A practical approach to zeolitic membranes and coatings: state of the art, opportunities, barriers and future perspectives

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Abstract

In this work, the concept of zeolite (zeolitic) membrane is discussed from a practical perspective. We consider the limitations of the existing synthesis methods and speculate on new opportunities of zeolites and zeolite-type materials such as metal organic frameworks for the production of membranes. This paper focuses on the barriers that need to be eliminated before the commercialization of these membranes becomes attractive. Additional opportunities for commercialization may arise in the shape either of mixed matrix membranes, taking advantage of composites with polymers, or as zeolite coatings useful for a plethora of new applications.

Keywords: Zeolite, MOF, Zeolite membrane, Zeolite coating, Mixed matrix membrane, Pervaporation, Gas separation.

Introduction

Membrane technology is attractive from the point of view of both energy cost and separation selectivity and efficiency. In particular, inorganic membranes such as those fabricated from zeolitic materials are especially fascinating because of their high thermal, mechanical and chemical stability. Zeolites are crystalline, hydrated aluminosilicates possessing microporous, regular structures. Several unique aspects of zeolites and zeotypes are responsible for their industrial success: (i) very high and adjustable adsorption capacity, (ii) catalytic sites of different strengths can be generated in the frameworks, (iii) the size of their channels and cavities is in the range of many molecules of interest, and (iv) excellent ion exchange capabilities. Furthermore, the concept of zeolite can be extended to the so-called tailored porous materials. This would include: oxide molecular sieves, metal organic frameworks (MOFs), porous carbons, sol-gel-derived oxides, and porous heteropolyanion salts. As a consequence, the term zeolitic material is frequently used in a very broad sense and so does the concept of zeolitic membrane. The crystallographic structure (pore size) and chemical composition (affinity) determine the separation properties of a given zeolitic material and might eventually allow the rational design of membranes.[1]

The field of zeolite membranes has been widely reviewed through several excellent articles in the last 15 years[2] announcing, or at least creating the expectation of the release of commercial products dealing with industrial applications in which *a priori* zeolite membranes would perform in a superior way. A few examples of these applications are solvent dehydration by pervaporation,[2e, 3] xylene isomers separation[4] or gas separations involving CO_2[5] and H_2.[6]

Even though many works claim the industrial application of zeolite membranes[7] only a few examples really deal with the large scale production and application of this kind of membranes.[8] In addition, recently very important advances have been achieved in the synthesis of membranes through alternative, low cost and reliable methodologies, while the discovery of new crystalline porous materials such as MOFs[9] opens the door to new types of zeolitic membranes.

Several decades after the first zeolitic membrane was reported[10] it is fair to admit that synthesis reproducibility is still the main drawback. As zeolites cannot be prepared as self-supported membranes in a practical way, porous supports commonly of alumina or stainless steel are used to grow the zeolite membranes on. The support can be either symmetric (less expensive) or asymmetric with a thin top layer chemically or texturally more fit to grow the zeolite. The only industrial application of zeolite membranes uses tubular symmetric supports,[8a] while planar supports[11] have been used for concept demonstration and easy testing.

Membrane synthesis can be made without[12] or with[13] support seeding. In principle, the seeding reduces the influence of the support in the flux and selectivity properties of the resulting zeolite membrane. These properties can be improved through support pretreatment[4c] and membrane post-treatment[14]. In addition, activation of zeolite membranes is not trivial[15] and a great deal of work has been devoted to alleviate this issue.[16] Finally, recent preparations of zeolite membranes without the use of hydrothermal[17] synthesis deserve special attention, since they may lead to the development of a new generation of industrial membranes obtained in an easier and more reproducible manner (using impregnation, filtration, and, in general, sol-gel based techniques).

In this manuscript we analyze the practical limitations arising from the existing synthesis methods of zeolite membranes. Simultaneously, we also speculate on new manufacturing opportunities. Traditional applications of crystalline microporous membranes have as main target gas separation[2c] and pervaporation.[2e] Indeed, both applications have been used as proof of concept in many reports dealing with zeolite membranes. Fortunately, during the last few years, in addition to outstanding works pushing the improvement of zeolite membrane synthesis, the development of new membrane concepts such as mixed matrix membranes (MMMs), although perhaps less challenging from the point of view of preparation, has advanced tremendously. Furthermore, the knowledge acquired in the synthesis of zeolite membranes has been transferred to the synthesis of high quality coatings[18] that may find application in many different industrial fields such as corrosion protection, optoelectronics, catalysis, microsystems and drug delivery.

Reproducibility of zeolite membrane synthesis

Zeolite membranes are always supported membranes on mainly stainless steel or alumina porous supports. A frustrating peculiarity is the lack of reproducibility.[19] at least when the behavior of membranes of the same zeolitic phase but prepared in different laboratories are compared. This means that one can find, for instance, MFI-type zeolite membranes (silicalite-1 and ZSM-5, the zeolites most studied as membranes) presenting not only different values of permeance and selectivity but also different qualitative behaviors. There are MFI-type membranes that separate the *n/i*-butane mixture at high temperature,[20] others only at low temperature[21] and others that cannot do this at all.[22] A few, very high quality membranes can separate xylene isomer mixtures,[4c, 23] some silicalite-1 membranes show activation with temperature for single H_2 permeance,[22] while others do not,[24] etc. These different behaviors can be related to the thickness of the membrane, the presence of different concentrations of intercrystalline defects[21] and also the distribution of the zeolite material in the support, since the resistance of the latter influences transport.[25]

As an example of reproducibility at laboratory scale, Navajas *et al.*[19] reported a study on the seeded hydrothermal synthesis of tubular (5-cm length) mordenite membranes on symmetric α-alumina tubular supports with 1.9 μm pores. The authors also studied the reproducibility of different alkaline post-synthetic treatments carried out to improve the performance of mordenite membranes. Water flux during pervaporation was compared for the different membranes. Figure 1 shows the decision diagram followed by the authors. Several mordenite membranes (N = 71) were prepared, and their N_2 permeation and weight change after synthesis were recorded. Since 52 membranes had N_2 permeation values below the threshold established (10^{-6} $mol \cdot m^{-2}s^{-1}Pa^{-1}$), the authors concluded that a 73 % of the syntheses yielded high-quality membranes. All of these membranes (M1 membranes in Figure 1) displayed water/ethanol separation factors higher than 35, in agreement with the membrane quality assessment based on N_2 permeation (a quick measurement). As shown in Figure ~~2~~1, the good quality M1 membranes were then subjected to alkaline treatment at pH 10 and 180 ºC in either 31 mL (N= 18) or 124 mL (N= 31) solutions during 5-72 h.[14] This gave rise to M2 (N= 16) and M3 (N= 13) type membranes. Water/ethanol separation factors for M2 and M3 type membranes were at least 150 and 19, respectively, and post-treatment yields (number of membranes with either 150 or 19 separation factor value divided by the respective number of initial membranes) to M2 and M3 were 89 % and 42 %, respectively. These threshold separation factors are of course arbitrary, and Figure 2 shows the distributions obtained with respect to water flux for as-synthesized M1 membranes and post-treated M2 and M3 membranes. It can be appreciated that M1 and M2 membranes were more reproducible than M3 (0.16±0.07, 0.40±0.11 and

0.87 ± 0.36 kg·m^{-2}·h^{-1}, respectively). Even though the alkaline post-treatment caused an increase of water pervaporation flux due to the selective membrane dissolution,[14] when a larger post-treatment volume was used the divergence of fluxes increased and in consequence a decrease in reproducibility was observed. Finally, the average water/ethanol separation factor values were 140±80, 420±230 and 200±270 for M1, M2 and M3, respectively. Clearly, the standard deviation of both membrane synthesis and post-treatment is industrially still far from viable.

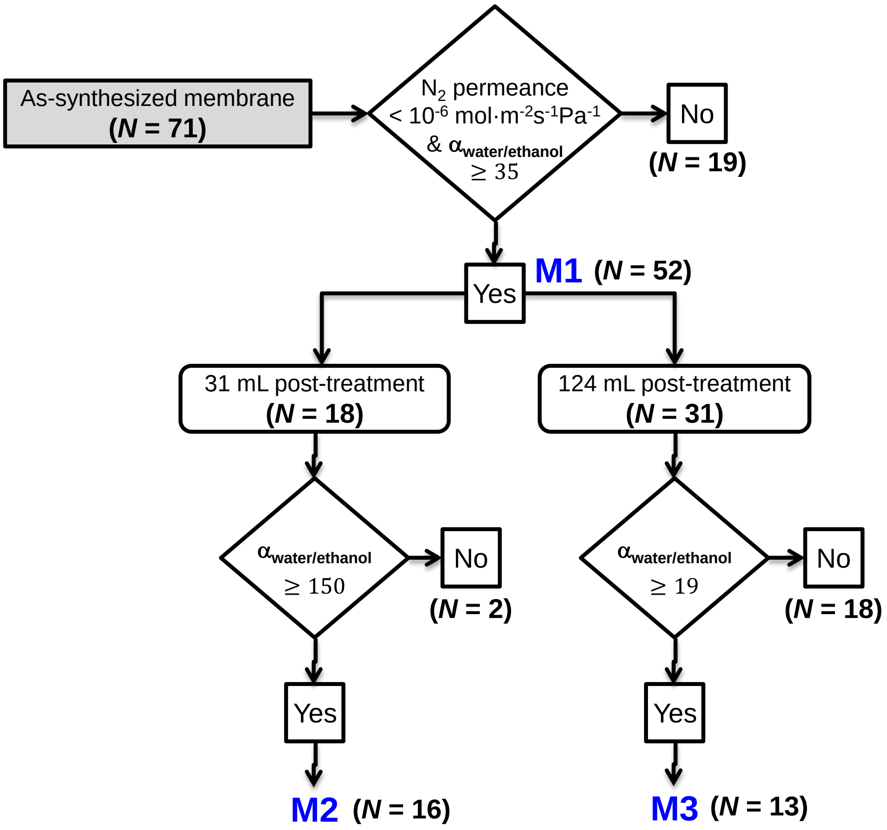

Figure 1. Decision diagram for as-synthesized and post-treated mordenite membranes.[19]

