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MFI型沸石分子筛膜在膜分离领域的应用

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摘 要

分离技术作为化工生产过程中的基本操作单元，为现代工业提供了大量的净化产品。分子筛膜的制备与使用已逐渐发展起来，已是当今薄膜科技发展的热点。MFI是目前研究最广泛和最成熟的一种分子筛，具有独特的孔道结构，不同取向的MFI沸石分子筛膜具有不同的分离效果。MFI分子筛膜已逐步应用于工业中各领域的分离中。本文总结了近年来用于MFI型分子筛膜在膜分离领域的应用，主要从不同的分离原料对其分离性能进行了分析。最后，对MFI型分子筛膜的发展前景做出了展望。

关键词

分子筛膜，膜分离，MFI型沸石

Application of MFI Type Zeolite Molecular Sieve Membrane in the Field of Membrane Separation

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Abstract

Separation technology, as a basic operating unit in the chemical production process, provides a large number of purification products for modern industry. The preparation and use of molecular sieve membranes has been gradually developed, has been a hot spot in the development of thin film technology today. MFI is currently the most widely studied and matured molecular sieve, with a unique pore structure, and different orientation of MFI zeolite molecular sieve membrane shave has different separation effects. MFI molecular sieve membranes have been gradually applied in

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the separation of various fields in industry. This paper summarizes the application of MFI molecular sieve membranes for membrane separation in recent years, mainly from different separation materials to analyze their separation performance. Finally, the prospect of the development of MFI type zeolite molecular sieve membrane is made.

Keywords

Molecular Sieve Membrane, Membrane Separation, MFI Zeolite

1. 引言

分子筛为一种水合铝硅晶体，其具有规则的孔道结构，它独特的化学性质和物理性质决定了它在催化、吸附、择形和离子交换等方面的优良性能[1] [2]。分子筛晶体间的交互作用和生长特征为分子筛膜的制备提供了基础，分子筛膜的研究扩大了分子筛的应用范围，如膜分离、膜反应器等[3]。从二十世纪九十年代开始，分子筛膜的制备与使用已逐渐发展起来，已是当今薄膜科技发展的热点[4]。分子筛有多种种类，按其骨架构造分类，迄今为止已有两百多种。MFI 是目前研究最广泛和最成熟的一种分子筛[5] [6]。根据其组成元素，MFI 型分子筛膜可分为 Silicalite-1 型、ZSM-5 型、TS-1 型分子筛膜。Silicalite-1 分子筛膜没有催化活性中心，通常用于混合物的分离；ZSM-5 膜具有酸性中心，TS-1 膜具有四配位的钛氧化中心；因此，ZSM-5 和 TS-1 膜可用于有机化合物的催化反应[7] [8]。本文主要讨论 Silicalite-1 型分子筛膜的分离。

MFI 型分子筛具有独特的孔道结构，平行于 a 轴的正弦通道(0.51 × 0.55 nm，截面近似圆形)和平行于 b 轴的直线通道(0.53 × 0.56 nm，截面近似椭圆)，平行于 c 轴的一条曲折的路径[9] [10]。沸石合成溶液一般包含：二氧化硅源、铝源、结构导向剂(SDA)、碱和水[11] [12]。一项研究表明，当选用四丙基氢氧化铵(TPAOH)为 SDA 时，制备出的 MFI 型分子筛颗粒具有明显的棺材状，即沿 c 轴的尺寸始终较长，沿 b 轴较短，面厚比高($L_c > L_a > L_b$) [13]。改变沸石分子筛膜的制备方式可制取不同取向的膜层，不同取向的 MFI 分子筛膜的传质路径和效率存在很大差异[14]。

在分离领域，渗透系数(膜通量)和分离因子是衡量沸石膜性能的指标。一般情况下，膜的渗透系数和分离因子越高，膜的性能越好。对混合物的分离过程中，膜层对物料的传质效率要求较高，若能使物料迅速穿过沸石薄膜的孔道，就可以大大地改善其渗透系数[9]。不同取向可带来不同的分离因子。所以，对 MFI 型沸石分子筛膜的取向进行有效的调控是十分必要的。

