

Xylene isomerization in a membrane reactor

Part I: The synthesis of MFI membranes for the *p*-xylene separation

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Abstract

The synthesis and characterization of silicalite and ZSM-5 films supported on porous SS tubes are described. Composite membranes were used to separate xylene isomers between 150 and 400 °C. Permeation measurements of the individual isomers and the ternary mixture were performed at each temperature within this interval. N₂ permeation measurements together with SEM observations were used to determine whether or not cracks and/or pinholes developed after exposure to the xylene isomers at high temperature. The ZSM-5 membrane was superior to the silicalite one because of its higher permeance flux ($1.16 \times 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$), separation factors (p/o 4.4), and up to 400 °C stability.

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1. Introduction

The naphtha reformer is the main source of xylenes in an oil refinery. The xylene fraction fed to the isomerization reactor together with H₂ mainly contains the three isomers and ethylbenzene. The most valuable product is the *p*-xylene. Therefore, the reactor exit stream is first distilled to separate the *o*-xylene while the *m*-xylene is crystallized out of the binary mixture. This two-step purification requires too much energy. This is why the use of a membrane becomes attractive, even more when energy costs have sky-rocketed [1]. This is reflected in a large number of papers being currently published concerning the development of composite membranes potentially applicable to selectively separate *p*-xylene from the isomers mixture [2–6].

The use of the MFI-zeolite membrane for xylene separation appears as a good choice to increase the *p*-xylene yield. The MFI-zeolite (silicalite or ZSM-5) presents a pore structure which consists of straight, circular pores (0.54 nm), interconnected with sinusoidal, elliptic pores (0.51 nm × 0.54 nm) [7]. These pore sizes are close to the kinetic diameter of *p*-xylene ($d_k = 0.58 \text{ nm}$), and it is expected that its bulkier isomers ($d_k = 0.68 \text{ nm}$) would diffuse at a slower rate through these pores.

Several groups have studied the separation of xylene isomers using MFI-zeolite membranes synthesized under different conditions [8,9]. Keizer et al. [10] reported equivalent single-component and binary *p*-xylene fluxes of $3 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ and a *p*-xylene/*o*-xylene flux ratio of 30 at 200 °C with a planar 3 μm MFI-membrane. The partial pressures of components in the feed were low (*p*-xylene 0.31 kPa, *o*-xylene 0.26 kPa). Gump et al. [11] studied the permeance of *p*-xylene, *o*-xylene and benzene through several molecular sieve membranes (SAPO-5, SAPO-11, mordenite) as well as three types of MFI-membranes (silicalite-1, ZSM-5 and boron-substituted ZSM-5) as a function of pressure and temperature. The boron-substituted ZSM-5 membrane was the most efficient one for the xylene separation with an ideal selectivity as high as 130 and a separation factor of ca. 60 at 151 °C.

Hedlund et al. [12,13] used an ultra thin MFI-membrane supported on porous α-alumina disks produced by a two-step support masking technique. High *p*-xylene permeance values were obtained together with *p*/*o*-xylene separation factors in the 3–17 range. Xomeritakis et al. [14,15] reported the preparation of an MFI-membrane synthesized on the surface of α-alumina disks and evaluated the separation of xylenes in the 22–275 °C temperature range. They found that the separation performance is directly related to the synthesis conditions and the resulting membrane microstructure. The membranes synthesized exhibited a *p*-xylene permeance of $2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 100–125 °C and *p*/*o* separation factors between 60 and

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300, when *n*-hexane was added to the binary *p/o* feed. This improvement is attributed to the preferential adsorption of *n*-hexane in non-zeolitic micropores/grain boundaries. Interesting results were recently obtained by Lai et al. [16,17] through b-oriented silicalite membranes on the surface of α -alumina disks. These membranes possess *p/o*-xylene separation factors (0.5 kPa/0.45 kPa) as high as 483 at 220 °C at a *p*-xylene permeance of $2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

Dalmon and coworkers [2] reported an interesting work about xylene isomerization in an extractor-type catalytic membrane reactor (CMR) using a silicalite membrane. They reported an increase of 10% in the *p*-xylene yield compared to their conventional fixed-bed reactor. This is the only work in the literature to report the improvement a catalytic membrane reactor brings about and together with the work by Gump et al. [11], the only studies to use tubular supports.

In order to use any of these composite membranes in a xylene isomerization reactor, the first requirement is that it should be thermally stable up to ca. 400 °C. The second requirement is that, for practical reasons, a porous stainless steel tube should be used as support. So far, no published data concerning xylene separation comply with these two requirements simultaneously.

In this work, we present the synthesis and characterization of MFI membranes on the surface of a porous stainless steel support tube. The performance of the silicalite is compared to that of the ZSM-5 membrane for the xylene separation. The membranes were characterized by XRD, SEM and nitrogen permeation. This is the first paper of a series of two. In the second one, permeation and selectivity data obtained at 370 °C with the best membrane will be used to evaluate the increase in *p*-xylene yield that could be obtained in an industrial reactor.

