



Modification of pore size in activated carbon by polymer deposition and its effects on molecular sieve selectivity

R.F.P.M. Moreira^{a,*}, H.J. José^a, A.E. Rodrigues^b

^a*Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, Campus Universitário, Trindade, 88040-970 Florianópolis, SC, Brazil*

^b*LSRE, Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia da Universidade do Porto, Rua dos Bragas, 4050-123 Porto, Portugal*

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Abstract

The separation of air for nitrogen production can be carried out by pressure-swing-adsorption over a carbon molecular sieve. The separation is kinetically controlled, since the equilibrium adsorption of both oxygen and nitrogen is very similar, but the adsorption kinetics for oxygen is faster than for nitrogen. Several methods to prepare carbon molecular sieves are reported. In this work, we synthesized a carbon molecular sieve from a commercial activated carbon. After deposition of polyfurfuryl alcohol, these materials were subjected to carbonization at 800°C under an inert atmosphere. All the microporous materials were characterized by analysis of kinetics and equilibrium adsorption data. The molecular sieve performance was assessed by the O₂/N₂ uptake ratio. The material prepared by two depositions has characteristics similar to those of commercial CMS. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon molecular sieves (CMS) are a special class of microporous materials used as adsorbents in separation processes. Due to the narrow pore size distribution, CMS find a wide range of applications in the field of separation, like nitrogen and oxygen from air [1,2] or carbon dioxide and methane [3] from their mixtures. The difference in kinetic adsorption characteristics of different gas species in CMS makes this adsorbent suitable for use in pressure-swing-adsorption processes (PSA).

While it is recognized that selectivity and gas sorption rates are important, the development of CMS of high capacity has attracted insufficient attention. For superior performance in the PSA process, a CMS should have high volumetric oxygen capacity which leads to both high recovery and higher productivity in the nitrogen PSA process [4]. A review of the properties of commercially

available activated carbons reveals a present limit of about 8 cm³/g of oxygen capacity.

In addition to high capacity and fast sorption rates, a superior CMS for air separation must also have high O₂/N₂ kinetic selectivity. This requirement makes the pore size distribution in the carbonaceous substrate very important. A substrate with a high micropore volume and some meso/macropores for transport is desirable. The difference in adsorption kinetics is thought to be related to molecular size. The kinetic diameter of oxygen (0.346 nm) is slightly smaller than that of nitrogen (0.364 nm). Recently, MacElroy et al. [5] reported that while aperture width is of fundamental importance, it is the pore length which is the central issue in the kinetic selectivity of CMS. When a carbon sample with molecular sieving characteristics comes into contact with air, an oxygen-enriched adsorbed phase and a corresponding nitrogen-rich gas phase are produced initially [6].

Several methods have been proposed for producing CMS since Emmett [7] reported the molecular sieving property of a carbonized Saran in 1948. The majority of methods are intended to slightly modify the pores created by carbonization of carbonaceous materials. Since the pore

*Corresponding author. Tel.: +55-048-331-9448; fax: +55-048-331-9687.

E-mail addresses: regina@enq.ufsc.br (R.F.P.M. Moreira), arodig@fe.up.pt (A.E. Rodrigues).

structure of carbonized materials is highly dependent on the starting materials, selection of a proper starting material is a key factor in the production of a CMS having the desired pore structure. Miura and Hayashi [8] have reported the preparation of CMS by modification of pore size distribution. The idea of this method is to modify the carbonization behavior of coal and consequently to change the pore structure of the char by adding modifiers, such as pitch and phenol–formaldehyde resin to coal. Only polymers that do not undergo transformation to the thermodynamically preferred graphite phase at high temperatures can be used for CMS synthesis [9]. This non-graphitizing character, which is present in materials like poly(acrylonitrile) (PAN), polyfurfuryl alcohol (PFA) and poly(vinylidene chloride) (PVDC), has been attributed to the presence of heteroatoms of cross-links between the polymer chains when pyrolyzed [9]. Several authors have shown that for most precursors, high temperature sintering leads to a diminution in porosity, with concomitant shrinkage of pores. Eventually, depending on the polymer precursor, a collapse of the structure and creation of macroporous defects occurs above a certain temperature, leading to a loss in sieving capability [10,11].