本文总结近年来 MFI 型沸石膜对混合物的分离应用，并分析了其面临的挑战及发展前景。

2. MFI 型沸石分子筛膜在膜分离领域的应用

2.1. 小分子气体分离

在小分子气体的分离中，由于分子筛的孔径比其粒径要大，因此在分子筛孔道中的吸附能也有很大差异，小分子气体是通过吸附与扩散来实现分离的[15] [16] [17]。在高温条件下，气体分子与薄膜间的交互作用减小，吸附作用减小，在分子筛孔道内，不同粒径的分子的扩散速度存在着一定的差异，此时分

离是由扩散来实现的。例如，MFI 分子筛膜在 H_2/N_2 [18]、O_2/N_2 [19]、H_2/CH_4 [20]等不同的体系中，都可以通过改变分离环境的条件进行高效的分离。

b 取向的沸石膜可用来将 CO_2 的混合气分离开。Zhou 等人利用所制得的 *b* 取向 silicalite-1 沸石薄膜将 CO_2/H_2 的混合物分开[21]。在-35 摄氏度时，CO_2/H_2 的分离因子为 109，CO_2 的渗透速度为 51,000 $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$，并且 *b* 取向沸石膜的分离效果远比随机取向沸石膜好得多。Korelskiy 等利用 b 取向沸石薄膜将 CO_2/CO 的混合气分开[22]。在−15~30 摄氏度之间，CO_2 的渗透速率随着温度的下降而增加，在−15 摄氏度时 CO_2/CO 的分离因子最大，达到了大约 26。Wang 等人利用 *b* 取向沸石薄膜对 CO_2/Xe 进行了分离[23]。在 25~200 摄氏度的温度下，渗透速率和分离因子都十分稳定，CO_2 的渗透速率为 1213 GPU，CO_2/Xe 的分离因子约为 5.6。

2.2. 液体分离

在液体分离领域，MFI 型沸石膜也有广泛的应用，可用于将极性较大的醇与极性较小的有机物或水分离。MFI 型沸石膜通常用于乙醇/水混合物分离[24] [25] [26] [27]。Zhao 等人制备的 Fe-silicalite-1 膜在 5 摄氏度下分离 5wt%乙醇/水混合物，总通量约为 3.5 $kg \cdot m^{-2} \cdot h^{-1}$，分离因子约为 40 [28]。Elyassi 等人研究了不同条件下制备的膜在 60 摄氏度下分离 5wt%乙醇/水混合物的性能，其中最好的膜表现出 85 的分离因子和 3.5 $kg \cdot m^{-2} h^{-1}$ 的总通量[29]。表 1 列出了文献中 MFI 型沸石分子筛对乙醇/水混合物的渗透蒸发(PV)性能。

MFI 型沸石分子筛的拓扑结构在脱盐中也是适用的，它具有比各种水合离子更小的孔道尺寸(大约 5.5Å) [30] [31] [32]。Li 与同事在 2004 年将 Silicalite-1 薄膜用于反渗透海水的脱盐工艺中。采用 0.1 M 的氯化钠水溶液为原料，得到了 0.112 $kg \cdot m^{-2} h^{-1}$ 的通量和 76.7%的排盐率[32]。同时，他们注意到，尺寸、扩散性和离子电荷都会对膜的水通量和离子排斥产生作用[33]。Zhou 等人通过在多孔载体上擦除沸石粉末获得晶种层，再经过二次生长获得的 MFI 型沸石分子筛膜可对含盐的化工废水进行反渗透，在 70 bar 压力差为下，获得了 4.0 $L \cdot m^{-2} \cdot h^{-1}$ 的通量和 80%的排盐率[34]。同时，还研究了这种薄膜对氯的耐受性，可以利用氯来清除残余有机物。MFI 型沸石分子筛膜用于脱盐虽然已有一定的研究价值，但是其制备方法的可重现性，以及大规模的工业化生产是两大难题。

Table 1. The pervaporation (PV) performances of zeolite MFI membranes for ethanol/water mixtures
表 1. MFI 型沸石分子筛膜对乙醇/水混合物的渗透蒸发(PV)性能

