH and NaOH, the use of the (A/P) molar ratio seems preferable to the (A/P) mass ratio. KOH is a more efficient activating agent for samples synthesized with $R/C = 300$ (micro–mesoporous carbons); in the case of carbon xerogels synthesized with $R/C = 1000$ (micro–macroporous carbons) both hydroxides produce samples with a very similar textural development.

The subproducts generated during the activation with NaOH are more easily trapped inside the microporosity of the samples (especially when texture is not very well developed) and therefore they are more difficult to remove during the washing step, leading to partial blockage of the final microporosity. For this reason, in certain applications where materials free of all mineral content are required, KOH would seem to be the preferable option in order to avoid long washing treatments necessary with NaOH. However, NaOH has the advantage to be a cheaper activating agent.

Acknowledgements L.Z. acknowledges the financial support received from the CSIC I3P Programme and cofinanced by the European Social Fund, for a PhD thesis grant and for a 5-month stay in the Laboratoire de Génie Chimique of the University of Liège (Belgium). N.J. is grateful to the F.R.S.-FNRS (Belgium) for a postdoctoral fellowship. The Belgian authors thank the Fonds de Recherche Fondamentale Collective, the Ministère de la Région Wallonne and the Interuniversity Attraction Pole (IAP/P6-17) for the financial support received and acknowledge the involvement of their laboratory in the Network of Excellence FAME of the European Union Sixth Framework Programme.

References

1. Al-Muhtaseb SA, Ritter A (2003) Adv Mater 15:101
2. Job N, Théry A, Pirard R, Marien J, Kocon L, Rouzaud J-N, Béguin F, Pirard J-P (2005) Carbon 43:2481
3. Job N, Pirard R, Marien R, Pirard J-P (2004) Carbon 42:619
4. Lillo-Ródenas MA, Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A (2001) Carbon 39:741
5. Lillo-Ródenas JA, Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A (2001) Carbon 39:751
6. Nabais JV, Carrott P, Ribeiro Carrott MML, Luz V, Ortiz AL (2008) Bioresour Technol 99:7224
7. Mora E, Blanco C, Pajares JA, Santamaria R, Menéndez R (2006) J Colloid Interface Sci 298:341
8. Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A (2007) Micropor Mesopor Mater 101:397
9. Raymundo-Piñero E, Azaïs P, Cacciaguerra T, Cazorla-Amorós D, Linares-Solano A, Béguin F (2005) Carbon 43:786
10. Lillo-Ródenas MA, Marco-Lozar JP, Cazorla-Amorós D, Linares-Solano A (2007) J Anal Appl Pyrolysis 80:166
11. Fierro V, Torné-Fernández V, Celzard A (2004) Micropor Mesopor Mater 101:419
12. Kunowsky M, Weinberger B, Lamari Darkrim F, Suárez-García F, Cazorla-Amorós D, Linares Solano A (2008) Int J Hydrogen Energy 33:3091
13. Jagiello J, Thommes M (2004) Carbon 42:1227
14. Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A (2004) Carbon 42:1233
15. Dubinin MM (1975) In: Danielli JF, Rosenberg MD, Cadenhead D (eds) Progress in surface and membrane science. Academic Press, New York
16. Parra JB, de Sousa JC, Bansal RC, Pis JJ, Pajares JA (1995) Adsorpt Sci Technol 12:51
17. Duong DD (1998) Adsorption analysis: equilibria and kinetics. Imperial College Press, London
18. Washburn EW (1921) Proc Natl Acad Sci 7:115
19. Bragg WH (1918) In: Bragg WH, Bragg WL (eds) X-rays and crystal structure. Bell and Song, London
20. Brunauer S, Deming LS, Deming WE, Teller E (1940) J Am Chem Soc 62:1723
21. Cuesta A (1994) PhD thesis, INCAR-CSIC, Oviedo, Spain