The objectives of this paper are:

- (i) to obtain CMS through the modification of activated carbon by deposition of polyfurfuryl alcohol;
- (ii) to analyze the role of the modifier during carbonization in the pore development;
- (iii) to assess the modified product behavior for O₂/N₂ separation.

2. Experimental

Several CMS were synthesized using the deposition of PFA on activated carbon (Norit Nederland B.V., The Netherlands) as support, designated as CA1. The activated carbon was used as powder (particle size: <100 µ). CMS supplied from Bergbau Forschung (Germany) was used to compare the performance of synthesized samples, in pellets of 2.5 mm diameter and 4 mm in length.

2.1. Synthesis

Furfuryl alcohol and formaldehyde (Merck) were mixed

in a flask containing activated carbon and were then heated to 80°C. H₃PO₄ (5%) was added to the flask and the temperature was increased up to 100°C. Following this, the hot mixture was filtered. The solid was dried at 100°C for 2 h and then carbonized at 800°C in an oven for 1.5 h under nitrogen atmosphere. Various microporous materials were synthesized as designated in Table 1.

2.2. Characterization

Nitrogen adsorption was carried out at 77 K with an ASAP/2000 Micromeritics (Norcross, GA, USA). All samples were pretreated at 350°C and 10^{−5} Torr. Sample sizes of approximately 0.25 g were used.

Mercury porosimetry (Micromeritics model 9320) was used to measure the macropore size distributions and densities. The porosimeter operated at a maximum pressure of 30 000 p.s.i. so that pores smaller than about 60 Å in diameter would not be detected.

2.3. Measurement of adsorption kinetics

The kinetics measurements were carried out using a microbalance CI Electronics (Wiltshire, UK). The sample was exposed to helium at a flow rate of 100 cm³/min at 350°C and kept at this temperature for 1 h. After the sample cooled and a stable baseline was obtained, the gas flow was switched to pure O₂ or N₂, also flowing at 100 cm³/min, and the weight uptake with time was monitored. The balance control unit was connected to an IBM PC enabling the weight reading to be accurately stored. The adsorption experiments were conducted at 25°C.

3. Results and discussion

3.1. Mercury porosimetry

This method is suitable for determining larger pores such as macropores of activated carbons. The macropore size distributions and densities are shown in Fig. 1 and Table 2. It is observed that after the first and second deposition of PFA, the total pore area diminishes about 19 times. After the second deposition, the total pore area decreases and the average pore size also decreases, indicat-

Table 1
Microporous materials prepared from activated carbon and polyfurfuryl alcohol

Designation	Treatments
CMS ^a	–
CA1 (activated carbon)	–
PFA2	Deposition of polyfurfuryl alcohol on CA1 + carbonization
PFA2-2	Deposition of polyfurfuryl alcohol on PFA2 + carbonization
PFA5	Carbonization of polyfurfuryl alcohol

^a CMS = Carbon molecular sieve (Bergbau Forschung).

