Silicalite-1 membranes supported on porous carbon discs

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Abstract

Silicalite-1 layers were successfully grown by standard hydrothermal syntheses on macroporous carbon discs and tested as membranes. All the carbon supports were previously oxidized to favor the anchoring of the zeolite-like material. The silicalite-1 crystals were synthesized using different templates, pHs, ageing times, and hydrothermal synthesis times and temperatures. Some synthetic routes proved to be more useful and reproducible for growing continuous and defect-free layers of silicalite-1 on the surface of a carbon disc. The control of the ageing time, oxidation of the support, use of clear solutions, and the pH of the synthesis solution are key parameters for a successful synthesis, as previously reported. Permeation studies of the prepared composites after removal of the template with both pure gases and gas mixtures proved that the prepared materials show good membrane properties.

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1. Introduction

Membranes are materials with a great importance from an industrial point of view, as they are involved in many separation processes both in the gas and in the liquid phase [1]. A membrane acts as a barrier that restricts the diffusion of specific components of a given mixture. These materials usually consist on a thin, homogeneous 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. Despite their many advantages, zeolites show some disadvantages. Since most of the zeolites are synthesized by means of hydrothermal synthesis [4], their crystal size is generally small, typically between 10 and 1 μm, and even smaller. The direct use of this kind of materials causes problems like high pressure drops and difficulties in separation and handling. To avoid such problems, pelletized zeolites are widely used. These materials, however, need the use of a binder that might block a significant part of the porosity.
Supporting zeolites on different materials is an alternative that has been suggested previously by Mintova and Valtchev [5]. Supported zeolites offer a wide range of possibilities, such as modifying the thickness of the zeolite layer and the use of various materials with different shapes. In the field of supported zeolites, there is an increasing interest in growing continuous, defect-free layers of zeolites on different supports for their use as membranes.

Zeolites have been successfully supported on many different materials like metals, ceramics, polymers, and carbon materials [6–26] by a wide variety of approaches [14,15,22,26–36]. Among these, ceramics and polymers are the most popular and widely used ones. However, these materials show some major drawbacks [6,21]: Polymers possess a relatively low chemical and thermal stability, which results in the decomposition of the support during the regeneration process at high temperatures, making its average lifetime relatively short. Ceramic materials are more stable, but they are expensive and brittle, and the use of such materials may alter the composition of the resulting zeolite (by dissolution of the support in the synthesis solution). One critical step in the preparation of supported zeolite membranes is the calcination, mainly due to the irregular thermal behavior of MFI-type zeolites [37]. It is worth mentioning that these zeolites show positive volume expansion coefficients in the low-temperature region near room temperature, and negative volume expansion coefficients at relatively high temperatures. This means that, whereas the support expands with increasing temperature, the zeolite layer shrinks at temperatures higher than approximately 120 °C. Thus, there is a problem during the calcination process due to the difference in the thermal expansion coefficients of the zeolite and the ceramic and, especially, the metallic support. The low thermal expansion coefficient of a carbon support can be an additional advantage.

However, scarce research has been carried out using carbon materials as supports, in spite of their interesting properties (low thermal expansion coefficients, availability of different shapes, such as discs, cylinders, etc. and the possibility to modify their porosity and surface chemistry). In previous studies, we succeeded in the synthesis of composites consisting of zeolites on different carbon materials with different pore textures and shapes [21], and we demonstrated the importance of the surface chemistry and porosity of the support for zeolite growth [21].

The main objective of this study is to grow continuous and defect-free silicalite-1 layers on macroporous carbon discs under different synthesis conditions in order to develop a procedure for controlling the formation of carbon-supported silicalite-1 membranes and to analyze their permeation properties. Thus, in the present work we will report the results obtained in the preparation and characterization of silicalite-1/carbon membranes. The synthesis of the silicalite-1 layer onto macroporous carbon was performed by hydrothermal methods, and the materials obtained were characterized by permeation measurements using pure gases and different gas mixtures.

