

Available online at www.sciencedirect.comMICROPOROUS AND
MESOPOROUS MATERIALS

Microporous and Mesoporous Materials 109 (2008) 21–27

www.elsevier.com/locate/micromeso

Effect of the stabilisation time of pitch fibres on the molecular sieve properties of carbon fibres

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

Department of Inorganic Chemistry, University of Alicante, E-03080 Alicante, Spain

Received 15 December 2006; received in revised form 3 April 2007; accepted 10 April 2007

Available online 24 April 2007

Abstract

The stabilisation of pitch fibres (PFs) is the most important step for their subsequent use in the preparation of carbon fibres (CFs) and their resulting characteristics. The present work studies the influence that the stabilisation time has on the porosity of the CFs, and on the subsequent properties as carbon molecular sieve (CMS). The increase of the stabilisation time carried out at 573 K, from 2 to 8 h favours their CMS properties producing a decrease in the microporosity accessible to N₂, which gets completely blocked after 6 and 8 h, while the narrow microporosity (V-DR CO₂) remains accessible. Adsorption kinetic studies with CH₄ and CO₂ were performed to assess the possibility of using these CFs as CMS by comparing them with Takeda 3A CMS. The results suggest that there is an optimal stabilisation time which allows the preparation of CFs from an abundant raw precursor with properties similar to Takeda 3A CMS.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Pitch; Stabilisation; Fibres; Carbon molecular sieve

1. Introduction

One of the most important steps in the preparation of carbon fibres (CFs) from pitches is the stabilisation of the pitch fibres (PFs) [1]. The stabilisation of PFs consists on the oxidation of the PF molecules in order to confer infusibility to the PFs before their carbonisation. Usually, stabilisation is performed in air [1,2]. Therefore, once the PFs are stabilised they will not melt during the subsequent carbonization process and, consequently, will not lose their fibre morphology. The obtained CFs have some porosity [3] which confers them molecular sieve properties [4]. However, it is not known if the porosity of the final CFs is importantly affected by the stabilisation process time at a fixed temperature, and if this parameter (time of stabilisation) is important in the molecular sieve properties of the CFs.

Carbon molecular sieves (CMSs), are microporous carbon materials whose special textural characteristics enable kinetic separation of gas mixtures, i.e., separation as a result of differences in the diffusion rates of the species involved. CMSs can be prepared from a wide variety of carbonaceous precursors, such as lignocellulosic materials [5], coals [6,7], carbon fibres [4,8,9] and pitches [10,11] by different methods [4–14]: (i) pyrolysis of polymers, (ii) controlled gasification of chars to increase the pore size, (iii) thermal treatment of carbon precursor to modify the pore size, (iv) chemical vapor deposition (CVD) of carbon at the entrance of the pores and, (v) modification of coals by mixing with tars and resins and subsequent carbonization. In most of these cases, several steps are required in their preparation method. As an example, the CMS preparation starting from coals involves different steps: demineralisation (by acid washing), activation (with the purpose of obtaining a high pore volume), moulding, carbonisation and, finally, chemical vapour deposition (CVD) of carbon to control the pore size. The step of moulding is carried out in order to confer a geometrical external form that

* Corresponding author. Fax: +34 965903454.

E-mail address: jalcaniz@ua.es (J. Alcañiz-Monge).

may reduce the hydrodynamic problems during their use for high flows of gases. Therefore, in general, CMS are presented in the form of pellets or monoliths.

As it has been previously commented, CFs show molecular sieve properties [4]. Their geometrical external shape presents interesting advantages compared to conventional CMS, such as: (i) low resistance to mass transfer at the surface and in the bulk due to their small diameter, (ii) a fast adsorption kinetic, (iii) very low hydrodynamic resistance, which is specially useful when these materials are to be applied in filters for high flows of gases, (iv) the fibres can be used in many different shapes (felts, cloths, etc.), (v) good mechanical properties, (vi) and finally, their use avoids the problems due to channeling and settling that exists in granular CMSs.

Taking into account all the previous comments, it seems quite interesting the development CF with appropriate molecular sieve properties. This study analyses the influence of the stabilisation time at 573 K in air in the preparation of CFs having molecular sieve properties, similar to those of commercial CMS, by a simple and novel preparation process.

2. Experimental

The CFs were prepared from an isotropic petroleum pitch. The raw pitch was characterised by Elemental analysis (CHNS Carlo Erba), solvent extraction tests (conducted with quinoline (QI) and toluene (TI) by applying the standards ASTM D 2318 and ASTM D 4072), DRIFTS (FTIR; ATI-Mattson Infinity Series) and Thermogravimetry (TG-DTA; Stanton Redcroft STA-780 Series). The softening point (SP) was measured by Thermo-mechanical Analysis (TMA 2940 TA Instruments) by using the expansion method. The chemical characterisation of the parent pitch is presented in Table 1.

