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Recent developments in zeolite membranes for gas separation

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ABSTRACT

The latest advances in the field of zeolitic membranes for gas separation are critically reviewed with special emphasis on new synthetic protocols. After introducing the most relevant aspects to membrane performance, including adsorption trends, permeation mechanisms and support effects, we review recent achievements in membrane synthesis and discuss in detail the effect of zeolite topology and chemical composition on membrane gas separation. We pay special attention to promising 8MR high-silica structures. As the formation of defects during synthesis remains one of the major challenges for large-scale production of such membranes, we review various approaches to either limit defect formation or decrease their adverse effect by post-synthesis modification. Finally, the current challenges for this field of research are summarized and an outlook is offered on approaches to decrease fabrication costs, improve reproducibility and rational design of zeolite membranes.

Contents

1. Introduction

Membrane technology constitutes an increasingly important, convenient and versatile way of separating gas mixtures. Compared with other approaches, membranes reduce energy and other

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operational cost for gas separation and, moreover, membrane operations are more scalable than conventional separation unit operations in the chemical industry [1,2]. Several important industrial processes would benefit from the use of membranes, such as air separation (N_2/O_2) [3], recovery of hydrogen from mixtures (H_2/N_2, H_2/CO, H_2/CO_2, H_2/hydrocarbons) [4], hydrocarbon separations (olefins/paraffins, linear/branched isomers, etc.) [5], and CO_2 capture from natural gas, flue gas, biogas and syngas (CO_2/air, CO_2/CH_4, CO_2/H_2) [6,7].

Membranes are usually categorized in four main groups based on the nature of the membrane material: polymeric, inorganic, mixed-matrix and liquid membranes. Polymeric membranes currently dominate the global membrane separation market [8], because of their good processability, economic competiveness, scalability and tuneability [9,10]. On the other hand, polymeric membranes suffer from several limitations such as their inherent permeability/selectivity trade-off [11,12] and low thermal and chemical instability limiting, respectively, the overall performance and the range of operation conditions. Similar issues disturb industrial implementation of liquid membranes [13–16]. Mixed matrix membranes (MMM) are obtained when selective inorganic fillers are introduced into a polymeric matrix. The advantage of the MMM concept is that it combines the ease of polymer film processing with the high selectivity and permeability of inorganic materials. Several inorganic materials have been explored in this approach such as carbon molecular sieves [17,18], zeolites [19,20] and metal-organic frameworks [21–23].

Inorganic membranes are particularly interesting, as these materials can usually withstand high temperature and pressure. Several materials have already been explored for the preparation of dense and porous inorganic membranes. Dense structures conduct only particular gases or ions by solution-diffusion or mixed ionic-electronic conductivity mechanisms. Examples of such membranes are thin metallic (palladium, vanadium, iron, etc.) films for recovery of hydrogen [4,24] and ceramics (perovskites, fluorites) for oxygen separation [25]. The advantages of dense inorganic membranes are high selectivity (approaching infinity for high quality membranes) and thermal stability. On the other hand, low permeability and/or sensitivity to poisoning of dense membranes are their main drawbacks. Porous inorganic membranes, including those made of carbon, amorphous silica, zeolites and metal-organic frameworks, generally offer much higher fluxes and chemical stability.

Microporous amorphous silica membranes are usually thermally stable supported films with a thickness of several tens of nanometers capable of separating gases with very high fluxes. Such films can be prepared by sol–gel or chemical vapor deposition (CVD) techniques [26,27]. Low hydrothermal stability is, however, often a major weakness of silica membranes. Some methods including surface grafting (silylation) [28,29] and preparation of hybrid silica membranes [30,31] have been explored to improve hydrothermal properties of amorphous silica.

Carbon membranes are prepared by conversion of polymer layers by pyrolysis or carbonization at high temperature in inert atmosphere [32]. In general, pore sizes and adsorption properties of carbon membranes may to a certain extent be tuned by varying pyrolysis conditions and/or the polymeric precursor [33–35]. Unfortunately, carbon membranes are usually brittle, sensitive to strongly adsorbing components and possess pores of random size distribution, which make them difficult to apply for many relevant separations.

Metal-organic frameworks (MOFs) constitute a relatively new class of materials, which already have been extensively studied for membrane applications [36]. MOFs are porous coordination polymers consisting of metal ions (clusters) interconnected by polytopic organic linkers to form ordered porous structures. The number of possible MOF structures is only limited by synthetic imagination, as there are myriads of cluster-linker combinations. Accordingly, it is possible, within certain limits [37], to tune structure properties for a particular separation [38]. There are many examples of the preparation and application of MOF membranes. The interested reader is referred to recent review papers describing in detail state-of-the-art techniques, concepts and achievements in the field [39–42].

Finally, zeolites, owing to the uniform system of pores with molecule-sized dimensions, high porosity, excellent thermal and chemical stability, are particularly promising for fabrication of molecular sieving membranes, capable of separating gases at industrially relevant conditions.

Several reviews discussing advances in zeolite membrane fabrication and their separation properties are available. These include contributions of Caro and co-workers [43,44] and, more recently, the work of Pera-Titus [45] that reviewed the performance of zeolite and other porous inorganic membranes in CO_2 capture. Tsapatsis, Caro and co-workers discussed the preparation of ultra-thin and oriented zeolite films and also compared the separation properties of MOF and zeolite membranes [46]. The current review focuses on gas separation applications of zeolite membranes. First, we discuss general aspects of gas separation by zeolite membranes, including separation mechanisms, the influence of the porous membrane support and the main issues involved in the preparation of high-quality membranes. Second, zeolites and zeotypes of different topology and chemical composition are reviewed in terms of potential for membrane applications; post-synthesis modifications of such membranes to enhance separation performance are highlighted as well. Finally, we summarize our work by providing some general conclusions about the state of the art and an outlook on important development directions.

2. Zeolite membranes: general aspects

2.1. Permeation: adsorption

Any zeolite membrane separation starts with the adsorption of the molecules from the gas phase onto the zeolite pore surface. Accordingly, adsorption affinity plays an important role in overall separation performance. At low to moderate operation temperatures (up to 100–200 °C depending on zeolite structure and polarity) zeolite membranes usually exhibit adsorption selectivity. That is, the more strongly adsorbing component of a mixture disturbs or blocks permeation of other components for which zeolite channels remain (partially) inaccessible. Adsorption based separations are particularly effective for dewatering and CO_2 capture, namely when a strong adsorbates needs to be removed. Adsorption of certain gas molecules on the surface of a given zeolite material depends on the adsorbate and the adsorbent. The most important adsorbate parameters are polarizability and dipole and quadrupole moments (see Table 1). These parameters determine the strength of the interaction between the adsorbing molecule and the zeolite surface. For instance, H_2O and CO_2 are usually the strongest adsorbed species on zeolites among the compounds considered in Table 1, because of their large dipole and quadrupole moments. As an example, Fig. 1 provides ambient temperature adsorption isotherms of CO_2, CH_4 and N_2 on high-silica SSZ-13 zeolite.

As for zeolite adsorbents, such properties as polarity, topology and flexibility of the framework, the type of counter cation compensating for possible negative framework charges and the zeolite pore size determine adsorption behavior. One of the most important parameters is polarity, which in turns depends on the

Table 1
Properties of some gas molecules [47,48].

Molecule	Kinetic diameter (Å)*	Polarizability (Å^3)	Dipole moment (D)	Quadrupole moment (D Å)
H_2O	2.65	1.450	1.870	2.30
H_2	2.89	0.80	0.000	0.66
CO_2	3.30	2.650	0.000	4.30
O_2	3.47	1.600	0.000	0.39
N_2	3.64	1.760	0.000	1.52
CO	3.69	1.95	0.112	2.50
CH_4	3.76	2.600	0.000	0.02
C_2H_4	4.16	4.260	0.000	1.50
C_2H_6	4.44	4.470	0.000	0.65
n-C_4H_{10}	4.69	8.20	0.050	–
i-C_4H_{10}	5.28	8.29	0.132	–
SF_6	5.50	6.54	0.000	0.00

* Derived by using the experimental second virial coefficients of gases at different temperatures and assuming that the intermolecular interaction follows the Lennard-Jones potential [49].

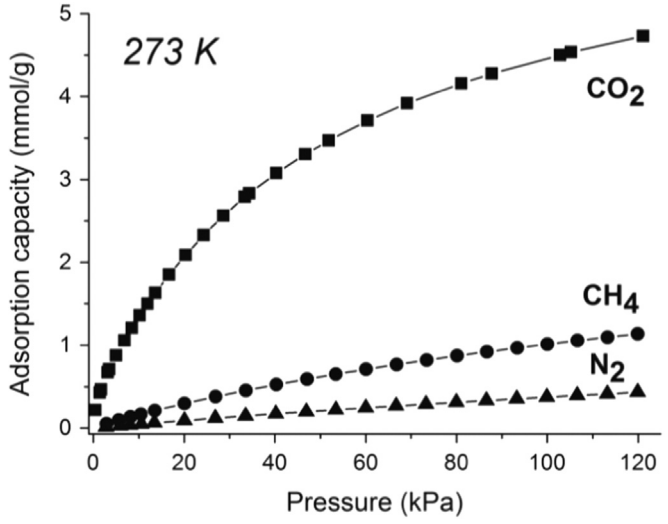

Fig. 1. Adsorption of CO_2 (■), CH_4 (●) and N_2 (▲) on high-silica SSZ-13 (Si/Al 85) at 273 K.

chemical composition of the zeolite. With increasing Al content, the framework becomes more polar. In general, the more polar the zeolite framework, the stronger it adsorbs various molecules through enhanced interactions. Fig. 2 illustrates this trend for the adsorption of CO_2 on zeolite LTA crystals with varying Si/Al ratio.

As these adsorption effects play a very important role in zeolite membrane separation, proper choice of the zeolite material is required to design an effective membrane for a given separation.

2.2. Permeation: diffusion

Permeation of gases through the zeolitic micropores at moderate temperature is generally controlled by surface (configurational) diffusion; it can be conveniently described in terms of hopping of molecules from one adsorption site to another [51,52]. Microporous transport of non-adsorbing as well as adsorbing molecules at higher temperature, that is when molecules keep the physical properties of the gas to a large extent because of weak adsorption, is defined by activated gaseous diffusion [53–55]. In general, excluding flow through defects, the overall flux through the zeolite film is a combination of surface and gaseous diffusion. The surface diffusion contribution (also indicated as zeolitic diffusion) to the overall permeance $\Pi_i^{surf.diff.}$ can be presented [56,57], assuming Langmuir adsorption, as:

$$\Pi_i^{surf.diff.} = \rho \bullet q_{sat,i} \bullet g \bullet D_i^{s,0} \bullet exp\left(\frac{-E_{a,i}^s}{RT}\right) \bullet \nabla \ln(1-\theta_i) \bullet \frac{1}{p_{i,r} - p_{i,p}}, \quad (1)$$

where ρ is the zeolite density, q_{sat} the saturation concentration of adsorbed phase, g a geometrical factor, D^s the surface diffusivity, E_a activation energy of diffusion, R the universal gas constant, T temperature, Θ occupancy and p_r and p_p the partial pressures of component i on the two sides of the membrane. The concentration of the gas in the adsorbed phase reaches saturation at certain pressure. At this point the surface diffusion flux does not increase further with increasing pressure. Increasing temperature, at constant pressure, leads to lowering of the concentration of adsorbed component and, accordingly, to lowered driving force while its activated character increases the flux. Thus, the contribution of surface diffusion may increase, decrease or have a maximum as a function of temperature, depending on the values of the activation

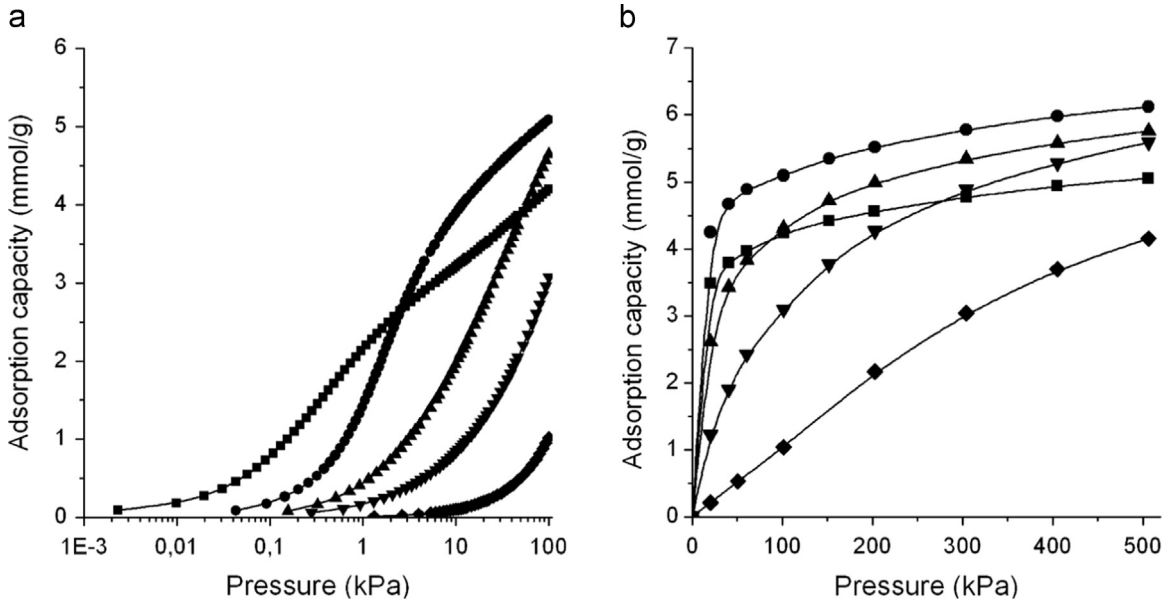

Fig. 2. CO_2 adsorption isotherms measured at 303 K in the (a) low- and (b) high-pressure ranges of LTA zeolites having Si/Al ratios of 1 (■), 2 (●), 3.5 (▲), 5 (▼), and ∞ (◆). Reprinted from [50]. Copyright 2010, with permission from the American Chemical Society.

