

Activated carbons from cork waste by chemical activation with K_2CO_3 . Application to adsorption of natural gas components

A.P. Carvalho *, M. Gomes, A.S. Mestre, J. Pires, M. Brotas de Carvalho

Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande Ed. C8, 1749-016 Lisboa, Portugal

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In a previous study [1] the potentialities of cork waste to produce activated carbons with high-developed porosity and with molecular sieve properties, by chemical activation with KOH, was shown. The preparation process used implied a great time and energy consumption, what can be a drawback for an eventual future production of these materials in industrial scale. In this sense, the first objective of the present work was to explore different methodologies to chemically activate cork with K_2CO_3 to minimize the cost of the preparation process. As a follow up, the potentiality of these materials towards the purification of methane by adsorption was ascertained. To this, the adsorption isotherms of methane, carbon dioxide, ethane and nitrogen, i.e., the main components of natural or landfill gas, were determined at ambient temperature on a granular sample obtained using a clay as binder.

The raw material was a representative sample of industrial waste, treated as reported elsewhere [1] and sieved for the fraction between 0.297 and 0.420 mm. Two types of impregnation were used: *physical impregnation*: cork powder was mixed with ground K_2CO_3 ; *impregnation with solution*: cork powder was mixed with a 30% solution of K_2CO_3 , and heated at 80 °C until complete evaporation. The mixtures, with weight ratios of K_2CO_3 :cork between 1:1 and 5:1, were calcined in a horizontal furnace, under N_2 flow ($2\text{ cm}^3\text{ s}^{-1}$). The temperature was raised (10 °C min^{-1}) up to the calcination temperature, T (°C), which attained values in the range 500–800 °C, and was kept for 1 h. After cooling, under N_2 flow, the samples were washed up to pH 7 and dried at 100 °C. The samples are named according with the expression: weight ratio K_2CO_3 :cork/ T (°C), followed by S in the case of the carbons where impregnation with solution was used. The granular form was prepared mixing the sample 1:1/700 with a montmorillonite (sup-

plied by Ward's) using a proportion clay/carbon of 0.25/1 and adding 3 cm^3 of water per gram of carbon. After the extrusion the samples were dried overnight at 60 °C. Cylindrical shape samples with, in average, 4 mm diameter and 9 mm long were obtained. N_2 adsorption isotherms at -196 °C were determined in a conventional volumetric apparatus (powder samples) and in an automatic apparatus Asap 2010 from Micromeritics (granular form). Adsorption studies of CH_4 , C_2H_6 , CO_2 and N_2 at $25 \pm 0.1\text{ °C}$, were made in a volumetric apparatus. Apparent surface areas, A_{BET} and microporous volumes, V_{DR} were estimated from, respectively, BET equation ($0.05 < p/p^0 < 0.15$) and Dubinin–Radushkevich (DR) equation. The mean micropore half width, L_0 , was evaluated from the characteristic adsorption energy, E_0 , obtained from the slope of the DR plots and applying the empirical equation $L_0 = (13.028 - 1.53 \times 10^{-5} E_0^{3.5})/E_0$ [2]. Microporosity characterization was complemented applying the α_s method, using as reference the isotherm reported in Ref. [3].

Physical mixing is an impregnation methodology seldom used [4], although this is simpler and much less time consuming than impregnation with solutions. The values of A_{BET} (Table 1) show that, although for $T = 500\text{ °C}$ the use of solution leads to a considerable gain in the porosity development, for higher temperatures the difference is small (A_{BET} – physical mixing $0.9 A_{BET}$ – solution). In this sense, this study was focused on samples prepared by physical mixing, because for operating conditions that lead to a considerable development of the porosity, i.e. 600–700 °C, there is no advantage to use impregnation with solution. In a first stage, the influence of the calcination temperature and K_2CO_3 content on the textural characteristics of the carbons was evaluated. The increase of the calcination temperature promotes a continuous development of the porosity, and A_{BET} and V_{DR} increase monotonously. On the other hand, the results of the α_s method reveal that, as observed for the samples activated with KOH [1], the porosity of carbons treated with K_2CO_3 presents ultra

* Corresponding author. Tel.: +351-217-500-897; fax: +351-217-500-088.