2. Experimental

2.1. Preparation of the supports

Macroporous carbon discs were cut from a macroporous carbon sheet (thickness: 0.5 mm, mean pore size: 0.7 μm) provided by Poco Graphite (DFP-1). These discs were 13 mm in diameter and 0.5 mm thick. In order to create as many surface oxygen groups as possible [21], the carbon discs were immersed in boiling HNO₃ (60% wt.) for 12 h under occasional stirring to ensure an appropriate contact of the carbon discs with the acid. After acid treatment, the carbon discs were thoroughly washed with distilled water and dried overnight in an oven at 125 °C.

2.2. Growth of silicalite-1 on the supports

Silicalite-1 layers were grown onto the carbon supports by standard hydrothermal synthesis procedures as described in Refs. [21,36]. The silicate solutions were obtained from fumed silica (Aldrich 112,945-52-5) by adding high-purity NaOH (Aldrich 30,657-6). Three different templates were used, viz. tetrapropylammonium hydroxide (TPA-OH) (Aldrich 25,453-3), tetra-
propylammonium bromide (TPA-Br) (Aldrich 2,556-8) and tetraethylammonium fluoride (TEA-F) (Aldrich 98,330-04-2). Typical compositions of the synthesis solutions were:

Silicalite-1 with TPA-OH:
$\text{1SiO}_2 \cdot 0.05\text{TPA-OH} \cdot 0.22\text{NaOH} \cdot 41.5\text{H}_2\text{O}$

Silicalite-1 with TPA-Br:
$\text{1SiO}_2 \cdot 0.047\text{TPA-Br} \cdot 0.278\text{NaOH} \cdot 41.48\text{H}_2\text{O}$

Silicalite-1 with TEA-F:
$\text{1SiO}_2 \cdot 0.052\text{TEA-F} \cdot 0.215\text{NaOH} \cdot 41.46\text{H}_2\text{O}$

The carbon supports were held vertically inside the autoclaves by means of a teflon piece inserted inside the autoclave, to reduce sedimentation of zeolite crystals on the support. The synthesis solution was poured inside the autoclave with the disc in it and the hydrothermal synthesis was carried out, after the ageing time, under static conditions. After the synthesis, the composites were washed and tested for mechanical stability in an ultrasonic bath for 15 min. The resulting materials were dried at 398 K overnight. Since zeolite growth occurred on both sides of the supports, one of the two zeolite layers was removed by treatment with an abrasive surface.

Regarding the membrane properties of the silicalite-1/carbon composites, not only the continuity of the zeolite layer is important, but also the thickness of the coating greatly influences the membrane characteristics. Thus, the effect of the composition of the synthesis mixture (NaOH content), the nature of the template (TPA-OH, TPA-Br and TEA-F), temperature (423–458 K), synthesis time (6–72 h) and ageing time (0–6 h) during the hydrothermal synthesis, on the quality of the composite and on the thickness of the membrane was studied.

The resulting composites were heat-treated at 973 K under a nitrogen flow of 100 cm$^3$/min for 2 h with a heating rate of 2 K/min in a horizontal furnace to remove the template.

The performance of the membranes for gas separation was studied by means of permeation experiments with pure gases and the separation of binary gas mixtures. The experimental set-up used has been described elsewhere [38]. Permeance experiments with pure gases were performed at 298 K on the as-synthesized and heat-treated membranes. The membranes were attached to a permeation cell (Millipore high-pressure filter holder). High-pressure high-purity gases supplied from compressed gas cylinders were introduced in contact with the membrane layer. A manometer measured the pressure. Vacuum was maintained on the low-pressure side of the membrane, and the permeate was pulled through a calibrated volume. The pressure was measured by means of a pressure transducer (Leybold CM 1000) and a digital equipment connected to a computer. The permeation and permeability of pure gases through the membrane were estimated from the variation of pressure with time at the low-pressure side of the device. In the case of separation of binary mixtures (1:1 mol:mol for all mixtures except for CO$_2$/N$_2$, where the molar ratio was 1:4), the penetrating gas mixtures were introduced at the upper side of the membrane (in contact with the zeolite microporous film). Helium was used as carrier gas and flowed through the permeate side. The gas concentration on the permeate side was measured by means of a TCD-GC (Hewlett-Packard, Model 5890) equipped with two columns (5A molecular sieve and Porapak Q).

