A durable ZSM-5/SS composite tubular membrane for the selective separation of *p*-xylene from its isomers

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Abstract

A ZSM-5 membrane synthesized on a stainless steel porous tube was used for the separation of *p*-xylene from its isomers, *m*- and *o*-xylene. The membrane was prepared by secondary growth on the outer surface of the support. The permeation regime through the membrane was described by a combination of adsorption–diffusion steps. In order to examine the durability of the membrane, a sequence of three thermal cycles was conducted. N_2 permeation measurements together with scanning electron microscopy (SEM) observations were the tools used to detect whether or not cracks developed after exposure to the xylene isomers up to 400 °C. After 1000 h on stream, the membrane was selective to *p*-xylene, the N_2 permeance fluxes remained unchanged and the SEM micrographs did not reveal any discontinuity.
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1. Introduction

In recent years, the availability of microporous zeolite membranes has opened up new fields of applications. The zeolite membranes allow difficult separations, such as those of mixtures of compounds with close boiling-points, i.e. of xylene isomers. In fact, the use of MFI-zeolite membranes appears as a potentially more energy-efficient xylene separation method. This is further supported by the difference in kinetic diameters of the isomers (0.58 nm for *p*-xylene and 0.68 nm for both *o*- and *m*-xylene).

Several groups have studied the separation of xylene isomers using MFI-zeolite membranes synthesized under different conditions [1–4]. The performance of these membranes during binary permeation of xylene isomers is generally poor. Hedlund et al. [5,6] used ultra thin MFI-membranes on porous α-alumina supports produced by a two-step masking technique. High *p*-xylene permeance values (3×10^{-7} mol m^{-2} s^{-1} Pa^{-1}) were obtained together with *p*/*o*-xylene separation factors in the 3–17 range between 100 and 390 °C. Xomeritakis et al.

[7,8] reported the synthesis of an MFI-membrane on the surface of an α-alumina support disk and evaluated the separation of xylene isomers vapors in the 22–275 °C temperature range. At 100–125 °C, the membranes synthesized exhibited a *p*-xylene permeance of 2×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and a p/o separation factor of 60–300. This selectivity was achieved through the addition of *n*-hexane to the binary p/o feed. The paraffin effect was attributed to the preferential adsorption of *n*-hexane in non-zeolitic micropores/grain boundaries. Interesting results were recently obtained by Lai et al. [9,10] through b-oriented silicalite membranes on the surface of an α-alumina support tube. They reported a p/o separation factor as high as 483 at 220 °C at a *p*-xylene permeance of 2×10^{-7} mol m^{-2} s^{-1} Pa^{-1}.

Dalmon and co-workers [11] performed the xylene isomerization in an extractor-type catalytic membrane reactor (CMR). They reported a 10% increase in the *p*-xylene yield compared to their conventional fixed-bed reactor. This is the only publication that reports data obtained for the *m*-xylene isomerization using a membrane reactor.

The geometry of the support is an important factor to consider. Much of the existing experimental work on MFI-zeolite membranes for the xylene separation has been performed using composite ceramic disks [5–8]. Only two groups have reported the use of tubular supports in the separation of xylene isomers

[4,11]. Various materials have been used as supports to produce composite membranes. The most common ones are alumina and stainless steel. The thermal expansion coefficients of both the support and the zeolite must be considered if the membrane is to be calcined and/or used at high temperature. The difference in thermal expansion may cause stress at the interface and cracks in the zeolite layer. A disadvantage presented by stainless steel is its higher thermal expansion coefficients compared to the alumina. Thus, stainless steel-supported zeolite membranes can be more susceptible to thermal cracking. However, stainless steel has the important advantage of ductility and is compatible with the most commonly used plant equipment parts. In order to improve the performance of the membranes supported on stainless steel, Tsapatsis and co-workers [12] have recently introduced an intermediate layer between the zeolite and the support. They have systematically studied the effects of different modifications in the deposition technique of the silica layer upon the membrane performance.