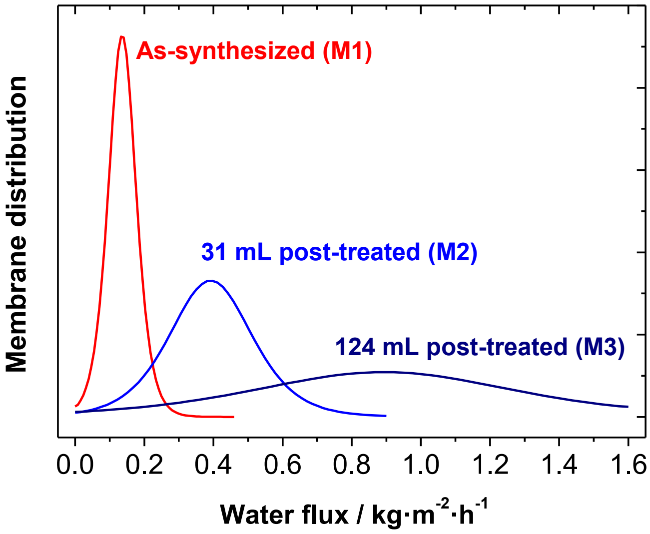

Figure 2. Mordenite membrane distributions based on water pervaporation flux. Water in the feed with ethanol: 10 wt.%; temperature: 150 ºC. As-synthesized membranes were compared with post-treated membranes with volumes of 31 and 124 mL of alkaline solution. Membrane distributions were obtained by derivation of the corresponding normalized cumulative number of membranes as a function of pervaporation water flux.[19]

Sato *et al.*[8c, d, 26] studied the reproducibility of zeolite Y membranes using two types of precursor solutions over 100 tubular samples (80 cm length). The reproducibility was confirmed by pervaporation of a 10/90 (wt.%) water/ethanol mixture at 75 ºC. The average permeation flux and separation factor were 8.1±1.5 kg·m^{-2}·h^{-1} and 220±80, and 9.8±1.4 kg·m^{-2}·h^{-1} and 210±40, respectively, for the two preparation methods. The authors claimed these results were good enough for the mass-production of zeolite Y membranes at industrial scale.

These two examples clearly demonstrate that, regarding selective transport properties, there is a quality distribution in the membrane types. This is not only caused by the different quality and crystallographic orientation (not considered in the previous examples) of the membranes,[27] but also the influence of the porosity and chemical composition of the support.[13b, 21] Quite often it is not possible to identify the effective thickness of the membrane separation layer and the contribution of the zeolitic material synthesized inside the support pores to the transport.[12b] On the other hand, the support may be attacked by the zeolite synthesis gel and the result is the incorporation of support components into the zeolitic phase, changing chemical composition of the latter[28] and, in consequence, its transport properties. In addition, membrane support properties may exhibit a quality distribution.

Recent improvements in the synthesis of zeolite membranes

The secondary (seeded) growth method implemented for silicalite-1 membranes,[27] allows, among other advantages, the reduction of the influence of the support over the permeation properties of the resulting zeolite membrane. For instance, crystallographically oriented silicalite-1 membranes can be obtained using nanometer sized silicalite-1 seeds.[29] Recently, the use of brittle seeds (obtained from polycrystalline zeolite particles prepared by confined growth)[30] has been proposed as an easy alternative for silicalite-1 membranes. However, the seeding with cheap commercial crystals has been used for several decades with different types of zeolite membranes.[3a, 13a, 31]

Already since the first zeolite membrane studies, supports have been pretreated to improve crystal growth on their surface. Common ceramic supports and aluminosilicates exhibit the same negative zeta potential under synthesis conditions; this results in electrostatic repulsion and therefore in defective membranes. Besides seeding, stainless steel supports have been oxidized by calcination to improve coverage with seeds,[32] impregnated with paraffin to avoid penetration of the synthesis dispersion,[4c] functionalized with APTES,[33] coated with ionic polymers that are positively charged under synthesis conditions,[34] manually rubbed with seeds[35] and submitted to chemical treatment to establish covalent bonding between support surface and seed crystals.[27a, 36] Recently, in the case of zeolite A coatings, by modifying the supports with a cationic polymer and even with glucose or polyethylene glycol and subsequent calcination at 673 K, a substantial improvement in terms of layer continuity and crystal intergrowth has been observed compared to coatings prepared on unmodified supports.[37]

In addition to different support pre-treatments and variations in the synthesis gel composition, membrane post-treatments have been proposed as a facile way to improve the performance of defective membranes: post-treatment by coating a polymer layer on microporous zeolite Y membranes resulted in a decrease of the flow through defects in gas separation,[38] while chemical vapor[39] and liquid[40] deposition of Si-species has been reported to heal intercrystalline defects improving membrane performance.

At all events, the rough estimate of the costs of a zeolite membrane without housing is 1000 €/m^2 (and that with housing is in the 3000-8000 €/m^2 range[41]).[9d] In fact, in 2000 the cost of a zeolite membrane module was already estimated to be about 2300 €/m^2 of installed membrane area.[2d] In such a membrane, most of the costs are attributed to the module and only 10-20 % to the membrane itself. This estimation compares favorably with metal membranes (*i.e.* Pd) (15000 €/m^2), and it has been suggested that, once in mass production and application, the cost may decline below 1000 €/m^2.[41a] Since the membrane costs are further dominated by the support costs and not by the zeolite layer, an interesting alternative is the replacement of the expensive ceramic supports by cheap alternatives such as metal grids[42] or simply perforated thin metal sheets.[43] Either way, since current commercial microfiltration and ultrafiltration ceramic supports appear to be the most realistic option for commercialization (as demonstrated by the zeolite A membranes already used at large scale, see below), for certain separations (*i.e.* gas mixtures) a drastic decrease in membrane thickness, which is expected to lead to a large increase in flux, from the current best values of about 1 μm to about 50 nm will be necessary.[41b] Following this strategy, Tsapatsis and co-workers have published the application of exfoliated zeolite nanosheets (ITQ-1[44] and the so-called multilayer silicalite-1[45]) with thicknesses of a few nanometers (2-3 nm), assembled horizontally onto porous alumina supports to produce very thin (200 nm) membranes.[46] Figure 3 shows the historical evolution of the N_2 permeance for MFI-type zeolite supported membranes, [4c, 28, 47] from the very thick (about 50 μm) Geus *et al.*[28] silicalite-1 membranes reported in 1992 ($0.3\cdot10^{-7}$ mol·m^{-2}s^{-1}Pa^{-1}) to the highest N_2 permeance ($129\cdot10^{-7}$ mol·m^{-2}s^{-1}Pa^{-1}) ever reported until now by Hedlund *et al.*[4c] for 500 nm thick membranes. The latter membranes were obtained by a support masking technique that avoided the penetration of the synthesis dispersion into the support. Similar ZSM-5 membranes have been reported as thin as 550 nm with good performance in the separation of mixtures containing H_2O, H_2 and *n*-hexane, characteristic of Fischer-Tropsch synthesis.[48]

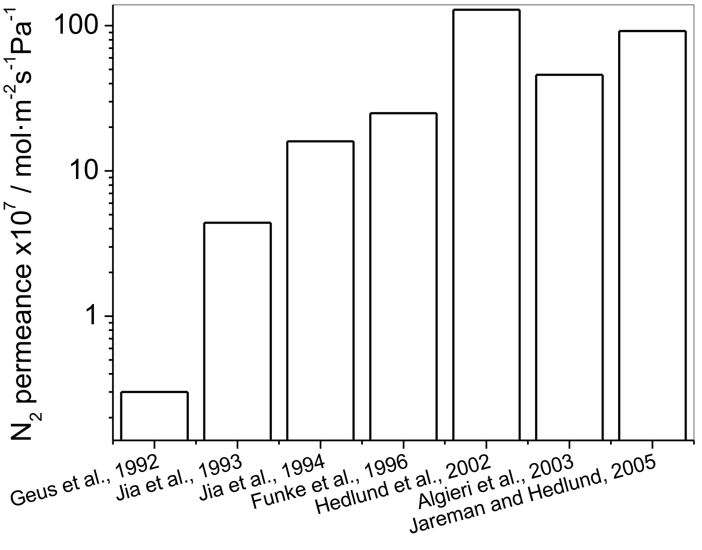

Figure 3. Evolution of N_2 permeance for MFI-type zeolite membranes.[4c, 28, 47]

Another interesting route towards zeolite membranes deals with sols of zeolitic nano-precursors (such as zeolite nanoslabs[49] and protozeolites[50]) that could be used to coat supports with very thin layers of zeotypes. A process like this would probably be more reproducible, avoiding the inherent risks associated to heterogeneous crystallization of a zeolitic phase on a given support, and closer to an industrial strategy. Along these lines, Nishiyama *et al.*[17] reported the preparation of a H_2-selective membrane from zeolite A nano-blocks obtained from the dissolution of commercial zeolite NaA crystals in HCl. In spite of the promising results, no follow-up on this publication has been reported, what perhaps may be related to the difficulty of obtaining molecular sieving membranes considering the large grain areas that must be closed off.

The last point of consideration when dealing with zeolite membranes is the calcination of the structure directing agent (SDA) used to conduct the formation of a given zeolite topology. The removal of the SDA requires a final activation stage that may lead to the formation of cracks and defects[15] with a higher probability in the case of small-pore zeolite membranes.[5c, 51] Consequently, important efforts have been devoted to the synthesis of zeolite membranes (typically obtained with SDA) in the absence of SDA,[22] as well as alternative activation routes such as the RTP (rapid thermal activation) using infrared radiation[16] or low temperature activation processes based on ozonication,[52] liquid extraction[a,b] and the use of degradable SDAs[c].

a C. W. Jones, K. Tsuji, T. Takewaki, L. W. Beck, M. E. Davis, *Microporous and Mesoporous Materials* **2001**, *48*, 57-64.

b B. Gautier, M. Smaihi, *New Journal of Chemistry* **2004**, *28*, 457-461.

c H. Lee, S. I. Zones, M. E. Davis, *J. Phys. Chem. B* **2005**, *109*, 2187-2191.