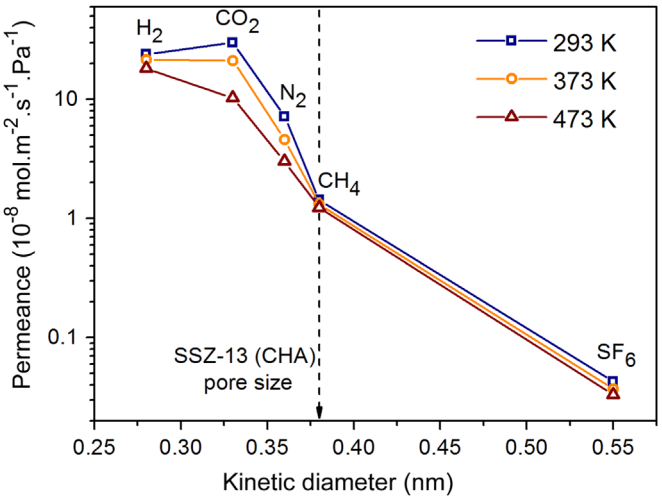

Fig. 3. Single gas permeance of several gases vs corresponding kinetic diameters through high-silica SSZ-13 membrane. Reproduced from [61] by permission of The Royal Society of Chemistry.

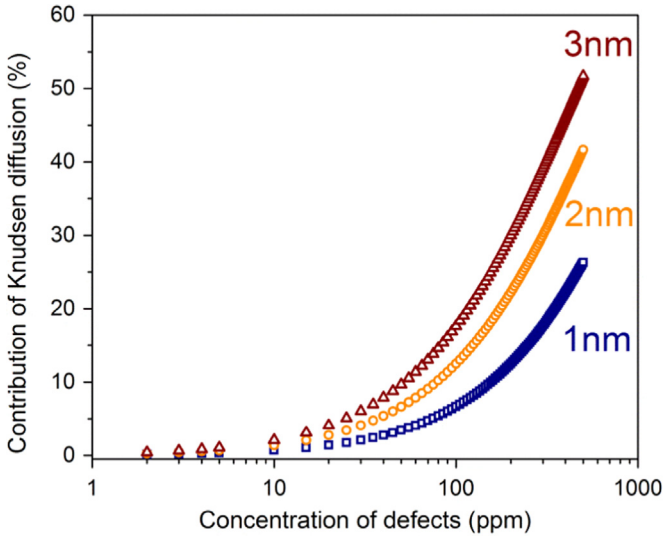

Fig. 4. Estimated contribution of Knudsen diffusion through defects of different size to the total flux of propane through an MFI membrane. The propane permeation through MFI layer is based on data from van de Graaf et al. [66].

energy and the adsorption enthalpy [58].

In turn, activated gaseous diffusion contribution to permeance $\Pi_i^{act.gas.diff.}$ can be defined [59] as:

$$\Pi_i^{act.gas.diff.} = \frac{1}{RT} \bullet \frac{g}{\delta} \bullet d \bullet \sqrt{\frac{8RT}{\pi M_i}} \bullet exp\left(\frac{-E_{a,i}^{g}}{RT}\right) \quad (2)$$

where δ is the membrane thickness, d the diffusion length and M_i the molar weight of component i. This contribution does not depend on pressure and, being an activated process, increases with temperature. Another important factor is that molecules significantly larger than the zeolite pores cannot adsorb and diffuse through. Fig. 3 demonstrates how the different diffusion contributions can vary with temperature. Expectedly, permeance of strongly adsorbing CO_2 molecules through small 8MR (eight-membered ring) pores of high-silica SSZ-13 membrane is the most affected by temperature, demonstrating a decrease of the surface diffusion contribution. SF_6 and CH_4 molecules, whose kinetic diameters are larger and similar to CHA pore size respectively, permeate much slower than smaller molecules. This is clearly an example of a molecular sieving effect, which can also be observed for DDR zeolites, another 8MR structure [60].

The main separation mechanisms by high quality (i.e., defect-free) zeolite membranes can be summarized in the following manner [62].

(1) Adsorption selectivity takes place when adsorption of one component is much stronger than that of another component; the zeolite occupancy with the more strongly adsorbing component is much higher and this leads to increased driving force. In addition, the strongly adsorbing component can block the micropores and hinder the transport of the other component, as for instance occurs in CO_2/H_2 separation [63]. Adsorption selectivity is usually the dominant separation mechanism at low temperatures.
(2) Diffusion selectivity takes place when molecules of one component are smaller and their diffusivity in zeolite micropores is much faster than that of the larger component (e.g., H_2/CH_4 in many 8MR zeolite membranes). The contribution of diffusion selectivity increase with temperature.
(3) Size exclusion (molecular sieving) – an extreme case of diffusion selectivity-when one component can scarcely or not at all permeate through zeolite pores (H_2/*i*-butane in 8MR membranes) [64].

It should be noted that these considerations pertain to high quality zeolite membranes. If many non-zeolitic pores of much larger size are present in the zeolite film, contributions of Knudsen diffusion, molecular diffusion, and even viscous flow can be significant and, eventually, become the dominant diffusion pathways [65]. Fig. 4 demonstrates how extremely low defect concentration can yield large contribution of unselective Knudsen flow. In addition, Knudsen diffusivity is proportional to the pore diameter, so that the size of defects plays an important role. Based on these results, the fraction of defect area should constitute less than 10 ppm for a zeolite membrane to render it operating in the molecular sieving regime.

2.3. Preparation of zeolite membranes

Two main techniques to prepare supported polycrystalline zeolite films are in situ synthesis and secondary growth. In situ synthesis was the first method used to obtain zeolite membranes [67,68]. A typical synthesis mixture contains an appropriate silica source (colloidal silica, fumed silica, sodium silicate, tetraethyl orthosilicate (TEOS), etc.), an alumina source (aluminum hydroxide, sodium aluminate, aluminum salts), a structure-directing agent (amines, tetralkylammonium salts, crown-ethers, etc.), base (e.g., alkali and/or organic bases) and water. After the mixture is homogenized, normally by stirring, the gel is poured in an autoclave vessel where the porous support is placed. During synthesis at elevated temperature zeolite crystals nucleate on the support surface and become intergrown upon crystallization. The main advantage of in situ synthesis is the minimal number of preparation steps. Furthermore, varying conditions of in situ synthesis allows obtaining either thin zeolite films on the support surface or infiltrated nano-composite membranes [69–71]. The latter method is called pore-plugging and it yields remarkably thermally and mechanically stable membranes [72–74]. The pore-plugging method, however, has a drawback of low permeance as the effective thickness of the infiltrated membrane can be extremely high [75,76]. To prevent zeolite crystallization in the support pores, its surface can be masked with polymer layers [77].

Another possibility to prepare zeolite films (*quasi*) in situ is the direct gel conversion method. The principle of the method is deposition (impregnation) of an aluminosilicate gel (dry or wet) on the support surface followed by crystallization [78]. A modification

of this method is a direct conversion of supported amorphous silica layers into zeolite films. In this case, the original support layer acts as a silica source so that crystallization is directed to occur on the support surface [79,80].

Secondary growth approaches involve preparation of nano-crystals (usually 50–1000 nm) of the targeted zeolite structure and their deposition as a thin layer on the support surface followed by hydrothermal secondary crystallization. Many methods exist to deposit thin layers of zeolite nano-crystals including dip-coating, filtration, rubbing, electrostatic and chemical deposition. Continuity, density and uniformity of the seed layer often determine the quality of the final membrane. By secondary growth, well-defined and sub-micron thin films may be crystallized, owing to the directed growth from the seed nano-crystals. Recently, Tsapatsis group reported extremely thin films (~200 nm) synthesized by secondary growth from MFI nano-sheet layers [81]. These ultra-thin membranes showed good selectivity in *p*-xylene/*o*-xylene separation and the permeance through such a thin zeolite layer was similar to the permeance through a bare porous support. Furthermore, secondary growth approach may be applied to control orientation of zeolite films by deposition of pre-oriented seed layers [82,83]. As zeolite crystals are often anisotropic, the orientation of the film may play an important role in the membrane performance, as it was convincingly shown for various MFI membranes by the Tsapatsis group [84,85].

Overall, it can be concluded that, despite the more laborious approach, secondary growth is a more versatile and convenient way to fabricate zeolite films. Accordingly, this approach prevails in recent research reports. As an illustration of secondary growth advantage, Fig. 5 provides a comparison between SSZ-13 (CHA) films synthesized on similar porous α-alumina supports at the same synthesis conditions in situ and by pre-seeding the support with SSZ-13 nanocrystals (ca. 120 nm). Clearly, thinner, more uniform and much higher quality membranes are obtained by directed crystallization on the support surface through secondary growth.

2.4. Supports

Zeolite membranes are usually supported thin films and the properties of porous support play a crucial role in successful membrane preparation. A rigid inorganic support is necessary to make the thin membrane layer mechanically stable. The main requirements to be fulfilled by the support are high stability in hydrothermal and alkaline synthesis conditions, low permeation resistance, a smooth surface without pinholes and affinity for the membrane layer material. Porous supports are mostly ceramic materials (α-alumina, titania, silica) or stainless steel, but examples of carbon [86], and even zeolite-based supports [87,88] have been reported. The choice of support material is to a high degree dictated by the compatibility of its thermal expansion with that of zeolite material. Zeolites usually have very specific negative thermal expansion coefficients, meaning that they contract upon heating [89]. In contrast, most ceramic materials expand upon heating. The mismatch between the thermal expansion coefficients is considered to be the main reason for the often encountered temperature-induced formation of defects within the zeolite layer upon calcination, which is the conventional way to (re-)activate (remove the structure-directing agent (SDA, template) molecules or other species occluded in the micropores) zeolite membranes [90,91].

Recent developments to avoid formation of thermally induced defects include application of rapid thermal processing (RTP) when a composite membrane is instantly heated by IR illumination to 600–900 °C, kept at this temperature for several minutes and then quickly cooled to room temperature [92]. Application of such a treatment to detemplate stainless steel and α-alumina supported zeolite (MFI) films was shown to yield membranes with much less intercrystalline defects and, hence, improved separation performance as compared with membranes calcined using conventional ramp rates. This phenomenon was explained by elimination of grain boundary defects because of strengthening the bonding between the grains [93–95]. Another viable alternative to conventional air calcination is ozonication performed in oxygen-ozone mixtures [96]. Owing to the high oxidation strength of ozone the temperature necessary for detemplation of MFI can be decreased to ca. 200 °C [97,98]. Accordingly, it was shown that ozonication is an efficient method to detemplate some zeolite membranes that cannot be treated at high temperature without deterioration [99]. More recently atmospheric pressure plasma treatment was shown to yield fast (ca. 60 s) and effective detemplation of thin MFI films [100].

The chemical, thermal, hydrothermal, and mechanical stability of the support material is also an important issue as zeolite films are usually prepared at elevated temperatures and hydrothermal conditions. Often, measures should be taken to prevent leaching of the support material. It was reported that Al from α- or γ-alumina supports can be incorporated into the zeolite layer during hydrothermal synthesis, which is often not desirable because of increased polarity of the resulting membranes.

In addition to zeolite film stability issues, properties of the support will often define the membrane separation performance. Textural characteristics of the support may influence both selectivity and permeance through a composite membrane. The driving force for permeation through any membrane is a partial pressure gradient. As Fig. 6 demonstrates, in case of highly permeable support: $(p_{feed}-p_{interface})\rightarrow(p_{feed}-p_{interface})=\Delta p$, and, thus, the overall membrane permeance approaches the intrinsic permeance of the zeolite film. On the other hand, in case a support has high diffusion resistance the pressure difference over the zeolite layer $(p_{feed}-p_{interface})\rightarrow 0$ and overall membrane permeance decreases. Hence, the key factor determining the membrane flux is the permeance ratio of the support material and the zeolite film; the higher this ratio, the less the support resistance

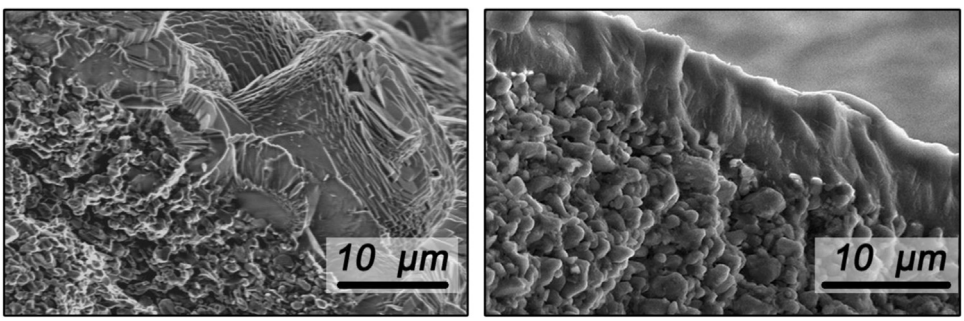

Fig. 5. SSZ-13 (CHA) films prepared in similar conditions by (left) in situ and (right) secondary growth method.

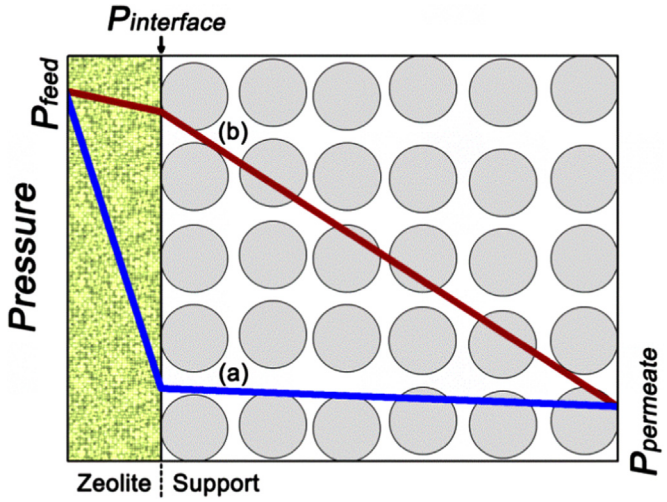

Fig. 6. Partial pressure drops over a zeolite membrane in case of low (a) and high (b) support diffusion resistance.

