

SYNTHESIS AND CHARACTERISATION OF SILICALITE/CARBON MEMBRANES

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Introduction

Membranes are materials with a great importance from an industrial point of view as they are involved in many separation processes in both gas and liquid phase⁽¹⁾. Membranes act as a barrier that restricts the diffusion of specific components of a given mixture. These materials usually consist on a thin, homogenous, and defect-free separation layer supported on an appropriate macroporous support. Regarding the separation layer, zeolites are widely used in the preparation of membranes for separation of molecular mixtures because they are crystalline aluminosilicates with a three-dimensional framework which, in general, form channels^(2,3). These characteristics make zeolites useful as molecular sieves, adsorbents, ion exchangers and catalysts. In this sense zeolite and zeolite-like membranes have given excellent results in gas separation^(4,6).

Zeolites have been successfully supported on different materials including metals, ceramics and polymers although all of them show remarkable drawbacks^(4,5). However, scarce research has been done using carbon materials as support in spite of their interesting advantages related to their inertness in oxygen-free atmospheres. Thus, carbon materials are stable at high temperatures in a non-oxidising atmosphere, they have a low thermal expansion coefficient, can be obtained in different forms (discs, cylinders,...) and both their porosity and surface chemistry can be easily modified⁽⁷⁾. The main drawback for the use of carbon materials is the hydrophobicity of the carbon surface that makes difficult the interaction with the zeolite synthesis solution. In previous studies, we succeeded in the synthesis of zeolite/carbon composites on different carbon materials with different porous texture and shapes⁽⁸⁾.

In the present work we will report the results obtained on the preparation and characterisation of silicalite/carbon membranes. The synthesis of the silicalite layer on a macroporous carbon has been performed through hydrothermal methods and the materials obtained have been characterised by permeation measurements of pure gases and different mixtures.

Experimental

Macroporous carbon discs (diameter 1.3 cm, 0.25 mm thickness, mean pore size 0.7 μm) were strongly oxidized using boiling concentrated HNO_3 prior to the synthesis of the composite. Silicalite synthesis mixture was prepared following a previously described method⁽⁸⁾. Different synthesis conditions such as the pH and template were studied. The templates used were tetrapropylammonium bromide (TPA-Br), tetrapropylammonium hydroxide (TPA-OH) and tetraethylammonium fluoride (TEA-F). A typical molar composition of the synthesis solution is $0.10\text{Na}_2\text{O}\cdot 0.05\text{TPA}\cdot\text{SiO}_2\cdot 40\text{H}_2\text{O}$. The synthesis solution was poured in an autoclave and the carbon discs were immersed in it for different ageing times. The carbon discs were held in a vertical position to avoid silicalite sedimentation. Finally, the autoclaves were heat treated in a furnace for different times (between 4 and 64 hours) and temperatures (150-185°C). After that, the membranes were washed thoroughly in a ultrasonic bath. The resulting membranes were calcined at 700°C in a horizontal oven to remove the organic template. The membranes were characterised by optical microscopy, scanning electron Microscopy and X-ray diffraction. The performance of the membranes for gas separation was studied by means of permeation experiments with pure gases and separation of binary gas mixtures. The experimental setup used in these experiments is described elsewhere⁽⁹⁾.

Results and Discussion

A proper oxidizing treatment of the carbon support is crucial to allow the growth of silicalite on its surface. Only when the carbon discs were strongly oxidized in concentrated HNO_3 , the formation of the silicalite layer was possible. These results corroborate previous studies about the necessity of the presence of oxygen surface groups on the carbon to grow a zeolite⁽⁸⁾.

The necessity of an ageing time to achieve the growth of the silicalite was also tested. Three membranes were synthesised without ageing time and there was no crystal growth, but gel deposition on the carbon disc. For this reason, all the other synthesis were carried out with different ageing times which varied from 5 to 39.5 hours

and, only in these materials, different crystal growth and disc coverage were observed.

In the case of TPA-Br and TPA-OH templates, it was found that a certain amount of NaOH favours the formation of a continuous layer of silicalite, being the optimum pH range quite narrow. In this range of pH, the higher the pH, the smaller the crystals. It was observed that for the same amount of NaOH added, bigger crystals are formed when TEA-F is used. The increase of the solubility of the silicate ions due to the presence of F⁻ ions seems to favour the increase of the silicalite crystals. As shown in Figure 1, by using TEA-F we managed to prepare a silicalite layer with crystals of about 20µm, whereas, as shown in Figure 2, by using TPA-OH the crystal size decreased up to 2µm.