As a partial conclusion of these last two sections, we can state that, even though some high performance zeolitic membranes have been synthesized in a very efficient way (mostly MFI-, LTA- and MOR-type zeolites), the cost of such membranes is still very high. The target cost for zeolite membranes with housing (below 1000 €/m^2) is so far below the actual cost (3000-8000 €/m^2), and the former is still high when compared to some economic estimations that require of a price of 200 €/m^2 for viability, [53] close to the polymer membrane module cost of 40-400 €/m^2 used for processing natural gas.[54]

Large scale production and application of zeolite membranes

A major issue of concern for membrane technology professionals and researchers is the scale up from laboratory to industrial practice.[55] In 2000 the first industrial scale separation plant using zeolite NaA tubular membranes was developed by Mitsui Engineering and Shipbuilding Co. Ltd. in Japan[56] for the dehydration of organic solvents by pervaporation. The plant is equipped with 16 modules, each consisting of 125 pieces of zeolite NaA tubular membranes with a thickness of 20-30 µm, hydrothermally synthesized on ceramic supports. This plant was reported to produce by pervaporation at 120 ºC 530 L/h of the different alcohols with less than 0.2 wt.% water from an initial 90 wt.% solvent concentration. Table 1 shows some of the zeolite membranes that have been commercially available and their membrane performance in the dehydration of organic solvents by pervaporation. The data reported in Table 1 have been either provided by the suppliers themselves or by independent researchers. The membranes developed by the Nano-Research Institute Inc (BNRI), a subsidiary of Mitsui, and by the European alliance between Smart (UK) and Inocermic (Germany) consisting of another hydrophilic LTA-type zeolite layer on a ceramic tubular support, have been upgraded to commercial pervaporation and vapor permeation plants that are still under operation in several countries. For instance, BNRI has installed vapor permeation units in Brazil (3000 L/d) and India (30000 L/d) working at 130 ºC for the dewatering of bioethanol using LTA-type membranes. Recently, Nanjing Jiusi Hi-Tech Co. from China has scaled up a NaA zeolite membrane to pilot plant for the dehydration of ethylene glycol (EG)/water mixtures. The water flux was seen to decrease from 4.0 kg·m^{-2}·h^{-1} at laboratory scale (Table 1) to 3.1 kg·m^{-2}·h^{-1} upon scaling-up.[57] These membranes have been also tested in the pharmaceutical industry for the dehydration of isopropanol obtaining high water fluxes of 7.3 kg·m^{-2}·h^{-1} and a permeate water content of 94 wt.% for 30 h operation time.[58]

Table 1. Commercial zeolite membrane performance in typical pervaporation conditions.

Membrane type	Membrane performance	Reference
NaA (Busan Nanotech Research Institute, BNRI)	Flux of 3.5-4 kg·m^{-2}·h^{-1} and separation factor of 20000-40000 for 10/90 wt.% water- ethanol mixture at 75 ºC	59
NaA (BNRI)	Flux of 8 kg·m^{-2}·h^{-1} with a separation factor of 10000 for a 10/90 wt.% water-ethanol mixture at 75 ºC	55
NaA (Inocermic GmbH)	Flux of 3 kg·m^{-2}·h^{-1} and separation factor of 100 for a 5/95 wt.% water-ethanol mixture at 75 ºC	59
NaA (SMART Chemical	Flux of 1 kg·m^{-2}·h^{-1} and separation	7b

company)	factor of 1240 for 7/93 wt.% water-tetrahydrofuran mixture at 55 ºC	
NaA (SMART Chemical company)	Flux of 1.5 $kg \cdot m^{-2} \cdot h^{-1}$ and separation factor of 16000 for 10/90 wt.% water-isopropanol mixture at 60 ºC	[60]
NaA (Nanjing Jiusi Hi-Tech Co.)	Flux of 4.0 $kg \cdot m^{-2} \cdot h^{-1}$ and separation factor of 5000 for a 20 wt.% water/EG mixture at 120 ºC	[57]

Since the pioneering development by Mitsui Engineering and Shipbuilding Co. Ltd., many efforts have been carried out to enhance the performance of the original NaA membranes to obtain membranes that can industrially separate organic[59] or acidic mixtures, or perform at high water content in the feed solution.[61] For example, Kühni AG provided pervaporation systems that use commercially available ceramic tubular membranes in addition to organic flat-sheets or hollow fiber membranes.[62] These systems were designed to operate at temperatures up to 130 ºC with life time over 18 months. Sulzer Chemtech has recently acquired Kühni AG activity on pervaporation membranes, and has started in 2009 the installation of a vapor permeation pilot plant in Asia that, using 100 m^2 of zeolite membrane (there is not information available about zeolite type), is able to dehydrate a 1500 kg/h water/isopropanol mixture from 20 wt.% to 0.3 wt.% water content, and purify ethanol to fuel grade 99.8 %.[63] These membranes are able to treat Hitachi Zosen Corporation commercializes membranes[59] for a hybrid distillation system that is suitable for the dehydration of ethanol and isopropanol. This membrane also consists of a thin NaA or NaY zeolite layer with mono-block structure, coated on a porous alumina tube with a pore size of 1 nm and claimed to dehydrate water-ethanol mixtures with less than 30 wt.% water. This company is expanding the production capacity of the membranes to reach 750000 million tons per year, and the hybrid system is reported to have been more than 1.5 years under continuous operation.[64] The zeolite NaA membrane from BNRI, Japan, has been tested at field pilot plant combined with a distillation column placed before the zeolite membrane vapor permeation process to produce anhydrous ethanol from sugar cane fermented beer.[65] In fact, commercial NaA membranes show the advantage of high thermal and mechanical stability and the disadvantage of low resistance at low pH and the expensive cost of fabrication, as compared to available polymeric membranes. However, in 2006 researchers were still expecting that the membrane cost would be reduced as the demand increased.[66]

Zeolite membranes that showed high performance at laboratory scale are usually fabricated on tubular supports by a secondary growth technique, and the improvement of the seeding of the support has been attempted by many different methods, as reviewed above. This has led to the industrial scale-up of 1500 m^2/year of NaA zeolite membranes 80 cm-long in China that are able to dehydrate 5000 ton/year isopropanol from 20 wt.% to 0.1 wt.% water content. These membranes are reported to last about two years in operation.[67] A possible alternative has been recently reported where a LTA-type zeolite layer was coated on a zeolite/polymer hollow fiber support configuration with the aim of avoiding the seeding procedure. This led to the production of a defect free layer that had high performance in the pervaporation of several aqueous organic mixtures.[68] Besides, the use of composite hollow fibers could reduce the cost of zeolite membranes by half.[63] The outer diameter of these composite hollow fibers is around 2 mm because of mechanical stability.[d] The latter can be improved by making monoliths containing multiple channels.[e] Other authors have achieved high permeabilities with MCM-48 molecular sieve layers prepared on 220 μm outer diameter polymeric hollow fibers.[f]

d Lai, L.; Shao, J.; Ge, Q.; Wang, Z.; Yan, Y., The preparation of zeolite NaA membranes on the inner surface of hollow fiber supports. Journal of Membrane Science 2012, 409-410, 318-328.

e Ge, Q.; Wang, Z.; Yan, Y., High-performance zeolite NaA membranes on polymer-zeolite composite hollow fiber supports. J. Am. Chem. Soc. 2009, 131 (47), 17056-17057.

f Jang, K.-S.; Kim, H.-J.; Johnson, J. R.; Kim, W.-g.; Koros, W. J., Chem. Mater. 2012, 23, 3025-3028.

The second most studied zeolite membranes after those of the LTA-type, whose industrial application in alcohol dehydration has been demonstrated, are of the MFI-type. Some of the first studies addressing the potential application of MFI-type membranes targeted the separation, by pervaporation or vapor permeation, of unconverted aromatic hydrocarbons from naphtha cracking. Zeolite membranes were thought easier to regenerate through calcination than conventional adsorption-based hydrocarbon separation processes.[69] Recently, the pervaporation and vapor performance of several zeolite membrane types (MFI, MOR, ZSM-5 and FAU) has been discussed regarding the energy savings their addition to a distillation process could originate in petrochemical industries.[70] More recently, all-silica small-pore DDR zeolite membranes have been produced by NGK Insulators, and their performance in the dewatering of ethanol tested at 373 K, with moderate to high water fluxes and selectivities.[71]

Another typical application is the zeolite membrane reactor (ZMR),[2f, 72] which aroused great interest but is still far from commercialization. ZMR concept would account, in general, for both zeolite membrane combined with a packed catalyst bed and catalytic zeolite membrane itself. In any event, the difficulty of controlling permeance, high-temperature sealing and reproducibility encumbers the development of zeolite membranes in membrane reactors as much as the membrane unit cost itself.[2f] In addition, two important parameters determine the membrane reactor performance: the activity of the catalyst and the permeation characteristics of the membrane, as represented by the Damköhler (Da) and membrane Péclet number (Pe_δ). For a significant improvement of the MR performance as compared to a plug flow reactor, $Da \geq 10$ and $Pe_\delta \leq 0.1$. $DaPe_\delta$ should be ≈ 1 to optimally utilize both catalyst and membrane.[73] These observations call for a parallel development of both membrane and catalyst, where the membrane surface area per volume is an adjustable parameter. Considering the above conditions, reported fluxes of membranes and the catalytic reactor productivity, learns that zeolite membrane reactors with diameters of 1-50 cm are required to match these requirements,[74] which is practically quite well feasible. As long as zeolite membranes are not common practice in industry the introduction of this new membrane reactor technology will not occur.

Recently, the commercial readiness of zeolite and catalytic membranes was evaluated as relatively moderate compared to other promising materials for waste water treatment applications, such as hybrid organic-inorganic nanocomposite and bio-inspired membranes. Still researchers are investing their efforts in developing zeolite membranes where the ion exchange ability and molecular sieve properties can constitute an improvement. In such a light, the effect of counter ions in reversed osmosis (RO) of oilfield brine desalination using MFI membranes has been optimized not only as a potential resource of potable water, but also as a way of reusing the subsurface reservoirs that could then become available for CO_2 storage.[75] More recently, sodalite membranes were reported to produce ultrapure water directly from seawater.[76]

Advances in the research on novel molecular sieves and the increased knowledge on pore size control to nanocomposite materials are thought to approach the dream of robust industrial-scale molecular sieving membranes.[77] Recently, some procedures to achieve the latter have been reported.[78] With the development of new hierarchical zeolites the preparation of thin films of nanoporous materials connected by mesopores enables specific separations and the use of expensive materials in small amounts, as demonstrated in the aqueous dehydration of fructose to 5-hydromethyl furfural.[79]

The molecular sieving properties of zeolite membranes constitute another opportunity for their commercialization in interesting applications, such as natural gas purification.[80] In an attempt to demonstrate industrial feasibility, Arruebo *et al.*[81] used silicalite-1 membranes to remove heavy hydrocarbons from natural gas. All-silica DD3R membranes have been reported as highly CO_2 selective and permeable for this application,[82] due to the narrow window in this cage type zeolite framework. SAPO-34 membranes have already been scaled up from 5 cm to 25 cm long obtaining acceptable CO_2/CH_4 selectivities and high CO_2 fluxes.[83] Air separation constitutes another field for investment on zeolite or zeotype membrane development, since zeolite pore size can be tuned by altering their framework but also by introducing extra framework cations in their structure, such as has been reported for Sr-ETS-4.[84] Although there are a few zeolite membranes industrially used for the dehydration of aqueous mixtures by pervaporation or vapor permeation, it is not expected that ceramic or inorganic membranes will fully replace polymeric ones. However, in special cases such as when high operation temperatures are used, when very low water content is required or when the chemical stability of polymer available membranes is insufficient, zeolites may find a foothold for massive application.