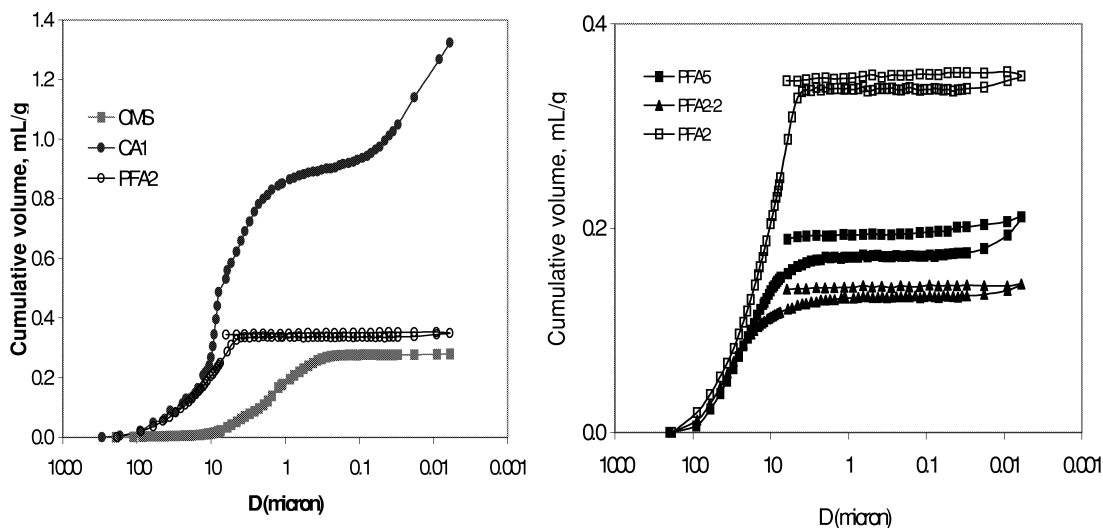


Fig. 1. Cumulative pore size distribution for CA1, PFA2, PFA2-2 and PFA5. CMS Bergbau Forschung is also shown.

ing that during the first and second deposition there is a filling of the macropores. The carbonized polymer shows a total pore area higher than the PFA2 and PFA2-2, but a lower average pore size.

3.2. Equilibrium isotherms

The equilibrium isotherms for O_2 and N_2 for different samples at 77, 204.5 and 296 K are shown in Figs. 2–4.

Nitrogen adsorption on CMS materials is difficult to measure, due to the high resistance to nitrogen diffusion or adsorption at 77 K. Adsorption in micropores does not take place by successive build-up of molecular layers, as supposed by the BET theory [12]. The microporous properties were calculated from Dubinin–Astakhov (DA) formalism [13] and the DA equation [Eq. (1)] was applied to obtain the micropore volume (W_o) and the characteristic energy (E_o). The DA formalism was applied in the range of relative pressures of $0 \leq P/P_o \leq 0.2$ [14].

$$W = W_o \exp \left[- \left(\frac{\varepsilon}{E_o} \right)^2 \right] \quad (1)$$

where W is the volume adsorbed at relative pressure P/P_o and $\varepsilon = RT \ln (P_o/P)$ is the adsorption potential, where R is the gas constant and T is the absolute temperature.

To estimate the micropore size, McEnaney [15] has

proposed that E_o and L_m , the micropore width, can be related by Eq. (2), where L_m is in nanometers.

$$L_m = 4.691 \exp (-0.0666E_o) \quad (2)$$

The adsorption equilibrium isotherms of nitrogen for different samples at 77 K are shown in Fig. 2. It can be observed that the isotherm of nitrogen for the precursor activated carbon (CA1) is typical of a mesoporous solid, where the hysteresis occurs because the mechanism of the adsorption in mesopores is different from that for desorption. The shape of hysteresis may be related to the dominant pore shape in the mesoporous solid. Hysteresis loop shapes have been classified by IUPAC [16]; the type shown for CA1 activated carbon is that found for slit-shaped pores, as expected for mesopores in activated carbons. All other materials show isotherms typical of microporous materials, and the N_2 adsorption isotherms are of type I. About 80–90% of the pore volume was filled below $P/P_o = 0.1$ indicating a narrow microporosity. The micropores of molecular sieve materials are usually considered to be slits between two carbon layer planes [17].

The analysis of isotherms at 77 K (Table 3) shows that the precursor activated carbon (CA1) has the lowest microporous volume and the highest width of micropores. After the first deposition, the microporous volume in-

Table 2
Analysis of mercury porosimetry

	CMS	CA1	PFA2	PFA2-2	PFA5
Total pore area (m^2/g)	2.40	94.6	5.02	4.86	14.40
Average pore size (4 V/A) (μm)	0.466	0.056	0.253	0.120	0.059
Apparent density (g/ml)	1.218	0.484	0.897	1.304	1.166
Skeletal density (g/ml)	1.848	1.349	1.254	1.610	1.548

