Catalysis Today 156 (2010) 261–267

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Nanocomposite MFI–alumina membranes prepared via pore-pugging synthesis: Application as packed-bed membrane reactors for m-xylene isomerization over a Pt-HZSM-5 catalyst

M.O. Daramola[a,*], Z. Deng[b,c], M. Pera-Titus[b], A. Giroir-Fendler[b], S. Miachon[b,1], A.J. Burger[a], L. Lorenzen[a,2], Y. Guo[c]

[a] Department of Process Engineering, Stellenbosch University, Private Bag X1, Matieland 7602, Stellenbosch, South Africa
[b] Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS, Université Lyon 1, 2 Av. A. Einstein, 69626 Villeurbanne Cedex, France
[c] Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, 200237 Shanghai, PR China

ARTICLE INFO

Article history:
Available online 18 May 2010

Keywords:
Xylenes
Catalytic membrane reactors
Xylene isomerization
Zeolite membrane
Nanocomposite
MFI

ABSTRACT

In this paper, we present m-xylene isomerization in an extractor-type catalytic membrane reactor using nanocomposite MFI–alumina membrane tubes packed with a Pt-HZSM-5 catalyst. The catalytic performance of the membrane reactor was compared with that of a conventional fixed-bed reactor with similar dimensions and at comparable operation conditions. The influence of the reaction temperature, gas hourly space velocity, reaction time and reactor configuration on the performance of membrane reactor was explored. The membrane reactor displayed a maximum p-xylene yield of 5.1% at 523 K when computed at permeate-only mode, decreasing with temperature. At combined mode, the p-xylene yield was ca. 28%, showing an increase of about 18% compared to an equivalent fixed-bed reactor. The catalytic membrane reactor showed 100% selectivity towards p-xylene at permeate-only mode, displaying a maximum value of ca. 42% at 523 K at combined mode. Higher performance was obtained when the catalyst packing was close to the inner top layer of the membrane support. In this configuration, xylene permeate compositions higher than 95% could be achieved on the basis of the high p/o and p/m-xylene separation factors offered by the membrane.

1. Introduction

P-xylene is an industrially valuable petrochemical intermediate, almost exclusively consumed in the production of terephthalic acid, which is further used in the manufacture of polyethylene terephthalate (PET) for polyester fibers, films and solid-state packaging resins. For the last three decades, there has been a significant evolution in p-xylene production technologies, with many equipment improvements being instituted in the industry. More recent research efforts have focused on the development of zeolite membranes (MFI) for the separation of p-xylene. Researchers in this field have channeled research efforts towards the development and applications of catalytic membrane reactors for p-xylene separation and production [1,2].

Catalytic membrane reactors (CMRs), where membrane separation is coupled with a catalytic reaction in the same unit, are attractive applications because they are potentially compact and have lower operating costs than more conventional processes. On the basis of how the membrane and the catalyst are combined, CMRs can be broadly classified as [3]: (1) extractor-type (e-CMR), (2) distributor-type (d-CMR), and (3) contactor-type (c-CMR). Extractor-type CMRs are by far the most widespread application of CMRs. Classical applications of this configuration range from dehydrogenation, isomerization and esterification/etherification reactions to chemical synthesis and biological treatment of wastewater (see for instance Refs. [4–9]). In this configuration, selective removal of one/more products from the reaction zone enhances the conversion of the reaction by shifting the equilibrium position or by promoting the catalytic activity.

The combination of a supported MFI membrane (film-like) with an isomerization catalyst in an e-CMR (hereinafter referred to as 'e-ZCMR') to promote p-xylene production has been proposed in a few number of previous studies. Tarditi et al. [10] have reported isomerization of m-xylene and ternary xylene vapour using a Ba-exchanged HZSM-5 membrane and a commercial

---

[*] Corresponding author. Tel.: +27 218083860; fax: +27 218082059.
E-mail address: daramola@sun.ac.za (M.O. Daramola).
[1] Deceased 21st January 2009.
[2] Current address: Snowden Group, 87 Colin Street, West Perth, WA 6005, Australia.

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.077

Pt/silica–alumina catalyst. In the case of ternary xylene mixtures, the feed p/m/o-xylene partial pressures were kept, respectively, at 0.26/0.83/0.26 kPa. These authors reported an enhancement of p-xylene yield up to 26% during m-xylene isomerization at 643 K compared to a fixed-bed reactor operated at similar experimental conditions. In the case of ternary xylene mixture isomerization, the increase of p-xylene yield in an e-ZCMR reached a value of 30%. In the same vein, Zhang et al. [11] reported m-xylene isomerization over a HZSM-5 catalyst in an e-CMR. The authors used a disk-shaped silicalite-1 membrane as separation unit displaying p/o-xylene separation factors up to 16. Finally, Deshayes et al. [12] have reported a modelling study of the xylene isomerization reaction in an industrial FBR focusing on the effect of incorporating multi-tubes containing Na-ZSM-5/SS membranes on the catalytic performance of the reactor. These last authors have predicted an increase of about 12% in p-xylene production over a conventional FBR.

In the case of catalytically active MFI membranes, the only example of application in the open literature has been reported by Haag et al. [13]. In this study, the membrane consisted of a HZSM-5 film grown on top of a porous stainless steel disk. These authors reported an increase by 15% of m-xylene conversion at 673 K compared to a fixed-bed reactor (FBR), while the p-xylene selectivity was enhanced by 10%. At higher temperatures, however, no further improvement of neither the conversion nor the p-xylene selectivity could be achieved, probably due to the poor separation quality of the membranes, ascribed in its turn to a high number of intercrystalline defects.

All the studies stated above involve the use of supported film-like MFI membranes. Film-like MFI membranes have some shortcomings such as a mismatch between the thermal expansion coefficients of the support and the zeolite material at higher operation temperatures. This enhances permeation of undesirable isomers through intercrystalline defects, contributing to a reduction of membrane selectivity. This occurrence becomes more pronounced if the membrane support is stainless steel because of the higher disparity between its thermal expansion coefficients and that of the MFI phase. Taking into account that xylene separation and isomerization is industrially carried out at temperatures about 673 K, this limitation acts in practice as a deterrent for the industrialization of MFI membranes.

