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Preparation and Characterization of Adsorption-Selective Carbon Membranes for Gas Separation

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Abstract. The preparation and characterisation of adsorption-selective carbon membranes (ASCMs) is described. ASCMs can separate the components of a gas mixture depending on their adsorption strength. These membranes allow the separation of non-adsorbable or weakly adsorbable components (e.g. N_2, H_2, O_2, etc) from the more strongly adsorbable components (e.g. hydrocarbons) in a gas mixture. They are prepared from the deposition of a thin film of a phenolic resin on the inner face of an alumina tube. Air oxidative treatment at temperatures in the range of 300–400°C, prior to carbonisation (pre-oxidation) or after carbonisation (under vacuum at 700°C) (post-oxidation) gives rise to an adsorption-selective carbon membrane. This membrane shows a high permeability and selectivity towards the separation of gas mixtures formed by hydrocarbons and N_2. Taking into account the permeation and separation properties of the membranes, post-oxidation treatment is shown to be more effective than pre-oxidation. The separation characteristics of the carbon membranes are dependent on the composition of the gas mixture (i.e. proportion of more strongly adsorbable components) and temperature.

Keywords: gas separation, carbon membrane, adsorption selectivity, hydrocarbon, phenolic resin

1. Introduction

In recent years there has been growing interest in the preparation of carbon membranes for use in gas separation applications (Morooka et al., 2000). Carbon membranes are prepared by carbonisation of polymeric films. Precursors of carbon membranes include synthetic polymers such as cellulose acetate (Soffer et al., 1987), poly(vinylidene chloride) (Centeno and Fuertes, 2000), polyimides (Suda and Hraya, 1997; Kusuki et al., 1997; Fuertes and Centeno, 1998), poly(furfuryl alcohol) (Shiflett and Foley, 1999) and phenolic resins (Kita et al., 1997; Centeno and Fuertes, 1999). These polymers are initially crosslinked or become crosslinked during pyrolysis preventing the formation of large graphite-like crystals during carbonisation and leading to the formation of disordered structures (non-graphiting carbons) with a very narrow porosity. Taking into account the gas transport mechanism through the microporous carbon film, two types of carbon membrane have been developed:

a. *Molecular Sieve Carbon Membranes* (*MSCM*). The separation of gas molecules by means of MSCM takes place via a molecular sieving mechanism. Since MSCM have micropores with sizes close to the dimensions of permanent gases (<4 Å), the diffusivity of these gases through the membrane varies abruptly with molecular size and shape. This means that gases with similar molecular sizes can be separated.
b. *Adsorption-Selective Carbon Membranes* (*ASCM*). The separation of gas molecules by means of ASCM can be achieved because of their different adsorption properties. The more easily condensable components are preferentially adsorbed on the micropores of the membrane, reducing open porosity and limiting the diffusion of the less adsorbable gases

into the micropores. The adsorbed species diffuse through the membrane by a surface diffusion mechanism, which has already been described by Barrer et al. (1955). The more strongly adsorbed components permeate preferentially through the ASCM membrane, and are separated as a permeate stream (low-pressure side) whereas the less adsorbed components in the feed gas mixture are mainly recovered on the high-pressure side (retentate stream). ASCMs therefore are effective in separating non-adsorbable or weakly adsorbable gases (e.g. He, H_2, air, O_2, N_2, CH_4, etc) from adsorbable gases such as hydrocarbons (C_{2+}), NH_3, SO_2, H_2S, CFCs, etc. In addition, high fluxes can be reached at relatively low-pressure gradients because the driving force for the permeation of the more strongly adsorbed molecules is the concentration gradient through the membrane, and high concentrations of adsorbed species can be attained at relatively low pressures (Sircar et al., 1999). Structurally, ASCMs consist of a carbon film with micropores that are slightly wider, probably in the range of 5–7 Å, than those characteristic of MSCMs.

In contrast with the extensive work on the preparation and characterisation of MSCM, only two types of ASCMs are described in the literature. In one case, researchers at Air Products and Chemicals Inc., prepared an ASCM by carbonising (N_2, 1000°C, 1 K/min) a PVDC latex layer deposited on macroporous carbon disks or ceramic tubes (SSF^{TM} carbon membranes) (Rao et al., 1992, 1995). The membrane structure consisted of a microporous carbon film (around 3 μm thickness) which contained micropores in the range of 5–6 Å. This membrane was tested for recovering H_2 from refinery gases (mixtures of 20–40% H_2 with C_1–C_4 hydrocarbons). A membrane module was successfully field tested at a refinery site for the separation of a mixture with these characteristics (Sircar et al., 1999). Recently, this author developed a new type of ASCM (Fuertes, 2000, 2001). The preparation method consisted of a) coating the inner face of a macroporous alumina tubular support with a phenolic resin; b) carbonisation of the polymeric film and, c) air oxidation of the carbonised film. The carbon membrane obtained was effective in recovering hydrocarbons (permeate stream) from multicomponent gas mixtures formed by hydrocarbons and nitrogen.

In this paper we explore a new method of preparing ASCM, consisting of the oxidation of the polymeric film with air, at temperatures in the range of 250–400°C, prior to the carbonisation step. In addition, the effect that temperature and hydrocarbon concentration have on the permeation and separation characteristics of adsorption-selective carbon membranes is analysed. The separation characteristics of the membranes were analysed via permeation tests, using pure gases and gas mixtures containing adsorbable and non-adsorbable components.

2. Theory: Gas Transport in Adsorption-Selective Carbon Membranes

Gas permeance through a membrane (mol.m^{-2}.s^{-1}.Pa^{-1}) can be defined as

$$F = \frac{\varepsilon}{\tau}\frac{J}{\Delta p} \tag{1}$$

where ε is membrane porosity, τ is the tortuosity factor, Δp the pressure drop through the membrane and J the transmembrane flux per unit of area (mol.m^{-2}.s^{-1}) which is given by

$$J = -D_F \frac{dc}{dx} \tag{2}$$

c is the concentration of the species diffusing through the membrane and D_F the Fickian diffusivity.