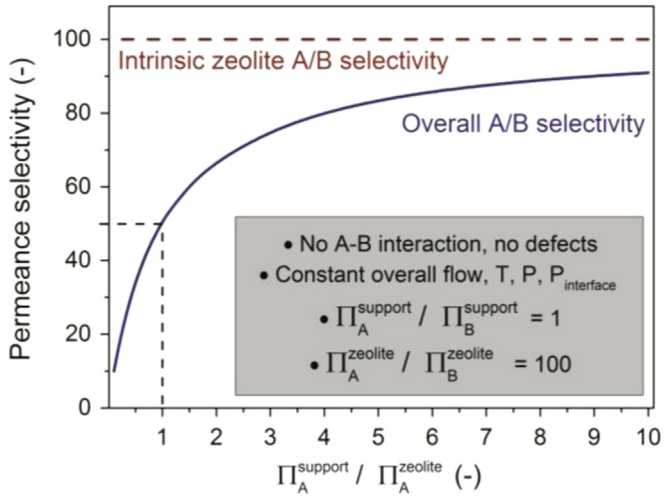

Fig. 7. Theoretical membrane A/B selectivity vs. support-zeolite permeance ratio.

limits the overall flux. Ultimately, since bare supports typically display negligible Knudsen selectivity, the overall membrane selectivity is also reduced, because diffusion of the faster permeating component would suffer more from support limitations than that of the retained one, as illustrated in Fig. 7. In this respect, the selective layer should face the feed side. Reversing the asymmetric membrane may result in a strongly reduced selectivity as the support induces then a polarization layer [101].

The support texture is of extreme importance for very thin zeolite films. High flux through such films requires avoiding an interface pressure build-up, otherwise the overall membrane performance might be strongly limited [57,102]. Korelskiy et al. evaluated ultra-thin (500 nm) hydrophobic MFI membranes, with less than 0.5% of defect flow contribution, for the recovery of ethanol and butanol from respective aqueous solutions [103]. Although the authors reported an unprecedentedly high flux for these separations, the selectivity was only low to moderate. Modeling showed that significant mass-transfer limitations, caused by the support, led to ca. 50% selectivity reduction of the composite membrane compared to the intrinsic selectivity of the zeolite film. In another work, comparison of high-silica SSZ-13 membranes of similar quality and thickness prepared on supports differing in porosity was made [99]. The gas separation results showed significantly higher (3–4 times) permeance of CO_2 and H_2 through membranes prepared on a more permeable support at similar CO_2/CH_4 and H_2/CH_4 selectivities. From this perspective, it is very important that researchers reporting separation properties of various zeolite membranes provide detailed textural data together with permeation data of the bare supports. Only in this case a fair comparison of zeolite membrane performance prepared by different groups can be made.

It is clear that supports possessing high porosity and as large as possible pores are preferred for fabrication of zeolite films. However, to facilitate formation of a thin and defect-free zeolite layer the support surface should be smooth, without microscopic roughness and imperfections. This condition practically limits the maximum support pore size to about 1 μm to prepare a zeolite film of ca. 1 μm thick. One solution for this problem is the fabrication of multilayered asymmetric supports, where a thin top layer provides the smoothness necessary for zeolite layer deposition and a coarse bottom layer provides sufficient transport properties. These advantages of asymmetric supports are, however, compromised by higher costs to fabricate them. Moreover, in case of asymmetric high aspect ratio hollow fiber supports, the thermal stability of zeolite (e.g., ZSM-5 and SSZ-13) films on smooth and highly curved surface has been shown to be impeded [99]. Overall, since the support may constitute up to 70% of total zeolite membrane cost [104], significant progress in production and application of cheaper and, at the same time, less diffusion resistant supports is necessary for large-scale commercialization of zeolite membranes for gas separation [105,106].

Recently, some efforts have been made to prepare high quality zeolite films on relatively cheap and large pore supports containing many microscopic imperfections. Yan et al. reported the synthesis of high-performance LTA membranes on the surface of coarse and inexpensive α-alumina tubes with 1–3 μm pores [107,108]. The preparation was based on rubbing the support surface with a synthesis gel (or LTA seeds embedded in the gel) followed by crystallization. The resulting membranes display high and reproducible performance in the dehydration of 10% water/90% ethanol mixtures by pervaporation. The same group reported the synthesis of MFI membranes on commercially available low-cost (150 $/m^2) α-alumina tubes [109,110]. The authors developed a so-called wetting rubbing method, which initially involves the impregnation of the support with solvent and then coating with MFI seeds layer by rubbing. Optimum results were obtained with *n*-butanol as the wetting agent. The hydrophilic membranes showed good performance in recovery of ethanol from a 5% aqueous solution by pervaporation. Li et al. synthesized LTA films on coarse α-alumina tubes by the hot dip-coating technique [111]. Using consequent dip-coating steps with decreasing seed particle sizes followed by secondary growth, the authors obtained high-performance hydrophilic membranes for the dehydration of organic solvents. In another work dip-coating at low pH to stabilize the precursor suspension was performed, yielding thin and dense seed layers of MFI and MEL zeolites on the rough surface of symmetric α-alumina hollow fibers [112]. After secondary growth, supports coated in this way yielded thin and good quality polycrystalline membranes for hydrophobic pervaporation and separation of butane isomers.

2.5. Chemical composition

The zeolitic Si/Al ratio not only influences framework polarity and adsorption properties but also has a strong effect on the integrity of the zeolite layer. Noack et al. observed that increasing the Si/Al ratio from 20 to 600 in ZSM-5 (MFI) membranes drastically enhanced membrane quality [113]; similar results were obtained by Kosinov et al. for a series of SSZ-13 membranes with Si/Al ratio varied from 5 to 85 [114]. It is generally accepted that the

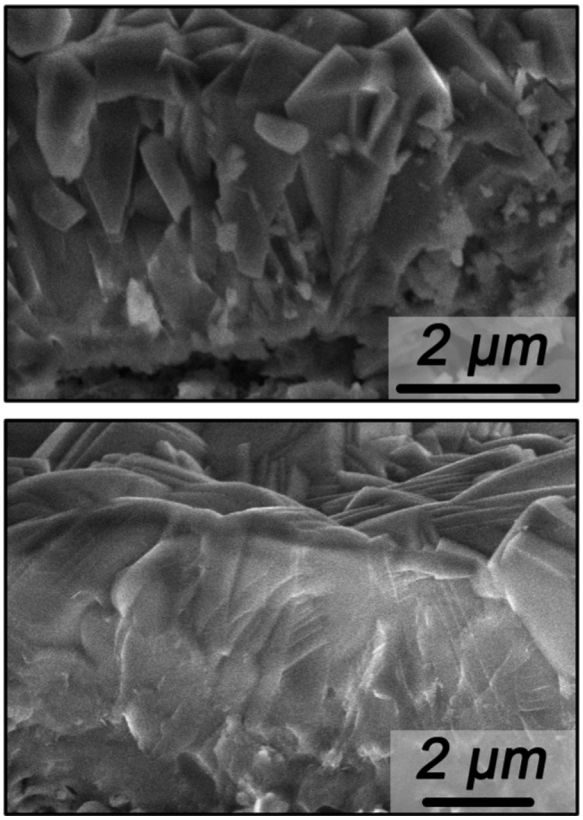

Fig. 8. Cross-section SEM images of SSZ-13 zeolite films synthesized at similar conditions from synthesis mixtures with an Si/Al ratio of 10 (left) and 100 (right).

repulsion between strongly negatively charged Al-rich zeolite crystals leads to formation of defects between the crystals and poor overall intergrowth [115]. Fig. 8 demonstrates how the synthesis mixture Si/Al ratio influences the integrity of SSZ-13 membranes prepared by the similar procedure. Clearly, the high-silica film is dense and uniform, while the low-silica film consists of barely intergrown single crystals.

Caro et al. developed a strategy of balancing the negative charge of Al-rich zeolite crystals by using "intergrowth supporting substances" (ISS) such as quaternary polyammonium salts, characterized by a high positive charge density [116]. Indeed, the membranes prepared with ISS addition contained less defects. Nevertheless, the contribution of defect flow for low-silica FAU and LTA membranes was still substantial leading to poor gas selectivities [117].

To summarize, the application of low-silica membranes appears currently to be restricted to moderate-temperature adsorption-controlled removal of H_2O, CO_2, H_2S and other highly polar compounds. In diffusion-controlled gas separation where the absence of defects is more important than adsorption properties, the Knudsen selectivity is rarely exceeded by using low-silica membranes. Thus, for genuine molecular sieving separations high-silica zeolite structures should be considered. In addition, it is important to note that the hydrothermal and chemical stability of zeolites increases with Si/Al ratio. For instance, Drobek et al. compared stability of ZSM-5 (Si/Al 100) and silicalite-1 membranes in long-term desalination runs (up to 560 h) and found much higher robustness for pure-silica zeolite [118]. Moreover, pure-silica DDR [119] and high-silica CHA membranes [120] were shown to have promising hydrothermal stability at industrially relevant conditions.

Silicoaluminophosphates (SAPOs) with stoichiometry of $Si_xAl_yP_zO_2$, where typically $0 < x < 0.2$, are a family of zeotype materials consisting of SiO_4, AlO_4 and PO_4 tetrahedra. The structure of SAPO materials corresponds to that of their aluminosilicate analogs, while the chemistry significantly differs. First of all, the intrinsic polarity of SAPO frameworks is higher than of aluminosilicate ones because of more ionic character of bonding – every PO_4 and AlO_4 tetrahedron is respectively positively and negatively charged. This fact leads to enhanced hydrophilicity and lower hydrothermal stability of SAPO materials as compared to high-silica zeolites [121]. Important consequence of increased polarity is the sensitivity of SAPO-based membranes to water vapor, which is often present in gas streams. Poshusta et al. studied the effects of short and long-term exposure of SAPO-34 membranes to water vapor. They found that SAPO-34 micropores were nearly blocked in the presence of 0.6–0.9% water vapor, leading to drastically decreased CO_2 permeance and negligible CO_2/CH_4 selectivity [122]. In addition, SAPO-34 membranes permanently degraded after long-term exposure to laboratory atmosphere (1–2% of water vapor, considering the average humidity and atmospheric pressure in Boulder, Colorado). It should, on the other hand, be noted that long-term exposure to an atmosphere with low water content (170 ppm) had only a slight effect on SAPO-34 membrane separation performance [123]. Nevertheless, the high sensitivity of SAPO structures to water vapor means that real gas streams must be thoroughly dehydrated before separation, which may turn application of SAPO membranes unfeasible.

To conclude, development of advanced seeding techniques made it possible to prepare high-quality zeolite films, even on very rough support surfaces. Further progress in this direction can significantly decrease fabrication costs and eventually help commercializing the gas separation and hydrophobic pervaporation zeolite membranes. In this respect, demonstration of synthesis reproducibility and membrane stability with respect to high temperature, pressure and presence of water and other typical components of gas streams will be key factors.

3. Zeolite topology

Many zeolite structures and their combinations with various substrates have been utilized for preparation of molecular sieving membranes. It is fair to say that zeolite topology plays an crucial role in zeolite membrane separations. A brief overview of selected existing membranes and their performance in various gas separations is given by Fig. 9.

3.1. 10MR and 12MR membranes

By far the most studied zeolite structure for preparation of membranes is ZSM-5 (MFI topology), named silicalite-1 in its pure-silica form. MFI possesses a 3-dimensional pore network consisting of intersecting sinusoidal (*a*-direction) and straight (*b*-direction) channels; the 10MR pores of MFI are ca. 5.5 Å in size. The popularity of this structure is explained by the relatively ease of preparation, which has led to many studies into MFI membrane growth enabling controlled synthesis of promising membranes [132]. Fig. 10 illustrates the dominance of MFI-type zeolites in scientific reports about zeolite membranes. Strikingly, there are nearly three times more publications on MFI membranes than on already commercialized LTA membranes.

From the perspective of gas separation, it should be noted that MFI pores are larger than the kinetic diameter of most permanent gases (Table 1). Thus, MFI and other 10MR and 12MR zeolite membranes can only be efficient for adsorption-controlled gas separations or separation of larger hydrocarbon molecules [133]. This fact limits application of these membranes to moderate temperatures, where adsorption still plays a significant role.

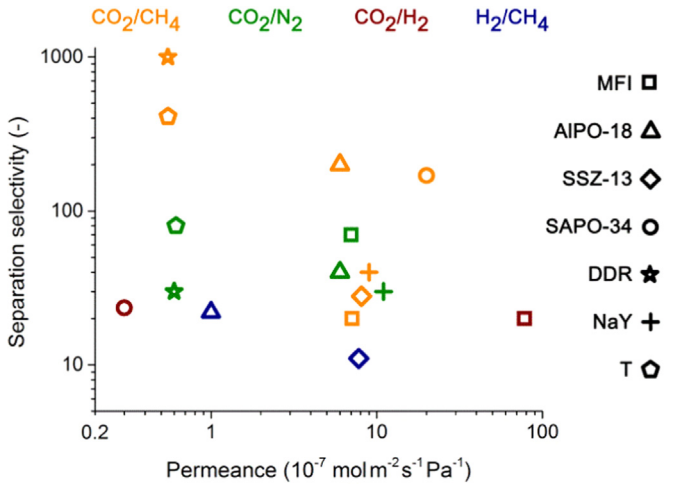

Fig. 9. Reported examples of mixture gas separation by various supported zeolite membranes [60,114,124–131]. In each case the measurements were performed in the temperature range of 20–35 °C, pressure range of 100–600 kPa with (nearly) equimolar mixtures.

