ELSEVIER

Catalysis Today 67 (2001) 101–107

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Tubular MFI zeolite membranes made by secondary (seeded) growth

María Pilar Bernal [a], George Xomeritakis [b], Michael Tsapatsis [b,*]

[a] *Department of Chemical and Environmental Engineering, University of Zaragoza, Zaragoza 50009, Spain*
[b] *Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003-3110, USA*

Abstract

Zeolite MFI membranes with thickness 15–20 μm were grown on the surface of macroporous α-alumina and stainless steel support tubes (pore size 200 and 500 nm, respectively) by the secondary (seeded) growth technique. The tubular supports were dipped vertically in an aqueous suspension of colloidal silicalite-1 seed crystals (particle size 100 nm) and withdrawn at a speed of 1–2 cm/h to allow for uniform formation of seed layers on the outer (for stainless steel) or inner (for α-alumina) cylindrical surface of the support tubes. The seeded tubes were treated hydrothermally with clear solutions of different composition and the resulting MFI membranes were characterized by SEM and permeation of butane isomers. For the best preparations, binary *n*-butane/isobutane ratios at 22°C were as high as 28 and 53 for stainless steel and α-alumina tubes, respectively, while the *n*-butane permeation flux varied in the range 0.8–3.8 mmol m^{-2} s^{-1}. The effect of temperature and feed partial pressure on permeation flux was also studied for binary mixtures of butane isomers and was found similar to that of planar membranes developed previously on α-alumina support disks by the same synthesis procedure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite MFI membranes; Secondary (seeded) growth; α-Alumina

1. Introduction

Current commercial applications of zeolites in powder form include ion-exchange, catalysis and gas/vapor separation by adsorption [1]. Recently, successful preparation of zeolite films and membranes by various groups has suggested new opportunities for applications in gas and liquid separations in the petrochemical industry [2]. Differences in chemical nature, molecule size and shape, and adsorption/diffusion in the zeolite channels can account for high separation selectivities between components of various mixtures such as hydrocarbon isomers, water/organics, etc. [3].

Zeolite membrane synthesis is more commonly carried out by the in situ crystallization technique which involves placing a porous support in contact with a synthesis solution or gel under hydrothermal conditions. For successful membrane formation, proper conditions are necessary to allow for preferential nucleation and growth of zeolite crystals on the support surface (possibly competing with solution events) in an interlocking fashion with minimal non-selective interzeolitic porosity [4]. An alternative approach for zeolite membrane formation is a technique referred to as secondary (seeded) growth, which involves attaching a closely packed layer of zeolite seed crystals on the surface of a support which act as nuclei for

---

[*] Corresponding author. Tel.: +1-413-545-0276;
fax: +1-413-545-1647.
E-mail address: tsapatsi@ecs.umass.edu (M. Tsapatsis).

PII: S0920-5861(01)00269-3

Table 1
Review of synthesis characteristics and butane permeation data for different MFI membranes

Reference	Synthesis characteristics			Permeation results		
	Support	Synthesis conditions	Thickness (μm)	Feed temperature (°C)/pressure (kPa)	n-Butane flux (mmol m^{-2} s^{-1})	Selectivity, n-C$_4$/i-C$_4$
[15]	Stainless-steel disk	In situ, 180°C	50	25/30	2.0	70
[16]	α-Al$_2$O$_3$ tube	In situ, 180°C	40	100/100	3.0	43
[17]	α-Al$_2$O$_3$ disk	In situ, 175°C	10	185/100	2.7	45
[18]	α-Al$_2$O$_3$ disk	In situ, 120°C	3	22/50	1.6	52
[7]	α-Al$_2$O$_3$ tube	Seeded growth, 130–150°C	5	110/100	0.19	80
[19]	γ/α-Al$_2$O$_3$ tube	In situ, 170°C	30	100/119	4.0	40
[20,21]	α-Al$_2$O$_3$ disk	Seeded growth, 175°C	20–30	22/50	3.0	62

further crystal growth under suitable hydrothermal conditions to fill the intercrystalline space [5–9].

Compared to the in situ crystallization scheme, seeded growth offers significant advantages such as better control over membrane microstructure (thickness, orientation), higher reproducibility, and a wider range of hydrothermal synthesis conditions leading to continuous film formation. Elimination of the constraints imposed by the need for crystal nucleation, due to the pre-existence of nuclei on the support surface, renders crystal growth as the main film formation mechanism and thus adds improved flexibility in zeolite film and membrane preparation [6].

