Low-cost hierarchical micro/macroporous carbon foams as efficient sorbents for CO₂ capture

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ABSTRACT

Hierarchical coal-based carbon foams with a low production cost and a high carbon yield have been synthesised using ZnCl₂ and KOH as activation agents and tested as adsorbents for CO₂, and a relation has been established between CO₂ uptake and their textural and chemical properties. The foams showed a porous structure consisting of macropores in the range of 100-10 μm , a surface area of 534-866 $\text{m}^2 \text{g}^{-1}$ and a total micropore volume of 0.21-0.25 $\text{cm}^3 \text{g}^{-1}$. The foams activated with ZnCl₂ at 500 $^{\circ}\text{C}$, which displayed a homogeneous microporosity in the range of 0.8-1.2 nm, showed moderate values of CO₂ uptake, ranging from 1.6 to 2.1 mmol g^{-1} . The CO₂ adsorption capacity of the foams prepared by KOH activation was as high as 2.8 mmol g^{-1} , as a result of their higher proportion of narrow micropores ($< 0.7 \text{ nm}$). This value is superior to those attained by commercial activated carbons and the highest ever reported for carbon foams. Regarding the chemical surface, the presence of acidic functionalities reduced the uptake of CO₂. The foam prepared with a low coal/KOH ratio (0.5) showed a very good selectivity for CO₂ adsorption over N₂, a low regeneration energy expenditure and a good recyclability.

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1. INTRODUCTION

CO₂ from fossil fuels accounts for about 60% of the global greenhouse gases (GHG) emitted nowadays, and it is considered as the main contributor to global warming and climate change (IEA) [1]. In 2014, the Intergovernmental Panel on Climate Change (IPCC) reported that total anthropogenic GHG emissions increased on average by 1.0 Gt CO₂ eq (2.2%) per year from 2000 to 2010, and that the increase in emissions can be expected to persist driven by the growing global population and economic activity [2]. In this scenario, if no additional measures are taken to reduce GHG emissions, beyond those already in place today, it has been estimated that, by 2100 the global surface temperature will have increased by 3.7-4.0 °C above pre-industrial levels [3]. Taking into account that over 30-40% of total GHG emissions are released by the energy supply sector and fossil fuels will continue to be the main energy source in the near future, CO₂ capture and storage (CCS) technologies can be expected to play a critical role in the short-term mitigation of global warming and climate change [3]. Technologies based on aqueous amine solutions are currently used by the fossil fuel extraction, refining and ammonia synthesis industries. However, its implantation for CO₂ capture in power plants (post-combustion flue gas) is not economically feasible, since it would involve an energy penalty of roughly 30% of the output of the power plant [4]. The main drawbacks of conventional scrubbing with amines are that these solutions are highly corrosive and toxic, have a low cycling performance and to regenerate the solvent would entail a high level of energy consumption [5]. To

overcome these drawbacks the use of porous solid sorbents is considered as the most promising alternative. Of the possible sorbents, carbon materials with a purpose designed microporous texture and chemical properties are known to show an excellent thermal and chemical stability. What is more, they are easy to apply and can be regenerated with very little energy consumption. Several studies have demonstrated that their CO₂ adsorption capacity at 25 °C and 1 bar is closely correlated with the content of narrow micropores [6-9]. Consequently, the synthesis of carbons with a large volume of small micropores for this purpose has recently attracted widespread interest among the scientific community [5, 10-12]. However, the majority of these carbon-based materials are at present in powder form. For practical purposes, it is necessary to use binders for granulation, which leads to pore blockage, thereby decreasing CO₂ adsorption while increasing production costs.

Until now, only a small number of carbon monoliths have been tested as sorbents for CO₂ adsorption. Bourlinos et al. prepared synthetic graphite oxide-like foam by calcining chloranilate disodium salt in air at 300 °C [13], for potential application in natural gas upgrading and for the purification of hydrogen produced from biomass, due to its high selectivity for CO₂ and CO over H₂, CH₄ and N₂. Narasimman et al. recently reported the synthesis of carbon foams with microporosity generated by means of a thermo-foaming process involving the use of molten sucrose and aluminum nitrate as blowing agent, followed by a carbonization step [14]. The foam obtained from carbonization at high temperature (up to 900 °C) using a high level of aluminum nitrate (5%) displayed a CO₂ adsorption capacity of 2.5 mmol g⁻¹ at 25 °C and a very good recyclability. On the other hand, Hao et al. reported CO₂ uptake values at 25 °C, of 2.6 to 3.3 mmol g⁻¹ for nitrogen-doped carbon monoliths derived from poly(benzoxazine-co-resol) [15], which are close to the values that have been estimated as optimal for

practical applications ($3\text{--}4\text{ mmol g}^{-1}$) [16]. However, the process for preparing these materials is costly and tedious, and hence unfavorable for large-scale production and application. Until now, the carbons synthesised by Wahby by means of a self-sintering process of activated mesophase pitches have provided the highest volume of narrow micropores, $1.42\text{ cm}^3\text{ g}^{-1}$, for monoliths, with CO_2 adsorption capacities of up to 4 mmol g^{-1} [17]. Recently, A. Arami-Niya et al. have reported the synthesis of activated carbon monoliths from mixtures of acid-treated tar pitch and KOH, using coal as a foam stabilizer [18]. These materials showed an open channel structure, reaching high CO_2 adsorption capacities at low pressures ($5\text{--}4.5\text{ mmol g}^{-1}$ at 303 K and 140 kPa) and reasonable uptakes of CO_2 and CH_4 at high pressure (~ 7.4 and 5.0 mmol g^{-1} , respectively, at 298 K and 350 kPa).