E-mail address: ana.carvalho@fc.ul.pt (A.P. Carvalho).

Table 1

Apparent surface area, A_{BET} microporous volumes evaluated by DR equation and α_s method, and characteristic adsorption energy and mean micropore half width estimated from the empirical equation proposed in Ref. [2]

Sample	A_{BET} (m ² g ^{−1})	DR equation			α_{s} method		
		V_{DR} (cm ³ g ^{−1})	E_0 (kJ mol ^{−1})	L_0 (nm)	$V_{\alpha\text{total}}$ (cm ³ g ^{−1})	$V_{\alpha\text{ultra}}$ (cm ³ g ^{−1})	$V_{\alpha\text{super}}$ (cm ³ g ^{−1})
<i>Impregnation with solution—effect of the calcination temperature</i>							
3:1/500-S	728	0.32	22.1	0.55	0.30	0.25	0.05
3:1/600-S	835	0.36	24.0	0.50	0.33	0.26	0.07
3:1/700-S	1173	0.51	20.4	0.61	0.48	0.36	0.08
<i>Physical mixing—effect of the calcination temperature</i>							
3:1/500	355	0.17	15.2	0.84	0.14	0.10	0.04
3:1/600	737	0.31	24.0	0.50	0.31	0.24	0.07
3:1/700	1025	0.44	22.7	0.54	0.41	0.31	0.10
3:1/800	1279	0.56	17.8	0.71	0.54	0.35	0.19
<i>Physical mixing—effect of the K₂CO₃:cork ratio</i>							
1:1/700	960	0.43	20.9	0.59	0.40	0.29	0.11
2:1/700	1033	0.45	20.0	0.62	0.42	0.33	0.09
3:1/700	1025	0.44	22.7	0.54	0.41	0.31	0.10
4:1/700	1027	0.44	21.3	0.58	0.41	0.31	0.10
5:1/700	1017	0.44	20.9	0.59	0.40	0.31	0.09

(width < 0.7 nm) and supermicropores (width between 0.7 and 2.0 nm). For calcinations up to $T = 700$ °C the volume correspondent to the narrowest pores, V_{ultra} , increase continuously, and represents 75% of the total microporous volume. Above 700 °C the creation of larger micropores became more important, resulting in the decrease of the percentage of V_{ultra} in the overall microporosity. This evolution of the textural parameters is in accordance with the mechanism accepted to this activation process, which states that the consumption of the carbonaceous matrix became more important for treatments above 700 °C. This fact is also reflected in the yields of preparation since, for calcinations at $T \leq 700$ °C yields are around 20%, and for $T = 800$ °C it decreases to 8%. These results lead us to choose the temperature of 700 °C to undergo the study of the influence of K_2CO_3 content.

The results for the samples with K_2CO_3 :cork weight ratio between 1:1 and 5:1 reveal that, in the experimental conditions used, the development of the samples porosity is almost independent of the K_2CO_3 content. Since the use of the smallest amount of the activating agent permits to achieve practically the same textural characteristics of the materials where highest amounts of K_2CO_3 was used, the sample 1:1/700 was selected to study of the adsorption of natural gas components.

It is interesting to confront the characteristics of the sample 1:1/700 with those of the sample previously prepared by chemical activation with KOH [1], using a similar amount of potassium ion and calcined at the same temperature. The sample 1:1/700 attains 90% of the A_{BET} value presented by the KOH treated cork. This activating agent develops slightly the narrowest micropores: $V_{\text{ultra}}/V_{\text{total}}$ is 0.84 and 0.72 for, respectively,

KOH and K_2CO_3 activated carbons. These differences can be important for some applications, but certainly do not prevent the use of the activated carbons prepared from K_2CO_3 . It must also be stressed that the experimental procedure used in this work leads to a considerable save in time and energy, what can be an important prerequisite to the use of these materials behind the laboratory scale. In fact, not only the impregnation method is much more expedited, but also the calcination regime takes 2 h instead of 7 h, required for the heat treatment of KOH activated carbons.

