

Zeolite based films, membranes and membrane reactors: Progress and prospects

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

The integration of reaction and separation in catalytic membrane reactors has received increasing attention during the past 30 years. The combination promises to deliver more compact and less capital-intensive processes with substantial savings in energy consumption. With the advent of new inorganic materials and processing techniques, there has been renewed interest in exploiting the benefits of membranes in many industrial applications. Zeolite membranes, however, have only recently been considered for *catalytic membrane* reactor applications. Despite the significant recent interest in these types of membranes there are relatively few reports of the application of such membranes in high-temperature catalytic membrane reactor applications. This can be attributed to a number of limitations that still need to be addressed such as the relatively high price of membrane units, the difficulty of controlling the membrane thickness, permeance, high-temperature sealing, reproducibility and the dilemma of upscaling. A number of research efforts, with some degree of success have been directed to finding solutions to the remaining challenges. This review makes a critical assessment of what has been achieved in the past few years in terms of hurdles that still stand in the way of the successful implementation of zeolite membrane reactors in industry. © 2005 Elsevier Inc. All rights reserved.

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1. Introduction

Increasingly stringent market and environmental demands, such as the minimization of energy consumption and ever-greater emphasis on process safety and superior product quality, mandate major revision of plant configurations. The manufacturing of fuel and chemicals has indeed been subject to large technological improvements during the past century. Headway has been made for instance in catalysis, heat integration, product purification

and effluent clean-up. The new millennium, however, still needs further improvements in processes and catalysts as well as novel manufacturing technologies. Membrane reactors are one of such evolving technologies that have huge promise to deliver processes that are more compact, less capital intensive, offer improved conversion for equilibrium limited reactions, allow controlled operation and have substantial savings in energy and resultant costs due to feed/product separation at elevated process temperatures [1].

Although the concept of membrane reactors has already been introduced in the 1950s, it was only with the advent of new inorganic materials and high-temperature membrane systems [2,3] in the last 30 years that considerable growth in the research and development of membrane reactor technology has been achieved. The significant interest in the

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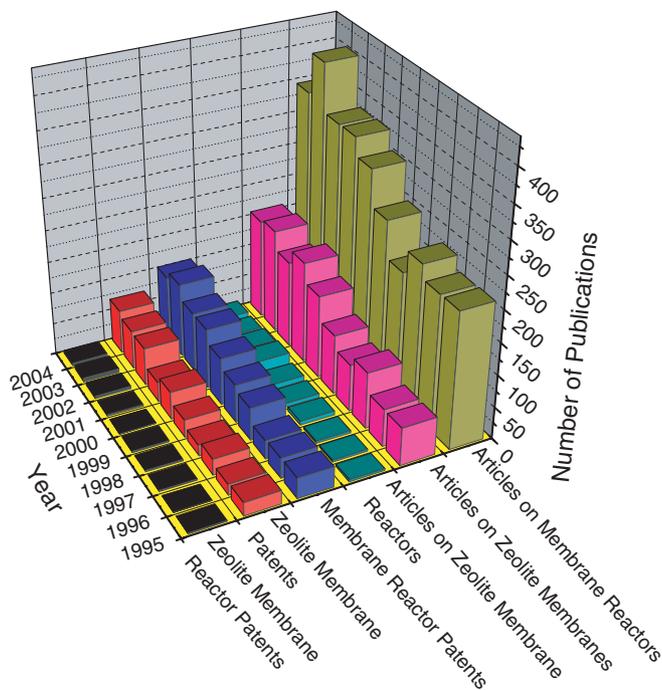


Fig. 1. Scientific publications on membrane reactors and zeolite membrane reactors, respectively (Scifinder search).

field is demonstrated by more than a 100 scientific publications (Fig. 1) on the subject per annum as well as several patents dealing with membrane reactors that have already been filed [4,5].

Most publications highlight the remarkable potential of membrane reactors such as the ability to shift the overall conversion beyond thermodynamic equilibrium by selective product removal, improvement in selectivity by distributed addition of reactants alongside the reactor and safety improvement through controlled reactant contact [6,7] (Table 1).

The clear advantages that exist for the combination of reaction and separation in a single unit and the multitude of possible applications reported in the scientific literature does not negate the fact that challenges remain which limits the large-scale industrial application of catalytic membrane reactors. This is acknowledged by several authors and evidenced by the shortage of commercialized high-temperature membrane reactor based processes (Table 2).

Several review papers have already been published, dealing with different aspects and applications of membrane reactors; Armor and Hsieh has published some of the earliest reviews in the field [2,25] highlighting the advantages as well as the major challenges for inorganic membranes to be used in catalytic devices. Saracco and Specchia [6,26] provided a survey on the reactions which have been performed in catalytic inert membrane reactors employing either dense (metals) or porous (mainly ceramic) membranes and also considered the practical difficulties to the commercialization of membrane reactors. In the more recent past, reviews on the subject were published by Sirkar

et al. [27], Dixon [7], Dalmon [28] and Tsotsis et al. [29–31]. Dittmeyer et al. [32] emphasized the role of palladium in a review on the subject and Noack et al. [33] looked at the developments in inorganic membranes and the implications for their practical application. Hsieh devoted the larger portion of a book to the subject of inorganic membrane reactors [34], while most recently, Marcano and Tsotsis authored a book, encompassing a broad treatment of catalytic membranes and membrane reactors [35].

Due to the multidisciplinary nature of membrane reactor technology, it is impossible to do justice to all aspects of the field in a single review article. It is also not the objective of the author to add to the already extensive list of reviews in the field but rather to focus on the progress made and the road forward to the industrial realization of zeolite-based, catalytic membrane reactors.

2. Zeolites applied in membrane reactor configurations

In zeolite-based membrane reactors the membrane normally consists of a thin film of a mesoporous or microporous zeolite on a macroporous support, typically α - Al_2O_3 , stainless steel or carbon. This thin film may simultaneously serve (i) as both a catalyst and a permselective membrane, (ii) as a permselective diffusion barrier or (iii) as an inert non-selective reactant distributor. Permselectivity depends on the size of the permeating molecules relative to the pore size of the membrane, the chemical nature of the permeating molecules and the membrane material—as well as the adsorption properties of the membrane—in a mixture of components with different adsorption characteristics the stronger adsorbing compound will permeate preferentially [36].

The common modes of application of zeolites in membrane reactors is; as a catalytic membrane reactor (CMR), a packed bed membrane reactor, a catalytic non-permselective membrane reactor, a non-permselective membrane and a reactant-selective packed bed reactor (RSPBR) (illustrated in Table 3). The zeolite-based catalytic membrane reactor generally consists of a supported permselective layer (membrane) that simultaneously acts as catalyst (CMR). The aforementioned catalytic membrane:

- could be inherently catalytic due to the presence of catalytic sites (Brönsted acid sites; Lewis acid sites; metal ions in cationic positions; transition metal ions in zeolite lattice positions; extra-lattice transition metal compounds in channels and cavities of a zeolite, metal particles in zeolite cavities) [4,37,38]. Zhu et al. recently synthesized metal nanoparticles encapsulated in mesoporous silicates as model porous catalysts with the aim to improve reaction selectivity [39].
- could have a separate catalytic and permselective layer. Van der Puil reported a composite hydrogenation catalyst, in which the catalytic phase (TiO_2 -supported platinum) was coated with a thin continuous layer of oriented silicalite crystals, creating separation

Table 1
Applications of membrane reactor processes reported in recent literature

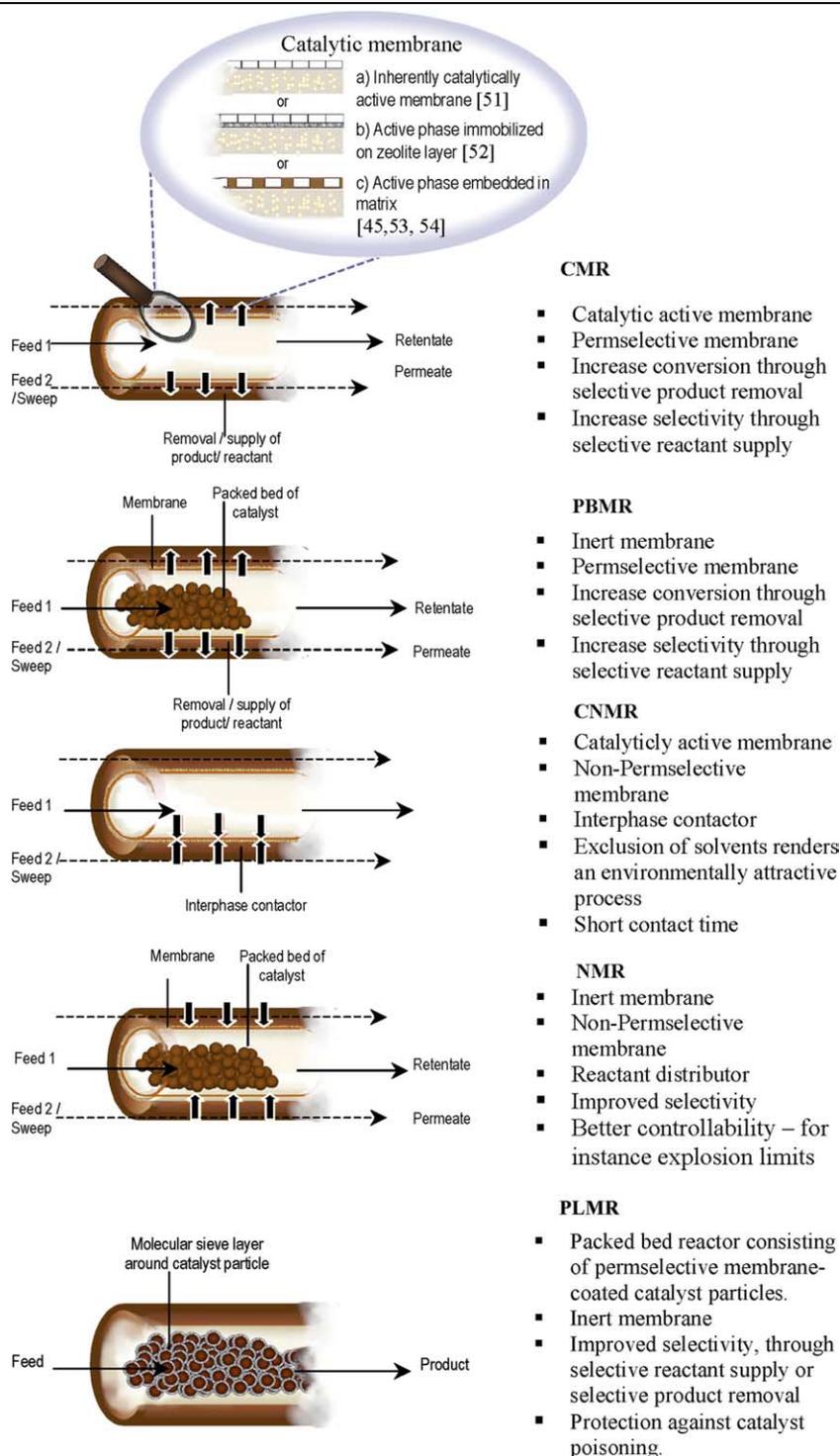
Reaction type	Reaction	Reactor config.	Operating conditions	Membrane	Advantages sought/obtained	Ref.
Dehydrogenation	Methanol oxidative dehydrogenation to formaldehyde	PBMR	200–250 °C Fe–Mo oxide	Non-permselective 316L stainless steel	Increased selectivity and yield due to distributed/controlled reactant addition	[8,9]
	Oxidative dehydrogenation of butane to butadiene	CMR	550 °C V/MgO	Alumina impregnated with MgO	Feed configurations that lead to a low partial pressure of oxygen also give rise to an improved selectivity	[10]
Hydrogenation	CO ₂ hydrogenation to methanol	CMR	210–230 °C Pd	MOR/ZSM-5/ chabazite	Higher CO ₂ conversion and CH ₃ OH selectivity	[11]
Oxidation	Oxidation of alkanes	PBMR	150–450 °C	MFI/Al ₂ O ₃ , SiO ₂ /Al ₂ O ₃ and AlPO ₄ /Al ₂ O ₃	AlPO ₄ membrane was the most efficient for O ₂ distribution	[12]
	Partial oxidation of ethane to syngas	CMR	800–900 °C LiLaNiO/γ-Al ₂ O ₃	Dense ceramic membrane	Ethane conversion of ~100%, the selectivity of CO was higher than 91%	[13]
	Partial oxidation of methane to syngas	PBMR	875 °C LiLaNiO/ γ-Al ₂ O ₃ catalyst	Dense ceramic membrane	94% methane conversion and higher than 95% CO selectivity	[14]
	Partial oxidation of methanol	NMR	Fe–Mo oxide catalyst bed 220–250 °C	316L-SS membrane	Observed increased operational stability	[15]
	Selective oxidation of ethane to ethylene	CMR	825–875 °C	Dense ceramic membrane	Ethylene yield of 56% with ethylene selectivity of 80%	[16]
	Selective oxidation of carbon monoxide	CMR	200–250 °C PtY	Y-type zeolite/ porous α-Al ₂ O ₃	Selective oxidation of CO—the CO conc. on the permeate side decreased below the detection limit	[17]
	Oxidation of benzene to phenol	CMR	<250 °C	Pd on Al ₂ O ₃	Phenol selectivities of 80–97% at benzene conversions of 2–16% below 250 °C; WHSV of 1.5 at 150 °C	[18]
Organic synthesis	Liquid-phase oligomerization of <i>i</i> -butene	PBMR	20 °C acid resin catalyst bed	MFI/SS	Significant increase in the selectivity, and as a consequence also in the yield of <i>i</i> -octenes	[19]
	Esterification between ethanol and acetic acid	CMR	60 °C	Polyetherimide/ γ-Al ₂ O ₃	Almost complete conversion was reached.	[20]
	Metathesis of propene to ethylene and 2-butene	PBMR	Re ₂ O ₇ /γ-Al ₂ O ₃ catalyst, 23 °C	Silicalite-1	Conversion could be increased above equilibrium to 38.4% with a <i>trans</i> -2-butene selectivity of 4.2	[21]