Coal-based carbon foams are light-weight materials with an interconnected network of pores in the range of macropores. They have a low surface area ($< 10\text{ m}^2\text{ g}^{-1}$) and micropore volume, which disqualifies them as sorbents or catalyst supports. However, recently, our group reported a simple method to develop micropores in carbon foams, which extends the range of applications beyond the typical thermal and mechanical ones [19]. The process consists in adding an activation agent to the coal prior to the foaming step. Activation then leads to the formation of micropores in the cell walls. Because of the low cost of the raw material, the high carbon yield, and the formation of a bimodal porosity (micro and macroporosity) such foams offer an interesting alternative for CO_2 capture. Moreover, the monolithic shape of the foam provides a high structural stability, which will facilitate their deployment on an industrial scale.

As already mentioned, the CO_2 adsorption capacity of carbon materials is closely related to their textural parameters (narrow micropore volume) and surface chemistry (basic functionalities). However, in most of the works found in the literature these

parameters are studied independently of each other. For example, results obtained for carbon materials, with a more basic surface character than their counterparts and different textural parameters (surface area and micropore volume), are discussed independently of their narrow microporosity [20-22]. In order to determine the influence of each individual parameter on CO₂ uptake, we prepared activated carbon foams with different properties by varying the activation agent, the activation agent/coal ratio and the activation temperature.

2. EXPERIMENTAL

2.1 Foam processing

A high volatile bituminous coal (P) was selected as precursor of the carbon foams. The characterisation data of the coal are summarized in Table 1. In some of the tests, the coal was previously subjected to a demineralization treatment (P*). The mineral matter was removed by acid washing in three steps: (i) HCl (5 M), (ii) HF (full-strength concentration, 22 M), (iii) HCl (full-strength concentration, 12M) [23]. In a typical experiment, 20 g of coal (< 212 µm) was mixed with 80 ml of acid solution by continuous shaking for 1 h at ~ 60 °C. Afterwards, the solids were isolated by filtration and washed with warm distilled water. The washed coal was used for the next step under the same experimental conditions. Finally, the acid-washed coal was dried in an oven at 60 °C during 12 h. By applying this procedure, the total ash content was reduced from 6.5 to 0.5%, representing ash reduction of more than 90%.

ZnCl₂ (Z) and KOH (K) were selected as the activation agents. The synthesis of the activated carbon foams was carried out in four sequential steps, in a procedure similar to

that previously reported [19]: (i) impregnation of the coal precursor with a chemical activation agent, (ii) foaming process, (iii) activation (carbonization of the green foam), and (iv) washing with HCl (0.5 M) and water to remove the residual compounds. The operational conditions employed in each step were carefully chosen to ensure that the fluidity during the foaming process was the proper one, and also to prevent structural breakdown of the carbon foam after the activation step. Thus, the experimental conditions were optimized depending on the activation agent to be used and the amount to be loaded (Figure 1).

Table 1. Analytical data of the coal (P) used as precursor for carbon foams

<i>Gieseler plasticity test</i>	
Softening temperature (°C)	391
Solidification temperature (°C)	482
Maximum fluidity temperature (°C)	443
Fluidity (ddpm)	12401
<i>Proximate analysis</i>	
Volatile matter (% , d.b.)	29.8
Ash (% , d.b.)	6.5

ddpm: dial divisions per minute recorded in the Gieseler plasticity test (ASTM D2639-98).

d.b.: dry basis.

The synthesis was initiated by the impregnation of the precursor coal (~15 g, <212 µm), with a solution of the activation agent (ZnCl₂ in ethanol and KOH in water), with an activation agent/coal mass ratio ranging from 0.5 to 2 for ZnCl₂ and from 0.5 to 1 for

KOH (with higher amounts of KOH it was not possible to obtain an integral piece). The dispersion was stirred for 2 h at 60-75 °C and dried at 105 °C for 2 days in the case of the ZnCl₂/coal mixture and until complete dryness for the KOH/coal mixture. Afterwards, the impregnated coal was subjected to a foaming step at 450 °C (temperature of maximum fluidity of the coal). The resulting “green” foams were carbonized in a horizontal tubular furnace under an Ar or CO₂ flow (100 ml min⁻¹) at temperatures in the 500-800 °C range. The activated foams thus obtained were subsequently washed with HCl (0.5 M) to remove any inorganic salts generated during the heat treatments, and then with hot water until neutral pH. Finally, the samples were dried in an oven at 120 °C.

Figure 1. Diagram of the activated foam producing process.

The samples were labelled according to the activating agent/coal ratio, the coal precursor (P, P*), the chemical activation compound (Z, K), and the activation temperature (500, 800). For example, 1PK800 corresponds to the foam activated with KOH at 800 °C with a KOH/coal ratio of 1.

In addition, several samples were subjected to an activation treatment under CO₂ (combined physical and chemical activation). The samples thus obtained were labelled including the code PA after the temperature.

For comparative purposes, two commercial activated carbons, Supra50 and Super50, were used as reference materials.

2.2 Characterization of materials

The apparent density, ρ_{Hg} , and the true density, ρ_{He} , of the samples were measured by mercury porosimetry (Micromeritics AutoPore IV) and helium pycnometry (Accupyc 1330 from Micromeritics), respectively. From these data the total pore volume (V_{Hg}) and the percentage of open porosity (s) were calculated according to equations E1 and E2. In addition, the macropore size distributions were determined by mercury porosimetry measurements between 0.0007 and 227 MPa.

$$V_{Hg} = (1/\rho_{Hg}) - (1/\rho_{He}) \quad (E1)$$

$$s = [1 - (\rho_{Hg}/\rho_{He})] \cdot 100 \quad (E2)$$

The microporous texture of the activated foams under study was analysed by the physical adsorption of N₂ and CO₂. The physical adsorption of N₂ at -196 °C was measured in a Micromeritics ASAP 2420 device, whereas the adsorption of CO₂ at 0 °C was measured in a Quantachrome NOVA 1200 instrument. In both cases, prior to the measurements, all the samples were degassed overnight at 120 °C under vacuum.

