Catal Lett (2008) 123:7–15
DOI 10.1007/s10562-008-9442-4

Xylene Isomerization in a ZSM-5/SS Membrane Reactor

Ana M. Tarditi · G. I. Horowitz · E. A. Lombardo

Received: 18 October 2007 / Accepted: 12 February 2008 / Published online: 5 March 2008

Abstract A membrane reactor containing different types of ZSM-5/porous SS membranes was used to perform the xylene isomerization reaction. The parent Na-ZSM-5 layer was synthesized by secondary growth on top of porous stainless steel tubes. The xylene isomerization reaction was carried out at different temperatures in the membrane reactor and in a fixed-bed reactor of identical geometry for comparison. Two different kinds of membranes were prepared by ion exchange: a Pt/H-ZSM-5 catalytic membrane and two Ba-ZSM-5 composites with different Ba^{2+} concentration. The *p*-xylene production using 100% exchanged Ba-membrane was about 28% higher than the fixed-bed reactor at 370 °C, when *m*-xylene was fed.

Keywords Xylene isomerization · Membrane reactor · Zeolite membrane

1 Introduction

Zeolite membrane reactors hold great promise for use in industrial practice due to their thermal and chemical stability. They are particularly useful to improve conversion, selectivity and yield in equilibrium-limited reactions by selective product removal [1, 2]. Furthermore, adequately tailored zeolites may develop catalytic activity for the above said reactions, thus providing an additional driving force when membrane reactors are used in certain applications. The combination of separation and reaction processes in a single unit is expected to provide a greater flexibility of operation as well as further enhancement in the system performance. In the last years, several kinds of membrane reactors have been developed using different types of membranes [2–5].

The xylene isomerization reaction is a thermodynamic equilibrium restricted reaction. The catalytic isomerization is industrially conducted in the presence of H_2 at temperatures between 350 and 400 °C and about 10 atm. The p/o/m feed ratios vary according to the operation conditions of the refinery. As is known from the literature, the use of MFI-zeolite membranes appears as a potentially more energy-efficient xylene separation method compared to the conventional separation technologies [6–9]. Thus, several groups have studied the separation of xylene isomers using MFI-zeolite membranes under different conditions. However, the reported data show a high dispersion and in most cases these data have been obtained at temperatures below 350 °C and low pressures. The most promising results were published by Lai et al. [8] using a b-oriented silicalite membrane on the surface of an α-alumina support disk. They reported a p/o separation factor as high as 483 at 220 °C and a *p*-xylene permeance of 2×10^{-7} mol s^{-1} m^{-2} Pa^{-1}. However, these authors acknowledged that data at higher temperatures were needed to use this membrane in a xylene reactor.

Dalmon and coworkers [10] reported an interesting study about xylene isomerization in an extractor-type membrane reactor using an inert silicalite film synthesized on top of a ceramic tubular support. Starting with pure *m*-xylene, they reported an increase of 10% in the *p*-xylene yield compared to their conventional fixed-bed reactor. On the other hand, Haag et al. [11] used a catalytic H-ZSM-5 layer synthesized

---

A. M. Tarditi · E. A. Lombardo (✉)
Instituto de Investigaciones en Catálisis y Petroquímica
(FIQ, UNL-CONICET), Santiago del Estero 2829,
3000 Santa Fe, Argentina
e-mail: nfisico@fiqus.unl.edu.ar

G. I. Horowitz
Repsol-YPF, Baradero S/N, 1925 Ensenada, Buenos Aires,
Argentina

on top of porous stainless steel disks to perform the isomerization reaction starting with either pure *m*-xylene or *o*-xylene. At 400 °C, they reported that the conversion of *m*-xylene and *o*-xylene was higher than the fixed-bed reactor by 15% and 4.4%, respectively. Moreover, the *p*-xylene selectivity increased by about 10% when *m*-xylene was fed to the reactor. A higher improvement in the *p*-xylene production and selectivity could not be obtained due to the low separation factor of the membrane they used.

Within our group, Deshayes et al. [12] modeled and simulated the isomerization reaction in an industrial fixed-bed reactor and studied the effect of the incorporation of multitubes containing Na-ZSM-5/SS membranes upon the catalytic performance. They reported an increase of 12% in the *p*-xylene production with the use of the membranes. Besides, we have recently studied the effect of Na, Ba, Sr and Cs upon xylene permeation across ZSM-5 membranes [13] and found that Ba-ZSM-5/SS was the most selective composite of this series. None of them, however, catalyze the isomerization reaction up to 400 °C.

The aim of the present work was to study the xylene isomerization reaction using ZSM-5/SS membranes in a catalytic reactor in order to improve the *p*-xylene production. A tubular porous SS support was used to improve the mechanical resistance and facilitate the sealing of the membrane to the reactor piping. Ba-ZSM-5 composite with different Ba^{2+} concentration and a catalytic Pt/H-ZSM-5 membrane were used. The catalytic data obtained in a membrane reactor (MR) and a catalytic membrane reactor (CMR), both operated in an extractor mode, were compared to those obtained in a fixed-bed reactor (FBR) of identical annular geometry.