As we have pointed out in a series of previous studies [14–17], this shortcoming ascribed to film-like membranes can be overcome by using nanocomposite MFI–ceramic membranes, where the zeolite crystals are embedded within the support pores instead of forming a film. The advantages of nanocomposite architectures compared to zeolite films include defect control and higher mechanical and thermal stability. These membranes have shown a promising xylene isomer separation performance, as we have reported in previous studies [18–20].

In the case of xylene isomerization using MFI–ceramic membranes with nanocomposite architecture, our group has reported in a preliminary study an increase of about 10% of p-xylene yield (when retentate and permeate amounts are combined) over a conventional FBR [18]. This paper pursues our research efforts carried out in the past for m-xylene isomerization over Pt-HZSM-5 catalyst in e-ZCMRs using nanocomposite MFI–ceramic membrane tubes as separation and catalyst packing units. The influence of operating parameters such as the gas hourly space velocity (GHSV = feed volumetric flow/catalyst volume), the reaction time and the catalyst location (i.e. packed in the membrane lumen or in the module shell) have been investigated. The results reported in this study open up an avenue for promoting the performance of e-ZCMRs when applied to m-xylene isomerization.

2. Experimental

2.1. Membrane preparation, quality test and xylene separation performance

The membrane used in this study was prepared by pore-plugging hydrothermal synthesis on an asymmetrical Pall-Exekia α-alumina tube (o.d. 10 mm, i.d. 7 mm, length 15 cm, active permeation area 26 cm^2) as described elsewhere [14,15]. The cross-sectional layers of the support had the following mean pore diameters: outer layer, 12 μm; intermediate layer, 0.8 μm; inner layer, 0.2 μm. The nanocomposite nature of the membranes was inspected by SEM (JSM-5800LV, 20 kV) coupled with EDX analysis (Edax Phoenix, 1-μm microprobe). The resulting nanocomposite membrane from this support has an effective membrane thickness <3 μm.

The quality of the membrane was preliminarily evaluated by pure hydrogen permeation and room temperature *n*-butane/H_2 binary mixture separation. Xylene ternary vapour permeation (VP) tests were performed by feeding the inner tube of the membrane with a ternary mixture of xylene isomers (Sigma–Aldrich, 99% purity for m- and p-xylenes and 97% purity for o-xylene), saturated in dry N_2 (Air Liquide, >99.9999% purity) at a feed flow rate of 10 mL(STP)/min and at 307 K saturation temperature. At these conditions, the p/m/o-xylene vapour pressures feeding the membrane were, respectively, 0.51, 0.34 and 0.59 kPa. Nitrogen gas was swept over the permeate side of the membrane at a flow rate in the range 5–40 mL(STP)/min to approach the xylene partial pressure in the permeate stream to zero. A pre-calibrated GC equipped with a sol–gel Wax capillary column and a FID detector was used for the analysis of the composition in the feed, retentate and the permeate streams. During the separation tests, all the lines were heated up to 393 K to prevent xylene condensation. More details on the set-up and experimental protocol used for performing the xylene separation tests can be found elsewhere [19,20].

Prior to the separation tests, the membrane was mounted into the membrane module and subjected to a high temperature pre-treatment at 673 K under a 20 mL(STP)/min N_2 flow in the retentate and permeate sides for 6 h to remove adsorbed species on the guidance of a previous study [21]. In all the xylene VP experiments, mass balances of each xylene isomer were closed with an experimental error <3%. Also, to prevent occurrence of viscous flow within the membrane during the separation, the transmembrane (total) pressure was kept as low as possible ($\Delta P \approx 0$, Wicke–Kallenbach method).

The vapour permeance of a given xylene isomer was computed as the quotient between the corresponding flux and the log-mean partial pressure difference between the feed/retentate and permeate. The separation factor ($Sf_{i/j}$) was defined as the enrichment factor of one component to another in the permeate, as compared to the feed composition ratio in the separation of xylene mixtures (Eq. (1)):

$$Sf_{i/j} = \frac{(y_i/y_j)_{\text{permeate}}}{(x_i/x_j)_{\text{feed}}} \tag{1}$$

where x_i and x_j and y_i and y_j are, respectively, the molar fractions of species *i* and *j* in the feed and permeate streams. In our case, *i* represents p-xylene while *j* represents either m- or o-xylene.

2.2. M-xylene isomerization

The set-up used for carrying out the m-xylene isomerization experiments is the same as that used for the VP tests. Specifically, in the catalytic tests, the lumen of the tubular MFI membrane was packed with 2.18 g of a commercial Pt-HZSM-5 catalyst supplied