编号	测试条件		流量($kg \cdot m^{-2} \cdot h^{-1}$)	分离因子	参考文献
	进料(wt%)	温度(K)			
M_1	5	333	0.93	106	[35]
M_2	5	348	1.36	58	[36]
M_3	5	333	1.81	89	[37]
M_4	5	333	1.38	45	[38]
M_5	10	333	2.55	72	[39]
M_6	5	333	2.85	60	[27]
M_7	10	323	0.85	52	[40]
M_8	5	333	1.22	88	[41]
M_9	4	303	0.1	24	[42]
M_{10}	4	333	0.76	58	[42]

2.3. 同分异构体分离

分级法是根据组分的分子量来分离混合物。分离异构体的原理与此不同，由于沸石膜对分子大小敏感，异构体的分离是根据吸附和扩散的性质及沸石的分子筛分效应。由于对/邻二甲苯的动力学直径(动态直径分别为 5.8 Å 和 6.8 Å)和正/异丁烷异构体的动力学直径(动态直径分别为 4.7 Å 和 5.3 Å)与 MFI 型沸石分子筛膜的孔径大小相似，因此常选用对/邻二甲苯和正/异丁烷异构体以测试 MFI 型沸石分子筛膜的分离性能[43]-[48]。

Tsapatsis 课题组[13]在对/邻二甲苯中的分离中比较了四种不同取向(*b*, *a*&*b*, *h0h*, *c*)的沸石膜的分离性能。在 100 摄氏度下，*c* 与 *h0h* 取向的膜的对二甲苯通量在 300 × 10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1} 数量级，而 *a*&*b* 与 *b* 取向膜表示出了高通量，对二甲苯通量在 3000 × 10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1} 数量级。同时，*h0h* 和 *b* 取向的分离因子有大约 20~80。而 *c* 与 *a*&*b* 取向的分离因子只有大约 2~3。Yoon 课题组制备了一种超高分离因子的 *b* 取向沸石膜，分离因子高达 1000，远高于其他沸石膜[49]。表 2 列出了不同取向的 MFI 型分子筛膜及相应的邻/对二甲苯的分离性能。

由于薄膜中存在的晶界缺陷或裂缝，会使渗透分子不能进行选择性的传递，从而使其分离的效果下降。这种非选择性的传输通道一般是由于除去模板剂的高温焙烧过程中产生的热应力导致的。为减小由于高温焙烧造成的膜层缺陷，Choi 等人研制出 RTP 工艺(使薄膜在 1 分钟之内迅速升温至 700 摄氏度，随后在该温度下保持 0.5~2 分钟) [50]。迅速升温会导致相邻近的晶种颗粒间的 Si-OH 基发生凝聚，并在消除 SDA 引起的面内拉应力之前，增强晶种颗粒之间的结合。传统焙烧手段获得的沸石膜选择因子只有 4；在常规焙烧前通过 RTP 处理了 *c* 取向的 10 μm 厚沸石膜，分离因子达到了 128，证明 RTP 工艺可以在减少焙烧过程中膜层的缺陷以达到二甲苯异构体分离效果的显著改善。Yoo 等人通过 RTP 处理沸石膜，得到了 123~139 分离因子的高质量膜层，对正丁烷的通量达到 2.6 × 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} [5]。因此，将 RTP 技术引入亚微米膜的处理过程中有两项优点，一是大大缩短了烧制时间；二是可以防止晶界缺陷和裂纹的形成，获得高质量的选择性膜。

Table 2. Zeolite MFI membrane with different orientations and their *p*-xylene/*o*-xylene separation performances
表 2. 不同取向的 MFI 型分子筛膜及相应的邻/对二甲苯的分离性能

取向	对二甲苯通量(10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1})	分离因子	参考文献
随机	60	3	[51]
随机/h0h	26 ± 4	123~139	[5]
h0h	1.75	278	[52]
b	24.6	378	[53]
b	19.6	483	[13]
b	21	~1000	[50]
c	4.8	126	[6]

3. 挑战及展望

分离被视为工业过程的关键技术[54]。在可持续发展的背景下，减少能源消耗和污染物排放的替代分离技术越来越受到关注，这些技术在很大程度上依赖于材料[55]。分子尺度上有序的微孔结构赋予了分子筛处理小分子的宝贵特性和巨大的分子分离潜力。近年来，分子筛膜在气体净化、空气分离等领域得到了广泛的运用，同时，在极具挑战性的苯衍生物的分离中也具希望。沸石分子筛的膜分离技术，是目前