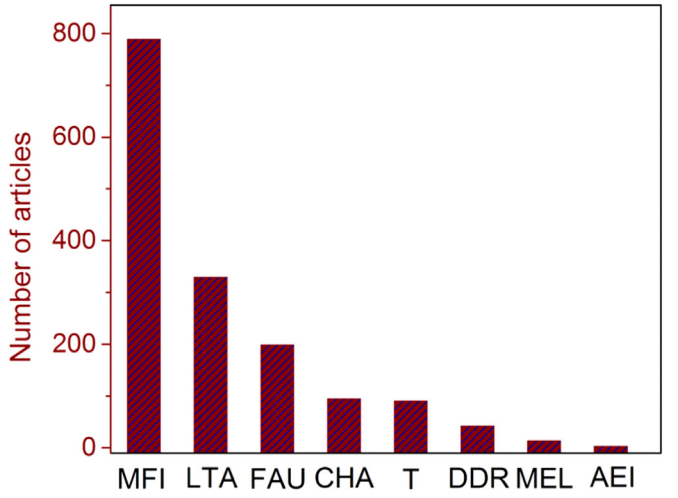

Fig. 10. Number of publications indexed in Scopus containing term "XXX zeolite membranes" (where XXX is zeolite topology code; note that zeolite T is an ERI-OFF intergrowth-type zeolite) in the article title, the abstract or the keywords. Different zeotypes belonging to one topology are combined, e.g. MFI=MFI+ZSM-5+silicalite-1; CHA=chabazite+CHA+SAPO-34+SSZ-13, etc.

Nevertheless, there are many examples of successful gas separations, especially CO_2-involving ones, by 10MR and 12MR zeolite membranes.

Recently, Hedlund et al. in a series of publications evaluated the performance of thin (<1 μm) α-alumina supported silicalite-1 membranes in low-temperature CO_2/H_2 and CO_2/CO separations [134,135]. These membranes displayed CO_2 permeances as high as 10^{-6}–10^{-5} mol m^{-2} s^{-1} Pa^{-1} and CO_2 selectivities as high as 10–100. Similar membranes were also applied for cryogenic O_2/N_2 separation with O_2 permeance of about 10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a separation factor of 5 at 80 K [136]. MFI membranes were also reported to be effective for separation of linear hydrocarbon isomers from their branched analogs. Separation of *n*-butane/*i*-butane mixtures is a common MFI membrane quality test [137].

Low-silica FAU type NaY and NaX membranes with 12MR pores (7.4 Å) are polar and thus highly CO_2 selective. Successful CO_2/CH_4 [129], CO_2/N_2 [138] and CO_2/H_2 [139] separations by FAU membranes have indeed been reported. Because of its large pores, FAU membranes offer high CO_2 flux at reasonable selectivity, which decreases with increasing temperature. An important advantage of FAU zeolites is that the use of organic SDAs is not always required in their synthesis. Thus, fabrication of FAU membranes is cheaper and consists of fewer steps as template removal can be omitted. On the other hand, the high Al content in FAU structures makes their synthesis in the shape of membranes quite challenging [140].

Organic-free mixtures are also applied for the synthesis of zeolite T membranes. Zeolite T is a low-silica (Si/Al 3–4) intergrowth of offretite (OFF, 1-dimensional, 12MR) and erionite (ERI, 3-dimensional, 8MR). Zeolite T membranes were evaluated in the separation of CO_2 from CH_4 [141] and other gases [124] and displayed decent performance at low temperature and pressure conditions.

Table 2
Properties of selected 8MR zeolite structures.

Zeolite structure (examples)	Pore size (Å × Å)[a]	Dimensions	Accessible volume (%)	Max. Si/Al[b]
AEI (SSZ-39, AlPO-18)[a]	3.8 × 3.8 3.8 × 3.8 3.8 × 3.8	3D	17.3	> 100
DDR (ZSM-58, DD3R)[a]	3.6 × 4.4	2D	9.2	∞
CHA (SSZ-13, SAPO-34)[a]	3.8 × 3.8	3D[c]	17.3	∞
LTA (Na-A, ITQ-29)[a]	4.1 × 4.1	3D[c]	21.4	∞
RHO (Rho, DNL-6 [188])[a]	3.6 × 3.6	3D[c]	20.6	5
ERI (UZM-12, AlPO-17)	3.6 × 5.1	3D[c]	15.1	10
AFX (SSZ-16, SAPO-56)	3.6 × 3.4	3D[c]	17.3	6
SFW (SSZ-52)	4.1 × 4.1	3D[c]	17.2	10
RTH (SSZ-50)	3.8 × 4.1 2.5 × 5.6	2D	16.0	∞
KFI (ZK-5)	3.9 × 3.9	3D[c]	17.9	5
ITE (ITQ-3)	3.8 × 4.3 2.7 × 5.8	2D	16.5	∞
IHW (ITQ-32)	3.5 × 4.3	2D	9.7	∞
ITW (ITQ-12)	2.4 × 5.4 3.9 × 4.2	2D	8.2	∞
NSI (Nu-6(2))	2.6 × 4.5 2.4 × 4.8	2D	3.5	∞
LEV (Levyne)	3.6 × 4.8	2D	14.3	50

[a] Structure has been applied for preparation of a thin film.
[b] Maximum reported Si/Al for aluminosilicates.
[c] Identical channels in *a, b, c*-directions.

3.2. 8MR membranes

Zeolites with smaller pores can offer real molecular sieving for separation of permanent gases, as typical pore size of these zeolites is below 4 Å, which is close to the kinetic diameter of many permanent molecules. To date, several 8MR structure have been utilized for preparation of gas selective zeolite membranes. Table 2 gives an overview of already applied and other promising 8MR structures.

LTA is a three-dimensional 8MR zeolite with very high accessible pore volume. Polar low-silica Na-A (Si/Al=1) membranes, commercialized for the dehydration of alcohols, rarely display selectivity above respective Knudsen values in separation of permanent gases [142,143]. The reason for this poor performance is the abundant presence of non-selective pathways in dehydrated Na-A membranes, caused by highly surface charged crystal nuclei during the synthesis [115], and the strong adsorption of traces of water vapor, blocking the permeation of other gases. On the other hand, recently developed pure-silica LTA (ITQ-29) [144] and neutral aluminophosphate AlPO-4 [145] membranes possess much

less defects and were accordingly shown to separate H_2/CH_4 mixture with a selectivity of ~6, well above the Knudsen value (2.6) [146]. The reasons for the superior quality of high-silica aluminosilicate membranes compared with their low-silica analogs will be discussed in the next section. Currently, the main problems associated with the fabrication of high-silica LTA membranes are the very expensive templates necessary for the synthesis (cryptand "Kryptofix 222" or alkyl-substituted polycyclic hydroxides) and the troublesome synthesis procedure involving hydrofluoric acid and a nearly dry initial mixture, making it difficult to grow uniform and thin zeolite layers. In addition, LTA pores of 4.1 Å are somewhat bigger than many light gas molecules, which limits the molecular sieving capacity of LTA membranes to separations involving hydrocarbons starting from ethylene and larger.

DDR is a two-dimensional zeolite with moderate porosity and 3.6×4.4 Å pores [147]. Excellent stability of high-silica DDR membranes, even at temperatures as high as 500 °C, has been reported [148,149]. Main applications of these membranes are CO_2 and H_2 separations [150]. For instance, selectivities of the order of 10^3 and 10^2 have been reported for CO_2/CH_4 and CO_2/air separations, respectively [60]. The DDR membranes were also shown to be effective for selective removal of hydrogen during catalytic dehydrogenation of isobutane [64].

The main drawback of DDR is the relatively low permeance that can be achieved, due to its two-dimensional pore structure and also the low porosity of DDR. Another pitfall is the troublesome synthesis of DDR, known to be poorly reproducible. So far, NGK is the only company that has been able to produce DDR membranes of high quality [119].

CHA membranes, high-silica SSZ-13 and zeotype SAPO-34 (silicoaluminophosphate), are currently considered the most promising candidates for light gases separation [151]. Excellent results were obtained using SAPO-34 membranes; they are highly selective and permeable for CO_2 in various mixtures as well as for H_2 and other small molecules [152,153]. More recently, high-silica SSZ-13 membranes have already been demonstrated to have at least comparable performance to SAPO-34 membranes [154], while possessing much higher thermal and hydrothermal stability. The open, highly symmetric 3-dimensional CHA structure is suitable for reproducible fabrication of membranes capable of separating various gas and liquid mixtures at close to industrial conditions [61].

Finally, zeotype AlPO-18 (AEI) membranes were recently reported to possess very promising separation properties towards CO_2 and H_2 [155,156].

3.3. 6MR membranes

Zeolites with exclusively 6MR pores (ca. 2.8 Å) are considered permeable to only very small molecules (e.g. water or hydrogen) [157–159]. For instance, low-silica sodalite (SOD) membranes displayed $H_2/n\text{-}C_4H_{10}$ ideal selectivities over 1000 [160]. The permeance through the extremely small 6MR pores is, however, very low which makes commercial application of sodalite membranes for gas separation unlikely. In addition, SOD hydrothermal stability is low because of the high Al content [161].

3.4. Post-synthesis modification

Post-synthesis modification is a convenient way to alter properties or reduce the number of defects within the zeolite film. This can include chemical modification by grafting, making use of surface silanols, to turn the surface hydrophobic or affinitive to specific compound. Such modification alters the zeolite adsorption properties and sometimes allows more selective separation [162].

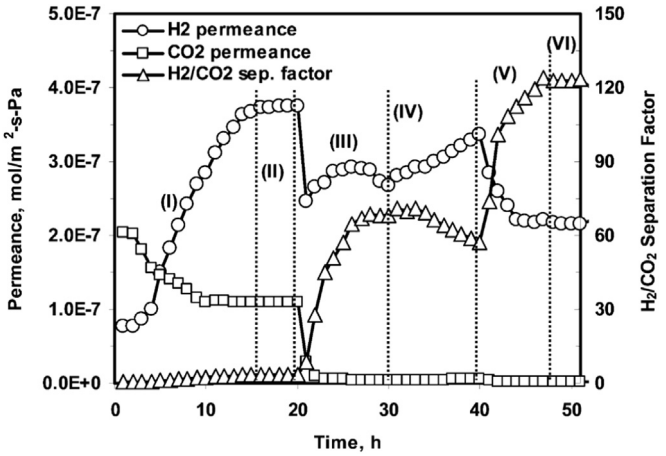

Fig. 11. Separation results for an equimolar H_2/CO_2 mixture during the CCD modification. (I) heating from ~298 to 723 K; (II) dwelling at 723 K; (III) first MDES CCD; (IV) annealing in H_2/CO_2 feed without MDES; (V) second MDES CCD; and (VI) H_2/CO_2 feed without MDES. Reprinted from [165]. Copyright 2009, with permission from the American Chemical Society.

Another approach involves tuning the zeolite pore size by CVD of silica or carbon layers [163]. For instance, Hong et al. tuned pores of B-ZSM-5 and SAPO-34 membranes by catalytic cracking deposition (CCD) of methyldiethoxysilane (MDES) and observed a significant improvement in H_2/CO_2 selectivity without proportional decrease of H_2 permeance [164]. Tang et al. observed an even more pronounced increase of the H_2/CO_2 selectivity (Fig. 11) after several consecutive CCD steps [165]. It should be noted that, although the separation selectivity increased ca. 40 times, the H_2 permeance of silylated membrane was just two times lower. Lin et al. performed similar CVD treatment on high-quality MFI membranes and concluded that, upon reducing the pore size, the transport of small molecules like H_2 and He was governed by activated gaseous diffusion instead of Knudsen flow [166]. Importantly, membranes silylated by MDES exhibited improved thermal and hydrothermal stability [167]. Thus, pore size tuning by deposition of molecular silica inside the zeolite pores offers a possibility to turn initially adsorption selective into stable and truly molecular sieving membranes with high selectivity towards small molecules (mainly H_2).

Expectedly, the combination of these properties led to application of pore tuned MFI membranes in catalytic membrane reactors. Among others, the use of membranes the thermodynamically limited water-gas shift reaction (WGSR) attracted a lot of attention [168]. In a catalytic membrane reactor, the equilibrium can be shifted towards the products by selectively removing the hydrogen from the reaction. It was shown by Dong et al. that, indeed, a catalytic membrane reactor based on high-quality MFI membrane modified by CCD is capable of surpassing the equilibrium limits in the WGS reaction. At 550 °C and 1.5 bar conversion of CO achieved in the zeolite membrane reactor was 81.7% well above the equilibrium value of 65% [169].

Post-synthesis modification can be also a way to decrease number of defects within zeolite film. Noble et al. applied soaking in cyclodextrin solution to improve the separation performance of SAPO-34 membranes [170]. Since cyclodextrin molecules are too large to penetrate into zeolite pores, they selectively block the intercrystalline defects. As a result, the CO_2/CH_4 separation tests showed significant increase of CO_2/CH_4 selectivity without affecting much the CO_2 permeance through the modified membranes. Similar methods to seal the defects including dip-coating of MFI membranes with amorphous silica layer [171], silicone rubber [172] and CVD of silica within defects by counter diffusion [173] have been proposed. Another relevant approach is fabrication of

poly-layer zeolite membranes in order to close defects in the bottom layer by another layer of the same material grown on top [174] or to combine desired properties of two different zeolite types in one structure [175].

Apart from blocking membrane defects and decreasing the pore size, post-synthesis modification can be used to tune zeolite adsorption properties. For example, grafting with methylamine enhances the performance of silicalite-1 membranes in CO_2/H_2 and CO_2/CH_4 separations [176]. The reason for the improvement is the much higher affinity of the modified material to CO_2, originating from the strong interaction of methylamine with the zeolite framework. As a result of Si–N–Si bridge formation the overall framework basicity strengthens, leading to increased CO_2 adsorption [177]. Another way to improve CO_2 affinity and, hence, membrane selectivity is impregnation with a calcium nitrate solution followed by its thermal decomposition, resulting in CO_2 specific adsorption sites [178]. A similar approach was applied to enhance the hydrophobicity of MFI membranes. Grafting with triethoxyfluorosilane yielded materials with drastically decreased affinity to water, authors explained this phenomena by partial replacement of polar Si–OH groups with Si–F ones within the zeolite layer [179].