2 Experimental

2.1 Membrane Preparation and Characterization

The membranes used in this work were obtained by secondary growth on the outer surface of porous stainless steel (PSS) tubular supports (Mott Metallurgical), 10 mm o.d. and 7 mm i.d. The average pore size was 0.2 μm. The support was cut into 30-mm-long pieces; then one end of the porous support was welded to a non-porous SS tube and the other end was sealed with a non-porous stopper. Through the open end, N_2 was injected to sweep the permeate. First, Na-ZSM-5 (Si/Al = 14) membranes were synthesized while the Ba and Pt/H-zeolite membranes were obtained by ion-exchange of the parent composite. In the case of the Ba-exchanged membranes, the cation-exchanges were carried out using barium nitrate. The Na membranes were immersed in a solution 0.1 M of $Ba(NO_3)_2$, at 80 °C for 24 h. After the ion-exchange treatment, the tubes were thoroughly washed with distilled water and dried in air at ambient temperature for 2 h, and then at 80 °C for 24 h. In the case of the higher Ba-exchanged membrane, the procedure was repeated three times under the same conditions.

The catalytic membrane (Pt/H-ZSM-5) was obtained by ion-exchange from the Na-ZSM-5 (Si/Al 14) form. First, the membrane was exchanged at 80 °C for 24 h with 1 M NH_4NO_3 solution during 24 h [14]. The NH_4^+-form of the membrane was exposed to air flowing at 450 °C for 1 h. After that, the Pt was introduced into the zeolite by ion exchange conducted at 25 °C for 24 h using a dilute aqueous solution (5×10^{-4} M) of $Pt(NH_3)_4NO_3$. The resulting Pt concentration in the zeolite was 0.5 wt.%.

The N_2 permeation was the first tool used to verify the formation of a continuous film on top of the support surface and to detect the presence of extra-zeolitic pores in the membrane. It was measured at 25 °C and a trans-membrane pressure of 80 kPa. The pressure difference across the membrane was controlled using a pressure regulator (Bronkhorst P-502C). All the permeation data are reported with a ±95% confidence interval.

Permporosimetry data were obtained in order to determine the contribution of the zeolitic and non-zeolitic pores (intercrystalline space and defects) to the total permeation flow through the membrane. In this case, nitrogen was used as the non-adsorbed permanent gas while *p*-xylene was the condensable vapor. The experiments were performed at 25 °C. The pressure difference across the membrane was kept at 60 kPa, and the permeate side was kept at atmospheric pressure.

2.2 Xylene Permeation Measurements

The vapor permeation experiments were conducted using a shell-and-tube membrane module. The zeolite side of the tube was flushed with a N_2 carrier stream which previously passed through the xylene saturator maintained at 35 °C, while the inside of the tube was flushed with N_2 as a sweep gas. 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).

Ternary mixture tests were performed in the 100–400 °C temperature range. The nitrogen feed flow rate and the sweep flow rate were set at 10 mL min^{-1} and 9 mL min^{-1}, respectively, using mass flow controllers (MKS Instruments). The sweep gas flux of 9 mL min^{-1} is in the range where the permeation reaches a plateau with increasing N_2 flow rate. This was verified by experiments in which the sweep gas was varied between 5 and

40 mL min^{-1}. The total pressure at either side of the membrane was 1.013×10^5 Pa (1 atm). The composition of the ternary mixture feed was 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, and 0.26 kPa *o*-xylene.

In order to make sure that the xylene isomerization did not occur, the Pt/H-ZSM-5 membrane was not activated before the xylene permeation measurement. The catalytic inactivity of the membrane was confirmed by the results obtained during the permeation measurements made with the *p*-xylene pure isomer up to 400 °C. In these experiments, neither other isomers (including ethyl benzene) nor aromatics such as toluene or benzene were detected in the retentate or in the permeate side.

2.3 Xylene Isomerization Reactions

2.3.1 *Membrane Reactor (MR)*

The isomerization reactions in the membrane reactor were carried out in the same module as the permeation measurement. In the case of an inert membrane (Ba-ZSM-5), the same catalyst used in the FBR was packed in the outer surface of the composite and the *m*-xylene and ternary mixture isomerization reactions were carried out at different temperatures (340, 370 and 390 °C). This range was controlled by the characteristics of the commercial catalyst used in these studies. The total pressure difference across the membrane was kept constant to zero, nitrogen being used as a sweep gas in the permeate side (20 mL min^{-1}) in order to secure the removal of the isomers. The reaction experiments were performed using two types of feed: *m*-xylene, and a ternary mixture with a composition ratio similar to that of the industrial reactor (65% *m*-xylene/14.5% *p*-xylene/20.5% *o*-xylene) corresponding to 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, and 0.26 kPa *o*-xylene. In all cases hydrogen was the carrier gas in the reaction side.