The apparent surface area (S_{BET}) was assessed by the standard BET method, using nitrogen adsorption data in the 0.01-0.2 relative pressure range. The total pore volume

(V_t) was calculated from the amount of N_2 adsorbed at a relative pressure of 0.975. The microporosity volume (< 2.0 nm; V_{DR-N_2}) and the narrow porosity (< 0.7 nm; V_{DR-CO_2}) of the samples were determined by fitting the Dubinin-Radushkevich (DR) equation to the N_2 and CO_2 adsorption isotherms, respectively. The mean micropore sizes ($L_{O(N_2)}$, $L_{O(CO_2)}$) were also calculated by applying the Stoeckli and Ballerini equation to both isotherms [24].

X-ray photoelectron spectroscopy (XPS) was employed to study the surface chemistry of the activated foams. XPS spectra were recorded on a Specs spectrometer equipped with a high performance Phoibos 100 hemispherical analyser and a 5 multiplier channeltron detector (5MCD). The X-ray radiation was non monochromatic $MgK\alpha$ (1253.6 eV) emitted from a twin anode at 50 w.

2.3 CO_2 adsorption measurements

The CO_2 uptake of the synthesised foams was investigated up to atmospheric pressure (1 bar) in a static volumetric analyser (Nova 1200 Quantachrome), at different temperatures (0, 25 and 50 °C). This equipment was also employed to measure the N_2 uptake at 25 °C in order to determine the selectivity of the activated foams for CO_2 over N_2 . Before the measurements, the samples were degassed at 120 °C overnight.

The heat of adsorption is related to the energy needed to regenerate the sorbent. This value was calculated by applying the Clausius-Clapeyron equation (E3) to the data obtained from the CO_2 isotherms at different temperatures [25].

$$\left[\frac{\partial \ln P}{\partial (1/T)} \right]_q = \frac{-\Delta H}{R} \quad (E3)$$

The recycling tests of CO₂ on the activated foams were performed at atmospheric pressure using a thermogravimetric analyser (TA Instruments). In a typical experiment, the sample was first purged at 200 °C under a He flow (100 ml min⁻¹) to remove the adsorbed substances, and then it was allowed to cool to 25 °C. After the temperature had stabilized, the inlet stream was switched to CO₂ (100 ml min⁻¹) and a weight gain was observed. After the sorbent was saturated, the inlet stream was switched back to He without varying the operational temperature to perform the desorption of CO₂. Adsorption-desorption cycles were repeated for five runs in order to test the ability of the sorbents to retain their CO₂ uptake.

3. RESULTS AND DISCUSSION

3.1 Characterization of activated foams

Carbon foams derived from graphitizable precursors, such as pitch or coal, are essentially macroporous carbons. However, recent studies have shown that a microporous texture can be developed by chemical activation [19, 26-28]. In many cases, the activation is performed after the synthesis of the carbon foam, which leads to the degradation of its monolithic shape. The strategy employed in the present work is based on the addition of different chemical agents (ZnCl₂ or KOH) to the coal before the foaming step, followed by the carbonization of the green foam. This methodology allows obtaining monoliths with high structural integrity that can be easily handled and molded to different sizes and shapes without breaking (Figure 2).

The SEM images displayed in Figures 3a and 3c show an open and interconnected cell structure, confirming that the characteristic microstructure of the carbon foams is not

compromised by the activation treatment. A closer inspection (Figures 3b and 3d) reveals the formation of porous texture on the walls of the cells due to the activation treatment. These pores show a spherical structure in the case of the activation with ZnCl_2 whereas the activation with KOH develops for more irregular and elongated pores.

Figure 2. Several pieces obtained from the foam 1P*Z500.

Figure 3. SEM microphotographs of the carbon foams obtained by chemical activation, 1P*Z500 (a,b) and 1PK800 (c,d).

3.1.1 Microporosity

The textural parameters calculated from N₂ volumetric analysis are summarized in Table 2. The BET surface area, S_{BET} , and the micropore volume, $V_{\text{DR-N}_2}$, increase as the ZnCl₂/coal ratio increases from 0.5 to 2, reaching a maximum of 866 m² g⁻¹ and 0.35 cm³ g⁻¹, respectively. The removal of mineral matter also leads to an increase in the S_{BET} , from 663 m² g⁻¹ for 1PZ500 to 720 m² g⁻¹ for 1P*Z500 (ΔS_{BET} , 8.6%) (Table 2). This result suggests that the mineral matter acts as an inactive phase, decreasing the volume of adsorbed gas per gram of sample, without affecting the formation of micropores or blocking their entrances.

Table 2. Textural properties of the activated carbon foams.

Sample	S_{BET} (m ² g ⁻¹)	V_t (cm ³ g ⁻¹)	$V_{\text{DR-N}_2}$ (cm ³ g ⁻¹)	$V_{\text{DR-CO}_2}$ (cm ³ g ⁻¹)	$L_{\text{O(N}_2)}$ (nm)	$L_{\text{O(CO}_2)}$ (nm)
0.5PZ500	390	0.20	0.16	0.13	1.0	0.66
1PZ500	663	0.28	0.25	0.21	1.1	0.71
2PZ500	866	0.41	0.35	0.25	1.3	0.72
1P*Z500	720	0.31	0.28	0.23	1.0	0.68
1P*Z800-PA	738	0.33	0.28	0.19	1.0	0.60
0.5PK800	534	0.24	0.21	0.26	0.9	0.55
1PK800	637	0.29	0.25	0.26	1.0	0.61

The narrow pore volume of the foams ($V_{\text{DR-CO}_2}$) follows a similar tendency to the micropore volume ($V_{\text{DR-N}_2}$), increasing as the ZnCl₂/coal ratio increases, and also when the coal is subjected to the demineralization process (Table 2). The close values of the

micropore volumes obtained from N₂ and CO₂ adsorption, 0.25 and 0.21 cm³ g⁻¹, respectively, indicate that the foam activated at a moderate ZnCl₂/coal ratio (1PZ500) has a narrow and homogenous pore size distribution. However, for higher concentrations of ZnCl₂ (2PZ500), the difference between both parameters is larger (0.35 and 0.24 cm³ g⁻¹), indicating a broader pore size distribution. Furthermore, in Figure 4a it can be observed that foam 2PZ500 possesses a higher proportion of supermicropores (< 1nm) than foam 1PZ500, in addition to greater amounts of narrow mesopores, between 2-3 nm. By other hand, the PSDs of foams 1PZ500 and 1P*Z500 are quite similar, confirming that the demineralization treatment does not affect the creation of microporosity (Figure 4b).

