



Evolution of porosity of activated carbon fibres prepared from pre-oxidized acrylic fibres

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ABSTRACT

Industrially pre-oxidized acrylic fibres were used to prepare activated carbon fibres (ACF). The results obtained show that pre-oxidation was effective in increasing the carbon yield during carbonization and reducing the reactivity of the char with CO₂ during activation, making it possible to obtain ACF with high pore volumes, up to 1.15 cm³ g⁻¹, with BET area of 2064 m² g⁻¹, even without a prior laboratory stabilization step. By controlling the activation temperature over the range 700–1000 °C and the activation time over the range 15–4320 min it was possible to obtain a range of materials varying from those which contained mainly ultramicropores, with a high capacity for the capture of CO₂, up to others with a broader distribution of pore sizes extending up to 4 nm. An interesting aspect of the results was the observation that the volume of ultramicropores was practically constant for different activation times and temperatures up to 900 °C. The importance of different processes which may contribute towards the development of porosity during activation is considered in the light of the results obtained.

1. Introduction

In comparison with the traditional granular (GAC), powder (PAC) and extruded (EAC) grades of activated carbon, activated carbon fibres (ACF) combine a number of advantages, including high rates of adsorption, easy separation, uniform tailored porosity and purity. They are currently manufactured by a number of companies, principally from cellulosic, PAN (polyacrylonitrile), phenolic and pitch precursor fibres, and find application in various areas related to health, energy, and environmental control [1,2]. A major limitation to their more widespread use is their high cost compared to GAC/PAC/EAC. In this respect, PAN based ACF are one of the less expensive [3] which is at least partially due to the fact that PAN, or acrylic, is a major textile fibre and PAN is also the principal precursor for fabrication of high performance structural carbon fibres [4].

Polymer fibres may be produced by a fibre company and then converted to ACF by a carbon company. In the case of PAN or acrylic fibres, the first stage of ACF production involves stabilization of the fibres by heating under tension in an inert or oxidizing atmosphere [5]. Relatively recently, a range of acrylic fibre based “technical fibres” have been commercialized by Fisipe SA (Portugal, member of SGL Group - The Carbon Company). These include pre-oxidized acrylic

fibres which in principle should not need to be stabilized by the ACF manufacturer prior to carbonization and activation, thereby reducing the manufacturing costs.

The production of ACF from this type of pre-oxidized fibre has not been reported before. Hence, the principal objectives of the work reported here were to assess the possibility of using them to prepare high surface area ACF with a view towards reducing the production costs of the ACF, and then to demonstrate the effect of systematically varying activation conditions on the pore structure of the materials obtained. In previous work [6] we prepared ACF from non-pre-oxidized acrylic textile fibres produced in the same factory but with stabilization under nitrogen in our laboratory prior to carbonization and activation in CO₂. Significant improvements were found in the present work. In addition, the importance of different processes which may contribute towards the development of porosity during activation is considered in the light of the results obtained.

Many works have been published on the development of porous materials for the capture of CO₂ [7–9] and in recent years good results have been obtained using activated carbons for the adsorption of CO₂ even at about 25 °C and near atmospheric pressure [10–16]. Hence the materials obtained in this work were tested as adsorbents for the capture of CO₂.

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2. Materials and methods

The precursor used in this work was a pre-oxidized acrylic fibre specially prepared by Fisipe SA, member of SGL Group - The Carbon Company. For the preparation of the ACF, a vertical tube furnace and constant gas flow of $85 \text{ cm}^3 \text{ min}^{-1}$ were used. Each sample was prepared from approximately 3 g of acrylic fibre carbonized by heating to 700, 800, 900 or 1000 °C at a rate of $10^\circ\text{C min}^{-1}$ under N_2 . Activation was carried out by switching to a CO_2 flow for between 15 and 4320 min, then switching back to the N_2 flow and allowing the sample to cool to below 50 °C before removing from the furnace. The samples are designated FXtq, where t is the activation temperature in °C divided by 100 °C and q is the burn-off. Each sample was subsequently characterized by adsorption of N_2 at 77 K using a Quantachrome Autosorb iQ after outgassing at 300 °C for 5 h. The N_2 adsorption-desorption isotherms were analysed using the following: the Quenched Solid Density Functional Theory (QSDFT) model for the determination of pore size distribution [17]; the BET method for the determination of apparent specific surface area, A_{BET} , and C parameter, C, applied using the criteria recommended by Rouquerol et al. [18] and subsequently endorsed by IUPAC [19]; the α_s method for the determination of pore volume, v_s , and specific external surface area, A_s ; the Dubinin-Astakhov (DA) equation for the determination of pore volume, v_o , and characteristic energy, E_o , which was subsequently converted to an estimate of mean pore size, L_o , from the relationship [20]:

$$L_o = 10.8/(E_o - 11.4)$$

The CO_2 adsorption and desorption performance of the samples was evaluated using a Perkin-Elmer STA6000 thermogravimetric analyzer. In this work, a CO_2/N_2 mixture was used for the measurements and its precise composition was determined using a Spectra Vacscan Plus quadrupole mass spectrometer with the tip of the capillary inlet placed as close as possible to the sample position. The CO_2 partial pressure was found to be 51 kPa. The sample, approximately 10 mg, was conditioned by heating at 300 °C under a $100 \text{ cm}^3 \text{ min}^{-1}$ flow of He. After cooling to 25 °C the subsequent experimental program was: constant temperature for 5 min; switch from He to CO_2 and leave for 20 min; switch from CO_2 to He and leave for 60 min. Blank runs with no sample were carried out in order to correct for the change in buoyancy between He and the CO_2/N_2 mixture.

