

Activated carbon fibre monoliths

E. Vilaplana-Ortego, J. Alcañiz-Monge, D. Cazorla-Amorós,
A. Linares-Solano*

Dpto. Química Inorgánica, Universidad de Alicante, E-03080 Alicante, Spain

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Abstract

Activated carbon fibre monoliths were prepared by physical activation of carbon fibre monoliths derived from two kinds of pitch-based carbon fibre (CF) (carbon fibres from a coal tar pitch and carbon fibres derived from a petroleum pitch). The monoliths were conformed using a coal tar pitch binder. The carbon fibre monoliths and the activated carbon fibre monoliths were studied by scanning electron microscopy (SEM) and gas adsorption (i.e. N₂ at 77 K and CO₂ at 273 K). The results obtained reveal that monoliths perform a good activation process that produce a quite high development of microporosity (BET surface areas around 2600 m²/g and N₂ micropore volume of 1.23 cm³/g). On the other hand, it is remarkable that the activation process used allow to easily control the degree of activation and hence to select the adsorption capacities of the activated carbon fibre monoliths. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, there has been a great interest in the development of new microporous monolithic materials from activated carbon (ACM), specially those based on fibres or bindered particles. Their applications in the field of gas treatment involve the preform of the materials in order to permit the circulation of gases and to avoid hydrodynamic problems.

The structures mostly used are those based on activated carbon particle conglomerates. When carbon fibres (CF) are utilised, the preparation procedure of monolithic CF needs

* Corresponding author. Fax: +34-965-90-34-54.

E-mail address: linares@ua.es (A. Linares-Solano).

the involvement of a binder. In this case, the employment of a phenolic resin [1] or starting from stabilised fibres by a hot briquetting method [2] is very common.

In this particular work, the activation process of the monoliths has been investigated with the purpose of producing high adsorption capacity microporous materials. Additionally, the use of a coal tar pitch as binder, and the use of two types of isotropic carbon fibres (a coal tar pitch and a petroleum pitch) has also been analysed.

2. Experimental

To prepare the activated carbon fibre monoliths, CF of different origin were used: chopped commercial carbon fibres (C) from an isotropic coal tar pitch precursor, and CF from an isotropic petroleum pitch (P) prepared at our laboratory. The pitch-based CF prepared from the isotropic petroleum pitch at our laboratory were spun in a monofilament spinning system. The obtained pitch fibres were stabilised in air up to 573 K, and latter on carbonised in N_2 up to 1273 K with a soaking-time period of 30 min [3].

In both cases, the CF were put in contact with a coal tar pitch solution in toluene. The blend was moulded in a cylinder (20 mm diameter and 40 mm length). The resultant material was heated in air up to 573 K to stabilise the coal tar pitch, and latter on carbonised at 1273 K in N_2 . The final material was labelled as M (carbon fibre monoliths). A different nomenclature has been used in each particular case, then, the carbon fibre monoliths prepared from commercial chopped fibres were labelled as CM and the carbon fibre monoliths obtained from CF prepared from the petroleum pitch P were named PM.

Two series of activated carbon fibre monoliths were obtained by controlled gasification of the carbon fibre monoliths (CM and PM) in CO_2 at 1165 K at several periods of time. The nomenclature for these activated carbon monoliths was ACM-X (for the commercial chopped carbon fibres) and APM-X (for those CF prepared at our laboratory). In both cases, X means the burn-off (BO).

The porous texture characterisation of the samples was performed by N_2 adsorption at 77 K and CO_2 adsorption at 273 K (Autosorb 6). The materials were also observed by scanning electron microscopy (SEM) (Jeol JSM-840).

3. Results and discussion

Fig. 1 shows the evolution of burn-off versus time for the two series of activated monoliths. In both series, the burn-off versus time evolution is linear up to burn-offs close to 80 wt.%. The slope of this plot indicates a higher reactivity of the PM monoliths. It is also important to remark that the monoliths do not change their dimensions when submitted to gasification in CO_2 , even at the highest BO reached (i.e. 80 wt.%), which reflects that the gasification mainly occurs homogeneously in the bulk of the monoliths.