It is well known that activation with ZnCl₂ at temperatures above 500 °C causes a severe reduction in microporosity due to the breakage of the dangling bonds induced by the activation agent [29]. However the use of an oxidant gas during treatment at high temperatures, referred to as simultaneous physical and chemical activation, may prevent the collapse of the micropore structure [30]. Accordingly, the green foam 1P*Z was subjected to carbonization at 800 °C under an oxidant atmosphere with CO₂ (1P*Z800-PA). It is important to note that an oxidant atmosphere should be employed during the heating from 500 to 800 °C (not only during the activation at 800 °C), since as ascertained in a previous paper [19], if the heating is carried out under an inert atmosphere, a reduction in the textural parameters is obtained (~ 50%, compared to when the foam is chemically activated at 500 °C).

As can be seen in Table 2, sample 1P*Z800-PA displays similar parameters of S_{BET} and V_{DR-N₂} to foam 1P*Z500, but its V_{DR-CO₂} has undergone a slight decrease from 0.22 to 0.19 cm³ g⁻¹. From these data, it can be inferred that the CO₂ atmosphere prevents the

collapse of the micropores during heating; at the same time, some gasification of the pore walls must have taken place causing the reduction of the narrow microporosity.

Figure 4. PSDs calculated by the NLDFT method from the N₂ adsorption isotherm at -196 °C for foams: a) 0.5PZ500, 1PZ500 and 2PZ500, b) 1PZ500 and 1P*Z500, c) 0.5PK800 and 1PK800.

By replacing the activation agent, the foams activated with the same activation agent:coal ratio, 1PK800 and 1PZ500, exhibit similar S_{BET} values, 637 and 663 $\text{m}^2 \text{g}^{-1}$, respectively. However, KOH induces the development of narrow microporosity to a greater extent than ZnCl_2 ($0.26 \text{ cm}^3 \text{g}^{-1}$ for 1PK800 vs $0.21 \text{ cm}^3 \text{g}^{-1}$ for 1PZ500) (Table 2). Moreover, it should be noted that even though the textural parameters calculated from N_2 isotherms at -196°C decrease when the amount of KOH falls to a ratio of 0.5, the CO_2 uptake remains unchanged, so both 0.5PK800 and 1PK800 show the same volume of narrow microporosity ($0.26 \text{ cm}^3 \text{g}^{-1}$). However, for foam 0.5PK800, $V_{\text{DR-N}_2} < V_{\text{DR-CO}_2}$, while for foam 1PK800, $V_{\text{DR-N}_2} \approx V_{\text{DR-CO}_2}$. The PSDs obtained from N_2 adsorption confirm that high ratios of KOH promote the development of pores between 1 and 2 nm (Figure 4c).

3.1.2 Macroporosity

As shown in Table 3, a rise in the amount of the chemical activation agent produces a decrease in the values of apparent density from 0.58 g cm^{-3} for 1PZ500 to 0.43 g cm^{-3} for 2PZ500, as a result of the increase in fluidity during the foaming process due to the presence of greater amounts of ZnCl_2 [19]. This fact also involves changes on the macroporous structure. Thus, in Figure 5a can be observed that the sample 2PZ500 presents a narrow pore size distribution centered around $100 \mu\text{m}$, while the sample 1PZ500 has a broader distribution with pore sizes between $100\text{-}10 \mu\text{m}$ (Figure 5a). The macroporosity of the foams is also influenced by the present of mineral matter and the chemical activation agent used. The demineralization treatment produces a decrease in the apparent density of the foams, from 0.58 g cm^{-3} (1PZ500) to 0.31 g cm^{-3} (1P*Z500) (Table 3). The total pore volume of foam 1P*Z500 was estimated taking into account

the total pore volume of the foam 1PZ500 ($1.11 \text{ cm}^3 \text{ g}^{-1}$), the yield of the synthesis (74%) and the fact that all mineral matter has been completely removed with the treatment. The difference between the calculated value ($1.21 \text{ cm}^3 \text{ g}^{-1}$) and the real one ($2.65 \text{ cm}^3 \text{ g}^{-1}$) indicates that the mineral matter prevents the formation of macropores, especially in the 10-45 μm range (Figure 5b). The macroporous structure is closely related to the coal fluidity and the pressure generated inside the reactor during the foaming process [19, 31]. Therefore, this effect is more than likely due to an increase in the fluidity as a consequence of the mineral matter removal from coal (inert phase).

Table 3. General properties of some of the activated carbon foams.

Carbon foam	True density (ρ_{He}, g cm^{-3})	Apparent density (ρ_{Hg}, g cm^{-3})	Open porosity (s, %)	Total pore volume (V_{Hg}, $\text{cm}^3 \text{ g}^{-1}$)
1PZ500	1.60	0.58	63.9	1.11
2PZ500	1.64	0.43	73.8	1.78
1P*Z500	1.80	0.31	82.7	2.65
1PK800	2.00	0.48	76.0	1.58

By other hand, the foam activated with KOH, 1PK800, has a higher pore volume (V_{Hg}) than the foam activated with ZnCl_2 , 1PZ500 (Table 3). This may be due to the fact that activation with KOH is carried out at a higher temperature than activation with ZnCl_2 , resulting in the removal of residual volatile matter blocking some of the pores. This is confirmed by the results obtained for the non-activated foams P500 and P800 (Figure 5c). Moreover, it is possible that gasification of the micropores takes place at

800 °C according to reactions R2 and R3 [32], which might give rise to the formation of macropores in the range of 10 to 0.1 µm (Figure 5d).