Among the different types of zeolites available, zeolite MFI (ZSM-5 and its Al-free analog, silicalite-1) have been more commonly employed in zeolite membrane synthesis, because of its pore size (~5.5 Å) suitable for several industrially important separations [10] and the relatively easy synthesis from a variety of silica sources and structure directing agents [11]. Permeation experiments with certain gas/vapor pairs, e.g. N_2/SF_6 [12], n-butane/isobutane [13] and p-xylene/o-xylene [14] have been often employed to characterize the quality of these MFI membranes. Table 1 gives an overview of the most successful zeolite MFI membranes on different flat or tubular ceramic or metallic supports together with representative butane permeation data for specific feed pressure and temperature conditions.

Our group has recently demonstrated reproducible synthesis of high-quality MFI type zeolite membranes by secondary growth of silicalite-1 seed layers of initial particle size ~100 nm deposited on α-alumina support disks (pore size, ~150 nm; permeation area, ~1.5 cm^2) as judged by n-butane/isobutane mixture separation factors in the range 40–70 and p-xylene/o-xylene single-component selectivities in the range 30–130 [14,20,21]. In this communication, we present preliminary results on the preparation of similar MFI membranes on tubular α-alumina and stainless steel supports (pore size, 200–500 nm) of much larger permeation area (13–15 cm^2). Permeation results with N_2, SF_6 and butane isomers are presented and utilized to evaluate membrane quality, especially as compared to the disk-shaped MFI membranes reported in our earlier publications.

2. Experimental

2.1. Membrane support

Two types of porous supports were used for zeolite membrane preparation: (a) α-alumina asymmetric tubes of 7 mm ID, 10 mm OD, with an inner top layer of pore size ~200 nm (NGK, Japan); (b) stainless steel tubes of similar dimensions and average pore size ~500 nm (Mott Metallurgical). The ends of the ceramic supports were sealed with a glazing compound while the ends of the metallic supports were welded with non-porous metal tubes (3/8 in. OD) to allow for mounting in a special glass holder for permeation measurements. In both cases, the length of the porous part available for permeation was 5–6 cm.

2.2. Membrane preparation

For surface seeding, the tubular supports were fixed vertically by their upper end and dipped in a glass vial containing an aqueous suspension of silicalite-1 seed crystals of particle size ~100 nm, concentration 20 g/l and pH ~9, prepared and characterized as described in [5,6,14,20]. This vial was in turn placed in a plastic bottle of larger diameter, floating inside a 2 in. OD glass tube filled with water. Removal of the water from the glass tube with the aid of a peristaltic pump resulted in slow withdrawal of the seed suspension at a speed of ~1–2 cm/h. After total withdrawal of the suspension, the support tube was dried in air and dip-coating was repeated with the tube inverted to allow for better uniformity of the seed layer. Typically, dip-coating was carried out four times for most of the tubes used for membrane preparation. During this process, the outer cylindrical surface of the ceramic tubes was wrapped with teflon tape (seed layer formed on the inner cylindrical surface) while the non-porous ends of the metallic tubes were closed with plastic caps (seed layer formed on the outer polished cylindrical surface). Fig. 1 is schematic representation of the experimental setup used for dip-coating.

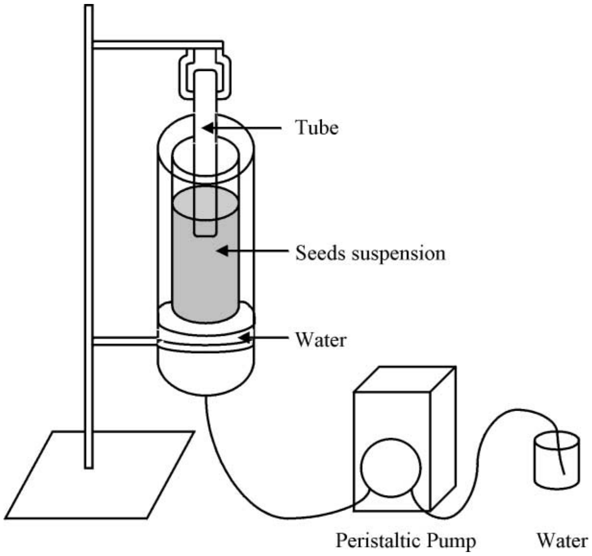

Fig. 1. Experimental setup for dip-coating of porous alumina and stainless-steel tubular supports.