Table 2
Industrial membrane reactor processes

Company	Separation technique	Application	Materials	Ref.
Degussa	Ultra-filtration	Production of enantiomerically pure L-amino acids	Acylase membrane	[22]
Air products/ ceramatec	Ion-conduction	Ion transport membrane syngas process for synthesis gas production to be implemented by 2010	Dense ceramic materials related to inorganic perovskite structures	[23]
Akzo Nobel	Micro-filtration	Polycondensation reaction	Microporous amorphous silica on alumina support, polyvinyl alcohol/nafiol/	[24]

Table 3

Classification of membrane reactor configurations according to membrane function and location [51,52,45,53,54]



selectivity and steric constraints at the zeolite/platinum interface [40].

(c) could have zeolite crystals with catalytic ability embedded in a matrix e.g. polymer membrane or another mesoporous zeolite/ceramic membrane.

Baron et al. recently investigated the use of a polymeric membrane with dispersed zeolite crystals encapsulating immobilized metal-complexes, acting as an interphase contactor during alkene oxidation in a CMR [41].

When the reactor consists of a membrane that is permselective but not catalytic with a conventional catalyst present in the form of a packed bed of pellets/extrudates in the flow stream, it is termed a packed bed membrane reactor (PBMR). Caro et al. reported the application of MFI zeolite membranes in the dehydrogenation of isobutane, for the selective removal of H₂, ultimately resulting in an increase in conversion. The catalytic reaction took place in a catalytic packed bed of Cr₂O₃ on Al₂O₃ spheres on the tube side of the membrane [42]. Although the majority of applications of zeolite membrane reactors reported in literature to date falls into the category of PBMR, more and more researchers are exploring the use of zeolite membranes as catalytically active centers and with different, more adventurous modes of operation. Slood et al. introduced a novel membrane reactor (termed a catalytic nonpermselective membrane reactor, CNMR) for the catalytic oxidation of H₂S to elemental sulfur, in which the membrane is although catalytically active, not permselective, and acts as reaction front, facilitating stoichiometrical feed rates of reactants [43]. When applied to the catalytic reduction of NO_x with NH₃ Slood et al. obtained high conversions of NO_x despite fluctuating reagent concentrations [44]. Wu et al. also later used a composite membrane (titanium silicalite-1/polydimethylsiloxane) as a catalytic interphase contactor in the two-phase reaction of *n*-hexane oxidation by dilute aqueous hydrogen peroxide [45]. In this reactor, the catalytic membrane was placed at the interface between the H₂O₂ aqueous phase and the *n*-hexane vapor phase. The two reactants, H₂O₂ and *n*-hexane, reach the catalyst surface by diffusion through the membrane, thereafter reacting with each other. After their formation, the products diffuse out of the membrane. An additional advantage of using such a membrane interphase contactor is that it avoids the use of co-solvent at industrial scale. In a non-permselective membrane reactor (NMR) the membrane does not have any catalytic activity, nor does it have permselectivity, it simply acts as a distributor of the reactant. Guizard and co-workers investigated the partial oxidation of alkanes in a membrane reactor where the membrane (MFI) acts as a O₂ distributor, allowing improved selectivity and preventing reaction run-away [12]. Increasing attention is being paid to particle-level membrane reactors (PLMR) which consists of catalyst particles coated with a permselective membrane layer allowing the selective addition of reactants to the reaction zone or the selective removal of products from the reaction zone when one product's diffusivity is much higher than those of the other products. The main benefit arising from this configuration is the increased membrane area per unit reactor volume compared to that of conventional membrane reactors. This is highly advantageous considering the difficulty to achieve a large membrane area with the absence of defects. Nishiyama et al. prepared a silica–alumina catalyst coated with a silicalite membrane and applied it to toluene disproportionation. Good selectivity for the *p*-xylene isomer, due to its selective removal, was achieved [46]. Nishiy-

ama et al. recently demonstrated the viability of membrane coated catalyst particles as a means to achieve selectivity again when they reported the use of spherical Pt/TiO₂ particles coated with a silicalite-1 for the selective hydrogenation of linear and branched alkenes. The composite silicalite-1/Pt/TiO₂ catalyst showed 1-hexene/3,3-DMB hydrogenation selectivities of 12–20 at 50 °C and 18–30 at 100 °C due to the selective permeation of 1-hexene through the silicalite-1 layer [47].

Marcano and Tsotsis [35], Perez et al. [48,49], Falconer et al. [50] as well as Coronas and Santamaria [49] introduced similar acronyms for ease of reference to the different membrane reactor types.

3. Progress in zeolite membrane synthesis for membrane reactor applications

Polymeric membranes allow both high permselectivity and fast permeation, well-developed technology to produce thin polymeric membranes already exists and are also relatively cheap, yet these membranes have important drawbacks that limit their use in membrane reactors. The shortcomings, namely their limited resistance to temperature, solvents and corrosive environments, limits the application of polymeric membranes to bioreactor and liquid-phase reaction systems [55]. Inorganic membranes, such as ceramics and metals however, do promise significant payoff in chemical processing, owing to their superior characteristics of thermal, mechanical and structural stabilities as well as chemical and solvent resistance. Inorganic membranes also allow regeneration through the oxidative removal of carbonaceous species at 400–500 °C and therefore have longer life expectancies than their polymeric counterparts.

Inorganic membranes can be classified into two types: non-porous (dense) and porous membranes. Dense membranes prepared from palladium or perovskites only allow certain gases (such as H₂ or O₂) to permeate via mechanisms such as solution–diffusion or solid-state ionic conduction. Such non-porous systems exhibit extremely high selectivities but have limited permeabilities, although here, substantial research effort during the last decade have produced fluxes within reach of targets [56]. These membranes further require high capital investment due to the use of precious metals and/or extreme synthesis and operating conditions [57] and may be mechanically unstable [58]. In contrast, microporous silica membranes have proven to be promising for molecular sieving applications. Precise pore size control (0.3–0.4 nm in diameter) to allow for separation on the basis of size by molecular filtration or ‘sieving’ has however not yet been achieved for amorphous inorganic membranes and they are also chemically, mechanically and thermally less robust [59] than zeolite membranes.

Zeolite membranes form one of the newest branches of the inorganic membrane field. Unlike the most microporous metal oxides (e.g., SiO₂, Al₂O₃ and TiO₂) that have

tortuous pore channels, zeolites are microporous aluminosilicate materials that have a well-defined, uniform pore system of molecular dimensions (enabling shape or size selective catalysis or separation) due to their porous crystalline structure. Zeolites are relatively stable at high temperatures, can be acidic or basic in nature and can exhibit hydrophilic or organophilic properties. These molecular sieves can be tailor made for a specific application through ion exchange, dealumination–realumination, isomorphous substitution and insertion of catalytically active guests such as transition-metal ions, complexes, basic alkali metal or metal oxide clusters. The molecular sieving abilities, Fig. 2, and selective sorption properties in combination with their catalytic activity, in addition to their thermal and chemical stability, make zeolites ideally suited for the combination of separation and reaction under process conditions.

Total selectivity, or sieving, results when the size of the pore apertures is similar to the dimensions of the gas molecules. Even the very critical separation of propane–propene is possible in this way [60]. However very high selectivity is also possible with mixtures of gases when the zeolite pore sizes are significantly larger than the molecules, due to adsorption selectivities and/or the differences in diffusivities of the various components in the mixture [61,62].

A great deal of progress in the science of zeolite membrane synthesis has been made since the first preparations of zeolite membranes by Suzuki in 1987 [37] the stand-alone, mechanically unstable membrane by Haag and Tsikoyiannis of Mobil in 1991 [4,63] and the first supported silicalite-1 membrane reported in literature by Geus et al. [64]. Since then there has been an exponential growth in

papers on the subject and literature abounds with reviews on zeolite membranes (van de Graaf et al. [65], Caro et al. [33,66], Tsapatsis et al. [67] and Lin et al. who recently summarized the significant progress made in the synthesis of microporous membranes [68]).