It is worth noting that the activated foams 1PZ500 and 0.5PK800 show lower density values than their non-activated counterparts P500 and P800, respectively. This phenomenon may be related to an increase in fluidity during the foaming, favouring the growth of bubbles and macropore development in this stage. ZnCl₂ promotes dehydrogenation reactions between aliphatic structures, as a result of which the radicals formed during the foaming are stabilized and remain in the metaplast instead of being so readily volatilized. In the case of KOH, the activation takes place by a redox process (R1). Consequently, to obtain a suitable green foam KOH must melt before the formation of metallic K, with this melting being the probably cause of the increase in fluidity.

Figure 5. PSDs obtained by mercury porosimetry for foams: a) 1PZ500 and 2PZ500, b) 1PZ500 and 1P*Z500, c) P500 and P800, d) 1PZ500 and 0.5PK800.

3.2 CO₂ adsorption studies

Figure 6 shows that the foams activated with ZnCl₂ under different experimental conditions display a CO₂ uptake at 1 bar and 25 °C proportional to their narrow pore

volume, with the exception of the foam activated at 800 °C, 1P*Z800-PA. This sample has a narrow pore volume ($V_{\text{DR-CO}_2}$: $0.19 \text{ cm}^3 \text{ g}^{-1}$), which is lower than that obtained for foams 1PZ500 and 1P*Z500 (0.21 and $0.23 \text{ cm}^3 \text{ g}^{-1}$, respectively), though it displays a higher CO_2 adsorption capacity (Figure 6). This observation can be clearly appreciated in Table 4, where the adsorption capacities have been normalized against the narrow pore volumes. The samples activated at 500 °C have an average micropore size of more than 0.7 nm, whereas the foam activated at 800 °C has an average micropore size of 0.6 nm (Table 4). Therefore, a possible explanation for the higher CO_2 uptake may be the smaller average micropore size, which is consistent with the results reported by Sethia et al. [33]. The role of pore size will be discussed in more detail later on.

Figure 6. Comparison between the CO_2 uptakes (25 °C, 1 bar) and narrow micropore volumes for the foams activated with ZnCl_2 (PZ series).

On the other hand, this phenomenon may be related to the surface chemistry, in spite of the interaction between the CO_2 and the coal foam being mainly a physical process, as can be deduced from the decrease in CO_2 uptake as the temperature increases (Table 4).

In other words, the surface properties of the foams may play an important role in CO₂ uptake [32].

The oxygen content as determined by XPS analysis for the foams activated at 500 °C is in the range of 16-10% at., but after the treatment at 800 °C this value drops abruptly to 5% at. Therefore, apart from the textural changes, the rise in temperature leads to a modification of the chemical composition of the foams.

Table 4. CO₂ adsorption capacity under different conditions (25 °C, 1 bar and 0 °C, 0.5 bar) and average micropore size calculated from CO₂ (0 °C) adsorption data for activated foams and commercial carbons.

Sample	C_{ads} (25°C, 1 bar) (mmol g⁻¹)	C_{ads} (0°C, 1 bar) (mmol g⁻¹)	L_o (CO₂) (nm)
1PZ500	1.6	2.6	0.75
2PZ500	2.1	3.4	0.76
1P*Z500	1.8	2.8	0.68
1P*Z800-PA	1.9	2.6	0.60
0.5PK800	2.8	3.2	0.57
1PK800	2.4	3.4	0.61
Super50	2.3	3.9	0.68
Supra50	2.3	3.8	0.70

Figure 7 shows the XPS results of 1P*Z500 and 1P*Z800-PA. The high resolution C 1s band of 1P*Z500 displays a main peak at 284.4 eV and a shoulder at 285.2 eV, associated to aromatic and aliphatic carbon, respectively. Moreover, two small peaks

appear at higher binding energy due to the existence of oxygen groups, C=O at 287.1 eV and O-C=O at 289.4 eV [19, 33]. The contribution of these bands decreases considerably in 1P*Z800-PA, indicating a rather poor surface in terms of oxygen functionalities, which is consistent with the higher temperature achieved during the activation step (800 °C vs 500 °C).

The basic or acidic nature of the oxygen functional groups present in the foams was also analysed by deconvoluting the high resolution O 1s band. In this region, five components were identified corresponding to: quinones or carbonyl oxygen (531 eV), lactones, phenols and ethers (532.5 eV), anhydrides (533.3 eV), carboxylic acids (534.2 eV) and chemisorbed water (536 eV) [34]. Figure 8 shows the XPS O 1s spectrum of foams 1P*Z500 and 1P*Z800-PA. It can be seen that the O 1s band shifts to lower energies as the temperature increases, confirming a reduction in the amount of acidic functionalities, such as anhydrides and carboxylic acids, whereas the amount of quinone type basic structures increases. Therefore, the activation at 800 °C enhances the hydrophobic character of the carbon foam and in consequence the affinity for CO₂ molecules may be greater in foam 1P*Z800-PA than in the foams activated at 500 °C. To corroborate this hypothesis, the heat of adsorption was calculated by applying the Clausius-Clapeyron equation to the adsorption isotherms assuming an adsorption uptake of ~0.7 mmol CO₂ g⁻¹. This parameter is a useful indicator of the strength of the interaction between the sorbent and the molecules of the adsorbate, in this case CO₂. Foam 1P*Z800-PA show a higher value (29 kJ mol⁻¹) than the foams activated at 500 °C (24-26 kJ mol⁻¹), indicating that CO₂ molecules have a greater affinity for foams activated at a higher temperature. Nevertheless, all of these values are in the same range as those reported in the literature for porous carbon materials, indicating that the sorbents only require a low amount of energy to be regenerated [10].

Figure 7. XPS C 1s spectra of foams 1P*Z500 and 1P*Z800-PA.

