

Molecular Sieve Carbons from PET for Separations Involving CH₄, CO₂, O₂ and N₂

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1. Introduction – Methane can be obtained from a number of different sources which include natural gas, biogas, landfill gas and abandoned coal mines. Most of these sources produce a CH₄ rich mixture containing significant amounts of other gases such as CO₂, O₂, N₂, H₂S and H₂O. Hence, in order to achieve a high calorific value it is necessary to remove these components using an appropriate separation process such as pressure swing adsorption (PSA) or membrane separation. In both cases, carbon molecular sieves (CMS), either in the form of pellets for PSA, thin films for asymmetric membranes or hollow fibres, have proven to be very effective and are currently commercialised by a number of companies such as Takeda (Japan), MAST (UK) and Carbon Membranes (Israel). There are a number of ways of preparing CMS. One of the most common, which has the advantage of using an established industrial technology, currently used for the production of C/C composites, nanotubes and synthetic diamonds, for example, is chemical vapour deposition (CVD). This involves the deposition of pyrolytic carbon on a microporous carbon material which has a homogeneous micropore structure with mean pore mouth dimension slightly larger than that required for effective molecular sieving action. The objective is to reduce the micropore mouth dimension by means of carbon deposition but without significantly reducing the adsorption capacity. A preliminary study of activated carbon production from PET had indicated that carbonised PET would be a suitable precursor [1]. Although other authors have also studied the use of PET as an activated carbon precursor [2-4], we believe this is the first report of CMS materials prepared from PET.

2. Experimental – The microporous carbon precursor, designated A4A0, was prepared from polyester (PET) textile fibres provided by Selenis (Portalegre) and carbonised in a horizontal tubular furnace under a N₂ flow of 85cm³min⁻¹ by heating at 1Kmin⁻¹ to 573K and holding for 60min, then at 10Kmin⁻¹ to 1073K and holding for 30min. CVD was carried out by passing N₂ saturated with benzene vapour over the sample at 1073K for *t* minutes and these samples are designated P8*t*. All materials were characterised by means of the adsorption of N₂ at 77K. A4A0 was also characterised by means of the adsorption of molecular probes of different dimensions at higher temperatures, namely, neopentane at 273K, dichloromethane at 298K, benzene at 298K and methanol at 298K. The molecular sieving properties of the PET derived CMS, as well as that of a commercial CMS, Takeda 3A, were evaluated by measuring single gas uptakes at 298K as a function of time at a contact pressure of approximately 1 bar. The gases used, and their respective molecular diameters, were CO₂ (0.330nm), O₂ (0.346nm), N₂ (0.364nm) and CH₄ (0.380nm).

3. Results and Discussion – Adsorption isotherms of N₂ at 77K and of the organic molecular probes on carbonised PET are shown in Figure 1. Analysis of the N₂ isotherm by means of the α_s and DR methods indicated that the sample was already microporous with micropore volume and mean micropore width of 0.26cm³g⁻¹ and 0.77nm, respectively. The high micropore volume is remarkable, considering that A4A0 was only carbonised and not activated. On the other hand, it can be seen from Figure 1 that the uptake of the organic adsorptives was lower and decreased with increasing molecular diameter. In particular, it is clear that the adsorption of the largest molecule (neopentane) was strongly activated, which indicates that the pore mouths contained constrictions smaller than the kinetic diameter of neopentane, that is, <0.62nm. This is an ideal starting point for pore mouth narrowing by CVD.

Figure 2 shows the adsorption isotherms of N₂ at 77K determined on the CVD treated samples. It can be seen that with increasing CVD time, the adsorption decreases and that the pore mouths were effectively narrowed. The most significant change occurred between 7 and 10 minutes of CVD and, for

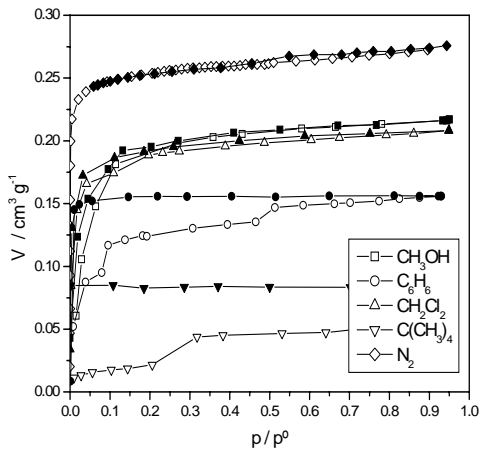


Figure 1 — Adsorption isotherms of $N_2/77K$ and organic probes on carbonised PET, A4A0