国内外具有工业前景的领域之一。

虽然目前已有很大的进展，但是关于分子筛的研究仍然有很多问题。分子筛膜的应用，其核心问题是怎样形成一个高品质的分子筛膜。理论上，沸石薄膜应该是没有缺陷的，以便最大程度地发挥其分离价值。但是，在开发具有重现性的、绿色的、经济的膜操作过程中，仍然存在着很大的困难。取向分子筛薄膜要达到工业化生产要求，必须具备优秀的机械强度和长时间工作稳定性。另外，沸石膜的大尺寸制备也提出了新的挑战。还有许多问题有待进一步的研究，包括：减少载体的成本、在粗糙或有曲度载体上制备有取向的沸石膜等。

参考文献

[1] Na, K., *et al*. (2011) Directing Zeolite Structures into Hierarchically Nanoporous Architectures. *Science*, **333**, 328-332. https://doi.org/10.1126/science.1204452

[2] Saha, D., Bao, Z., Jia, F. and Deng, S. (2010) Adsorption of CO_2, CH_4, N_2O, and N2 on MOF-5, MOF-177, and Zeolite 5A. *Environmental Science & Technology*, **44**, 1820-1826. https://doi.org/10.1021/es9032309

[3] Wang, S. and Peng, Y. (2010) Natural Zeolites as Effective Adsorbents in Water and Wastewater Treatment. *Chemical Engineering Journal*, **156**, 11-24. https://doi.org/10.1016/j.cej.2009.10.029

[4] Lu, X., Yang, Y., Zhang, J., Yan, Y. and Wang, Z. (2019) Solvent-Free Secondary Growth of Highly *b*-Oriented MFI Zeolite Films from Anhydrous Synthetic Powder. *Journal of the American Chemical Society*, **141**, 2916-2919. https://doi.org/10.1021/jacs.9b00018

[5] Yoo, W.C., Stoeger, J.A., Lee, P.-S., Tsapatsis, M. and Stein, A. (2010) High-Performance Randomly Oriented Zeolite Membranes Using Brittle Seeds and Rapid Thermal Processing. *Angewandte Chemie International Edition*, **49**, 8699-8703. https://doi.org/10.1002/anie.201004029

[6] Pham, T.C.T., Nguyen, T.H. and Yoon, K.B. (2013) Gel-Free Secondary Growth of Uniformly Oriented Silica MFI Zeolite Films and Application for Xylene Separation. *Angewandte Chemie International Edition*, **52**, 8693-8698. https://doi.org/10.1002/anie.201301766

[7] Wang, X., Zhang, B.Q., Liu, X.F. and Lin, J.Y.S. (2006) Synthesis of *b*-Oriented TS-1 Films on Chitosan-Modified α-Al_2O_3 Substrates. *Advanced Materials*, **18**, 3261-3265. https://doi.org/10.1002/adma.200502772

[8] Ji, M., Liu, G., Wang, L. and Zhang, X. (2014) Controllable Fabrication and Catalytic Activity of Highly *b*-Oriented HZSM-5 Coatings. *AIChE Journal*, **60**, 1964-1968. https://doi.org/10.1002/aic.14464

[9] Li, Y., Zhu, G., Wang, Y., Chai, Y. and Liu, C. (2021) Preparation, Mechanism and Applications of Oriented MFI Zeolite Membranes: A Review. *Microporous and Mesoporous Materials*, **312**, Article ID: 110790. https://doi.org/10.1016/j.micromeso.2020.110790

[10] Ueno, K., *et al*. (2019) Effects of Seed Crystal Type on the Growth and Microstructures of Silicalite-1 Membranes on Tubular Silica Supports via Gel-Free Steam-Assisted Conversion. *Microporous and Mesoporous Materials*, **289**, Article ID: 109645. https://doi.org/10.1016/j.micromeso.2019.109645

[11] Geus, E.R., Den Exter, M.J. and Van Bekkum, H. (1992) Synthesis and Characterization of Zeolite (MFI) Membranes on Porous Ceramic Supports. *Journal of the Chemical Society Faraday Transactions*, **88**, 3101-3109. https://doi.org/10.1039/ft9928803101

[12] 李良清. 无模板剂制备 MOR 和 ZSM-5 沸石膜及其渗透蒸发脱水应用研究[D]: [硕士学位论文]. 大连: 大连理工大学, 2016.