A Pt/silica-alumina commercial xylene isomerization catalyst was used. It had a particle diameter of 1.58×10^{-3} m and a surface area of 116 m^2 g^{-1}. It was grounded between 0.147 and 0.183 mm. The catalyst was diluted with quartz of the same size in a proportion of 1.25 to 98.75. The same mass of 3.9 g of the obtained mechanical mixture was used in every experiment. Before the catalytic runs, the solid was activated in situ under flowing H_2 at 350 °C for 3 h. The weight hourly space velocity (WHSV) was chosen high enough to maintain the conversion below equilibrium, in order to avoid undesired by-product (toluene or ethylbenzene) formation.

The *p*-xylene yield (*R*) is the amount of formed *p*-xylene (permeate + retentate) divided by the total xylene feed. The selectivity (*S*) value is the percentage of *p*-xylene present (permeate + retentate) divided by the amount of reaction products (*p*-xylene + *o*-xylene).

2.3.2 *Catalytic Membrane Reactor (CMR)*

In this case, the mass of solid considered (0.108 ± 0.00054 g) was estimated from the amount of zeolite deposited in the tubular support. The WHSV (210 h^{-1}) was maintained high enough to stay away from the equilibrium so as to avoid the formation of undesired products. The reaction experiments were carried out feeding *m*-xylene diluted in a H_2 stream to the reactor, and in the permeate side nitrogen was used as the sweep gas (20 mL min^{-1}).

2.3.3 *Fixed-Bed Reactor (FBR)*

The zeolite membrane was replaced by a non-porous stainless steel tube of identical dimensions, and the reaction conditions were kept as close as possible to the CMR operation. (i) For the experiments where the Pt/silica-alumina catalyst diluted in quartz was used, the same mass as in the membrane reactor (3.9 g) was loaded to the reactor. (ii) For the CMR, the data were compared to those obtained in the FBR using the Pt/H-ZSM-5 catalyst. This solid was obtained from Na-ZSM-5 power exchanged with the corresponding salts under the same conditions used for the membrane. The amount of catalyst used was equal to the estimated amount of zeolite deposited on and into the stainless steel support.

The estimated error of the permeation flux, selectivity and *p*-xylene yield is ±4%. This number was calculated from the standard deviations of both the chromatographic analysis and the flow measurements using the error propagation law.

3 Results and Discussion

3.1 Membrane Synthesis and Characterization

In all cases, the XRD patterns show that all the Na-ZSM-5 (Si/Al = 14) membranes synthesized and calcined were composed of pure MFI zeolite, as revealed by the presence of its characteristic reflections (not shown). It is important to note that the patterns were modified by neither the ion-exchange process nor the xylene permeation measurements [13]. Largely intergrown polycrystalline films with a randomly oriented structure were observed in the SEM micrographs.

From the N_2 permeation experiments, it was possible to verify the formation of a continuous zeolite layer on top of the stainless steel support. The membranes were non-permeable to N_2 before calcination for a trans-membrane pressure of 80 kPa at room temperature due to the presence of the template in the pores of the zeolite. The flow rate of N_2 was below the detection limits of our system (1×10^{-10} mol s^{-1} Pa^{-1}). The nitrogen permeance increased substantially to the range of 10^{-8} mol s^{-1} m^{-2} Pa^{-1} after removal of the template. The N_2 permeances of the calcined membranes are shown in Table 1. These values are in the range of those usually reported for good quality membranes synthesized on top of stainless steel supports [15, 16]. These data should be considered as a first test for the assessment of the quality of the membrane, in terms of cracks and defects.

From the permporosimetry data, it was possible to calculate that the contribution of non-zeolite pores to the total flux through the three membranes was between 4 and 4.5%. This is an indication of both the membrane quality and the reproducibility of the synthesis procedure [13]. A complete description of the porosimetry results obtained with these membranes have been published elsewhere [13, 17].

3.2 Xylene Permeation Measurements and Membrane Stability

Table 1 shows the xylene permeation and p/o separation factors at 370 °C obtained feeding the ternary mixture. The three membranes were selective to *p*-xylene between 100 and 400 °C, Fig. 2. The Pt/H-ZSM-5 membrane showed a slightly higher permeance than the Ba-exchanged membranes but the selectivity of the former was much lower (Table 1). The p/o and p/m selectivity for the three membranes decreased with increasing temperature due to the difference in the temperature dependence of the isomer fluxes. The Ba-ZSM-5 totally exchanged membrane (M-21) presented the highest p/o separation factor, 19 at 370 °C (Table 1, column 4).