Secondary growth of the seed layers deposited on the support tubes was carried out hydrothermally with clear solutions of compositions given in Table 2. Corresponding amounts of KOH pellets (Fisher Scientific), TPABr (98%, Aldrich), TPAOH (1 M solution, Aldrich), TEOS (98%, Aldrich) or Ludox AS-40 (Aldrich) were added in deionized water and stirred for 2–3 h until a clear solution was obtained. The solution was transferred in teflon-lined stainless steel autoclaves with the support tubes fixed vertically and hydrothermal reaction was carried out for 20–24 h under static conditions in a convection oven preheated at 175°C. In the case of the ceramic tubes, hydrothermal reaction was carried out only one time. In the case of the metallic tubes, however, two or three hydrothermal reactions were necessary to secure a final membrane of satisfactorily low N_2 permeance before calcination. After each synthesis, the tubes were rinsed several times with hot water and were finally calcined for 8 h at 450°C for removal of the tetrapropylammonium template occluded in the zeolite pores.

Table 2
Molar compositions of clear solutions for secondary growth

Code	KOH	TPABr	TPAOH	SiO_2	H_2O
A[a]	1.0	1.0	–	4.5	1000
B[a]	–	–	3.0	25	1500
C[a]	1.0	1.0	–	9.0	1000
D[b]	1.6	2.0	–	40	1000

[a] Silica source is TEOS.
[b] Silica source is Ludox AS-40.

2.3. Characterization

For SEM observation of the membrane surface and cross-section, test samples were cut out of selected tubes with a wafering blade (Buehler), attached on copper specimen boats with conductive carbon tape and sputter coated with gold. SEM micrographs were obtained with a JEOL 100CX microscope operated at 20 kV.

For permeation experiments, the tubular support ends were connected with non-porous glass tubes of $\frac{1}{4}$ in. OD with the aid of Ultratorr fittings (Swagelok) and fixed in a custom-made separable glass holder. Permeation measurements were conducted in either the Wicke-Kallenbach mode (feed of binary butane mixture) or with the pressure rise method (feed of pure N_2 or SF_6). In either case, the feed was always introduced at 100 kPa total pressure from the side of the zeolite layer, while the opposite side was flushed with 100 cm^3/min of helium (for the butane mixture experiments of Figs. 3–5) or kept in vacuum (for the

N_2 or SF_6). Permeation data were obtained with the aid of an HP 5890 Series II gas chromatograph (feed of butane isomers) or an absolute pressure transducer (Omega) connected to a PC for data acquisition. The separation factor for the binary butane mixture, $\alpha_{n,i}$, is calculated as follows:

$$\alpha_{n,i} = \frac{C_n{}^{\text{perm.}}/C_i{}^{\text{perm.}}}{C_n{}^{\text{feed}}/C_i{}^{\text{feed}}},$$

where C_n and C_i are the concentrations of *n*-butane and isobutane in the feed (C^{feed}) and permeate ($C^{\text{perm.}}$).

3. Results and discussion

Fig. 2 shows SEM micrographs of: (a) and (b) surface and cross-section of an MFI membrane grown on NGK α-alumina support by one growth using composition B; (c) surface of an MFI membrane grown on stainless steel support by one growth using composition B; (d) cross-section of an MFI membrane grown on stainless steel support by two growths using composition A. It is generally observed that the membranes grown on the ceramic tubes have lower concentration of surface defects compared to the metal-supported