The thermal resistance of the membrane is then an important characteristic of these composite materials, albeit scarcely addressed in the open literature. Lai and Tsapatsis [10] used an MFI membrane supported on an α-alumina disk and reported that the separation factor did not change and the permeance was only reduced (10%) after 100 heating and cooling cycles up to a maximum temperature of 220 °C. Masuda et al. [13] reported the use of a ZSM-5 catalytic membrane synthesized on the outer surface of an alumina tube to obtain olefins from methanol. To test the durability of the membrane they ran a sequence of three mechanical and thermal shocks. The membrane was heated up to 500 °C, held for 1 h at that temperature, cooled in air and then the permeabilities of the xylenes and diethylbenzene isomers were measured at room temperature. The p/o permeability ratio remained constant along the sequence of thermal cycles.

The main objective of this work was to prepare a ZSM-5 zeolite membrane without pinholes, useful for xylene isomers separation and thermally stable up to 400 °C. The ZSM-5 membrane was synthesized on the outer surface of a stainless steel tubular support. The membrane was characterized by XRD, scanning electron microscopy (SEM) and nitrogen permeation. The 400 °C limit to evaluate thermal stability was selected in view that the xylene isomerization carried out in industrial practice at ca. 370 °C.

2. Experimental

2.1. Membrane preparation

The ZSM-5 membrane employed in this work was obtained using the secondary growth technique on the outer surface of a porous stainless steel (PSS) tubular support (Mott Metalurgical), 10 mm o.d. and 7 mm i.d. The average pore size was 0.2 μm. One end of the porous support was welded to a non-porous metal tube and the other end was sealed with a non-porous stopper. Through the open end, nitrogen was injected to sweep the permeate. First, silicalite crystal seeds were synthetized under hydrothermal synthesis conditions in a Teflon-lined autoclave. Then, the porous support was seeded with silicalite crystals (ca.

250 nm). The gel used to prepare the crystalline seeds contained Aerosil 300 as the Si source, tetra-propylammonium hydroxide (TPAOH) as the template and NaOH as the mineralizing agent plus deionized water. The molar proportion was $25SiO_2:125NaOH:6TPAOH:333H_2O$ [14]. This gel was heated at a fixed temperature of 125 °C for 8 h in the Teflon-lined autoclave. The suspension obtained was centrifuged and washed with deionized water several times, until a pH of 7 was reached. The seed suspension was then diluted by adding the water needed to yield a seed concentration of 20 g/l.

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, tetrapopylammonium bromide (TPABr) as a template, sodium hydroxide, deionized water and sodium aluminate as the Al source with the composition: $21SiO_2:1TPABr:3NaOH:0.105Al_2O_3:987H_2O$ [15]. The as-synthesized membrane was washed with deionized water, dried at 80 °C for 24 h and tested for N_2 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

X-ray diffraction patterns of the membrane and of the residual powder collected at the bottom of the autoclave after synthesis were obtained with an XD-D1 Shimadzu instrument using Cu Kα radiation at 30 kV and 40 mA. The scan rate was $1° \, min^{-1}$ in the range $2\theta = 5–40°$. The XRD patterns of the membrane were obtained from smaller samples, which were synthesized in the same vessel as the full size specimen. These samples were cut in smaller pieces and placed in the sample holder of the instrument. The evidence for the removal of the template was furnished by FT-IR spectroscopy. FT-IR spectra of as-synthesized and calcined ZSM-5 powders collected after synthesis were obtained using a Shimadzu 8101M spectrometer. Samples were prepared in the form of pressed wafers (ca. 1% sample in KBr). All spectra involved the accumulation of 40 scans at $4 \, cm^{-1}$ resolution.

The surface and cross-section of the ZSM-5 membrane were examined by scanning electron microscopy using a JEOL JSM-35C instrument. The Si, Al and Fe composition was measured using an energy dispersive analytical system (EPMA) attached to the SEM instrument.

2.3. Permeation measurements

2.3.1. N_2 permeation
The N_2 permeation data was used as a criteria to evaluate the extent of extra-zeolitic pores present in the membrane. It was measured at 25 °C and transmembrane pressure of 80 kPa. The pressure difference across the membrane was controlled using a pressure regulator (Bronkhorst P-502C).

2.3.2. Mixture and single-component xylenes separation
The vapor permeation experiments were conducted using a shell-and-tube membrane module. For these experiments, the membrane was connected to the permeation module using Teflon

ferrules kept at temperatures lower than 200 °C. 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 a N₂ carrier stream which previously passed 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 total pressure in either side of the membrane was 1.01325×10^5 Pa (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.