Note that when the Ba^{2+} concentration increased, the membrane presented a better performance (Figs. 1 and 2). The *o*- and *m*-xylene permeation fluxes increased with temperature in both cases but both fluxes were lower in the fully exchanged membrane (Fig. 2). The *o*-xylene flux decreased from 1.9×10^{-6} mol s^{-1} m^{-2} up to 7.5×10^{-7} mol s^{-1} m^{-2} at 370 °C for the partially and fully exchanged membranes, respectively. On the other hand, the *p*-xylene flux increased with the Ba^{2+} concentration (Fig. 1), and clearly presented a maximum at 250 °C with the fully exchanged membrane. The xylene permeation fluxes were the same after the second and third ion-exchange cycles. This confirms that the exchange capacity of the membrane was saturated with Ba^{2+}. In a previous work [13], we presented the effect of the ion exchange on the xylene transport through ZSM-5 membranes; it was possible to verify that the synthesis method and the exchange procedure were reproducible. In that case, nine Na-ZSM-5 (Si/Al = 14) membranes were evaluated with N_2 and xylene permeation and in all cases both data were reproducible, within the experimental error. The back exchange with $NaNO_3$ of a Ba-ZSM-5 membrane further confirmed that the cation exchange procedure does not affect the membrane quality since the permeation flux of the xylene isomers after the back-exchange was similar to the parent Na-ZSM-5 (Si/Al = 14) membrane.

The three membranes were characterized using DRX and SEM-EPMA before and after the xylene permeation test. These tools were used to study the morphology of the composite and to confirm the thermal stability up to 400 °C. The stability of this type of membranes was discussed in our previous work [18] and it was found that the membranes were stable after 1000 h of operation including several cycles between 25 and 400 °C. Neither the selectivity nor the permeation of the membranes changed after this long time on stream.

3.3 Xylene Isomerization Reactions

3.3.1 *m-Xylene Isomerization*

Figure 3a compares the *p*-xylene yield obtained in the FBR with the values retrieved from the membrane reactor (MR) fitted with the Ba-exchanged membranes. Both reactors were fed pure *m*-xylene diluted in H_2. The incorporation of a membrane to the reactor leads to an increase in the *p*-xylene production. This is due to the

Table 1 Permeation characteristics of the membranes used in this work

Membrane[a]	N_2 permeance $\times 10^8$ (mol s^{-1} m^{-2} Pa^{-1})[b]	*p*-xylene permeance $\times 10^8$ (mol s^{-1} m^{-2} Pa^{-1})	Separation factor p/o[c]
M-11 (40% Ba^{2+})	6.2 ± 0.24	5.5 ± 0.22	8.1
M-21 (100% Ba^{2+})	6.0 ± 0.24	6.5 ± 0.26	19.0
M-20 (Pt/H-ZSM-5)[d]	6.3 ± 0.24	7.2 ± 0.29	4.9

[a] The three composites were prepared by ion exchange of a Na-ZSM-5/SS membrane

[b] Pressure difference across membranes, 80 kPa at 25 °C

[c] Temperature: 370 °C, feed partial pressure: 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene

[d] Contains 0.5 wt.% of Pt

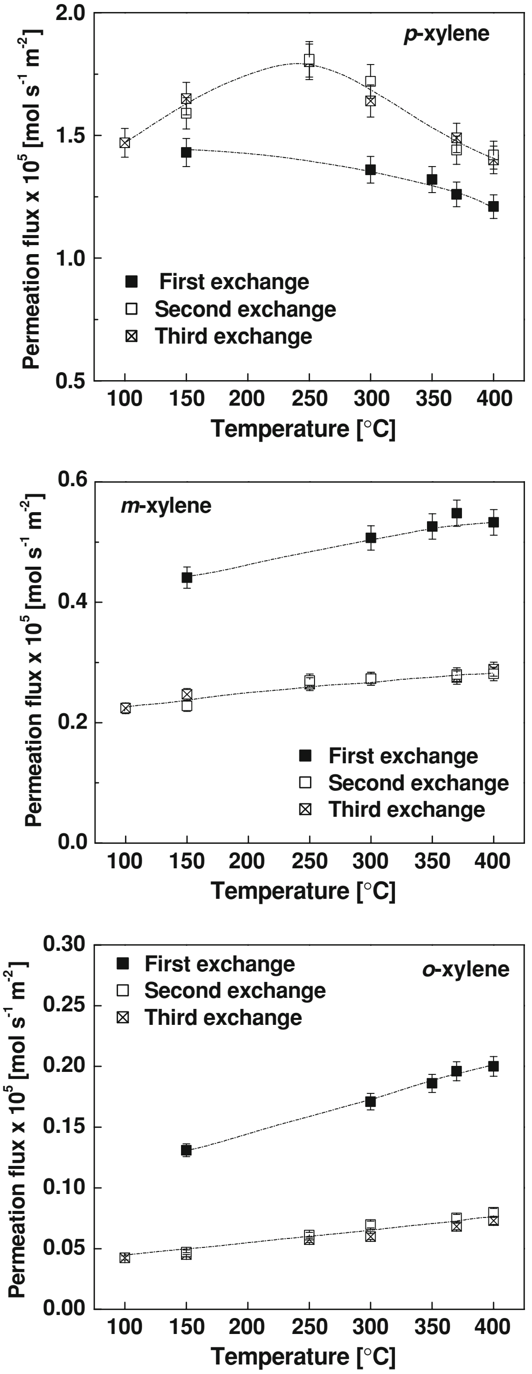


Fig. 1 Fluxes of the xylene isomers from ternary mixtures through the Ba-exchanged membranes with different Ba^{2+} loads. Feed partial pressure: 0.23 kPa *p*-xylene, 0.83 kPa *m*-xylene, 0.26 kPa *o*-xylene, $\Delta P = 0$, sweep gas flow rate 9 mL min^{-1}