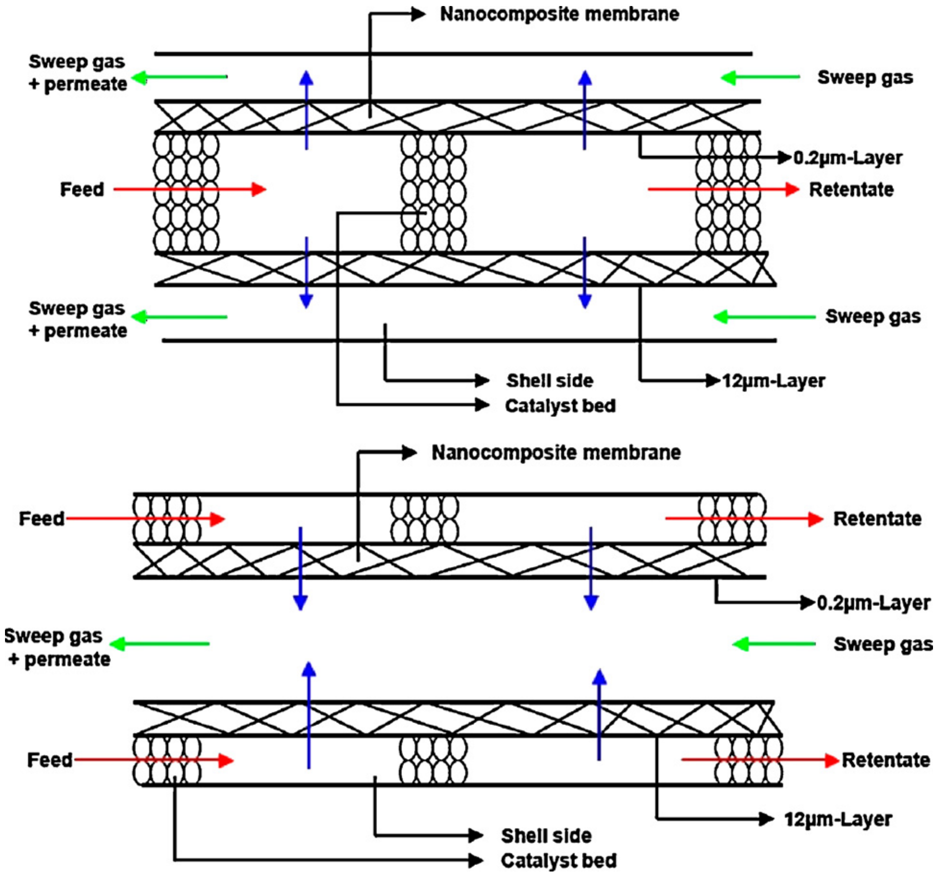

Fig. 1. Scheme of an e-ZCMR based on MFI–alumina catalytic membrane reactor with the catalyst packed in the lumen of the membrane tubes (on top) and between the membrane tube and the module shell (on bottom).

by Süd-Chemie (specific surface >500 $m^2\,g^{-1}$; skeletal density, 1.7 $g\,cm^{-3}$) to the configuration schematically depicted in Fig. 1. The catalyst was mixed with glass beads, increasing the total weight of the bed to 4.86 g. The catalytic bed was activated by passing H_2 over the catalytic bed for 3 h at 673 K [14].

M-xylene saturated in N_2 was fed into the reactor at a partial pressure in the range 2.45–2.84 kPa and at a flow rate of 10 mL(STP)/min, while the permeate side (for e-ZCMR) was swept with N_2 in counter-current mode at a flow rate of 40 mL(STP)/min. The temperature was kept in the range 523–673 K and feed fed at a high flow rate to operate far from the chemical equilibrium, inhibiting the formation of undesirable byproducts (e.g., toluene and trimethylbenzene). For comparison with a conventional FBR, a stainless steel tube with the same dimensions as the e-ZCMR was used and packed with the same amount of fresh Pt-HZSM-5 catalyst, the isomerization reaction being carried out at the same operation conditions. Also for comparison, some experiments were carried out packing the catalyst between the outer side of the membrane tube, close to the outermost layer and the module shell.

For each experiment, m-xylene conversion (X_{MX}), p-xylene yield (Y_{PX}) and p-xylene selectivity (S_{PX}) were calculated using the set of Eqs. (2)–(6):

$$X_{MX} = \frac{w_{MX}^{feed} - w_{MX}^{ret+perm}}{w_{MX}^{feed}} = \frac{w_{MX}^{feed} - w_{MX}^{ret} - w_{MX}^{perm}}{w_{MX}^{feed}} \quad (2)$$

$$Y_{PX}^{ret} = \frac{w_{PX}^{ret}}{w_{PX}^{ret} + w_{PX}^{perm} + w_{OX}^{ret} + w_{OX}^{perm} + w_{byproducts}^{ret} + \Delta w} \quad (3)$$

$$Y_{PX}^{perm} = \frac{w_{PX}^{perm}}{w_{PX}^{ret} + w_{PX}^{perm} + w_{OX}^{ret} + w_{OX}^{perm} + w_{byproducts}^{ret} + \Delta w} \quad (4)$$

$$S_{PX}^{ret} = \frac{w_{PX}^{ret}}{w_{PX}^{ret} + w_{OX}^{ret} + w_{Arom}^{ret}} \quad (5)$$

$$S_{PX}^{perm} = \frac{w_{PX}^{perm}}{w_{PX}^{perm} + w_{OX}^{perm} + w_{Arom}^{perm}} \quad (6)$$

where w_{PX}, w_{MX} and w_{OX} are, respectively, the p-xylene, m-xylene and o-xylene weight fractions, and the superscripts '*feed*', '*ret*', and '*perm*' refer, respectively, to the feed, retentate and permeate streams.

The analysis of the results was based on permeate-only and combined modes. Permeate-only mode considers the product distribution in the permeate stream, while the combined mode considers the addition of products in both the permeate and retentate streams. Some replicated experiments showed that m-xylene conversion, p-xylene yield and selectivity were accurate to within ±10%.

3. Results

3.1. Membrane quality and xylene mixture separation

After pre-treatment, the membrane prepared in this study shows a room temperature pure hydrogen permeance of 0.31 $\mu mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ and a separation factor of 66 for *n*-butane/H_2 separation. This latter value reflects a good membrane quality in terms of low amount of intercrystalline defects. Furthermore, the SEM micrographs (see Fig. 2) confirm the formation of a nanocomposite material on the substrate, namely no continuous MFI film was formed on top of the support. Fig. 2 also shows good pore plugging of the 0.2-μm layer with zeolite crystals. The