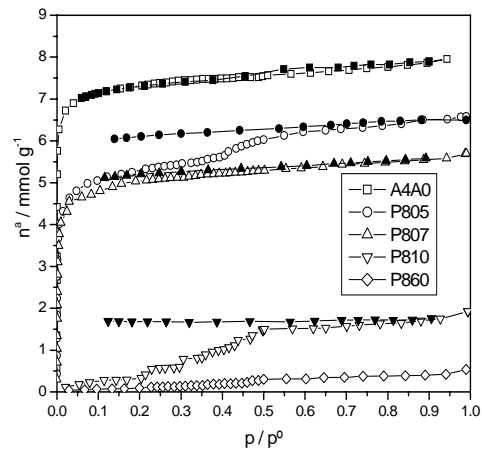


Figure 2 — Adsorption isotherms of $N_2/77K$ on A4A0 and the CVD treated samples

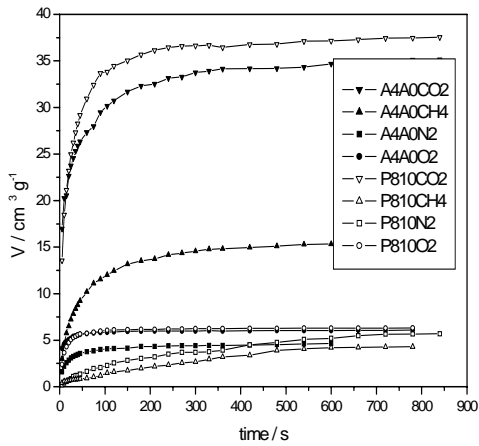


Figure 3 — Uptake curves for CO_2 , O_2 , N_2 and CH_4 at 298K on A4A0 and P810

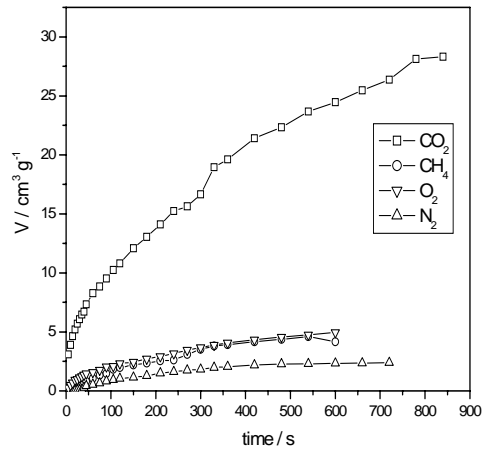


Figure 4 — Uptake curves for CO_2 , O_2 , N_2 and CH_4 at 298K on P860

CVD times of 10 minutes or more, N_2 at 77K is almost completely excluded. This is very similar to the behaviour which is also observed with commercial CMS used for O_2/N_2 separation.

Figure 3 shows the uptake curves for CO_2 , O_2 , N_2 and CH_4 at 298K on A4A0 and P810. It can be seen that the uptakes of the smaller molecules, CO_2 and O_2 , were not significantly altered by the CVD treatment. This confirms that the carbon deposition took place at the pore mouth, as intended, but not inside the pores. The equilibrium uptake of N_2 was also unaltered. However, its rate of uptake at low contact times was much lower. This indicates that the pore mouths had been narrowed to a size very similar to that of the N_2 molecule. As might be expected in this case, both the rate of uptake and the equilibrium uptake of the larger CH_4 molecule were significantly decreased. Figure 4 shows the uptake curves determined on P860 and it can be seen that with this sample the rate of uptake of all the molecules, including the smallest (CO_2) were decreased.

