

Carbon aerogels used in carbon dioxide capture

Aerogeles de carbono utilizados en la captura de dióxido de carbono

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Abstract

In this work the maximum carbon dioxide adsorption capacity of carbon aerogels, obtained by a sol-gel process using 2,4-dihydroxybenzoic acid/formaldehyde (DHBAF) and resorcinol/formaldehyde (RF) as precursors, was studied. The effect of increasing the temperature of carbonization and physical activation of the samples DHBAF was also studied. The results showed that the maximum adsorption capacity is favoured at lower temperatures, adsorption and desorption are rapid and the performance is maintained over several cycles of CO₂ adsorption/desorption. A comparison with samples of commercial carbons was also made and it was concluded that carbon aerogels exhibit a behaviour comparable or superior to that obtained for the commercial carbons studied.

Resumen

En este trabajo se ha estudiado la capacidad máxima de adsorción de dióxido de carbono de aerogeles de carbono, obtenidos mediante un proceso sol-gel utilizando ácido 2,4-dihidroxibenzoico / formaldehído (DHBAF) y resorcinol / formaldehído (RF) como precursores. También fue estudiado el efecto del aumento de la temperatura de carbonización y la activación física de las muestras DHBAF. Los resultados mostraron que la capacidad máxima de adsorción se ve favorecida a temperaturas más bajas, la adsorción y desorción son rápidas y el rendimiento se mantiene durante varios ciclos de adsorción/desorción de CO₂. También se hizo una comparación con las muestras de carbones comerciales donde se concluyó que los aerogeles de carbono exhiben un comportamiento comparable o superior a la obtenido para los carbones comerciales estudiados.

1. Introduction

Climate change is regarded as one of the biggest environmental threats worldwide as a result of global warming [1]. According to the scientific community the CO₂ emitted by burning fossil fuels is the main cause of the drastic global warming [2, 3] and ways of reducing its emission are currently investigated and developed, based on strategies of capture, transport and storage of CO₂ [4, 5].

The technology of CO₂ capture and storage, “carbon capture and storage” (CCS), drawn up by the G8 (eight major industrial countries) in the year 2008, allows the CO₂ emitted by various industrial sources to be captured, transported and stored in adapted geological formations. Currently CO₂ capture technology consists of three methods (pre-combustion, post-combustion and oxy-combustion) with several technical options [6] indicated in Figure 1.

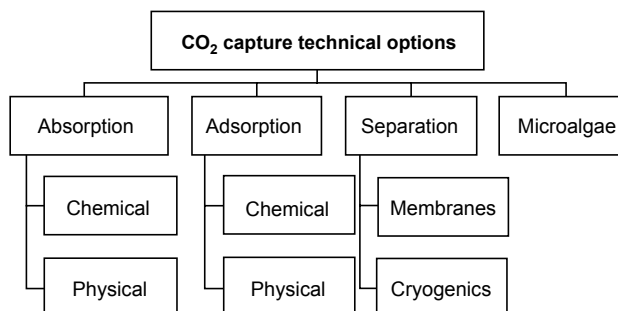


Figure 1: CO₂ capture technical options.

Figura 1: Opciones técnicas para la captura de CO₂.

In the present work adsorption was studied. As key features, the solid adsorbent should present a high selectivity, high rate of adsorption or desorption, regenerative capacity and energy efficiency. The various adsorbents usually studied include zeolites [7], activated carbons [8, 9] and mesoporous silicas [10]. Currently MOFs (Metal Organic Frameworks) [11] and carbon aerogels [12] show potential as adsorbents in the medium and long term. A carbon aerogel is a form of microporous carbon obtained by carbonization or activation of a polymer precursor which is prepared by a sol-gel route followed by supercritical drying. This procedure results in products with monolithic form and high mesopore surface area, which makes them interesting materials for use in fuel cells, supercapacitors, lithium batteries, gas separation, hydrocarbon vapour recovery, electric conductors and carbon capture [13-15].

In this article we will focus just on the performance of some unmodified low density carbon aerogels. Results for carbon aerogels modified by CVD or amine deposition have previously been published [15, 16].

2. Experimental

2.1. Preparation of organic and carbon aerogels

Polymer aerogels were prepared from 2,4-dihydroxybenzoic acid (DHBA) or resorcinol (R) and formaldehyde (F) under basic conditions using the procedure described by Carrott *et al* [17]. All the aerogels were synthesized using the stoichiometric molar ratio (0.5) and a solids content of 4%, equivalent to dilution ratios of 80 (RF) or 100 (DHBAF).