MFI zeolite membranes (silicalite-1, ZSM-5), on flat or tubular supports, have been investigated extensively for application in gas separation, catalytic reactors and pervaporation. Silicalite-1 has for instance been applied in the separation of *n*-hexane from its branched isomers in a hydroisomerization membrane reactor [69]. The linear alkanes are preferentially adsorbed by the zeolite and supplied to a packed bed of catalyst. The control of the feed composition to the reaction resulted in an increased selectivity and conversion. Zeolite A membranes have often been the target of investigations because their small pore size would in principle exclude molecules with a size larger than 4.1 Å thereby opening the field to highly selective separations in the gas and liquid-phases [70]. Other zeolite membranes that have been reported include FAU [71], MOR [72,73], FER [74], GIS(P) [75], SAPO-34 [76], zeolite T [77,78], BEA [51] and mesoporous UTD-1 [79]. The hydrophilic LTA zeolitic membrane has been the first to find industrial application. The first large-scale pervaporation plant, which produces 530 l/h of solvents (EtOH, IPA, MtOH, etc.) at less than 0.2 wt.% of water from 90 wt.% solvent at 120 °C, has been put into industrial operation recently by Mitsui Engineering and Shipbuilding Co. Ltd. [80]. The plant is equipped with 16 modules, each of which consists of 125 pieces of NaA zeolite membrane tubes. The excellent water separation is however based on the strong hydrophilic nature of the LTA membrane and not on molecular sieving [81]. Few reports exist for the

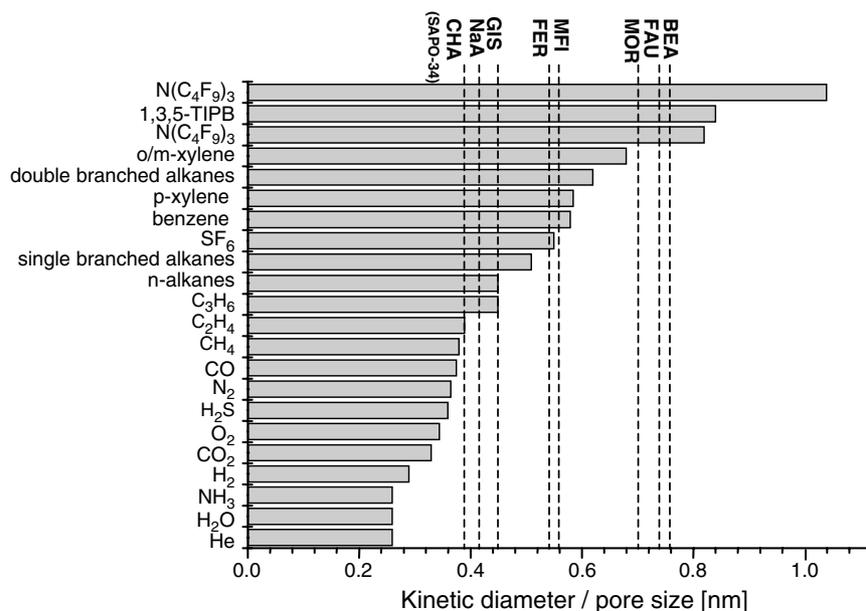


Fig. 2. Comparison between the effective pore sizes of different zeolites and the kinetic diameters of gas molecules featured in reports on zeolite-based membrane reactor applications.

successful application of zeolite A membranes to gas separation. Most authors report selectivities similar to those expected for Knudsen flow through the membrane—an indication of the presence of intercrystalline pores.

Despite the measurable success achieved in supported zeolite membranes during the past decade, few reports on the practical application of such membranes in high-temperature catalytic membrane reactors exist. To some respect this can be contributed to the diminishing interest of industry in novel catalytic and separation materials and processes that provide only moderate performance improvements to established processes. The current economic climate and the fact that material uncertainties and associated development costs rarely counterbalance potential benefits fuel this somewhat discouraging view of industry. However, the lack of implementation of zeolite membrane reactor technology cannot solely be blamed on industrial scepticism. In order to bring zeolite membrane reactors to commercial applications, there are a number of criteria that still have to be met and/or further explored:

1. The synthesis of membranes with high permeability and selectivity, i.e. oriented, thin layers i.e. small effective thicknesses are required which must be highly uniform and free of defects. Optimal membrane reactor operation requires the membrane flux to be in balance with the reaction rate [82].
2. Reproducibility and long-term stability of membrane performance. Coke deposition, triggered to a large extent by the acidic nature of the zeolite framework, necessitates the possibility of repeated membrane regeneration and a technology for repairing defective membranes.
3. “Ultramicroporous” membranes, i.e. those with sufficiently small pores (~ 3 Å) to allow separation on the basis of size exclusion, and without intercrystalline pores. The majority of the membranes synthesized so far are MFI-type zeolite membranes that have pore diameters (~ 5 Å), which are still too big to selectively separate small gaseous molecules.
4. The sealing of the membranes at high-temperatures (>250 °C) and pressures.
5. Scaling-up of membrane modules, requiring the ability to prepare large defect-free membranes at reasonable costs.
6. Cost of membranes and membrane modules.
7. Clarification of multicomponent transport and separation behaviour through zeolitic and non-zeolitic pathways in the membranes at industrially relevant operating conditions.

Recent research efforts have therefore been directed to finding solutions to the above challenges. For this reason the advances made in the field of membrane reactors mirror the advances made in the production of new and improved membranes.

3.1. The synthesis of high-flux, selective membranes

The quality of zeolite membranes is determined by intercrystalline porosity (defects) [83], the crystal orientation relative to the membrane layer [84], size of the crystals [85] and the thickness and uniformity of the zeolite layer [86]. In recent years, several groups have reported preparations of high quality zeolite membranes: MFI [87,88], mordenite [89,90], Y-type [91], A-type [92] and ferrierite [93]. A variety of methods for the fabrication of zeolite thin films exists which includes dip coating, spin coating, sputtering, chemical vapour deposition (CVD) and laser ablation [94]. The three most common methods used to produce membranes for gas separation have been (a) the formation of a composite, by embedding zeolite crystals in a matrix, such as a polymer, (b) in situ crystallization in the presence of a substrate, such as a porous ceramic, to give a supported zeolite membrane and (c) the more recently developed secondary growth process which involves the deposition of colloidal zeolite crystals on a macroporous support followed by hydrothermal synthesis.

Most papers written on zeolite membranes, and most development in the field have been targeted at MFI type molecular sieves. Table 4 gives a summary of recent progress made in the synthesis of silicalite-1 membranes.

In order to control and direct the synthesis of thin, oriented, selective zeolite membranes, crucial to the success of membrane reactors, a fundamental understanding of the mechanism of zeolite crystallization *and* membrane growth needs to be gained. The preparation of zeolite membranes is still often conducted in conditions similar to zeolite powder synthesis, which are not optimized for membrane formation. Finding the proper conditions to prepare a desired zeolite membrane is often largely based on trial and error, limiting the reproducibility of membrane preparation. As a result, substantial effort has recently been put into the elucidation of the mechanism of crystal growth [104] and zeolite film formation [105–107], as well as the role of structure directing agents (SDAs) in the assembly of long-range ordered materials. More importantly the correlation between the mechanism, the membrane synthesis procedure and composition and the resulting zeolite film has been investigated. De Moor et al. [108], using a combination of in situ SAXS, USAXS and WAXS (ultrasmall and wide-angle X-ray scattering), found the nucleation of Si-TPA MFI to be a two-step process: first nutrients must assemble into composite species (~ 2.8 nm). Aggregation of these nanometer-scale primary units to 10–15-nm-sized particles is found to be an essential step in nucleation of the zeolite since it enhances the nucleation rate. By varying the alkalinity, it was found that 2.8 nm particles were always present unlike their aggregates which were not formed at high alkalinities (Si/OH ratio > 2.65) [109]. Although the size of the primary units for MFI was shown to be independent of the structure-directing agent used (a dimer of TPA, a trimer of TPA or trimethylene-bis(*N*-hexyl, *N*-methyl-piperidium)), the organic species does have

Table 4
Overview of synthesis for thin, high flux, oriented silicalite-1 membranes

Ref.	OH ⁻ /Si	Na ⁺ /TPA ⁺	Synthesis temp. (°C)	Synthesis method	Support	Membrane thickness (μm)	Crystal Orientation	Membrane performance
[95]	0.32	0.00	165	In situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 plates	1	<i>b</i> -Oriented	Flux and selectivity not given
[95]	0.50	0.00	165	In situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 plates	0.6	<i>b</i> -Oriented	Flux and selectivity not given
[96]	0.32	0.00	165	In situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 Aluminium alloy	<0.4	<i>b</i> -Oriented	Flux and selectivity not given
[97]	4.23	0.00	175 and 140	Secondary growth of precursor layers with no calcinations step prior to secondary growth	non-porous glass slides	4/7.5/13	Primarily <i>c</i> -oriented/or <i>c</i> -axis tilted by 35°	Flux and selectivity not given
[98]	0.44	1.00	175	Seeded synthesis, by two successive secondary synthesis for 24 h, from clear solution	α-Al ₂ O ₃ disks	25–40	Primarily <i>c</i> -oriented	50% mixture binary para:ortho flux ratio <4 as opposed to almost 40 for the single-component
[84]	0.23	1.00	140/175	Secondary growth procedure consisting of deposition of MFI microcrystals from a colloidal suspension on the substrate to form seed layers, followed by hydrothermal growth of the seed crystals to form a film	α-Al ₂ O ₃ disks and non-porous glass	12–15	<i>c</i> - or [<i>h0h</i>]-out-of-plane	N ₂ :SF ₆ single-component selectivity is 8–10, flux of <i>n</i> -C ₄ H ₁₀ and the <i>n</i> -C ₄ H ₁₀ : <i>i</i> -C ₄ H ₁₀ flux ratio from 50/50 mixtures at 223 °C is in the range 1.5–5.5 × 10 ⁻³ mol m ⁻² s ⁻¹ and 28–62, respectively. <i>N</i> -butane/ <i>i</i> -butane selectivity of 50–90
[99]	4.00	0.00	175	Sol–gel dipcoating of mesoporous silica, followed by the covalent linking of oriented seed layer and secondary growth	α-Al ₂ O ₃ disks	1	<i>a</i> - and <i>b</i> -oriented	<i>o/p</i> -selectivity at 180 °C: 3 <i>p</i> -xylene permeance at 180 °C: 2 × 10 ⁻⁷ mol/m ² s Pa
[99]	4.20	0.00	175	Sol–gel dipcoating of mesoporous silica, followed by the covalent linking of oriented seed layer and secondary growth	α-Al ₂ O ₃ disks	1	Primarily <i>b</i> -oriented	High flux + <i>o/p</i> -xylene selectivity >4
[100]	0.25	0.00	130	Seeded, secondary growth	γ/α-Al ₂ O ₃ disks	2.0	101/002 or <i>c</i> -oriented	Ideal selectivities were 2.59 and 5.24 for He/Ar and He/SF ₆ , He permeance at avg. <i>trans</i> -membrane pressure = 1.20 bar, <i>T</i> = 323 K: 58 cm ³ min ⁻¹ cm ⁻² bar ⁻¹ He permeance at avg. <i>trans</i> -membrane pressure = 1.20 bar, <i>T</i> = 323 K: 2 cm ³ min ⁻¹ cm ⁻² bar ⁻¹
[100]	0.28	10.00	150	Seeded, secondary growth	γ/α-Al ₂ O ₃ disks	3.0	101/002 or <i>c</i> -oriented	Flux and selectivity not given
[101]	0.13	0.00	175	In situ, hydrothermal	Silicon disks		(020) plane parallel to the surface initially	Flux and selectivity not given
[101]	0.25	0.00	125	Charge reversal with 3-mercaptopropyl trimethoxy silane, seeded, secondary growth	Silicon disks	1.1	<i>c</i> -axis nearly normal	Flux and selectivity not given
[102]	4.12	0.00	100	Seeded, secondary growth, hydrothermal	Silicon wafers		<i>b</i> -oriented, however in thick films, most of the crystalline material is <i>a</i> -oriented	Flux and selectivity not given
[103]	4.12	0.00		Seeded, secondary growth, hydrothermal	Silicon wafers	240, 500, 1200 nm	<i>a</i> - and <i>b</i> -oriented	3.2 for 0.27 kPa <i>p</i> -xylene/0.59 kPa <i>o</i> -xylene

a pronounced influence on the crystal growth step and, therefore, on the crystal growth rate, size, and morphology [110]. The suggested growth mechanism agrees with a mechanism proposed earlier by Schoeman et al. [111] essentially the same growth mechanism was also suggested by den Exter et al. [112].