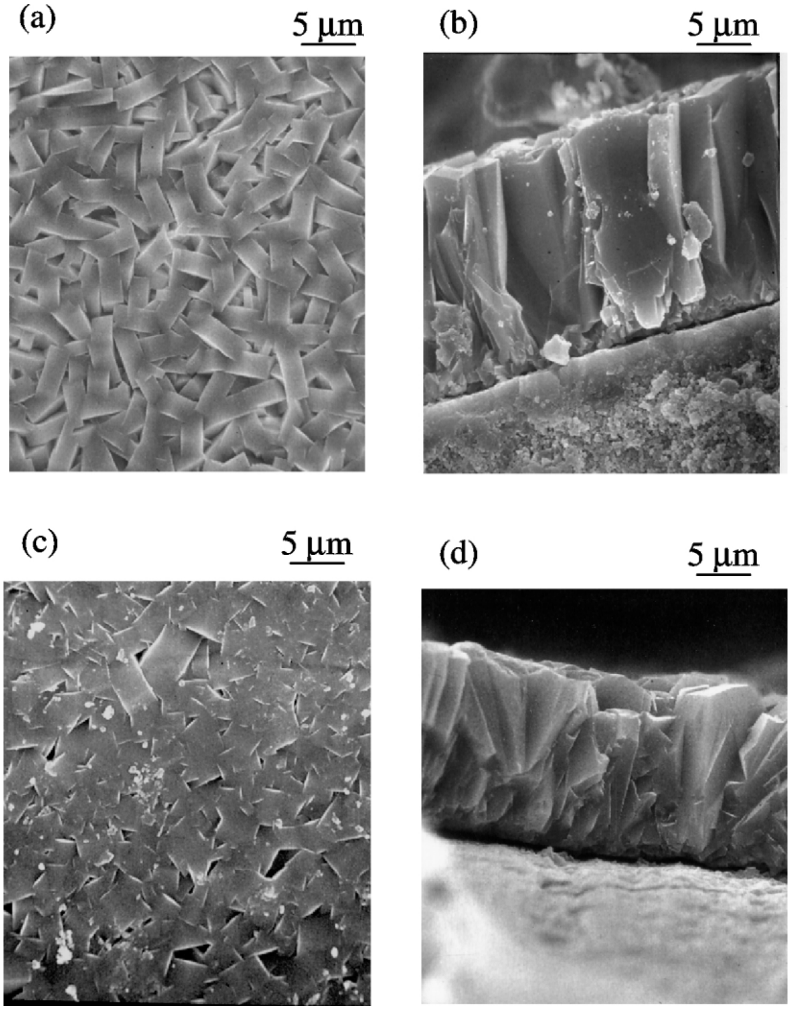

Fig. 2. SEM micrographs of MFI membranes grown on: (a) and (b) NGK alumina; (c) and (d) stainless steel tubular supports.

membranes due to the higher quality of the top layer of the ceramic tubes compared to the more rough metallic supports. The membrane grown in one step on the α-alumina support tube was 20 μm thick, in agreement with membranes grown on α-alumina disks, while the membrane grown in two steps on the stainless steel support had a thickness of only 17 μm, lower than that of membranes grown on α-alumina disks (thickness 25–30 μm) [20,21]. Although the exact reason for this discrepancy is not known yet, it is likely that iron leached in the solution from the stainless steel support during hydrothermal reaction may have decreased the film growth rate, hence resulting in smaller thickness for the metal-supported MFI membranes. Nevertheless, both types of tubular MFI membranes exhibit a columnar microstructure as evidenced from the cross-sectional SEM photos, which is characteristic of films and membranes grown on planar supports by the secondary growth process, as documented extensively in our earlier publications [6,20,22].

Table 3 summarizes room-temperature permeation results of butane isomers through different MFI membrane samples prepared on α-alumina and stainless steel support tubes. The binary *n*-butane/isobutane flux ratio was above 30 for the α-alumina supported membranes, while it varied typically in the range 15–20 for the stainless-steel supported membranes, with the exception of membrane SS-5 which had an *n*-butane/isobutane ratio of 28. The higher separation factor for butane isomers achieved with the ceramic support tubes can be possibly associated to the lower concentration of defects present on these membranes, as compared to the metal-supported ones. The single-component N_2/SF_6 ratio was ∼10 for all tubular MFI membranes, in agreement with the previous results obtained with good quality MFI membranes made on α-alumina support disks [20]. Similar results were reported by Burrgraaf et al. [23] with 3 μm thick MFI membranes on α-alumina disks, whereas Coronas et al. [12,19] obtained N_2/SF_6 ratios an order of magnitude higher (200–300) with MFI membranes grown in/on α-alumina support tubes. At this moment, the reason for this discrepancy is not fully understood, although it may be associated with possible incorporation of Al in the MFI structure during synthesis of membranes on tubular α-alumina supports reported by Coronas et al.