The feed, permeate and retentate streams were analyzed with a Shimadzu GC-9A gas chromatograph equipped with a flame-ionization detector and a packed column containing Bentona 34% and SP-1200 5% (Supelco). Single-gas and mixture tests were performed in the temperature range of 150–400 °C. 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.

2.3.3. Membrane stability

In order to examine the thermal stability of the membrane a sequence of three thermal cycles were realized. First, the single-component and mixture fluxes of the xylene isomers were measured in the 150–370 °C temperature range. Then, the membrane was cooled to ambient temperature. In a second cycle, the system was first heated to 370 °C and the xylene mixture fluxes were measured. After reaching 400 °C both the single-component and the mixture fluxes were obtained. The same sequence of cooling and heating at 400 °C was repeated once more (ca. 1000 h on stream all together).

3. Results

3.1. ZSM-5 powder

The residual zeolite powder obtained from the hydrothermal syntheses presented a well defined MFI-structure as revealed by the presence of all its characteristic reflections, which were not modified by calcination in air at 470 °C (Fig. 1). The XRD pattern of the as-synthesized powder shows that the intensities of the first two reflections at 2θ 7.9° and 8.8° are lower due to the presence of the template in the intracrystalline voids (Fig. 1a). When the sample was calcined, the relative intensity changed, the first two lines became more intense whereas the lines at ca. 11.9° and 12.5° 2θ slightly decreased in intensity (Fig. 1b). These intensity changes may be explained as the expected consequence of the removal of extra framework organic and inorganic species incorporated into the structure voids during synthesis [16,17].

The evidence for the removal of the template was obtained by FT-IR spectroscopy. Fig. 2 compares the FT-IR spectra of the
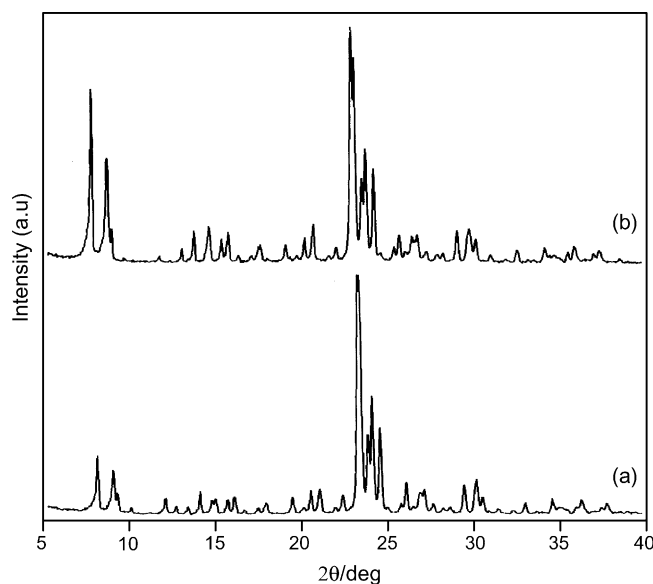

Fig. 1. X-ray diffraction patterns of the ZSM-5 powder (a) as-synthesized and (b) calcined at 470 °C.

powder before and after calcination and the spectrum of the template (TPABr). The presence of the template molecules in the as-synthesized samples is easily identified. The IR spectra of the template containing powders include two well defined groups of IR bands at about 3000 and 1500 cm⁻¹ (Fig. 2(B)), characteristic of the TPABr [18]. Note the template peaks with a maxima at about 2883, 2943 and 2981 cm⁻¹. These peaks can be assigned to methylene (–CH₂–) and methyl (–CH₃) C–H vibrations [17]. The lower frequency bands correspond to the methyl bending mode (1460–1470 cm⁻¹). These bands disappear in the IR spectrum of the calcined ZSM-5 powder. Thus, the calcination was effective in removing TPABr.

In the low frequency range (Fig. 2), the spectra present the characteristic absorption peaks of ZSM-5 at 550, 850, 1100 and 1225 cm⁻¹. Particularly, the band at about 550 cm⁻¹ has been assigned to the five-membered ring of the pentasil zeolite structure [19].