The PFs were prepared by melt spinning in a monofilament spinning system. Details of the spinning process are available in the literature [15]. The stabilisation of the PFs was performed by placing 1 g of PFs in an alumina crucible into a horizontal furnace and heating the PFs with variable heating rates and using an air flow of 500 ml/min. The stabilisation treatment was carried out up to 573 K, and the soaking times at 573 K varied from 2 to 8 h (a conventional stabilisation process only uses 2 h of soaking time at 573 K [15]). In order to gain insight into the processes

occurring during the stabilisation of the pitch fibres, DRIFT spectroscopy was used to analyse the structural characteristics of the fibres after the oxidation. Thermogravimetry (TG) was utilised to follow the weight variations during the stabilisation process.

The carbonisation of the stabilised PFs was performed in the same horizontal furnace at three different temperatures: 773, 1023 and 1273 K, in an inert atmosphere of N₂ and by using a gas flow of 100 ml/min. Additionally, the carbonisation of the 8 h stabilised PFs was analysed by TG under similar conditions than those used with the horizontal furnace during the carbonisation process.

The porous texture characterisation of the stabilised and carbonised PF was carried out by physical adsorption of gases (N₂ at 77 K and CO₂ at 273 K) (Quantachrome. Autosorb 6 and 6B). The samples were outgassed at 523 K under a vacuum of 1 Pa for at least 4 h. The Dubinin Radushkevich (DR) equation [16] was used to calculate the micropore volume (VDR N₂ and VDR CO₂).

Adsorption kinetic studies with CH₄ and CO₂ were carried out to assess the molecular sieve properties of the obtained CF as CMS, these CF were compared to commercially available Takeda 3A CMS. Adsorption kinetics of CH₄ and CO₂ have been followed in a constant volume DMT high pressure microbalance (Sartorius 4406) at 298 K and 0.1 MPa. The experimental results have been corrected for buoyancy effects related to the displacement of gas by sample, sample holder, adsorbed phase and pan [17].

3. Results and discussion

3.1. Study of stabilisation of pitch fibres in air

Thermogravimetry (TG) and DRIFTS were used to follow the variations produced in the fibres during the stabilisation process. Fig. 1 shows the corresponding TG profile of PFs at 573 K during 8 h.

The TG of Fig. 1 shows the variable heating rates used during the stabilisation process followed: 5 K/min up to 403 K, 1 K/min up to 493 K (soaking time of 60 min) and 1 K/min up to 573 K (soaking time of 480 min). It can be seen that the weight gain produced on the PFs as the temperature increases, which is related with the oxygen that is oxidised the pitch molecules [18–22]. This weight gain reaches a maximum of 7 wt.% at 573 K, when this temperature is kept constant, a decrease of the weight takes place. This weight loss (balance of oxygen uptake and carbon oxidation consumption) indicates that the material is being gasified by oxygen as well as suffering decomposition of the pitch molecules. In this sense, it must be remarked that DRIFT-TG studies [18] of this stabilisation process shows (even at low temperatures) oxidation of pitch molecules, intermolecular bond formation and evolution of H₂O, CO and CO₂. Even though all these processes may be occurring, the weight loss between 2 and 8 h only amounts about 3 wt.%.

Table 1
Characterisation of the parent pitch

Precursor	Elemental analysis (wt.%)					Solvent fractionation		
	C	H	N	S + O ^a	H/Cat ^b	IT	IQ	SP (K)
Petroleum pitch	93.73	6.16	0.09	0.01	0.79	0	0	493

^a Oxygen and sulphur content measured by difference.

^b Atomic ratio of hydrogen and carbon content.

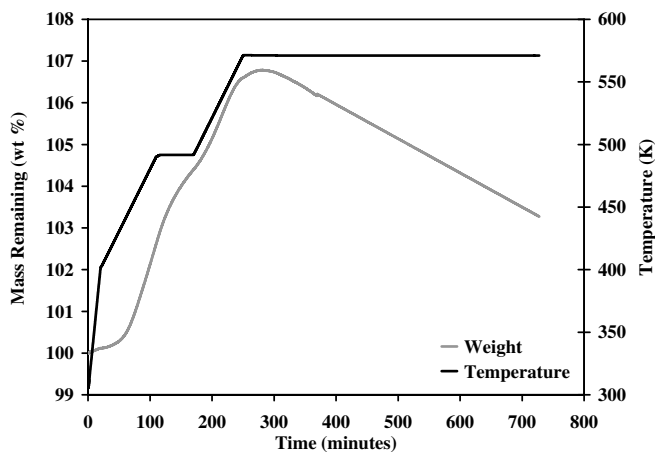


Fig. 1. TG curve of the stabilisation of PFs during 8 h analysis.