For adsorbable gases, Fickian diffusivity is concentration-dependent. A relationship between D_F and the concentration of adsorbed species (c) can be deduced from the thermodynamic theory (Darken equation).

$$D_F = D\frac{d\ln(p)}{d\ln(c)} \tag{3}$$

D being the intrinsic diffusivity, which is independent of the amount adsorbed. Combining Eqs. (2) and (3), gives

$$\begin{aligned} J &= -D\frac{d\ln(p)}{d\ln(c)}\frac{dc}{dx} = -D\frac{d\ln(p)}{d\ln(c)}\frac{dc}{dp}\frac{dp}{dx} \\ &= D\frac{d\ln(p)}{d\ln(c)}\frac{dc}{dp}\frac{\Delta p}{\delta} \end{aligned} \tag{4}$$

where δ is the membrane thickness. By combining (4) and (1), the permeance of a gas through the membrane can be written as

$$F = \frac{\varepsilon}{\tau\delta}D\frac{d\ln(p)}{d\ln(c)}\frac{dc}{dp} \tag{5}$$

Transport of Pure Non-Adsorbable Gases through the Membrane. In this case, transport occurs exclusively by gas diffusion, in which case the derivative terms of Eq. (5) are

$$\frac{d\ln(p)}{d\ln(c)} = 1 \tag{6}$$

$$\frac{dc}{dp} = \frac{1}{RT} \tag{7}$$

and the gas permeance for a non-adsorbable gas (F_g) will be given by

$$F_g = \frac{\varepsilon}{\tau\delta}\frac{1}{RT}D_g = \frac{\varepsilon}{\tau\delta}\frac{1}{RT}D_o^g e^{-E_g/RT} \tag{8}$$

where E_g is the activation energy for the activated diffusion in gas phase.

Transport of Strongly Adsorbable Gases through the Membrane. For strongly adsorbable gases, gas permeation will take place exclusively by a superficial diffusion mechanism. If the Langmuir equation is used to relate the pressure to the adsorbed phase concentration

$$\theta = \frac{c}{c_{\text{sat}}} = \frac{Kp}{1+Kp} \tag{9}$$

where K is the Langmuir constant and c_{sat} is the maximum amount adsorbed on carbon at a given temperature. Parameters K and c_{sat} are temperature-dependent and decrease as temperature increases. By using Eq. (9), the derivative terms of Eq. (5) are

$$\frac{d\ln(p)}{d\ln(c)} = \frac{1}{1-\theta} = 1 + Kp \tag{10}$$

$$\frac{dc}{dp} = c_{\text{sat}}\frac{K}{(1+Kp)^2} \tag{11}$$

By substituting (10) and (11) in Eq. (5), the permeance of an adsorbable gas (F_{a}) is given by

$$\begin{aligned} F_a &= \frac{\varepsilon}{\tau\delta}c_{\text{sat}}D_a\frac{K}{1+Kp} = \frac{\varepsilon}{\tau\delta}c_{\text{sat}}D_aK(1-\theta) \\ &= \frac{\varepsilon}{\tau\delta}c_{\text{sat}}(1-\theta)D_o^aK_oe^{-(E_a-Q)/RT} \end{aligned} \tag{12}$$

E_a being the activation energy of superficial diffusion and Q the heat of adsorption. In this case, the gas permeance shows an apparent activation energy of $(E_a - Q)$. As shown in Eq. (12) permeance increases with temperature if $E_a > Q$ and decreases if $E_a < Q$.

For low adsorption degrees ($\theta \to 0$; low partial pressures, Henry region), the permeance of the adsorbed species is given by

$$F_a = \frac{\varepsilon}{\tau\delta}c_{\text{sat}}D_o^aK_oe^{-(E_a-Q)/RT} \tag{13}$$

whereas at high adsorption degrees ($\theta \to 1,\ Kp \gg 1$; low temperature, high partial pressures),

$$F_a = \frac{\varepsilon}{\tau\delta}c_{\text{sat}}D_o^a\left(\frac{1}{p}\right)e^{-E_a/RT} \tag{14}$$

In this case, the activation energy of the process is that corresponding to superficial diffusion. From Eq. (14) it can be seen that for a high surface coverage, the permeance depends on the inverse of the partial pressure of the adsorbed species.

In general, both mechanisms, superficial diffusion and gas diffusion can contribute to transport through the membrane simultaneously. This is particularly true for permeation through the carbon membranes of the moderately adsorbable gases (i.e. C_1, C_2 and C_3 hydrocarbons) or the more condensable hydrocarbons (i.e. C_4) at high temperatures. An expression for overall permeance (F_{ag}) must therefore take into account both contributions. Thus,

$$\begin{aligned} F_{\text{ag}} = \frac{\varepsilon}{\tau\delta}\Bigg(&c_{\text{sat}}(1-\theta)D_o^aK_oe^{-(E_a-Q)/RT} \\ &+\frac{1}{RT}D_o^ge^{-E_g/RT}\Bigg) \end{aligned} \tag{15}$$

Transport of Non-Adsorbable Gases in the Presence of Adsorbable Gases. In the presence of an adsorbable species, the transport of non-adsorbable gas is hindered because a part of the open porosity is occupied by the adsorbed species. Consequently, the gas permeance (F_g^*) will be lower than that predicted by Eq. (8) for pure gas permeance. The hindering effect the adsorbed components have on the permeation of a non-adsorbing component can be analysed following the theoretical approach proposed by Yang et al. (1999). These authors postulate that the presence of adsorbed molecules creates a potential barrier to the diffusion of non-adsorbed molecules. From this hypothesis, they deduced the following equation for the permeance of non-adsorbed species in the presence of an adsorbable gas

$$F_g^* = F_g e^{-(E_o\theta)/RT} \tag{16}$$

where θ is the surface coverage of the adsorbed species and E_o the potential barrier introduced at $\theta = 1$. By combining Eqs. (8) and (16) we get

$$\begin{aligned} F_g^* &= \frac{\varepsilon}{\tau\delta}\frac{1}{RT} D_g e^{-(E_o\theta)/RT} \\ &= \frac{\varepsilon}{\tau\delta}\frac{1}{RT} D_o^g e^{-(E_g+E_o\theta)/RT} \end{aligned} \tag{17}$$

The apparent activation energy will be $(E_g + E_o\theta)$. The parameter E_o increases with the adsorption strength of the species. From the above equation, it can be seen that the permeance of a non-adsorbable species will depend on the nature of the adsorbable gas (E_o) and on the degree of coverage (θ), which is in turn dependent on temperature and pressure. It can be predicted that the lowest permeance for the non-adsorbable gas will be reached for mixtures with strongly adsorbable gases (i.e. n-butane) at low temperatures (i.e. room or sub-zero temperatures) and high partial pressures (a high proportion of hydrocarbon in the mixture).