The monoliths and activated monoliths were studied by SEM (Jeol JSM-840). From the SEM photographs (Figs. 2 and 3), it can be appreciated that the CF in the monoliths form a three-dimensional carbon network, with inter-fibres spaces in the range of macroporosity size. On the other hand, a small amount of binder particles can be observed. This suggests

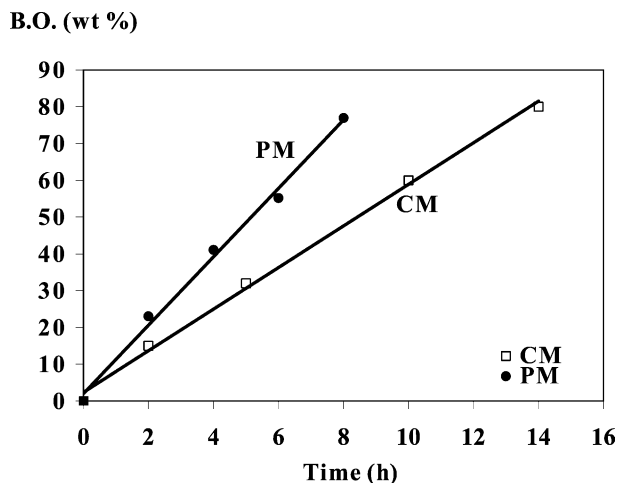


Fig. 1. Evolution of burn-off versus time of the carbon fibre monoliths (□: chopped commercial carbon fibre monoliths, ●: carbon fibre monoliths obtained from isotropic petroleum pitch P).

that a very thin layer of binder covers the CF surface, allowing their conformation as a monolithic preform. This three-dimensional carbon network is also present in the activated monoliths, as it can be appreciated from Fig. 3, and no important differences in the monoliths before and after the activation can be observed. Thus, the activated monoliths might favour the transport of gases through the macropore structure of the composite to the

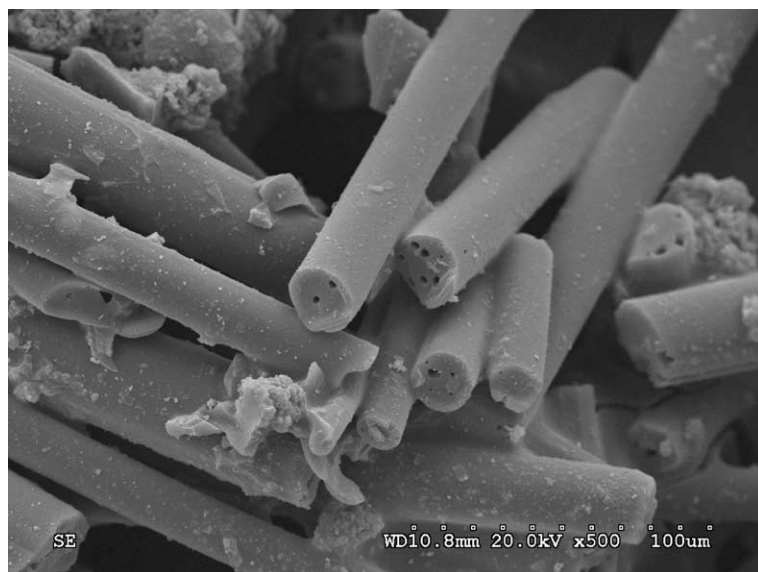


Fig. 2. SEM photograph of a carbon fibre monolith (PM series).