In order to study the changes happening in the pitch fibres during the stabilisation soaking time (2–8 h), at 573 K a DRIFTS study was carried out (see Fig. 2).

Other works [18–22], have studied the air stabilisation process of PFs. From these studies it has been observed that as the stabilisation progresses, a decrease in the hydrogen bands (Haro and Hali, indicating, respectively, hydrogen bonded to aromatic carbons and hydrogen bonded to aliphatic carbon) is observed (3100–2800, 1440, 900–700 cm^{-1}). Besides that, new bands related to oxygen groups appear. The development of these oxygen group bands depends on the stabilisation temperature. At temperatures below 500 K the band at 1700 cm^{-1} attributed to carbonyl groups gets more intense as the process temperature increases [23]. At around 500 K, an important band in the region between 1740 and 1650 cm^{-1} (carbonyl and carboxylic groups [24]) begins to be apparent in the spectrum of PFs. Finally, while holding the temperature at 573 K, a progressive development of the bands around 1850–1735 cm^{-1} (aromatic anhydrides, esters and aromatic esters [22–24]) and at 1300–1200 cm^{-1} (related to –OH groups and C–O bonds, respectively) occurs.

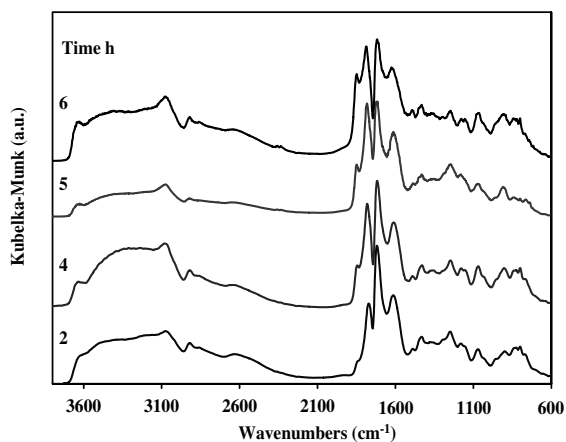


Fig. 2. DRIFTS spectra of the stabilised pitch fibres at different soaking times (from 2 to 6 h) at 573 K.

In Fig. 2, the main changes described above, can be seen in the spectrum of PFs stabilised for a soaking time of 2 h at 573 K. Thus, during this period of time the main reduction of the intensity of hydrogen bands has already occurred, and soaking times higher than 2 h do not produce significant changes on these bands. It must be noted that the increase in the stabilisation soaking time does not affect the bands due to C–H vibrational modes. The main changes in the DRIFT spectra can be appreciated in the region attributed to anhydrides and carbonyl groups (1850–1690 cm^{-1}) [23].

Fig. 3 shows a detail of the DRIFT spectra in the 2000–1400 cm^{-1} region. It can be clearly observed that the relative intensity of the bands assigned to anhydrides (1850 cm^{-1}) and esters (1800–1735 cm^{-1}) increase with soaking time, while the bands assigned to carbonyl and carboxylic groups (1740–1650 cm^{-1}) decrease as soaking time goes from 2 to 6 h.

The increase of the band at 1850 cm^{-1} (anhydrides) and the decrease of the band at 1740–1650 cm^{-1} (carboxylic and others) supports the idea that condensation reactions between carboxylic groups that are in adjacent pitch molecules are occurring. The formation of these functionalities would contribute to the stabilisation of pitch molecules.

It can be concluded from TG and DRIFTS experiments that an increase in the soaking time above the usual 2 h [15] does not produce important changes in the already stabilised pitch molecules but introduces variations in the distribution of oxygen functionalities that may affect the reticulation of PFs.