For a binary gas mixture formed by a strongly adsorbable gas (i.e. n-butane at room temperature) and a non-adsorbable gas (i.e. nitrogen), the separation factor $(\alpha_{a/g})$ is given by

$$\begin{aligned} \alpha_{(a/g)} &= F_a/F_g^* \\ &= RT c_{\text{sat}} K_o \left(\frac{D_o^a}{D_o^g}\right)(1-\theta)e^{-(E_a-Q-E_g-E_o\theta)/RT} \end{aligned} \tag{18}$$

For a binary gas mixture formed by a non-adsorbable gas (i.e. nitrogen) and a moderately adsorbable gas (i.e. ethylene at room temperature), an expression for the separation factor can be deduced by using Eq. (15) for the permeance of the adsorbing component.

For multicomponent gas mixtures (i.e. $C_1 + C_2 + C_3 + C_4$ hydrocarbons and nitrogen), both the amount adsorbed and the surface diffusion of each component through the membrane are the result of a complex equilibrium of all the adsorbing components. In general, the presence of strongly adsorbable components (i.e. n-butane) reduces the adsorbed amount of the less adsorbing gases (i.e. C_1, C_2 and C_3 hydrocarbons) due to a competitive adsorption occurring between the various species. This is a very complex problem, which lies outside the scope of the present work. Van de Graaf et al. (1999) have presented a solution for simple cases such as the separation of ethane/methane or propane/methane mixtures through zeolite membranes.

3. Experimental

3.1. Preparation of Carbon Membranes

Ceramic tubular membranes manufactured by US Filter for ultrafiltration processes were used as carbon membrane supports. The dimensions of the substrates are 10 mm o.d., 7 mm i.d. and 20 mm length. The tubes consist of four layers: the inner layer is made up of γ-alumina film (Pore size: 20 nm); the other layers are made up of α-alumina. The selective carbon film was prepared from a commercial novolak-type phenolic resin. A thin phenolic resin film was deposited on the inner face of the porous substrate. The supported phenolic resin film was cured in air at 150°C for 2 hours. Carbonisation of the polymeric film was carried out in a vertical tubular furnace (Carbolite) at a temperature of 700°C, under vacuum (<0.01 mbar). Pre-oxidation treatments with air were carried out upon deposited and cured phenolic resin films. Post-oxidation treatments upon carbonised samples were performed with air at temperatures between 300°C and 400°C, for a period of time of 30 minutes.

3.2. Permeation Measurements

In order to analyse the permeation characteristics of the membranes, the following gases were selected: He (2.6 Å), CO_2 (3.3 Å), O_2 (3.46 Å), N_2 (3.64 Å), CH_4 (3.8 Å), C_2H_4 (3.9 Å), C_2H_6 (4.0 Å), C_3H_6 (4.5 Å), C_3H_8 (4.3 Å), n-C_4H_{10} (4.3 Å), i-C_4H_{10} (5.0 Å). The values in brackets correspond to the kinetic diameters of the gases (Breck, 1974).

The permeance of pure gases was measured at ambient temperature (20 ±1°C). The carbon membrane (Area $\approx 2 \times 10^{-4}$ m^2) was attached to a permeation cell. To measure the permeation of pure gases, high-pressure high-purity gases supplied from compressed gas cylinders were placed in contact with the membrane. A manometer was used to measure the pressure. A vacuum was maintained on the low-pressure side of the membrane, and the permeate was pulled through a calibrated volume. The variation in pressure was determined by using a pressure transducer

(Leybold CM 1000) and a digital unit connected to a computer. The permeance and permeability of pure gases throughout the membrane was estimated from the variation of pressure with time on the low-pressure side of the device up to a pressure of 100 mbar.

An analysis of the separation of gas mixtures was carried out at ambient temperature (20 ± 1°C) by means of a system described elsewhere (Centeno and Fuertes, 1999). A gas mixture was injected into the inner face of the tubular membrane (in contact with the carbon microporous film). As a rule the feed pressure was 1 bar, but some experiments were carried out at a feed pressure of 2 bar. Helium was used as carrier gas and was made to flow through the permeate side (Pressure: 1 bar). The gas concentration on the permeate side was measured by means of a TCD-GC (Hewlett-Packard, Mod. 5890) equipped with a Porapak Q column. In order to operate under quasi-differential conditions, the stage cut ((Permeate flow rate/feed flow rate) × 100) was maintained in the range of 5–10%. By modifying the flow rate of the carrier gas, concentrations of permeating gases in the permeate stream were kept below 5%.

4. Results and Discussion

4.1. Structure of Carbon Membranes

The carbon membranes prepared are formed by a thin carbon film supported on a macroporous ceramic substrate. An SEM microphotograph of a pre-oxidised (350°C, 1 h) carbon membrane is shown in Fig. 1. As can be seen, the carbon film has a thickness of around 2–3 microns and is well adhered to the ceramic substrate.

In a previous paper (Fuertes, 2001) it was reported that non-oxidised sample exhibits a mean micropore size in the range of 4.0–4.5 Å whereas an oxidised membrane (in air at 400°C, 0.5 h) shows a slight enlargement of micropore size.