3.2. ZSM-5 membrane

X-ray diffraction patterns of the ZSM-5 membrane before and after calcination were obtained (Fig. 3a and b). Note that the pattern is not affected by the xylene measurement (Fig. 3c). The XRD patterns clearly depict the presence of a highly crystalline MFI-type structure. Besides, the XRD data show that the crystals are randomly oriented since the relative intensity ratio of the peaks is the same as the one calculated from the powder diffractogram (Fig. 1b). No characteristic reflections of the stainless steel were observed, indicating a good coverage of the support by the zeolite layer. The lower signal to noise ratio of the diffractograms shown in Fig. 3 compared to those shown in Fig. 1 is due to the curvature of the membrane that distorts the diffraction patterns.

Fig. 4 shows SEM micrographs of (a) the surface of the support; (b) the support seeded; (c and d) two different
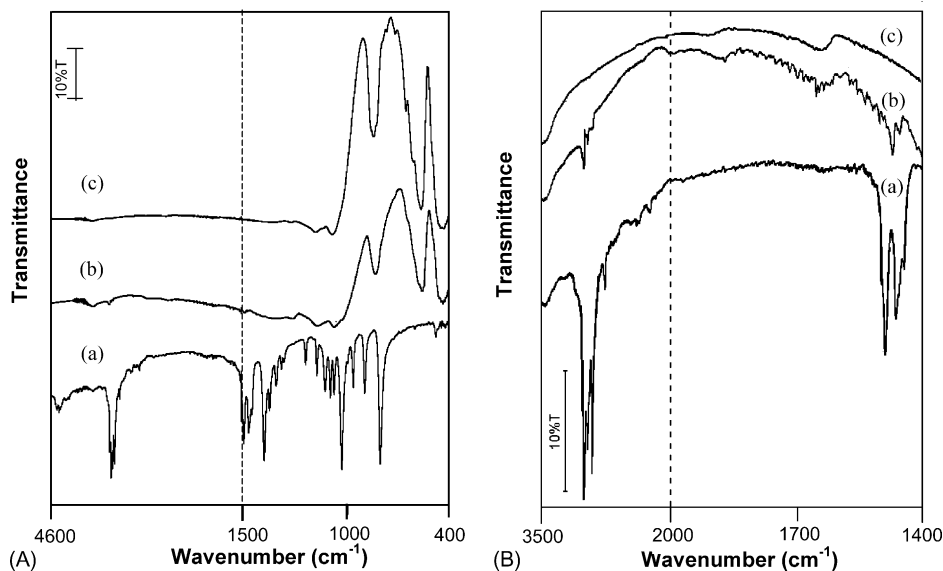
Fig. 2. FT-IR spectra of the (a) template (TPABr), (b) as-synthesized ZSM-5 powder and (c) calcined ZSM-5 powder. (A) Full spectra and (B) intermediate wavenumber region.

magnifications of the ZSM-5 membrane. The images reveal the formation of continuous films displaying densely packed crystals with a surface free of cracks and pinholes. A largely intergrown polycrystalline film with a randomly oriented structure was observed consistent with the XRD patterns.

Fig. 5a shows a cross-sectional view of the top layer of the membrane. A zeolite film with a thickness of ca. 20 μm can

be seen on top of the support. No precise determination can be made due to the roughness of the support. The zeolite film probably extends into the pores of the support. The image shows a relatively homogeneous and continuous film, even though significant thickness variations are possible due to the roughness of the support. The Si/Al ratio is also shown (Fig. 5b). The Si/Al ratio drops in the vicinity of the support surface. Note that near the support surface, the iron concentration picks up.
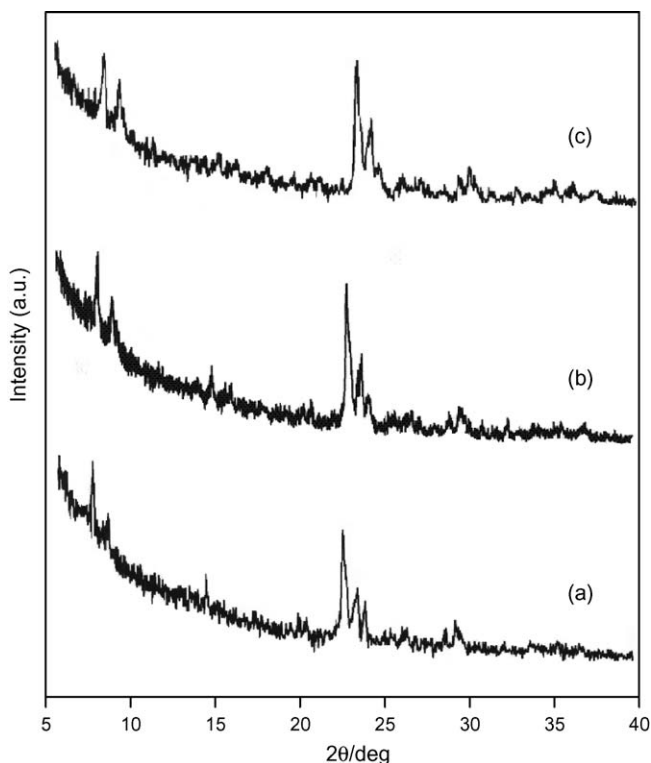
3.3. Permeation measurement