The influence of different synthesis times and temperatures for the hydrothermal treatment were also studied. Increasing the temperature of the hydrothermal synthesis made crystals to grow less. This effect was less notorious in the case of TPA-OH, probably due to the high pH of the synthesis solution. The effect of the time of the hydrothermal synthesis is not completely straightforward, as it seems to depend on the template used.

The thickness of the silicalite layer was estimated by the weight gain before and after the synthesis (assuming the density of silicalite was 1.8 g/cm³). The obtained values were quite similar to those observed by SEM. This result suggests that there is not a significant amount of silicalite in the porosity of the support.

It is quite remarkable that, for certain synthesis conditions, well crystalline silicalite was grown on the carbon whereas the material which was not anchored on the carbon remains as a gel. This observation suggests that the carbon surface favours the nucleation and final crystallization of the silicalite in agreement with previous results⁽⁸⁾.

Finally, the membranes were heat-treated in N₂ at 700°C in order to remove the template. After this, the resulting membranes were tested in a conventional permeation device to check the quality of the coverage.

Figure 3 and Table 1 shows the pure gas permeance values for both the carbon disc (support) and one silicalite membrane versus the square root of the molecular weight of different gases. The permeance for different gases is much higher for the carbon discs than for the membrane. This observation suggests that there are no important defects in the silicalite layer. Also, in the case of the carbon disc, there is a linear trend between the permeation of the gases and the square root of their molecular weight. This behaviour is typical of Knudsen diffusion. However, for the silicalite layer there is no correlation between the permeation and the molecular weight. On the contrary, CO₂ exhibits a

permeance which is more than two times higher than that measured for He. It indicates that CO₂ transport through the silicalite membrane takes place by a surface diffusion mechanism, that involves adsorption and diffusion of the molecules, which is characteristic of zeolite membranes. These facts corroborate that the silicalite layer behaves as a proper membrane.

Results obtained from the separation of binary gas mixtures of CO₂, N₂ and hydrocarbons are indicated in Table 2. The separation factors for analysed gas mixtures are higher than those obtained from the ratio of pure gas permeances. This fact shows that the more permeable gases (Hydrocarbons, CO₂ etc) are adsorbed on the membrane micropores, occupying part of the void space and partially inhibiting the diffusion of non-adsorbable species (N₂). The separation factors obtained for the mixtures propane/N₂ and propylene/N₂ are specially high. Also for *n*-butane/*i*-butane mixture, the separation factor shows that the membrane prepared by the aforementioned method presents good properties.

Conclusions

Continuous layers of silicalite have been successfully grown on carbon discs by direct conventional hydrothermal treatment. An oxidizing pre-treatment of the carbon is necessary to allow the anchoring of the silicalite crystals on the support. A minimum ageing time is also necessary to obtain some crystal growth on the carbon surface, as it favours the interaction between the dissolved silica and the carbon.

The modification of the synthesis conditions allows the control of the crystal size of the silicalite. In this sense, high pH and temperature, short synthesis time and the use of TPA-OH favour the formation of small silicalite crystals (2 µm). The weight gain after the hydrothermal treatment suggests that no silicalite is formed in the porosity of the support. Carbon discs are very interesting as supports inasmuch as they are hydrophobic (do not let the synthesis solution into their porosity) and also favour the nucleation of the crystals.

Both the permeation for different gases and separation of binary mixtures studies show clearly that the silicalite/carbon membranes prepared by the previously described method show good permeation and separation properties and are almost free of cracks and large-sized defects.

It is quite remarkable that the synthesised composite materials maintain good properties as membranes after being heat treated at 700 °C. This is an important advantage compared to other supports (i.e., steel, alumina,...), what is a consequence of the low thermal expansion coefficient of carbon materials.