Figure 8. XPS O 1s spectra of foams 1P*Z500 and 1P*Z800-PA.

Taking into account that both the textural parameters (pore volume and pore size) and the presence of acidic functionalities play an important role in determining the capacity of CO₂ uptake, it is to be expected that the foams activated with KOH at 800 °C, which have a large volume of narrow pores, will exhibit a higher CO₂ adsorption capacity than the foams activated with ZnCl₂.

As can be seen in Table 4, the foams activated with KOH, show the highest CO₂ uptake at 1 bar and 25 °C (2.4-2.8 mmol g⁻¹), a value that is much greater than those achieved

by the commercial activated carbons, Super50 and Supra50 (2.3 mmol g^{-1}). In terms of their textural parameters, the commercial carbons exhibit a high adsorption of N_2 at -196°C , with specific areas higher than $1000 \text{ m}^2 \text{ g}^{-1}$ and micropore volumes of the order of $0.65\text{--}0.70 \text{ cm}^3 \text{ g}^{-1}$, values that are 2 and 3 times higher than those obtained by the foams activated with KOH. In contrast, the PK foams have a greater narrow pore volume (0.26 and $0.24 \text{ cm}^3 \text{ g}^{-1}$ for 0.5PK800 and 1PK800, respectively, and $0.23 \text{ cm}^3 \text{ g}^{-1}$ for both Supra50 and Super50). These results suggest that only pores below 0.8 nm are suitable active centers for CO_2 capture, whereas the presence of wider pores might even favour the diffusion of the CO_2 molecules into narrow pores. This possibility that has already been reported in the literature [33], is confirmed by Figure 9, where it can be seen that the CO_2 uptake at 25°C and 1 bar obtained for the samples does not show any correlation with the total microporosity (Figure 9b), but when these results are plotted against the narrow pore volume two different linear trends are apparent, one of which concerns the commercial activated carbons (AC) and the foams activated at high temperature (PK series and 1P*Z800-PA), and the other the PZ series activated at 500°C (Figure 9a). The latter has shifted to lower values as a consequence of the surface chemistry of the foams, since, as mentioned above, these samples, which were treated at a low temperature, display a more acidic character that reduces their capacity to adsorb CO_2 .

Figure 9. Correlation between the CO₂ uptakes (25 °C, 1 bar) and the narrow micropore volume (a), the total micropore volume (b) and the CO₂ uptakes at 0 °C and 0.5 bar (c). The dashed line shows the fitting of the data. The triangles represent the foams activated with KOH, the circles the foams activated with ZnCl₂ and the squares the commercial activated carbons.

A comparative analysis of the CO₂ isotherms at 0 and 25 °C for foam 0.5PK800 and the commercial activated carbons is presented in Figure 10. It can be seen that at 25 °C the foam displays a higher CO₂ adsorption capacity over the whole range of sub-atmospheric pressures, while at 0 °C the commercial carbons adsorb a greater amount of CO₂ than the foam above 0.6 bar. From the PSDs calculated by applying the NLDFIT method to the CO₂ isotherms at 0 °C it can be observed that foam 0.5PK800 has a greater fraction of pores below 0.5 nm, with an average micropore size of 0.57 nm,

whereas in the case of the commercial carbons this value is slightly higher, in the range of 0.7 nm (Figure 11). These results are in agreement with those reported by Presser [35], confirming that, at sub-atmospheric pressures, CO₂ adsorption is proportional to the amount of pores below 0.5 nm, whereas the micropores below 0.8 nm play an important role in the adsorption process at atmospheric pressure and ambient temperature. This is due to the fact that these narrow micropores have a strong adsorption potential that favours the ingress of CO₂ molecules at low pressures [6].

In this work a good correlation between the adsorption capacity of CO₂ at 0 °C and 0.5 bar and that corresponding to 25 °C and 1 bar was also observed (Figure 9c), which suggests that pores below 0.5 nm are also essential for achieving a good CO₂ capture performance at 25 °C.

Figure 10. Comparison of CO₂ adsorption isotherms for samples 0.5PK800, Super50 and Supra50 at several temperatures: a) 0 °C and b) 25 °C.

The adsorption capacity at 25 °C attained by the foams synthesised in this work, by KOH activation, is the highest value ever recorded for any coal foam, and is similar to those reported for other porous carbon materials in monolithic shape (Table 5). Even though some carbon materials have adsorption capacities higher than 3 mmol g⁻¹ [5], it needs to be taken into account that the majority of such materials are prepared by the activation of polymers or pitches and with a high ratio of activation agent (>2), that increases the chemical consumption and reduces the process yield. From an industrial point of view, it has been reported that a suitable adsorbent material should exhibit an adsorption capacity in the range of 3-4 mmol g⁻¹ at a cost lower than 10 \$ kg⁻¹ [16]. The second condition is satisfied by the foams presented in this work and the capacity (2.8 mmol g⁻¹) is reasonably close to the industrial target value. Further research into the modification of their surface using amine groups, metal oxides or fluorination treatments, can be expected to lead to the development of foams with an even more enhanced performance [5].

A good sorbent must also be able to retain the same capacity and structural integrity over numerous adsorption-desorption cycles. Moreover, in low-pressure postcombustion systems the flue gas usually contains less than 15% of CO₂, and, in consequence, the adsorbent needs to show a greater selectivity for CO₂ over other compounds present in the gas mixture.

Given that foam 0.5PK800 exhibited the greatest capacity to adsorb CO₂, this sample was selected to evaluate the selectivity of the sorbent for CO₂ over several regeneration cycles.

Figure 11. PSDs calculated by the NLDFT method from the CO₂ isotherm (0 °C) for samples 0.5PK800, Super50 and Supra50.

Table 5. Comparison of the CO₂ adsorption capacity (25 °C and 1 bar) of 0.5PK800 with different carbon monoliths.