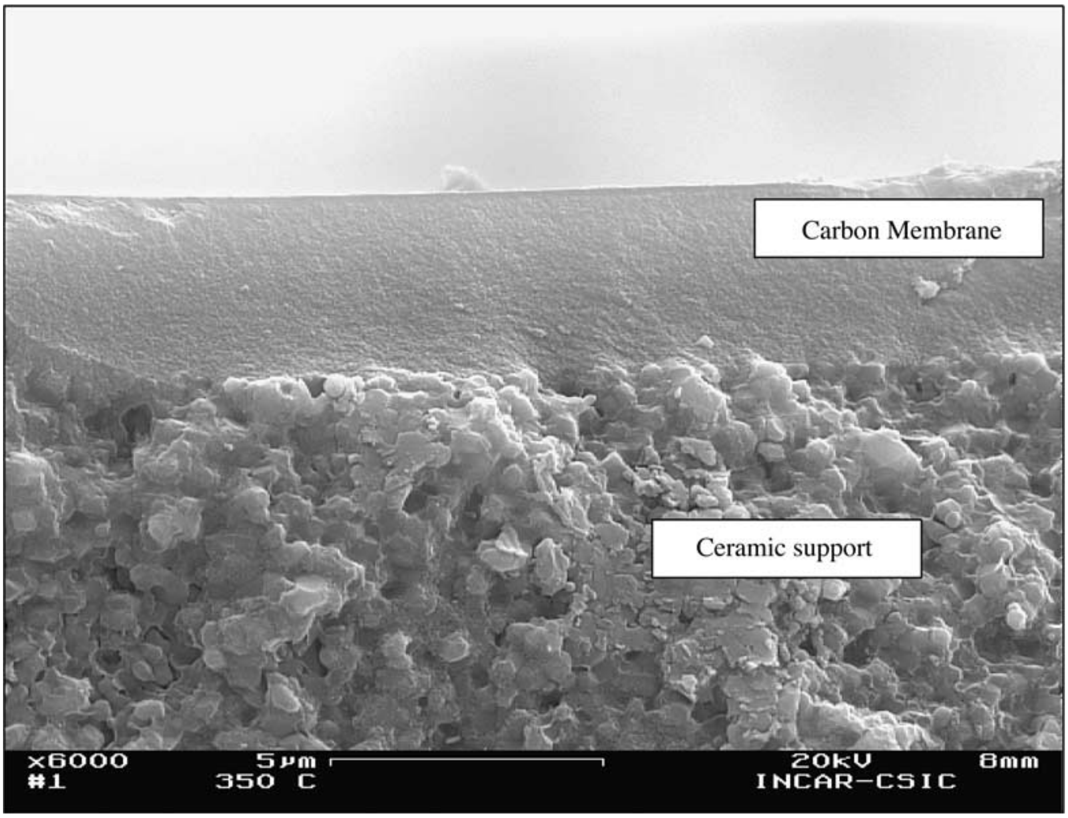

Figure 1. SEM microphotograph of a carbon membrane (pre-oxidised at 350°C, 1 h).

4.2. Effect of the Air Oxidation of the Polymeric Film on the Separation Characteristics of Carbon Membranes

It well known that air oxidation of some polymers allows the formation of oxygen bridges between aromatic molecules, which inhibits the rearrangement and growth of aromatic crystallites during carbonisation (Jenkins and Kawamura, 1976). It allows that carbons formed after carbonisation of pre-oxidised samples show a more open porosity. Based in this hypothesis, air pre-oxidation of deposited phenolic resin films was explored as a way to prepare carbon membranes with a wider porosity with respect to non-oxidised samples. Then, it is expected that pre-oxidised materials show adsorption-selective properties.

The effect that air pre-oxidation has on permeances of pure gases through carbonised membranes is illustrated in Fig. 2 for different samples pre-oxidised at temperatures ranging from 250°C to 400°C. The gas permeances show an increase with the pre-oxidation temperature. The sample pre-oxidised at 250°C exhibits molecular sieving properties and the gas permeances decrease with molecular size, but to a lesser extent than for the non-oxidised membrane. For the samples pre-oxidised at higher temperatures, the permeances do not show a regular variation with kinetic diameter. Helium ($d_k = 2.6$ Å) shows a lower gas permeance than that of ethylene ($d_k = 3.9$ Å). This indicates that for the pre-oxidised membranes adsorption effects have an important role in the transport of pure gases and, in consequence, the diffusion of more adsorbable gases (i.e. hydrocarbons) through the membrane takes place by means of a surface diffusion mechanism.

Separation experiments of binary gas mixtures formed by a non-adsorbable gas (nitrogen) and an adsorbable gas (hydrocarbon) conducted with a pre-oxidised carbon membrane demonstrate the importance of adsorption effects on gas separation. Figure 3 shows, for a carbon membrane pre-oxidised at 350°C (1 h), the modification of N_2 permeance (Fig. 3(a)) and of the (N_2/hydrocarbon) separation factor (Fig. 3(b)) against the critical volume of hydrocarbon (permeant). Here, the critical volume can be taken as a measure of adsorption strength. As the critical volume of the permeant increases, the nitrogen permeance decreases (Fig. 3(a)) and the separation factor increases (Fig. 3(b)). This suggests that, as hydrocarbon molecules are adsorbed into the micropores of the carbon membrane, they occupy a part of the void space and partially inhibit the diffusion of non-adsorbable species. The degree of hindrance to N_2 diffusion increases from ethylene to *n*-butane because the more condensable gases are adsorbed more strongly. This can be understood better if one takes into account the concepts developed in Section 2. Thus, since critical volume can be considered as a measure of hydrocarbon-carbon adsorption strength, the modification observed is a consequence of the fact that more condensable hydrocarbons establish higher potential barriers (E_o). This has been observed by Yang et al. (1999), who found that $E_{o(\text{BUTANE})} > E_{o(\text{PROPANE})} > E_{o(\text{ETHANE})} > E_{o(\text{METHANE})}$. From Eq. (17) the permeance of non-adsorbable gas decreases as the potential barrier (E_o) increases. The observed decrease in nitrogen permeance (Fig. 3(a)) is in accordance with the trend predicted from Eq. (17). Moreover, from Eq. (18), an increase in the potential barrier (E_o) leads to a rise in selectivity (adsorbable/non-adsorbable), which is confirmed by the tendency shown in Fig. 3(b).

From an analysis of the data given here and those reported by other authors (Rao et al., 1992, 1995; Fuertes, 2000, 2001), it can be established that for an effective separation of adsorbable and non-adsorbable species by a carbon membrane, the micropore size distribution must be in the range of 5–10 Å and more probably around 5–7 Å. Membranes with micropores below 5 Å exhibit molecular sieving properties and so are effective for separating mixtures of permanent gases such as O_2–N_2, CO_2–CH_4, He–N_2, etc. For membranes with micropores in the range of 5–7 Å, the adsorption of more condensable gases effectively hinders the diffusion of less adsorbable species. In the case of membranes with micropores larger than 7–10 Å, the non-adsorbable gases are able to diffuse through the membrane more easily in spite of the adsorption of the more condensable species into the micropores. Consequently, the separation factor is low and the separation is ineffective. Clearly, for optimal separation between adsorbable and non-adsorbable species, the micropore size distribution of the carbon membrane must be carefully controlled, the optimum size probably to be found in the range of 5–7 Å.

The influence of pre-oxidation temperature on the separation characteristics of carbon membranes is shown in Table 1 where the results of the permeances and the separation factor for the separation of 50/50 (v/v) N_2-hydrocarbon mixtures are shown. For the carbon membrane pre-oxidised at 250°C, both hydrocarbon permeance and selectivity are very low, indicating