2. Experimental

2.1. Membrane synthesis

MFI membranes were synthesized on the outer surface of a porous stainless steel tubular support provided by Mott Metallurgical. It had an outer diameter of 10 mm and an inner diameter of 7 mm (thickness 1.5 mm). The average pore size was 0.2 μm . Before use, the tubes were ultrasonicated in acetone for 30 min to remove organic contaminants and dirt. The ZSM-5 membrane was prepared by first casting layers of silicalite seed crystals (ca. 250 nm). The silicalite crystal seeds were synthesized under hydrothermal synthesis conditions in a Teflon-lined autoclave at a fixed temperature of 125 °C for 8 h. The seeded support was subsequently subjected to two hydrothermal reaction steps for 8 h each at 165 °C. The starting hydrogel for the ZSM-5 membrane consisted of Aerosil 200 as the Si source, tetrapropylammonium bromide (TPABr) as a template, sodium hydroxide, deionized water, and sodium aluminate as the Al source with the following composition: 21SiO₂:1TPABr:3NaOH:0.105Al₂O₃:987H₂O [18]. The silicalite membrane was synthesized on the support modified by washcoating with γ -Al₂O₃ using a suspension made up of 15 wt% of γ -Al₂O₃ in acid deionized water. Afterwards, the support was calcined in air at 500 °C for 6 h. The N₂ permeation

decreased from 16.2×10^{-6} to $4.5 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The silicalite films were synthesized by two hydrothermal reactions steps treatment for 8 h at 175 °C each, with a gel composition of 0.32TPAOH:1TEOS:165H₂O [19]. In this case, the tetrapropylammonium hydroxide (TPAOH) was used as the template and tetraethyl orthosilicate (TEOS) as the Si source. In order to improve the performance of the membrane, several silicalite membranes were synthesized with different treatments of the support. In this work, the best silicalite membrane obtained is compared with the ZSM-5 membrane. The as-synthesized membranes were washed with deionized water, dried at 80 °C for 24 h, and tested for N₂ permeation. The template in the zeolite pores was removed by heating in air at 470 °C for 3 h with a heating rate of 0.3 °C/min and a cooling rate of 0.5 °C/min.

2.2. Characterization

The morphology of the membranes was examined by scanning electron microscopy (SEM) using a JEOL JSM-35C instrument. X-ray diffraction patterns of the membranes and of the residual powders collected at the bottom of autoclaves after synthesis were obtained with an XD-D1 Shimadzu instrument, using Cu K α radiation at 30 kV and 40 mA. The scan rate was 1° min⁻¹ in the range $2\theta = 5\text{--}40^\circ$.

2.3. Permeation measurements

2.3.1. N₂ permeation

The N₂ permeation data were used as a criterion to evaluate the extent of extra-zeolitic pores present in the membrane. It was measured at 25 °C and transmembrane pressures between 40 and 100 kPa.

2.3.2. Xylene permeation

The vapor permeation experiments were conducted using the set-up schematically shown in Fig. 1. For these experiments, the membranes were connected to the permeation module using Teflon ferrules. Before testing, the MFI membrane was pre-treated at 150 °C under nitrogen flow for 4 h. The zeolite side of the tube was flushed with N₂ carrier streams passing through the xylene saturator maintained at 35 °C, while the inside of the tube was flushed with N₂ as a sweep gas. The nitrogen feed flow rate and the sweep flow rate were set at 10 and 9 ml/min, respectively, using mass flow controllers (MKS Instruments). The sweep gas flux of 9 ml/min is in the range where the permeation reaches a plateau with increasing N₂ flow rate. This was verified by experiments in which the sweep gas was varied between 5 and 40 ml/min. The total pressure in either side of the membrane was 1 atm. To prevent condensation of the organics and ensure correct xylene vapor pressure values, all system lines were kept at 150 °C using heating tape.

A Shimadzu GC-9A gas chromatograph equipped with a flame-ionization detector and a packed column containing Bentona 34 5% and SP-1200 5% (Supelco), was used to analyze the feed, permeate and retentate streams. The volumetric flow rates of the retentate and the permeate streams were measured at

