

MOLECULAR SIEVE PROPERTIES OF GENERAL PURPOSE CARBON FIBERS

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Introduction

Carbon molecular sieves (CMS) are valuable materials for the separation and purification of gas mixtures. CMS are active carbons with a homogeneous pore size distribution, having a pore size of several angstroms. In these materials, gas separation is based on the different adsorption kinetics of the gases, existing the possibility that the amounts adsorbed in the equilibrium be similar. Considering the technological relevance of CMS, an important number of studies and patents can be found in the literature. In all the cases, the research is focused in the preparation of CMS with a large kinetic selectivity and with a high adsorption capacity in a reasonably short period of time [1].

Recently, we have studied the preparation of General Purpose Carbon Fibers (GPCF) from different materials [2] and, from them, activated carbon fibers (ACF) [3]. ACF are essentially microporous materials with a homogeneous pore size distribution which are very promising to obtain suitable CMS. Additionally, the analysis of the porous texture of the original GPCF (i.e., unactivated carbon fiber), revealed that these materials could contain, after an adequate preparation process, porosity accessible to CO₂ at 273 K and not accessible to N₂ at 77 K. These preliminary results could be an indication that GPCF could exhibit molecular sieve properties. In this work, we analyze the behaviour of GPCF obtained from different starting materials as CMS and its performance will be compared with commercial CMS in the separation of CO₂ and CH₄.

Experimental

GPCF prepared from four coal tar pitches and from a petroleum pitch [2] have been used in this study. A commercial GPCF from petroleum pitch and CMS (denoted CF and CMS respectively) have been also analyzed. Table 1 includes the porous texture of the materials analyzed determined from N₂ and CO₂ adsorptions at 77 K and 273 K, respectively. It contains the volume of micropores calculated from the application of the Dubinin-Radushkevich (DR) equation.

Kinetics of CH₄ and CO₂ adsorption has been followed in a DMT high-pressure microbalance (Sartorius 4406) in a range of pressures between 0.1 and 0.4 Mpa and at temperatures from 273 to 313 K. The experimental results have been corrected for buoyancy effects [4].

Table 1. Micropore volume of samples studied (cc/g)

Sample	CO ₂	N ₂
CF Coal pitch A	0.17	-
CF Coal pitch B	0.19	-
CF Coal pitch C	0.09	0.05
CF Coal pitch D	0.05	-
CF Petrol. pitch	0.25	-
CF	0.18	-
CMS	0.18	-

Results and discussion

Porous texture of the materials analyzed (Table 1) shows that all the samples are characterized by the absence of N₂ adsorption at 77 K, because the entrance of this adsorptive in the narrow micro-porosity of the carbon samples, is kinetically restricted. Nevertheless, the samples contain some narrow-microporosity (pore size lower than 0.7 nm) that is accessible to CO₂ adsorption at 273 K. This preliminary characterization can be an indication of molecular sieving properties of these samples.

If GPCF obtained from coal tar pitch are compared with those prepared from petroleum pitch, it can be observed that the pore volume accessible to CO₂ is higher for the second type of carbon fibers. Additionally, the results indicate that the pore volume achieved with the carbon fibers can be similar or, even larger, than that of the commercial CMS.

However, to obtain conclusions about the performance and of the molecular sieve properties of the different materials, the kinetics of adsorption of the gases which should be separated must be analyzed. In fact, this is necessary because the separation by carbon molecular sieves is based on the different adsorption kinetics of the gases that will be determined by their kinetic diameter. Because the

kinetic diameter of CO₂ is smaller than that for CH₄ (0.33 and 0.38 nm, respectively), an adequate carbon molecular sieve should selectively adsorb CO₂.

Figure 1 shows, as an example, the uptake of CO₂ at 298 K for the commercial CMS and carbon fibers obtained from coal tar pitch B and petroleum pitch. CH₄ uptake is not shown in the figure as it is not observed in the period of time studied. From this type of experiments, selectivity of the adsorbents can be calculated as the ratio of the diffusion time constants (i.e., D/r^2) for CO₂ and CH₄ adsorptions.