[13] Lai, Z., *et al*. (2003) Microstructural Optimization of a Zeolite Membrane for Organic Vapor Separation. *Science*, **300**, 456-460. https://doi.org/10.1126/science.1082169

[14] Lu, X., Wang, H., Yang, Y. and Wang, Z. (2022) Microstructural Manipulation of MFI-Type Zeolite Films/Membranes: Current Status and Perspectives. *Journal of Membrane Science*, **662,** Article ID: 120931. https://doi.org/10.1016/j.memsci.2022.120931

[15] Gin, D.L. and Noble, R.D. (2011) Designing the Next Generation of Chemical Separation Membranes. *Science*, **332**, 674-676. https://doi.org/10.1126/science.1203771

[16] Pandey, P. and Chauhan, R.S. (2001) Membranes for Gas Separation. *Progress in Polymer Science*, **26**, 853-893. https://doi.org/10.1016/S0079-6700(01)00009-0

[17] 王婷. 二维卟啉基共价有机骨架及其膜材料的制备与气体分离性能研究[D]: [硕士学位论文]. 长春: 吉林大学, 2021.

[18] Masuda, T., *et al*. (2021) Modification of Pore Size of MFI-Type Zeolite by Catalytic Cracking of Silane and Application to Preparation of H_2-Separating Zeolite Membrane. *Microporous and Mesoporous Materials*, **48**, 239-245. https://doi.org/10.1016/S1387-1811(01)00358-4

[19] Naskar, M.K., Kundu, D. and Chatterjee, M. (2011) Understanding the Role of Process Parameters on the Preparation of Silicalite-1 Zeolite Seed Crystals and Thin Films. *International Journal of Applied Ceramic Technology*, **8**, 1163-1172. https://doi.org/10.1111/j.1744-7402.2010.02551.x

[20] Dong, J., Lin, Y.S. and Liu, W. (2000) Multicomponent Hydrogen/hydrocarbon Separation by MFI-Type Zeolite Membranes. *AIChE Journal*, **46**, 1957-1966. https://doi.org/10.1002/aic.690461008

[21] Zhou, M., Korelskiy, D., Ye, P., Grahn, M. and Hedlund, J. (2014) A Uniformly Oriented MFI Membrane for Improved CO_2 Separation. *Angewandte Chemie International Edition*, **53**, 3492-3495. https://doi.org/10.1002/anie.201311324

[22] Korelskiy, D., Grahn, M., Ye, P., Zhou, M. and Hedlund, J. (2016) A Study of CO_2/CO Separation by Sub-Micron *b*-Oriented MFI Membranes. *RSC Advances*, **6**, 65475-65482. https://doi.org/10.1039/C6RA14544B

[23] Wang, X., *et al*. (2018) One-Pot Synthesis of High-Flux *b*-Oriented MFI Zeolite Membranes for Xe Recovery. *ACS Applied Materials and Interfaces*, **10**, 33574-33580. https://doi.org/10.1021/acsami.8b12613

[24] Chai, L., *et al*. (2015) Pervaporation Separation of Ethanol-Water Mixtures through B-ZSM-11 Zeolite Membranes on Macroporous Supports. *Journal of Membrane Science*, **491**, 168-175. https://doi.org/10.1016/j.memsci.2015.01.054

[25] Lan, J., *et al*. (2020) Synthesis of Ethanol Perm-Selective MFI Zeolite Membranes by Binary Structure Directing Agents. *Journal of Membrane Science*, **598**, Article ID: 117647. https://doi.org/10.1016/j.memsci.2019.117647

[26] Zou, X., *et al*. (2012) Ethanol Recovery from Water Using Silicalite-1 Membrane: An Operando Infrared Spectroscopic Study. *ChemPlusChem*, **77**, 437-444. https://doi.org/10.1002/cplu.201200048