Zeolite coatings versus separative zeolite membranes

Zeolite membranes or coatings as sensors, microreactors and drug delivery systems have been reviewed recently.[2h] Hence, this part is mainly excluded from our perspective. However, it is worth mentioning here that besides separation membranes and membrane reactors, zeolite films have found commercial development with millions of dollars invested [18] in interesting applications which do not rely on the molecular sieve effect: low dielectric constant insulators [85], and several coatings with corrosion-resistance,[86] hydrophilicity,[87] biocide,[88] biocompatibility,[89] wear-resistance,[90] and antifouling[91] properties.

Zeolites exhibit excellent corrosion resistance (Figure 4), strong adhesion to substrates, and extraordinary thermal and mechanical properties.[85b] The combination of these properties, together with the nontoxic character of zeolites, suggests that zeolite coatings have the potential to become an environmentally friendly alternative for the most commonly used, toxic, carcinogenic and strictly regulated, chromate conversion coatings.[92] Nevertheless, high quality zeolite coatings require a hydrothermal deposition process which is considered inconvenient by the surface-finishing industry, because it involves high pressure/temperature conditions. On the other hand, the chromate conversion coating can be deposited at ambient pressure. Cai *et al.*[92] overcame this drawback by finding a new route to synthesize zeolite corrosion-resistant coatings under ambient pressure (Figure 5a-b). This route is based on ionothermal synthesis, using ionic liquids as solvent/template. Along with the chemical properties of the zeolite framework, the uncalcined coatings (in case of zeolites containing structure directing agents) can physically block corrosive compounds and consequently are promising candidates for chromium-free corrosion-resistant coatings.[93] Anticorrosive properties of zeolites can also be improved by using the excellent ion-exchange capacity, hosting useful extra-ions such as molybdenum ions in their framework ~~(Figure 5c)~~.[94] Zeolite coatings are also key to protect titanium alloy Ti_6Al_4V, which is widely used in dental and orthopedic implants, from corrosion and consequently from the release of harmful metals such as vanadium and aluminum ~~(Figure 5d)~~.[89] Furthermore, zeolite coatings have an elastic modulus which closely matches that of bones and that is more appropriate than that of titanium alloys, avoiding bone resorption.

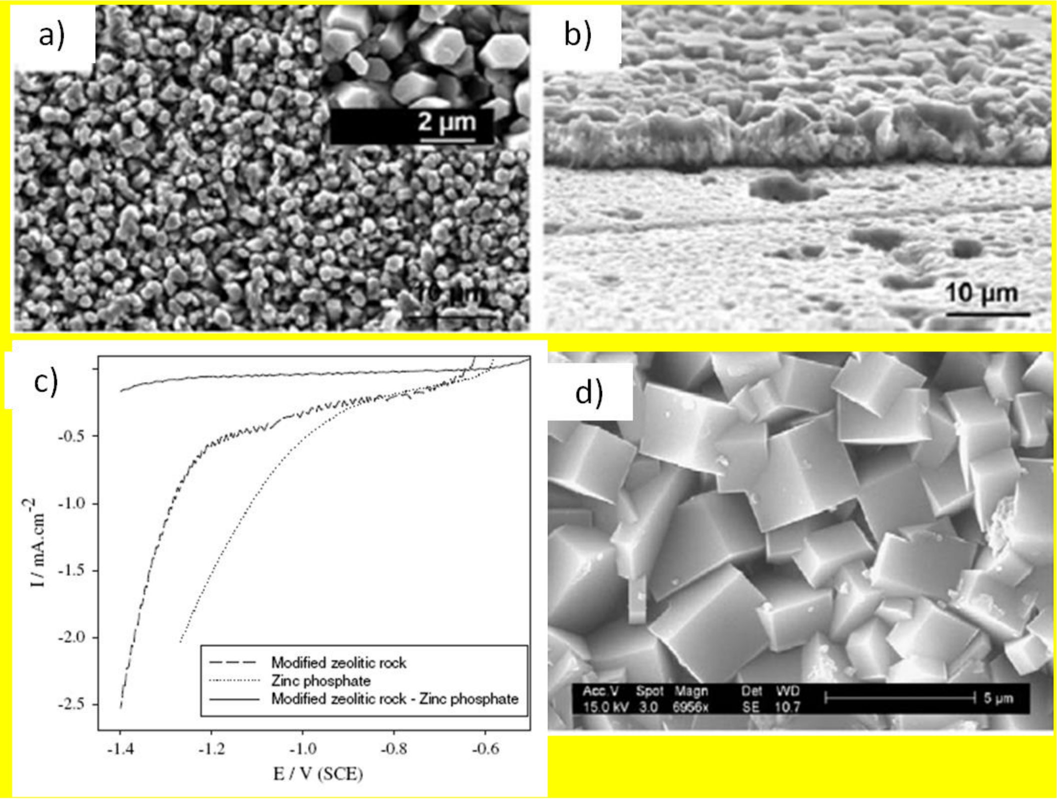

Figure 4. SEM images of corrosion-resistant coatings. SAPO-11 obtained by ionothermal treatment (reproduced from ref.[92]) a) surface, b) cross-section. c) Cathodic polarization curves of steel in contact with a smart anticorrosion pigment zeolite-zinc phosphate (reproduced from ref.[94]). d) MFI-type zeolite on Ti_6Al_4V surface (reprinted from publication[89] with permission from Elsevier).

Efficient heat exchangers are critical to numerous industrial processes and practical devices. The extraction or injection of the latent heat from or to liquid water is generally enhanced by a hydrophilic coating (Figure 5a).[87] A hydrophilic surface causes the distribution of water droplets into a thin film which helps to reduce the pressure drop of the air forced through the system, decreasing the operation noise and the pumping cost. In this sense, zeolite coatings are also an environmentally friendly alternative to increase the hydrophilicity of stainless steel, improving the heat transfer coefficients by 500 % over the bare metal.[87]

Biofouling, the undesired attachment of organisms to surfaces (bio-film) in an aquatic environment, has been recognized as a widespread problem in the field of materials' design.[95] Aqueous environments have seriously affected the efficient operation of military equipment and industrial processes due to the increase of mass on marine structures and boats, promotion of hydrodynamic drag and fouling/clogging of water pipes and filters.[96] For instance, a fouled ship burns up to 40 % more fuel in order to maintain the same speed[97]. Zeolites have shown an excellent performance to inactivate viruses and bacteria.[98] Consequently, zeolite coatings are not only interesting because of their improved heat transfer and extremely corrosion-resistance but also because of their excellent biocide properties. In fact, hydrophilic zeolite coatings decrease the bacteria attachment, a key issue to minimize biofouling.[91] Furthermore, silver-exchanged zeolites inhibit bio-film formation because the release of Ag ions inhibits the transport functions in the cell wall (respiration), the cell division (reproduction) and the cell energy generation (metabolism).[99] In addition, silver-exchanged zeolites have been extensively used in various technological fields, such as water treatment,[100] food packaging,[101] hospital equipment,[102] healthcare furnishing,[103] medical packaging and cosmetics[104] and PVC-based zeolite composites.[105]

As described in this perspective, zeolite thin films find their way toward future commercial implementation, but it is highly necessary to evaluate their mechanical, interfacial and tribological properties as these are critically important in providing the necessary mechanical strength, fracture and wear resistance for the final purpose.

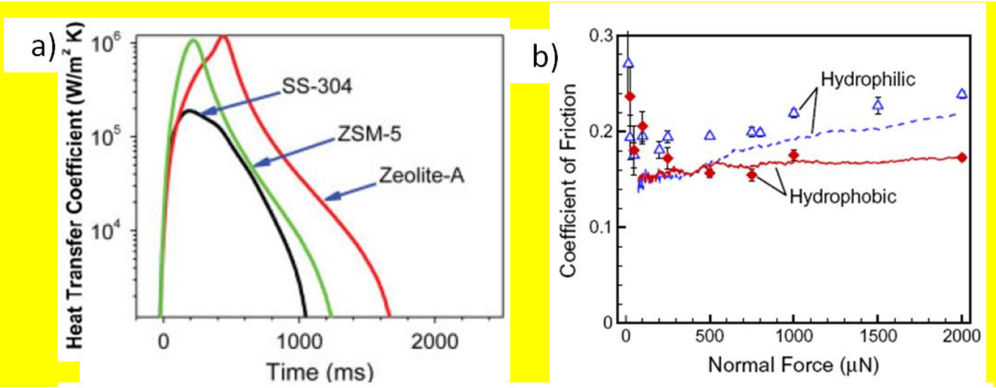

Figure 5. a) Heat transfer coefficient variation with time for different hydrophilic zeolite coatings. Initial surface temperature = 200 ºC (reproduced from ref.[87]), b) coefficient of friction vs. normal force for hydrophobic and hydrophilic MEL-type zeolite films (reprinted from publication[90] with permission from Elsevier).

Jonhson *et al.*[90] used a vapor-phase silylation process to control the hydrophobicity of the zeolite surface, demonstrating that there is a clear difference in the wear resistance between hydrophilic and hydrophobic films. Reporting that at low normal load the two films, hydrophilic and hydrophobic, exhibited similar friction behavior. Nevertheless, at higher normal load, the hydrophobic zeolite film showed significantly lower friction and greater wear resistance (Figure 5b). This fact is of outstanding importance since both hydrophobic and hydrophilic zeolite thin films have potential applications in various technological fields. A foreseeable application of zeolite coatings which is directly related with their mechanical properties is as anti-reflection layer in optical devices. Amorphous silica coatings are usually used to face this issue but their mechanical durability is of concern. Zeolite coatings show strong anti-reflection properties, with a scatter enhancing surface texture. In fact, after a steaming treatment, Chen *et al.*[106] achieved a strong zeolite film with a pencil hardness better than 6H, with added benefit of self-cleaning effects.