The uptake versus time curves show that adsorption of CO₂ in the CMS happens in a short period of time whereas CH₄ adsorption is absent. This shows the good molecular sieve properties of this material which has a high selectivity in the separation of these gases. On the contrary, whereas the adsorption capacity of the GPCF can be as high as that of the CMS, the time needed to reach a nearly constant weight is much larger. These differences in adsorption kinetics make the GPCF not adequate for application purposes.

Additionally, important differences can be observed if the adsorption kinetics of GPCF prepared from coal tar pitch are compared with the materials obtained from petroleum pitch. In general, either adsorption kinetics for GPCF from coal tar pitch is slower than for GPCF from petroleum pitch or much lower adsorption capacity is reached after the same period of time, even though both materials can have similar pore volumes (compare GPCF B with GPCF from petroleum pitch in Table 1). These results show that GPCF from coal tar pitch contain a lower pore volume and/or that the porosity is narrower than for GPCF from petroleum pitch. The differences between both materials should be related to the higher aromaticity of coal tar pitch that will introduce differences during the carbonization process of the petroleum and coal tar pitch fibers.

GPCF from petroleum pitch have been subjected to different treatments to improve their molecular sieve characteristics. In this sense, the commercial GPCF has been heat treated to 1173 K. We observed a weight loss by TG in these carbon fibers when heated in N₂ to 1173 K, which could indicate that the carbonization temperature in their manufacture was lower. The second treatment performed has consisted in a selective gasification by putting the sample in contact with air at 473 K and further heating to 973 K in N₂. Both treatments have produced materials with good molecular sieve properties. The kinetic selectivity attained with the first procedure was close to 48 and near to 12 for the second one. Considering that, from an economic point of view, the selectivity should be close to 20 for an efficient separation [5], both treatments are very promising to get good molecular sieve carbon fibers from GPCF.

Conclusions

GPCF exhibit molecular sieve properties but kinetics of adsorption is too slow for application purposes. Hence, these materials must be subjected to an adequate treatment to improve their performance as molecular sieves. GPCF from coal tar pitch have less possibilities than those prepared from petroleum pitch due to the lower pore volume and narrower porosity of the first type of materials.

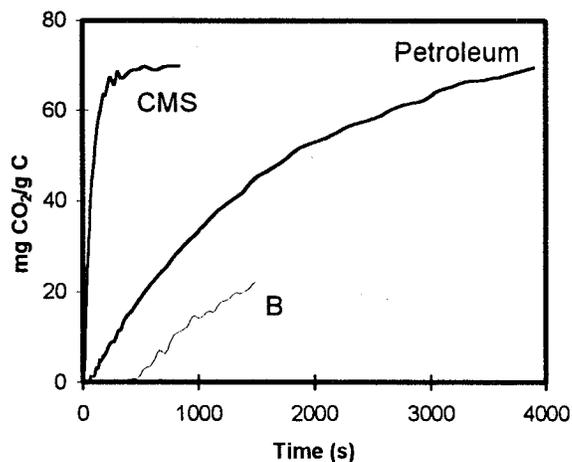


Figure 1. Uptake of CO₂ at 298 K for commercial CMS and CFs derived from coal tar pitch B and petroleum pitch.

Acknowledgments

The authors thank OCICARBON (project C23-353) and DGICYT (project PB93-0945) for financial support and MEC for the Thesis grant of M.A.C.L.

References

1. Moore, S.V. and Trimm, D.L., *Carbon*, 1977, 15, 177.
2. Alcañiz-Monge, J., Cazorla-Amorós, D., Linares-Solano, A., Oya, A., Sakamoto, A. and Hoshi, K., *Carbon*, 1997, accept.
3. Alcañiz-Monge, J., Cazorla-Amorós, D., Linares-Solano, A., Yoshida, S., and Oya, A., *Carbon*, 1994, 32, 1277
4. Cazorla-Amorós, D., Alcañiz-Monge, J., and Linares-Solano, A., *Langmuir*, 1996, 12, 2820.
5. Tao, J.C., *Separation Technology*, ed. E.F. Vansat, 1994, Elsevier Sci. B.V., 499.