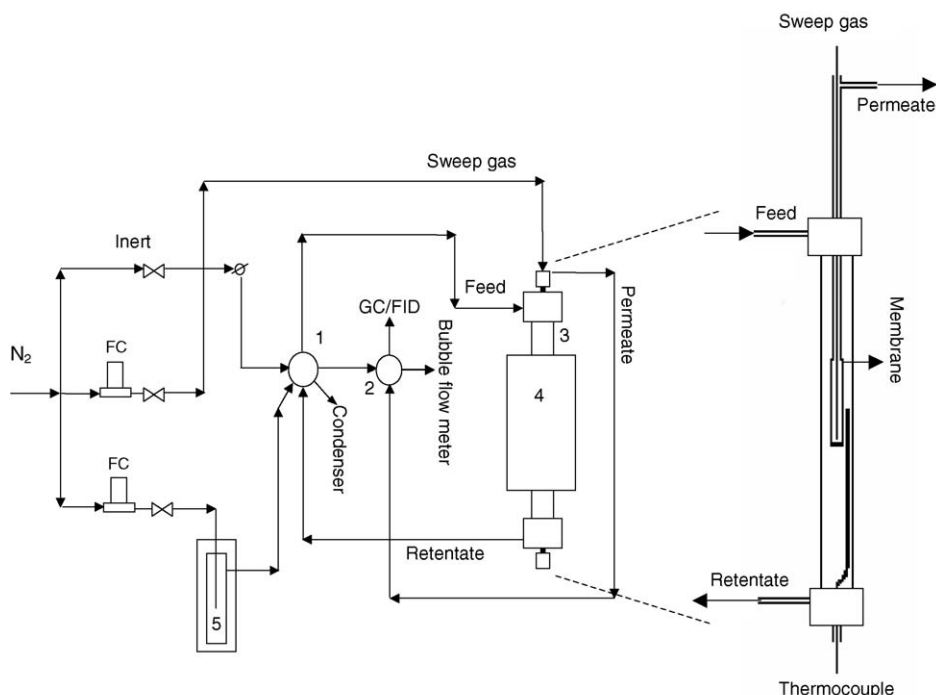


Fig. 1. Schematic diagram of the experimental set-up for xylenes measurements (1, six-way valve; 2, four-way valve; 3, membrane module; 4, furnace; 5, saturator).

atmospheric temperature and pressure using bubble flow meters. Single-gas and mixture tests were performed in the temperature range of 150–400 °C. The composition of the ternary mixture feed was 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene. This is the ratio of the thermodynamic equilibrium, composition of the isomers at 35 °C. The single-component measurements were carried out with 2.026 kPa *p*-xylene, 1.92 kPa *m*-xylene and 1.52 kPa *o*-xylene. The permeation flux of each component was calculated from its molar fraction (determined by GC), the flow rate of the permeate stream and the membrane area available for permeation ($7.5 \times 10^{-4} \text{ m}^2$ for the silicalite and $7.3 \times 10^{-4} \text{ m}^2$ for the ZSM-5 membranes). The experimental error in the molar fraction determination was less than 4%.

The single-component permselectivity (ideal selectivity) was defined as the ratio of their fluxes while the mixture separation factor was defined by the following equation:

$$\text{Separation factor} = \frac{(X_p/X_i)_{\text{permeate}}}{(X_p/X_i)_{\text{feed}}}$$

where X_p represents mole fraction of *p*-xylene and X_i represents mole fraction of either *m*-xylene or *o*-xylene.

3. Results

3.1. Characterization

Fig. 2 shows the XRD patterns of the ZSM-5 and silicalite membranes after calcination. A comparison with standard powder diffraction patterns of ZSM-5 and silicalite, respectively, confirms that the zeolite layers on the support consist of pure MFI zeolite. Note that the patterns of the powders are very

similar because they have the same MFI structure. The XRD patterns of the membranes before calcination were similar to those of the calcined membranes. No characteristic reflections of the stainless steel were observed, indicating a good coverage of the support by the zeolite layer. As suggested by the intensity ratio

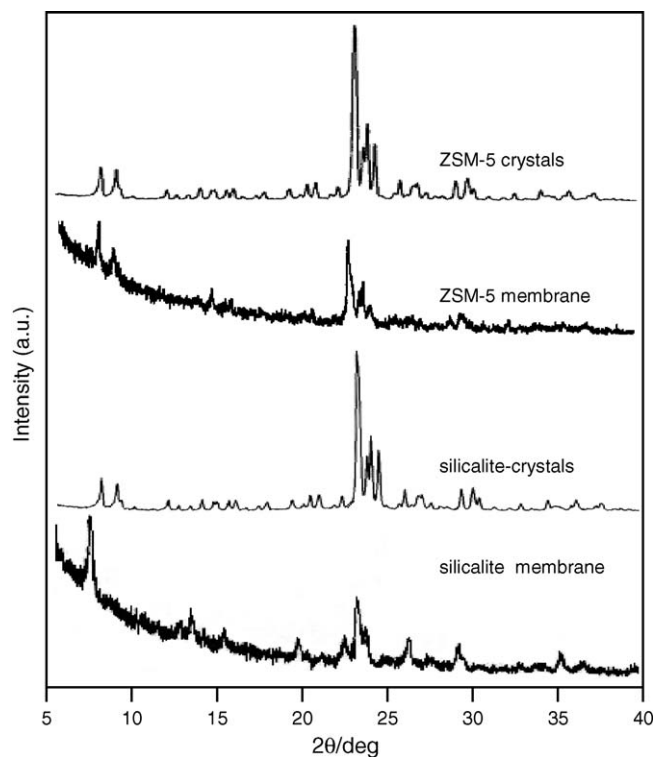


Fig. 2. XRD patterns of the MFI crystals and the membranes after calcination.

of the characteristic reflections, the ZSM-5 membrane exhibits a random orientation while the silicalite membrane shows a preferential orientation with the *c*-axis perpendicular to the surface.