Recent development of zeolite thin film technology has pushed the applications of these materials into low-dielectric constant (low-*k*) insulating materials for computer chips.[107] A new generation of materials is required in the top-down nanotechnology approach as the feature sizes of next-generation microprocessors reach into the 32 nm node. A suitable dielectric interconnect material with a *k* value lower than 2.5 units and an elastic modulus of at least 6 GPa is required by semiconductor industry to continue the development along Moore's Law.[108] Pure-silica zeolite coatings offer several of the necessary properties for low-*k* applications: high porosity, mechanical strength, heat conductivity, thermal stability, and hydrophobicity.[109] A spin-on manufacturing-friendly process was developed by Wang *et al.*[110] in which hierarchical silicalite-1 films with bimodal pore size distribution were used. The authors were able to obtain a *k*-value and an elastic modulus of 2.1 and 16-18 GPa, respectively.

The increasing environmental concerns and stringent regulations have spurred the development and implementation of advanced emission control technologies. Zeolites have also been successfully used as hydrocarbon adsorbents during engine cold start for diesel and gasoline powered vehicles, trapping the hydrocarbons up to high temperatures enough to be decomposed by the three-way catalyst.[111]

Finally, zeolite coatings have been stated in the design of novel 'capsule' catalysts, first explored by Nishiyama *et al.*[112] The capsule catalyst has a core/shell structure, with a zeolite coating (shell) enwrapping a catalyst (core). The zeolite shell offers a unique spatial selectivity, which enables the design of selective catalysts for specific functions. For instance, the shell can induce reactant selectivity,[112-113] selective product removal[114] or reactant delivery,[115] reduce the core poisoning or even simultaneously offer catalytic properties.[116] The topological coating of silicalite-1 on H-ZSM-5 crystals and application in the selective production of *p*-xylene by the alkylation of toluene with methanol is an ultimate result of this approach. The high selectivity, better than the industrially required 99.5 %, is even maintained at high toluene conversions, due to the absent xylene isomerization at the outside surface of these catalyst particles.[117] Other examples of core-shell particles possessing zeolite single-crystal cores and zeolite polycrystalline shells have dealt with BEA-STO,[g] BEA-MFI,[118] MOR-MFI[119] and SOD-LTA, BEA-LTA, FAU-MFI, MFI-BEA and MFI-MFI[120] structure type pairs.

[g] S. Nair, L. A. Villaescusa, M. A. Camblor, M. Tsapatsis, *Chemical Communications* **1999**, 921-922.

Zeolite applications take advantage of the inherent molecular-sieve characteristic of these porous tailored materials. Nevertheless, novel research discloses the feasibility of zeolitic coatings in a wide number of fields such as electronics, biomechanics, corrosion-resistance, optics, automotive, and material science. Zeolitic coatings circumvent the drawbacks originated by the materials used up to now in those fields, being deemed to be essential in future material science development. On the other hand, zeolitic coatings still suffer from a lack of convenient deposition techniques to avoid the typical high pressure/temperature conditions, but these techniques are still in progress.

Metal organic framework based membranes

The first reports on metal organic frameworks (MOFs) or, more widely speaking, on coordination polymers date from the late 1950s[121] and early 1960s,[122] although it was not until the end of the last century when Robson and co-workers [123], followed by Kitagawa *et al.*,[124] Yaghi and Li,[125] and Férey and co-workers,[126] rediscovered and boosted the field. MOFs cover a much wider pore size range than zeolites, even bridging micro- and mesoporous materials, and present an unprecedented topological richness. The combination of organic and inorganic building blocks offers an almost infinite number of combinations, enormous flexibility in pore size, shape and structure, and lots of opportunities for functionalization, grafting and encapsulation. These materials hold world records in adsorption capacities, specific surface areas and pore volumes. Their porosity is much higher than that of zeolites (up to 90 %), justifying the designation 'framework'. Their thermostability, even in presence of steam,[127] is sometimes unexpectedly high, reaching temperatures above 400 °C. [128] Obviously, MOFs have attracted a lot of attention, with the major studies dealing with the synthesis of new structures,[129] and the majority of applications being on adsorption/separation,[130] storage,[131] catalysis,[132] encapsulation,[133] and even medical applications.[134]

Given the high topological richness of MOFs, the fact that no calcination is required after synthesis and the flexibility of many structures together with the applicability of the synthetic tools developed for zeolite membranes, the interest of MOFs in the field of membranes has grown exponentially during the last few years. The analogy with zeolites as crystalline porous material with molecular dimensions is obvious, but there are also some clear differences. Thinking in terms of membranes the highly accessible porosity infers high fluxes, while the wide range of pore sizes (sometimes into the mesopore range) would allow not only to tackle classical, though extremely important molecular separations as hydrogen from other gases, removal of

CO_2, alkanes from alkenes, linear from branched alkanes, and aromatic isomers, but also separation of larger molecular isomers.

After some early works on MOF dense coatings[135] on porous substrates and layer by layer deposition of MOFs on non-porous supports,[136] the first MOF membranes displaying separation properties different from Knudsen diffusion control were reported by the groups of Tsapatsis[137] and Caro.[138] At the same time, the first self-supported MOF membrane was reported by Guo *et al.*[139] In the latter, a HKUST-1 membrane was produced by hydrothermally oxidizing part of a copper wire mesh. This created a local supersaturation that promoted the formation of the MOF material that filled up the space in between the mesh wires, resulting in a kind of reinforced self-supported membrane. This material showed selectivity for hydrogen over other permanent gases, although this was not anticipated based on the pore size of this MOF structure. This work together with the electrochemical synthesis of MOF coatings reported by Ameloot *et al.*[140] clearly exemplify some of the most peculiar advantages (*i.e.* fast and reproducible synthesis) that MOFs may eventually offer over zeolites for the production of membranes.

In Table 2 the MOF membranes reported to date together with their main properties are summarized. Table 2 gives a complete picture of the separation performance achieved using this type of membranes so far, completing very recent reviews.[9d, 141] Synthetic methods utilized vary from direct hydrothermal synthesis[37] to the use of secondary growth in combination with microwave heating[138b] and the use of covalent linkers like 3-aminopropyltriethoxysilane to favor crystal attachment to a support.[142] At the same time, some groups have made use of the intrinsic properties of MOFs to promote the growth of dense membranes: Hu *et al.*[143] used the porous support as the inorganic source reacting with the organic precursor to grow a seeding layer used afterwards in the synthesis of MIL-53(Al) membranes. Along the same line, Jeong *et al.*[144] developed a surface modification involving the hot treatment of the support with the methyl imidazole linker used for the synthesis of ZIF-8 membranes.

Table 2. MOF membranes reported in the literature.

MOF	**Type of support**	**Synthesis method**	**Layer thickness**	**Separation (Separation factor) (Ideal selectivity*)**	**Temp. (°C)**	**Permeance ($mol\cdot m^{-2}s^{-1}Pa^{-1}$)**	**Ref**
MOF-5	Symmetric α- Al_2O_3 disks		≈10 μm	--	R.T.	H_2: $1.5\cdot10^{-6}$	[145]
HKUST-1	Self supported (copper mess)	Support oxidation + hydrothermal	≈20 μm	H_2/N_2 (7) H_2/CO_2 (6.8) H_2/CH_4(5.9)	R.T.	H_2: $1.5\cdot10^{-6}$	[139]
MMOF	Symmetric α- Al_2O_3 disks	Direct hydrothermal	≈15 μm	H_2/N_2 (22*) H_2/CO_2 (4*) CO_2/N_2 (5*)	25 - 200	H_2:$1.5\cdot10^{-8}$	[137]
ZIF-8	Asymmetric TiO_2 disks	Microwave-Assisted	≈30 μm	H_2/CH_4 (11.2) C_2H_4/C_2H_6 (2.6)	R.T.	H_2: $6.7\cdot10^{-8}$	[138a, 146]
ZIF-7	Asymmetric α-Al_2O_3 disks	Secondary growth	≈1 μm	H_2/N_2 (18) H_2/CO_2 (13.6) H_2/CH_4 (14)	25 - 200	H_2: $4.5\cdot10^{-8}$	[138b, 147]
HKUST-1	Symmetric α-Al_2O_3 disks	Secondary growth	≈8 μm	H_2/N_2 (7*) H_2/CH_4 (5*) H_2/CO_2 (4*)	25 - 200	H_2: $1.5\cdot10^{-6}$	[148]
ZIF-22	Asymmetric TiO_2 disks modified with APTES ligand	Direct hydrothermal	≈30 μm	H_2/N_2 (6.4) H_2/CO_2 (7.2) H_2/O_2 (6.4) H_2/CH_4 (5.2)	R.T.	H_2: $2\cdot10^{-7}$	[142]

ZIF-90	Asymmetric α-Al_2O_3 disks modified with APTES ligand	Direct hydrothermal	≈15 µm	H_2/N_2 (7.3) H_2/CO_2 (11.7) H_2/CH_4 (15.3) H_2/C_2H_4 (62.8)	R.T.	H_2: $2.5\cdot10^{-7}$	[149]
ZIF-69	Symmetric α- Al_2O_3 disks	Direct hydrothermal	≈30 µm	CO_2/CO (3.5)	R.T.	H_2: $6.5\cdot10^{-8}$	[150]
ZIF-8	Symmetric α- Al_2O_3 disks	Secondary growth	≈20 µm	H_2/N_2 (11.6) H_2/CH_4 (13)	R.T	H_2: $2\cdot10^{-7}$	[144]
ZIF-8	Symmetric α- Al_2O_3 tubes	Secondary growth	≈5 µm	CO_2/CH_4(5.1)	R.T.	CO_2: $2\cdot10^{-5}$	[151]
SIM-1	Asymmetric α-Al_2O_3 tubes	Direct hydrothermal	≈25 µm	CO_2(10)/N_2(87)/ H_2O(3) (CO2/N2=4.5)	25-200	H_2: $8\cdot10^{-8}$	[152]
ZIF-8	Asymmetric α-Al_2O_3 disks	Secondary growth	≈10 µm	H_2/CO_2 (6) H_2/CH_4 (10) H_2/C_2H_6 (10) H_2/C_3H_8 (400)	R.T.	H_2: $1\cdot10^{-7}$	[153]
MIL-53(Al)	Symmetric α-Al_2O_3 disks	Reactive seeding	≈10 µm	EtAc/H_2O (>100)	R.T. (gas) 60 (Pervap)	H_2: $5\cdot10^{-7}$	[143]
ZIF-90 PSM	Symmetric α-Al_2O_3 disks	Direct hydrothermal	≈20 µm	H_2/N_2 (16) H_2/CO_2 (16) H_2/CH_4 (20)	25 - 200	H_2: $5\cdot10^{-7}$	[154]
HKUST-1	Symmetric α-Al_2O_3 disks	Layer by layer seeding + secondary growth	≈15 µm	H_2/N_2 (3.7*) H_2/CO_2 (5.1*) H_2/CH_4 (2.9*)	R.T.	H_2: $7.5\cdot10^{-7}$	[155]
IRMOF-3 (PSM)	Symmetric α-Al_2O_3 disks	Secondary growth	≈10 µm	H_2/CH_4 (2*)	R.T.	H_2: $1.1\cdot10^{-6}$	[156]
MOF-5	Symmetric α-Al_2O_3 disks	Secondary growth	≈14 µm	H_2/N_2 (4*) H_2/CO_2 (4.1*)	R.T.	H_2: $4.3\cdot10^{-7}$	[157]