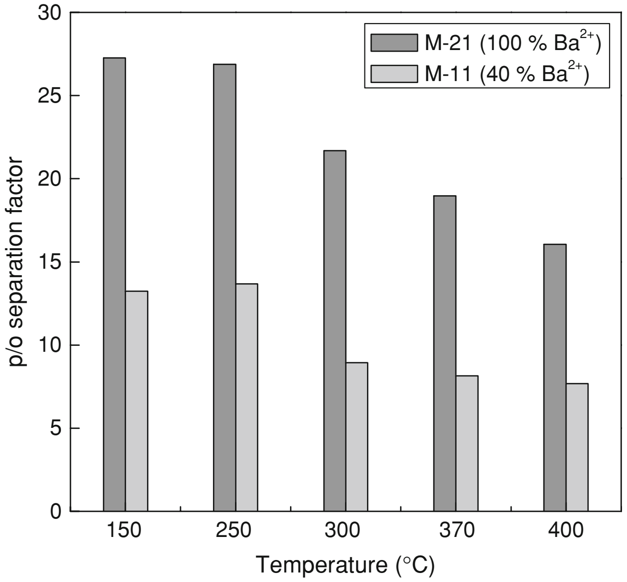


Fig. 2 Comparison of the p/o separation factor for the partially and fully exchanged barium composites

selective extraction of *p*-xylene from the reaction side. Note that with the fully Ba-exchanged membrane (M-21) a higher yield and *p*-xylene production increase were obtained due to the better performance of this composite. As shown in Table 1 and Fig. 2, the 100% exchanged zeolite presented the highest p/o separation factor. Therefore, more *p*-xylene can be extracted from the reaction side, improving its production.

No products (such as toluene or ethylbenzene) other than the xylene isomers were detected during the catalytic runs reported in this work. The detection limit of by products was ca. below 0.5% conversion of the reactants.

At 370 °C, a relative increase of the yield of *p*-xylene by 28% was observed in the membrane reactor with the 100% Ba-exchanged membrane (Fig. 3a). At this point, the *p*-xylene yield increase in the MR presents a maximum. Even though the *p*-xylene yield at 390 °C somewhat rises, the relative increase is lower than at 370 °C. This can be attributed to the permeation limit of the membrane which does not allow the extraction of more *p*-xylene from the reaction side; as a consequence, a higher increase in the yield could not be obtained. This is consistent with the effect of temperature on the permeation flux, as seen during the permeation test (Fig. 1).

In the case of the catalytic membrane (Pt/H-ZSM-5) (CMR) the *p*-xylene yield increased by 22% with respect to the FBR at 370 °C (Fig. 3b). It is important to note that a strict comparison with the other membranes cannot be made, considering the different catalysts used and the membrane configuration, extractor membrane reactor for the Ba-exchanged composites and catalytic membrane reactor for the Pt/H-ZSM-5.

3.3.2 Ternary Mixture Isomerization

In order to obtain first-hand information about the different responses of the MR and the FBR when fed a ternary

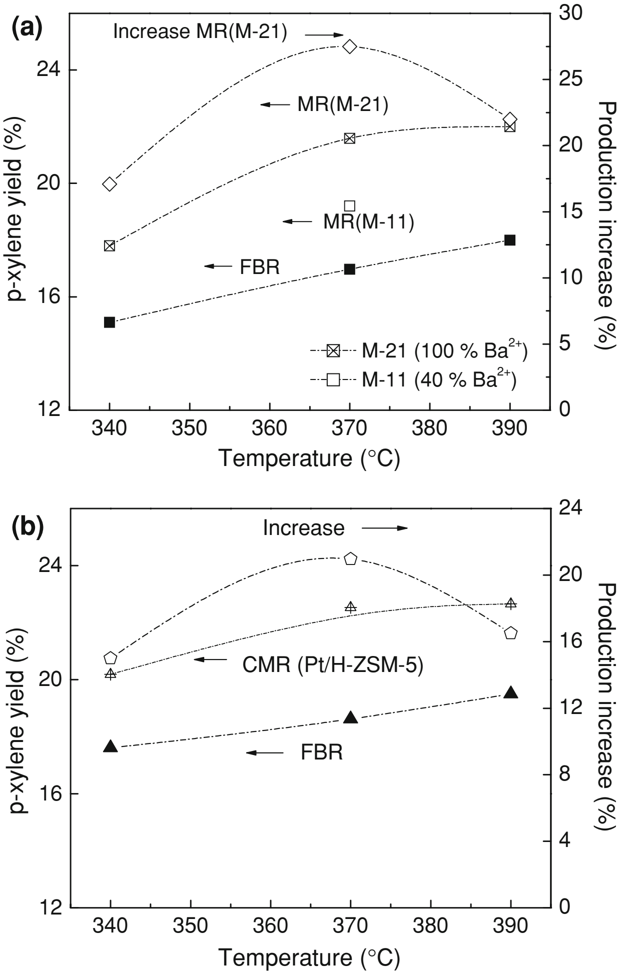


Fig. 3 *m*-Xylene isomerization in a fixed-bed reactor (FBR) and in membrane reactors: (**a**) Using Ba-exchanged composites (MR, WHSV = 410 h^{-1}), and (**b**) Using the catalytic Pt/H-ZSM-5 membrane (CMR, WHSV = 210 h^{-1})

mixture with a relative composition similar to those characteristic of industrial practice (petrochemical plant), the data reported in Table 2 and Fig. 4 was obtained.