[27] Zhang, X., Zhu, M., Zhou, R., Chen, X. and Kita, H. (2011) Synthesis of Silicalite-1 Membranes with High Ethanol Permeation in Ultradilute Solution Containing Fluoride. *Separation and Purification Technology*, **81**, 480-484. https://doi.org/10.1016/j.seppur.2011.08.009

[28] Zhao, C., Liu, X. and Zhang, B. (2016) Submicrometer-Thick *b*-Oriented Fe-Silicalite-1 Membranes: Microwave-Assisted Fabrication and Pervaporation Performances. *RSC Advances*, **6**, 108265-108269. https://doi.org/10.1039/C6RA23327A

[29] Elyassi, B., *et al*. (2016) Ethanol/Water Mixture Pervaporation Performance of *b*-Oriented Silicalite-1 Membranes Made by Gel-Free Secondary Growth. *AIChE Journal*, **62**, 556-563. https://doi.org/10.1002/aic.15124

[30] Kazemimoghadam, M. and Mohammadi, T. (2007) Synthesis of MFI Zeolite Membranes for Water Desalination. *Desalination*, **206**, 547-553. https://doi.org/10.1016/j.desal.2006.04.063

[31] Li, L., Liu, N., McPherson, B. and Lee, R. (2007) Enhanced Water Permeation of Reverse Osmosis through MFI-Type Zeolite Membranes with High Aluminum Contents. *Industrial & Engineering Chemistry Research*, **46**, 1584-1589. https://doi.org/10.1021/ie0612818

[32] Li, L., Dong, J., Nenoff, T.M. and Lee, R. (2004) Desalination by Reverse Osmosis Using MFI Zeolite Membranes. *Journal of Membrane Science*, **243**, 401-404. https://doi.org/10.1016/j.memsci.2004.06.045

[33] Lia, L., Dong, J., Nenoff, T.M. and Lee, R. (2004) Reverse Osmosis of Ionic Aqueous Solutions on a MFI Zeolite Membrane. *Desalination*, **170**, 309-316. https://doi.org/10.1016/j.desal.2004.02.102

[34] Zhu, B., *et al*. (2015) Application of Robust MFI-Type Zeolite Membrane for Desalination of Saline Wastewater. *Journal of Membrane Science*, **475**, 167-174. https://doi.org/10.1016/j.memsci.2014.09.058

[35] Lin, X., Chen, X., Kita, H. and Okamoto, K. (2003) Synthesis of Silicalite Tubular Membranes by *in Situ* Crystallization. *AIChE Journal*, **49**, 237-247. https://doi.org/10.1002/aic.690490122

[36] Ma, X., Wu, X., Caro, J. and Huang, A. (2019) Seeding-Free Synthesis of High-Performance MFI Zeolite Membranes on Superhydrophobic Supports Inspired by "Like Grows Like" Principle. *Microporous and Mesoporous Materials*, **288**, Article ID: 109589. https://doi.org/10.1016/j.micromeso.2019.109589

[37] Lin, X., Kita, H. and Okamoto, K.-I. (2001) Silicalite Membrane Preparation, Characterization, and Separation Performance. *Industrial and Engineering Chemistry Research*, **40**, 4069-4078. https://doi.org/10.1021/ie0101947

[38] Shen, D., *et al*. (2011) Synthesis of Silicalite-1 Membrane with Two Silicon Source by Secondary Growth Method and Its Pervaporation Performance. *Separation and Purification Technology*, **76**, 308-315. https://doi.org/10.1016/j.seppur.2010.10.021

[39] Lin, X., Kita, H. and Okamoto, K.-I. (2000) A Novel Method for the Synthesis of High Performance Silicalite Membranes. *Chemical Communications*, No. 19, 1889-1890. https://doi.org/10.1039/b005180m

[40] Ueno, K., Negishi, H., Miyamoto, M., Uemiya, S. and Oumi, Y. (2018) Effect of Si/Al Ratio and Amount of Deposited MFI-Type Seed Crystals on the Separation Performance of Silicalite-1 Membranes for Ethanol/Water Mixtures in the Presence of Succinic Acid. *Microporous and Mesoporous Materials*, **267**, 1-8.

https://doi.org/10.1016/j.micromeso.2018.03.005

[41] Peng, Y., Lu, H., Wang, Z. and Yan, Y. (2014) Microstructural Optimization of MFI-Type Zeolite Membranes for Ethanol-Water Separation. *Journal of Materials Chemistry A*, **2**, 16093-16100. https://doi.org/10.1039/C4TA02837F