3.3.1. N_2 permeation

Before removal of the template, the membrane was impermeable to N_2 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. These values are in the range of those usually reported for good quality membranes [20,21].

3.3.2. Xylene permeation

Fig. 6 shows the single-component permeance fluxes of the xylene isomers through the ZSM-5 membrane between 150 and 400 °C. The *p*-xylene flux presents a maximum at about 300 °C, while the *m*-xylene and *o*-xylene fluxes continuously increase with temperature. The permeances of *o*-xylene and *m*-xylene are very similar while the *p*-xylene permeance varies between 8.5 and 4 times higher than the other two isomers as temperatures gives from 150 to 400 °C. Note that the membrane is selective to *p*-xylene over the entire temperature range with a maximum ideal p/o separation factor of 12 at 150 °C.

Fig. 7 shows the xylene fluxes obtained from the ternary mixture measurements. Note that the permeances of the three isomers increase with temperature but the increase of *m*-xylene and *o*-xylene is more pronounced. The p/o and p/m separation factors for this membrane are 8 and 6.9, respectively, at 150 °C.

Fig. 3. X-ray diffraction patterns of the membrane (a) before calcination, (b) after calcinations and (c) after xylene permeation.
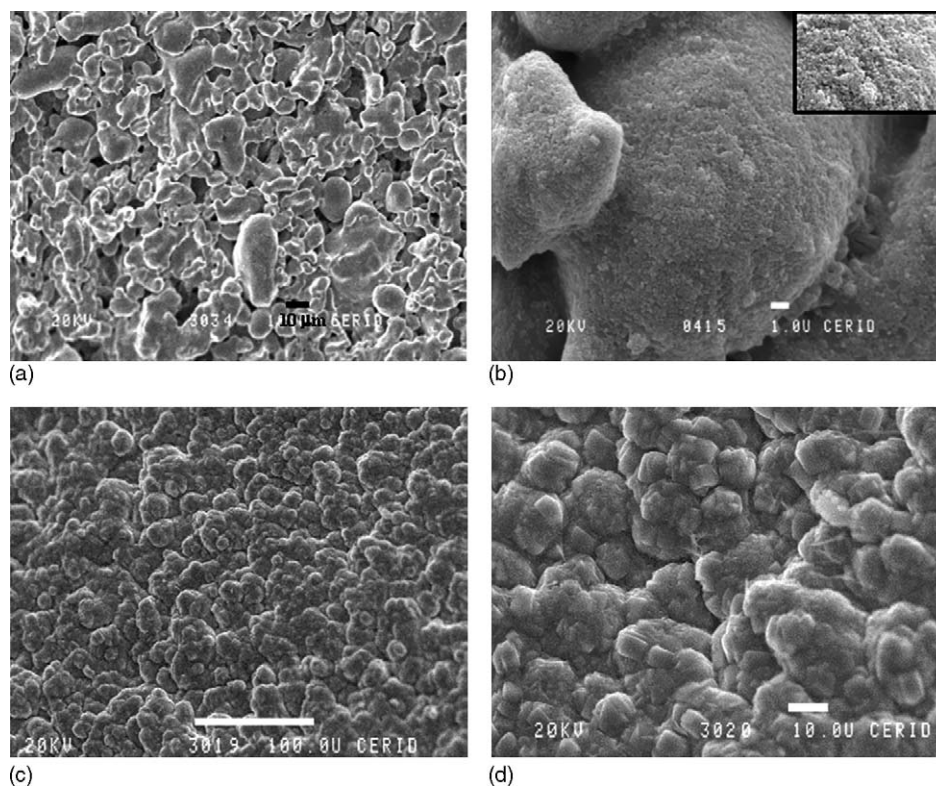
Fig. 4. SEM top views of the (a) surface of support, (b) the support seeded and (c and d) different views of the membrane surface.
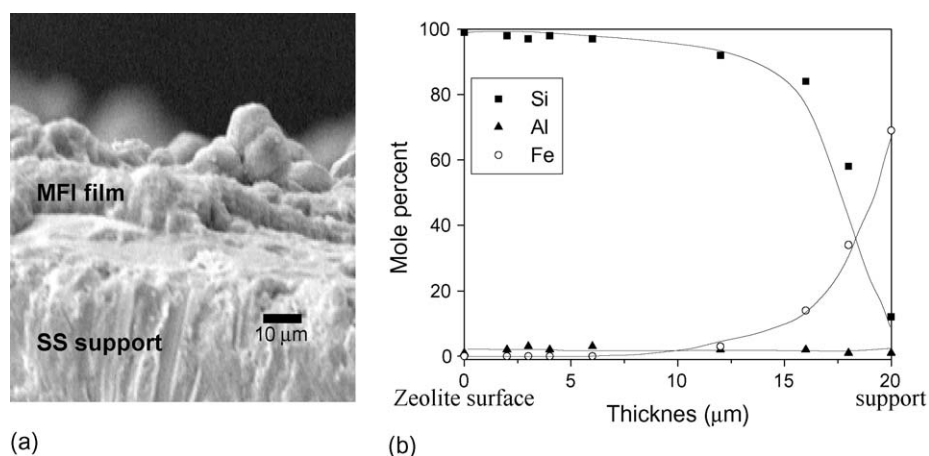