### 2.3. Characterization of the materials

The crystalline phases synthesized were characterized by X-ray powder diffraction in a Seifert 2002 equipment. CuK$\alpha$ (1.54 Å) radiation was used. The scanning velocity was 2°/min, and the 20 range was scanned from 2° to 60°.

The morphology of the synthesized composites was studied by scanning electron microscopy (SEM) using a Hitachi S-3000N equipment. The chemical composition of the samples was analyzed by EDX (coupled to the SEM equipment, Link QX-200). IR spectra were recorded in an FTIR Mattson spectrophotometer model Infinity with an MCT detector coupled with a diffuse reflectance accessory model COLLECTOR from Spectra-Tech. Thermal analysis was carried out in a Stanton Redcroft 780 TG-DTA equipment.

XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer, by using MgK$\alpha$ (1253.6 eV) radiation of a twin anode in the
constant analyzer energy mode with a pass energy of 50 eV. The pressure of the analysis chamber was maintained at $5 \times 10^{-10}$ mbar. The binding energy and the Auger kinetic energy scale were calibrated by setting the C 1s transition at 284.6 eV. The accuracy of the BE and KE values was ±0.2 and ±0.3 eV, respectively. The BE and KE values were obtained by using the Peak-fit program implemented in the control software of the spectrometer.

The zeolite content was estimated by weighing the membrane before and after the hydrothermal synthesis. The difference in both masses was attributed to the zeolite layer grown on the support.

3. Results and discussion

3.1. Zeolite growth

In previous studies [21,36], the importance of surface oxygen groups for the growth of silicalite-1 and ZSM-5 on carbon materials was demonstrated. It was stressed there that the presence of a sufficient amount of oxygen groups on the surface of the support is essential for an adequate zeolite growth. Additionally, it has been reported that the presence of strongly acidic groups on the surface of the support favors the anchoring of the sol aggregates that form on the support before crystal formation in the presence of Na$^+$ ions [19]. Then, the oxidation of the support used in this study has been analyzed as it is of great relevance, since experimentally there is no silicalite-1 growth on the non-oxidized support.

In order to precisely determine whether the oxidizing pretreatment of the carbon discs yielded a significant amount of oxygen surface groups on the support, TPD and FTIR experiments were carried out on the discs before and after the oxidation process. Due to the small surface area of the support, none of the two techniques proved useful to identify the oxygen surface groups of the carbon discs. For that reason, XPS analysis was carried out. Fig. 1 shows the XPS oxygen 1s region for the oxidized and non-oxidized carbon discs. The figure clearly shows that the oxidized support has a higher oxygen content. The calculated surface O/C ratio for the two samples is 0.189 for the oxidized support and 0.052 for the non-oxidized sample.

By using the synthetic route described in Section 2, it is possible to obtain a layer of well-crystallized zeolite on the oxidized carbon discs under certain synthesis solution compositions (the effect of the different experimental parameters will be described in the following sections). As an example, Fig. 2 shows the cross-section and the upper view of one of the composites prepared in the present study which exhibits membrane properties (composition of synthesis solution: $1\text{SiO}_2\cdot 0.049\text{TPA-Br}\cdot 0.198\text{NaOH} \cdot 41.77\text{H}_2\text{O}$; two consecutive syntheses). It is clear that the crystal morphology is that of zeolite MFI. Additionally, Fig. 3 shows the X-ray diffractogram of the silicalite-1/carbon composite, containing three characteristic peaks at $2\theta \approx 23^\circ$ corresponding to the most intense reflections of zeolite MFI [39]. Fig. 4 shows the IR spectra of one of the silicalite-1/carbon membranes obtained and that of the zeolite crystals obtained by hydrothermal synthesis in the same autoclave but without using the carbon support. It is clear from the spectra that silicalite-1 is present in both materials, due to the characteristic bands at 2020, 1890, 1640, 1360 and 1225 cm$^{-1}$ [40].