The transport properties of the tubular MFI membranes made by seeded growth were further investigated with binary permeation experiments of butane isomers at different conditions of feed partial pressure and temperature. Fig. 3 shows permeation flux data of butane isomers at 22°C for the stainless-steel supported membrane SS-5 as a function of feed partial pressure for a binary feed consisting of: (a)

Table 3
Summary of permeation results of tubular MFI-type zeolite membranes made by seeded growth, (temperature = 22°C)

Membrane code	Synthesis conditions	*n*-Butane flux ($mmol\,m^{-2}\,s^{-1}$)	Separation factor, *n*-C_4/*i*-C_4
NGK-1	B	2.39	36.0
NGK-2	B	1.95	44.2
NGK-3	B	2.90	31.6
NGK-4	B	2.54	38.1
NGK-5	B	2.20	36.1
NGK-6	B	2.67	37.7
NGK-7	A	3.11	32.6
NGK-8	A	3.13	25.8
NGK-9	A	3.82	35.8
NGK-10	D	2.03	48.4
NGK-11	D	1.55	53.0
SS-5	C–C	0.83	28.0

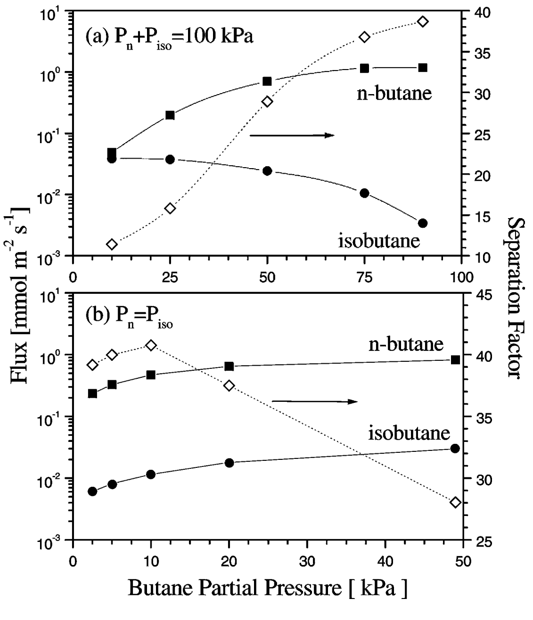

Fig. 3. Permeation of butane isomers through the stainless-steel supported MFI membrane SS-5 vs. feed partial pressure. Permeation temperature = 22°C.

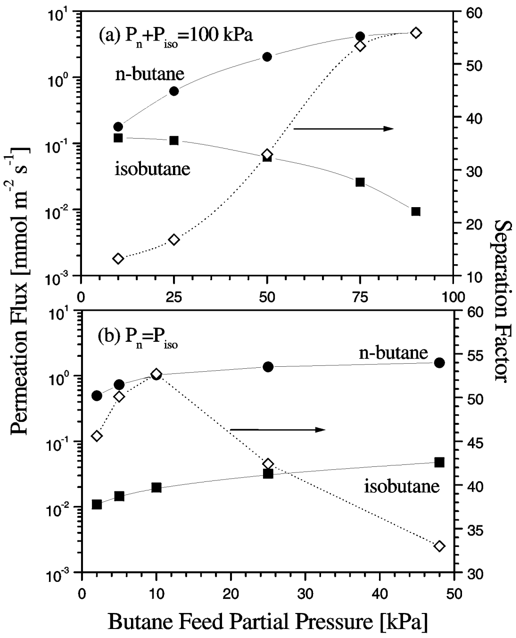

Fig. 4. Permeation of butane isomers through the alumina supported MFI membrane NGK-1 vs. feed partial pressure. Permeation temperature = 22°C.

n-butane of partial pressure 10–90 kPa, balanced to a total of 100 kPa by isobutane; (b) equimolar *n*-butane/isobutane mixture of partial pressure 2.5–50 kPa, balanced to a total of 100 kPa by helium. The corresponding *n*-butane/isobutane separation factor, $\alpha_{n,i}$, is also given in the figure (open symbols). Fig. 4 shows corresponding data for the α-alumina supported membrane NGK-1.