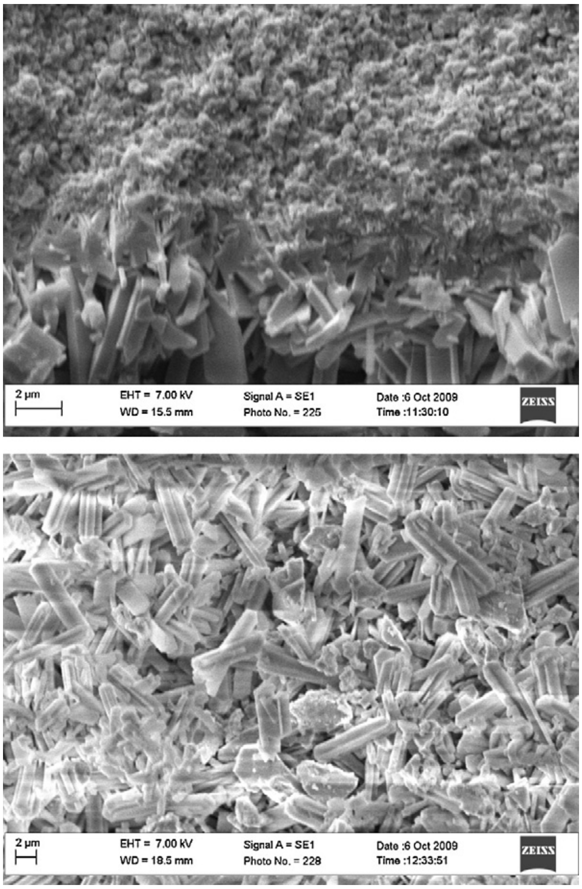

Fig. 2. SEM micrographs of the membrane showing formation of a nanocomposite zeolite material embedded in the support top layer. On top, cross-sectional view micrograph of the 0.2-μm layer pore-plugged with zeolite crystals; on bottom, surface view micrograph of the 0.2-μm layer pore-plugged with zeolite crystals.

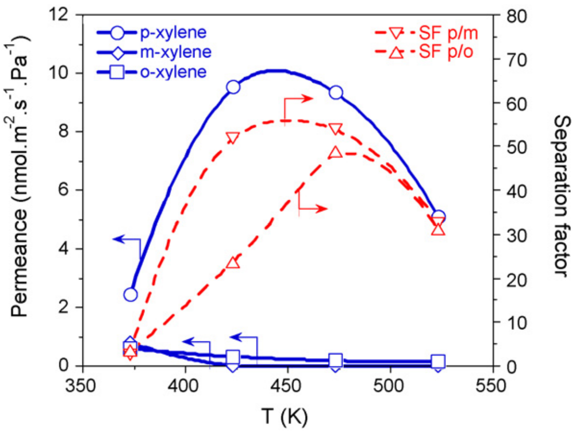

Fig. 3. Separation performance of nanocomposite MFI–alumina membranes as a function of temperature. *Experimental conditions*: feed flow rate, 10 mL(STP)/min; sweep gas flow rate, 15 mL(STP)/min; feed composition (p/m/o), 0.51/0.34/0.59 kPa.

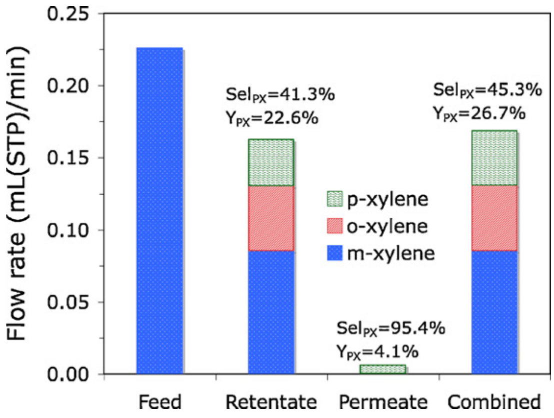

Fig. 4. M-xylene isomerization over Pt-HZSM-5 in an e-ZCMR at 573 K with the catalyst packed in the tube lumen. The combined mode corresponds to the addition of the retentate and permeate streams. *Experimental conditions*: feed composition, 2.30 kPa m-xylene in 10 mL(STP)/min N_2; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min; reaction time, 30 min.

Table 1
P- and o-xylene productivity in FBR, ZCMR-IN and ZCMR-OUT configurations at permeate-only mode (top values) and combined mode (bottom values). *Experimental conditions*: temperature, 573 K; m-xylene feed partial pressure, 2.84 kPa; feed flow rate, 10 mL(STP)/min; sweep gas flow rate, 40 mL(STP)/min.

Product	Productivity (nmol s^{-1} $g_{cat}{}^{-1}$)		
	FBR	ZCMR-IN	ZCMR-OUT
p-Xylene	–/10.7	2.0/12.1	1.4/11.2
o-Xylene	–/14.9	0.1/15.4	0.8/15.4

EDX analysis showed an average Si/Al ratio about 10–20 (semi-quantitative analysis) on the inner active layer. The material in the active layer corresponds accordingly to an Al-enriched HZSM-5 zeolite.

Fig. 3 confirms the p-xylene preferential separation of the membrane, achieving a maximum p-xylene flux of about 3.5 μmol m^{-2} s^{-1} at 450 K, corresponding to a maximum p-xylene permeance of ca. 10 nmol m^{-2} s^{-1} Pa^{-1}, and p/o and p/m mixture separation factors up to 50 and 55, respectively. In most permeation experiments, no m-xylene was found in the permeate streams. Accordingly, the corresponding partial pressures have been estimated from the detection limit of the GC (0.001 kPa). Also, during the separation tests, no isomerization products were detected in both the permeate and retentate streams, indicating that the membrane was catalytically inert to xylene isomerization. Furthermore, the membrane kept a repeatable separation performance after several thermal cycles, this testifying to its high thermal stability.

3.2. M-xylene isomerization

Fig. 4 plots the results for a representative m-xylene isomerization experiment performed on a ZCMR at 573 K. A significant transformation of m-xylene into p-xylene is obtained, with a p-xylene yield and selectivity, respectively, about 25 and 45% for combined mode operation.