3.2. Porous texture characterisation of CFs carbonised at 1273 K after stabilisation at different soaking times

The above stabilised fibres at different soaking times were carbonised at 1273 K to obtain the corresponding CFs. The carbon fibre yield obtained relative to the starting

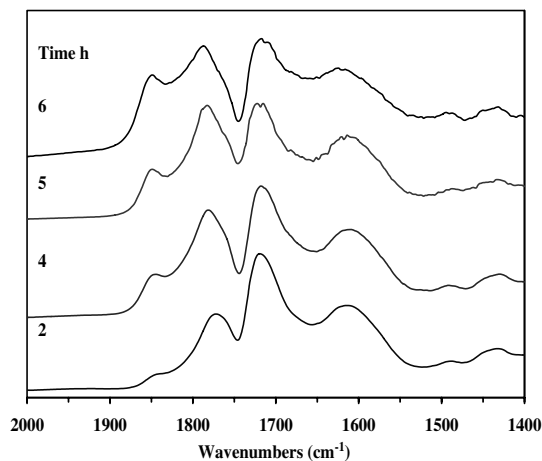


Fig. 3. Detail of the DRIFT spectra in the region of 1400–2000 cm^{-1} of the stabilised pitch fibres at different soaking times (from 2 to 6 h) at 573 K.

pitch fibre is presented in Table 2. The porous texture of the different CFs obtained was analysed by gas adsorption (N_2 and CO_2). Fig. 4 presents the N_2 adsorption isotherms of the prepared CFs.

In general, the isotherms are of Type I, as corresponds to microporous materials [25]. Interestingly, it can be appreciated that stabilisation has an effect on the final porosity of the CFs. It can be observed that soaking times lower than 5 h produces CFs with porosity accessible to N_2 . Samples CF-2h and CF-4h show higher adsorption capacity isotherms with narrow isotherm knees, which is related to a narrow micropore size distribution. Samples stabilised at higher soaking (6–8 h) do not present N_2 adsorption while the CF-5h isotherm behaves in between presenting a different shape maybe due to diffusional problems on the N_2 adsorption at low relative pressure ($P/P_0 < 0.2$). The narrow micropores cause a kinetic restriction to the N_2 adsorption at 77 K [26–28]. The shape of the CF-5h isotherm would indicate the presence of narrower micropores compared to the other samples (CF-2h and CF-4h) but bigger than samples CF-6h and CF-8h.

Regarding narrow microporosity (pores < 0.7 nm), CO_2 adsorption is useful to characterise the pores not accessible to N_2 [26,28–30]. Table 2 collects all the information about the porous texture characterisation of the CFs using both adsorptives (i.e., N_2 and CO_2). As it can be appreciated, the CF obtained from the stabilised PF by a conventional stabilisation method (soaking time of 2 h at 573 K) present both N_2 and CO_2 adsorption. The increase of the stabilisation time up to 4 h produces an important development of porosity, as detected by the increase of both N_2 and CO_2 adsorption. This indicates a development of porosity and a widening of the microporosity. Soaking times larger than 4 h produce CF with a lower micropore volume and a narrower microporosity, decreasing the porosity assessed by N_2 adsorption (see Fig. 4 and Table 2). Therefore, CF-5h shows a 50% reduction on its VDR_{N_2} with respect to CF-4h, while for soaking times higher than 5 h, the CFs the N_2 adsorption is nill and only CO_2 adsorption occurs. The VDR_{CO_2} for stabilisation soaking times higher than 5 h remained unaltered and similar to those obtained after 2 h of stabilisation (see Table 2). Hence, the increase of stabilisation soaking times from 6 to 8 h, does not affect the porosity accessible to CO_2 .

Table 2
Porous texture characterisation of the prepared CF at 1273 K, and the commercial carbon molecular sieve Takeda 3A

Sample	Stabilisation soak time at 573 K (h)	VDR_{CO_2} (cc/g)	VDR_{N_2} (cc/g)	BET (m^2/g)	CF yield (wt.%)
CF-2h	2	0.27	0.22	473	62
CF-4h	4	0.36	0.32	653	58
CF-5h	5	0.26	0.17	322	60
CF-6h	6	0.27	0.00	0	60
CF-8h	8	0.27	0.00	0	59
Takeda 3A	–	0.20	0.00	0	–

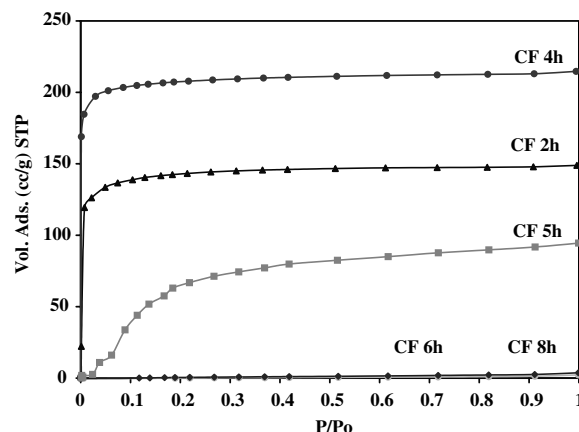


Fig. 4. N_2 adsorption isotherms performed at 77 K of the CFs obtained after carbonisation at 1273 K (the number after the letters CFs corresponds to the hours of stabilisation soaking time at 573 K).