[42] Sano, T., Yanagishita, H., Kiyozumi, Y., Mizukami, F. and Haraya, K. (1994) Separation of Ethanol/Water Mixture by Silicalite Membrane on Pervaporation. *Journal of Membrane Science*, **95**, 221-228. https://doi.org/10.1016/0376-7388(94)00120-0

[43] Lee, T., Choi, J. and Tsapatsis, M. (2013) On the Performance of *c*-Oriented MFI Zeolite Membranes Treated by Rapid Thermal Processing. *Journal of Membrane Science*, **436**, 79-89. https://doi.org/10.1016/j.memsci.2013.02.028

[44] Hedlund, J., *et al*. (2002) High-Flux MFI Membranes. *Microporous and Mesoporous Materials*, **52**, 179-189. https://doi.org/10.1016/S1387-1811(02)00316-5

[45] Keizer, K., Burggraaf, A.J., Vroon, Z.A.E.P. and Verweij, H. (1998) Two Component Permeation through Thin Zeolite MFI Membranes. *Journal of Membrane Science*, **147**, 159-172. https://doi.org/10.1016/S0376-7388(98)00133-1

[46] O'Brien-Abraham, J., Kanezashi, M. and Lin, Y.S. (2007) A Comparative Study on Permeation and Mechanical Properties of Random and Oriented MFI-Type Zeolite Membranes. *Microporous and Mesoporous Materials*, **105**, 140-148. https://doi.org/10.1016/j.micromeso.2007.05.045

[47] Agrawal, K.V., *et al*. (2015) Oriented MFI Membranes by Gel-Less Secondary Growth of Sub-100 nm MFI-Nanosheet Seed Layers. *Advance Materials*, **27**, 3243-3249. https://doi.org/10.1002/adma.201405893

[48] Motuzas, J., Julbe, A., Noble, R.D., van der Lee, A. and Beresnevicius, Z.J. (2006) Rapid Synthesis of Oriented Silicalite-1 Membranes by Microwave-Assisted Hydrothermal Treatment. *Microporous and Mesoporous Materials*, **92**, 259-269. https://doi.org/10.1016/j.micromeso.2006.01.014

[49] Choi, J., *et al*. (2009) Grain Boundary Defect Elimination in a Zeolite Membrane by Rapid Thermal Processing. *Science*, **325**, 590-593. https://doi.org/10.1126/science.1176095

[50] Hedlund, J., Jareman, F., Bons, A.-J. and Anthonis, M. (2003) A Masking Technique for High Quality MFI Membranes. *Journal of Membrane Science*, **222**, 163-179. https://doi.org/10.1016/S0376-7388(03)00285-0

[51] Xomeritakis, G., Lai, Z. and Tsapatsis, M. (2001) Separation of Xylene Isomer Vapors with Oriented MFI Membranes Made by Seeded Growth. *Industrial & Engineering Chemistry Research*, **40**, 544-552. https://doi.org/10.1021/ie000613k

[52] Lai, Z., Tsapatsis, M. and Nicolich, J.P. (2004) Siliceous ZSM-5 Membranes by Secondary Growth of *b*-Oriented Seed Layers. *Advanced Functional Materials*, **14**, 716-729. https://doi.org/10.1002/adfm.200400040

[53] Hoang, V.-T. and Kaliaguine, S. (2013) Predictive Models for Mixed-Matrix Membrane Performance: A Review. *Chemical Reviews*, **113**, 4980-5028. https://doi.org/10.1021/cr3003888

[54] Yue, B., *et al*. (2022) Zeolites for Separation: Fundamental and Application. *Journal of Energy Chemistry*, **71**, 288-303. https://doi.org/10.1016/j.jechem.2022.03.035

[55] Bastani, D., Esmaeili, N. and Asadollahi, M. (2013) Polymeric Mixed Matrix Membranes Containing Zeolites as a Filler for Gas Separation Applications: A Review. *Journal of Industrial and Engineering Chemistry*, **19**, 375-393. https://doi.org/10.1016/j.jiec.2012.09.019