Sample	$C_{ads,25^{\circ}C}$ (mmol g ⁻¹)
0.5PK800 (<i>This work</i>)	2.8
Cellular carbon foam derived from sucrose [14]	2.2
GO-like foam [13]	~ 2.5 ^a
Carbon monoliths from polymers [15]	2.6-3.3
Porous carbon monoliths from deep eutectic solvents [36]	2.2
Carbon monoliths from tar pitch and coal powder [36]	~ 4 ^b
N-enriched porous carbon monoliths [6]	3.1
^a at 20 bar	
^b at 1.3 bar and 30 °C	

3.3 Adsorbent selectivity and reuse

From an industrial point of view the sorbents must demonstrate a good selectivity for CO₂ over N₂ molecules. Figure 12a shows the single-component isotherms of CO₂ and N₂ for the 0.5PK800 foam at 25 °C. The CO₂/N₂ selectivity coefficient measured from the uptakes of the pure gases at 1 bar is ~ 8, which is consistent with the data reported for other porous carbon materials (about 7) [37].

Figure 12. a) Adsorption isotherms of CO₂ and N₂ at 25 °C for foam 0.5PK800, and b) CO₂ adsorption/desorption cycles for foam 0.5PK800 at 25 °C.

The reuse of sorbents is another important issue to be considered, since it affects the efficiency and cost of a CO₂ capture process. The reusability of the foam was tested in a thermobalance by performing several adsorption/desorption cycles at 25 °C. The affinity of the carbon foam towards CO₂ was found to be weak, as can be deduced from the enthalpy adsorption value (30 kJ mol⁻¹), indicating that the energy requirement for the release of CO₂ is low. Indeed, the CO₂ can be easily desorbed at ambient temperature by switching the carrier gas from CO₂ to He. As shown in Figure 12b, the CO₂ adsorption capacities were similar under the same conditions over six repeated runs, indicating that 0.5PK800 is exceptionally stable and can be recycled without any significant loss of CO₂ capture performance.

4. CONCLUSIONS

Hierarchical carbon foams with macro and microporosity were successfully prepared by means of a simple activation route. By adjusting the synthesis conditions (the type of activation compound, the amount of compound and the activation temperature),

activated foams with different textural and chemical properties can be obtained. Thus, chemical activation with ZnCl_2 at 500 °C generates highly microporous foams, with surface areas between 866 and 720 $\text{m}^2 \text{g}^{-1}$ and a homogeneous micropore size distribution centered at 0.8 and 1.2 nm. On the other hand, foams activated with KOH at 800 °C present a lower surface area ($< 640 \text{ m}^2 \text{g}^{-1}$) and their microporosity is dominated by micropores of less than 1 nm. The CO_2 uptake of the foams at 25 °C and 1 bar correlates well with the volume of narrow micropores, with foam 0.5PK800 achieving a maximum CO_2 adsorption of 2.8 mmol g^{-1} . Given that this value is one of the highest ever reported for carbon foams, coal-based carbon foams can be considered as good potential sorbents for CO_2 capture. Moreover, in comparison with other porous carbons, the foams reported in this work offer important advantages from the point of view of industrial application such as: i) the low cost of the raw material, which can be employed without the need for pretreatment, ii) a simple synthesis method in comparison to other techniques (e.g., nanotemplates), iii) the need for only a small amount of activation agent, which reduces chemical consumption and the process cost, iv) a high yield (75% as against 15% for activated biomass), and v) a monolithic structure which gives them a great mechanical strength and an easy manageability. Furthermore, these materials also offer a good selectivity for CO_2 over N_2 and can be used repeatedly over many cycles without any loss of adsorption capacity.

REFERENCES

- [1] IEA, CO₂ emissions from fuel combustion. Highlights, OECD/IEA, Paris, 2013.
- [2] R.K. Pachauri, L.A. Meyer, IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, 2014.
- [3] Intergovernmental Panel on Climate Change, Climate Change 2014: Mitigation of Climate Change, Cambridge University Press, 2015.
- [4] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long, Carbon Dioxide Capture in Metal–Organic Frameworks, *Chemical Reviews*, 112 (2012) 724-781.
- [5] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, Recent advances in solid sorbents for CO₂ capture and new development trends, *Energy & Environmental Science*, 7 (2014) 3478-3518.
- [6] M. Sevilla, A.B. Fuertes, Sustainable porous carbons with a superior performance for CO₂ capture, *Energy & Environmental Science*, 4 (2011) 1765-1771.
- [7] M. Sevilla, J.B. Parra, A.B. Fuertes, Assessment of the Role of Micropore Size and N-Doping in CO₂ Capture by Porous Carbons, *ACS Applied Materials & Interfaces*, 5 (2013) 6360-6368.
- [8] S.-Y. Lee, S.-J. Park, Determination of the optimal pore size for improved CO₂ adsorption in activated carbon fibers, *Journal of Colloid and Interface Science*, 389 (2013) 230-235.
- [9] N.P. Wickramaratne, M. Jaroniec, Importance of small micropores in CO₂ capture by phenolic resin-based activated carbon spheres, *Journal of Materials Chemistry A*, 1 (2013) 112-116.