Table 2 Xylene mixture isomerized in a fixed-bed reactor and in a membrane reactor[a]

Reactor type	η_p[b] (%)	Sel. (%)	*p*-xylene production (mol s^{-1})	Increase (%)
FBR	21	52	2.86×10^{-8}	–
MR (40% Ba^{2+})	24	59	3.50×10^{-8}	22.0
MR (100 % Ba^{2+})	25	69	3.74×10^{-8}	30.7

[a] 370 °C, WHSV = 550 h^{-1}, feed: *m*-xylene 65%, *p*-xylene 14.5%, *o*-xylene 20.5%

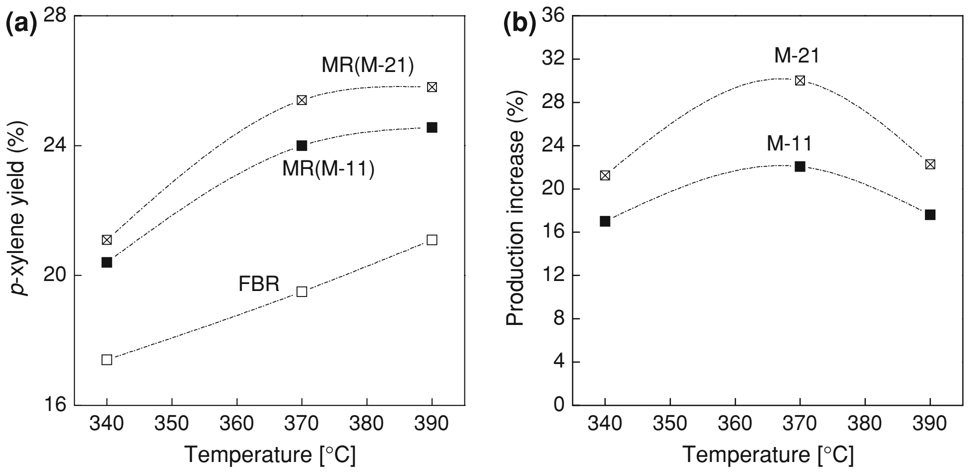
[b] η_p = *p*-xylene yield (retentate + permeate)

This figure shows the *p*-xylene yield and its increase compared to the FBR when the ternary mixture isomerization reaction was carried out at different temperatures using the Ba-exchanged membranes. Here, as was observed in the case of pure *m*-xylene, the relative increase in the *p*-xylene production presented a maximum at 370 °C. The improvement observed, when a fully exchanged membrane was incorporated to the reactor was higher than that obtained with the partially exchanged composite. Under these conditions, a maximum increase of 31% was observed in the case of the M-21 (100% Ba^{2+}) membrane reactor. The production in the MR at 390 °C is slightly lower than at 370 °C, probably due to the decrease in the permeation of the *p*-xylene at higher temperatures.

3.3.3 *Pressure Effects*

The xylene isomerization reaction is carried out industrially at temperatures between 350 and 400 °C, and pressures around 1000 kPa (10 atm). The following partial pressures of the isomers were reported for an industrial reactor: 8.6 kPa, 40.7 kPa and 13.5 kPa for *p*-, *m*- and *o*-xylene, respectively [12]. The balance is made up of ethyl benzene, hydrogen and methane. These pressures

Fig. 4 Xylene isomerization reaction feeding a ternary mixture in a membrane reactor with the two Ba-exchanged membranes: (**a**) *p*-Xylene yield, (**b**) Increment with respect to the fixed-bed reactor. Feed: 65% *m*-xylene, 14.5% *p*-xylene, 20.5% *o*-xylene, WHSV = 550 h^{-1}



are higher than those used in this work. Our reaction system cannot operate at high pressure, thus in order to ascertain the pressure effect upon the membrane performance, we used a transport model recently developed in our group [17]. This model takes into account the flux of the three isomers through both the zeolite pores and the intercrystalline space. It is based on the contribution of different transport mechanisms: Knudsen flux, surface diffusion and activated translation diffusion. Pertinent literature data were used to obtain numerical estimates of permeation fluxes at different pressures. The data calculated in this way are reported in Fig. 5. As expected, the selectivity decreases with pressure but the membrane is still selective to *p*-xylene up to 100 kPa. Therefore, if the xylene isomerization reaction is carried out using a membrane reactor with these membranes, a significant increase in the *p*-xylene production should be obtained. However, experimental measurements should be made in order to further explore the practical application of these membranes at higher pressures.