The SEM micrographs of the membranes synthesized in this work are shown in Fig. 3. It can be seen that the two membranes exhibit different morphologies. No cracks were detected in the as-synthesized films. Crystal aggregates were present on the film surfaces. Note that the orientation of the crystals is consistent with the XRD patterns.

EPMA profile was obtained to ascertain whether or not aluminum atoms of the γ -Al₂O₃ layer have diffused in the silicalite matrix. Fig. 4 shows that not significant migration of this element has occurred even after heating the composite at 470 °C. Table 1 shows the weight gain (mg g⁻¹) and thickness (μ m) of both membranes.

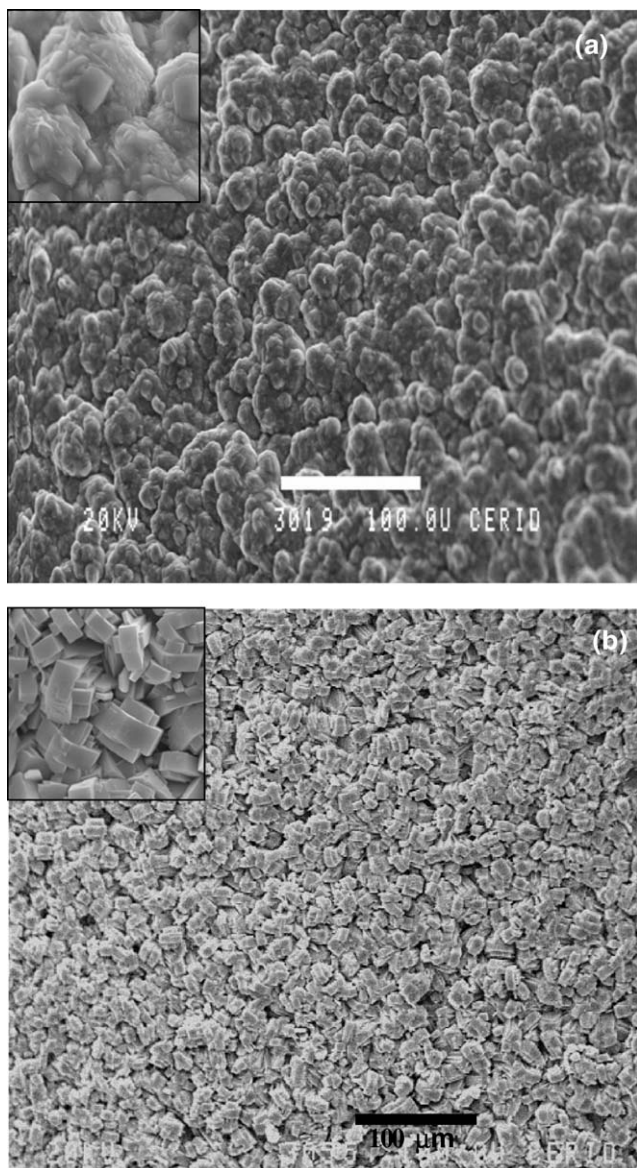


Fig. 3. SEM top views of the surface of the calcined membranes (a) ZSM-5 and (b) silicalite.

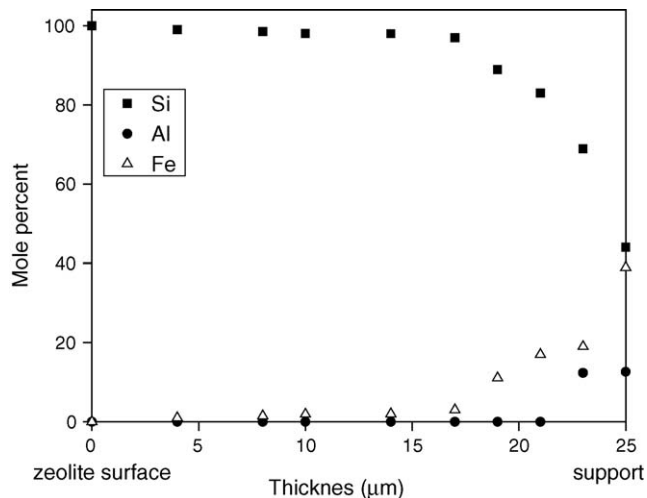


Fig. 4. EPMA profile of the silicalite membrane after calcination.