Fig. 5. SEM-EPMA data (a) cross section of the membrane and (b) Si, Al, Fe elemental composition percentage.

As the temperature increases, the selectivity decreases but the membrane is still 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.

3.4. Membrane stability

Fig. 8 shows the xylene mixture permeance fluxes and separation factors at 370 °C for the first thermal cycle and 400 °C for the second and third cycles. Their values remained practically constant during the sequence of thermal cycles. To further confirm the durability of the membrane, the N_2 permeation was checked after each heating and cooling cycle. Table 1 shows the N_2 per-

Table 1
N_2 permeation through the ZSM-5 membrane

Cycle	N_2 permeance $\times 10^8$ (mol s^{-1} m^{-2} Pa^{-1})	Time (h)
Before[a]	7.81	0
1[b]	7.49	670
2[b]	7.75	840
3[b]	7.63	1000

Transmembrane pressure of 80 kPa and 25 °C.
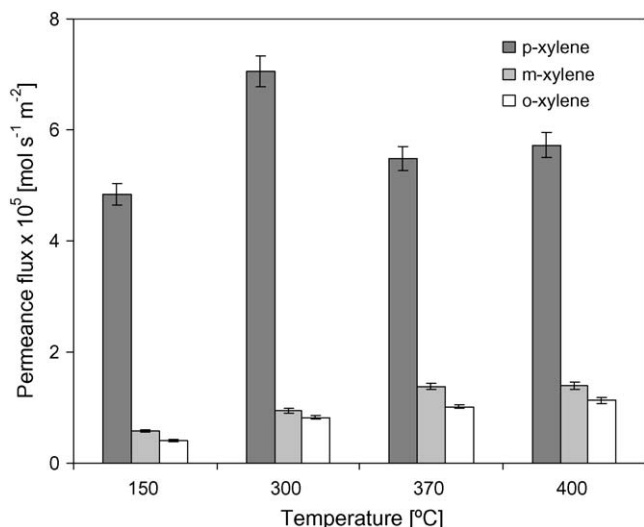[a] Before the xylene permeation.
[b] Measured after each cycle.