From Figs. 3(a) and 4(a), we observe that the separation factor increases monotonically with increasing *n*-butane feed partial pressure from ∼11 (feed rich in isobutane) to ∼40 (56) (feed rich in *n*-butane) for the stainless-steel (α-alumina) supported MFI membrane. This result suggests that the ability of *n*-butane to block isobutane from entering the zeolite pores increases with *n*-butane feed partial pressure. In the case of the equimolar mixtures (Figs. 3(b) and 4(b)), however, the behavior is quite different since the separation factor shows a maximum at about 10 kPa feed partial pressure for both the stainless-steel and α-alumina supported MFI membranes. This behavior can be qualitatively explained if the adsorption isotherms of butane isomers in silicalite-1 are taken into account [24]. Adsorption of *n*-butane in silicalite-1 at 30°C follows a normal Langmuir isotherm and saturation of 1.2 mol/kg is reached at partial pressure ∼10 kPa. Instead, isobutane exhibits a two-step adsorption behavior with an initial sharp followed by a slower increase of adsorbed amount up to about 200 kPa partial pressure. Therefore, it is suggested that the observed drop in the separation factor after 10 kPa is a result of preferential intrusion of isobutane in the zeolite pores with increasing partial pressure.

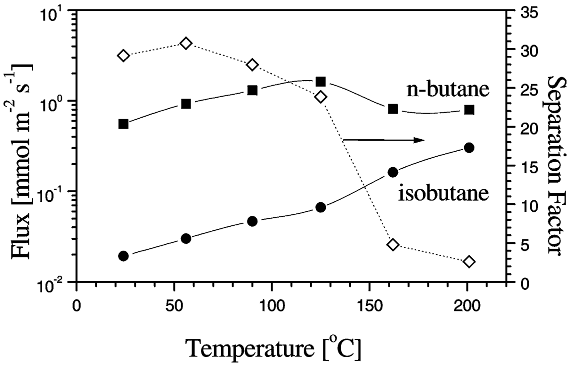

Fig. 5. Permeation of butane isomers through stainless-steel supported MFI membrane SS-5 vs. temperature. Feed is a binary 50/50 kPa *n*-butane/isobutane mixture.

Fig. 5 shows permeation flux data of butane isomers for the stainless-steel supported membrane SS-5 as a function of temperature for a 50/50 kPa *n*-butane/isobutane binary mixture. The flux of *n*-butane shows a maximum at ∼130°C, while the flux of isobutane increases monotonically up to 200°C, and the separation factor remains high up to about 130°C but drops considerably at higher temperatures. A very similar behavior has been observed with MFI membranes prepared on α-alumina tubes (not shown here) and previously on α-alumina disks [19,21,25] and can be generally described by the interplay and the relative temperature dependence of diffusion and adsorption of the permeating molecules through MFI.

4. Conclusions

Zeolite MFI membranes with thickness 15–20 μm were successfully prepared on tubular α-alumina and stainless-steel supports by the secondary (seeded) growth technique. The membranes exhibited *n*-butane/isobutane mixture ratios in the range 15–30 and 30–50 for stainless-steel and α-alumina supports membranes, respectively. The dependence of the permeation flux of butane isomers on temperature and feed partial pressure was found consistent with previously published results of MFI membranes made on disks by the same technique. The results indicate that the seeded growth technique has potential for successful scale-up of zeolite membranes if optimized conditions and strict procedures are employed.

Acknowledgements

Financial support for this work was provided by Amoco Corporation, the National Science Foundation (CAREER, CTS-9624613), the David & Lucile Packard and the Henry and Camille Dreyfus Foundations. We are grateful to Dr. Ruth Ann Doyle of Amoco Corporation for providing the tubular NGK supports for MFI membrane synthesis. Maria Pilar Bernal acknowledges partial support from DGICYT, Spain, Project QUI97-1085.

References

[1] M.E. Davis, Zeolites and molecular sieves: not just ordinary catalysts, Ind. Eng. Chem. Res. 30 (1991) 1675.

[2] H.H. Funke, A.M. Argo, J.L. Falconer, R.D. Noble, Separation of cyclic, branched and linear hydrocarbon mixtures through silicalite membranes, Ind. Eng. Chem. Res. 36 (1997) 137.

[3] K. Kusakabe, T. Kuroda, K. Uchino, Y. Hasegawa, S. Morooka, Gas permeation properties of ion-exchanged Faujasite-type zeolite membranes, AIChE J. 45 (1999) 1220.

[4] Y. Yan, M.E. Davis, G.R. Gavalas, Preparation of zeolite ZSM-5 membranes by in situ crystallization on porous α-Al_2O_3, Ind. Eng. Chem. Res. 34 (1995) 1652.

[5] M.C. Lovallo, M. Tsapatsis, Preferentially oriented submicron silicalite membranes, AIChE J. 42 (1996) 3020.