Table 1
Depth of the MFI layers

Membrane	Weight gain (mg g ⁻¹)	Thickness (μ m) ^a
ZSM-5	12.04	20
Silicalite	15.50	25

^a Measured in the SEM micrographs.

3.2. Permeation measurements

3.2.1. N₂ permeation

Before removal of the template, the membranes were impermeable to N₂ for a transmembrane pressure of 80 kPa at room temperature. Nitrogen permeance increased substantially to the range of 10⁻⁸ mol s⁻¹ m⁻² Pa⁻¹ after removal of the template. Table 2 shows the results of the single-gas permeation of nitrogen before and after the xylenes permeation tests were conducted up to 400 °C.

The N₂ permeance of the silicalite composite membrane, when measured after the xylene measurements, was 15% higher than the initial values (Table 2). This result indicates that the membrane was not stable at 400 °C. For the ZSM-5 membrane, the N₂ permeance did not change after exposure to the xylene isomers at the same temperature (Table 2).

3.2.2. Xylene permeation

The single-gas fluxes of *p*-xylene, *m*-xylene and *o*-xylene are shown as a function of temperature in Fig. 5 for the

Table 2
N₂ permeation through the MFI membranes supported on porous SS tubes at 25 °C and ΔP : 80 kPa

Membrane	N ₂ permeance $\times 10^8$ [mol s ⁻¹ m ⁻² Pa ⁻¹]	
	Before ^a	After ^b
Silicalite	9.05	10.40
ZSM-5	7.80	7.75

^a Before the xylene permeation measurements.

^b After the xylene permeation at 400 °C.

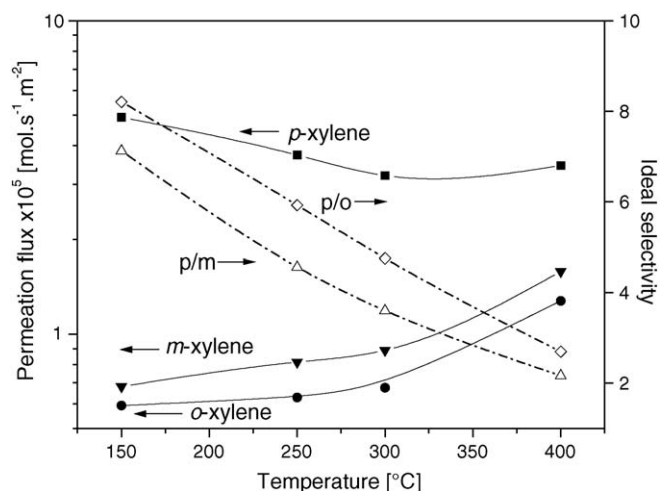


Fig. 5. Single-component fluxes of the xylene isomers through the silicalite membrane. Feed partial pressure: 2.026 kPa *p*-xylene, 1.92 kPa *m*-xylene and 1.52 kPa *o*-xylene.

silicalite membrane. This system presents a maximum *p/o* ideal separation factor of about 8.5 at 150 °C. The permeance of *p*-xylene decreases with temperature but between 300 and 400 °C it increases slightly. The permeances of *m*-xylene and *o*-xylene increase slowly at low temperature but at 400 °C they both exhibit a sharp increase.

The mixture fluxes of *p*-xylene, *m*-xylene and *o*-xylene through this membrane are shown in Fig. 6. The permeance trends are similar to those of the single-gas fluxes but flows increases above 300 °C are more pronounced. Note that the ternary mixture measurements at 400 °C were made after the single-gas data were obtained. These results and those obtained with the individual isomers suggest the formation of cracks consistent with the recorded increase of N₂ permeation after the xylene tests (Table 2). The maximum *p/o* and *p/m* separation factors were 5.6 and 4.6, respectively, at 150 °C.

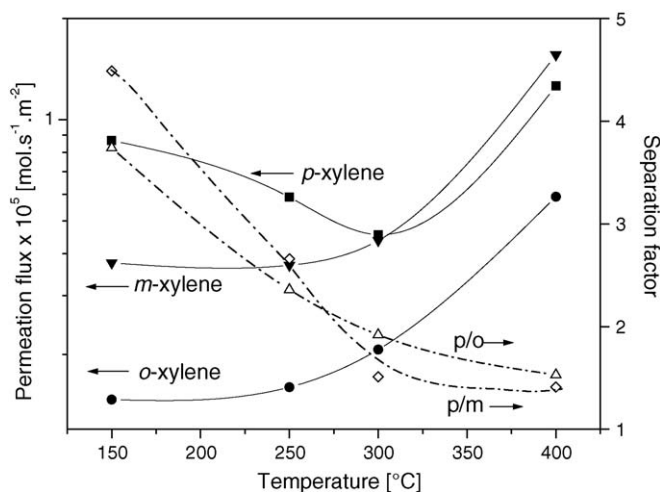


Fig. 6. Fluxes of the xylene isomers from ternary mixtures through the silicalite membrane. Feed partial pressure: 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene.