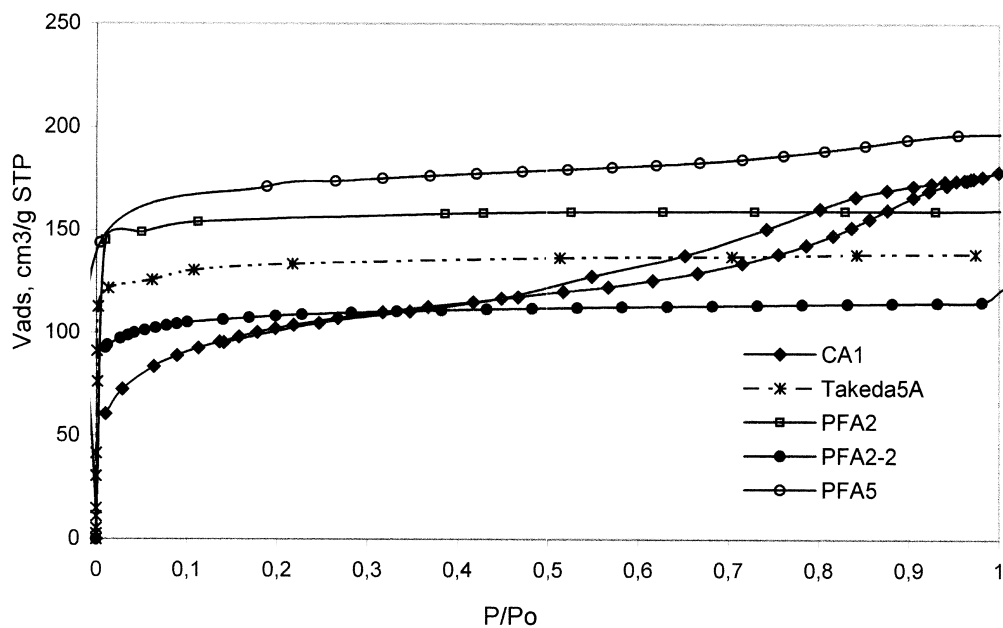


Fig. 2. N_2 Isotherms of adsorption at 77 K on PFA2, PFA2-2, PFA5 and activated carbon CA1. Data on CMS Takeda 5A. Ref. [22] is shown for comparison.

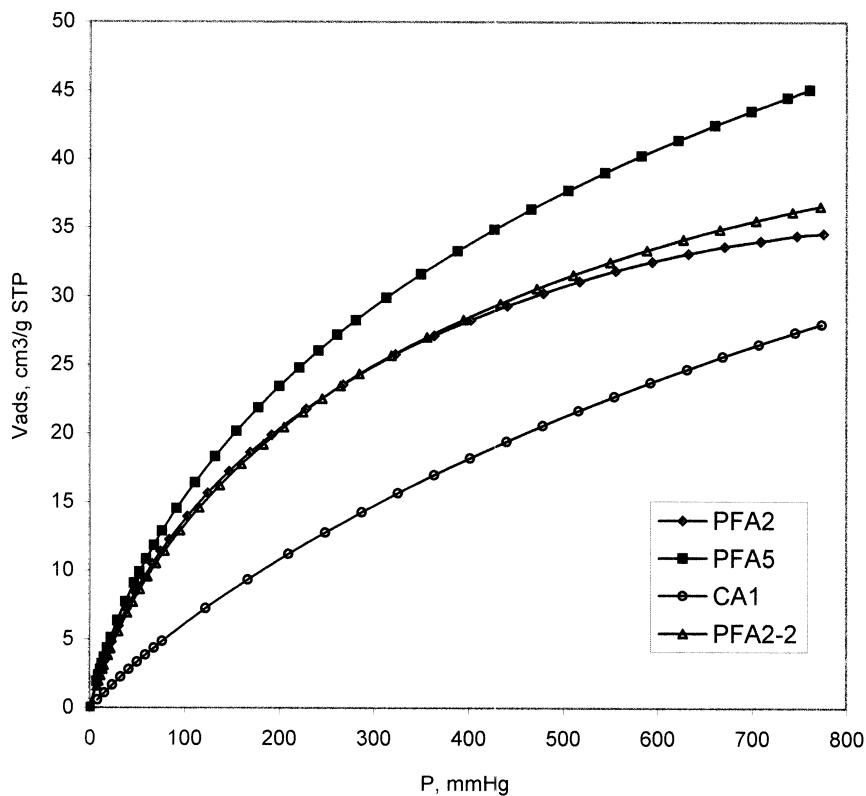


Fig. 3. Adsorption equilibrium isotherms of adsorption of nitrogen at 204.5 K.