Concerning the CF yield, Table 2 compiles the results obtained. It must be mentioned that this parameter is not significantly affected by the increase of the soaking time at 573 K during the stabilisation as expected from the TG results of Fig. 1. Therefore, an increase of stabilisation time at times larger than 2 h does not improve the CF yield. If this is so, another interesting observation, regarding the CF porosity is that their different adsorption capacities can not be related to a higher decomposition suffered by the PFs during their carbonisation.

3.3. Development of microporosity during the carbonisation of stabilised pitch fibres (at different soaking times) as a function of the carbonisation temperature

In order to complete the analysis of the effect of the PFs stabilisation soaking time, additional carbonisation temperatures (773 and 1023 K) have been carried out on all the PFs. The resulting CFs have been analysed by N_2 and CO_2 adsorption at 77 and 273 K. The micropore volumes of the samples studied are plotted in Fig. 5 (a, for CO_2 adsorption showing the temperature effect and b, to compare N_2 and CO_2 micropore volumes at 1273 K).

We can appreciate in Fig. 5a, that: (i) Independently of the temperature used, and for a given temperature the PF stabilised at different soaking times contain similar CO_2 micropore volume, with the exception of sample obtained at 1273 K and soaking time of 4 h, (ii) the V_{CO_2} increases continuously with the carbonisation temperature, (iii) at temperatures lower than 1273 K, all the samples present a narrow microporosity (< 0.7 nm) which is only accessible to CO_2 (there is not adsorption of N_2 at 77 K) and (iv) CFs carbonised at 1273 K have highest porosity. In addition, Fig. 5b shows that the carbonisation temperature at 1273 K produces samples that present N_2 adsorption at 77 K, except for the sample with stabilisation times above 5 h in which, microporosity is only accessible to CO_2 and not to N_2 .

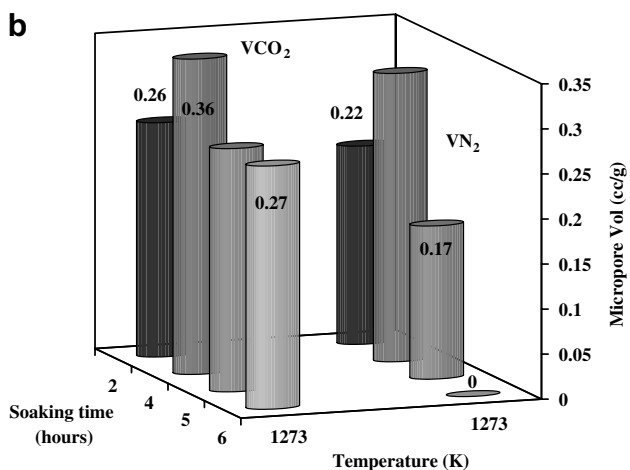
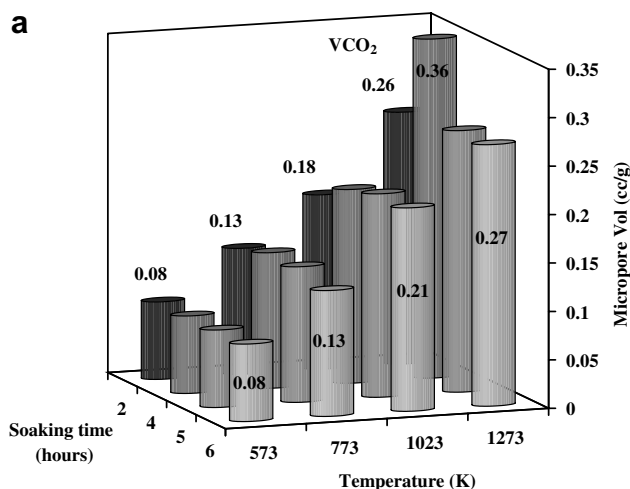


Fig. 5. (a) and (b) Micropore volume from CO₂ and N₂ adsorption of stabilised PFs at different soaking times as function of the carbonisation temperature (numbers indicated the value of micropore volume).

Considering, (i) that the weight loss during carbonisation up to 1273 K (see carbonisation yields of Table 2) is quite constant (≈ 40 wt.%) for all the stabilised samples and, (ii) that also their VCO₂ gradually increases with the carbonisation temperature, we can suggest that there is a relationship between porosity and weight loss of the stabilised fibres (related to the release of volatile matter from the stabilised pitch fibres) that generates microporosity in the carbon fibres.