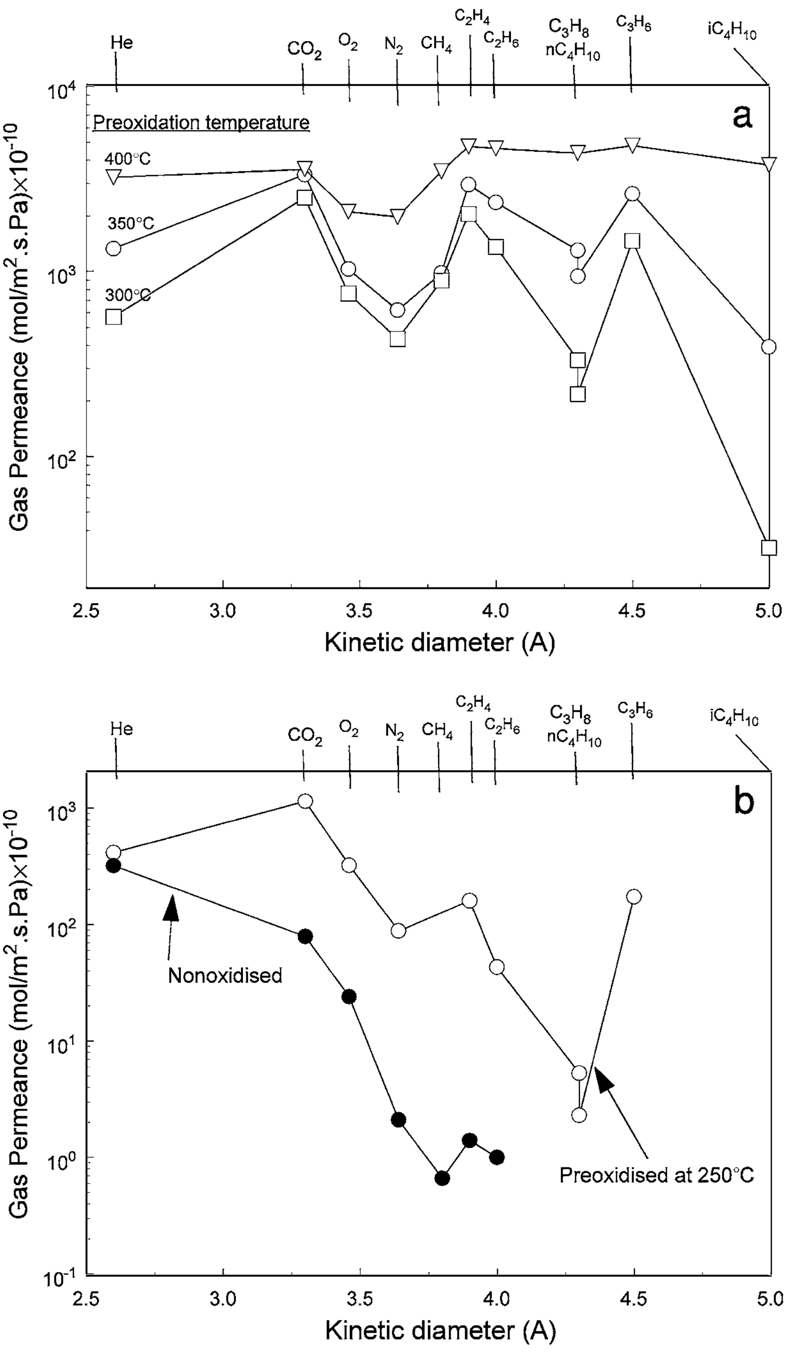

Figure 2. Modification of pure gas permeance with kinetic diameter. (a) Pre-oxidised membranes at temperatures of 300°C, 350°C and 400°C. (b) Non-oxidised membrane and pre-oxidised at 250°C. (Oxidation time: 1 h).

that pre-oxidative treatment hardly affects the structure of the carbonised sample. This membrane still retains molecular sieving properties as indicated in Fig. 2(b). Moreover, the carbon membrane pre-oxidised at 400°C exhibits very low selectivity towards the separation of C_4–N_2 mixtures, suggesting that as a consequence of the pre-oxidation treatment, the carbon membrane contains micropores of too large a size for an effective separation. With pre-oxidation treatments of 300°C (1 h) and 350°C (1 h) carbon membranes with better

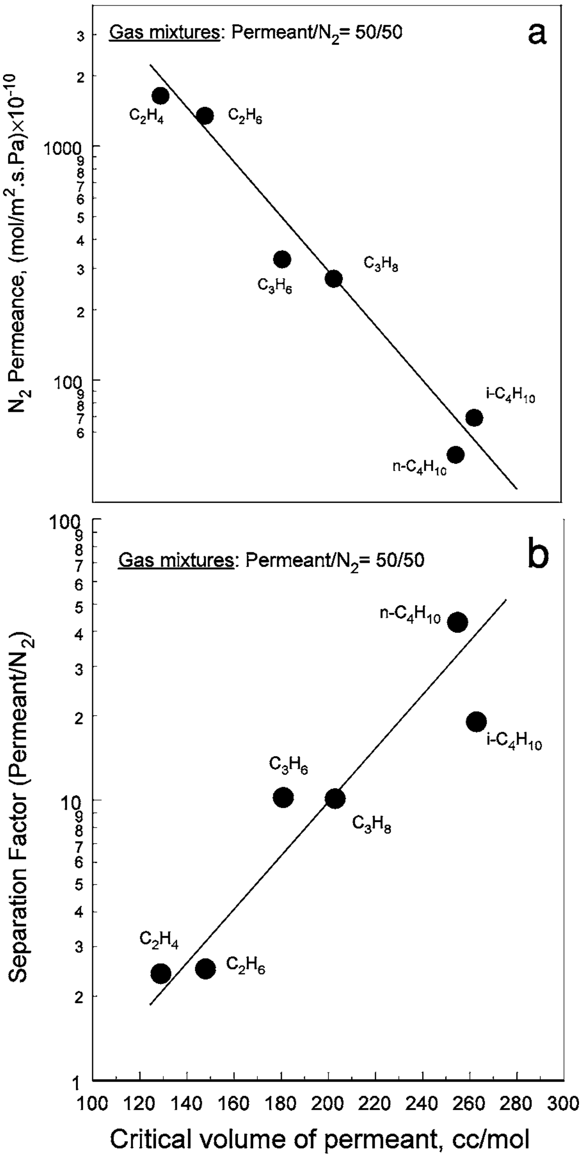

Figure 3. Change of N_2 permeance (a) and separation factor (b) with the critical volume of the permeant for a carbon membrane pre-oxidised at 350°C (1 h).

separation properties can be obtained. Notably, pre-oxidation at 350°C leads to a carbon membrane with a good permeance-selectivity combination.

A better evaluation of the performance of a carbon membrane can be obtained from an analysis of the separation of a complex mixture made up of hydrocarbons (CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}) and N_2, the results of which are shown in Table 2. These confirm the main conclusions deduced from the experiments with binary gas mixtures (Table 1). Furthermore, the data corresponding to the sample pre-oxidised at 350°C and a comparison of these data with those obtained from the binary gas mixture experiments (Table 1) (permeances of ethylene–ethane are very similar and the same applies to propylene-propane), show that the presence of the more strongly adsorbed species (i.e. n-butane) drastically reduces the permeances of the other hydrocarbons and increases their selectivity with respect to N_2. This shows that the more strongly adsorbed species (i.e. n-butane) also hinder diffusion of the less adsorbable species (C_1, C_2 and C_3 hydrocarbons) through the membrane due to competitive adsorption. A detailed analysis of this is given elsewhere (Fuertes, 2001).