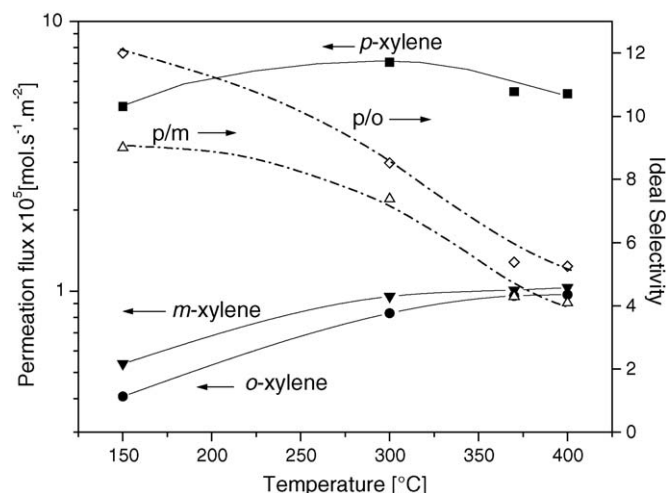


Fig. 7. Single-component fluxes of the xylene isomers through the ZSM-5 membrane. Feed partial pressure: 2.026 kPa *p*-xylene, 1.92 kPa *m*-xylene and 1.52 kPa *o*-xylene.

The ZSM-5 membrane exhibits higher fluxes and selectivities for the xylene isomers than its silicalite counterpart. Fig. 7 shows single-component permeation flux data in the 150–400 °C temperature range. Note the different temperature dependence of the *p*-xylene permeation flux.

Fig. 8 shows the xylene fluxes obtained from the ternary mixture permeation through the ZSM-5 membrane. Note that the fluxes of the three isomers increase with temperature but those of *m*-xylene and *o*-xylene are more pronounced. This membrane has *p/o* and *p/m* separation factors of 8 and 6.9, respectively, at 150 °C. As the temperature increases, the selectivities decrease but the membrane is selective for *p*-xylene at temperatures as high as 400 °C, where the separation factors are *p/o* 4.4 and *p/m* 4.3.

After the measurement of mixtures at 370 °C, the membrane was cooled at 300 °C and the *p*-xylene flux was measured again. Going up in temperature, the flux was $7.05 \times 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$

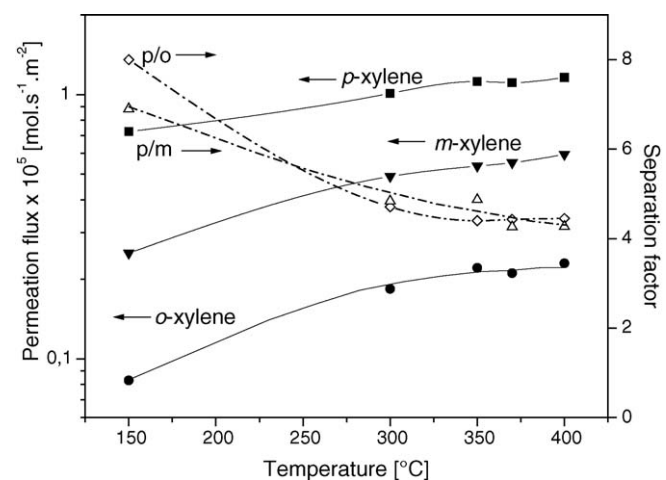


Fig. 8. Fluxes of the xylene isomers from ternary mixtures through the ZSM-5 membrane. Feed partial pressure: 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene.

Table 3
Xylenes permeation through the MFI membranes at 300 °C

	Feed pressure [kPa]	Permeance $\times 10^8$ [mol s ⁻¹ m ⁻² Pa ⁻¹]	
		ZSM-5	Silicalite
Pure			
<i>p</i> -Xylene	2.026	3.48	1.59
<i>m</i> -Xylene	1.92	0.49	0.46
<i>o</i> -Xylene	1.52	0.54	0.44
Mixture			
<i>p</i> -Xylene	0.83	4.42	1.19
<i>m</i> -Xylene	0.20	0.69	0.61
<i>o</i> -Xylene	0.25	0.71	0.62