Although most of the earlier molecular sieve membranes prepared were freestanding, the vast majority of zeolite membranes prepared today are supported, owing to their greater structural stability and reduced mass-transfer resistance. Two critical stages can be distinguished during the formation of supported zeolite membranes, namely nucleation on the support followed by crystal growth to form a continuous zeolite film covering the support. Nucleation and crystal growth processes during zeolite membrane synthesis are very sensitive to experimental conditions such as synthesis solution/gel composition (which Wang et al. proved can be manipulated to control the crystal growth orientation [95]), pH, temperature, chemical and structural nature of the support [113], support position [75,114], structure directing agents (SDAs) [99] used to assemble long-range ordered materials and even nutrient sources [115,116].

Synthesis of zeolite membranes or thin films on a support can broadly be classified as either in situ, a one-step hydrothermal synthesis where the support is placed in direct contact with the alkaline precursor solution, or *secondary (seeded) growth* in which an existing zeolite phase (seed crystals), is attached to the support followed by hydrothermal growth of the applied seeds to a continuous layer. In essence both these techniques involve nucleation and crystal growth steps, although nucleation sites are created and applied separately and with more control to the surface of the support during secondary synthesis. Since secondary growth techniques enable improved control of nucleation site location and density, it renders the nature of the support less important for membrane growth with growth proceeding from a layer of seed crystals covering the support [117]. Nevertheless good adherence of the zeolite seed crystals (nucleation sites), as well as the zeolite film to the support is still as important as is the case for in situ synthesis in order to guarantee the mechanical, thermal and chemical stability of the composite membrane.

The above constitutes the main difference between zeolite powder and zeolite membrane synthesis as well as one of the difficulties inherent to the preparation of zeolite membranes, namely the existence of an additional parameter, the substrate and the linking of zeolite crystals to that substrate so as to obtain a continuous thin composite zeolite membrane. Various techniques have been developed to facilitate nucleation and crystal growth on the substrate and to tailor the interaction between the zeolite layer and the substrate.

It has been well established that the quality of the underlying support determines, to a high degree, the quality of the selective membrane layer on top. A thin zeolite film is less likely to adhere in a continuous fashion to a rough

or large-pore substrate, therefore whenever attempting to prepare a supported zeolite membrane; one of the first steps taken is to ensure that the substrate surface is smooth. Smooth porous surfaces for deposition of a zeolite layer could be created in its simplest form by mechanical polishing of the substrate [84,118]. However this method is tedious and repetitive while more importantly, the polishing of tubular support interiors are unfeasible. More recently the deposition of a thin meso-/micro-porous film on the support have been used to create a smooth surface for zeolite film growth. The layer has the additional benefit of serving as a diffusion barrier, preventing the zeolite layer from penetrating the support, which would result in a longer effective diffusion path, whilst also protecting the support against possible leaching [64]. Lai et al. [99] dip-coated an α -alumina support with a mesoporous silica layer according to the method developed by Tsai et al. [119] to improve the surface finish of the substrate for seed crystal deposition. They reported not only an improved flux due to a shorter effective diffusion path, but also increased selectivity partly due to the elimination of stress-induced crack formation during calcinations. A *p*-xylene/*o*-xylene selectivity as high as ~ 400 at a *p*-xylene permeance of 3×10^{-7} mol/(m² s Pa) with an essentially *b*-oriented MFI film of 1 μ m was obtained.

Hedlund et al. [103,120] reported what they termed “a two-step support masking technique” to prevent support invasion and leaching. They applied a coating of PMMA on the surface of the support and plugged the pores of the support with a polyethylene wax. The PMMA layer was removed by rinsing in acetone for a week while the polyethylene wax was later removed during calcination. A monolayer of colloidal nucleation seeds was adsorbed electrostatically on the support, followed by hydrothermal growth, producing a defect-free film, although grain boundaries are still clearly visible, with a thickness of 0.5 μ m. High-pressure xylene separation tests were carried out at 400 °C at 100 kPa hydrocarbon partial pressure (200 kPa total pressure). The *p*-xylene/*m*-xylene selectivity was 13 at a *p*-xylene permeance of 1.1×10^{-7} mol/(m² s Pa).

One of the challenges faced during in situ synthesis is ensuring a high nucleation site density on the support, often giving rise to higher film thickness than desired to close all defects. Techniques that have been used to ensure that nucleation takes place on the support are multitude.

The adherence of the zeolite crystals to the support surface is to a large extent determined by the hydrophilicity of the support surface, e.g. the number of OH-groups per nm². Treatment of the support with NaOH in order to increase the number of surface hydroxyl groups would therefore impart the support with more nucleation points as well as sites where crystals could adhere by means of Van der Waals interactions and H-bonding. Kim et al. reported treatment of the support with trimethylchlorosilane to create Si–Cl bonds on the surface of the support in order to enhance adhesion of a mesoporous layer to

the support [121]. Pretreatment of the support surface by impregnation or spin-coating with the appropriate template was also shown to direct the formation of crystallites on the support. Chau et al. found that a coating of a metal oxide (e.g. Fe_2O_3) on the support surface provided a simple technique to control the number and type of nucleation sites available on the support surface [117]. Their results indicated that there was a direct correlation between the number of nucleation sites and the amount of iron(III)oxide present on the surface of the support and allowed the synthesis of a more complete and uniform zeolite film. Synthesis conditions, such as a highly alkaline synthesis mixture, have also been shown to favor a high nucleation density [118,122]. In a more recent report of Van den Berg et al. UV-radiation was used to increase the number of defect sites and hydroxyl groups to promote the hydrophilicity of a TiO_2 -coated support. The authors reported an increased nucleation and the resultant formation of a uniform, monolithic zeolite A film, well attached to the support [123,124].

Other approaches that rely on limiting/directing nutrient sources or other conditions necessary for synthesis, to the surface of the support have also been examined. Electrophoretic deposition can be used to coat substrates with charged particles from colloidal suspension. Zeolite particles formed during hydrothermal synthesis assume a negative/positive charge due to electrical double layer effects. These charged zeolite particle would be attracted to a support to which an opposite charge is applied. Oonkhanond et al. made use of this principal to attract ZSM-5 particles to the surface of a porous alumina tube in order to obtain a 10–15 μm thick, continuous layer [125]. Mohammadi and Pak synthesized a zeolite A membrane from Kaolin that was electrophoretically deposited on a cylindrical anode and treated hydrothermally [126]. Heating only the support while the rest of the synthesis solution is cooled would rule out nutrient depletion by competing nuclei and crystal growth in the bulk solution and result in crystallization being limited to the support surface. Yamazaki and Tsutsumi used a plate heater to apply heat to the substrate area alone with a static solution, as well as a circulated solution system [127]. In both scenarios zeolite membrane formation was not accompanied by powder formation in the bulk solution. Deposition of films within a substrate can be achieved by using the countercurrent reactor configuration, where each reagent enters from the opposite side of the substrate. This method would effectively eliminate nucleation and growth from occurring outside the support [128]. The vapor phase transfer synthesis method is a variation of the in situ synthesis method, developed by Xu et al. that consists of two steps: covering the support with a synthesis gel and crystallization of the dried gel under autogeneous pressure. Since one of the nutrient sources is limited to the support surface, zeolite membrane formation would also be limited to the support surface [129,130].

Seeded synthesis tends to produce continuous films a lot more readily and with better reproducibility due to better

control over nucleation site density. One of the determining factors for the successful synthesis of a thin, defect-free zeolite film on the support with this two-stage method, is the application of a thin, uniform and continuous layer of seed crystals to the support. The simplest and often used method is to apply seed crystals to the substrate with mechanical rubbing [130,92]. This method is not ideal however since it is quite difficult to obtain a continuous and even seed layer. Several authors applied seed crystals to the support by dipcoating the substrate in a suspension of zeolite particles, followed by drying at room temperature and calcination in order to fix the crystals to the support surface. This process is often repeated a few times in order to ensure a sufficiently high coverage of the support with zeolite seed crystals [84,131,132]. Electrostatic attraction could be used to limit the number of times the dipcoating procedure has to be repeated. This involves charge modification of the substrate surface by adsorption of an anionic or cationic polymer, which would then effect the electrostatic attraction of colloidal zeolite particles in suspension to the surface of the support [115]. The electrostatic deposition process generally achieves a high coverage of the substrate with well-adhered particles and is one of the most-effective techniques developed to date for seed crystal deposition. Electrophoretic deposition (EPD) offers a way to coat a substrate uniformly with a variety of charged particles without the need to pretreat the substrate. Seike et al. [133] prepared a zeolite Y membrane through EPD of NaY zeolite seed crystals on a stainless steel support. Shan et al. [134] were recently able to prepare zeolite films through electrophoretic deposition in a non-aqueous medium, allowing the application of a higher voltage and better control over the thickness and density of the prepared films. The self-assembly of micrometer-sized zeolite crystals on supports via covalent linkers has received increasing attention during the last five years. This method of preparation, although promising for yielding well-oriented monolayers, is however rather complicated and to date no membrane suitable for gas separation has been obtained [135,136]. Other methods that have been investigated for the deposition of oriented monolayers of zeolite seed crystals include Langmuir–Blodgett deposition [137] and pulsed laser ablation [79].

The MFI crystal has an anisotropic two-dimensional channel network consisting of straight channels of elliptical cross-section ($0.51 \times 0.54 \text{ nm}$) along the *b*-direction and sinusoidal channels of nearly circular cross-section (0.54 nm) along the *c*-direction, Fig. 3. Due to the anisotropic nature of this zeolite, the orientation of the crystals will have a significant influence on the molecular sieving performance.

Preferred crystal orientation could impact the molecular sieving and permeation of the zeolite film that are crucial for their application in membrane reactors. Due to the attractive features of oriented thin films, there has been intense effort during the last ~ 5 years to prepare zeolite

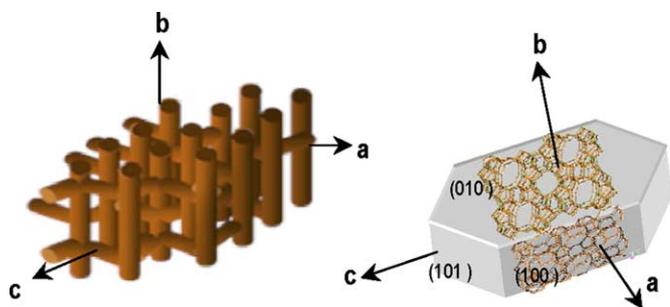


Fig. 3. MFI crystal with stylistic pore structure and crystallographic axis [66].

films with controlled orientation and several approaches have been developed:

(a) Identifying and controlling conditions to promote growth rates along certain crystallographic directions. Progress towards the fundamental understanding of the origin of shape and habit of zeolite crystals will greatly facilitate the task of engineering zeolite film microstructure according to design. Some degree of preferred orientation could always be expected since most of the zeolite structure types have anisotropic growth rates. MFI crystals most often have a coffin shape, elongated along the c -crystallographic direction, indicative of fast growth along the c -axis. Many authors have noted that the growth morphology of zeolite varies with the composition of the synthesis mixture, i.e. composition of the starting mixture, as well as the synthesis temperature. This means that the growth process for each crystal face is strongly dependent on the synthesis conditions. Systematic variations of MFI synthetic conditions can lead to particle shapes ranging from symmetric to elongated needle or coffin. Iwasaki et al. [138] and Wang and Yan [95] performed a systematic study on the correlation between the crystal orientation in MFI films on stainless steel plates and the composition of the synthesis solution. The goal of their respective studies was to show that manipulation of crystal orientation in a continuous thin

film could be achieved with in situ crystallization through systematic optimization of the synthesis composition. They found that within the synthesis system of TPAOH:NaOH:TEOS:H₂O:NaCl, OH⁻/Si and Na⁺/TPA⁺ ratios play a critical role in controlling crystal orientation. For sodium-free or low sodium syntheses, only random-oriented films are formed at OH⁻/Si ≥ 0.64, (a,b)-oriented films at 0.64 > OH⁻/Si > 0.5 or at 0.2 ≥ OH⁻/Si > 0.1, and b -oriented films at 0.5 ≥ OH⁻/Si > 0.2. For a given OH⁻/Si ratio, addition of Na⁺ leads to change of crystal orientation from b -oriented, to (a,b)-oriented, to (a,b,c)-oriented, and eventually to random oriented. Wang et al. explained this by the fact that Na⁺ tends to cause agglomeration of silicate precursors leading to large aggregates of random-oriented crystals. Wang et al. also found that the crystallization temperature and time as well as the chemical nature and roughness of the support are important for orientation and film continuity.