4.3. *Comparison of Adsorption-Selective Carbon Membranes Prepared in Different Ways*

A comparison of the performances of the adsorption-selective carbon membranes prepared by pre-oxidation and post-oxidation treatments is given in Table 3. The permeance values for the membrane prepared by pre-oxidation are similar to those obtained for a post-oxidised membrane (350°C, 0.5 h). In contrast, the selectivities for the pre-oxidised membrane are considerably lower.

Table 3 also compares adsorption-selective carbon membranes (ASCM) prepared by means of air oxidative treatments and SSF^{TM} carbon membranes prepared by the researchers of Air Products (Rao et al., 1992, 1995). For the ASCM, N_2 was selected as the non-adsorbable component, whereas H_2 was used to test SSF^{TM} membranes. It is reasonable to assume that N_2 and H_2 play a similar role during the separation of multicomponent gas mixtures. Thus, the permeability of H_2 through a five-coated SSF^{TM} membrane (130 Barrer) is not very different from the value obtained for N_2 (75 Barrer) (Rao and Sircar, 1993). A comparison of the results obtained for an ASCM (Post-oxidised at 350°C, 0.5 h) (mixture A) and a five coated SSF^{TM} membrane (mixture C), shows that ASCM exhibit higher values of permeance and selectivity. The permeances obtained for ASCM are more than ten times higher. The preparation procedure of improved (by air oxidation) SSF^{TM} membranes has been described by Rao et al. (1995). From a comparison of an improved SSF^{TM} (mixture D) and ASCM (mixture B), it can be seen that, although ASCM show lower selectivities, the permeances through an ASCM membrane are more than five times higher.

Table 1. Separation of binary gas mixtures (hydrocarbon–nitrogen: 50/50, v/v) using carbon membranes prepared by the pre-oxidation of the polymeric film at different temperatures (oxidation time: 1 h.).

Pre-oxidation temperature (°C)	Ethylene–N_2		Propylene–N_2		n-Butane–N_2		i-Butane–N_2	
	F^a	SF^b	F^a	SF^b	F^a	SF^b	F^a	SF^b
250	56	3	55	3.2	–	–	–	–
300	1890	6.2	1660	34	456	64	72	4
350	3970	2.4	3340	10.2	2072	43	1280	19
400	–	–	–	–	3200	4.4	2830	3.6

[a] F, Gas permeance of hydrocarbon in $(mol.m^{-2}.s^{-1}.Pa^{-1}) \times 10^{-10}$.

[b] SF, Separation factor (hydrocarbon/N_2).

Table 2. Separation of a multicomponent gas mixture (31.4% N_2, 16.3% CH_4, 16.1% C_2H_6, 16.2% C_3H_8, 20% n-C_4H_{10}) using carbon membranes prepared by the pre-oxidation of the polymeric film at different temperatures (oxidation time: 1 h.).

Pre-oxidation temperature (°C)	Gas permeances, $(mol/m^2.s.Pa) \times 10^{-10}$					Separation factor			
	N_2	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	CH_4/N_2	C_2H_6/N_2	C_3H_8/N_2	n-C_4H_{10}/N_2
250	20	35	20	4.6	7.9	1.8	1	0.2	0.4
300	12	28	91	138	476	2.2	7.3	11	38
350	78	202	605	1166	2680	2.6	7.8	14.9	34
400	820	1212	1520	2330	4444	1.5	1.9	2.8	5.4

Table 3. Comparison of adsorption-selective carbon membranes prepared by air oxidative treatments (pre-oxidation and post-oxidation) and SSF™ carbon membranes. [1 Barrer = 10^{-10} $(cm^3 (STP).cm.cm^{-2}.s^{-1}.cmHg^{-1})$]

	Pre-oxidised (350°C, 1h) This work		Post-oxidised (350°C, 0.5 h) (Fuertes, 2000)				SSF™ carbon membrane (Air Products)			
	Gas mixture A[d]		Gas mixture A[d]		Gas mixture B[e]		Gas mixture C[f] (Rao et al., 1992)		Gas mixture D[g] (Rao et al., 1995)	
Gases	P^a	$SF_{N2}{}^b$	P^a	$SF_{N2}{}^b$	P^a	$SF_{N2}{}^b$	P^a	$SF_{H2}{}^c$	P^a	$SF_{H2}{}^c$
H_2	–	–	–	–	–	–	1.2	1	11	1
N_2	47	1	18	1	125	1	–	–	–	–
CH_4	121	2.6	51	2.8	320	2.6	1.3	1.1	72	6.5
C_2H_4	–	–	–	–	–	–	–	–	141	12.7
C_2H_6	363	7.8	216	12	1104	9.1	7.2	6	135	12.2
C_3H_6	–	–	–	–	2930	23.4	–	–	489	44
C_3H_8	700	15	600	33	2850	22.8	24.1	20.1	417	38
n-C_4H_{10}	1608	34	1760	98	–	–	120	100	–	–

[a] P = permeability (Barrer).

[b] SF_{N2}: (Gas/N_2) separation factor.

[c] SF_{H2}: (Gas/H_2) separation factor.

[d] Gas mixture A: 16.3% CH_4, 16.1% C_2H_6, 16.2% C_3H_8, 20% n-C_4H_{10}, 31.4% N_2.

[e] Gas mixture B: 16.3% CH_4, 16.1% C_2H_6, 16.2% C_3H_8, 20% C_3H_6, 31.4% N_2.

[f] Gas mixture C: 20.2% CH_4, 9.5% C_2H_6, 9.4% C_3H_8, 19.9% n-C_4H_{10}, 41% H_2.

[g] Gas mixture D: 20.2% CH_4, 8.0% C_2H_4, 8.3% C_2H_6, 28.6% C_3H_6, 14.9% C_3H_8, 20% H_2.