Carbon aerogels were obtained using a vertical tube furnace by heating individual monoliths in a 90 cm³ min⁻¹ N₂ flow to 1073 and 1223 K (only the samples of type DHBAF) at a rate of 5 K min⁻¹ and maintaining the monoliths at this temperature for 180 minutes. The temperature was then allowed to fall below 323 K before removing the carbon aerogel from the furnace.

The activation of the sample DHBAF was carried out at 1073 K in a horizontal tubular furnace by heating under N₂ from room temperature to 1073 K at a rate of

5 K min⁻¹, maintaining at this temperature for 180 min before switching to CO₂ for 5 h and then allowing it to cool down to room temperature under N₂ flow. The N₂ and CO₂ flow rates were both 90 cm³ min⁻¹.

2.2. Characterization by nitrogen adsorption

The characterization of the porosity of the aerogels produced was performed by nitrogen adsorption at 77 K using a Quantachrome Quadrasorb automated N₂ adsorption analyser and analysis of the adsorption isotherms by application of the BET, DR and α_s methods. The mesopore size distributions were calculated by the NLDFT method.

2.3. CO₂ adsorption/desorption

The CO₂ adsorption and desorption performance of the samples was evaluated using a Perkin-Elmer STA6000. CO₂ capture tests at 298, 308, 328, 348 and 373 K were carried out, with repeat run cycles at 298 K to evaluate the suitability of the samples for cyclic operation. In each case, the sample mass was allowed to stabilize at the selected temperature and then the carrier flow was changed from He (100 cm³min⁻¹) to CO₂ (100 cm³min⁻¹) in order to measure the adsorption capacity. Once the mass had stabilized, the carrier gas was changed back to He in order to measure the desorption of CO₂. In the case of stability testing, this procedure was repeated during 6 cycles of adsorption/desorption at 298 K.

3. Results and discussion

3.1. Characterization of organic aerogels

The N₂ at 77 K isotherms determined on the organic aerogels were similar to previously published results [18]. The N₂ isotherms were analysed by the BET and α_s methods and the results are given in Table 1. It can be seen that the values of A_s and A_{BET} are very similar. Additionally, the values of C are low which indicates the absence of microporosity.

Also included in the table are the total mesopore volumes and mesopore sizes obtained from the NLDFT analysis. The NLDFT mesopore size distributions indicated that the samples have mesopore widths greater than 40 nm.

3.2. Characterization of carbon aerogels

The N₂ at 77 K isotherms determined on the carbon

aerogels were similar to previously published results [19]. In the case of the carbon aerogels, it is observed that the values (shown in Table 1) of A_s are lower than the values of A_{BET} since they correspond to the external surface area only. In all cases, the C values are much larger than those determined on the samples of organic aerogels, which indicates the presence of ultramicropores.

It should be noted that both an increase in the temperature of carbonization as well as physical activation allowed an increase of ultramicroporosity in the aerogel structure, since the C values are larger when compared with the sample DHBAF-1073. By application of the α_s method, it can be seen that the values of V_{mic} are between 0.19-0.24 cm³g⁻¹. By applying the DR method, it is observed that the d_{mic} values are approximately 1 nm for the DHBAF samples and close to 2 nm for the RF sample. As pointed out previously [19] the DR method overestimates the micropore width of carbon aerogels due to their large specific external surface area. However, the C values indicate that the DHBAF aerogels have narrower ultramicropores than RF. Modification of the DHBAF sample induces only a small change in the average width of the micropores. By application of NLDFT, it is observed that the modification of the DHBAF aerogel results in only a small decrease in mesopore volume but a significant reduction in mesopore diameter of the carbon aerogels in comparison with the DHBAF-1073 sample. The RF sample is the sample with the highest mesopore volume.

3.3. CO₂ adsorption/desorption

3.3.1. Stability tests

In order to assess the stability of the adsorbents, multiple adsorption/desorption cycles were performed at 298 K. The CO₂ adsorption capacity after six cycles confirmed the stability. The same type of study was carried out with some commercial carbons and the results can also be observed in Table 2. Based on the results obtained it is possible to observe that the behaviour observed in the case of commercial carbons is similar to that obtained with carbon aerogels prepared in the laboratory.

It is also possible to infer that the differences in adsorption capacity of the samples presented are due to the difference in the width of the micropores, as

Table 1: Textural parameters determined in organic and carbon aerogels.