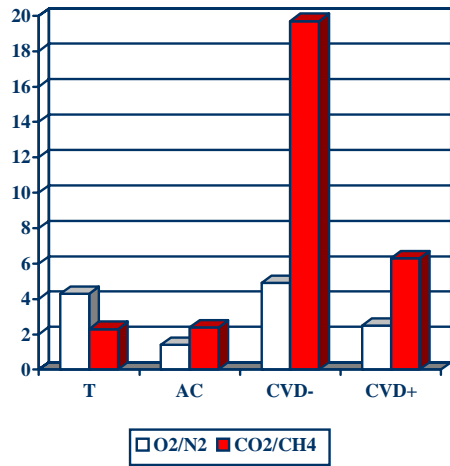


Figure 5 — O₂/N₂ and CO₂/CH₄ selectivities at 30s contact time (T=Takeda 3A; AC=A4A0; CVD-=P810; CVD+=P860)

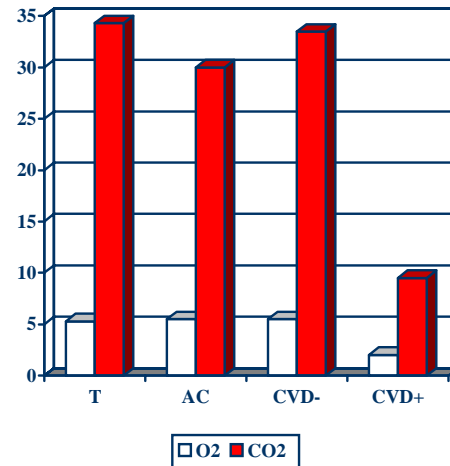


Figure 6 — O₂ and CO₂ capacities at 30s contact time (T=Takeda 3A; AC=A4A0; CVD-=P810; CVD+=P860)

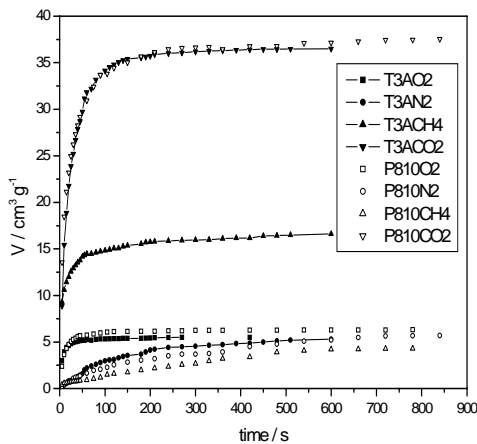


Figure 7 — Uptake curves for CO₂, O₂, N₂ and CH₄ at 298K on Takeda 3A and P810.

A comparison of the results in Figures 3 and 4 therefore suggests that a CVD time of about 10 minutes would be suitable for increasing O₂/N₂ and especially CO₂/CH₄ selectivity, but that a CVD time of 60 minutes would be excessive.

As a first estimate of the separation performance of the materials, in comparison with commercial CMS, selectivities for the separation of O₂/N₂ and CO₂/CH₄ were calculated from the ratio of the corresponding uptakes after 30s contact time [5] and are shown in Figure 5. The adsorption capacities for the smaller molecules at the same contact time are shown in Figure 6. The results in the Figures refer to a commercial CMS, Takeda 3A, as well as to A4A0, P810 and P860. It can be seen that the carbonised PET already had a performance similar to that of the Takeda CMS for the CO₂/CH₄ separation, but somewhat inferior for the O₂/N₂ separation. After 10min CVD treatment the selectivity for the O₂/N₂ separation was improved to a value slightly superior to that of the Takeda 3A, while the selectivity for the CO₂/CH₄ separation was greatly improved. In both cases, the O₂ and CO₂ capacities were not significantly altered.

After 60min CVD treatment, the selectivities were reduced, although that for the CO₂/CH₄ separation was still much higher than the Takeda selectivity. However, there was also a large decrease in the adsorption capacity. These results confirm that about 10 minutes CVD treatment produced materials with good performance but that 60 minutes CVD treatment was excessive. A more rigorous analysis of the uptake curves, with a view to estimating diffusion coefficients, is currently being carried out.

Finally, it is worthwhile comparing the uptake curves determined on P810 and Takeda 3A, shown in Figure 7. It is clear that the uptake of CO₂ was almost identical, while that of O₂ and N₂ was very similar. The most significant difference between the two samples is in relation to the uptake curve for CH₄, which was found to be much lower with P810. This indicates that in comparison to Takeda 3A the PET derived CMS had a pore size distribution with a lower upper cut-off, which is probably the main reason for its superior separation performance.

4. Conclusions – The results presented here show that commercial PET textile fibres could be used as precursors for the production of carbon molecular sieves. The PET fibres were first carbonised and then the pore mouths were narrowed by CVD of benzene. The best materials were obtained after 10 minutes CVD time and had a performance for O₂/N₂ and CO₂/CH₄ separations superior to that of commercial CMS.

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