Acknowledgements

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References

- (1) Separation Technology, Process Technology, Proceedings, E.F. Vansant, Elsevier (1994)
- (2) W.M. Meir, D.H. Olson, Ch. Baerlocher, "Atlas of zeolite structures" 4th edition, Elsevier (1996)
- (3) D.W. Breck, Zeolite molecular sieves, Wiley, New York, (1974)
- (4) J. Caro, M. Noak, P. Kölsch, R. Schäfer, Zeolite membrane-state of the development and perspective, Microporous and Mesoporous Materials, 38, 1, (2000)
- (5) M.J. den Exter, J.C. Jansen, J.M. van Graaf, F. Kapteijn, J.A. Moulijn, H. van Bekkum, in: H. Chon, S.I. Woo, E.E. Park (Eds.), Zeolites-based membranes: Preparation, Performance and Prospects, Recent Advantages and New Horizons in Zeolite science and Technology, Elsevier Science B.V., Amsterdam, (1996)
- (6) B.J. Schoeman, A. Erdem-Senatalar, J. Hedlund, J. Sterte, Zeolites 19, 21 (1997)
- (7) H. Marsh, E.A. Heintz, F. Rodriguez-Reinoso, Introduction to Carbon Technologies, Publicaciones de la Universidad de Alicante, 1997
- (8) Javier García-Martínez, D. Cazorla-Amorós, A. Linares-Solano and Y.S. Lin, Microporous and Mesoporous Materials, 42, 255, (2001)
- (9) T. A. Centeno, A. B. Fuertes, J. Memb. Sci., 160, 201, (1999)

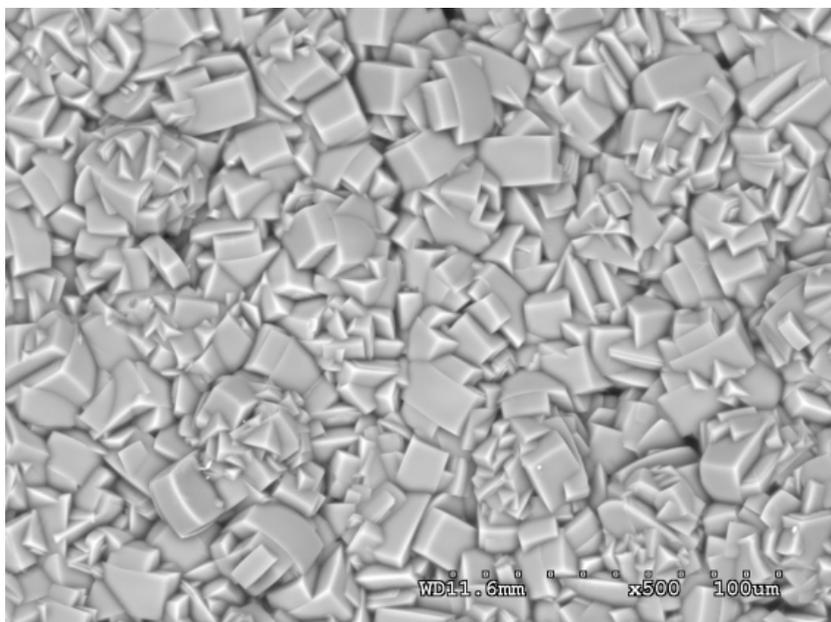


Figure 1. Silicalite crystals synthesised using TEA-F. The size of these crystals is about 20 μ m.

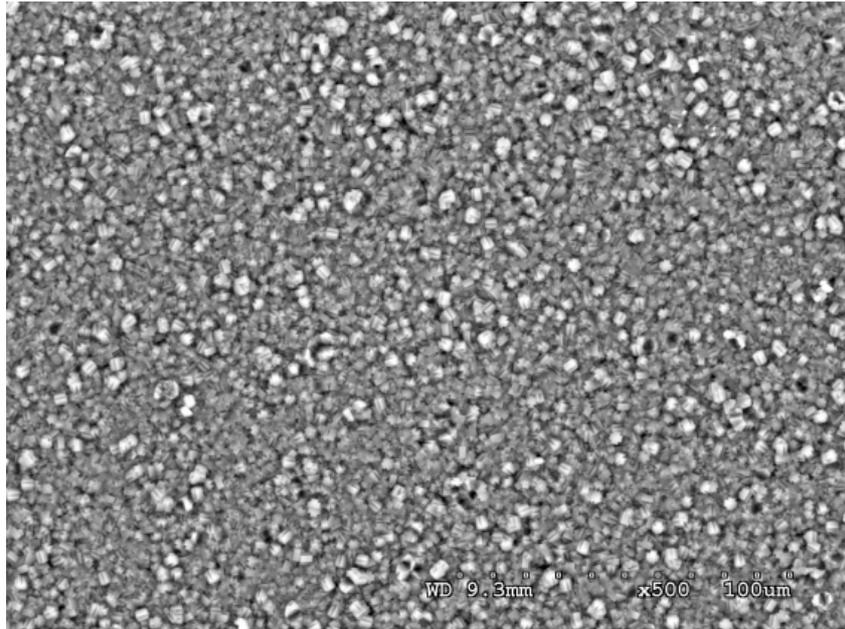


Figure 2. Silicalite crystals synthesised using TPA-OH. The size of these crystals is about 2-4µm.