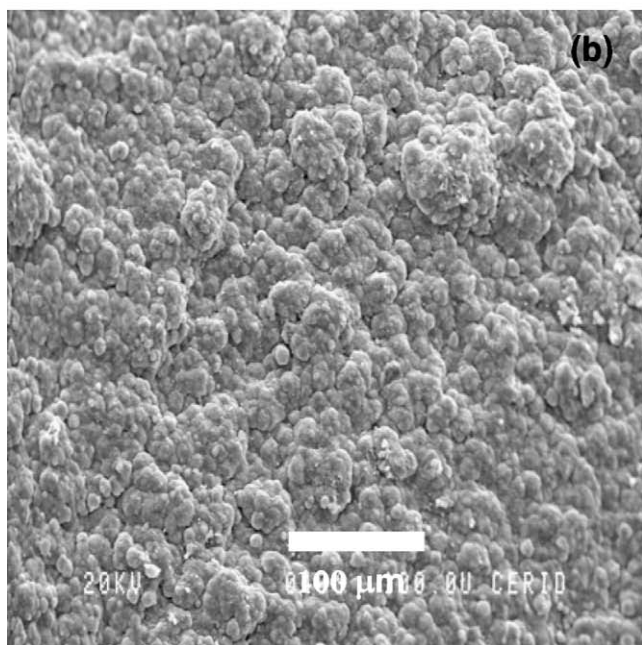
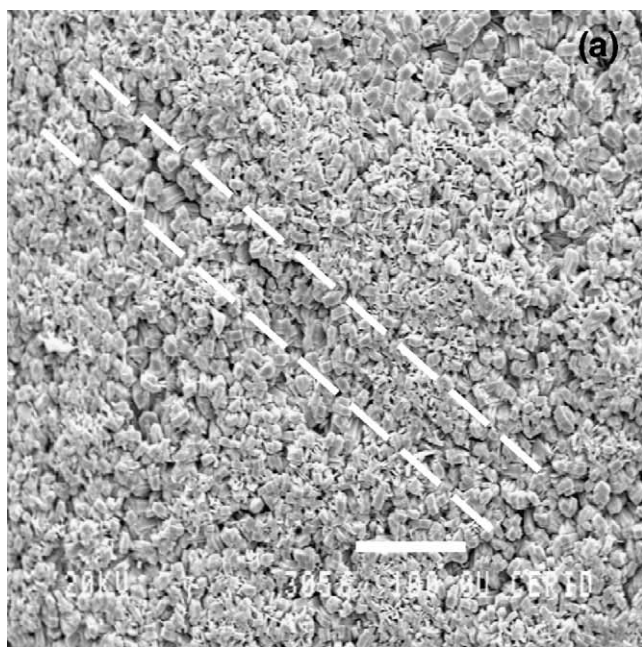


Fig. 9. SEM top view of: (a) the silicalite membrane surface and (b) the ZSM5 surface, both taken after the xylene permeation measurements.

and coming back 7.15×10^{-5} mol s⁻¹ m⁻², the same within the experimental error.

Table 3 summarizes the xylene permeances obtained through both membranes at 300 °C. The *p*-xylene permeance is higher in the ZSM-5 membrane but those of the other xylenes are similar in both the ZSM-5 and the silicalite membrane. In the case of the ZSM-5 membrane, the *p/o* separation factor of the xylene isomers is about 38% lower than the ideal separation. For the silicalite membrane, this separation factor decreases by 60% at 300 °C.

3.3. SEM micrograph of the used membranes

The higher after use N₂ permeation (Table 2) and the sharp increase in xylene permeation fluxes at 400 °C of the silicalite membrane (Fig. 6) are symptomatic of the appearance of extra zeolitic channels. This was confirmed by the crack shown in the micrograph (Fig. 9a). In the ZSM5 system on the other hand, the N₂ permeation before and after xylene measurements remained constant (Table 2) indicating that the ZSM-5 membrane was thermally stable. Accordingly, the micrograph of this membrane after the xylene measurements did not present any cracking (Fig. 9b).

4. Discussion

The molecules of xylenes can migrate through the MFI membranes via both the crystalline homogeneous pores and the larger intercrystalline spaces and cracks. The transport regime is not only controlled by the different sizes but also by the differences in adsorption interaction. In the zeolitic pores, the bulkier *m*- and *o*-xylenes with larger kinetic diameters are expected to diffuse much slower than *p*-xylene. However, this difference in diffusivities is somewhat attenuated due to the well-documented framework expansion upon *p*-xylene adsorption [20,21]. The variation of the permeation fluxes with temperature yields important clues about the contribution of the two types of membrane channels to the xylenes transport. In what follows, the transport mechanisms through the silicalite and ZSM-5 membranes will be discussed.

4.1. Silicalite membrane

First of all, note that there is an abrupt change of tendency in the evolution of permeation fluxes between 300 and 400 °C. This effect is more pronounced in the case of mixtures (Fig. 6) than in the case of single isomer permeance flux (Fig. 5). Note that the mixture measurements were made after the single runs. Therefore, the membrane had been kept at 400 °C for a longer time (100 h). The origin of this behavior is the development of cracks and/or pinholes in the silicalite layer for: (i) the N₂ permeation increased by 15% after the xylene exposure at 400 °C (Table 2), and (ii) the SEM micrograph (Fig. 9a) clearly shows the appearance of cracks in the composite membrane.