To conclude, post-synthesis modification is a convenient and versatile method to adjust specific separation and adsorption properties as well as to improve the overall quality of zeolite membranes.

4. Perspectives

Although during the last decade the field of zeolite membranes has witnessed very important developments, several promising directions should be explored further. Among them, development and improvement of preparation methods, design of novel membranes by combining the existing synthetic repertoire with appropriate zeolite structures and reduction of costs associated with the preparation of zeolite membranes are of special interest.

4.1. Improvement of synthesis techniques

In this section we will briefly discuss several perspective directions in the fabrication of zeolite films. As highlighted above secondary growth remains the predominant technique for synthesizing high-quality thin and often oriented zeolite films. Normally, the secondary growth method requires nano-crystals to be used as seeds. Synthesis of zeolite nano-crystals is often difficult [180] and a ball-milling step can be a convenient strategy to prepare seed crystals of suitable size. For instance, it was shown for NaA and CHA crystals (originally 5–10 μm) that ball-milling led to highly crystalline nano-crystals with relatively narrow particle size distributions which could be successfully applied for surface coating [181,182].

Use of fluoride anions as mineralizing agents has some advantages compared with conventional hydroxyl media [183]. Fluoride-mediated synthesis is well-known to result in zeolite crystals with much lower density of silanol defects and, hence, higher overall zeolite hydrophobicity and hydrothermal stability [184]. Now, the first examples of successful fluoride route membrane preparations are emerging. For instance, the group of Hedlund recently reported fabrication of high-quality and thin (<0.5 μm) F-silicalite-1 films on α-alumina discs [185]. The synthesis was performed in fluoride media at near neutral pH. The quality of the resulting membranes was determined by high-resolution permporometry; in this way, it was found that more than 99.5% of He flow through the [F]-MFI membrane passes through zeolite pores. In accordance with permporometry results [F]-MFI membranes performed well in CO_2/H_2 and *n*-butanol/water separations. Liu et al. reported the possibility to heal the lattice defects of as-synthesized [OH]-zeolites by simple hydrothermal treatment in NH_4F solution [186]. By using ^{29}Si, ^{19}F and ^{1}H NMR, the authors proved that zeolites (silicalite-1, ITQ-13 and ZSM-48), originally synthesized in basic media, after treatment with NH_4F, possess all the properties of the fluoride route synthesized materials. Crystal shape and zeolite structure were not disturbed after the modification, as demonstrated by SEM and XRD. This concept can be particularly interesting for the fabrication of zeolite membranes. By converting conventional [OH]-zeolite films into [F]-zeolite films, high-quality hydrophobic membranes can be obtained without dealing with troublesome fluoride route synthesis, which involes HF as a reagent and often very viscous gels making it difficult to grow a uniform membrane layer [187].

As discussed in previous sections, post-synthesis modification, which include blocking the defect pathways or tuning the zeolite pores as well as altering the surface or framework chemistry is a promising strategy worth further exploring. For instance, polymeric membranes have been widely applied in practice after defect healing strategies were developed. In addition post-synthesis treatment can help overcoming issues with synthesis reproducibility, which is often inherent to zeolite membrane synthesis.

4.2. Rational zeolite membrane design

To properly choose a zeolite structure for a given separation several factors should be taken into account. These include the size and adsorption properties of the molecules to be separated, operational conditions, presence of impurities (e.g. water vapor), etc. For instance, polar low-silica structures often display high adsorption selectivity for CO_2 separations (CO_2/CH_4, CO_2/N_2, CO_2/H_2); however, the presence of even low amounts of water is detrimental for their performance. Thus, if the target separation involves water or other strongly adsorbing impurities, high-silica 8MR zeolites offering molecular sieving properties, hydrothermal stability and low polarity should be considered. Table 2 and Fig. 12 highlight 8MR frameworks promising for preparation of molecular sieving gas selective membranes.

Some of these structures (AEI, CHA, DDR, LTA and the silicoaluminophosphate version of RHO) have already been applied for membrane preparation. For instance, the aluminosilicate version of one of the most interesting frameworks – RHO – has only been prepared with a rather low Si/Al ratio of about 5, which is hardly suitable for membrane preparation. RHO is characterized by a very open framework (density of only 14.5 T-atoms/1000 $Å^3$), a highly symmetric system of channels (i.e. the same channels in *a, b* and *c* directions, which usually has positive effect on the film synthesis because of isotropic growth), a cage-like pore structure (as discussed above, often advantageous for adsorption discrimination), and last and probably the most important – pores of 3.6×3.6 Å that would favor high molecular-sieving selectivity. High-silica RHO membranes would be particularly promising for industrially important separations involving He (He/air), H_2 (H_2/CH_4) and other small molecules.

Currently, novel approaches of rational zeolite design and necessary structure-directing agents are being developed. According to the International Zeolite Association there are over 220 discovered frameworks and,among them, there are over 70 8MR structures. This number constantly increases owing to advances in zeolite chemistry. Although the complete mechanism of zeolite growth remains unclear, the progress in the field of rational zeolite design is remarkable. Starting from a nearly alchemical trial and error approach, now it is possible to model geometrical properties of organic SDAs in view of their fit into zeolite channels and cages and interaction with the framework, and accordingly suitable

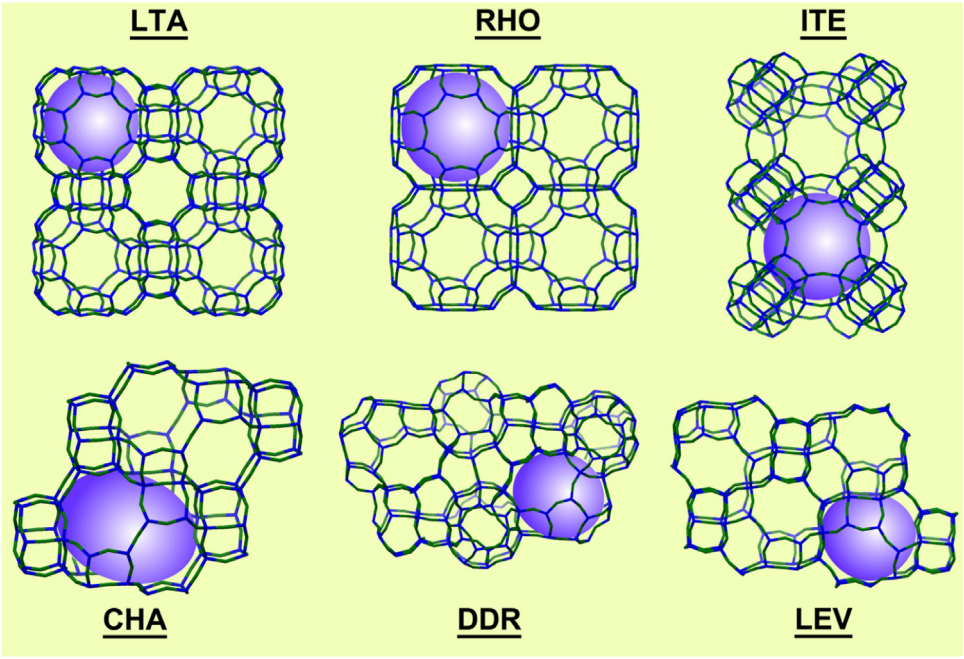

Fig. 12. Structures of selected 8MR zeolite structures suitable for fabrication of gas separation membranes.

templates for novel zeolite structures can be designed [189,190]. The progress in synthesis of new zeolites will undoubtedly lead to an increased number of zeolite structures suitable for preparation of thin films and membranes with optimal separation properties.

4.3. Cost reduction

The main pitfall en route to practical gas separation zeolite membranes is high fabrication cost. Some promising approaches to decrease fabrication expenses are discussed below.

(1) The support may constitute up to 70% of the total zeolite membrane cost; thus research efforts should be made to decrease the cost of the support. Optimization of seeding and secondary growth processes may lead to the possibility of synthesizing high-quality thin zeolite films on rough surfaces of cheaper extruded supports and several such membranes were discussed in this review.

(2) Recently, the library of zeolites that can be prepared in organic-free media has been significantly expanded. The method is based on adding the targeted zeolite as seeds to a synthesis gel that can yield another zeolite, containing common building units with the target structure, when the reaction is performed without seeds [191]. According to such approaches, several 8MR zeolites including RUB-13 (RTH) [192], RUB-50 (LEV) [193], ECR-18 (PAU) [194] have already been successfully synthesized. Further propagation of these methods to higher silica zeolites and their implementation in membrane synthesis can reduce the preparation costs by saving expensive organic SDAs. Such preparations would be also faster and more energy-efficient as it is not necessary to detemplate the as-synthesized membranes. A recent example is a SAPO-34 membrane with excellent CO_2/CH_4 separation performance prepared in organic-free media by microwave heating [195]. In addition, elimination of the calcination step can help avoiding formation of thermally-induced defects, which would positively influence membrane quality and reproducibility [196–199].

(3) The use of phosphorous-based molecules as templates for zeolite synthesis is another way to reduce costs associated with organic SDAs. Phosphorous-containing molecules are more stable than conventional nitrogen-based compounds that are usually decomposed during the membrane synthesis. Phosphonium cations and phosphazenes, on the other hand, can be recovered and re-used for further preparations [200]. In addition, the unique properties of phosphorous-based SDAs have already led to the discovery of several new zeolite structures [201,202].

5. Conclusions

Although usually separation performance, as well as thermal and chemical stability of zeolite membranes are unsurpassed by other materials, their commercialization for gas separation requires significant reduction of fabrication costs and improvement of preparation reproducibility. To this end, implementation of cheaper extruded porous supports for fabrication of membranes is crucial. It is now becoming possible because of remarkable advances recently achieved in coating very rough support surfaces with zeolite seed layers and healing/blocking the membrane defects by post-synthesis modification methods. Synthesis reproducibility is another critical factor closely related to the support properties. In most cases reproducible production of novel zeolite films requires parallel development of zeolite and support layers in terms of permeability, chemical properties and morphology. The importance of the support would only increase with inevitable and ever ongoing decrease of membrane thickness. Additionally, detailed long-term stability studies (high temperature, pressure, presence of aggressive impurities) are necessary to evaluate the robustness of zeolite membranes, which is often considered to be their main advantage.

Finally, improvement of existing and design of novel high-silica 8MR membranes deserves more attention of the scientific community than they currently attract. After major synthetic advances, it is now clear, that suitable ultra-thin and defect-free high- or pure-silica 3-dimensional 8MR membrane would be the ultimate material for highly efficient recovery/removal of small gas

molecules in a wide temperature and pressure range.