From the cross-section of Fig. 2a, corresponding to one of the composites synthesized, it is clear that the zeolite crystals do not grow inside the pores of the support. This observation is corrobor-
orated by comparing the silicalite-1 layer thickness obtained by SEM with that calculated from the measured weight increase after calcination (assuming a silicalite-1 density of 1.8 g cm\(^{-3}\) [41]). As can be seen from Table 1, the silicalite-1 layer thicknesses calculated from the weight gain after the hydrothermal treatment are in agreement with those measured by SEM. One of the main disadvantages of using ceramic or metallic supports is that there is a very important zeolite growth inside the pores of the support, giving rise to a significant decrease in the permeability of the membrane [42]. Therefore, when hydrophilic supports are used, more than one hydrothermal synthesis is needed (in some cases, up to five hydrothermal treatments are needed [42]). This is because the first crystal nuclei grow inside the pores of the support, hence the surface is only covered when all pores of the support is filled. The fact that zeolite crystals do not grow inside the pores of carbon strongly suggests that this is due to the hydrophobic nature of the carbon support which will prevent a significant penetration of the synthesis solution into the pores of the support and hence the zeolite from growing inside the pores of the support. In fact, contact angles measured for water on the carbon support before (contact angle 104°) and after (contact angle 65°) oxidizing treatment indicate that the hydrophilic character of the carbon support is significantly enhanced due to the surface oxygen groups. However, the measured contact angle for the oxidized support is still far bigger than that
found for more hydrophilic supports (with an angle between $5^\circ$ and $15^\circ$). The high contact angle after oxidation agrees with the difficulty to oxidize this carbon sample (prepared by graphite agglomeration). Thus, considering the low reactivity of the carbon material and its hydrophobic nature, the oxidation with HNO₃ will be rather heterogeneous and will mainly focus on the external surface of the disc.

It is remarkable that zeolite crystals from the mother liquor and from the membrane, both obtained in the same autoclave, do not have the same size. More precisely, crystals recovered from the mother liquor after the hydrothermal treatment are larger than those found on the surface of the membrane. This is possibly due to the fact that the surface of the support acts as a source of nucleation sites, favoring the crystallization kinetics and the presence of a higher amount of crystal nuclei, giving rise to smaller crystals. Additionally, for certain synthesis conditions and using short synthesis times, well crystalline silicalite-1 was grown on the carbon discs, whereas the material which was not anchored remained a gel. These observations suggest that the carbon surface favors the nucleation and final crystallization of silicalite-1 in agreement with previous results [21].

It must be emphasized that the use of clear synthesis solutions was necessary to achieve a good coverage of the support, in agreement with previous results [21].

Having presented the main aspects concerning the synthesis of zeolite/carbon composites using some specific examples, we will discuss in more detail the influence of different synthesis parameters that affect the properties of the composites. All examples reported correspond to nearly identical synthesis mixtures, thus being essentially comparable. Additionally, the experimental conditions used for the syntheses presented in each section were kept constant except for the variable being analyzed (i.e., 6 h ageing time, 423 K synthesis temperature, 24 h synthesis time and just one hydrothermal treatment).

### 3.1.1. Effect of the ageing time

The importance of the ageing time in the crystallization process was studied keeping the composition of the synthesis solution constant. A representative composition of the synthesis solution was:

$$1\text{SiO}_2 \cdot 0.048\text{TPA-Br} \cdot 0.215\text{NaOH} \cdot 41.45\text{H}_2\text{O}$$

Fig. 5 shows the SEM images of two composites obtained with different ageing times. The composite synthesized without ageing (Fig. 5a) does not exhibit crystal growth, but gel deposition on the carbon disc. However, if an ageing time of 6 h is applied (Fig. 5b), then the presence of MFI-type crystals anchored on the carbon support is clear. A minimum ageing time is essential for the anchoring of silicate species on the surface of the support that favors crystal growth during the hydrothermal treatment [21].

Additionally, the influence of the ageing time was tested in other experiments carried out using different templates and synthesis solution compositions, and in all cases similar results were obtained when no ageing was applied.