From the results shown in Figs. 5 and 6, it is concluded that the crystalline pores are the dominant pathway for xylene transport between 150 and 300 °C due to the following reasons:

Table 4
Performance comparison of MFI composite membranes

Support	Feed (kPa)			T (°C)	Separation factor p/o	Permeance _{<i>p</i>-xylene} × 10 ⁷ (mol s ⁻¹ m ⁻² Pa ⁻¹)	Sweep (ml/mi)n	Reference
	<i>p</i> -Xylene	<i>o</i> -Xylene	<i>m</i> -Xylene					
SS tubular ^a	0.23	0.26	0.83	150–400	9–4.4	0.51 (400 °C)	9	This work
α-Al ₂ O ₃ , tubular ^b	1.5	1.35	4.5	127–400	21–7	0.01 (400 °C)	15	[2]
SS tubular ^c	2.1	2.1		127–237	60–2.8	0.05 (237 °C)	40	[11]
α-Al ₂ O ₃ , disk ^b	0.27	0.59		100–390	16 (390 °C) ^d	3 (390 °C)	^e	[12]

^a ZSM-5.

^b Silicalite.

^c Boron-substituted ZSM-5.

^d Maximum value.

^e Not reported.

- (i) The higher flux of *p*-xylene compared to the other isomers.
- (ii) The *p*-xylene flux decrease with temperature is symptomatic of the strong adsorption of this isomer in silicalite [22].
- (iii) The increase in *o*- and *m*-xylene fluxes with temperature is also consistent with the weaker adsorption of these isomers in the crystalline pores [22,23].

4.2. ZSM-5 membrane

The first thing to note is that in this case, the MFI membrane did not develop any discontinuity at 400 °C. This was checked by the constancy of the N₂ permeation flux before and after running the xylene permeation experiments (Table 2). In the same vein, the micrograph of this membrane does not show any defect (Fig. 9b) as in the case of its silicalite counterpart (Fig. 9a).

In this case, all the fluxes (but one) monotonically increased with temperature (Figs. 7 and 8). This change in tendency of the *p*-xylene isomer would indicate that it is not so strongly adsorbed on ZSM5 compared to the silicalite. As a matter of fact, it has been reported that the incorporation of aluminum in the MFI lattice decreases the adsorption strength of the C₈ isomers [24,25].

It has been reported [2,14] that the *p*-xylene flux presents a maximum at relatively low temperatures. Again, the interplay between adsorption and diffusion may be responsible for this maximum. At low temperatures, the surface coverage is relatively high. At increasing temperatures, the coverage decreases but is counterbalanced by the higher values of the diffusion coefficient. Beyond the maximum temperature, coverage becomes so low that this effect predominates and a slight decrease of the flux is observed between 300 and 400 °C. From all these experimental data, it is concluded that the crystalline pores are the main pathway for the transport of the xylenes across the ZSM-5 membrane between 150 and 400 °C, with little contribution from intercrystalline pores and/or pinholes.

4.3. Our data compared to the published information

Table 4 provides a summary of the published data of xylene permeance through composite MFI membranes at high temper-

atures. The first thing to be remembered is that most published papers provide data obtained with composite ceramic supported disks. Only two groups worked with tubular supports and only one of them used stainless steel porous tubes. The cylindrical membranes show lower separation factors than the discs. This seems to be due to a higher concentration of defects that are generated on non-flat surfaces. As a matter of fact, several groups have reported data obtained with flat MFI composite membranes [12–17]. They are not included in Table 4, however, because they show measurements carried out at low temperatures (ca. 200 °C) and cannot be compared with ours at 400 °C. Observing the first three entries of the Table, it is concluded that our membrane is the best of them taking into account both permeance and separation factors. Only one membrane can be strictly compared to ours [2] because in the other case [11] the maximum temperature is much lower than 400 °C. Furthermore, in Part II of this sequence it will be shown how the use of the ZSM-5 membrane would improve the yield of *p*-xylene in an industrial isomerization reactor.

5. Conclusions

Both composite membranes synthesized in this work were selective to *p*-xylene between 150 and 300 °C. The ZSM-5 composite exhibited the highest p/o, p/m separation factors. The silicalite membrane became thermally unstable at ca. 400 °C while the ZSM-5/SS system was not affected by xylene exposure at the same temperature. The permeation regime is described by a combination of adsorption–diffusion steps whose balance is modified by the introduction of aluminum in the MFI lattice. Taking into account both permeance and separation factors, the ZSM-5 membrane compares favorably with other similar tubular composites reported in the literature (Table 4).

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