The N_2 adsorption isotherms at -196 °C in the powder and in the granular form of the 1:1/700 (Fig. 1) show that, although both curves can be assigned to highly microporous solids, there is a decrease in the external area as consequence of the aggregation. The

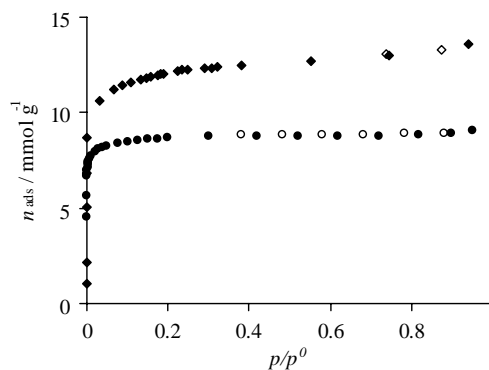


Fig. 1. Nitrogen adsorption-desorption isotherms at -196 °C on the sample 1:1/700 in powder (◆) and in granular form (●). Open and closed symbols represent adsorption and desorption points, respectively.

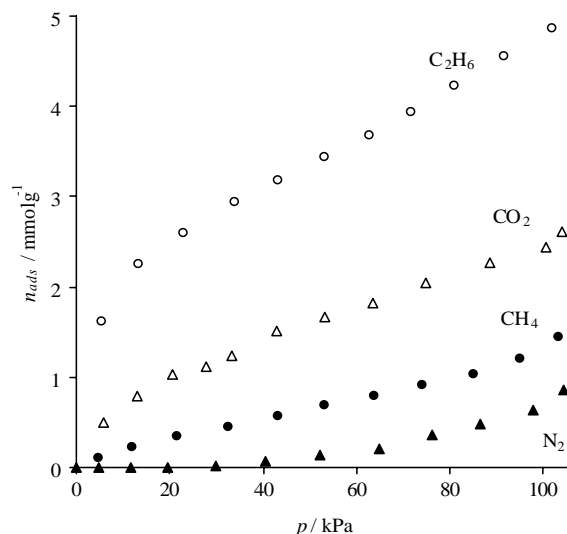


Fig. 2. Adsorption isotherms, at 25 °C, of the indicated gases in the granular form of the sample 1:1/700.

adsorption capacity is lower in the granular form, the microporous volume being reduced from $0.43 \text{ cm}^3 \text{ g}^{-1}$, in the powder, to $0.30 \text{ cm}^3 \text{ g}^{-1}$. This reduction (30%) is almost directly related to the mass effect, due to the amount of binder (25%).

The adsorption isotherms of CH_4 , C_2H_6 , CO_2 and N_2 , at 25 °C (Fig. 2) compare favourable with the literature data for the adsorption in commercial activated carbons. The sequence of the isotherms is, qualitatively, in line with the polarization forces involved and, so, it is expected that the separation of the studied molecules will occur by the differences in the adsorption equilibrium and not as a consequence of molecular sieving effects. To quantify the separation ability of the carbons the selectivity values for the binary mixtures were estimated: from the values of the Henry constants (S_{Henry}), obtained in the low coverage region and from the theory of the ideal adsorbed solution— S_{IAS} [5]. The latter were calculated for a pressure near the atmospheric pressure and for binary compositions near the averaged natural gas composition. The calculation of the S_{IAS} values for

Table 2

Selectivity values obtained from the initial slope of the isotherms (S_{Henry}), and from the IAS theory (S_{IAS}), at 25 °C. In the latter case the values are estimated for pressures near the atmospheric pressure and for a typical natural gas composition

	S_{Henry}	S_{IAS}
$\text{CH}_4\text{--C}_2\text{H}_6$	13.1	20.9
$\text{CH}_4\text{--CO}_2$	3.6	6.4
$\text{CH}_4\text{--N}_2$	96.5	—
$\text{C}_2\text{H}_6\text{--CO}_2$	3.6	8.2

$\text{CH}_4\text{--N}_2$ was not made since data for higher pressures would be necessary in the case of the N_2 adsorption in order to obtain the appropriate spreading pressure values which was not possible with the experimental apparatus used. Selectivity values (Table 2) are always very favourable, what suggest that with these materials would be even possible to purify ethane from carbon dioxide in a by-product mixture of the methane purification.

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