- [10] M. Sevilla, C. Falco, M.-M. Titirici, A.B. Fuertes, High-performance CO₂ sorbents from algae, *RSC Advances*, 2 (2012) 12792-12797.
- [11] J. Wang, A. Heerwig, M.R. Lohe, M. Oschatz, L. Borchardt, S. Kaskel, Fungi-based porous carbons for CO₂ adsorption and separation, *Journal of Materials Chemistry*, 22 (2012) 13911-13913.
- [12] Z.H. Chen, S.B. Deng, H.R. Wei, B. Wang, J. Huang, G. Yu, Activated carbons and amine-modified materials for carbon dioxide capture - a review, *Frontiers of Environmental Science & Engineering*, 7 (2013) 326-340.
- [13] A.B. Bourlinos, T.A. Steriotis, M. Karakassides, Y. Sanakis, V. Tzitzios, C. Trapalis, E. Kouvelos, A. Stubos, Synthesis, characterization and gas sorption properties of a molecularly-derived graphite oxide-like foam, *Carbon*, 45 (2007) 852-857.
- [14] R. Narasimman, S. Vijayan, K. Prabhakaran, Carbon foam with microporous cell wall and strut for CO₂ capture, *RSC Advances*, 4 (2014) 578-582.
- [15] G.-P. Hao, W.-C. Li, D. Qian, G.-H. Wang, W.-P. Zhang, T. Zhang, A.-Q. Wang, F. Schüth, H.-J. Bongard, A.-H. Lu, Structurally Designed Synthesis of Mechanically Stable Poly(benzoxazine-co-resol)-Based Porous Carbon Monoliths and Their Application as High-Performance CO₂ Capture Sorbents, *Journal of the American Chemical Society*, 133 (2011) 11378-11388.
- [16] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-Combustion CO₂ Capture Using Solid Sorbents: A Review, *Industrial & Engineering Chemistry Research*, 51 (2011) 1438-1463.
- [17] A. Wahby, J.M. Ramos-Fernández, M. Martínez-Escandell, A. Sepúlveda-Escribano, J. Silvestre-Albero, F. Rodríguez-Reinoso, High-Surface-Area Carbon Molecular Sieves for Selective CO₂ Adsorption, *ChemSusChem*, 3 (2010) 974-981.

- [18] A. Arami-Niya, T.E. Rufford, Z. Zhu, Activated carbon monoliths with hierarchical pore structure from tar pitch and coal powder for the adsorption of CO₂, CH₄ and N₂, *Carbon*, 103 (2016) 115-124.
- [19] E. Rodriguez, R. Garcia, Microporosity Development in Coal-Based Carbon Foams, *Energy & Fuels*, 26 (2012) 3703-3710.
- [20] M.G. Plaza, K.J. Thurecht, C. Pevida, F. Rubiera, J.J. Pis, C.E. Snape, T.C. Drage, Influence of oxidation upon the CO₂ capture performance of a phenolic-resin-derived carbon, *Fuel Processing Technology*, 110 (2013) 53-60.
- [21] C. Pevida, M.G. Plaza, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, Surface modification of activated carbons for CO₂ capture, *Applied Surface Science*, 254 (2008) 7165-7172.
- [22] Y. Xia, R. Mokaya, G.S. Walker, Y. Zhu, Superior CO₂ Adsorption Capacity on N-doped, High-Surface-Area, Microporous Carbons Templated from Zeolite, *Advanced Energy Materials*, 1 (2011) 678-683.
- [23] P. Samaras, E. Diamadopoulos, G.P. Sakellariopoulos, The effect of mineral matter and pyrolysis conditions on the gasification of Greek lignite by carbon dioxide, *Fuel*, 75 (1996) 1108-1114.
- [24] D. Cazorla-Amorós, J. Alcañiz-Monge, M.A. de la Casa-Lillo, A. Linares-Solano, CO₂ As an Adsorptive To Characterize Carbon Molecular Sieves and Activated Carbons, *Langmuir*, 14 (1998) 4589-4596.
- [25] C. Chen, J. Kim, W.S. Ahn, Efficient carbon dioxide capture over a nitrogen-rich carbon having a hierarchical micro-mesopore structure, *Fuel*, 95 (2012) 360-364.
- [26] B. Tsyntsarski, B. Petrova, T. Budinova, N. Petrov, L.F. Velasco, J.B. Parra, C.O. Ania, Porosity development during steam activation of carbon foams from chemically modified pitch, *Microporous and Mesoporous Materials*, 154 (2012) 56-61.

- [27] J. Yang, Z. Shen, Z. Hao, Preparation of highly microporous and mesoporous carbon from the mesophase pitch and its carbon foams with KOH, *Carbon*, 42 (2004) 1872-1875.
- [28] J. Yang, Z.M. Shen, R.S. Xue, Z.B. Hao, Study of mesophase pitch-based graphite foam used as anodic materials in lithium ion rechargeable batteries, *J Mater Sci*, 40 (2005) 1285-1287.
- [29] A. Ahmadpour, D.D. Do, The preparation of active carbons from coal by chemical and physical activation, *Carbon*, 34 (1996) 471-479.
- [30] Z. Hu, H. Guo, M.P. Srinivasan, N. Yaming, A simple method for developing mesoporosity in activated carbon, *Separation and Purification Technology*, 31 (2003) 47-52.
- [31] M. Calvo, R. Garcia, A. Arenillas, I. Suarez, S.R. Moinelo, Carbon foams from coals. A preliminary study, *Fuel*, 84 (2005) 2184-2189.
- [32] J. Wang, S. Kaskel, KOH activation of carbon-based materials for energy storage, *Journal of Materials Chemistry*, 22 (2012) 23710-23725.
- [33] G. Sethia, A. Sayari, Comprehensive study of ultra-microporous nitrogen-doped activated carbon for CO₂ capture, *Carbon*, 93 (2015) 68-80.
- [34] A. Stein, Z. Wang, M.A. Fierke, Functionalization of Porous Carbon Materials with Designed Pore Architecture, *Advanced Materials*, 21 (2009) 265-293.
- [35] V. Presser, J. McDonough, S.H. Yeon, Y. Gogotsi, Effect of pore size on carbon dioxide sorption by carbide derived carbon, *Energy & Environmental Science*, 4 (2011) 3059-3066.
- [36] J. Patino, M.C. Gutierrez, D. Carriazo, C.O. Ania, J.B. Parra, M.L. Ferrer, F.d. Monte, Deep eutectic assisted synthesis of carbon adsorbents highly suitable for low-

pressure separation of CO₂-CH₄ gas mixtures, *Energy & Environmental Science*, 5 (2012) 8699-8707.

[37] G.K. Parshetti, S. Chowdhury, R. Balasubramanian, Biomass derived low-cost microporous adsorbents for efficient CO₂ capture, *Fuel*, 148 (2015) 246-254.