Fig. 6, showing the thermogravimetric profile of the carbonisation process of the PFs soaked for 6 h at 573 K, confirms such existing relationship between porosity and weight loss of the stabilised pitch fibres (decomposition of oxygen functional groups and pitch molecules). It can be appreciated that the main weight loss occurs up to 1023 K and that increase in the porous volume is quite similar for all samples prepared up to 1023 K.

Interestingly, see Fig. 5b, the carbonisation at 1273 K of stabilised PF at different soaking times, produces, as it was discussed in Section 3.2, CFs with pronounced differences

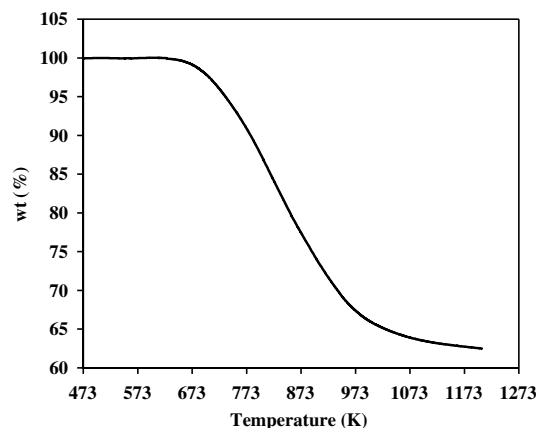


Fig. 6. Thermogravimetric curve of the carbonisation of the PF soaked for 6 h at 573 K.

in their microporosity evidenced by their different N₂ (77 K) adsorption behaviours. Taking into account the previous comments, it can be suggested that the main differences in the development of porosity of these samples take place during the carbonisation from 1023 K to 1273 K. In this range of temperature the narrow microporosity (VCO₂) develops in a similar trend as it does at lower temperatures (773 and 1023 K), presenting similar values for all samples (VCO₂) except for the sample stabilised for 4 h at 573 K. On the other hand, in this range of temperature, the widening of the microporosity is observed, as deduced from N₂ adsorption (Fig. 4). Thus, initially, an important widening on the microporosity happens, which increases with the soaking time of stabilisation up to 4 h, whereas at higher stabilisation times the microporosity becomes narrower, and samples stabilised for soaking times higher than 5 h do not present N₂ adsorption. It must be pointed out that between 1023 and 1273 K there is a small weight loss (Fig. 6). Hence, the development of narrow microporosity cannot be related with the release of volatiles, it must be related with a structural rearrangement of graphene layers from pitch molecules [31]. These processes could explain the observed evolution on the size of the microporosity. Therefore, larger stabilisation times may produce more rigid structures (i.e., via crosslink reactions between opposite pitch molecules) that avoid the widening of microporosity. This agrees with the DRIFT results that reveal that an increase of stabilisation time produces an increase in the formation of anhydride groups on pitch molecules.

3.4. Adsorption kinetic studies

The higher CO₂ micropore volumes than N₂ micropore volume of samples carbonised at 1273 K (see Fig. 5b) specially for the PFs stabilised at 6 h which has null N₂ adsorption, suggests that these CFs may exhibit CMS properties [4,26]. Interestingly, all the prepared samples have higher CO₂ micropore volumes than the Takeda 3A CMS (T3A)

(0.20 cc/g) (see Table 2). As a consequence, the presence of this type of porosity, as well as this appreciable micropore volume, makes these materials interesting candidates for their application in gas separation. The performance of different materials as CMS is normally evaluated in terms of adsorption kinetics of different gases [4,5,8,9,32]. In this work, individual adsorption kinetics of CO₂ and CH₄ (kinetic diameter 0.38 and 0.33 nm, respectively) were carried out as explained in Section 2 in samples carbonised at 1273 K and stabilised at different times (4, 5 and 6 h). Fig. 7a and b shows the adsorption kinetic data for CO₂ and CH₄, respectively. Fig. 7a shows the results corresponding to the kinetic of CO₂ adsorption for the four samples studied whereas Fig. 7b presents only the kinetic of CH₄ adsorption for sample CF-4h because the other samples do not have adsorption on the time scale of these measurements. In Fig. 7a, we can see that sample CF-4h has the highest CO₂ uptake although as it can be seen in Fig. 7b it also adsorbs CH₄. This observation agrees with data of Fig. 4 where sample CF-4h has the highest adsorption capacity for N₂ adsorption at 77 K. Therefore, at first glance, the sample Takeda 3A, CF-6h and CF-5h present more interesting behaviours, as CMS, than CF-4h, which

is not suitable for the separation of a mixture of these gases (CH₄ and CO₂).