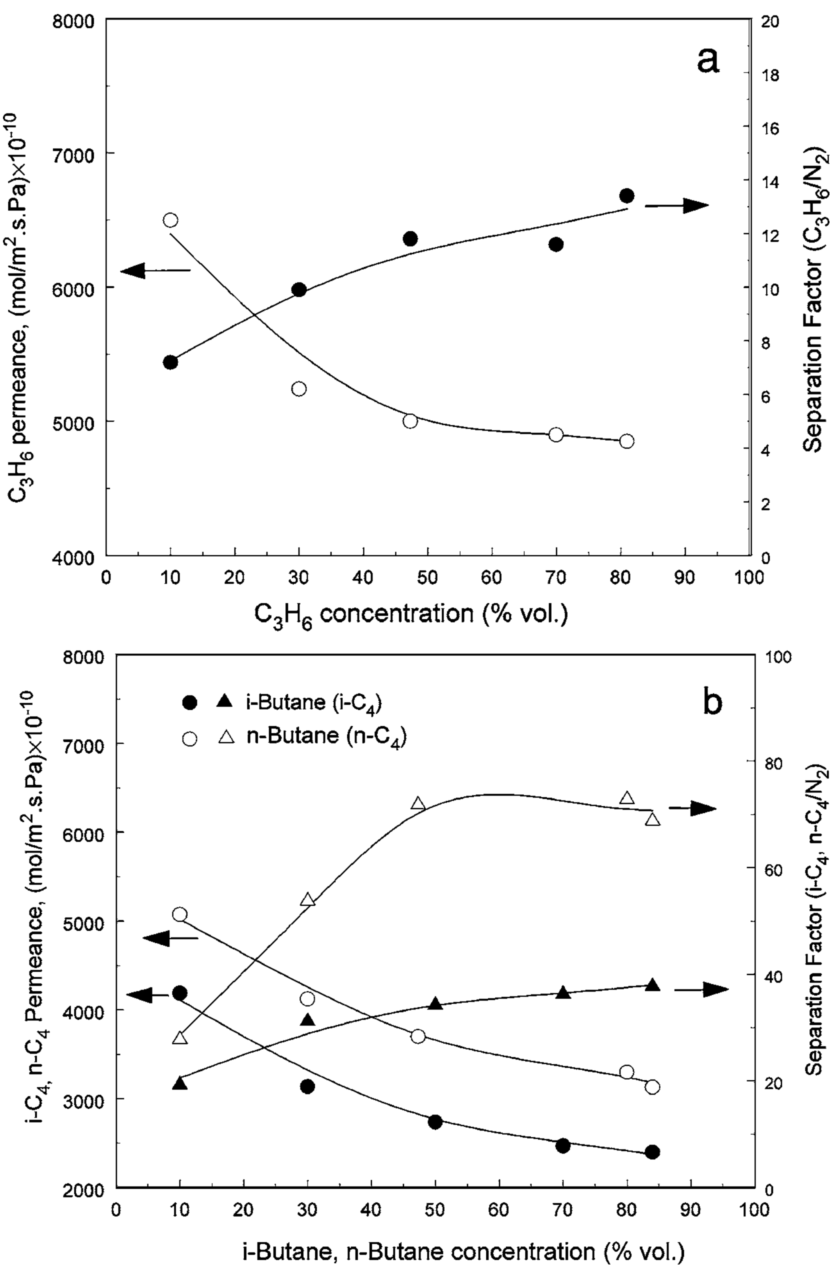

Figure 4. Effect of hydrocarbon concentration on permeance and selectivity. (a) Propylene–N_2 mixtures. (b) *n*-butane–N_2 and isobutane–N_2 mixtures. (Carbon membrane post-oxidised at 400°C for 0.5 h).

4.4. Effect of Composition on the Separation of Binary Gas Mixtures

The composition of the gas mixture (Hydrocarbon–N_2) affects both the permeance and the separation factor considerably, as can be seen in Fig. 4(a) (mixtures of propylene with N_2) and Fig. 4(b) (mixtures of *n*-butane or *i*-butane with N_2). In general, as the hydrocarbon concentration increases, hydrocarbon permeance decreases. This behaviour is in accordance with that predicted from Eq. (12) for strongly adsorbable gases (i.e. *n*-butane and *i*-butane) and Eq. (15) for moderately adsorbable gases (i.e. propylene). The increase in hydrocarbon concentration produces an increase in surface coverage (θ). Thus, in accordance with Eqs. (12) or (15), as surface coverage augments, a drop in permeance takes place. By contrast, nitrogen permeance decreases with hydrocarbon concentration. This is consistent with Eq. (17). Furthermore, Figures 4a and 4b, show that the (hydrocarbon/N_2) separation factor increases with hydrocarbon concentration. From a phenomenological point of view, the increase in the (hydrocarbon/N_2) separation factor with hydrocarbon concentration (partial pressure) is a consequence of enhanced restriction to N_2 diffusion, as the amount of adsorbed hydrocarbon increases. It can be seen that the extent of permeance and separation factor modification is a function of the strength of hydrocarbon adsorption in the order n-butane > i-butane > propylene. The strength of adsorption is represented in Eqs. (17) and (18) by the potential energy term which, as commented in Section 2, is a function of the nature of hydrocarbon.

4.5. *Modification of Permeance and Selectivity with Temperature*

The influence of the temperature on the separation of a gas mixture formed by adsorbable and non-adsorbable gases is illustrated in Fig. 5, which shows the modification with temperature of permeance and the separation factor for the separation of a binary gas mixture (N_2/n-butane) by means of a carbon membrane (post-oxidised at 300°C, 0.5 h). It can be seen that whereas n-butane permeance exhibits a maximum at around 100°C, nitrogen permeance increases continuously from room temperature up to 150°C. Consequently, as the temperature rises from room temperature to 150°C, the separation factor decreases drastically, from 65 to 5. Similar behaviour has been observed by Bakker et al. (1996) and Coronas et al. (1997) for the separation of H_2/n-butane mixtures using a zeolite membrane. Temperature dependence may be envisaged as follows. The modification of n-butane permeance with temperature is the result of two opposite effects, adsorption (the adsorbed amount decreases with temperature) and diffusion (diffusivity increases with temperature). This explains the observed maximum of n-butane permeance at 100°C. Equation (15) can be used to analyse the change of permeance of adsorbable gases over a wide range of temperatures. At low and moderate temperatures this equation is reduced to Eq. (12). As the temperature increases, the two opposite effects are represented by a decrease in the adsorbed amount $c_{\text{sat}}(1 - \theta)$ and an increase in the exponential term (if $E_a > Q$). At high temperatures, Eq. (15) is reduced to Eq. (8) and an increase in hydrocarbon permeance with temperature can be expected.