[6] M.C. Lovallo, A. Gouzinis, M. Tsapatsis, Synthesis and characterization of oriented MFI membranes prepared by secondary growth, AIChE J. 44 (1998) 1903.

[7] R. Lai, G.R. Gavalas, Surface seeding in ZSM-5 membrane preparation, Ind. Eng. Chem. Res. 37 (1998) 4275.

[8] J. Hedlund, M. Noack, P. Kolsch, D. Creaser, J. Caro, J. Sterte, ZSM-5 membranes synthesized without organic templates using a seeding technique, J. Membr. Sci. 159 (1999) 263.

[9] W.F. Lai, H.W. Deckman, J.A. McHenry, J.P. Verduijn, Supported zeolite membranes with controlled crystal width and preferred orientation grown on a growth enhancing layer, US Patent 5,871,650 (1999).

[10] H.H. Funke, M.G. Kovalchick, J.L. Falconer, R.D. Noble, Separation of hydrocarbon isomer vapors with silicalite zeolite membranes, Ind. Eng. Chem. Res. 35 (1996) 1575.

[11] E.R. Geus, Preparation and characterization of composite inorganic zeolite membranes with molecular sieve properties, Ph.D. Dissertation, Delft University of Technology, The Netherlands, 1993.

[12] J. Coronas, J.L. Falconer, R.D. Noble, Characterization and permeation properties of ZSM-5 tubular membranes, AIChE J. 43 (1997) 1797.

[13] Z.A.E.P. Vroon, K. Keizer, A.J. Burggraaf, H. Verweij, Preparation and characterization of thin zeolite MFI membranes on porous supports, J. Membr. Sci. 144 (1998) 65.

[14] G. Xomeritakis, M. Tsapatsis, Permeation of aromatic isomer vapors through oriented MFI-type membranes made by secondary growth, Chem. Mater. 11 (1999) 875.

[15] E.R. Geus, H. van Bekkum, W.J.W. Bakker, J.A. Moulijn, High-temperature stainless steel supported zeolite (MFI) membranes: preparation, module construction and permeation experiments, Micropor. Mater. 1 (1993) 131.

[16] K. Kusakabe, S. Yoneshige, A. Murata, S. Morooka, Morphology and gas permeance of ZSM-5-type zeolite membrane formed on a porous α-alumina support tube, J. Membr. Sci. 116 (1996) 39.

[17] Y. Yan, M.E. Davis, G.R. Gavalas, Preparation of highly selective zeolite ZSM-5 membranes by a post-synthetic coking treatment, J. Membr. Sci. 123 (1997) 95.

[18] K. Keizer, A.J. Burggraaf, Z.A.E.P. Vroon, H. Verweij, Two component permeation through thin zeolite MFI membranes, J. Membr. Sci. 147 (1998) 159.

[19] J. Coronas, R.D. Noble, J.L. Falconer, Separations of C_4 and C_6 isomers in ZSM-5 tubular membranes, Ind. Eng. Chem. Res. 37 (1998) 166.

[20] G. Xomeritakis, A. Gouzinis, S. Nair, T. Okubo, M. He, R. Overney, M. Tsapatsis, Growth, microstructure and permeation properties of supported zeolite (MFI) films and membranes prepared by secondary growth, Chem. Eng. Sci. 54 (1999) 3521.

[21] G. Xomeritakis, S. Nair, M. Tsapatsis, Transport properties of alumina supported MFI membranes made by secondary (seeded) growth, Micropor. Mesopor. Mater. 38 (2000) 61.

[22] A. Gouzinis, M. Tsapatsis, On the preferred orientation and microstructural manipulation of molecular sieve films prepared by secondary growth, Chem. Mater. 10 (1998) 2497.

[23] A.J. Burggraaf, Z.A.E.P. Vroon, K. Keizer, H. Verweij, Permeation of single gases in thin zeolite MFI membranes, J. Membr. Sci. 144 (1998) 77.

[24] W. Zhu, J.M. van de Graaf, L.J.P. van den Broeke, F. Kapteijn, J.A. Moulijn, TEOM: a unique technique for measuring adsorption properties: light alkanes in silicalite-1, Ind. Eng. Chem. Res. 37 (1998) 1934.

[25] Z.A.E.P. Vroon, K. Keizer, M.J. Gilde, H. Verweij, A.J. Burggraaf, Transport properties of alkanes through ceramic thin zeolite MFI membranes, J. Membr. Sci. 113 (1996) 293.