### Table 1

<table>
<thead>
<tr>
<th>Composite</th>
<th>Weight A$^a$ (g)</th>
<th>Weight B$^b$ (g)</th>
<th>Weight gain (g)</th>
<th>Calculated thickness$^c$ (μm)</th>
<th>Observed thickness$^d$ (μm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0622</td>
<td>0.0680</td>
<td>0.0058</td>
<td>12.1</td>
<td>≈11–12</td>
</tr>
<tr>
<td>2</td>
<td>0.0630</td>
<td>0.0741</td>
<td>0.0111</td>
<td>23.0</td>
<td>≈23–24</td>
</tr>
<tr>
<td>3</td>
<td>0.0622</td>
<td>0.0636</td>
<td>0.0014</td>
<td>2.9</td>
<td>≈2–3</td>
</tr>
</tbody>
</table>

$^a$ Before hydrothermal synthesis.

$^b$ After hydrothermal synthesis and calcination.

$^c$ Assuming that no crystals grow inside the pores of the support.

$^d$ Observed by SEM.
3.1.2. Effect of temperature of the hydrothermal synthesis

Various composites were synthesized in order to study the effect of temperature of the hydrothermal synthesis on the resulting material. The materials were prepared using the following composition of the synthesis solution:

$$1\text{SiO}_2 \cdot 0.048\text{TPA-Br} \cdot 0.215\text{NaOH} \cdot 41.45\text{H}_2\text{O}$$

Fig. 5b shows the SEM image of a composite prepared at 458 K and Fig. 6 that for a material prepared at 458 K. It can be seen that the composite shown in Fig. 6 has some areas on which silicalite-1 did not grow. The image in Fig. 5b shows a higher coverage of silicalite-1 on the surface of the support. We found that the optimal synthesis temperature is 423 K, since it leads to a better coverage of silicalite-1 crystals than the same synthesis performed at 458 K. It is probable that, at such high temperatures, anchoring of the zeolite crystals on the carbon support is hindered, and thus 423 K turns out to be a more suitable synthesis temperature in this case.

3.1.3. Effect of time of the hydrothermal synthesis

In order to study the influence of the time of hydrothermal synthesis, different zeolite–carbon composites were prepared using nearly the same composition as before:

$$1\text{SiO}_2 \cdot 0.047\text{TPA-Br} \cdot 0.225\text{NaOH} \cdot 41.50\text{H}_2\text{O}$$

Fig. 7 presents the SEM images of these two materials prepared at 423 K and a synthesis time of 18 h (Fig. 7a) and 72 h (Fig. 7b), respectively. From Fig. 7 it can be clearly seen that, as it is well known, the longer the hydrothermal synthesis time the larger the crystals and the better the continuity of the zeolite layer.

3.1.4. Effect of the NaOH content

To study the effect of the amount of NaOH added to the synthesis solution, different silicalite-1/carbon composites were synthesized. It has to be borne in mind that templates like TPA-Br, which give a slightly acidic solution when dissolved, need a minimum of added NaOH so that the pH is high enough for an adequate dissolution of the fumed...
silica. This is a crucial parameter since only clear synthesis solutions led to an efficient surface coverage of the supports. Some syntheses were carried out using a gel as a synthesis mixture and no zeolite growth was observed on the carbon surface. As a matter of fact, if one considers the relatively poor wetability of the oxidized carbon support, when a gel (with high viscosity) is used, the interaction between the two phases is extremely poor and thus no zeolite growth is observed. Examples for two representative synthesis solutions were

\[ \text{1SiO}_2 \cdot 0.048\text{TPA-Br} \cdot 0.215\text{NaOH} \cdot 41.45\text{H}_2\text{O} \]
\[ \text{1SiO}_2 \cdot 0.049\text{TPA-Br} \cdot 0.307\text{NaOH} \cdot 41.93\text{H}_2\text{O} \]