Concerning sample CF-6h, that only presents microporosity accessible to CO₂ (it does not adsorb N₂ as shown in Fig. 5b) and has not CH₄ adsorption (as shown in Fig. 7b), exhibits a very slow CO₂ adsorption kinetics, which confirms it is a very narrow microporosity. Such narrow microporosity not only impedes the CH₄ adsorption, but it also makes difficult the CO₂ diffusion. Sample CF-5h has an intermediate situation as it can be seen in Table 2: it has a wider porosity than CF-6h, (it presents N₂ adsorption whereas CF-6h does not), and a narrower porosity than CF-4h (higher differences between VCO₂ and VN₂ values). As a result the sample that has an optimum pore size for CH₄/CO₂ separation is CF-5h (since it does not adsorb CH₄ but it adsorbs CO₂ in a comparable rate to T3A, see Fig. 7a). Moreover, for times longer than 180 s, CF-5h has a higher CO₂ adsorption capacity than T3A.

4. Conclusions

CFs with molecular sieve properties, have been successfully prepared, from an isotropic petroleum pitch with properties similar to Takeda 3A carbon molecular sieve.

The CFs derived from the PFs stabilised at 573 K during 5 h show an optimum pore size for CH₄/CO₂ separation, since it does not adsorb CH₄ but it adsorbs CO₂ in a comparable rate to Takeda 3A commercial carbon molecular sieve. Therefore by controlling the soaking time during the stabilisation it is possible to prepare in one step CFs with molecular sieve properties.

Consequently, this process is much simpler than conventional methods of preparing CMS that involve several steps (i.e., pre-treatments, carbonisation, activation and/or pore blockage by carbon deposition).

Additionally, the results obtained indicate that the development of narrow microporosity accessible to CO₂ at 273 K, increases with the carbonisation temperature. Interestingly, the porous texture remains unaltered for all samples prepared up to 1023 K at different soaking times during the stabilisation, showing a relationship between the development of porosity and the decomposition of the stabilised fibres. The main differences in the development of porosity can be observed during the carbonisation from 1023 K to 1273 K.

Acknowledgments

The authors would like to thank the financial support to the project MCYT (PPQ2003-03884).

References

- [1] J.B. Donnet, S. Rebouillat, T.K. Wang, J.C.M. Peng, *Carbon Fibers*, third ed., Marcel Dekker, New York, 1998.
- [2] I. Matsumoto, I. Mochida, *Carbon* 30 (1992) 1041.

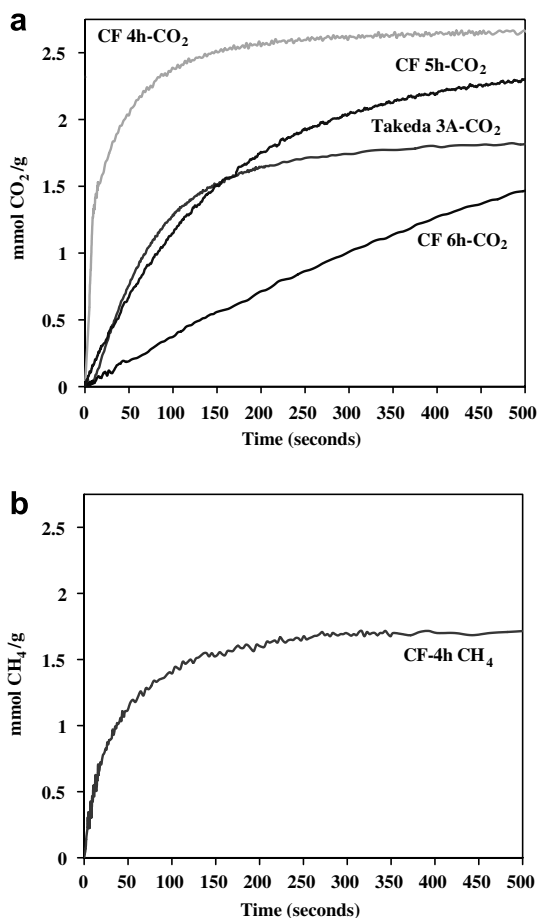


Fig. 7. CO₂ (a) and CH₄ (b) adsorption kinetics of CFs stabilised at different times and for Takeda 3A (the number after the letters CF corresponds to the number of hours of stabilisation at 573 K).