By studying the nucleation and growth rates of MFI crystals along different crystallographic directions, Lai et al. were able to manipulate relative growth rates along different crystallographic directions of MFI, and by doing so, obtained highly selective oriented molecular sieve films [99,139]. Membranes of the high silica molecular sieve MFI with c -out-of-plane preferred orientation showed low selectivity for p - o -xylene, Fig. 4, left, due to the presence of grain boundary defects. MFI membranes with a small difference in preferred orientation (c -axis inclined by about 35°, ($h0h$) plane normal to the support) showed no evidence for the presence of similar defects at the grain boundaries. These membranes show excellent selectivity for p -xylene. The relationship between membrane microstructure and the transport properties of ZSM-5 membranes were also investigated by Au and Yeung [100]. Experiments conducted by the authors suggested that grain boundaries form the main non-zeolitic pathway in the membrane diffusion and their elimination through grain growth can result in better membrane performance.

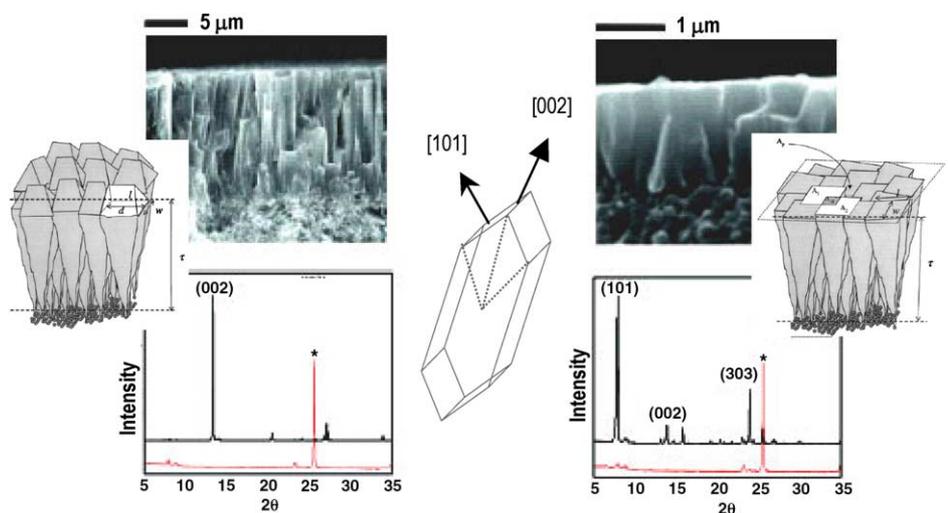


Fig. 4. Molecular sieve membranes with small differences in microstructure showing drastically different performance [97,100].

(b) The second approach involves starting the membrane synthesis with oriented seeds and proceeding with the seeded growth in the absence of further nucleation. Several different strategies have been used for oriented seed layer deposition. These include dip coating [131], charge reversal of the support with a cationic polymer followed by seed deposition [101,140], and recently there has been a trend to make use of chemical linkers such as iso-cyanates to covalently bond the seed crystals to the support [135].

Tsapatsis et al. [141] prepared a silicalite membrane by growing a layer of oriented silicalite-1 crystals on a composite precursor nanocrystalline silicalite/alumina unsupported film using controlled secondary growth. The orientation of the crystals was primarily with the *c*-direction perpendicular to the support, in other words both straight and sinusoidal channel networks ran nearly parallel to the membrane surface. Although oriented seed crystals give rise to a zeolite layer of the same orientation initially, it was found that as the film grew thicker during secondary growth, randomly oriented films formed due to anisotropic growth rates of the different crystal faces. In 1998 Gouzinis and Tsapatsis [97] further studied the growth of an oriented zeolite layer. They succeeded in manipulating the out-of-plane grain orientation by secondary growth conditions, in such a way that the *c*-axis of the grains range from being oriented perpendicular to the substrate to being oriented at an angle of $\sim 35^\circ$ from the direction normal to the substrate. More recently Lai et al. [99] succeeded in preparing a primarily *b*-oriented layer on α -Al₂O₃ disks, by following a three-step approach. First the supports were coated with a mesoporous silica layer, masking the support and providing a smooth layer for membrane growth (see Fig. 5). This was followed by the deposition of an essentially single layer of seed crystals through the use of chemical linking groups according to the method of Ha et al. [135]. Finally the seeded supports were hydrothermally treated at 175 °C for 24 h in a synthesis solution containing trimer TPA as structure directing agent. Lai et al. obtained superior *o*-xylene/*p*-xylene separation whilst maintaining high permeances with the above described membrane.

Hedlund et al. [142] treated an alumina support with a cationic polymer in order to reverse the charge of the support. They subsequently deposited the negatively charged

LTA seed crystals electrostatically on the support. Film crystallization on the seeded substrate was effected by hydrothermal treatment in synthesis solution with the same composition that was used for the seed crystal preparation. They obtained an essentially continuous 280 nm LTA film with the (100) plane of the crystals primarily oriented parallel to the substrate surface. In 1998 Mintova et al. [143] reported the synthesis of ZSM-5 films on quartz substrates from template free precursors. The substrates were covered with a monolayer of seed crystals. These crystals were grown into continuous films with thicknesses in the range 230–3500 nm by hydrothermal treatment. The preferential orientation of the crystals constituting the film was initially with the *c*-axis close to parallel to the substrate surface. During the course of crystallization this orientation changed to one with the most of the crystals having the axis directed (as in the case of Tsapatsis et al. [97]) approximately 35° from perpendicular to the substrate surface. In 1999 Hedlund et al. [102] investigated certain parameters in the film formation process. These included the seed crystal size, amount of adsorbed seed crystals and film thickness after hydrothermal treatment of the seeded substrates. They concluded that the shape and orientation of the adsorbed seed crystals and their growth rate in different directions determine the orientation of the final film. By controlling the seed size and amount of seed crystals they could attain some control of the orientation of the crystals constituting the film.

In 2001 Yeung et al. [86] also succeeded in preparing a (101)-oriented MFI zeolite membrane on seeded supports by tailoring the synthesis conditions and composition.

(c) Changing the direction of the highest nutrient concentration from the out-of-plane to the in-plane direction. The presence of a precursor gel can be used to provide high nutrient concentrations on the surface of the substrate. Direct hydrothermal synthesis with this approach can lead to *a*- and/or *b*-out-of-plane oriented films since the fastest growing crystallographic plane (along the *c*-axis) is now *in-plane*, confined by nutrient availability. Essentially *b*-oriented MFI films, prepared according to this approach were previously reported on silicon wafer and glass supports by Jansen et al. [144], den Exter et al. [112] and Kogler et al. [106]. However, these films were often non-continuous.

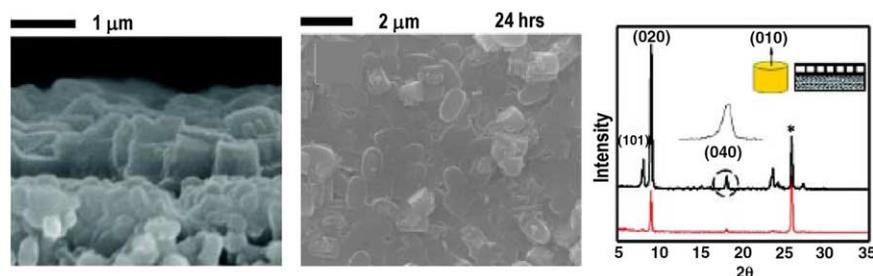


Fig. 5. Cross-section and top view of the primarily *b*-oriented silicalite-1 membrane, and corresponding XRD trace of the seed layers (bottom trace) and the membranes (top trace) [99].

3.2. Reproducibility and long-term stability of membranes

Reliability and durability are key criteria in the process industry and one of the main obstacles for industrial zeolite membrane reactors. It is well-known that poor reproducibility of zeolite membrane preparations is a commonly encountered problem [83] due to the large number of factors that play a role in zeolite membrane formation. Van de Graaf et al. for instance reported that only 4 out of 12 silicalite-1 membranes had an acceptable quality. Noack et al. [145] also concluded that reproducibility of membrane preparation was severely lacking with only 10–30% of preparations producing high quality membranes. By varying the synthesis composition and conditions, the authors could however increase the yield of high-quality membranes to 70% of their preparations.

One of the key contributing factors to the difficulty of obtaining reproducibility is the lack of attention that has been paid to temperature trajectories within synthesis reactors. Several authors have shown that the synthesis temperature and profile has a significant influence on the microstructure and the overall quality of the membrane [100,146]. Li et al. [147] obtained notably improved results when use was made of a two-stage temperature synthesis, allowing the formation of a larger amount of nuclei and a resultant continuous membrane. Even though temperature profiles within reactors clearly have a major influence on the final quality of the membrane, very few authors have mentioned synthesis reactor characteristics or temperature profiles within those reactors. This necessitates the re-optimization of synthesis procedures whenever the experimental setup and conditions are slightly altered.

For the successfully implementation of zeolite membranes in industrial processes, permeances and selectivities should also be maintained over long periods of time. Coronas et al. [85] studied the separation properties as a function of time on stream for several membranes and observed a reduction in the *n*-hexane permeance and *n*-hexane/2,2-dimethylbutane selectivity that increased with increasing operating temperature. The degraded membranes could however be regenerated by calcination at elevated temperature to obtain their original permeances and selectivities. Van den Broeke et al. [148] studied the reproducibility of permeation results for carbon dioxide and the robustness of silicalite-1 membranes prepared by them with a time span of about a year between runs. During this period a large number of temperature and pressure cycles were performed, with various gases. Their results indicated only minor changes in performance. Van de Graaff et al. [83] investigated the long-term stability of a silicalite-1 membrane using the *n*-butane/*i*-butane permselectivity at 30 °C as a standard test and found that there was only a slight decrease in selectivity over a period of two years. Studies on the reliability of membrane syntheses and the reproducibility of membrane performance has also been conducted by Gora et al. [149] and Hedlund et al. [150] Current efforts to produce reproducible high quality mem-

branes overall indicates that a satisfactory success rate could be obtained with optimization of conditions and compositions for zeolite membrane formation.