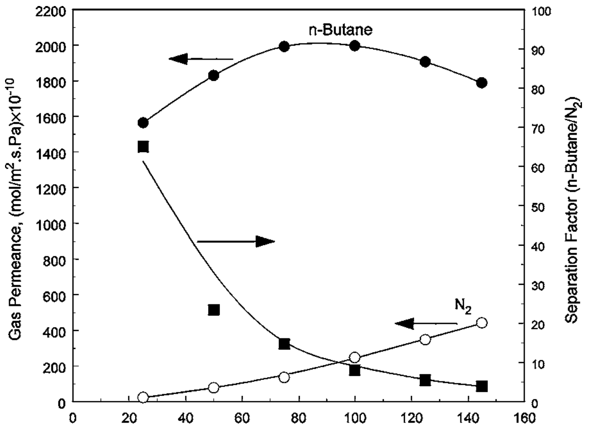

Figure 5. Influence of temperature on the separation of a binary gas mixture (n-butane/N_2: 50/50 v/v). (Carbon membrane post-oxidised with air at 300°C for 0.5 h).

Moreover, according to Eq. (17), the observed change in nitrogen permeance with temperature is the sum of two effects, the increase in gas diffusivity (D_g) and the drop in potential barrier ($E_o\theta$). At low temperatures n-butane adsorption dominates the separation ($\theta \to 1$). N_2 diffusion through the micropores is hindered considerably by the amount of hydrocarbon adsorbed. At high temperatures $\theta \to 0$ and nitrogen permeance is given by $F_g^* = F_g$. The nitrogen permeance undergoes a strong increase whereas n-butane permeance hardly changes with temperature, leading to a huge drop in the separation factor.

The effect of temperature on the separation of a multicomponent gas mixture (Nitrogen + methane + ethane + propane + propylene) is shown in Fig. 6. The permeances of the less adsorbing components (nitrogen and methane) increase continuously with temperature whereas for the more adsorbable gases (propane and propylene) a continuous decrease can be observed (Fig. 6(a)). Ethylene permeance shows a maximum at around 80°C. The separation factors (hydrocarbon/nitrogen) decrease rapidly with temperature, this change being even greater for the more strongly adsorbable components (Fig. 6(b)).

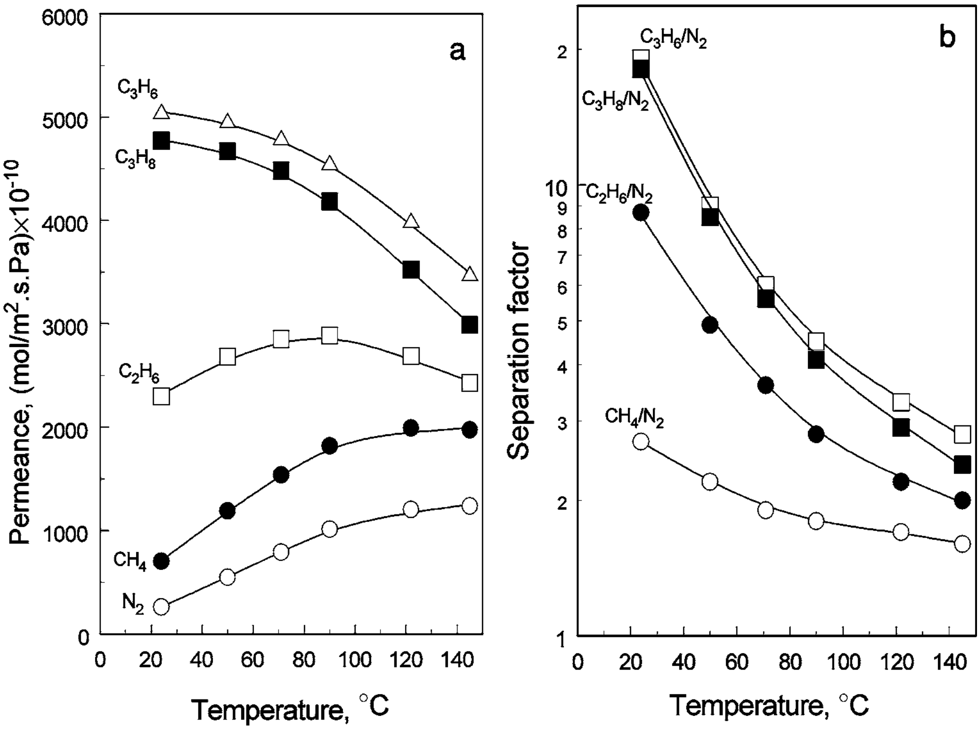

Figure 6. Modification of permeance (a) and separation factor (b) with temperature, for the separation of a multicomponent gas mixture (31.4% N_2, 16.3% CH_4, 16.1% C_2H_6, 16.2% C_3H_8, 20% C_3H_6) by means of a carbon membrane (Post-oxidised at 350°C, 0.5 h).

The results discussed above suggest that a more effective separation of adsorbable and non-adsorbable gases using a carbon membrane can be achieved by operating at low temperatures for which $\theta \rightarrow 1$.

5. Conclusions

Adsorption selective carbon membranes can be prepared following two different procedures: a) pre-oxidation (before the carbonisation step) with air of a phenolic resin film coated on the inner face of a macroporous alumina tubular support at a temperature around 300–350°C and, b) post-oxidation (after carbonisation step) with air of a microporous carbon film coated on the inner face of a macroporous alumina tubular support. The measurements of the gas permeances in the membranes prepared by the pre-oxidation or post-oxidation are similar. However, the selectivities of the post-oxidised membranes are considerably higher.

Carbon membranes are effective for the separation of a gas mixture formed by adsorbable (i.e. hydrocarbons) and non-adsorbable components (i.e. nitrogen). For example, the values of permeability and selectivity ($\alpha =$ hydrocarbon/N_2) for the separation of a complex gas mixture (16.3% CH_4, 16.1% C_2H_6, 16.2% C_3H_8, 20% n-C_4H_{10}, 31.4% N_2), by means of a pre-oxidised carbon membrane (350°C, 1 h), are: CH_4, 121 ($\alpha = 2.6$); C_2H_6, 363 ($\alpha = 7.8$); C_3H_8, 700 ($\alpha = 14.9$) and n-C_4H_{10}, 1608 Barrer ($\alpha = 34$).

The permeances and separation factor in a mixture formed by adsorbable and non-adsorbable components is strongly dependent on the concentration of adsorbable species. Thus, selectivity (hydrocarbon/nitrogen) increases and hydrocarbon permeance diminishes as the hydrocarbon concentration rises. The extent of these changes is a function of the strength of hydrocarbon adsorption, in the order n-butane > i-butane > propylene > ethylene.

The separation characteristics of ASCMs are based on the adsorption of hydrocarbons onto microporous carbon film. Because of this, a rise in the separation temperature produces a significant reduction of the separation factor as a consequence of the desorption of hydrocarbon molecules. This suggests that high separation selectivities can be achieved at low temperatures, below room temperature.

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