3.3.4 Our Data Compared to the Literature

In the open literature there are only two articles on the xylene isomerization reaction using membrane reactors. They report data obtained during the isomerization of pure isomers. Table 3 compares the data obtained from *m*-xylene isomerization in this work with those found in the literature. Note that the improvement obtained by Dalmon and coworkers [10] was lower than ours obtained with the Ba-exchanged composites. This could be due to the higher *p*-xylene permeance of our membranes. If a comparison is made between the permeance performance of their composites (p/o separation factor 7 and *p*-xylene permeance 4×10^{-9} mol s^{-1} m^{-2} Pa^{-1} at 400 °C) and the data presented in this work, it is seen that a higher *p*-xylene permeance was obtained with our Ba-ZSM-5 composites (6.48×10^{-8} mol s^{-1} m^{-2} Pa^{-1} for the 100% Ba-exchanged composite). In this point it is important to note that the xylene pressure used in both cases was different.

On the other hand, Haag et al. [11] reported the isomerization reaction of the three pure isomers using a catalytic H-ZSM-5 membrane synthesized on top of stainless steel disks. When the *m*-xylene isomerization was carried out, they observed an increase of 15% in the *p*-xylene production when compared to their FBR at 400 °C. If a comparison is made between our data obtained with the catalytic membrane (Pt/H-ZSM-5) and the data reported by Haag et al. (Table 3) at 400 °C, it is observed that a somewhat higher increase in the production was obtained with our system. The separation performance of the composite synthesized by Haag et al. (p/o ideal selectivity of 4.3 and *p*-xylene permeance of 6.14×10^{-8} mol s^{-1} m^{-1} Pa^{-1} at 300 °C) was similar to our data for the Pt/H-ZSM-5 composite.

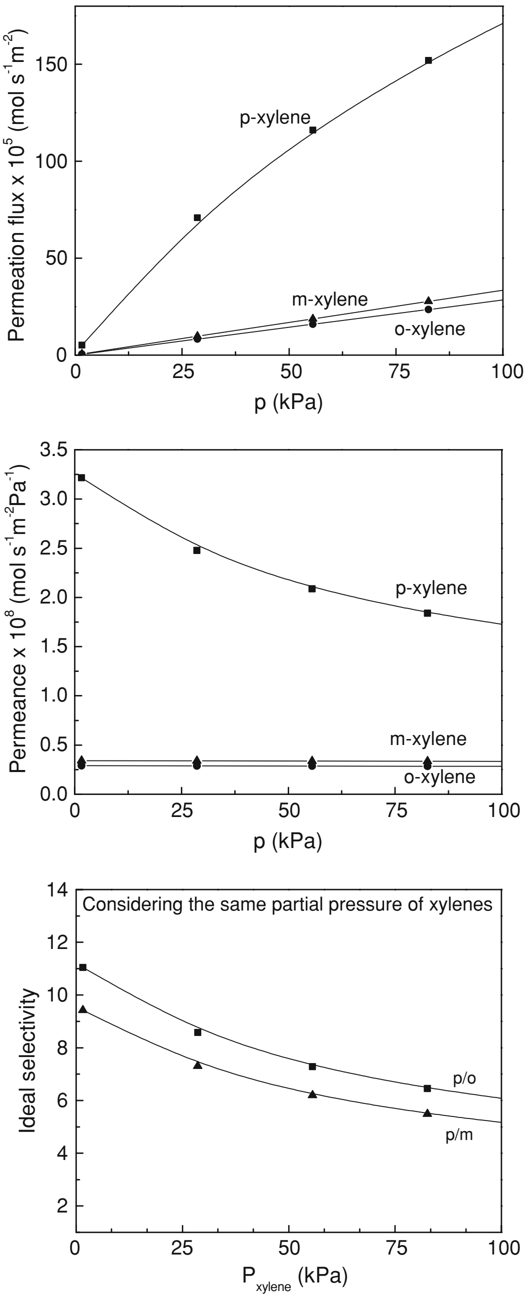


Fig. 5 Effect of pressure upon the xylene permeation through the Ba(100%)-ZSM-5 membrane. Estimated using the model developed in [17]

Our Ba-exchanged membranes present the highest increase in the *p*-xylene production and highest selectivity when they are compared to the other two membranes reported in the literature (Table 3). However, it should be noted that this is not a completely fair comparison due to the different reaction conditions (temperature, WHSV and

Table 3 *m*-Xylene isomerization in membrane reactors (comparison with the literature)

Membrane	Temperature (°C)	WHSV (h^{-1})	Production increase (%)	*p*-Xylene selectivity[a]	Reference
Silicalite	304	215	10	65	[10]
H-ZSM-5	400	21,672	17	66	[11]
Ba-ZSM-5 (40%)	370	410	16	66	This work
Ba-ZSM-5 (100%)	340	410	19	70	This work
Ba-ZSM-5 (100%)	370	410	26	72	This work
Ba-ZSM-5 (100%)	390	410	23	69	This work
Pt/H-ZSM-5	370	210	20	67	This work