$Co_3(HCOO)_6$	Macroporous glass-frit disks	Secondary growth	≈11 µm	CO_2/CH_4 (10-15)	0-60	CO_2: $2\cdot10^{-6}$	[158]

Abbreviations: MOF systems: HKUST-1 = $Cu_3(btc)_2$; MOF-5 = $Zn_4O(bdc)_3$; IRMOF-3 = $Zn_4O(bdc\text{-}NH_2)_3$ MIL-53(Al) = Al(OH)(bdc); ZIF-7 = $Zn(BIM)_2$; ZIF-8 = $Zn(MeIM)_2$; ZIF-22 = $Zn(ABIM)_2$; ZIF-69 = $Zn(ClBIM)_2$; ZIF-90 = $Zn(ICA)_2$; SIM-1 = $Zn(MeIMC)_2$; MMOF: (Cu-4,4'-(hexafluoroisopropylidene)-bis(benzoic acid). Linker and functional groups: bdc = 1,4-terephthalate; bdc-NH_2 = 2-amino-1,4-terephthalate; btc = 1,3,5-benzene- tricarboxylate; BIM: benzimidazole; MeIM = 2-methylimidazole; ICA = imidazolate-2-carboxyaldehyde; MeIMC: 4-methyl-5-imidazolecarboxaldehyde; ClBIM: 5-chlorobenzimidazole; ABIM: 5-azabenzimidazole. PSM: Post-synthetic modification.

Considering Table 2, it is easy to realize that membranes based on the so-called zeolite imidazolate frameworks (ZIFs) have been most studied. ZIFs are a sub-family of MOFs named after the resemblance of the metal-imidazolate-metal bond angles to the Si-O-Si angles of zeolites.[159] Most ZIFs are built by connecting metal clusters (mainly Zn or Co) through modified imidazole linkers, resulting in the formation of small pore solids displaying zeotype architectures based on cage connections such as SOD, RHO or LTA. The full saturation of the metal together with the use of imidazole linkers provide ZIF materials with an outstanding thermal stability (up to 400 °C) and, more importantly, with a highly hydrophobic character.[160] In analogy to zeolites, hydrophobic MOFs seem to be much more suitable (as the silicalite-1 zeolite has probably given rise to the best zeolite membranes) for the synthesis of membranes. We attribute this to the highly negative electric surface charge of hydrophilic MOF crystals and to the absence of "interacting surface hydroxyls", as it is the case with zeolites. This negative surface charge is expected to prevent the negatively charged linker anions to enter the space between the growing crystallites in a MOF membrane layer and close this layer, as discussed earlier and as shown by Bux *et al.*[161] for highly hydrophilic zeolites.

In terms of flux, although most MOF-based membranes are of the order of magnitude of zeolite membranes,[82b, 162] already the first examples of outstanding fluxes have been published. Venna and Carreon[151] reported the preparation of high permeation flux (J_{CO2}=$2\cdot10^{-5}$ mol·$m^{-2}s^{-1}Pa^{-1}$) ZIF-8 membranes on tubular supports using secondary growth. One year later, Zou *et al.*[158] synthesized $Co_3(HCOO)_6$ membranes on glass frit disks with CO_2 permeation fluxes as high as $2\cdot10^{-6}$ mol·$m^{-2}s^{-1}Pa^{-1}$.

Regarding selectivity, it is fair to admit that MOF membranes are still far from expectations based on pore dimensions. This might be due to a great extent to the intrinsic flexibility of many MOF structures.[9b] Recently, ZIF-7 has been shown to be able to adsorb olefins and paraffins much larger than the crystallographic pore size of the structure (0.3 nm). This was attributed to the reversed shape selectivity to a “gate-opening” effect due to the rotation of the benzimidazole linkers in which specific threshold pressures control the rotation of the linker and therefore the uptake and release of individual molecules.[130b, 163] Aguado *et al.*[164] later discussed a similar gate opening behavior of ZIF-7 upon CO_2 adsorption accompanied by a phase transformation of the framework. These results combined with work of Luebbers *et al.*,[165] who demonstrated the high flexibility of ZIF-8 towards adsorption of bulky hydrocarbons, and with recent patents dealing with the application of ZIF-7 in the selective separation of CO_2 and the separation of CH_4 from different hydrocarbons[166] indicate that ZIFs may be much more flexible than expected [160]. Thinking of membranes, this type of flexible behavior results in lower separation factors, as a too large flexibility will deteriorate real molecular sieving. On the other hand, it may be more forgiving towards differences in thermal expansion between support and selective layer, and avoiding crack formation at elevated temperatures, as suggested elsewhere.[9b] In fact, Li *et al.*[167] have shown an improved separation performance of their ZIF membranes up to temperatures of 200 °C and even in the presence of moisture. Similarly, Aguado *et al.*[152] reported an activated permeation of H_2 at 200 °C and a negligible effect of water on the separation of CO_2/N_2 mixtures at room temperature when using membranes of the so-called ZIF SIM-1.

The extension of synthetic procedures to different MOF topologies has been demonstrated, but the reproducibility of MOF membrane synthesis based on solvo/hydrothermal protocols seems to be an issue to be considered and much more work is needed on this specific topic. Most probably the questions that remained unresolved for zeolite membranes are also problems to overcome with MOFs membranes.

As we have shown, the field of MOF membranes is developing rapidly and the first opportunities (high fluxes) and limitations (fair selectivities and low reproducibility) of these membranes have already been identified. At this moment, we cannot forecast whether MOF membranes will be able to find their way towards commercial applications. It is experienced that the first barrier to overcome is the low reproducibility. In this sense new manufacturing methods, differing from those known in zeolite membrane production, like electrochemical synthesis,[168] may play an important role. Moreover, in view of their unprecedented topological richness, MOFs can be victims of their own success. In this sense, the recent development of high-throughput computational and experimental screening methods for identifying useful MOFs for separations will certainly help select the most promising structures[h-k]. On the other hand, MOFs offer important advantages for industrial production: in principle, their interaction with cheaper support materials should be better.[139, 158] In addition, it should even be possible to grow MOF membranes on top of polymeric hollow fibers, resulting in highly attractive membrane module prices.

h-kBeatriz, las referncias que comentamos.

In addition to economic considerations, further experimental work is needed in order to fully evaluate the potential of MOF membranes, more specifically for liquid phase applications and at higher temperatures:

- So far, MOF based membranes have been applied to the separation of small gases, while liquid phase separations have scarcely been reported.[169] This is counter-intuitive, since one would expect that much bigger molecules can be separated based on the pore dimensions of many MOFs. Some liquid phase adsorptive separation has been reported,[170] so selectivities can be expected.
- In most cases, room temperature separation has been reported, only a few examples of separation performance at high temperatures are available in literature.[171]

Other possible industrial applications of zeolite (composite) membranes

Polymeric membranes have been extensively developed in the field of pervaporation and gas separation. The development of membranes for gas separation dates back to 1961 with the production of high-flux asymmetric membranes by Loeb and Sourirajan.[172] Polymer materials, and predominantly those prepared from glassy polymers, have received considerable attention in membrane technology providing good mechanical properties and better size separation characteristics compared to rubbery polymers.[173] Different polymer families have been widely investigated for gas separation, such as polycarbonate, polyester, polysulfone, polyethersulfone, polyetherimide or polyimide, among others.[174] In 1980, Permea (now a division of Air Products) launched the first large industrial application of gas separation membranes. A polysulfone hollow fiber membrane was used for the separation and recovery of hydrogen from the purge gas streams of ammonia plants.[175] By the mid-1980s, Cynara (part of Natco), Separex (part of UOP), and GMS (part of Kvaerner) used cellulose acetate membranes for CO_2 removal from natural gas.[176] Later on, in 1994, Medal (part of Air Liquid) installed a plant for CO_2/CH_4 separation using a polyimide hollow fiber membrane.[175]

The above mentioned commercial polymer materials have the benefits of being (i) inexpensive to process, (ii*)* highly reproducible (easy to control the thickness and easy to prepare defectiveness dense membranes), and (iii) physically robust,[176-177] therefore, solving the difficulties and addressing the opportunities pointed out along the paper for pure zeolite membranes. Nevertheless, polymeric membranes, both at lab and commercial scale, still do not meet the requirements for the current advanced membrane technology due to their lower separation performance (moderate selectivities), when compared with the ones based only on crystalline materials with well-defined pore systems like zeolites[2c, 2g] or metal organic frameworks (MOFs).[9b]

In 1991, and updated in 2008, Robeson plotted the data of many polymer membranes in a selectivity versus permeability graph for different gas mixtures obtaining the defined “upper bound trade-off” line,[178] which conventional polymer membrane materials cannot overcome. This bound marks, to a certain extent, the polymer material performance for a specific gas mixture and emphasizes the need for choosing innovative materials or combining them within the polymer matrix with the purpose of overcoming the Robeson’s upper-bound achieving a synergetic separation performance.

The performance of polymers versus inorganic molecular sieving materials along with the economically viable region is shown for carbon dioxide/methane separation in Figure 6. For comparison purposes, the estimated permeability-selectivity couple of pure porous materials commonly used for inorganic membranes such as zeolites[179] or carbon molecular sieves (CMSs)[180] have been added to the graph. In addition, Erucar *et al.*[181] predicted the behavior of ten different MOF structures (from the Cambridge Structural Database) containing similar topologies, either with one-, two- or three-dimensional pores with the same metal sites but with different CO_2 affinities. From theoretical permeation models, these authors placed the pure MOF materials beyond the attractive region. These results point towards the combination of high performance polymers and fillers to create new composite membranes *i.e.* mixed matrix membranes (MMMs).

Generally, MMMs are composed of nanostructured porous fillers embedded in a polymer matrix. This novel membrane approach adds better transport properties and higher thermal and chemical stability to the polymer phase, solving the inherent brittleness problems found in the pure inorganic membranes. The most important advances in MMMs have been extensively revised[177, 182] since the pioneering study of Zimmerman *et al.*,[183] indicating the polymers and the fillers used in conjunction with the results of permeability and selectivity for different gas mixtures.