Tabla 1: Parámetros texturales determinados en aerogeles orgánicos y de carbono.

Aerogel	BET		a _s		DR	NLDFT	
	A _{BET} / m ² g ⁻¹	C	A _s / m ² g ⁻¹	V _{mic} / cm ³ g ⁻¹	d _{mic} / nm	d _{p(mes.)} / nm	V _{T(mes.)} / cm ³ g ⁻¹
Organic							
DHBAF	557	158	532	n.a	n.a	> 40	1.33
RF	619	85	612	n.a	n.a	>40	4.36
Carbon							
DHBAF-1073	798	1587	323	0.20	0.98	> 40	1.50
DHBAF-1223	811	3249	264	0.22	1.01	17.30	1.39
DHBAF-(AC)	942	34509	349	0.24	1.08	27.39	1.49
RF-1073	1083	626	656	0.19	1.92	> 40	4.03

A_{BET} = Apparent specific surface area obtained by the BET method; C = BET C parameter; A_s = Specific external surface area obtained by a_s the method; V_{mic} = Total micropore volume obtained by a_s the method; d_{mic} = DR micropore width; d_{p(mes.)} = Mesopore mean width obtained from the maximum of the NLDFT pore size distribution; V_{T(mes.)} = Mesopore volume calculated by the NLDFT method; n.a = not applicable.

Table 2. Comparison of the CO₂ maximum adsorption capacity achieved for carbon aerogels and commercial carbons at 298 K.

Tabla 2. Comparación de la capacidad de adsorción máxima de CO₂ alcanzada para aerogeles de carbono y carbones comerciales a 298 K.

Sample	1 cycle	2 cycle	3 cycle	4 cycle	5 cycle	6 cycle
	n (CO ₂) / mmolg ⁻¹					
DHBAF-1073	2.13	2.13	2.13	2.13	2.13	2.13
DHBAF-1223	2.15	2.11	2.11	2.11	2.11	2.11
DHBAF-(AC)	2.06	2.07	2.07	2.07	2.06	2.06
RF-1073	1.87	1.88	1.88	1.90	1.90	1.91
Carbosieve	2.15	2.11	2.13	2.13	2.15	2.14
Maxorb	1.87	1.88	1.88	1.90	1.90	1.91
Takeda 4A	1.15	1.23	1.23	1.22	1.21	1.20

reported by other authors [20-22]. Higher and lower CO₂ adsorption capacity are presented by the DHBAF and RF samples, respectively.

3.3.2. Influence of temperature

Figure 2 shows representative TGA curves for 2 cycles of adsorption and desorption of CO₂ at different temperatures. Values of the maximum adsorption capacity for all samples are given in Table 3. The comparison of CO₂ adsorption capacity at different temperatures, shown in Table 3, indicates that the results obtained in this work for carbon aerogels are comparable or superior to those obtained with other carbon adsorbents.

The same results also show that the increase in temperature of analysis contributed to a sharp decrease of the maximum capacities of adsorption, indicating a physical adsorption process between the adsorbent and CO₂ molecules. Additionally, it can be seen that in the case of the carbon aerogels the highest and lowest adsorption capacities are obtained for the samples DHBAF (1073 or 1223, depending on the temperature) and RF, respectively. The results corroborate the view of several authors [20, 22, 23] who have pointed out that the maximum adsorption capacity of CO₂ at atmospheric pressure on carbon materials depends on the presence of narrow micropores.

The values in Table 3 of adsorption capacity at different temperatures allow us to estimate values of adsorption capacity at other temperatures. Of particular interest is the adsorption capacity at 273 K, as many authors quote results for this temperature. As found in previous work [16], plots of ln(n(CO₂)) as a function of 1/T are linear. Representative examples are given in Figure 3 for the two samples with the highest

adsorption capacity at 298 K, namely, the carbon aerogel DHBAF-1073 and the carbon molecular sieve Carbosieve. At 298 K Carbosieve has a slightly higher adsorption capacity. However, it is one of the samples with the lowest temperature dependence, with a slope of 1695 K on Figure 3. On the other hand, DHBAF-1073 is the sample with the greatest temperature dependence, the slope on Figure 3 being 1977 K. As a result, the predicted adsorption capacity of DHBAF-1073 becomes greater than that of Carbosieve at temperatures below about 293 K. In fact, it is the only sample which has a predicted adsorption capacity greater than 4 mmol g⁻¹ at 273 K.