3.3. “Ultramicroporous” membranes

Zeolite molecular sieves, having high porosities and well-defined pore sizes in the range of 3–12 Å, are clearly good candidates for membrane reactors. The difficulty to produce ultramicroporous zeolite membranes however remains and is of dual-nature: firstly zeolite membranes with pores in the ~3 Å range to separate small gas molecules on the basis of size exclusion should be produced, and secondly a method to produce zeolite membranes without non-zeolite pores or defects has to be found.

Until recently the attention of the research community had been focused on MFI zeolites due to its suitability for the separation of several industrially important raw materials. The development of zeolite membranes with channel sizes small enough to achieve high separation factors for gas mixtures is however also attractive for the separation of small gas molecules such as carbon dioxide (CO₂) and methane (CH₄) which typically have small differences in adsorption strengths. The small pore size of, for instance, zeolite NaA (0.41 nm) could improve separation of small gas molecules such as nitrogen (0.364 nm) and oxygen (0.346 nm) by exploiting differences in size between them. Xu et al. [151] made use of this fact in order to separate nitrogen and oxygen and achieved a permselectivity of 1.8 for O₂/N₂. Further investigation however indicated the presence of defects with a larger diameter than the pore size of zeolite NaA. More recently Kazemimoghadam et al. [152] investigated the dehydration of water/1-1-dimethylhydrazine mixtures by zeolite NaA and hydroxy sodalite membranes. Separation factors of >10000 were obtained for both NaA and hydroxy sodalite membranes at 25 °C and a pressure of 1.5 mbar on the permeate side. The hydroxysodalite membrane had a slightly lower flux but also a higher selectivity due to its smaller pore size. Other small pore zeolite membrane that have been investigated include the zeolite P membrane (examined by Dong and Lin [75] for the separation of H₂/Ar, CH₄/Ar and H₂/SF₆), zeolite T [153] and a DDR type zeolite membrane, examined by Tomita et al. [154]. Tomita et al. concluded that the prepared DDR membrane had few defects and worked well as molecular sieving membrane, obtaining a separation factor of 220 for a 1:1 CO₂/CH₄ mixture at 28 °C and 0.5 MPa total gas feed pressure. Poshusta et al. [76] demonstrated that a SAPO-34 membrane also hold promise for the separation of light gas molecules. The authors achieved a CO₂/CH₄ separation factor of 30 at 27 °C.

The intercrystalline diffusion via defects in the structure of the zeolite membrane has a large negative impact on the performance of the membrane. In Fig. 6, Nelson et al. [155] showed that the flux through the imperfect membrane has a similar functional form to that for the perfect membrane,

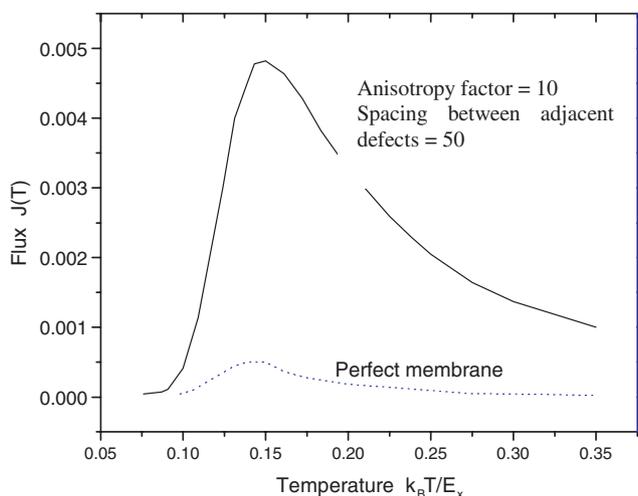


Fig. 6. Comparison of fluxes through an anisotropic imperfect membrane with nanoscopic defects and a perfect membrane as a function of temperature [153].

but with a maximum flux that is about ten times larger. This increase in flux was attributed to the decrease in the effective thickness of the membrane due to the presence of voids. Since the effective membrane thickness is much smaller than the actual thickness Nelson et al. also predict lower permselectivities for this imperfect, anisotropic membrane compared to those for defect-free membranes.

Since defect size and defect density determines the separation performance of the membrane:

- (a) The number and size of defects that form during membrane crystallization and post-synthesis thermal treatment have to be limited to a minimum.
- (b) The defects that do form should be repaired through a suitable technique.

Several groups have shown the deleterious effect of calcination on the membrane quality and performance. Both Den Exter et al. [112], Geus et al. [156] and Dong et al. [157] found that compression stresses that developed during cooling after calcination induced cracks in the supported zeolite film. In response to the mentioned findings, endeavors to prepare zeolite membranes in the absence of an organic template have been reported by for instance Mintova et al. [143] and Hedlund et al. [150] reported the in situ synthesis of a MFI membrane while Lai and Gavallas [158], Pan and Lin [159] and Lassinanti et al. [160] reported the preparation of a MFI membrane according to the secondary growth method. Most authors reported reduced flux and slightly increased selectivity.

Efforts that have been made to eliminate defects that did form during synthesis, include post-synthetic coke treatment [161], chemical vapor deposition of silica by reaction with silicon alkoxide or silylation agents and treatment with a silane coupling reagent [162]. In a study performed by Nomura et al., the separation selectivity for a *n/i*-

C_4H_{10} mixture increased from 9.1 to 87.8 after modification of the membrane pore structure by a TEOS- O_3 counter-diffusion chemical vapor deposition technique [163,164]. Van den Broeke et al also demonstrated that the permeation behaviour of a silicalite-1 membrane can be modified selectively by the reaction of a silane $(CH_3)_3Si$ (TMCS), with accessible zeolitic OH-groups [148]. Xomeritakes et al. [165,166] selectively sealed cracks that formed during the calcination of MFI membranes by dip-coating the membranes in a surfactant-templated silica. After drying, the mesostructured surfactant-silica layer that formed on top of the MFI membrane exhibited extensive cracking and could be easily peeled off by blowing the membrane surface with compressed air. However, the sol infiltrated inside large cracks during dip-coating, permanently plugged the cracks after transformation to an impervious surfactant-silica composite and improved the membrane selectivity. Although this method is successful in increasing the selectivity, it could lead to pore blocking and is therefore done at the cost of the flux. Van den Broeke et al. reported a reduction in *n*-butane flux by a factor 17 after silanation.

Lai et al. [99] recently made a large contribution to the art of membrane synthesis when the authors showed that it is possible to prepare highly selective zeolite membranes with a very low defect density. They were the first to report a zeolite membrane showing excellent separation with high permeance that relies on discrimination between molecules on the basis of differences in size and shape. The oriented film of the siliceous zeolite ZSM-5 prepared, showed *p*-xylene/*o*-xylene selectivities of ~ 200 – 800 whilst maintaining high flux.

3.4. Addressing the problem of sealing

The property of inorganic zeolite membranes that set them apart from polymeric and amorphous membranes is their thermostability, which allows operation under severe conditions as well as the ability to be reactivated which in turn gives rise to increased life expectancies for these membranes. It is however, generally acknowledged that the high-temperature application of zeolitic membranes is strongly limited by high-temperature resistant sealing of the module by which feed and permeate are separated from each other [167]. Despite the technical importance of high-temperature seals for zeolite membrane research, studies with emphasis on high-temperature seals themselves are seldom reported in literature.

One possibility is the parting of the locations of sealing and separation in order to be able to apply already known technology for sealing at low temperature. This however necessitates a much more complex membrane module in which a large temperature gradient exists over the different sections (that for separation and that for sealing) of the equipment. This has been achieved by providing a cooling system (e.g. water cooling) in a fully heated apparatus [168].

Of the many joining processes available, brazing is one of the most established techniques for ceramic to metal joining. In its simplest form, a brazing alloy that wet ceramics is applied to the support surface and subsequently heated in a controlled atmosphere such as nitrogen or argon [26]. Due to large differences in thermal expansion coefficients between the brazing material and the ceramic, this process often generates high residual stresses in the ceramic with resultant cracking and an inability to form gas impermeable seals. Another innovation has a ceramic incorporated in the braze alloy, to both increase its strength and reduce its coefficient of thermal expansion [169].

Ceramic glazes can also be used to seal the porous surface around the ends of a ceramic membrane. Ceramic glazes will limit the difference in thermal expansion coefficients between the seal and the membrane and reduce the development of thermal stresses. However some ceramic glazes have a lower chemical resistance and could dissolve in the high pH zeolite synthesis solution. Reed et al. [170] addressed the dilemma in their patent for a gas impermeable, glass-based glaze that can withstand high temperatures, for sealing the ends of a porous tubular alumina support containing a microporous separation membrane on the inside.

Geus et al. [113] solved the problem by preparing MFI membranes on porous, sintered stainless steel supports within stainless steel membrane modules in order to perform (high temperature) permeation experiments whilst avoiding high-temperature sealing by the formation of the zeolite layer on both porous and non-porous stainless steel parts. Although the as-synthesized layers were found to be gas-tight, even for small molecules such as neon, this method severely complicates the synthesis procedure. Later Gora et al. [149] obtained a gas-tight seal by preparing zeolite A and MFI membranes on porous stainless steel supports to which swagelok connections had been welded.

Another approach, often used for lab-scale reaction systems, involves the lamination of the ends of the membranes combined with the use of graphite O-ring seals. The high-temperature enamel (Aremco 617) that can tolerate temperatures up to 1100 K was for instance used by Wong et al. to coat the tube ends while viton or graphite O-rings were used along with modified compression fittings to provide leak-free sealing [146]. The major problem of this technique is that, if not properly designed, the system can experience substantial thermally induced stress due to the differences in the thermal expansion coefficients between the seal, the ceramic support and the zeolite membrane and this could cause the membrane to crack during heating or cooling.

Recently Min et al. [171] reported a new approach to membrane module design using a porous metal support and a tapered sealing technique. To perform the permeation measurements of single gases and xylene isomers at temperatures of up to 723 K, Min et al. developed an all-stainless steel module in which the membrane module

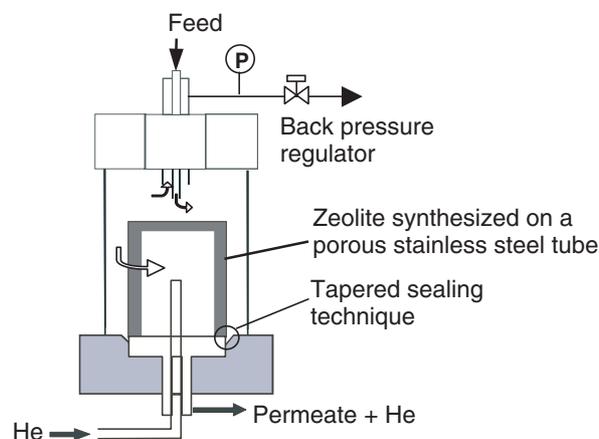


Fig. 7. Schematic cross-sectional view of the membrane module [171].

was constructed by tightly mounting the sintered metal support into a tapered hole to fasten the metal support in the module as shown in Fig. 7. Afterwards the membrane module and support was placed in a stainless steel autoclave and a hydrothermal synthesis repeatedly carried out at 180 °C until the zeolite membrane was rendered impermeable to N₂. By following the tapered sealing method, no special sealant was needed to seal the metal support and membrane module in order to perform the permeation experiments above 473 K.