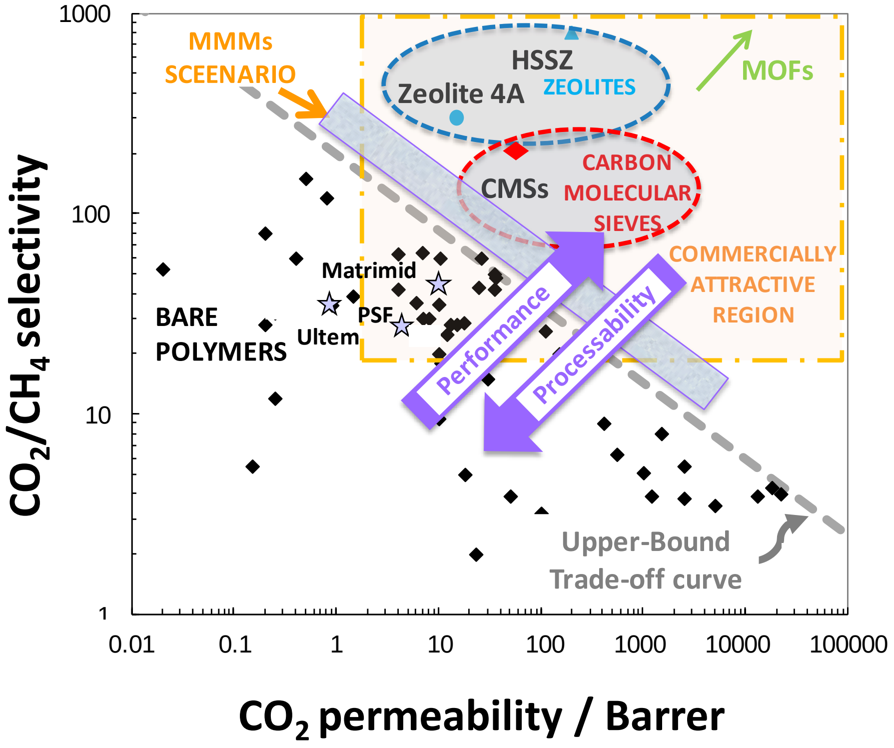

Figure 6. Robeson's plot for the CO_2/CH_4 separation. The permselectivity values of different bare polymers and pure nanostructured porous materials (zeolites,[179] CMSs[180] and MOFs[181]) including the mixed matrix membrane scenario are represented. Values for MOFs are estimated outside the graph area with a CO_2 permeability close to 10^7 Barrer (for BAHGUN MOF) and a CO_2/CH_4 selectivity better than 10^5 (for MMIF MOF).[181] CMSs and PSF are carbon molecular sieves and polysulfone, while Ultem and Matrimid correspond to commercial polyetherimide and polyimide, respectively.

Difficulties in obtaining a good interaction between the continuous (polymer) and disperse (filler) phases have been recognized, which is considered the first factor influencing the MMM success. If polymer chains are not completely able to surround the particles, undesirable channels may be created between both phases.[184] This induces higher permeabilities because of gas bypassing accompanied by losses of selectivity. Koros and co-workers[184a, 185] have identified two key requirements that would be necessary for the success of hybrid membranes with glassy polymers, in addition to the matching filler and polymer transport properties: molecular adsorption of the polymer onto the filler surface, and polymer flexibility during the membrane formation.

Various polymers (mostly polyetherimides, polysulfones and polyimides due to their good transport properties) have been modified with inorganic fillers such as zeolites,[186], porous titanosilicates,[187] mesoporous silicas,[184b, 186c, 188] CMSs,[180, 189] carbon nanotubes[190] and even non-porous solids such as fumed silica[191] to produce MMMs displaying gas separation performances that overpass the pure polymer. For instance, adding 8 wt.% of ordered mesoporous silica spheres (MSSs) of 2-4 μm in diameter to a glassy polymer matrix resulted in a selective membrane with an increase in H_2/CH_4 selectivity of 35 and 25 %, for polysulfone and polyimide as a continuous phase, respectively.[186c, 188] Incorporating 4 wt.% of high aspect ratio delaminated titanosilicate UZAR-S1 to polysulfone, a similar enhancement was reached.[187b] Moreover, other delaminated materials obtained from a layered AlPO,[l] and lamellar zeolites AMH-3[m,n] and Nu-6(1)[o] have been also applied successfully to MMMs. In addition, Up to 38 vol.% of CMSs integrated to a polymer resulted in a profound improvement in CO_2/CH_4 and O_2/N_2 selectivities (as much as 45 and 20 % for polyetherimide and polyimide, respectively).[180, 189b] In many other MMMs studies a significant selectivity enhancement was also found. Adding 10 vol.% of Grignard reagent modified HSSZ-13 zeolite in polyetherimide revealed increases of 25 % in selectivity for the CO_2/CH_4 pair,[186b] while 4-8 wt.% of hollow zeolite spheres embedded in polysulfone or polyimide matrix led to CO_2/N_2 and O_2/N_2 selectivity improvements of 35-50 %. The spherical filler molecular sieve structure minimizes agglomeration and hence improves dispersion and interaction with the polymer phase.[186c]

[l] H. K. Jeong, W. Krych, H. Ramanan, S. Nair, E. Marand, M. Tsapatsis, *Chemistry of Materials* **2004**, *16*, 3838-3845.

m S. Choi, J. Coronas, E. Jordan, W. Oh, S. Nair, F. Onorato, D. F. Shantz, M. Tsapatsis, *Angewandte Chemie-International Edition* **2008**, *47*, 552-555.
n S. Choi, J. Coronas, Z. Lai, D. Yust, F. Onorato, M. Tsapatsis, *Journal of Membrane Science* **2008**, *316*, 145-152.
o P. Gorgojo, D. Sieffert, C. Staudt, C. Tellez, J. Coronas, *Journal of Membrane Science* **2012**, *411-412*, 146-152.

With the discovery of MOFs the interest in MMMs has been revitalized. The use of MOFs as fillers provides several advantages over conventional inorganic materials. First, the interaction of both phases is easier to control due to the better affinity of the MOF linkers with the polymer chains. Second, the size, shape and chemical functionalities of the MOF cavities can be easily adjusted by choosing the appropriate linker-metal couples. Indeed, since the seminal work of Yehia *et al.*,[192] MOF-MMMs have experienced a rapid growth[193] and we expect the first examples of industrial application in the near future.[9d] A detailed review on MOF based MMMs can be found elsewhere.[194]

The MMM approach offers a clear opportunity for improving the already commercial polymer membranes regarding (i) the *processability* in terms of costs, reproducibility and the facility to prepare non-defective membranes, and (ii) the membrane *performance*, resulting in an overall superior gas separation efficiency.[182a, 183, 189b, 195]

In response to the urgent need to reduce material costs, the idea of using membranes comprising nanostructured porous materials and polymers in the same film would lead to an economic compromise. Considering the price of the individual phases, a pure polymer gas separation membrane system boils down to 80 €/m^2 (e.g. membrane applied for CO$_2$ capture),[196] while the fully inorganic membranes are estimated 10- to 50-fold more expensive.[175] This difference in price could be accepted only by specific applications where the polymer membranes fail (shape selective separation behavior and thermal and chemical stability limitations).[197] Therefore, an intermediate position of MMMs regarding cost-price, between polymer and zeolite membranes, is attractive, next to the outlook of selectivity improvement of these membranes.

The economic arguments towards commercialization also involve membrane configurations that maximize intensification (area to volume ratio) and performance.[198] In gas phase separations, intensification can be achieved with thinner membranes or by increasing the active surface of the membrane. Commercially, the membranes of growing demand and popularity have the optimized geometry of hollow fibers.[199] Preparation of asymmetric polyetherimide hollow fiber membranes with high gas selectivity was reported for He/N_2 separation.[200] Such membranes have a selective layer on the outside of the fiber and an inner porous support layer.[201] Figure 7 shows a diagram of a hollow fiber mixed matrix membrane with asymmetric structure. The enlarged area shows the selective layer containing the filler (zeolitic material) within the polymer matrix. Recently, Dai *et al.*[p] have incorporated ZIF-8 into a polyetherimide (Ultem® 1000) matrix and produced dual-layer asymmetric hollow fibers membranes making Figure 7 a reality.

[p] Y. Dai, J. R. Johnson, O. Karvan, D. S. Sholl, W. J. Koros, *Journal of Membrane Science* **2012**, *401–402*, 76-82.

The final success of MMMs towards industrial implementation greatly depends on the selection of the membrane materials and the filler-polymer compatibility with homogeneous dispersion of filler within the polymer. Starting from a polymer located near or on the upper-bound, the surface chemistry, textural properties, particle size distribution and aspect ratio should be taken into account as the most critical variables to obtain a high performance MMM. A remaining challenge for MMMs relates to the availability of materials simultaneously featured with nanometer size (to produce thin, high flux membranes), good dispersibility (avoiding agglomeration) and chemical interaction with polymer phase (to minimize filler-polymer gaps). Finally, the achievement of improvements at low filler loading is also of interest, since this would reduce MMM cost while preserving the mechanical properties of the pure polymer.

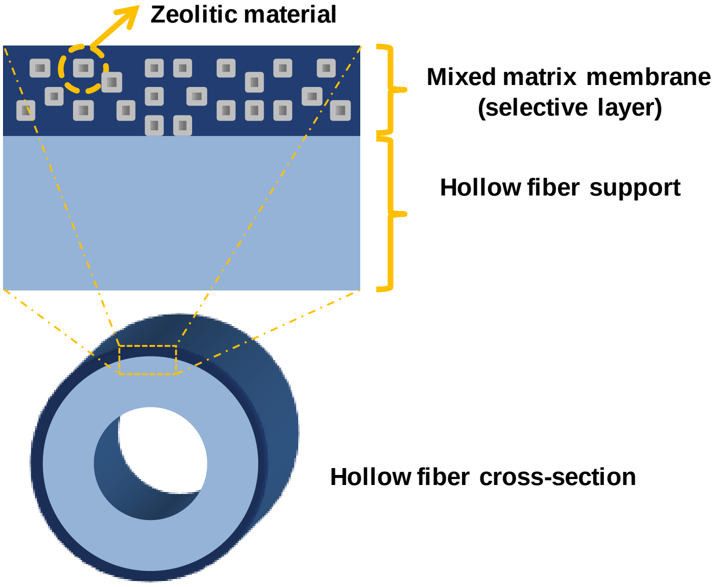

Figure 7. Scheme of a hollow fiber mixed matrix membrane with asymmetric structure.