Acknowledgments

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References

[1] R.W. Baker, Future directions of membrane gas separation technology, Ind. Eng. Chem. Res. 41 (2002) 1393–1411.
[2] H. Strathmann, Membranes and membrane separation processes. 1 Principles, Ullmann's Encycl. Ind. Chem. 22 (2011) 413–454.
[3] R. Surya Murali, T. Sankarshana, S. Sridhar, Air separation by polymer-based membrane technology, Sep. Purif. Rev. 42 (2013) 130–186.
[4] N.W. Ockwig, T.M. Nenoff, Membranes for hydrogen separation, Chem. Rev. 107 (2007) 4078–4110.
[5] R. Faiz, K. Li, Olefin/paraffin separation using membrane based facilitated transport/chemical adsorption techniques, Chem. Eng. Sci. 73 (2012) 261–284.
[6] Y. Zhang, J. Sunarso, S. Liu, R. Wang, Current status and development of membranes for CO_2/CH_4 separation: a review, Int. J. Greenh. Gas. Control. 12 (2013) 84–107.
[7] C.A. Scholes, K.H. Smith, S.E. Kentish, G.W. Stevens, CO_2 capture from pre-combustion processes – strategies for membrane gas separation, Int. J. Greenh. Gas. Control. 4 (2010) 739–755.
[8] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B. D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: a review, Polymer 54 (2013) 4729–4761.
[9] C.A. Scholes, S.E. Kentish, G.W. Stevens, Carbon dioxide separation through polymeric membrane systems for flue gas applications, Rec. Pat. Chem. Eng. 1 (2008) 52–66.
[10] H.A. Mannan, H. Mukhtar, T. Murugesan, R. Nasir, D.F. Mohshim, A. Mushtaq, Recent applications of polymer blends in gas separation membranes, Chem. Eng. Technol. 36 (2013) 1838–1846.
[11] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390–400.
[12] B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, Macromolecules 32 (1999) 375–380.
[13] L. Boyadzhiev, Liquid membranes, in: I.D. Wilson, E.R. Adlard, C. Poole, M. Cooke (Eds.), Encyclopedia of Separation Science, 2002, pp. 1739–1748.
[14] L.J. Lozano, C. Godinez, A.P. de los Rios, F.J. Hernandez-Fernandez, S. Sanches-Segado, F.J. Alguacil, Recent advances in supported ionic liquid membrane technology, J. Membr. Sci. 376 (2011) 1–14.
[15] R.D. Noble, D.G. Lin, Perspective of ionic liquids and ionic liquid membranes, J. Membr. Sci. 369 (2011) 1–4.
[16] S. Kasahara, E. Kamio, T. Ishigami, H. Matsuyama, Amino acid ionic liquid-based facilitated transport membranes for CO_2 separation, Chem. Commun. 48 (2012) 6903–6905.
[17] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed-matrix membranes using carbon molecular sieves: I. Preparation and experimental results, J. Membr. Sci. 211 (2003) 311–334.
[18] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed-matrix membranes using carbon molecular sieves: II. Modelling permeation behaviour, J. Membr. Sci. 211 (2003) 335–348.
[19] Y. Li, T.S. Chung, S. Kulprathipanja, Novel Ag+-zeolite/polymer mixed matrix membranes with a high CO_2/CH_4 selectivity, AIChE J. 53 (2007) 610–616.
[20] A.M.W. Hillock, S.J. Miller, W.J. Coros, Crosslinked mixed matrix membranes for the purification of natural gas: Effects of sieve surface modification, J. Membr. Sci. 314 (2008) 193–199.
[21] T. Rodenas, M. van Dalen, E. Garcia-Perez, P. Serra-Crespo, B. Zornoza, F. Kapteijn, J. Gascon, Visualizing MOF mixed matrix membranes at the nanoscale: towards structure-performance relationships in CO_2/CH_4 separation over MIL-53(Al)@Pl, Adv. Funct. Mater. 24 (2014) 249–256.
[22] T. Rodenas, I. Luiz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabres, I. Xamena, J. Gascon, Metal-organic framework nanosheets in polymer composite materials for gas separation, Nat. Mater. 14 (2015) 48–55.
[23] B. Seoane, J. Coronas, I. Gascon, M.E. Benavides, O.X.U. Karvan, J.X.R. Caro, F. Kapteijn, J. Gascon, Metal-organic framework based mixed matrix membranes: a solution for highly efficient CO_2 capture, Chem. Soc. Rev. 44 (2015) 2421–2454.
[24] S. Yun, S.T. Oyama, Correlations in palladium membranes for hydrogen separation: a review, J. Membr. Sci. 375 (2011) 28–45.
[25] J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenberg, S. Liu, Y.S. Lin, J.C. Diniz de Costa, Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation, J. Membr. Sci. 320 (2008) 13–41.
[26] S.J. Khatib, S.T. Oyama, Silica membranes for hydrogen separation prepared by chemical vapor deposition (CVD), Sep. Purif. Technol. 111 (2013) 20–42.
[27] R.M. de Vos, W.F. Maier, H. Verweij, Hydrophobic silica membranes for gas separation, J. Membr. Sci. 158 (1999) 277–288.
[28] D.H. Park, N. Nishiyama, Y. Egashira, K. Ueyama, Enhancement of hydrothermal stability and hydrophobicity of a silica MCM-48 membrane by silylation, Ind. Eng. Chem. Res. 40 (2001) 6105–6110.
[29] H.H. El-Feky, K. Briceno, E. de Oliveira Jardim, J. Silvestre-Albero, T. Gumi, Novel silica membrane material for molecular sieve applications, Microporous Mesoporous Mater. 179 (2013) 22–29.
[30] H.M. van Veen, M.D.A. Rietkerk, D.P. Shanahan, M.M.A. van Tuel, R. Kreiter, H. L. Castricum, J.E. ten Elshof, J.F. Vente, Pushing membrane stability boundaries with HybSi® pervaporation membranes, J. Membr. Sci. 380 (2011) 124–131.
[31] G.G. Paradis, D.P. Shanahan, R. Kreiter, H.M. van Veen, H.L. Castricum, A. Nijmeijer, J.F. Vente, From hydrophilic to hydrophobic HybSi® membranes: a change of affinity and applicability, J. Membr. Sci. 428 (2013) 157–162.
[32] A.F. Ismail, L.I.B. David, A review on the latest development of carbon membranes for gas separation, J. Membr. Sci. 193 (2001) 1–18.
[33] P.S. Tin, T.S. Chung, Y. Liu, R. Wang, Separation of CO_2/CH_4 through carbon molecular sieve membranes derived from P84 polyimide, Carbon 42 (2004) 3123–3131.
[34] Y. Xiao, M.L. Chung, T.S. Chung, M. Toriida, S. Tamai, H. Chen, Y.C.J. Jean, Asymmetric structure and enhanced gas separation performance induced by in situ growth of silver nanoparticles in carbon membranes, Carbon 48 (2010) 408–416.
[35] S.S. Hosseini, T.S. Chung, Carbon membranes from blends of PBI and polyimides for N_2/CH_4 and CO_2/CH_4 separation and hydrogen purification, J. Membr. Sci. 328 (2009) 174–185.
[36] J. Gascon, F. Kapteijn, B. Zornoza, V. Sebastian, C. Casado, J. Coronas, Practical approach to zeolitic membranes and coatings: state of the art, opportunities, barriers, and future perspectives, Chem. Mater. 24 (2012) 2829–2844.
[37] J. Gascon, F. Kapteijn, Metal-organic framework membranes – high potential, bright future? Angew. Chem. Int. Ed. 49 (2010) 1530–1532.
[38] R. Krishna, J.M. van Baten, *In silico* screening of metal-organic frameworks in separation applications, Phys. Chem. Chem. Phys. 13 (2011) 10593–10616.
[39] M. Shan, M.C. McCarthy, S. Sachdeva, A.K. Lee, H.K. Jeong, Current status of metal-organic framework membranes for gas separations: promises and challenges, Ind. Eng. Chem. Res. 51 (2012) 2179–2199.
[40] O. Shekhan, J. Liu, R.A. Fischer, C. Wöll, MOF thin films: existing and future applications, Chem. Soc. Rev. 40 (2011) 1081–1106.
[41] A. Betard, R.A. Fischer, Metal-organic framework thin films: from fundamentals to applications, Chem. Rev. 112 (2012) 1055–1083.
[42] J. Gascon, F. Kapteijn, Metal-organic framework membranes – high potential, bright future? Angew. Chem. Int. Ed. 49 (2010) 1530–2532.
[43] J. Caro, M. Noack, P. Kolsch, R. Schafer, Zeolite membranes-state of their development and perspective, Microporous Mesoporous Mater. 38 (2000) 3–24.
[44] J. Caro, M. Noack, Zeolite membranes – recent developments and progress, Microporous Mesoporous Mater. 115 (2008) 215–223.
[45] M. Pera-Titus, Porous inorganic membranes for CO_2 capture: present and prospects, Chem. Rev. 114 (2014) 1413–1492.
[46] N. Rangnekar, N. Mittal, B. Elyassi, J. Caro, M. Tsapatsis, Zeolite membranes – a review and comparison with MOFs, Chem. Soc. Rev. 44 (2015) 7128–7154.
[47] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, 5th Edn, McGraw-Hill, New York, NY, USA, 2000.
[48] S. Sircar, A.L. Myers, Gas separation by zeolites, in: S.M. Auerbach, K. A. Carrado, P.K. Dutta (Eds.), Handbook of Zeolite Science and Technology, 2003, pp. 1063–1104.
[49] N. Mehio, S. Dai, D. Jiang, Quantum mechanical basis for kinetic diameters of small gaseous molecules, J. Phys. Chem. A 118 (2014) 1150–1154.
[50] M. Palomino, A. Corma, F. Rey, S. Valencia, New insights on CO_2-methane separation using LTA zeolites with different Si/Al ratios and a first comparison with MOFs, Langmuir 26 (2010) 1910–1917.
[51] A.B. Shelekhin, A.G. Dixon, Y.H. Ma, Theory of gas diffusion and permeation in inorganic molecular-sieve membranes, AIChE J. 41 (1995) 58–67.
[52] T. Yoshioka, E. Nakanishi, T. Tsuru, M. Asaeda, Experimental studies of gas permeation through microporous silica membranes, AIChE J. 47 (2001) 2052–2063.
[53] J.R. Xiao, J. Wei, Diffusion mechanism of hydrocarbons in zeolites – I. theory, Chem. Eng. Sci. 47 (1992) 1123–1141.
[54] J. van der Bergh, J. Gascon, F. Kapteijn, Diffusion in zeolites-Impact on catalysis. In Zeolites and catalysis, synthesis, reactions and applications., in: J. Cejka, A. Corma, S. Zones (Eds.), Wiley-VCH Verlag GmbH & Co., KGaA: Weinheim, 2010, pp. 361–387.
[55] J. van der Bergh, N. Nishyama, F. Kapteijn, Zeolite membranes in catalysis: What is new and how bright is the future? In Novel concepts in catalysis and chemical reactors: Improving the efficiency for the future, in: A. Cybulski, J. A. Moulijn, A. Stankiewicz (Eds.), Wiley, Weinheim, 2010, pp. 211–234.
[56] J.M. van de Graaf, F. Kapteijn, J.A. Moulijn, Methodological and operational aspects of permeation measurements on silicalite-1 membranes, J. Membr. Sci. 144 (1998) 87–104.
[57] F. Kapteijn, W. Zhu, J.A. Moulijn, T.Q. Gardner, Zeolite membranes: modeling and application, in: A. Cybulski, J.A. Moulijn (Eds.), In Structured Catalysts and Reactors, second edition,CRC Taylor & Francis, Boca Raton, USA, 2006, pp. 700–746.
[58] F. Kapteijn, J.M. van de Graaf, J.A. Moulijn, One-component permeation maximum: diagnostic tool for silicalite-1 membranes? AIChE J. 46 (2000) 1096–1100.
[59] J.M. van de Graaf, F. Kapteijn, J.A. Moilijn, Permeation of weakly adsorbing