It does seem as if some progress has been made in the high-temperature sealing of zeolite/ceramic membranes, especially at laboratory scale. The gas-tight, high-temperature resistant sealing of tubular zeolite membranes in an industrial scale module, where each individual tube in a tube bundle has to be sealed and fixed to metal tube sheets in the module, with differences in thermal expansion, whilst still preserving the integrity of the membrane film on the ceramic support, remains problematic and a possible bottleneck for this technology.

3.5. Up-scaling

Up-scaling is faced with a number of challenges; such as the synthesis of large continuous membranes. Although seeded synthesis may improve nucleation density and therefore increase the ease of synthesizing a large continuous membrane, the two-step synthesis procedure also poses problems and decreased ease of synthesis when one considers for instance the application of the seed layer in a uniform and continuous way on a large scale.

Temperature control in large synthesis reactors is another subject that needs more thorough investigation. Larger volumes would lead to the existence of a large temperature trajectory within the reactor, which means that synthesis conditions will have to be optimized for larger volume preparations. Obtaining a clear picture of the effect of synthesis temperature as a parameter on the nucleation and crystal growth rate of zeolites on a support is very difficult due to insufficient/incomplete information that are

given regarding the subject in reports of membrane syntheses. Microwave heating could provide better control over the temperature-time profile. Compared to conventional hydrothermal synthesis, microwave synthesis of zeolite membranes provide fast homogeneous heating throughout a reaction vessel and more simultaneous nucleation on the support surface, uniform small zeolite crystals and a resulting thin membrane, as well as a reduction in processing time and energy cost compared to conventional heating [172].

Membrane reactor modules will have to be designed in order support large surface area membranes, especially when dealing with potentially fragile ceramic units. Ease and effectiveness of sealing inside the module will also need attention.

3.6. Cost considerations

The estimation of the feasibility of a membrane reactor process is not merely as straightforward as the comparison of yield and selectivity with that of a fixed bed process (although this is the approach generally used) and actually requires a full economic assessment. However, due to the fact that zeolite membrane technology is relatively new and very few long-term commercial processes exist, an economic evaluation of a zeolite membrane reactor process is very difficult and reports of such evaluations in literature are scarce.

An initial study of the limited number of cost assessments of zeolite membranes and zeolite membrane reactors that have been reported in literature, paints a rather gloomy picture for the future of zeolite membrane reactor technology. Costs of about US\$3000/m² for zeolite modules of which 10–15% is contributed to the membrane itself has been reported by Caro et al. [66]. Meindersma and de Haan [173] concluded in a feasibility study done by them for the separation of aromatics from Naphtha feedstocks, that unless membrane module costs were reduced by a factor of 10 and the flux were increased by a factor of 25 the investments would be uneconomical. Tennison also reported that due to selectivity limitations of zeolite membranes, membrane processes are uneconomical and a considerable reduction in membrane costs is required to make such processes feasible [174]. Tennison emphasized that very few processes would be able to tolerate costs of more than €1000/m² and operation would also occur under far more demanding conditions than were generally used in modelling studies [175].

Besides variable and fixed costs in processes, increasing consideration will have to be paid in future to the costs for minimizing the environmental damages of manufacturing. The disposal of toxic or dangerous waste, such as spent catalysts and chemicals, easily amounts to US\$250–US\$750 per ton [176]. It is therefore critical to minimize waste production and emission, both from a conservation responsibility as well as a cost perspective. Zeolites and zeolite membrane reactors are ideally suited for environmentally

friendly operation and their respective properties suggest that they will have a key role to play in sustainable process technology in the new millennium.

The economics of a plant could be improved by improving the overall selectivity and the productivity of the plant. Zeolite membrane reactors are known to be beneficial for product selectivity and using zeolite membranes/catalysts, which have an improved resistance to deactivation and could already separate species that could lead to deactivation, before reaching the catalyst, could limit plant downtime—thereby increasing productivity. The losses and transfers of energy, which dictate the investment costs, can be potentially minimized by zeolite membrane reactor technology by maximizing the reaction selectivity and the concentration of the various streams, and by minimizing changes in temperature.

Therefore, although at first glance economic feasibility of zeolite membrane reactors seems unattainable, there are a lot of possible benefits that should be taken into careful consideration and which will play an increasingly important role in future developments. In light of the above as well as the recent reports of submicron, highly selective, high flux [99,103,142], reproducible, and reduced cost membranes [177], economic feasibility might well be reached.

3.7. Multicomponent transport and separation behaviour

Transport in zeolite membranes is a complex process that is governed by adsorption and diffusion. The irregular nature of the zeolite membrane with intercrystalline pores [155], and the further contribution of a support layer to the permeation resistance [178] add to the complexity of the process. In order to employ zeolite membranes on a large scale, improved experimental methods for the measurement of intracrystalline diffusion has to be developed and our understanding of the mass transport properties, the factors governing separation behaviour and our ability to predict the permeation of molecules through these membranes have to be increased.

The diffusivity in zeolites depends strongly on the pore diameter, the structure of the pore wall, the interactions between the surface atoms and the diffusing molecules, the shape of the diffusing molecules and the way the channels are connected as well as, most important in mixtures, adsorbate–adsorbate interactions [179]. The quantitative prediction of diffusion rates inside zeolites with modelling techniques is often hard to relate to the aforementioned properties and the underlying microscopic mechanisms [180,181]. A contributing factor to the difficulty of diffusion prediction is the large discrepancies that often exist between diffusivities determined from different experimental techniques [182–184].

When used as a catalyst or molecular sieve, at least two, and often more, species are present inside the zeolite pore structure. A number of studies have indicated that mixture separation selectivities could not be predicted from the

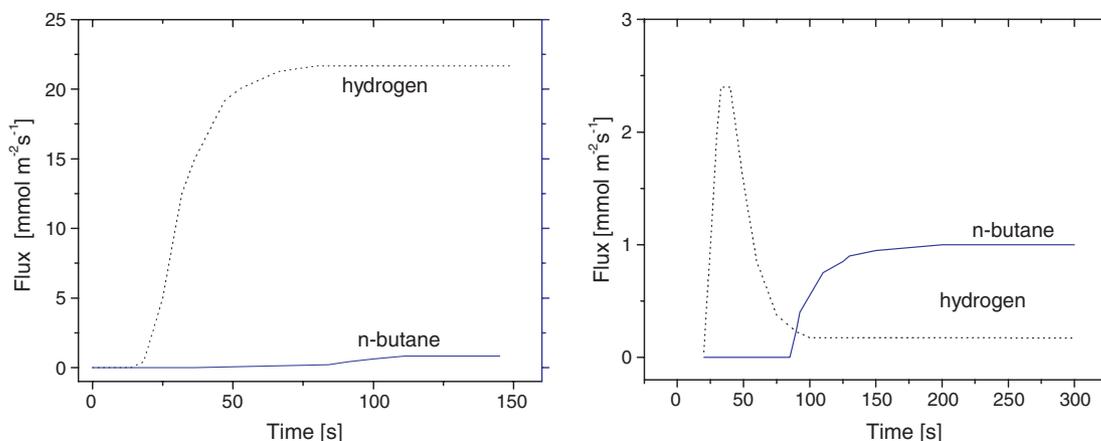


Fig. 8. Breakthrough curves of the (a) single components hydrogen and *n*-butane and a hydrogen/*n*-butane mixture (95 kPa/5 kPa, $T = 295$ K) indicating the difference in fluxes of components in single component and mixture permeation [178,185].

permeances of single components alone since competitive adsorption, pore mouth blocking and/or single file diffusion may govern the molecular transport through the zeolite channels, Fig. 8 [178,185–187]. However despite its practical importance, mixture transport through zeolites and zeolite membranes has only recently received more substantial attention. This can be contributed to the difficulty of experimentation with mixtures as well as the exponential increase in complexity of simulations with an increasing number of components.

Currently two classes of experiments to measure intracrystalline diffusion through zeolites can be distinguished; macroscopic techniques, or visible uptake measurements (gravimetry, volumetry, Fourier transform infrared (FTIR) spectroscopy), including the frequency response technique and zero-length-column chromatography and secondly microscopic techniques such as pulsed field gradient NMR (PFG NMR) [188,189] and quasi-electron neutron scattering (QENS) [190]. Unlike macroscopic techniques, the microscopic techniques take place under equilibrium conditions. The difference in diffusivities obtained by these two classes of techniques has sparked further development of experimental techniques to measure diffusion such as the fast pulse technique for the simultaneous determination of both the pore diffusion coefficients in, and the rate constants for adsorption and desorption at zeolitic materials reported by Nijhuis et al. [191], Schumacher et al. [192] reported tracer-exchange experiments with positron emission profiling (TEX-PEP) which allowed the measurement of self-diffusion coefficients of adsorbates in zeolites on a macroscopic time-scale and at elevated temperature; while Zhu et al. [193] used the novel tapered element oscillating microbalance (TEOM) technique to determine the intracrystalline diffusivities of *n*-hexane, 2-methylpentane, 3-methylpentane and 2,3-dimethylpentane in silicalite-1 and obtained good agreement with ZLC results.

A number of simulation techniques have been used and sometimes combined to describe mixture transport through zeolites and zeolite membranes such as Monte-Carlo [194],

molecular dynamics (MD), transition-state theory (TST), Fick and Onsager formulations and the Maxwell–Stefan model to name a few. Among these it is generally accepted that the generalized Maxwell–Stefan formulation offers the most convenient and the nearest quantitative prediction of multicomponent diffusion through zeolite membranes [61,181]. This model is based on the principle that frictional interactions (characterized by Maxwell–Stefan diffusivities) experienced between different molecules in a mixture as well as with a solid matrix, balances the driving force (often the chemical potential gradient in the case of membranes) exerted on each molecule and gives rise to the different velocities of molecules. The strength of this model lies in the fact that it intrinsically encompasses intra-crystalline diffusion phenomena as well as sorption processes, allowing it to predict multicomponent diffusion based on pure component Maxwell–Stefan diffusivities and mixture adsorption isotherms. Configurational-bias Monte-Carlo (CBMC) simulations demonstrated that due to the inefficient packing of higher branched alkanes and aromatic molecules, their saturation loadings will be lower than that of linear short alkanes and these molecules might even be expelled from the zeolite, as a result of configurational entropy effects [195]. Adsorption isotherms of mixtures consisting of components with widely different saturation loadings would therefore show an inflection, which is not described by multicomponent Langmuir isotherms in a thermodynamically consistent way. Kapteijn et al. [196] extended the generalized Maxwell–Stefan equations for multi-component diffusion to also account for molecules with different saturation loadings by using the ideal adsorbed solution theory (IAST) of Myers and Prausnitz [197] which shows good agreement with adsorption isotherms predicted from CBMC simulations [198]. Krishna and Paschek [199] made use of CBMC simulations to develop the required mixture isotherms and followed the approach of Kapteijn et al. [196] using the Maxwell–Stefan theory for describing hydrocarbon mixture diffusion across a silicalite-1 membrane. Both authors emphasized the influ-

ence of mixture non-ideality effects on separation selectivities and recommended the use of the IAST in the Maxwell–Stefan formulation in order to account for size and configurational entropy effects.

4. Catalytic activity of zeolites in membrane reactors

The high internal surface area of zeolites, coupled with the ability to control the number and strength of acid sites and shape and size selective effects, allow the application of zeolites as versatile heterogeneous catalysts and catalyst supports. The intrinsic catalytic activity of zeolites coupled with the possibility to tune adsorptive properties makes them good candidates for bringing about simultaneous reaction and separation. The symbiosis that exists between the catalyst and membrane in the membrane reactor however also limits the degrees of freedom of both the membrane and the catalyst. Besides an appropriate membrane, membrane reactors will therefore also require the design of a customized catalyst, owing to the different conditions that catalysts are exposed to in membrane reactors compared to conventional reactors.