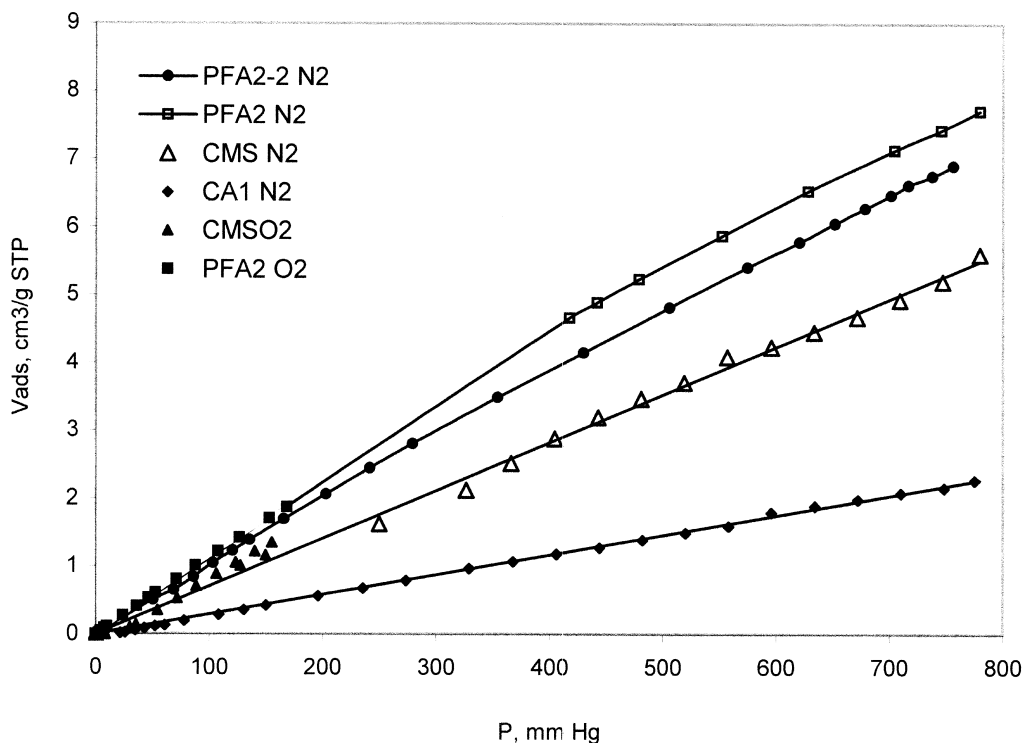


Fig. 4. Comparison of adsorption equilibrium isotherms at 296 K O_2 on PFA2 and CMS and N_2 on PFA2, PFA2-2, CA1 and CMS. CMS Bergbau Forschung is shown as comparison.

creases about 50% and concomitantly the width of micropore decreases, indicating that the PFA was deposited mainly on macro and mesopores. After the second deposition, the micropore width and microporous volume decrease, possibly as a consequence of filling the pores of the activated carbon precursor. The micropore width approaches 0.70 nm, from the first to second deposition, which is the micropore width of carbonized polymer PFA5.

The experimental isotherms for nitrogen at 204.5 K are shown in Fig. 3. The isotherms are favorable in form (type I) and fitted (Table 4) the ideal Langmuir model [Eq. (3)], as reported by Ruthven [18]. At this temperature, the

curvature of isotherm in the subatmospheric pressure range is similar to that encountered at ambient temperatures over the working pressure range of most nitrogen PSA processes [18].

$$\frac{V}{V_s} = \frac{bP}{1 + bP} \quad (3)$$

where V_s is the saturated amount adsorbed. We may observe that PFA5 has the highest V_s and the results obtained at 77 K (Table 4) show that micropore volume is the highest for these materials.