Figs. 5–9 plot the influence of temperature (range 523–673 K), gas hourly surface velocity, reaction time and catalyst position in the reactor (i.e. in the tube lumen or in the module shell) on the m-xylene isomerization performance of a FBR and an e-ZCMR packed with Pt-HZSM-5 catalyst in terms of p-xylene yield and selectivity, m-xylene conversion and coke formation rate. As can be seen in Fig. 5, higher m-xylene conversions and p-xylene yields can be obtained in an e-ZCMR compared to a FBR with the catalyst packed in the tube lumen due to selective p-xylene extraction from the reaction zone by the membrane. The m-xylene conversion reaches a value about ca. 62% at 523 K in the e-ZCMR, the p-xylene yield and selectivity attaining values, respectively, up to 28 and 46% (combined mode).

Table 1 lists the p-xylene and o-xylene productivities at 573 K at permeate-only and combined operation modes for the three reactor configurations considered in this study, namely FBR, ZCMR-IN

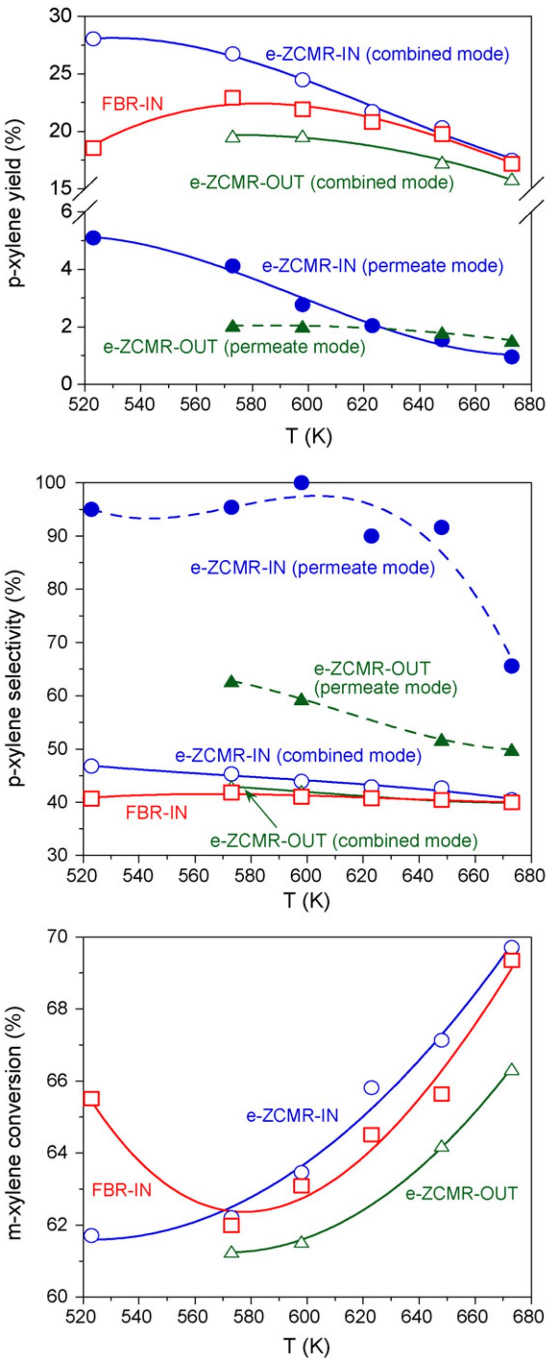

Fig. 5. M-xylene isomerization over Pt-HZSM-5 in an e-ZCMR and a FBR as a function of temperature and catalyst packing (IN, catalyst packed in the tube lumen; OUT, catalyst packed in the shell). From top to bottom, p-xylene yield, p-xylene selectivity and m-xylene conversion. *Experimental conditions*: feed composition, 2.30 kPa m-xylene in 10 mL(STP)/min N_2; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min; reaction time, 30 min.

(e-ZCMR-IN) and ZCMR-OUT (e-ZCMR-OUT). As can be seen, the higher p-xylene productivity corresponds to the ZCMR-IN mode, reaching a value about 12.1 nmol s^{-1} $g_{cat}{}^{-1}$ (combined mode).

4. Discussion

4.1. Xylene mixture separation

The permeation behaviour of p-xylene as a function of temperature depicted in Fig. 3 is qualitatively consistent with the

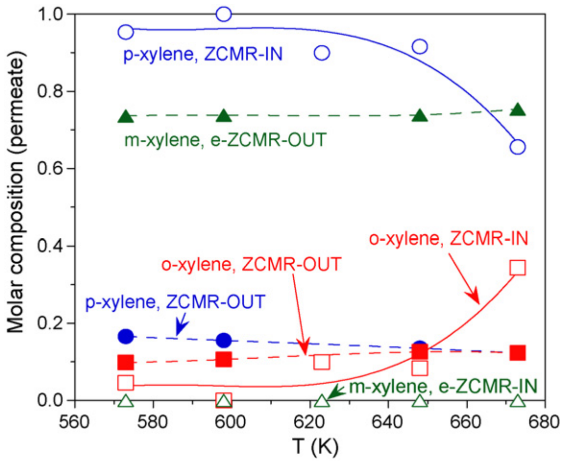

Fig. 6. P-, m- and o-xylene molar composition in permeate in ZCMR-IN and ZCMR-OUT configurations as a function of temperature. *Experimental conditions*: feed composition, 2.30 kPa m-xylene in 10 mL(STP)/min N_2; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min; reaction time, 30 min.

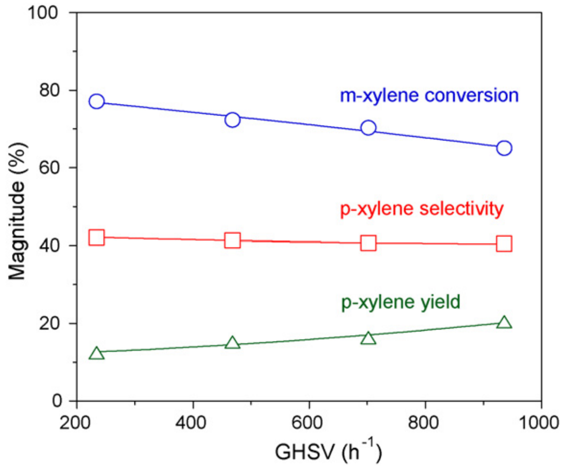

Fig. 7. M-xylene isomerization over Pt-HZSM-5 in an e-ZCMR as a function of the GHSV. *Experimental conditions*: temperature, 673 K; feed composition, 2.30 kPa m-xylene; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min; reaction time, 30 min.