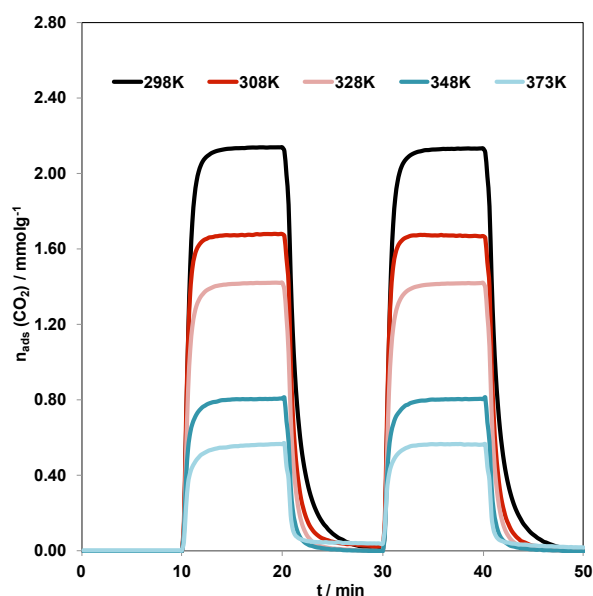

Figure 2. Adsorption/desorption cycles corresponding to the sample DHBAF-1073.

Figura 2. Adsorción/desorción de ciclos correspondiente a la muestra DHBAF-1073.

Table 3. Average maximum capacity for adsorption of CO₂ at different temperatures, at atmospheric pressure obtained on samples of carbon aerogels and commercial carbons.

Tabla 3. Promedio de la capacidad máxima de adsorción de CO₂ a diferentes temperaturas, a presión atmosférica, obtenidos en muestras de aerogeles de carbono y carbones comerciales.

Sample	298 K	308 K	328 K	348 K	373 K
	n (CO ₂) / mmolg ⁻¹				
DHBAF-1073	2.13	1.68	1.42	0.81	0.56
DHBAF-1223	2.12	1.89	1.42	1.06	0.68
DHBAF-(AC)	2.07	1.60	1.08	0.87	0.59
RF-1073	1.89	1.59	1.23	0.86	0.57
Carbosieve	2.15	1.96	1.41	1.02	0.70
Maxorb	1.87	1.58	1.07	0.80	0.49
Takeda 4A	1.15	1.49	1.13	0.83	0.55

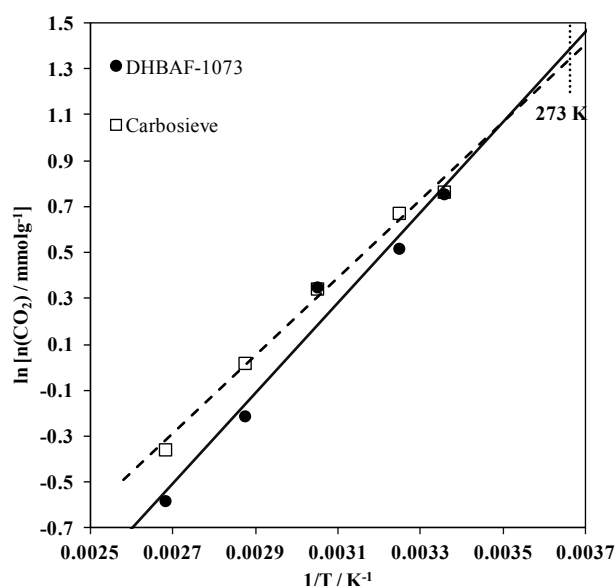


Figure 3. CO₂ maximum capture capacities determined at different temperatures.

Figura 3. Capacidades máximas de captura CO₂ determinadas a diferentes temperaturas.

4. Conclusions

In the current work, a set of different porous carbon samples, including carbon aerogels and commercial carbons was studied. The carbon aerogels featured high stability and reproducible performance in the CO₂ adsorption/desorption tests. Furthermore, the maximum CO₂ adsorption capacities of the carbon aerogels were found to be comparable or superior to those of the commercial carbons studied. Additionally, the results also showed that the adsorption and desorption are very fast, a feature suitable for future applications of these carbon aerogels in CO₂ capture.