The adsorption equilibrium isotherms of nitrogen and oxygen at 298 K (Fig. 4) are almost linear, as reported by Ruthven et al. [1]. It is evident that there is little difference between the isotherms for oxygen and nitrogen for both CMS Bergbau Forschung and PFA2.

Table 3
Analysis of isotherms of adsorption at 77 K^a

	CA1	PFA2	PFA2-2	PFA5
W_o (cm ³ /g)	0.153	0.231	0.165	0.270
E_o (KJ/mol)	14.78	27.73	28.37	28.60
L_m (nm)	1.75	0.74	0.71	0.70
S_{mi} (m ² /g)	30.17	403.27	307.63	260.34
S_{ext} (m ² /g)	329.01	74.18	54.30	251.86
S_{BET} (m ² /g)	359.15	447.45	402.19	512.20

^a S_{mi} = Microporous area; S_{ext} = external area; S_{BET} = BET surface area.

Table 4
Analysis of adsorption isotherms at 204.5 K

Microporous materials	Langmuir parameters	
	V_s (cm ³ /g STP)	$10^3 b$ (mmHg) ⁻¹
CA1	55.53	1.25
PFA2	43.10	5.03
PFA2-2	46.29	4.28
PFA5	57.47	3.91

3.3. Kinetics of adsorption

The activated carbon, CA1, did not show any appreci-

able sieve effect or kinetic separation for oxygen and nitrogen (Fig. 5). To reduce the pore sizes, PFA was deposited on activated carbon and then carbonized.