One of the main aspects that received attention is the correlation of the membrane throughput with the catalyst activity. Van Dyk et al. [200] did a comparative study of the dehydrogenation of isobutane in an extractor-type CMR fitted firstly with a MFI membrane and secondly with a Pd-membrane, which showed superior performance compared to the zeolite membrane, and found that the reactor performance was in fact limited by the catalyst. The authors concluded that in order to draw the full benefit of the separation–reaction synergism, very active catalysts that were able to comply with the high extraction ability of the membrane had to be developed. Also Miachon et al. [201] highlighted that although a catalyst could be active enough to achieve equilibrium in a conventional reactor this was not necessarily the case in an extractor type membrane reactor. Membrane reactors might also require catalysts with improved stability. Such is the case for catalysts used for dehydrogenation reactions in an extractor-type membrane reactor, where selective hydrogen removal might in fact promote coke formation due to a decrease in the H/C ratio and result in a decrease in catalytic activity. Larachi et al. [202] for instance reported that an increase in conversion during methane aromatization due to hydrogen removal from the reaction zone was offset by a drop-off ascribed to a carbon build-up on catalytic active sites. The authors were however able to regenerate the catalytic sites by an interruption in permeation with either autogeneous hydrogen or an external source of hydrogen to reduce the deposited carbon.

The presence of a membrane however does not always adversely affect the catalyst function. It could also protect the catalyst from poisons and increase selectivity by suppressing undesirable side reactions from taking place. Lai et al. [203] reported one such case when they investigated the Knoevenagel condensation reaction of benzaldehyde

and ethyl cyanoacetate to produce ethyl 2-cyano-3-phenylacrylate. Here, the presence of a ZSM-5 membrane in a PBMR and microreactor enabled the continuous and selective removal of water during the reaction, protecting the Cesium-exchanged NaX faujasite catalyst from deactivation by the water which is formed as byproduct during the reaction. Espinoza et al. [204] applied the same principle to the Fischer–Tropsch process, protecting the cobalt and iron-based catalysts from deactivation by water produced during the reaction. An increase in the contact time or effective reactor volume due to product extraction from the reactive zone and a resultant improvement in conversion and yield could also be effected by the presence of a membrane. The dimerization of *i*-butene into branched octenes not only produces *i*-octenes, but also undesired C₁₂ or even C₁₆ species. Piera et al. [19] reported that by removing the C₈ intermediate product from the reaction environment through a silicalite-1 membrane further reaction to give undesired C₁₂ and C₁₆ compounds was prevented, and an increased residence time of the reactants effected, consequently, increasing both the *i*-butene conversion and *i*-octene reaction selectivity considerably with respect to a conventional FBR.

Although inert membranes simply function as a distributor of reactants or a separator of products, inorganic membranes with catalytic activity are able to simultaneously function as a distributor, a separator and a catalytic reactor. The benefit most often reported by authors is the improved selectivity and resistance to deactivation of catalytic membranes as compared to the same catalyst, employed in a packed bed configuration. In a study by Yeung et al. [82] the effect of catalyst location in membrane reactors was investigated. The authors demonstrated that for a PBMR, a CMR and a fixed bed reactor (FBR), for a first-order reversible reaction, a non-uniform distribution of catalyst, located on the feed/external side in either the membrane (CMR) or the pellet (PBMR and FBR) gave superior performance compared to uniformly distributed catalyst. In addition it was found that the performance of the CMR and PBMR was identical when the catalyst location is at the feed side of the membrane (for the CMR) or at the external surface of the pellet (for the PBMR), due to the absence of mass transfer resistance. These two membrane configurations exceeded the performance of the FBR configuration over the full range of residence times.

Santamaria and co-workers [205] also compared three reactor configurations for the catalytic esterification of ethanol with acetic acid, loaded with the same amount of catalyst, namely: (i) packed bed reactor, with the H-ZSM-5 catalyst packed as powder inside an impervious tube, (ii) packed bed membrane reactor (PBMR), with the H-ZSM-5 catalyst packed as powder inside a tubular Na-ZSM-5 membrane which acted as an extractor of product, (iii) a catalytic membrane reactor (CMR), where there was no catalyst other than the H-ZSM-5 membrane itself resulting in the efficient integration of product extraction and reaction. As a result the conversion obtained at the

same feed rate and catalyst loading was greater than in conventional fixed bed reactors, or even in reactors where the zeolite membrane was kept separated from the catalyst.

When Liu et al. [52] applied a $\text{La}_2\text{NiO}_4/\text{NaA}$ zeolite composite membrane to CH_4/CO_2 reforming, the conversions of CH_4 and CO_2 in a catalytic membrane reactor (CMR) were remarkably higher than those over a fixed-bed reactor, while coke deposition was lower. Here the membrane also acted as an extractor of the products CO and H_2 resulting in a decrease of carbon deposition although the separation selectivity was quite low. Masuda et al. [206] applied a ZSM-5 type zeolite membrane to the catalytic dehydrogenation of methanol to olefins. In this instance the membrane served as a contactor, allowing the control of the residence time of species inside the reactive zone. Optimising the reaction rate and the diffusion rate in the membrane could minimize further dehydrogenation of the olefins to aromatics. A selectivity of 80–90% for high methanol conversions of 60–98% was obtained. Torres et al. [207] made use of a zeolite- β membrane for the oligomerization of isobutene, which is an acid catalysed reaction. Also in this application, the membrane did not function as a separator, but was used as a contact medium, with which the residence time could be controlled, limiting secondary reactions and improving selectivity. Compared to a conventional fixed-bed zeolite catalyst, here too, the beta membrane reactor showed improved performance and resistance to deactivation.

The development of mesoporous molecular sieve films, such as MCM-41 and UTD-1 in the past decade has made the encapsulation of nanometer size guest compounds or clusters possible. Furthermore, the reactive hydroxyl groups on the internal surface of these mesoporous hosts could be easily modified by covalently anchoring of organometallic complexes or grafted by silane coupling agents. These mesoporous membranes expand the range of reactions that can be catalyzed by zeolite membranes and the possible applications in membrane reactors.

5. Applications of zeolite membrane reactors

In the majority of zeolite-based membrane reactor applications, the zeolite membrane used, is only applied to separation and is not catalytically active. An example of this is the dehydrogenation of isobutane to isobutene reported by Casanave et al. [208]. They applied a MFI zeolite membrane supported on a mesoporous alumina tube to the dehydrogenation reaction of isobutane to isobutene with modest gains in yield; in 1999 Casanave et al. [209,210] resumed their study on the dehydrogenation of isobutene this time making use of two sweeping modes: co-current and countercurrent and varying the sweep and flow rates. The lower the feed and the higher the sweep flow, the higher the conversion. High sweep flows is however economically unfavourable for industrial applications and therefore not recommended. Their studies indicated that the limiting parameter could be either the membrane or

the catalyst depending on the sweeping configuration that is used. Although Dalmon and coworkers obtained a certain degree of success applying MFI membranes (10-membered oxygen ring zeolite with 0.56 nm pore diameter) to the dehydrogenation of alkanes, it seems difficult to get high enough hydrogen separation factors to make the process industrially viable. Since the zeolite membrane membranes have pore diameters larger than the sizes of the components to be separated, separation will not be based on molecular exclusion but on the combination of competitive adsorption and the different mobilities of molecules, arising from differences in molecular shape, within the zeolite pore [61,196]. Small pore, defect-free zeolite membranes with pore sizes between the size of hydrogen (0.29 nm) and *n*-alkanes (0.45 nm) have yet to be developed to a satisfactory extent. Possible candidates, in addition to LTA, include the 8 membered ring zeolites such as GIS, CHA and SOD.

Van de Graaf et al. applied an inert stainless steel supported, silicalite-1 membrane in a packed bed membrane reactor to study the effect of selective product removal in the equilibrium limited metathesis of propene to ethene and 2-butene and of *cis*-2-butene to *trans*-2-butene [211,212]. Depending on the operating conditions that were used, the propene conversion was 13% higher than the thermodynamic equilibrium conversion obtained in a conventional packed bed reactor. Van de Graaf et al. showed in their study, that when the separation selectivity of the membrane is not absolute, the performance of the membrane reactor is a balance between reactant loss and sufficient removal of the products. They compared the flux through the reactor wall (areal time yield, ATY) to the productivity per unit volume (space time yield, STY) for the silicalite-1 membrane reactor and found the values to be between 20 and 5000. This represents the necessary volume to area ratio of the reactor. For a cylinder this implies diameters of ~ 0.1 –20 cm—a good perspective for the application of zeolite membranes in industrial reactors.

A zeolite membrane (mordenite or NaA zeolite) was recently employed by Santamaria and co-workers [213] to selectively remove water during the gas-phase synthesis of MTBE obtaining higher performances than in a traditional reactor. An increase of conversion in the Fischer–Tropsch process by selective water removal with a ZSM5 membrane was reported [204]. In this case the reason for the conversion increase is not the shifting of an equilibrium through product removal; the presence of water decreases the reaction rate by dilution of the gases and causes deactivation of the Mordenite catalyst. Nomura et al. [214] selectively extracted ethanol from an ethanol fermentation broth through a silicalite membrane. A high separation factor of 218 for ethanol over water was obtained and maintained for at least 48 h.

The dimerization of isobutene in a zeolite membrane reactor, recently studied by Santamaria et al. [19], involved the removal of a valuable intermediate product before it reacted further in consecutive reaction networks. In this

case, a considerable increase in the yield to the desired product can be obtained, provided that the membrane is sufficiently selective to the intermediate product under reaction conditions.

The ability of a membrane reactor to control the addition and mixing of reactants, and the selective removal of products, results in better material utilization, less waste and pollution, and safer operation. Zeolite membrane reactors, when applied to the oxidative dehydrogenation of alkanes, are potentially useful to (a) control the oxygen feed, thereby limiting highly exothermic, total combustion [215] and (ii) improving the contact between the reactant and the catalyst. Zeolite membranes can be used as active contactors if they are catalytically active. Immobilizing transition metal ions in zeolites by ion exchange or by incorporation into the lattice leads to stable isolated and well-defined redox active catalytic sites. Julbe et al. [38] compared the catalytic performance of MFI and V-MFI membrane reactors for the oxidative dehydrogenation of propane. Better conversion was obtained with the V-MFI membrane. The NCMR configuration was however, not found to improve the reactor performance compared to the conventional flow through one.

6. Outlook of zeolite based membrane reactors

Significant progress has been made during the last decade in the understanding of separation mechanisms of zeolite membranes and the synthesis of thin, high flux, defect-free zeolite membranes applying new techniques of preparation [216], modification [217] and new materials [218]. The reproducible preparation of superior quality membranes seems to finally be within reach. As a result of the groundwork made numerous, new prospective applications of zeolite membrane reactors have emerged [219]. The end line has, however, not yet been crossed. More studies on the economic feasibility of zeolite membrane reactor processes, long-term stability of membranes and up scaling are needed. A closer look at temperature profiles and control within the synthesis autoclave is necessary for large-scale membrane production, here microwave heating, feasible at small-scale preparation [220], might be a solution to the problem although this should be further explored. Further improvements in especially cost reduction and membrane reliability should still be endeavoured to facilitate the wide introduction of zeolite-based membrane reactors into industrial practice.

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