It is clear from the SEM images presented in Figs. 5b and 8 that the composite synthesized with the higher amount of NaOH (Fig. 8) yields smaller crystals and a higher coverage. A larger NaOH content in the solution (i.e. a higher pH) increases the solubility and thus allows a higher SiO\textsuperscript{4+} saturation concentration, which favors the formation of a large quantity of small nuclei, giving rise to a large amount of small crystals (Fig. 8). However, there is an upper limit for the NaOH that can be added to the synthesis solution in order to obtain silicalite-1. If an excessive amount of NaOH is added, then either quartz crystals begin to form on the support (the diffractogram of the composite shown in Fig. 8 exhibited a huge peak at 2\(\theta = 26.515^\circ\)) or no solid material is obtained. This effect was also observed when TEA-F was used as a template. Apart from the pH of the synthesis solution, the NaOH content plays a very important role during the hydrothermal synthesis. It is well known that Na\textsuperscript{+} ions have a strong effect in the growth of MFI zeolite crystals [43], causing the formation of a sol phase in the synthesis solution and giving rise to sol aggregates that make zeolite crystals grow with a random orientation [19]. The effect of the NaOH content in the synthesis solution and its significance has been previously studied by other authors [44].

3.1.5. Effect of the template

Since the template is the compound that “directs” the synthesis, it must play a very important role for the final result. To show the effect of the
template the following synthesis solutions were used:

\[
\begin{align*}
&\text{1SiO}_2 \cdot 0.048\text{TPA-Br} \cdot 0.215\text{NaOH} \cdot 41.45\text{H}_2\text{O} \\
&\text{1SiO}_2 \cdot 0.052\text{TEA-F} \cdot 0.178\text{NaOH} \cdot 41.77\text{H}_2\text{O} \\
&\text{1SiO}_2 \cdot 0.05\text{TPA-OH} \cdot 0.22\text{NaOH} \cdot 41.5\text{H}_2\text{O}
\end{align*}
\]

The SEM images of the resulting composites are shown in Figs. 5b, 9a and 9b, respectively. From these figures it can be seen that the surface coverage of the three materials is not the same and that the differences between the crystal sizes is quite remarkable. Composites synthesized using TPA-OH (Fig. 9b) as a template have smaller crystal sizes and a much higher coverage than those prepared with TPA-Br (Fig. 5b) and TEA-F (Fig. 9a).

Of course, as discussed above, the pH of the synthesis solution affects the final result. This effect is less pronounced in the case of TPA-OH, probably due to the high pH of the synthesis solution. Membranes synthesized with TPA-OH as a templating agent possess crystals with sizes varying from 2 to 4 μm, whereas TPA-Br and TEA-F yield crystals with sizes of 10 and 25 μm, respectively. Also worth mentioning is the role that the fluoride ions play in the crystal growth. The formation of SiF$_2$ ions increases the solubility of the fumed silica during the synthesis and favors the formation of larger and better intergrown crystals.

3.1.6. Template removal from the composites

As mentioned in Section 1, the removal of the template from the resulting composites is a very troublesome step in the synthesis of zeolite membranes. With the aim of optimizing this process, thermal analyses were carried out on the prepared samples. Fig. 10 shows the evolution of the TG and DTA signals with temperature, both for the synthesized silicalite-1 crystals and for the support used. The experiments were carried out in air; additionally, the zeolite crystals were heat-treated in nitrogen for comparison purposes. The weight loss of the silicalite-1 crystals beginning at approximately 673 K corresponds to the removal of the template, whereas the weight loss of the support, beginning at around 723 K, is due to the burn-off of the carbon disc. Since carbon burning occurs close to the template removal, the use of air should be avoided. For this reason, a pyrolysis at 973 K in N$_2$, as described in the experimental section, has been used in all the cases.

3.2. Permeation studies

The results presented and discussed in the above sections permit us to conclude that, selecting appropriate synthesis conditions, a large coverage of the support can be achieved. However, permeation experiments are necessary to corroborate the membrane properties of these materials.
The membrane properties of the synthesized compounds were tested by two experiments: firstly, different pure gases (He, N₂, CO₂, O₂, ethane, ethylene, propane, propylene, n-butane and i-butane) were passed through the composite to check that the amount of cracks present in the material was not significant and, secondly, the quality of the membrane was tested by passing through different mixtures of gases (i.e. i-butane/n-butane or n-butane/N₂). It must be noted that the as-synthesized membranes showed no permeation at all, thus indicating the absence of significant pinholes and/or defects.