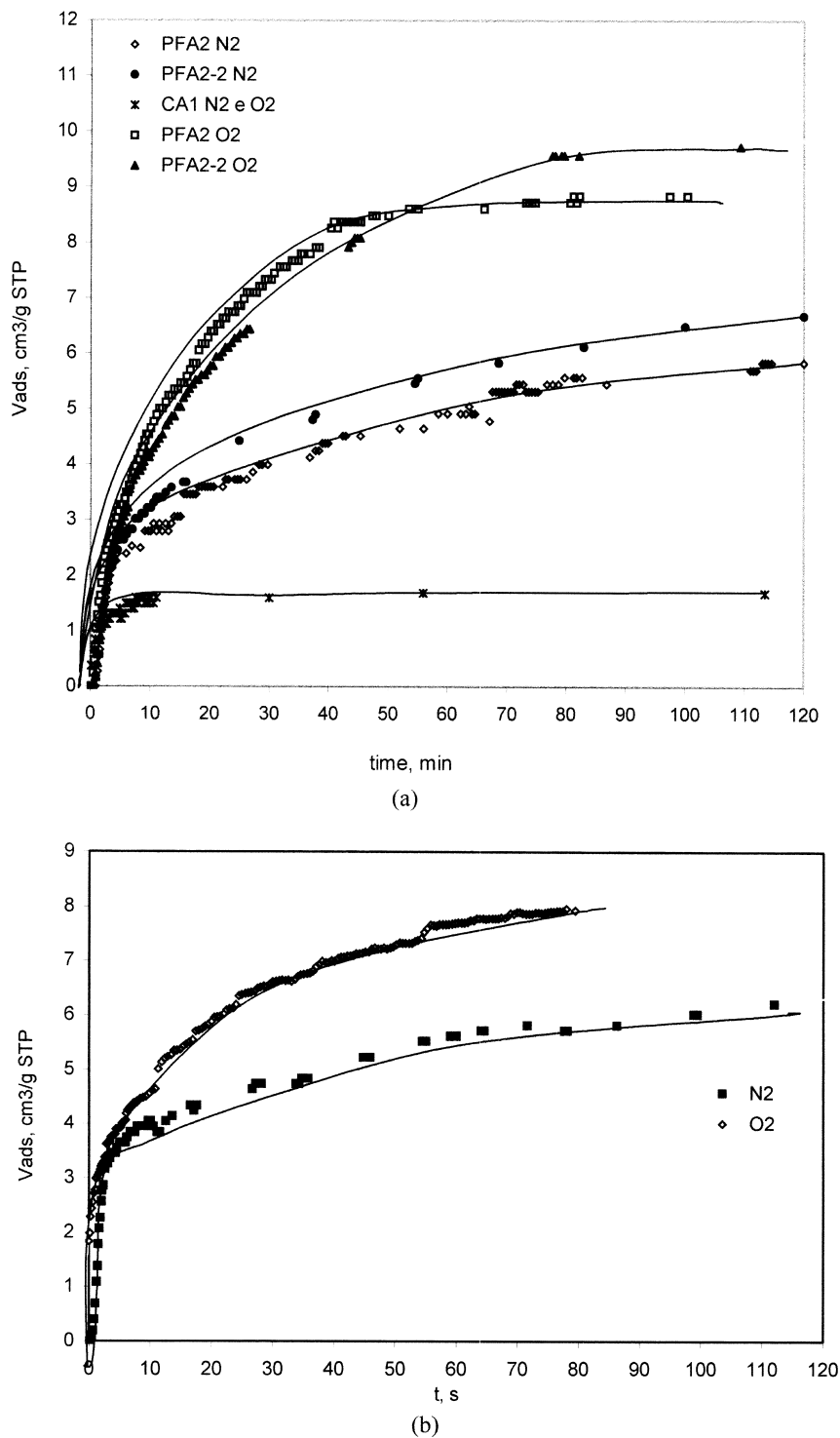


Fig. 5. Kinetics of adsorption of oxygen and nitrogen on CA1, PFA2 and PFA2-2 (a) and PFA5 (b) at 298 K.

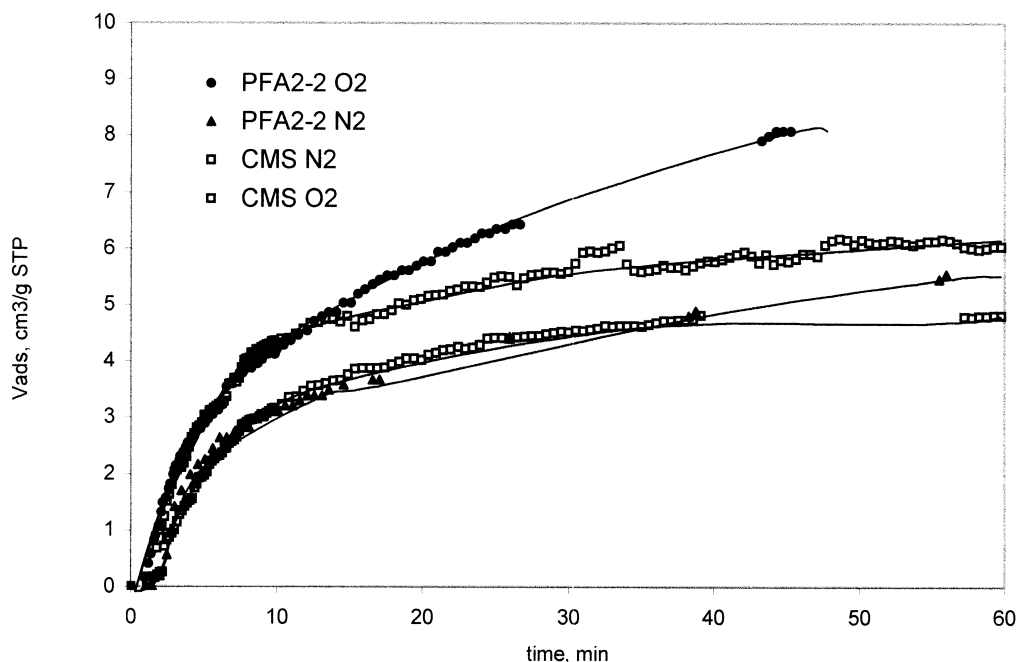


Fig. 6. Kinetics of adsorption of oxygen and nitrogen on PFA2-2 and CMS Bergbau Forschung at 298 K.