- [3] D.M. McKee, V.J. Mimeault, in: P.L. Walker Jr., P. Thrower (Eds.), *Chemistry and Physics of Carbon*, vol. 8, Marcell Dekker Inc., New York, 1988, pp. 151–232.
- [4] M.A. De la Casa-Lillo, J. Alcañiz-Monge, E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, *Carbon* 36 (1998) 1353.
- [5] Z. Hu, E.F. Vansant, *Microporous Materials* 3 (1995) 603.
- [6] J. Alcañiz-Monge, D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, *Economical Monolithic Coal Molecular Sieves. Extended Abstracts*, Carbon Conference, Charleston, SC, USA, 1999, p. 682.
- [7] K. Miura, J. Hayashi, K. Hashimoto, *Carbon* 29 (1991) 653.
- [8] P.J.M. Carrot, J.M.V. Valente, M.M.L. Ribeiro Carrot, J.A. Menéndez, *Carbon* 42 (2004) 227.
- [9] M.A. De la Casa-Lillo, B.C. Moore, D. Cazorla-Amorós, A. Linares-Solano, *Carbon* 40 (2002) 2489.
- [10] T.D. Burchell, R.R. Judkins, M.R. Rogers, A.M. Willians, *Carbon* 35 (1997) 1279.
- [11] Y. Kawabuchi, C. Sotawa, M. Kishiro, S. Kawano, D.D. Whitehurst, I. Mochida, *Langmuir* 13 (1997) 2314.
- [12] D. Lozano-Castelló, J. Alcañiz-Monge, D. Cazorla-Amorós, A. Linares-Solano, W. Zhu, F. Kapteijn, J.A. Moulijn, *Carbon* 43 (2005) 1643.
- [13] S.K. Verma, P.L. Walker Jr., *Carbon* 28 (1990) 175.
- [14] S. Villar-Rodil, R. Navarrete, R. Denoyel, A. Albinia, J.I. Paredes, A. Martínez-Alonso, J.M.D. Tascón, *Microporous and Mesoporous Materials* 77 (2005) 109.
- [15] J. Alcañiz-Monge, D. Cazorla-Amorós, A. Linares-Solano, A. Oya, A. Sakamoto, K. Hoshi, *Carbon* 35 (1997) 1079.
- [16] M.M. Dubinin, *Carbon* 27 (1989) 457.
- [17] R.K. Agarwal, J.A. Schwarz, *Carbon* 26 (1988) 873.
- [18] J.G. Lavin, *Carbon* 30 (1992) 351.
- [19] J. Alcañiz-Monge, D. Cazorla-Amorós, A. Linares-Solano, A. Oya, *Anales de Química* 90 (2) (1994) 201.
- [20] Y. Korai, M. Nakamura, I. Mochida, *Carbon* 29 (1991) 561.
- [21] T. Matsumoto, I. Mochida, *Carbon* 30 (1992) 1014.
- [22] C.C.Q. Yang, J.R. Simms, *Carbon* 31 (1993) 451.
- [23] P. Painter, R.W. Zinder, M. Starnisic, M.M. Coleman, D.W. Kuehn, A. Davids, *Applied Spectroscopy* 35 (5) (1981) 475.
- [24] J.F. McKay, P.J. Amend, T.E. Cogswell, P.M. Harnsberger, R.B. Erickson, D.R. Latham, in: P.C. Uden, S. Siggia, H.B. Jensen (Eds.), *Analytical Chem. of Liquid Fuels Sources: Tar Sands, Oil Shale, Coal, and Petroleum*, vol. 9, American Chemical Society, ACS, Washington, DC, 1978.
- [25] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Applied Chemistry* 57 (1985) 603.
- [26] F. Rodríguez-Reinoso, A. Linares-Solano, in: P. Thrower (Ed.), *Chemistry and Physics of Carbon*, vol. 21, Marcell Dekker, Inc., New York, 1988, pp. 2–146.
- [27] S.J. Gregg, S.K.W. Sing, *Adsorption, Surface Area and Porosity*, second ed., Academic Press, London, 1982.
- [28] D. Cazorla-Amorós, J. Alcañiz-Monge, A. Linares-Solano, *Langmuir* 12 (1996) 2820.
- [29] H. Marsh, B.J. Rand, *Journal of Colloid and Interface Science* 33 (1970) 101.
- [30] A. Linares-Solano, C. Salinas-Martínez de Lecea, J. Alcañiz-Monge, D. Cazorla-Amorós, *Tanso* 185 (1998) 316.
- [31] I.C. Lewis, *Carbon* 20 (1982) 519.
- [32] T. Orfanoudaki, G. Skodras, I. Dolios, G.P. Sakellariopoulos, *Fuel* 82 (2003) 2045.