Fig. 11 shows the pure gas permeance values for both the carbon disc (support) and one heat-treated silicalite-1 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 membrane. Also, in case of the carbon disc, there is a linear trend between the permeation of the gases and the square root of their molecular weight (see Fig. 11). This behavior is typical of Knudsen diffusion. However, for the silicalite-1 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. This indicates that CO₂ transport through the silicalite-1 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-1 layer behaves as a proper membrane. This observation can be stated far more
clearly in Fig. 12, where the permeance of several gases is plotted versus their kinetic diameter. The lack of correlation between the permeation and the kinetic diameter discards the possibility of the transport occurring by a molecular sieving mechanism. This, however, does not eliminate the possibility that some steric factors might be of importance in the diffusion. The permeation values for some hydrocarbons like ethane, ethylene, and propylene are higher than that corresponding to He. This observation is in agreement with what has been previously said about CO$_2$. In the case of $i$-butane, there seem to be some steric problems due to the similar size of $i$-butane (5.0 Å) and the pores of silicalite-1 (5.4 Å × 5.6 Å for the straight channels and 5.0 Å × 5.5 Å for the sinusoidal channels).

Results obtained from the separation of binary gas mixtures of CO$_2$, N$_2$ and hydrocarbons are collected in Table 2. The table includes the preparation conditions of each membrane. The separation factors for the gas mixtures are higher than those obtained from the ratio of pure gas permeances. This indicates that the more permeable gases (hydrocarbons, CO$_2$ etc.) are adsorbed in the membrane micropores, occupying part of the void space and partially inhibiting the diffusion of non-adsorbable species (N$_2$). The separation factors obtained for the mixtures propane/N$_2$ and propylene/N$_2$ are especially high. Also for $n$-butane/$i$-butane mixtures, the separation factor shows that the membrane prepared by the aforementioned method presents good properties. These results are comparable to those obtained by other authors using different supports like $\alpha$-alumina [45,46], $\gamma$-alumina [47] or porous metals [48], their separation factors for $n$-butane/$i$-butane mixtures being typically around 10 and 30 when in situ synthesis methods were used. Higher separation factors can be achieved by the secondary growth (seeded) method [49].

4. Conclusions

The present work shows a clear progress in the preparation of zeolite/carbon composites. Not
only were the need for an ageing time, the use of clear synthesis mixtures, and an oxidizing pre-
treatment confirmed (as we have already pointed 
out in Ref. [21]), but continuous layers of silicalite-
1 were also successfully grown on carbon discs by 
conventional hydrothermal treatment. Such ma-
terials show adequate membrane properties and 
thus clearly show the applicability of these com-
posites. It must also be emphasized that using 
carbon as a support shows advantages compared 
to metal oxides such as higher thermal stability 
after calcination, the lack of zeolite growth inside 
the pores of the support, simplicity of the synthesis 
method, and the wide range of shapes which can 
be fabricated from carbon.

The modification of the synthesis conditions 
allows the control of the crystal size of silicalite-1. 
In this sense, a high pH, short synthesis times and 
the use of TPA-OH favor the formation of small 
silicalite-1 crystals (2 \( \mu m \)). The weight gain after 
the hydrothermal treatment suggests that no sili-
calite-1 is formed inside the pores of the support.
Carbon discs are very interesting as supports since 
they are hydrophobic and do not let the synthesis 
solution enter into their pores and also favor the 
nucleation of the crystals.

Both the permeation of pure gases and the 
separation of binary mixtures clearly show that 
the silicalite-1/carbon membranes prepared by the 
previously described method have good perme-
ation and separation properties and are almost 
free of cracks and large-sized defects. It is quite 
remarkable that the synthesized composite mate-
rials maintain good properties as membranes after 
heat treatment at temperatures as high as 973 K. 
This is an important advantage over other sup-
ports (steel, alumina, etc.) and a consequence of 
the low thermal expansion coefficient of carbon 
materials.

Nevertheless, the reproducibility of these ma-
terials in the separation performance is an issue of 
crucial importance that needs further investiga-
tion. In this sense it must be noted that not only 
the synthesis solution and the synthesis condi-
tions play a key role for the resulting materials, 
but also the support (hydrophilic character, surface 
roughness, etc.) is an important subject to deal 
with.

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