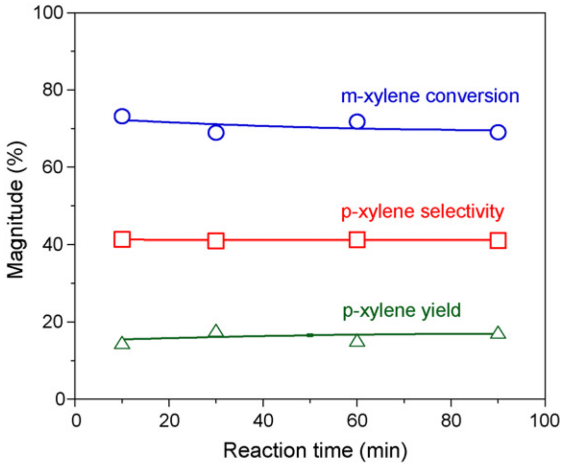

Fig. 8. M-xylene isomerization over Pt-HZSM-5 in an e-ZCMR as a function of the reaction time. *Experimental conditions*: temperature, 673 K; feed composition, 2.84 kPa m-xylene in 10 mL(STP)/min N_2; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min.

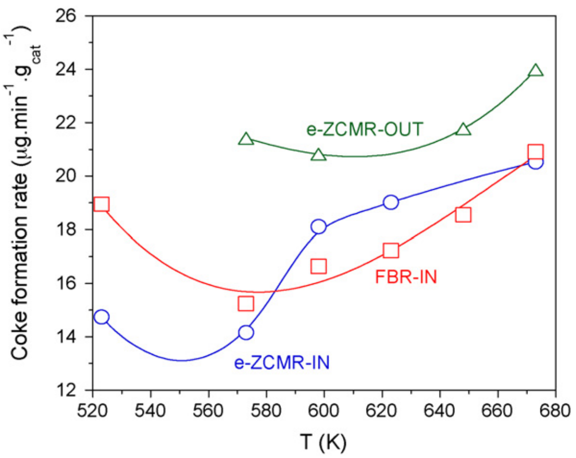

Fig. 9. Coke formation rate as a function of temperature in FBR, ZCMR-IN and ZCMR-OUT configurations. *Experimental conditions*: feed composition, 2.30 kPa m-xylene in 10 mL(STP)/min N_2; sweep gas flow rate into e-ZCMR, 40 mL(STP)/min; reaction time, 30 min.

trends already found in previous studies on either nanocomposite MFI–alumina membrane tubes or hollow fibres [18–20]. The p-xylene flux shows a maximum value of 3.5 μmol m^{-2} s^{-1}, at about 450 K, corresponding to a permeance ca. 9.5 nmol m^{-2} s^{-1} Pa^{-1}. The highest attainable p/o- and p/m-xylene separation factors are, respectively, about 50 and 55. It is noteworthy that, compared to our previous studies, the membrane shows comparable p/o and p/m separation factors at the maximum temperature, while usually the former separation factors are about one order of magnitude higher. The lower capacity of our membrane to discriminate o-xylene should be attributed to a higher amount of intercrystalline defects in our membrane, as can be deduced from the lower *n*-butane/H_2 separation factors at room temperature (66 vs. >100).

4.2. e-ZCMR vs. FBR

The results plotted in Figs. 5 and 6 reflect that, by packing the catalyst in the membrane lumen, an increase about 18% in the p-xylene yield (from 18 to 28%) at 523 K can be reached in an e-ZCMR over a conventional FBR due to selective p-xylene removal by the membrane (the p-xylene selectivity in permeate-only mode approaches to 100% at a temperature <573 K). The difference matches the p-xylene yield measured for permeate-only mode (~5%). The higher p-xylene yield at lower temperatures (i.e. 523 K) can be attributed to a higher concentration between the membrane and catalyst activities, providing a higher efficiency of the membrane reactor and consequently a higher differential in terms of p-xylene yield compared to a FBR. Note that the maximum p-xylene permeance and membrane selectivity to p-xylene is obtained at about 473 K (see Fig. 3). Moreover, lower temperatures are also beneficial due to the reduction of formation of byproducts (i.e. toluene and trimethylbenzene).

Regarding the effect of the GHSV on the isomerization in an e-ZCMR, Fig. 7 shows that the residence time does not exert a remarkable influence on neither the p-xylene yield nor selectivity. This observation, also reported by Zhang et al. [11], can be attributed to a reduced influence of p-xylene production through an intermolecular transalkylation mechanism responsible for toluene and trimethylbenzene formation, the diphenylmethane intermediates of this reaction acting as promoters of coke formation on strong acid sites [22].

4.3. Catalyst and membrane stability

As depicted in Fig. 8, the p-xylene yield, p-xylene selectivity and m-xylene conversion remain practically unchanged by increasing the reaction time from 10 to 90 min, this reflecting that a 'true' steady state was attained during the period. It is good to notice that we conducted the experiments continuously for about 8 h to collect the data for the points reported in Fig. 8. Therefore the time indicated in Fig. 8 is the reaction time before sampling to obtain the data for each point. This observation suggests that, although coke might be formed on the catalyst surface during the reaction, as evidenced from the mismatch in mass balances (see Fig. 4), this does not promote catalyst deactivation throughout the experimental period. As a matter of fact, the maximum computed coke loading on the catalyst after 90 min continuous operation is lower than 0.1 wt.% for both FBR and ZCMR configurations.