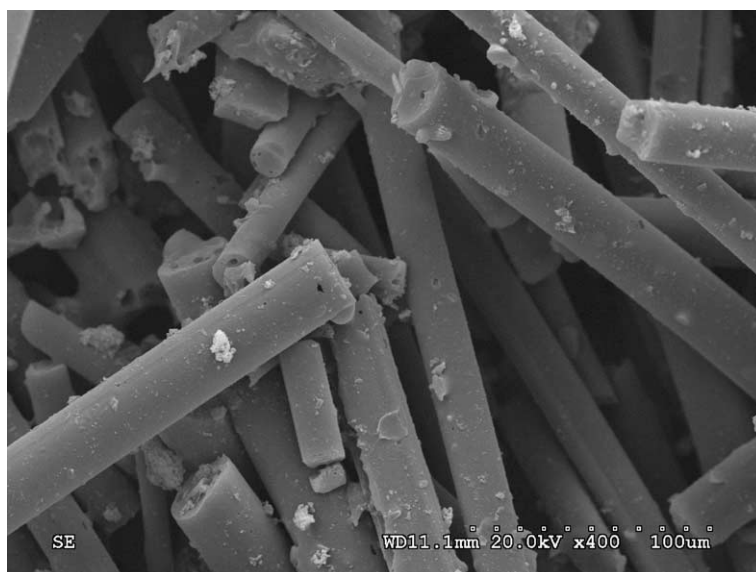


Fig. 3. SEM photographs of an activated carbon fibre monolith (APM series).

high area regions where adsorption takes place. On the other hand, it must be noted that the diameter of the fibres does not decrease considerably even when higher BO were reached (60–80 wt.%). Hence, taking into account this observation, and that the monolith dimensions do not change, we deduced that the gasification of the monoliths with CO_2 occurs mainly through inside the bulk of the fibres [4].

Table 1 presents the characterisation of the porous texture of the monoliths, including the BET surface area and the N_2 and CO_2 micropore volumes obtained by applying the Dubinin–Radushkevich equation to the monoliths and activated monoliths were prepared.

Table 1
Characterisation of the porous texture of the monoliths and activated monoliths

Sample	DR-Micropore vol. CO_2 (cm^3/g)	DR-Micropore vol. N_2 (cm^3/g)	Surface area BET (m^2/g)	Burn-off (wt.%)
CM	0.26	0.27	582	0
ACM-15	0.26	0.25	570	15
ACM-32	0.36	0.35	762	32
ACM-60	0.53	0.73	1920	60
ACM-80	0.50	0.99	2663	80
PM	0.22	0.13	299	0
APM-23	0.42	0.40	868	23
APM-41	0.57	0.63	1421	41
APM-55	0.62	0.87	1975	55
APM-77	0.61	1.23	2600	77

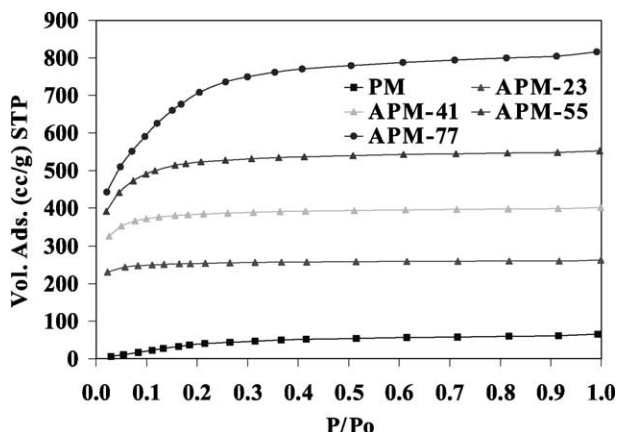


Fig. 4. N₂ adsorption isotherms of activated carbon fibres monoliths derived from PM.

Fig. 4 contains the N₂ adsorption isotherms of monoliths and activated monoliths of P series. The monoliths and activated monoliths obtained by this method are essentially microporous, presenting in all the cases type I isotherms (Fig. 4). Figs. 5 and 6 present the micropore volumes for N₂ and CO₂ adsorption data obtained from DR equation. It should be noted that the porous texture was determined for each sample by taking small portions of different parts of the monoliths (i.e. surface, bulk, ...), without differences in their porous texture. These results indicate that the activation process occurs homogeneously inside the bulk of the monoliths.