Fig. 6. Single-component permeance flux of the xylene isomers through the ZSM-5 membrane. Feed partial pressures: 2.026 kPa *p*-xylene, 1.92 kPa *m*-xylene, 1.52 kPa *o*-xylene.
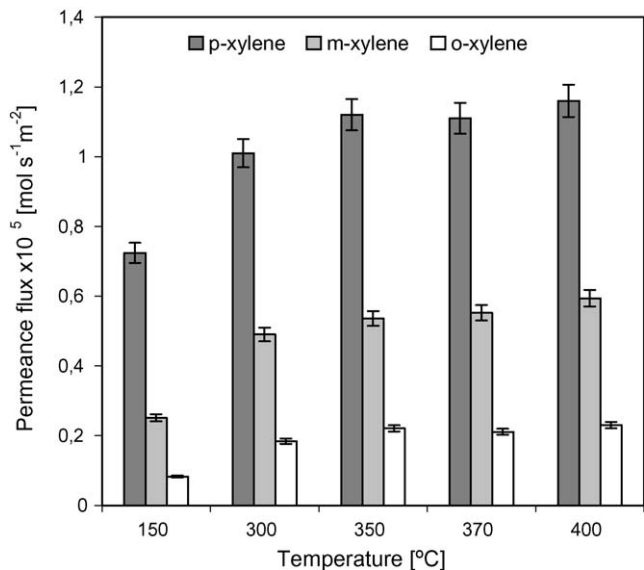

Fig. 7. Permeation fluxes of the xylene isomers from ternary mixtures through the ZSM-5 membrane. Feed partial pressure: 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene.

Fig. 8. Permeation fluxes of the xylene isomers from ternary mixture and separation factors measured at 400 °C along the sequence of thermal cycles.

meation values obtained. These data confirm that the membrane was thermally stable after 1000 h on stream in agreement with the xylene permeance flux data and the SEM micrographs taken after the xylene measurements (Fig. 9).

4. Discussion

As described in Section 1, the two published contributions concerning the stability of MFI-membranes for xylene separation were made over alumina supported composites either flat [10] or cylindric [13]. The use of stainless steel tubes to support the ZSM-5 film poses the most severe challenge to thermal stability due to both the shape and the difference in expansion coefficients of the two parts of the composite membrane.
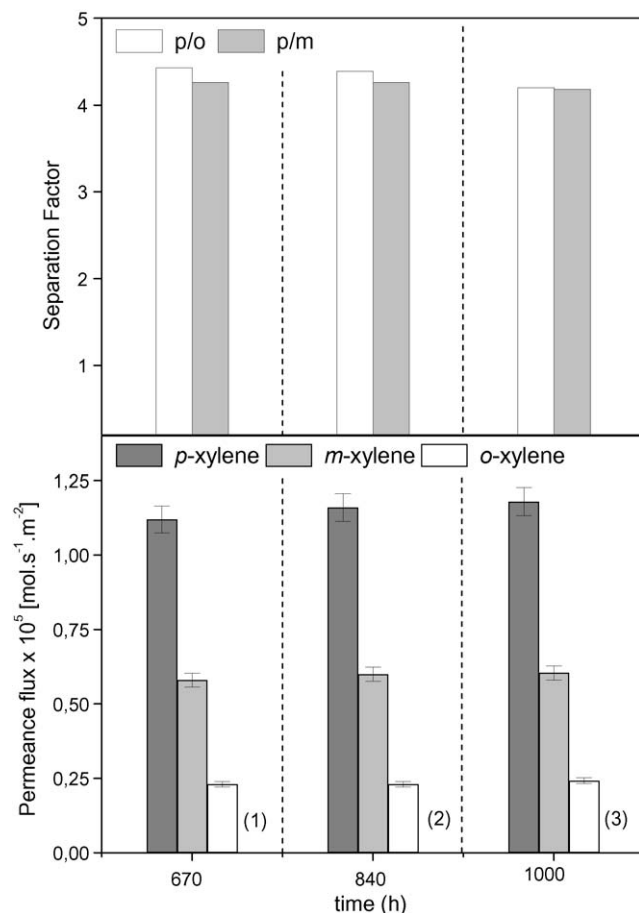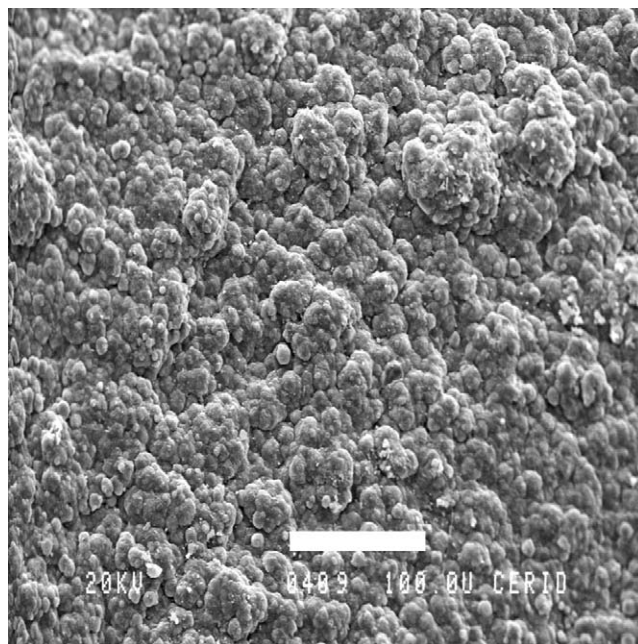