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6. References

- [1] Olajire AA. CO₂ capture and separation technologies for end-of-pipe applications – A review. *Energy*. 2010;35:2610-28.
- [2] Arenillas A, Smith KM, Drage TC, Snape CE. CO₂ capture using some fly ash-derived carbon materials. *Fuel*. 2005;84:2204-10.
- [3] Plaza MG, Pevida C, Arenillas A, Rubiera F, Pis JJ. CO₂ capture by adsorption with nitrogen enriched carbons. *Fuel*. 2007;86:2204-12.
- [4] Orr JFM. CO₂ capture and storage: are we ready? *Energy & Environmental Science*. 2009;2:449.
- [5] Gibbins J, Chalmers H. Carbon capture and storage. *Energy Policy*. 2008;36:4317-22.
- [6] Pires JCM, Martins FG, Alvim-Ferraz MCM, Simões M. Recent developments on carbon capture and storage: An overview. *Chemical Engineering Research and Design*. 2011;89:1446-60.
- [7] Cheung O, Bacsik Z, Liu Q, Mace A, Hedin N. Adsorption kinetics for CO₂ on highly selective zeolites NaKA and nano-NaKA. *Applied Energy*. 2013;112:1326-36.

[8] Builes S, Roussel T, Ghimbeu CM, Parmentier J, Gadiou R, Vix-Guterl C. Microporous carbon adsorbents with high CO₂ capacities for industrial applications. *Physical chemistry chemical physics : PCCP*. 2011;13:16063-70.

[9] Sevilla M, Fuertes AB. CO₂ adsorption by activated templated carbons. *Journal of colloid and interface science*. 2012;366:147-54.

[10] Chandrasekar G, Son W-J, Ahn W-S. Synthesis of mesoporous materials SBA-15 and CMK-3 from fly ash and their application for CO₂ adsorption. *Journal of Porous Materials*. 2008;16:545-51.

[11] Zhao Z, Li Z, Lin YS. Adsorption and Diffusion of Carbon Dioxide on Metal-Organic Framework (MOF-5). *Industrial & Engineering Chemistry Research*. 2009;48:10015-20.

[12] Martín CF, Plaza MG, García S, Pis JJ, Rubiera F, Pevida C. Microporous phenol-formaldehyde resin-based adsorbents for pre-combustion CO₂ capture. *Fuel*. 2011;90:2064-72.

[13] Fricke J, Tillotson T. Aerogels: production, characterization, and applications. *Thin Solid Films*. 1997;297:212-23.

[14] Akimov YK. Fields of Application of Aerogels (Review). *Instruments and Experimental Techniques*. 2003;46:287-99.

[15] Marques LM, Carrott PJM, Carrott MMLR. Amine-modified Carbon Aerogels for CO₂ Capture. *Adsorption Science & Technology*. 2013;31:223-32.

[16] Marques LM, Conceição FL, Ribeiro Carrott MML, Carrott PJM. Diffusion of gases in metal containing carbon aerogels. *Fuel Proc Technol*. 2011;92:229-233.

[17] Carrott PJM, Marques LM, Ribeiro Carrott MML. Core-shell polymer aerogels prepared by co-polymerisation of 2,4-dihydroxybenzoic acid, resorcinol and formaldehyde. *Microporous and Mesoporous Materials*. 2012;158:170-4.

[18] Carrott PJM, Marques LM, Carrott MMLR. Characterisation of the porosity of polymer and carbon aerogels containing Fe, Ni or Cu prepared from 2,4-dihydroxybenzoic acid by n-nonane pre-adsorption and density functional theory. *Microporous and Mesoporous Materials*. 2010;131:75-81.

[19] Carrott PJM, Conceição FL, Carrott MMLR. Use of n-nonane pre-adsorption for the determination of micropore volume of activated carbon aerogels. *Carbon*. 2007;45:1310-3.

[20] Olivares-Marin M, Garcia S, Pevida C, Wong MS, Maroto-Valer M. The influence of the precursor and synthesis method on the CO₂ capture capacity of carpet waste-based sorbents. *Journal of environmental management*. 2011;92:2810-7.

[21] Rashidi NA, Yusup S, Hameed BH. Kinetic studies on carbon dioxide capture using lignocellulosic based activated carbon. *Energy*. 2013;61:440-6.

[22] Zhang Z, Zhou J, Xing W, Xue Q, Yan Z, Zhuo S. Critical role of small micropores in high CO₂ uptake. *Physical chemistry chemical physics : PCCP*. 2013;15:2523-9.

[23] Yoo H-M, Lee S-Y, Park S-J. Ordered nanoporous carbon for increasing CO₂ capture. *Journal of Solid State Chemistry*. 2013;197:361-5.