The coke formation rate is inhibited at lower temperatures (i.e. 523 K) in configuration ZCMR-IN compared to a FBR (see Fig. 9). This result is accompanied by a reduction of the m-xylene conversion and an increase of the p-xylene yield, as can be observed in Fig. 5. The reduction of coke formation in ZCMR-IN configuration at lower temperatures suggests a higher role of meta-xylene isomerization through an intramolecular catalytic mechanism based on benzenium-ion intermediates instead of an intermolecular transalkylation mechanism promoting coke generation by disproportionation. Therefore, the reduction of coke formation in ZCMR-IN configuration should necessarily involve a reduction of diphenylmethane intermediates due to selective p-xylene extraction by the membrane, promoting isomerization through an intramolecular mechanism. This effect is expected to be more intense in the case of HZSM-5 catalysts than for HFAU zeolites due to the reduced pore size of the ZSM-5 channels, providing higher steric hindrance and inhibiting therefore the formation of bulky diphenylmethane intermediates.

4.4. Effect of reactor configuration

Fig. 5 shows that, for the three configurations here considered (i.e. e-ZCMR-IN, e-ZCMR-OUT and FBR), the p-xylene yield is enhanced at lower temperatures in the range 523–673 K (combined mode). However, while the p-xylene yield increases practically linearly in configuration e-ZCMR-IN while reducing the temperature, the trend becomes inhibited at lower temperatures for the other two configurations, showing a plateau. These observations might be ascribed to positive role of the membrane in p-xylene extraction in the former case. In the case of configuration e-ZCMR-OUT, the GHSV used in these experiments is significantly lower than in configuration e-ZCMR-IN, allowing in principle the catalyst activity to be more concerted with that of the membrane. However, the trend of the p-xylene yield with the temperature suggests a reduced effect of the membrane on the catalytic performance. This lack of membrane efficiency might be explained on the basis of diffusion limitations in the membrane support, as permeation proceeds from the outer surface to the inner top layer. Similar conclusions have been recently addressed by Zhang et al. [11].

4.5. Results compared with literature

Table 2 collects the results reported in the literature on m-xylene isomerization in ZCMRs using Pt-HZSM-5 and Pt/alumina–silica catalysts. Despite the different reaction conditions considered by these authors (e.g., GHSV, feed composition and membrane geometry), the results presented are comparable in terms of p-xylene yield and selectivity enhancement. This could be attributed to the higher quality of the nanocomposite membranes prepared in this study, with permeances up to 9.5 nmol m^{-2} s^{-1} Pa^{-1} and p/o and p/m-

Table 2
Comparison of the results obtained in this study with the literature.

Membrane type/support	Feed composition	T (K)	P-xylene yield (%)		P-xylene sel. (%)		References
			e-ZCMR	FBR	e-ZCMR	FBR	
Film-like inert Ba-ZSM-5/SS e-CMR	Ternary mixture	643	25	21	69	52	[10]
Inert silicalite/α-alumina disk	m-Xylene	603	21.3	18.5	44.6	35	[11]
Catalytic H-ZSM-5/SS disk e-CMR	m-Xylene	673	6.9	5.87	66.7	55.6	[13]
Nanocomposite inert silicalite-1/tubular ∝-alumina e-ZCMR	m-Xylene	577	11.2	10.2	65	58	[18]
Nanocomposite MFI–alumina e-ZCMR	m-Xylene	523	27	23	49	42	This work

xylene separation factors >50. Another positive consequence of the selectivity of our membranes is the high purity of p-xylene in the permeate, achieving molar fractions >95% at 573 K. Note that, for comparison, Zhang et al. [11] achieved p/m-xylene separation factors of only 16. Also, our results improve remarkably the p-xylene yields previously reported by van Dyk et al. [18].

5. Conclusions

The results presented in this study confirm the potential of e-ZCMRs compared to the conventional FBRs for m-xylene selective isomerization to p-xylene. However, more research efforts are needed in terms of membrane development to increase p-xylene permeances while keeping the p-xylene selectivity at present values. Recently, our group has demonstrated that the application of nanocomposite MFI–ceramic hollow fibre membranes for xylene isomer separation could increase p-xylene flux by ca. 30% over conventional membrane tubes [19]. Another advantage of hollow fibres is ascribed to their higher surface-to-volume ratios. These modules when used in e-CMR increase p-xylene productivity while reducing the module layout. However, taking into account the results presented in this study on configurations, e-ZCMR-IN and e-ZCMR-OUT, the main challenge of hollow fibres when applied to m-xylene isomerization is how to achieve effective catalyst packing between the hollow fibres and supporting tubes and how to reduce diffusion limitations in the hollow fibres. In this case, hollow fibres with the MFI effective layers on the outer surface would be in principle preferential.

Furthermore, catalytically active MFI membranes may be a good option. In general terms, catalytically active membranes are thought to be about 10 times more active than in the FBRs provided that the membrane thickness and porous texture, as well as the quantity and location of the catalyst in the membrane are adapted to the reaction kinetics [23,24]. Meanwhile, research in the application of catalytically active membranes for p-xylene production is still limited.

Acknowledgements

The authors hereby acknowledge the financial assistance of the French Embassy in Pretoria and the CNRS (France) and the NRF (South Africa) for funding this work through a PICS joint program. The authors thank Süd-Chemie for kindly providing the Pt-HZSM-5 catalyst.

References

[1] Y.Y. Fong, A.Z. Abdullah, A.L. Ahmad, S. Bhatia, Development of functionalized zeolite membrane and its potential role as reactor combined separator for para-xylene production from xylene isomers, Chem. Eng. J. 139 (1) (2008) 172–193.

[2] M.O. Daramola, A.J. Burger, M. Pera-Titus, A. Giroir-Fendler, S. Miachon, J.-A. Dalmon, L. Lorenzen, Separation and isomerization of xylene using zeolite membranes: a short overview, Asia-Pac J. Chem. Eng. (2009), doi:10.1002/apj.414 (in press).