The activation process seems to depend on the origin of the carbon fibres. From the analysis of the carbon fibre monoliths (CM) and activated carbon fibre monoliths (ACM series) data (Table 1 and Fig. 5), it can be appreciated that a low increment in N₂ adsorption until a 32 wt.% B.O. (0.35 cm³/g for sample ACM-32 versus 0.27 cm³/g for the

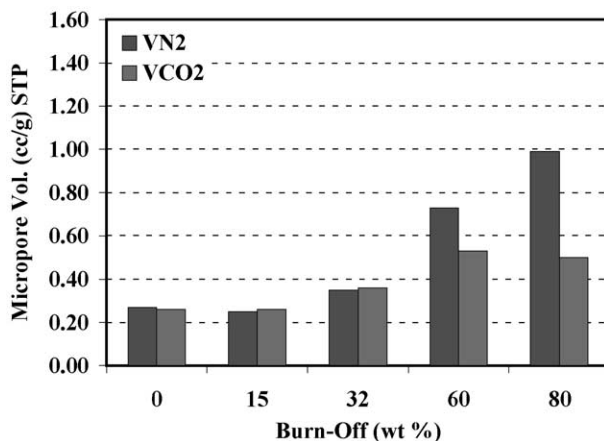


Fig. 5. Characterisation of the porous texture of the CM and ACM.

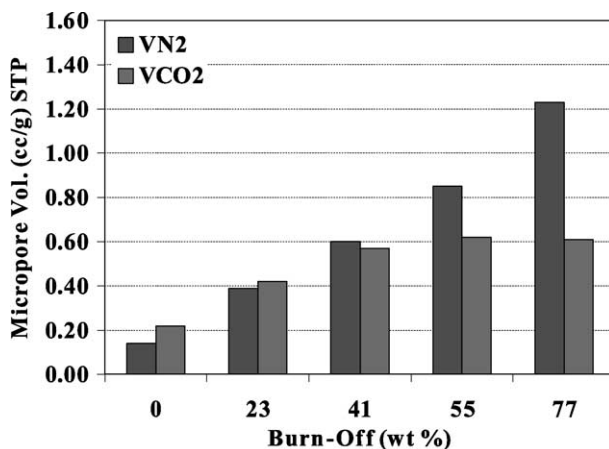


Fig. 6. Characterisation of the porous texture of the PM and APM.

CM) exists. However, from this point there is a considerable increase in porosity, reaching micropore volumes of $0.73 \text{ cm}^3/\text{g}$ at 60 wt.% BO and $0.99 \text{ cm}^3/\text{g}$ at 80 wt.%. This trend could indicate that, at low burn-offs, CO_2 reacts mainly with the carbonised binder that covers the commercial CF. This phenomenon does not occur when the CFs prepared at our laboratory are used (APM series). In this sense, from Table 1 and Fig. 6, it can be observed that the development of porosity is more homogeneous in the activated carbon fibre monoliths derived from a petroleum pitch, APM monoliths (compared to ACM monoliths), as the burn-off increases. This different behaviour on the activation process of the carbon fibre monoliths (CM and PM) might suggest a different CF–binder interaction, as well as an effect of the different CF nature (and reactivity; see Fig. 1) of both type of fibres.

4. Conclusions

The activation process of CF monoliths has been studied. The gasification process alters neither the CF diameter or the dimensions of the monoliths of both series (ACM and APM), and it has been observed that the activation of the carbon fibre monoliths is homogeneous in the bulk of the monoliths. These observations allow an easy control of the activation process and hence permit to select the adsorption capacities.

As result, activated carbon fibre monoliths have been successfully prepared from CF of different nature, reaching apparent BET surface areas close to $2600 \text{ m}^2/\text{g}$, and micropore volume of $1.23 \text{ cm}^3/\text{g}$.

Acknowledgements

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