components through a silicalite-1 membrane, Chem. Eng. Sci. 54 (1999) 1081.
[60] J. van der Bergh, W. Zhu, J. Gascon, J.A. Moulijn, F. Kapteijn, Separation and permeation characteristics of a DD3R zeolite membrane, J. Membr. Sci. 316 (2008) 35–45.
[61] N. Kosinov, C. Auffret, C. Gücüyener, B. Szyja, J. Gascon, F. Kapteijn, E.J. M. Hensen, High flux high-silica SSZ-13 membrane for CO_2 separation, J. Mater. Chem. A 2 (2014) 13083–13092.
[62] M. Yu, R.D. Noble, J.L. Falconer, Zeolite membranes: microstructure characterization and permeation mechanisms, Acc. Chem. Res. 44 (2011) 1196–1206.
[63] F. Kapteijn, W.J.W. Bakker, J.M. van de Graaf, G. Zheng, J. Poppe, J.A. Moulijn, Permeation and separation behaviour of a silicalite-1 membrane, Catal. Today 25 (1995) 213–218.
[64] J. van der Bergh, C. Gucuyener, J. Gascon, F. Kapteijn, Isobutane dehydrogenation in a DD3R zeolite membrane reactor, Chem. Eng. J. 166 (2011) 368–377.
[65] F. Jareman, J. Hedlund, D. Creaser, J. Sterte, Modelling of single gas permeation in real MFI membranes, J. Membr. Sci. 236 (2004) 81.
[66] J. van de Graaf, F. Kapteijn, J.A. Moulijn, Diffusivities of light alkanes in a silicalite-1 membrane layer, Microporous Mesoporous Mater. 35–36 (2000) 267–281.
[67] H. Suzuki, Composite membrane having a surface layer of an ultrathin film of cage-shaped zeolite and processes for production thereof, US Pat. 4,699,892 (1987).
[68] E.R. Geus, M.J. den Exter, H. van Bekkum, Synthesis and characterization of zeolite (MFI) membranes on porous ceramic supports, J. Chem. Soc. Faraday Trans. 88 (1992) 3101–3109.
[69] S. Miachon, E. Landrivon, M. Aouine, Y. Sun, I. Kumakiri, Y. Li, O. Pachtová Prokopová, N. Guilhaume, A. Giroir-Fendler, H. Mozzanega, J.-A. Dalmon, Nanocomposite MFI-alumina membranes via pore-plugging synthesis: preparation and morphological characterization, J. Membr. Sci. 281 (2006) 228–238.
[70] Y. Li, M. Pera-Titus, G. Xiong, W. Yang, E. Landrivon, S. Miachon, J.-A. Dalmon, Nanocomposite MFI-alumina membranes via pore-plugging synthesis: genesis of the zeolite material, J. Membr. Sci. 325 (2008) 973–981.
[71] M. Tawalbeh, F.H. Tezel, B. Krucxek, S. Letaief, C. Detellier, Synthesis and characterization of silicalite-1 membrane prepared on a novel support by the pore plugging method, J. Porous Mater. 20 (2013) 1407–1421.
[72] A. Giroir-Fendler, J.D.F. Ramsay, A. Julbe, J.A. Dalmon, Porous inorganic composite materials, structure, especially membranes, and their manufacture, Int. Pat. Appl. WO, 1994, 9, 529–751.
[73] S. Miachon, P. Ciavarella, L. van Dyk, I. Kumakiri, K. Fiaty, Y. Schuurman, J.-A. Dalmon, Nanocomposite MFI-alumina membranes via pore-plugging synthesis: specific transport and separation properties, J. Membr. Sci. 298 (2007) 71–79.
[74] A. Alshebani, M. Pera-Titus, E. Landrivon, Th Schiestel, S. Miachon, J.-A. Dalmon, Nanocomposite MFI – ceramic hollow fibers: prospects for CO_2 separation, Microporous Mesoporous Mater. 115 (2008) 197–205.
[75] A. Julbe, Zeolite membranes – synthesis, characterization and application, in: J. Cejka, H. van Bekkum, A. Corma, F. Schuth (Eds.), Introduction to Zeolite Science and Practice, 3rd edition,Elsiever, Amsterdam, 2007, pp. 181–219.
[76] B.M. Kang, G.R. Gavalas, Intrapore synthesis of silicalite membranes at temperatures below 100 °C, Ind. Eng. Chem. Res. 41 (2002) 3145–3150.
[77] J. Hedlund, J. Sterte, M. Anthonis, A.-J. Bons, B. Carstensen, N. Corcoran, D. Cox, H. Deckman, W. De Gijnst, P.-P. de Moor, F. Lai, J. McHenry, W. Mortier, J. Reinoso, J. Peters, High-flux MFI membranes, Microporous Mesoporous Mater. 52 (2002) 179–189.
[78] M. Matsukata, N. Nishiyama, K. Ueyama, Preparation of a thin zeolitic membrane, Stud. Surf. Sci. Catal. 84 (1994) 1183–1190.
[79] S. Aguado, E.E. McLeary, A. Nijmeijer, M. Luiten, J.C. Jansen, F. Kapteijn, *b*-oriented MFI membranes prepared from porous silica coatings, Microporous Mesoporous Mater. 120 (2009) 165–169.
[80] L.A. Truter, V.V. Ordomskiy, T.A. Nijhuis, J.C. Schouten, Preparation of ZSM-5 zeolite coatings within capillary microchannels, J. Mater. Chem. 22 (2012) 15976–15980.
[81] K.V. Agrawal, B. Topuz, Z. Jiang, K. Nguenkam, B. Elyassi, L.F. Francis, M. Tsapatsis, Solution-processable exfoliated zeolite nanosheets purified by density gradient concentration, AIChE J. 59 (2013) 3458–3467.
[82] Z. Lai, G. Bonilla, I. Diaz, J.G. Nery, K. Sujaoti, M.A. Amat, E. Kokkoli, O. Terasaki, R.W. Thompson, M. Tsapatsis, D.G. Vlachos, Microstructural optimization of a zeolite membrane for organic vapor separation, Science 300 (2003) 456–460.
[83] T.C.T. Pham, H.S. Kim, K.B. Yoon, Growth of uniformly oriented silica MFI and BEA zeolite films on substrates, Science 334 (2011) 1533.
[84] J. Choi, S. Ghosh, Z. Lai, M. Tsapatsis, Uniformly a-oriented MFI zeolite films by secondary growth, Angew. Chem. Int. Ed. 45 (2006) 1154–1158.
[85] Z. Lai, M. Tsapatsis, J.P. Nicolich, Siliceous ZSM-5 membranes by secondary growth of b-oriented seed layers, Adv. Funct. Mater. 14 (2004) 716–729.
[86] S. Dominguez-Dominguez, A. Berenger-Murcia, E. Morallon, A. Linares-Solano, D. Cazorla-Amoros, Zeolite LTA/carbon membranes for air separation, Microporous Mesoporous Mater. 115 (2008) 51–60.
[87] F. Akhtar, A. Ojuva, S.K. Wirawan, J. Hedlund, L. Bergstrom, Hierarchically porous binder-free silicalite-1 discs: a novel support for all-zeolite membranes, J. Mater. Chem. 21 (2011) 8822–8828.
[88] Y. He, X. Cui, X. Liu, Y. Wang, J. Zhang, K. Lin, Preparation of self-supporting NaA zeolite membranes using geopolymers, J. Membr. Sci. 447 (2013) 66–72.
[89] P. Lightfoot, D.A. Woodcock, M.J. Maple, L.A. Villaescusa, P.A. Wright, The widespread occurrence of negative thermal expansion in zeolites, J. Mater. Chem. 11 (2001) 212–216.
[90] M.J. den Exter, H. van Bekkum, C.J.M. Rijn, F. Kapteijn, J.A. Moulijn, H. Schellevis, C.I.N. Beenakker, Stability of oriented silicalite-1 films in view of zeolite membrane preparation, Zeolites 19 (1997) 13–20.
[91] J. Dong, Y.S. Lin, M.Z.C. Hu, R.A. Peascoe, E.A. Payzant, Template-removal-associated microstructural development of porous-ceramic-supported MFI zeolite membranes, Microporous Mesoporous Mater. 34 (2000) 241–253.
[92] M.C. Schillo, I.S. Park, W.V. Chiu, H. Verweij, Rapid thermal processing of inorganic membranes, J. Membr. Sci. 362 (2010) 127–133.
[93] J. Choi, H.K. Jeong, M.A. Snyder, J.A. Stoeger, R.I. Masel, M. Tsapatsis, Grain boundary elimination in a zeolite membrane by rapid thermal processing, Science 325 (2009) 590–593.
[94] T. Lee, J. Choi, M. Tsapatsis, On the performance of c-oriented MFI zeolite membranes treated by rapid thermal processing, J. Membr. Sci. 436 (2013) 79–89.
[95] J.A. Stoeger, J. Choi, M. Tsapatsis, Rapid thermal processing and separation performance of columnar MFI membranes on porous stainless steel tubes, Energy Env. Sci. 4 (2011) 3479–3486.
[96] J. Kuhn, S. Sutanto, J. Gascon, J. Gross, F. Kapteijn, Performance and stability of multi-channel MFI zeolite membranes detemplated by calcination and ozonication in ethanol/water pervaporation, J. Membr. Sci. 339 (2009) 261–274.
[97] S. Heng, P.P.S. Lau, K.L. Yeung, M. Djafer, J.C. Schrotter, Low-temperature ozone treatment for organic template removal from zeolite membrane, J. Membr. Sci. 243 (2004) 69–78.
[98] J. Kuhn, J. Gascon, J. Gross, F. Kapteijn, Detemplation of DDR type zeolites by ozonication, Microporous Mesoporous Mater. 120 (2009) 12–18.
[99] N. Kosinov, C. Auffret, G. Sripathi, C. Gücüyener, J. Gascon, F. Kapteijn, E.J. M. Hensen, Influence of support morphology on the detemplation and permeation of ZSM-5 and SSZ-13 zeolite membranes, Microporous Mesoporous Mater. 197 (2014) 268–277.
[100] H.-T. Chien, M.-C. Chen, P.-S. Yang, J.-Y. Lai, C.-C. Hsu, D.-Y. Kang, Reactive atmospheric pressure plasma for highly efficient removal of structure-directing agents from zeolite thin films, Chem. Commun. 51 (2015) 13910–13913.
[101] J.M. van de Graaf, E. van der Bijl, A. Stol, F. Kapteijn, J.A. Moulijn, Effect of operating conditions and membrane quality on the separation performance of composite silicalite-1 membranes, Ind. Eng. Chem. Res. 37 (1998) 4071–4083.
[102] F.T. de Bruijn, L. Sun, Z. Olujic, P.J. Jansens, F. Kapteijn, Influence of the support layer on the flux limitation in pervaporation, J. Membr. Sci. 223 (2003) 141–156.
[103] D. Korelskiy, T. Leppäjärvi, H. Zhou, M. Grahn, J. Tanskanen, J. Hedlund, High flux MFI membranes for pervaporation, J. Membr. Sci. 427 (2013) 381–389.
[104] J. Caro, Are MOF membranes better in gas separation than those made of zeolites? Curr. Opin. Chem. Eng. 1 (2011) 77–83.
[105] Y.S. Lin, M.C. Duke, Recent progress in polycrystalline zeolite membrane research, Curr. Opin. Chem. Eng. 2 (2013) 209–216.
[106] L. Zhang, I.S. Park, K. Shqau, W.S.W. Ho, H. Verweij, Supported inorganic membranes: promises and challenges, JOM 4 (2009) 61–71.
[107] Z. Wang, Q. Ge, J. Gao, J. Shao, C. Liu, Y. Yan, High-performance zeolite membranes on inexpensive large-pore supports: highly reproducible synthesis using a seed paste, ChemSusChem 4 (2011) 1570–1573.
[108] J. Ma, J. Shao, Z. Wang, Y. Yan, Preparation of zeolite NaA membranes on macroporous alumina supports by secondary growth of gel layers, Ind. Eng. Chem. Res. 53 (2014) 6121–6130.
[109] Y. Peng, Z. Zhan, L. Shan, X. Li, Z. Wang, Y. Yan, Preparation of zeolite MFI membranes on defective macroporous alumina supports by a novel wetting-rubbing seeding method: role of wetting agent, J. Membr. Sci. 444 (2013) 60–69.
[110] Y. Peng, H. Lu, Z. Wang, Y. Yan, Microstructural optimization of MFI-type zeolite membranes for ethanol-water separation, J. Mater. Chem. A 2 (2014) 16093–16100.
[111] H. Li, J. Wang, J. Xu, X. Meng, B. Xu, J. Yang, S. Li, J. Lu, Y. Zhang, X. He, D. Yin, Synthesis of zeolite NaA membranes with high performance and high reproducibility on coarse macroporous supports, J. Membr. Sci. 444 (2013) 513–522.
[112] N. Kosinov, E.J.M. Hensen, Synthesis and separation properties of an α-alumina-supported high-silica MEL membrane, J. Membr. Sci. 447 (2013) 12–18.
[113] M. Noack, P. Kolsch, V. Seefeld, P. Toussaint, G. Georgi, J. Caro, Influence of the Si/Al-ratio on the permeation properties of MFI-membranes, Microporous Mesoporous Mater. 79 (2005) 329–337.
[114] N. Kosinov, G.J. Borghuis, G. Sripathi, C. Auffret, E.J.M. Hensen, Influence of Si/Al ratio on the separation properties of SSZ-13 membranes, J. Membr. Sci. 484 (2015) 140–145.
[115] J. Caro, D. Albrecht, M. Noack, Why is it so extremely difficult to prepare shape-selective Al-rich zeolite membranes like LTA and FAU for gas separation, Sep. Purif. Technol. 66 (2009) 143–147.
[116] M. Noack, P. Kölsch, A. Dittmar, M. Stöhr, G. Georgi, R. Eckelt, J. Caro, Effect of crystal intergrowth supporting substances (ISS) on the permeation properties of MFI membranes with enhanced Al-content, Microporous Mesoporous Mater. 97 (2006) 88–96.
[117] M. Noack, P. Kölsch, A. Dittmar, M. Stöhr, G. Georgi, M. Schneider,