Fig. 9. SEM top view of the membrane surface after the xylene permeation measurements.

Table 2
Comparison with data reported in the literature for tubular membranes

Support	Feed (kPa)			Max. T (°C)	Permeance$_{p\text{-xylene}} \times 10^7$ (mol s^{-1} m^{-2} Pa^{-1})	Separation factor p/o	Reference
	p-xylene	o-xylene	m-xylene				
SS	0.23	0.26	0.83	400	0.51	4.4	This work
α-Al$_2$O$_3$	1.50	1.35	4.50	400	0.01	7.0	[11]
SS	2.10	2.10		237	0.05	2.8	[4]

The ZSM-5 membrane synthesized did not present any abrupt increase in the permeance fluxes of the xylenes that would be symptomatic of crack formation after 1000 h on stream. This was further confirmed by the constancy of the N$_2$ permeation flux before and after the thermal cycles (Table 1). This result and the SEM micrographs taken after the xylene permeation experiments (Fig. 9) confirmed that the membrane was thermally stable.

Table 2 shows the data reported in the literature for tubular membranes. Note that only one entry can be strictly compared to ours [11] for in the third entry the maximum temperature is much lower than 400 °C [4]. Besides, at present we are studying other factors that may influence the performance of ZSM-5 composite membranes and we have so far synthesized ten of them; they are all thermally stable up to 400 °C.

Although the expansion coefficients of ZSM-5 (-10^{-6} °C^{-1}) and stainless steel ($10–19 \times 10^{-6}$ °C^{-1}) are quite different, the membrane stability is not affected by exposure to the xylenes at 400 °C. A possible explanation of this thermal stability might be found in the rugosity and porosity of the support that allows a degree of flexibility at the interface. Moreover, a reactive interaction between the zeolite and the steel surface could develop which would strengthen the interfacial anchoring suggested to occur in related systems [22,23]. The EPMA iron profile of the membrane (Fig. 5b) is consistent with both interpretations of the thermal stability.

It is well established in the literature that p-xylene adsorbs selectively on MFI from mixtures of the three isomers [24]. This selectivity is attributed to the much higher diffusivity of p-xylene compared to that of the bulkier m- and o-isomers. This difference in diffusivities is somewhat attenuated due to the well-documented framework expansion upon p-xylene adsorption [25,26].

The results of this study show that the transport of the xylene isomers through the ZSM-5 membrane is not only controlled by their different sizes but also by the differences in adsorption interaction. First of all, note that the fluxes of m-xylene and o-xylene (single-component and mixture) and the flux of p-xylene, in mixture, monotonically increase with temperature. In the case of single-component permeance (Fig. 6), the p-xylene flux presents a maximum at ca. 300 °C. 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, the coverage decreases and this effect predominates so that a slight decrease

of the flux is observed between 300 and 400 °C. Other groups [4,8] have also reported that the p-xylene flux presents a maximum at relatively low temperatures. They also assigned the maximum to the competition between adsorption and diffusion. Their membranes were synthesized on top of alumina support, in one case disk [4] and in the other tubular [8].

From the data presented here, it is then concluded that the main pathway for the transport of the xylenes across the ZSM-5 membrane between 150 and 400 °C are the crystalline pores with very little contribution from intercrystalline pores and/or pinholes.

5. Conclusions

The ZSM-5 membrane synthesized in this work is selective to p-xylene between 150 and 400 °C. At 400 °C, the p/o and p/m separation factors are 4.4 and 4.3, respectively, and the p-xylene permeance is 5.1×10^{-8} mol s^{-1} m^{-2} Pa^{-1}. The membrane remains thermally stable after a sequence of three thermal cycles that last ca. 1000 h. This is the feature that distinguishes this membrane among those reported in the literature.

Acknowledgements

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