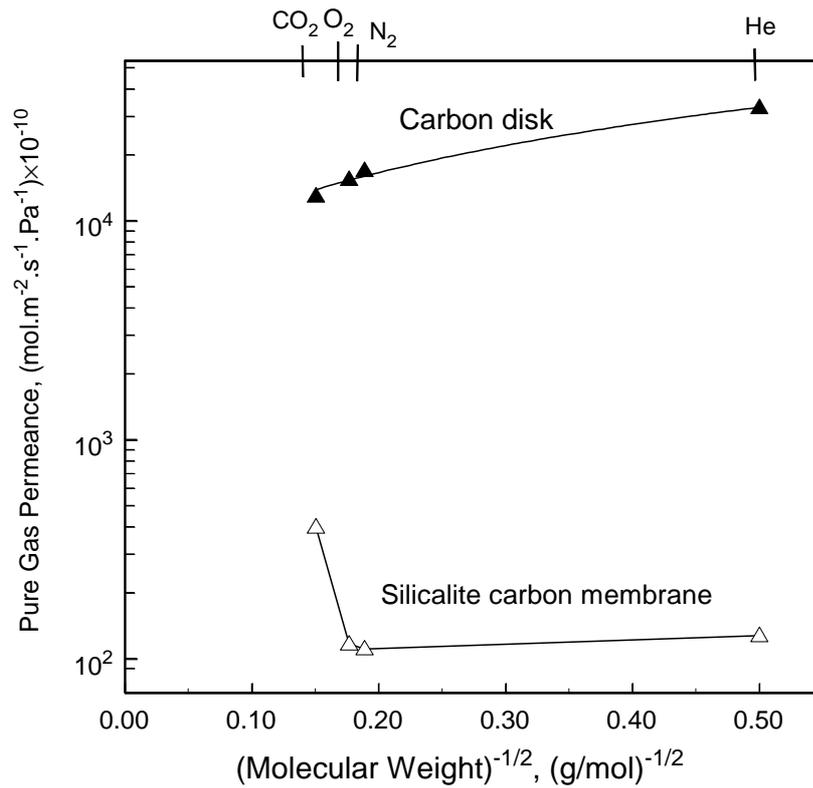


Figure 3. Pure gas permeance versus square of molecular weight for the graphite disc and the silicalite-carbon membrane.

Table 1. Permeation values of pure gases (T=20°C).

Gases	Graphite disc (blanc)	Membrane
	P en (mol.m ⁻² .s ⁻¹ .Pa ⁻¹)×10 ⁻¹⁰	P en (mol.m ⁻² .s ⁻¹ .Pa ⁻¹)×10 ⁻¹⁰
He	33000	145
CO ₂	13000	400
O ₂	15500	155
N ₂	17000	157
Ethane	-	350
Ethylene	-	440
Propane	-	155
Propylene	-	204
n-Butane	22000	93
i-Butane	-	28

Table 2. Separation of binary gas mixtures (50/50: mol/mol) by means of the silicalite-carbon membrane at 20°C. (Composition of CO₂/N₂ mixture: 20/80)

Gas mixture	Permeance (mol.m ⁻² .s ⁻¹ .Pa ⁻¹)×10 ⁻¹⁰		Separation factor (P _A /P _B)
	P _A	P _B	
CO ₂ /N ₂	CO ₂ : 278	N ₂ : 77	3.6
Ethane/N ₂	Ethane: 219	N ₂ : 33	6.7
Ethylene /N ₂	Ethylene: 257	N ₂ : 50	5.2
Propane/N ₂	Propane: 134	N ₂ : 14	9.3
Propylene/N ₂	Propylene: 167	N ₂ : 16	10.4
n-Butane/N ₂	n-Butane: 89	N ₂ : 14	6.5
n-Butane/i-Butane (20°C)	n-Butane: 44	i-Butane: 11	4
n-Butane/i-Butane (100°C)	n-Butane:103	i-Butane: 12	8.5