U. Dingerdissen, A. Feldhoff, J. Caro, Proof of the ISS-concept for LTA and FAU membranes and their characterization by extended gas permeation studies, Microporous Mesoporous Mater. 102 (2007) 1–20.
[118] M. Drobek, C. Yacou, J. Motuzas, A. Julbe, L. Ding, J.C. Diniz da Costa, Long term pervaporation desalination of tubular MFI zeolite membranes, J. Membr. Sci. 415–416 (2012) 816–823.
[119] T. Tomita, K. Nakayama, H. Sakai, Gas separation characteristics of DDR type zeolite membrane, Microporous Mesoporous Mater. 68 (2004) 71–75.
[120] Y. Zheng, N. Hu, H. Wang, N. Bu, F. Zhang, R. Zhou, Preparation of steam-stable high-silica CHA (SSZ-13) membranes for CO_2/CH_4 and C_2H_4/C_2H_6 separation, J. Membr. Sci. 475 (2015) 303–310.
[121] M.H. Simonot-Grange, A. Waldeck, D. Barthomeuf, G. Weber, Contribution to the study of framework modification of SAPO-34 and SAPO-37 upon water adsorption by thermogravimetry, Thermochim. Acta 329 (1999) 77.
[122] J.C. Poshusta, R.D. Noble, J.L. Falconer, Characterization of SAPO-34 membranes by water adsorption, J. Membr. Sci. 186 (2001) 25–40.
[123] S. Li, G. Alvarado, R.D. Noble, J.L. Falconer, Effect of impurities on CO_2/CH_4 separations through SAPO-34 membranes, J. Membr. Sci. 251 (2005) 59–66.
[124] Y. Cui, H. Kita, K. Okamoto, Preparation and gas separation performance of zeolite T membrane, J. Mater. Chem. 14 (2004) 924–932.
[125] M. Hong, S. Li, J.L. Falconer, R.D. Noble, Hydrogen purification using a SAPO-34 membrane, J. Membr. Sci. 307 (2008) 277–283.
[126] B. Wang, N. Hu, H. Wang, Y. Zheng, R. Zhou, Improved AlPO-18 membranes for light gas separation, J. Mater. Chem. A 3 (2015) 12205–12212.
[127] H. Guo, G. Zhu, H. Li, X. Zou, X. Yin, W. Yang, S. Qiu, R. Xu, Hierarchical growth of large-scale ordered zeolite silicalite-1 membrane with high permeability and selectivity for recycling CO_2, Angew. Chem. Int. Ed. 118 (2006) 7211–7214.
[128] Y. Hasegawa, K. Watanabe, K. Kusakabe, S. Morooka, Influence of alkali cations on permeation properties of Y-type zeolite membranes, J. Membr. Sci. 208 (2002) 415–418.
[129] Y. Hasegawa, T. Tanaka, K. Watanabe, B.-H. Jeong, K. Kusakabe, S. Morooka, Separation of CO_2–N_2 and CO_2–CH_4 systems using ion-exchanged FAU-type zeolite membranes with different Si/Al ratios, Korean J. Chem. Eng. 19 (2002) 309–313.
[130] M.A. Carreon, S. Li, J.L. Falconer, R.D. Noble, Alumina-supported SAPO-34 membranes for CO_2/CH_4 separation, J. Am. Chem. Soc. 130 (2008) 5412–5413.
[131] M. Zhou, D. Korelskiy, P. Ye, M. Grahn, J. Hedlund, A uniformly oriented MFI membrane for improved CO_2 separation, Angew. Chem. Int. Ed. 53 (2014) 3492–3495.
[132] C.S. Cundy, P.A. Cox, The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism, Microporous Mesoporous Mater. 82 (2005) 1–78.
[133] C. Ji, Y. Tan, Y. Li, Y.S. Lin, Thin oriented AFI zeolite membranes for molecular sieving separation, Microporous Mesoporous Mater. 186 (2014) 80–83.
[134] E. Sjoberg, S. Barnes, D. Korelskiy, J. Hedlund, MFI membranes for separation of carbon dioxide from synthesis gas at high pressures, J. Membr. Sci. 486 (2015) 132–137.
[135] D. Korelskiy, P. Ye, S. Fouladvand, S. Karimi, E. Sjoberg, J. Hedlund, Efficient ceramic zeolite membranes for CO_2/H_2 separation, J. Mater. Chem. A 3 (2015) 12500–12506.
[136] P. Ye, D. Korelskiy, M. Grahn, J. Hedlund, Cryogenic air separation at low pressure using MFI membranes, J. Membr. Sci. 487 (2015) 135–140.
[137] J. Choi, S. Ghosh, L. King, M. Tsapatsis, MFI zeolite membranes from *a*- and randomly oriented monolayers, Adsorption 12 (2006) 339–360.
[138] K. Kusakabe, T. Kuroda, S. Morooka, Separation of carbon dioxide from nitrogen using ion-exchanged faujasite-type zeolite membranes formed on porous support tubes, J. Membr. Sci. 148 (1998) 13–23.
[139] K. Kusakabe, T. Kuroda, K. Uchino, Y. Hasegawa, S. Morooka, Gas permeation properties of ion-exchanged faujasite-type zeolite membranes, AIChE J. 45 (1999) 1220–1226.
[140] J. Caro, M. Noack, P. Kolsch, Zeolite membranes: from the laboratory scale to technical applications, Adsorption 11 (2005) 215–227.
[141] S.M. Mirfenderski, T. Mazaheri, M. Sadrzadeh, T. Mohammadi, CO_2 and CH_4 permeation through T-type zeolite membranes: effect of synthesis parameters and feed pressure, Sep. Purif. Technol. 61 (2008) 317–323.
[142] X. Xu, W. Yang, J. Liu, L. Lin, Synthesis of a high-permeance NaA zeolite membrane by microwave heating, Adv. Mater. 12 (2000) 195–197.
[143] W. Zhu, L. Gora, A.W.C. van der Berg, F. Kapteijn, J.C. Jansen, J.A. Moulijn, Water vapour separation from permanent gases by a zeolite-4A membrane, J. Membr. Sci. 253 (2005) 57–66.
[144] I. Tiscornia, S. Valencia, A. Corma, C. Tellez, J. Coronas, J. Santamaria, Preparation of ITQ-29 (Al free zeolite A) membranes, Microporous Mesoporous Mater. 110 (2008) 303–309.
[145] A. Huang, F. Liang, F. Steinbach, T.M. Gesing, J. Caro, Neutral and cation-free LTA-type aluminophosphate (AlPO4) molecular sieve membrane with high hydrogen permselectivity, J. Am. Chem. Soc. 132 (2010) 2140–2141.
[146] A. Huang, J. Caro, Steam-stable hydrophobic ITQ-29 molecular sieve membrane with H_2 selectivity prepared by secondary growth using Kryptofix 222 as SDA, Chem. Commun. 46 (2010) 7748–7750.
[147] Jvd Bergh, S. Banm, T.J.H. Vlugt, F. Kapteijn, Modeling the loading dependency of diffusion in zeolites: the relevant site model extended to mixtures in DDR-type zeolite, J. Phys. Chem. C. 113 (2009) 21856–21865.
[148] M. Kanezashi, J. O'Brien-Abraham, Y.S. Lin, Gas permeation through DDR-type zeolite membranes at high temperature, AIChE J. 54 (2008) 1478–1486.
[149] J. van der Bergh, A. Tihaya, F. Kapteijn, High temperature permeation and separation characteristics of an all-silica DDR zeolite membrane, Microporous Mesoporous Mater. 132 (2010) 137–147.
[150] J. van der Bergh, W. Zhu, F. Kapteijn, J.A. Moulijn, K. Yajima, K. Nakayama, T. Tomita, S. Yoshida, Separation of CO_2 and CH_4 by a DDR membrane, Res. Chem. Intermed. 34 (2008) 467–474.
[151] S. Li, Z. Zong, S.J. Zhou, Y. Huang, Z. Song, X. Feng, R. Zhou, H.S. Meyer, M. Yu, M.A. Carreon, SAPO-34 membranes for N_2/CH_4 separation: Preparation, characterization, separation performance and economic evaluation, J. Membr. Sci. 487 (2015) 141–151.
[152] J.C. Poshusta, V.A. Tuan, E.A. Pape, R.D. Noble, J.L. Falconer, Separation of light gas mixtures using SAPO-34 membranes, AIChE J. 46 (2000) 779–789.
[153] Y. Huang, Z. Song, S. Li, M. Yu, Growth of high-quality, thickness-reduced zeolite membranes towards N_2/CH_4 separation using high-aspect-ratio seeds, Angew. Chem. Int. Ed. 54 (2015) 10843–10847.
[154] H. Kalipcilar, T.C. Bowen, R.D. Noble, J.L. Falconer, Synthesis and separation performance of SSZ-13 zeolite membranes on tubular supports, Chem. Mater. 14 (2002) 3458–3464.
[155] T. Wu, B. Wang, Z. Lu, R. Zhou, X. Chen, Alumina-supported AlPO-18 membranes for CO_2/CH_4 separation, J. Membr. Sci. 471 (2014) 338–346.
[156] M.L. Carreon, S. Li, M.A. Carreon, AlPO-18 membranes for CO_2/CH_4 separation, Chem. Commun. 48 (2012) 2310–2312.
[157] S. Khajavi, J.C. Jansen, F. Kapteijn, Production of ultra pure water by desalination of seawater using a hydroxyl sodalite membrane, J. Membr. Sci. 356 (2010) 52–57.
[158] S. Khajavi, F. Kapteijn, J.C. Jansen, Synthesis of thin defect-free hydroxy sodalite membranes: new candidate for activated water permeation, J. Membr. Sci. 299 (2007) 63–72.
[159] S. Khajavi, J.C. Jansen, F. Kapteijn, Performance of hydroxy sodalite membranes as absolute water selective materials under acidic and basic conditions, J. Membr. Sci. 356 (2010) 1–6.
[160] X. Xu, Y. Bao, C. Song, W. Yang, J. Liu, L. Lin, Microwave-assisted hydrothermal synthesis of hydroxyl-sodalite zeolite membrane, Microporous Mesoporous Mater. 75 (2004) 173–181.
[161] S. Khajavi, S. Sartipi, J. Gascon, J.C. Jansen, F. Kapteijn, Thermostability of hydroxy sodalite in view of membrane applications, Microporous Mesoporous Mater. 132 (2010) 510–517.
[162] M.H. Kassaee, Internal Surface Modification of Zeolite MFI Particles and Membranes for Gas Separation (Ph.D. thesis), Georgia Institute of Technology, USA, 2012.
[163] Y. Yan, M.E. Davis, G.R. Gavalas, Preparation of highly selective zeolite ZSM-5 membranes by a post-synthesis coking treatment, J. Membr. Sci. 123 (1997) 95–103.
[164] M. Hong, J.L. Falconer, R.D. Noble, Modification of zeolite membranes for H_2 separation by catalytic cracking of methyldiethoxysilane, Ind. Eng. Chem. Res. 44 (2005) 4035–4041.
[165] Z. Tang, J. Dong, T.M. Nenoff, Internal surface modification of MFI-type zeolite membranes for high selectivity and high flux for hydrogen, Langmuir 25 (2009) 4848–4852.
[166] X. Zhu, H. Wang, Y.S. Lin, Effect of the membrane quality on gas permeation and chemical vapor deposition modification of MFI-type zeolite membranes, Ind. Eng. Chem. Res. 49 (2010) 10026–10033.
[167] X. Gu, Z. Tang, J. Dong, On-stream modification of MFI zeolite membranes for enhancing hydrogen separation at high temperature, Microporous Mesoporous Mater. 111 (2008) 441–448.
[168] H. Wang, X. Dong, Y.S. Lin, Highly stable bilayer MFI zeolite membranes for high temperature hydrogen separation, J. Membr. Sci. 450 (2014) 425–432.
[169] Z. Tang, S. Kim, G.K. Reddy, J. Dong, P. Smirniotis, Modified zeolite membrane reactor for high temperature water gas shift reaction, J. Membr. Sci. 354 (2010) 114–122.
[170] Y. Zhang, A.M. Avila, B. Tokay, H.H. Funke, J.L. Falconer, R.D. Noble, Blocking defects in SAPO-34 membranes with cyclodextrin, J. Membr. Sci. 358 (2010) 7–12.
[171] S. Nair, Z. Lai, V. Nikolakis, G. Xomeritakis, G. Bonilla, M. Tsapatsis, Separation of close-boiling hydrocarbon mixtures by MFI and FAU membranes made by secondary growth, Microporous Mesoporous Mater. 48 (2001) 219.
[172] H. Matsuda, H. Yanagishita, H. Negishi, D. Kitamoto, T. Ikegami, K. Haraya, T. Nakane, Y. Idemoto, N. Koura, T. Sano, Improvement of ethanol selectivity of silicalite membrane in pervaporation by silicone rubber coating, J. Membr. Sci. 210 (2002) 433.
[173] M. Nomura, T. Yamaguchi, S.-i Nakao, Silicalite membranes modified by counter diffusion CVD technique, Ind. Eng. Chem. Res. 36 (1997) 4217.
[174] A. Huang, N. Wang, J. Caro, Synthesis of multi-layer zeolite LTA membranes with enhanced gas separation performance by using 3-aminopropyl-triethoxysilane as interlayer, Microporous Mesoporous Mater. 164 (2012) 294–301.
[175] Y. Kiyozumi, T. Nagase, Y. Hasegawa, F. Mizukami, A process for synthesizing bilayer zeolite membranes, Mater. Lett. 62 (2008) 436–439.
[176] J. Lindmark, J. Hedlund, Modification of MFI membranes with amine groups for enhanced CO_2 selectivity, J. Mater. Chem. 20 (2010) 2219–2255.
[177] A. Han, H. He, J. Gou, H. Yu, Y. Huang, Y. Long, Studies on structure and acid-base properties of high silica MFI-type zeolite modified with methylamine, Microporous Mesoporous Mater. 79 (2005) 177–184.
[178] J. Lindmark, J. Hedlund, S.K. Wirawan, D. Creaser, M. Liu, D. Zhang, X. Zou, Impregnation of zeolite membranes for enhanced selectivity, J. Membr. Sci. 365 (2010) 188–197.
[179] N. Kosinov, V.G.P. Sripathi, E.J.M. Hensen, Improving separation performance

of high-silica zeolite membranes by surface modification with triethoxyfluorosilane, Microporous Mesoporous Mater. 194 (2014) 24–30.
[180] L. Tosheva, V.P. Valtchev, Nanozeolites: synthesis, crystallization mechanism, and applications, Chem. Mater. 17 (2005) 2494.
[181] Z. Yang, Y. Liu, C. Yu, X. Gu, N. Xu, Ball-milled NaA zeolite seeds with submicron size for growth of NaA zeolite membranes, J. Membr. Sci. 392–393 (2012) 18–28.
[182] J. Jiang, X. Wang, Y. Zhang, D. Liu, X. Gu, Microporous Mesoporous Mater. 215 (2015) 98–108.
[183] G. Bellussi, A. Carati, C. Rizzo, R. Millini, New trends in the synthesis of crystalline microporous materials, Catal. Sci. Technol. 3 (2013) 833.
[184] K. Zhang, R.P. Lively, J.D. Noel, M.E. Dose, B.A. McCool, R.R. Chance, W.J. Koros, Adsorption of water and ethanol in MFI-type zeolites, Langmuir 28 (2012) 8664–8673.
[185] H. Zhou, D. Korelskiy, E. Sjoberg, J. Hedlund, Ultrathin hydrophobic MFI membranes, Microporous Mesoporous Mater. 192 (2014) 76–81.
[186] X. Liu, U. Ravon, A. Tuel, Evidence of F-/SiO- anion exchange in the framework of as-synthesized all-silica zeolites, Angew. Chem. Int. Ed. 50 (2011) 5900–5903.
[187] J. Caro, M. Noack, Zeolite membranes – status and perspective, Adv. Nanoporous Mat. 1 (2010) 1–96.
[188] N. Kosinov, High-Silica Zeolite Membranes for Gas and Liquid Separation (Ph. D. thesis), Eindhoven University of Technology, The Netherlands, 2014.
[189] Z. Wang, J. Yu, R. Xu, Needs and trends in rational synthesis of zeolite materials, Chem. Soc. Rev. 41 (2012) 1729–1741.
[190] A. Jackowski, S.I. Zones, S.-J. Hwang, A.W. Burton, Diquaternary ammonium compounds in zeolite synthesis: cyclic and polycyclic N-heterocycles connected by methylene chains, J. Am. Chem. Soc. 131 (2009) 1092–1100.
[191] K. Iyoki, K. Itabashi, T. Okubo, Progress in seed-assisted synthesis of zeolites without using organic structure-directing agents, Microporous Mesoporous Mater. 189 (2014) 22–30.
[192] T. Yokoi, M. Yoshioka, H. Imai, T. Tatsumi, Diversification of RTH-Type zeolite and its catalytic application, Angew. Chem. Int. Ed. 48 (2009) 9884–9887.
[193] B. Xie, H. Zhung, C. Yang, S. Liu, L. Ren, L. Zhang, X. Meng, B. Yilmaz, U. Muller, F.-S. Xiao, Seed-directed synthesis of zeolites with enhanced performance in the absence of organic templates, Chem. Commun. 47 (2011) 3945–3947.
[194] K. Itabashi, Y. Kamimura, K. Iyoki, A. Shimojima, T. Okubo, A working hypothesis for broadening framework types of zeolites in seed-assisted synthesis without organic structure-directing agent, J. Am. Chem. Soc. 134 (2012) 11542–11549.
[195] H. Shi, Organic template-free synthesis of SAPO-34 molecular sieve membranes for CO_2–CH_4 separation, RSC Adv. 5 (2015) 38330–38333.
[196] S. Gopalakrishnan, T. Yamaguchi, S. Nakao, Permeation properties of template and template-free ZSM-5 membranes, J. Membr. Sci. 274 (2006) 102–107.
[197] G. Li, E. Kikuchi, M. Matsukata, The control of phase and orientation in zeolite membranes by the secondary growth method, Microporous Mesoporous Mater. 62 (2003) 211–220.
[198] J. Hedlund, M. Noack, D. Creaser, J. Caro, J. Sterte, ZSM-5 membranes synthesized without organic templates using a seeding technique, J. Membr. Sci. 159 (1999) 263–273.
[199] R. Lai, G.R. Gavalas, ZSM-5 membrane synthesis with organic-free mixtures, Microporous Mesoporous Mater. 38 (2000) 239–245.
[200] M. Moliner, F. Rey, A. Corma, Towards the rational design of efficient organic structure-directing agents for zeolite synthesis, Angew. Chem. Int. Ed. 52 (2013) 13880–13889.
[201] A. Corma, M.J. Diaz-Cabanas, J.L. Jorda, F. Rey, G. Sastre, K.G. Strohmaier, A zeolitic structure (ITQ-34) with connected 9- and 10-ring channels obtained with phosphonium cations as structure directing agents, J. Am. Chem. Soc. 130 (2008) 16482–16483.
[202] D.L. Dorset, G.J. Kennedy, K.G. Strohmaier, M.J. Diaz-Cabanaz, F. Rey, A. Corma, P-derived organic cations as structure-directing agents: synthesis of a high-silica zeolite (ITQ-27) with a two-dimensional 12-ring channel system, J. Am. Chem. Soc. 27 (2006) 8862–8867.