3. Results and discussion

3.1. Carbonization and activation

The carbonization yields decreased with increase in carbonization temperature, being 64, 60, 53 and 50% at 700, 800, 900 and 1000 °C respectively. In previous work [6], where the acrylic fibres were stabilized in N_2 but not pre-oxidized, the carbonization yield at 800 °C was found to be approximately 50%. The objective of stabilization is to promote the formation of cross-links and partial aromatization and to increase the average molar mass at relatively low temperatures. It follows that when the material is carbonized at higher temperatures the loss of volatile matter, due to chain scission, for example, will be lower. In addition, the cross-linked and aromatic structures formed will have a higher thermal stability than the C-C bonds of the linear polymer precursor. The significantly higher carbonization yield of 60% obtained in this work at 800 °C indicates that the pre-oxidation was effective in stabilizing the fibres and hence in decreasing the loss of material during the carbonization.

The values of burn-off during subsequent activation are included in Table 1. At each activation temperature there was a linear increase in burn-off with increasing activation time. In the previous work, two distinct regimes of reactivity were observed, but this behaviour was not found here with the pre-oxidized fibres. A comparison of reactivity can be made by estimating the activation energies for activation from an

Table 1

Sample preparation conditions, burn-offs, and pore volumes determined by the application of the QSDFT method to N_2 adsorption isotherms determined at 77 K.

Designation	Temperature/°C	Time/min	Burn-off/%	V_p (< 0.7 nm)/ $\text{cm}^3 \text{g}^{-1}$	V_p (0.7–4 nm)/ $\text{cm}^3 \text{g}^{-1}$
FX714	700	360	14	nd	nd
FX719	700	660	19	nd	nd
FX724	700	1002	24	nd	nd
FX735	700	1980	35	0.20	0.06
FX756	700	4320	56	0.24	0.16
FX817	800	60	17	0.11	0.04
FX829	800	150	29	0.18	0.07
FX843	800	300	43	0.22	0.12
FX862	800	480	62	0.22	0.27
FX871	800	660	71	0.20	0.42
FX911	900	20	11	nd	nd
FX934	900	60	34	0.20	0.12
FX944	900	80	44	0.20	0.24
FX960	900	120	60	0.19	0.46
FX983	900	150	83	0.21	0.64
FX1013	1000	15	13	0.07	0.06
FX1029	1000	30	29	0.13	0.14
FX1049	1000	45	49	0.15	0.29
FX1051	1000	60	51	0.17	0.41
FX1071	1000	72	71	0.13	0.59
FX1078	1000	90	78	0.14	0.99

V_p (< 0.7 nm), V_p (0.7–4 nm) – cumulative pore volumes corresponding to 0.7 nm and between 0.7 and 4 nm, obtained from the pore size distributions; nd – not determined.

Arrhenius plot. For this purpose, the slopes of the plots of burn-off as a function of activation time were used as a measure of rate of activation. It was found that the points at the three lowest temperatures gave a straight line and from the corresponding slope a value of 187 kJ mol^{-1} was obtained for the activation energy for activation of the carbonized fibres. The results previously obtained, only at the two temperatures 800 and 900 °C, and for the first regime of (lower) reactivity, lead to a value of 163 kJ mol^{-1} . The higher value obtained in this work confirms that the pre-oxidation step resulted in the production of stabilized fibres with a reduced intrinsic reactivity.

3.2. Adsorption of N_2 at 77 K

Representative adsorption-desorption isotherms of N_2 at 77 K are shown in Fig. 1. Almost all of the isotherms determined on the different samples were found to be Type I of the IUPAC classification [19] with a

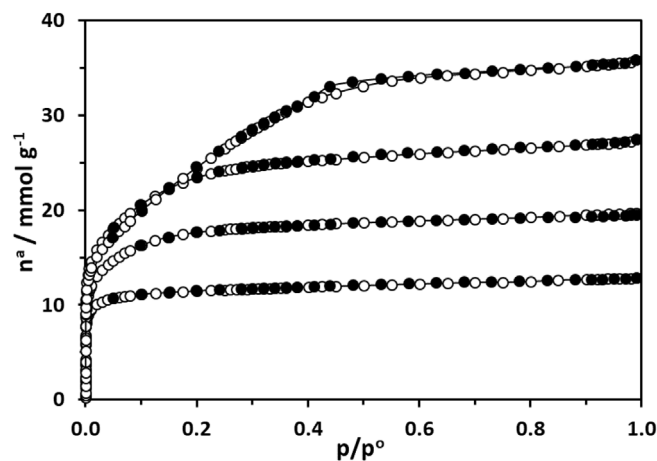


Fig. 1. Representative N_2 adsorption-desorption isotherms determined at 77 K. From top to bottom at 0.9 p^o – FX1078, FX983, FX871, FX756.

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