Fig. 5 shows the nitrogen and oxygen uptake versus time. It can be observed that although the adsorption capacities for oxygen and nitrogen are very similar to those reported in Fig. 4, the rates of adsorption differ markedly. In the nitrogen adsorption there is initially a very rapid uptake, followed by a slow approach to equilibrium, and so a simple single-step diffusion model evidently cannot properly represent uptake curves [1]. The most reasonable explanation for this behavior is that there is significant adsorption capacity and very little diffusion resistance within the macropores. The macropore surface equilibrates rapidly in the first instances. This is followed by slow diffusion into the micropores where most of adsorption occurs. After this initial uptake in both PFA2 and PFA5, the O_2 and N_2 curves are very different, indicating that

these materials have molecular sieve properties. After the second deposition, the fast initial uptake is not observed (Fig. 6) and the material has nearly the same initial uptake as a commercial CMS, although with higher capacity.

The solutions of small and long time behavior can be derived from Fick's law for isothermal diffusion for a concentration C into a homogeneous sphere of radius r , with D being the diffusivity constant [19].

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (4)$$

The complete solution for the uptake is:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp \left(- \frac{D n^2 \pi^2 t}{a^2} \right) \quad (5)$$

Table 5
Summary diffusivity data for carbon materials

	T (K)	D_{O_2}/r^2 (s^{-1})	D_{N_2}/r^2 (s^{-1})	D_{O_2}/D_{N_2}	Ref.
CMS* ^a	298	2.5×10^{-4}	4.7×10^{-5}	6	This work
CMS*	300	$0.8-2.0 \times 10^{-4}$	$3.5 \times 10^{-5}-10 \times 10^{-7}$	2–200	Ruthven et al. [1]
CMS*	300	1.7×10^{-4}	0.7×10^{-5}	24	Knoublauch [20]
CMS*	300	3.5×10^{-4}	1.0×10^{-5}	35	Chen et al. [21]
CMS*	273	2.4×10^{-4}	0.35×10^{-5}	68	Ruthen [18]
CA1	298	1.02×10^{-4}	1.02×10^{-4}	1	This work
PFA2	298	0.99×10^{-4}	1.0×10^{-5}	10	This work
PFA2-2	298	0.77×10^{-4}	1.4×10^{-5}	6	This work
PFA5	298	0.93×10^{-4}	1.5×10^{-5}	6	This work

^a CMS* = Carbon molecular sieve (Bergbau Forschung).

For short times this approximates to:

$$\frac{M_t}{M_\infty} = \frac{6D^{1/2}t^{1/2}}{\pi^{1/2}a} \quad (7)$$

For short times ($M_t/M_\infty < 0.25$) therefore, a plot of M_t/M_∞ versus $t^{1/2}$ will have a slope of $(6D^{1/2}/\pi^{1/2}r)$. The major problem with this approach is that the experimental data obtained in the initial uptake period are less accurate because of the time required to change the gases and experimental limitations.

For longer times, the higher order in Eq. (5) becomes negligible so that the expression simplifies to Eq. (8).

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} e^{-\pi^2 D t / r^2} \quad (8)$$

Diffusion of oxygen is clearly very much faster than that of nitrogen and no break is evident between the macropore and micropore uptakes. The diffusional time constants were evaluated from the plot of M_t/M_∞ versus $t^{1/2}$ and are shown in Table 5. The values found for CMS Bergbau Forschung are similar to those reported by several authors.

It can be also observed in Table 5 that the diffusional time constants for oxygen are at least one order in magnitude higher than those for nitrogen, for all microporous materials synthesized in this work, indicating that these materials are able to separate the components of air.

4. Conclusions

Carbon molecular sieves were prepared by deposition and carbonization of polyfurfyl alcohol on activated carbon. These materials are characterized by a high selectivity towards O_2 and a large uptake of this gas when compared with nitrogen. The equilibrium isotherms are essentially the same both for N_2 and O_2 . After the first deposition of polyfurfuryl alcohol, the micropore volume increases and the pore width decreases. A second deposition decreases the pore width, which approximates the pore width of the carbonized polyfurfuryl alcohol. The material prepared by two depositions has characteristics similar to those of commercial CMS.

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