[3] S. Miachon, J.-A. Dalmon, Catalysis in membrane reactors: what about the catalyst? Top. Catal. 29 (2004) 59–65.

[4] A. Pantazidis, J.-A. Dalmon, C. Mirodatos, Oxidative dehydrogenation of propane on catalytic membrane reactors, Catal. Today 25 (1995) 403–408.

[5] D. Casanave, P. Ciavarella, K. Fiaty, J.-A. Dalmon, Zeolite membrane reactor for isobutane dehydrogenation: experimental results and theoretical modelling, Chem. Eng. Sci. 54 (1999) 2807–2815.

[6] M. Pera-Titus, J. Llorens, F. Cunill, Technical and economical feasibility of zeolite NaA membrane-based reactors in liquid-phase etherification reactions, Chem. Eng. Process.: Process Intensif. 48 (2009) 1072–1079.

[7] O. de la Iglesia, R. Mallada, M. Menendez, J. Coronas, Synthesis of MTBE in zeolite membrane reactors, Chem. Eng. J. 131 (2007) 35–39.

[8] T. Inoue, T. Nagase, Y. Hasegawa, Y. Kiyozumi, K. Sato, M. Nishioka, S. Hamakawa, F. Mizukami, Stoichiometric ester condensation reaction processes by pervaporative water removal via acid-tolerant zeolite membranes, Ind. Eng. Chem. Res. 46 (2007) 3743.

[9] B. Perrin, K. Fiaty, C. Charcosset, H. Moueddeb, R. Couturier, B. Maisterrena, A composite enzymatic membrane for the specific separation and concentration of l glycerophosphate from a racemic d/l glycerophosphate mixture, Enzyme Microb. Technol. 40 (2009) 1604–1607.

[10] A.M. Tarditi, G.I. Horowitz, E.A. Lombardo, Xylene isomerization in a ZSM-5/SS membrane reactor, Catal. Lett. 123 (2008) 7–15.

[11] C. Zhang, Z. Hong, X. Gu, Z. Zhong, W. Jin, N. Xu, Silicalite-1 zeolite membrane reactor packed with HZSM-5 catalyst for meta-xylene isomerization, Ind. Eng. Chem. Res. 48 (2009) 4293–4299.

[12] A.L. Deshayes, E.E. Miro, G.I. Horowitz, Xylene isomerization in a membrane reactor. Part II. Simulation of an industrial reactor, Chem. Eng. J. 122 (2006) 149–157.

[13] S. Haag, S.M. Hanebuth, G.T.P. Mabande, A. Avhale, W. Schwieger, R. Dittmeyer, On the use of a catalytic H-ZSM-5 membrane for xylene isomerization, Micropor. Mesopor. Mater. 96 (2006) 168–176.

[14] A. Giroir-Fendler, J. Peureux, H. Mozzanega, J.-A. Dalmon, Characterization of a zeolite membrane for catalytic membrane reactor application, Stud. Surf. Sci. Catal. 101 (1996) 127–136.

[15] S. Miachon, E. Landrivon, M. Aouine, Y. Sun, I. Kumakiri, Y. Li, O. Pachtova Prokopova, N. Guilhaume, A. Giroir-Fendler, H. Mozzanega, J.-A. Dalmon, Nanocomposite MFI–alumina membranes via pore-plugging synthesis: preparation and morphological characterization, J. Membr. Sci. 281 (2006) 228–238.

[16] S. Miachon, P. Ciavarella, L. van Dyk, I. Kumakiri, K. Fiaty, Nanocomposite MFI–alumina membranes via pore-plugging synthesis: Specific transport and separation properties, J. Membr. Sci. 298 (2007) 71–79.

[17] Y. Li, M. Pera-Titus, G. Xiong, W. Yang, E. Landrivon, S. Miachon, J.-A. Dalmon, Nanocomposite MFI–alumina membranes via pore-plugging synthesis: Genesis of the zeolite material, J. Membr. Sci. 325 (2008) 973–981.

[18] L. Van Dyk, L. Lorenzen, S. Miachon, J.-A. Dalmon, Xylene isomerization in an extractor type catalytic membrane reactor, Catal. Today 104 (2005) 274–280.

[19] M.O. Daramola, A.J. Burger, M. Pera-Titus, A. Giroir-Fendler, L. Lorenzen, S. Miachon, J.-A. Dalmon, Nanocomposite MFI hollow-fibre membranes via pore-plugging synthesis: prospects for xylene isomer separation, J. Membr. Sci. 337 (2009) 106–112.

[20] M.O. Daramola, A.J. Burger, M. Pera-Titus, A. Giroir-Fendler, L. Lorenzen, J.-A. Dalmon, Xylene vapour mixture separation in nanocomposite MFI–alumina tubular membranes: influence of operating variables, Sep. Sci. Technol. 45 (1) (2009) 21–27.

[21] A. Alshebani, M. Pera-Titus, K.L. Yeung, S. Miachon, J.-A. Dalmon, Influence of pre-treatment on the *n*-butane/hydrogen separation performance of nanocomposite MFI zeolite membranes, J. Membr. Sci. 314 (2008) 143–151.

[22] M. Guisnet, N.S. Gnep, S. Morin, D.E. Ozokwelu, Mechanisms of xylene isomerization over acidic solid catalysts, Micropor. Mesopor. Mater. 35–36 (2000) 47–59.

[23] V.T. Zaspalis, W. Van Praag, K. Keizer, J.G. Van Ommen, J.R.H. Ross, A.J. Burggraaf, Reaction of methanol over catalytically active alumina membranes, Appl. Catal. 74 (2) (1991) 2005–2222.

[24] M.P. Harold, C. Lee, A.J. Burggraaf, K. Keizer, V.T. Zaspalis, R.S.A. De Lange, Catalysis with inorganic membranes, MRS Bull. 19 (4) (1994) 34–39.