[a] *p*-xylene/(*p*-xylene + *o*-xylene)

Table 4 Comparison of transport properties of our Ba(100%)-ZSM-5 membrane with the literature at the same xylene partial pressures

Membrane	Total xylene pressure (kPa)	Temperature (°C)	*p*-Xylene permeation flux × 10^8 (mol s^{-1} m^{-2})	Ideal selectivity[c] p/o	Reference
Ba(100%)-ZSM-5	17	370	3.19(a)	11.0	This work
H-ZSM-5	17	300	6.14	4.3	[11]
Ba(100%)-ZSM-5	6.5	370	3.23(b)	11.5	This work
Silicalite	6.5	400	0.35	7.0	[10]

[a,b] Values calculated using the transport model developed in a recent work [17]. Partial pressures: [a]2.4 kPa *p*-xylene; 3.7 kPa *o*-xylene; 10.9 kPa *m*-xylene (same as in [11]), [b]0.9 kPa *p*-xylene; 1.4 kPa *o*-xylene; 4.2 kPa *m*-xylene (same as in [10])

[c] Ratio of permeation fluxes for both isomers

geometry) and the type of catalysts used in MR and CMR.

In order to achieve a more realistic comparison of our data with those reported in the literature, values of ideal selectivity and permeance of single-components were calculated with our model [17] at the same pressures used by Dalmon and coworkers [10] and Haag et al. [11] (Table 4). Note, that even taking into account the pressure effect, higher permeances and ideal selectivities can be obtained with our membrane.

4 Conclusions

Using a fully exchanged Ba-ZSM-5/SS composite in an extractor type membrane reactor, the yield of *p*-xylene obtained from *m*-xylene increased 28% compared to a fixed-bed reactor operated both at the same temperature and space velocity. When a Pt/H-ZSM-5/SS composite was used in a catalytic membrane reactor, the *p*-xylene yield increased 22% always compared to the fixed-bed reactor operated at the same temperature and space velocity.

Although both the non-catalytic and the catalytic membranes selectively permeated *p*-xylene, the Ba-ZSM-5/SS composite exhibited the highest separation factor. The three membranes used in this study were stable after 1000 h on stream, which included several thermal cycles between 25 and 400 °C. Studies at higher pressures are needed to further explore the applicability of this concept in industrial practice.

Acknowledgements The authors wish to acknowledge the financial support received from UNL, CONICET and ANPCyT. Thanks are given to Elsa Grimaldi for the English language editing. A.M.T. thanks the YPF Foundation for the support received for her doctoral scholarship.

References

1. Saracco G, Neomagus HWJP, Versteeg GF, van Swaaij WPM (1999) Chem Eng Sci 54(13–14):1997–2017
2. Coronas J, Santamaría J (1999) Catal Today 51:377
3. Jeong BH, Sotowa KI, Kusakabe K (2003) J Membr Sci 224:151
4. Gora L, Jansen JC (2005) J Catal 230:29
5. Dalmon J-A, Cruz-López A, Farrusseng D, Guilhaume N, Iojoiu E, Jalibert J-C, Miachon S, Mirodatos C, Pantazidis A, Rebeilleau-Dassonneville M, Schuurman Y, van Veen AC (2007) Appl Catal A 325:198
6. Xomeritakis G, Lai Z, Tsapatsis M (2001) Ind Eng Chem Res 40:544
7. Gump ChJ, Tuan VA, Noble RD, Falconer JL (2001) Ind Eng Chem Res 40:565
8. Lai Z, Bonilla G, Díaz I, Nery JG, Sujaoti K, Amat MA, Kokkoli E, Terasaki O, Thompson RW, Tsapatsis M, Vlachos DG (2003) Science 300:456

9. Hedlund J, Jareman F, Bons A-J, Anthonis M (2003) J Membr Sci 222:163
10. van Dyk L, Lorenzen L, Miachon S, Dalmon J-A (2005) Catal Today 104:274
11. Haag S, Hanebuth M, Mabande GTP, Avhale A, Schwieger W, Dittmeyer R (2006) Micropor Mesopor Mater 96:109
12. Deshayes AL, Miró EE, Horowitz GI (2006) Chem Eng J 122:149
13. Tarditi AM, Lombardo EA (2007, in press) Influence of exchanged cations (Na^+, Cs^+, Sr^{2+}, Ba^{2+}) on xylene permeation through ZSM-5/SS tubular membranes. Sep Purif Tech
14. Nishi K, Kamiya N, Yokomori Y (2007) Micropor Mesopor Mater 101:83
15. Algieri C, Bernal P, Goléeme P, Barbieri G, Drioli E (2003) J Membr Sci 222:181
16. Sebastián V, Kumakiri I, Bredesen R, Menéndez M (2007) J Membr Sci 292:92
17. Tarditi AM, Lombardo EA, Avila AM (in press) Ind Eng Chem Res
18. Tarditi AM, Horowitz GI, Lombardo EA (2006) J Membr Sci 281:692