Conclusions

During the last few decades, a great deal of work has been devoted to the development of zeolitic membranes and coatings. Already great advances have been achieved, with the first examples of industrial separation processes in the market. Having said this, we should admit that it is not been an easy ride: in spite of the high expectations, there is still a long road ahead for the massive implementation of this type of membranes. The main barriers that need to be eliminated along with opportunities for future developments to be mentioned are:

i) The lack of reproducibility to meet industrial and commercial requirements. This may be due to the unfit orientation of the polycrystalline membranes, but also to the influence of the porosity and chemical composition of the support, activation process and difficulty to control membrane thickness. In this sense, the parallel development of both support and membrane would help to overcome this limitation.

ii) The estimated actual cost of zeolite membrane modules has to drop by a factor of *ca*. 5 in order to compete with polymers. This cost limitation should be circumvented by synthesizing thinner membranes, resulting in higher fluxes per unit area and by developing cheaper supporting materials.

iii) For certain applications, the state of the art zeolite membranes already outperform other separation technologies: i.e. for high temperature applications, when very low water content is required or when the chemical stability of polymer membranes is insufficient.

iv) Concerning MMMs, since many polymeric membranes have already been commercialized, the final success of zeolites as fillers for industrial implementation greatly depends on filler-polymer compatibility with homogeneous dispersion, good interaction and low loading.

v) Last but not least, we should not forget that the knowledge generated during the development of zeolite membranes has opened the door to the application of zeolite coatings in adjacent fields like electronics, biomechanics, corrosion-resistance, optics and automotive, with already exciting results. In addition, such knowledge has been transferred to MOF membranes. The latter offer important advantages for industrial production. Their interaction with cheaper support materials can be easily tuned, and it should even be possible to grow MOF membranes on top of economical polymeric hollow fibers, resulting in highly attractive membrane module prices.

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References

1. Yu, M.; Noble, R. D.; Falconer, J. L. *Acc. Chem. Res.* **2011,** *44* (11), 1196-1206.

2. (a) Bein, T. *Chem. Mater.* **1996,** *8* (8), 1636-1653; (b) Tavolaro, A.; Drioli, E. *Adv. Mater.* **1999,** *11* (12), 975-996; (c) Coronas, J.; Santamaria, J. *Separ. Purif. Method.* **1999,** *28* (2), 127-177; (d) Caro, J.; Noack, M.; Kolsch, P.; Schafer, R. *Microporous Mesoporous Mater.* **2000,** *38* (1), 3-24; (e) Bowen, T. C.; Noble, R. D.; Falconer, J. L. *J. Membr. Sci.* **2004,** *245* (1-2), 1-33; (f) McLeary, E. E.; Jansen, J. C.; Kapteijn, F. *Microporous Mesoporous Mater.* **2006,** *90* (1-3), 198-220; (g) Caro, J.; Noack, M. *Microporous Mesoporous Mater.* **2008,** *115* (3), 215-233; (h) Pina, M. P.; Mallada, R.; Arruebo, M.; Urbiztondo, M.; Navascues, N.; de la Iglesia, O.; Santamaria, J., *Microporous Mesoporous Mater.* **2011,** *144*, 19-27; (i) van den Bergh, J.; Nishyama, N.; Kapteijn, F., *edited by A. Cybulski, J. A. Moulijn, and A. Stankiewicz, Weinheim: Wiley* **2010**, 211-234.

3. (a) Kita, H.; Horii, K.; Ohtoshi, Y.; Tanaka, K.; Okamoto, K. I. *J. Mat. Sci. Lett.* **1995,** *14* (3), 206-208; (b) Wee, S. L.; Tye, C. T.; Bhatia, S. *Sep. Purif. Technol* **2008,** *63* (3), 500-516.

4. (a) Matsufuji, T.; Nishiyama, N.; Matsukata, M.; Uyama, K.,. *J. Membr. Sci.* **2000,** *178* (1-2), 25-34; (b) Xomeritakis, G.; Lai, Z. P.; Tsapatsis, M. *Ind. Eng.Chem. Res.* **2001,** *40* (2), 544-552; (c) Hedlund, J.; Sterte, J.; Anthonis, M.; Bons, A. J.; Carstensen, B.; Corcoran, N.; Cox, D.; Deckman, H.; De Gijnst, W.; de Moor, P. P.; Lai, F.; McHenry, J.; Mortier, W.; Reinoso, J. *Microporous Mesoporous Mater.* **2002,** *52* (3), 179-189; (d) Daramola, M. O.; Burger, A. J.; Pera-Titus, M.; Giroir-Fendler, A.; Miachon, S.; Dalmon, J. A.; Lorenzen, L. *Asia-Pac. J. Chem. Engi.* **2010,** *5* (6), 815-837.

5. (a) Kusakabe, K.; Kuroda, T.; Murata, A.; Morooka, S. *Ind. Eng.Chem.Res.* **1997,** *36* (3), 649-655; (b) Poshusta, J. C.; Tuan, V. A.; Falconer, J. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **1998,** *37* (10), 3924-3929; (c) Tomita, T.; Nakayama, K.; Sakai, H. *Microporous Mesoporous Mater.* **2004,** *68* (1-3), 71-75; (d) Olajire, A. A. *Energy* **2010,** *35* (6), 2610-2628.

6. (a) Tuan, V. A.; Falconer, J. L.; Noble, R. D. *Microporous Mesoporous Mater.* **2000,** *41* (1-3), 269-280; (b) Sebastian, V.; Lin, Z.; Rocha, J.; Tellez, C.; Santamaria, J.; Coronas, J. *Chem. Commun.* **2005,** (24), 3036-3037; (c) Li, Y.; Pera-Titus, M.; Xiong, G.; Yang, W.; Landrivon, E.; Miachon, S.; Dalmon, J. A. *J. Membr. Sci.* **2008,** *325* (2), 973-981; (d) Wirawan, S. K.; Creaser, D.; Lindmark, J.; Hedlund, J.; Bendiyasa, I. M.; Sediawan, W. B. *J. Membr. Sci.* **2011,** *375* (1-2), 313-322.

7. (a) Meindersma, G. W.; de Haan, A. B. *Desalination* **2002,** *149* (1-3), 29-34; (b) Urtiaga, A.; Gorri, E. D.; Casado, C.; Ortiz, I. *Sep. Purif. Technol.* **2003,** *32* (1-3), 207-213; (c) Sommer, S.; Melin, T. *Chem. Eng. Process.* **2005,** *44* (10), 1138-1156; (d) Gorri, D.; Urtiaga, A.; Ortiz, I. *Ind. Eng. Chem. Res.* **2005,** *44* (4), 977-985; (e) Deshayes, A. L.; Miro, E. E.; Horowitz, G. I. *Chem. Eng. J.* **2006,** *122* (3), 149-157; (f) Urtiaga, A. M.; Gorri, E. D.; Gomez, P.; Casado, C.; Ibanez, R.; Ortiz, I. *Dry. Technol.* **2007,** *25* (11), 1819-1828; (g) Sato, K.; Sugimoto, K.; Nakane, T. *Microporous Mesoporous Mater.* **2008,** *115* (1-2), 170-175.

8. (a) Morigami, Y.; Kondo, M.; Abe, J.; Kita, H.; Okamoto, K. *Sep. Purif. Technol.* **2001,** *25* (1-3), 251-260; (b) Sato, K.; Nakane, T. *J. Membr. Sci.* **2007,** *301* (1-2), 151-161; (c) Sato, K.; Sugimoto, K.; Nakane, T. *J. Membr. Sci.* **2008,** *319* (1-2), 244-255; (d) Sato, K.; Sugimoto, K.; Nakane, T. *J. Membr. Sci.* **2008,** *310* (1-2), 161-173.

9. (a) Zacher, D.; Shekhah, O.; Woll, C.; Fischer, R. A. *Chem. Soc. Rev.* **2009,** *38* (5), 1418-1429; (b) Gascon, J.; Kapteijn, F. *Angew. Chem. Int. Edit.* **2010,** *49* (9), 1530-1532; (c) Shekhah, O.; Liu, J.; Fischer, R. A.; Woll, C. *Chem. Soc. Rev.* **2011,** *40* (2), 1081-1106; (d) Caro, J. *Curr. Opin.Chem. Eng.* **2011,** *1* (1), 77-83.

10. Ishikawa, A.; Chiang, T. H.; Toda, F. *J. Chem. Soc.Chem. Comm.* **1989,** (12), 764-765.

11. Yan, Y. S.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995,** *34* (5), 1652-1661.

12. (a) Coronas, J.; Falconer, J. L.; Noble, R. D . *AIChE J.* **1997,** *43* (7), 1797-1812; (b) Miachon, S.; Landrivon, E.; Aouine, M.; Sun, Y.; Kumakiri, I.; Li, Y.; Prokopova, O. P.; Guilhaurne, N.; Giroir-Fendler, A.; Mozzanega, H.; Dalmon, J. A., *J. Membr. Sci.* **2006,** *281* (1-2), 228-238.

13. (a) Lovallo, M. C.; Tsapatsis, M.; Okubo, T. *Chem. Mater.* **1996,** *8* (8), 1579-&; (b) Chau, J. L. H.; Tellez, C.; Yeung, K. L.; Ho, K. C. *J. Membr. Sci.***2000,** *164* (1-2), 257-275.

14. Navajas, A.; Mallada, R.; Tellez, C.; Coronas, J.; Menendez, M.; Santamaria, J. *J. Membr. Sci.e* **2006,** *270* (1-2), 32-41.

15. Dong, J. H.; Lin, Y. S.; Hu, M. Z. C.; Peascoe, R. A.; Payzant, E. A. *Microporous Mesoporous Mater.* **2000,** *34* (3), 241-253.

16. Choi, J.; Jeong, H. K.; Snyder, M. A.; Stoeger, J. A.; Masel, R. I.; Tsapatsis, M. *Science* **2009,** *325* (5940), 590-593.

17. Nishiyama, N.; Yamaguchi, M.; Katayama, T.; Hirota, Y.; Miyamoto, M.; Egashira, Y.; Ueyama, K.; Nakanishi, K.; Ohta, T.; Mizusawa, A.; Satoh, T. *J. Membr. Sci.* **2007,** *306* (1-2), 349-354.

18. Lew, C. M.; Cai, R.; Yan, Y. S. *Accounts Chem. Res.* **2010,** *43* (2), 210-219.

19. Navajas, A.; Mallada, R.; Tellez, C.; Coronas, J.; Menendez, M.; Santamaria, J., *J. Membr. Sci.* **2007,** *299* (1-2), 166-173.

20. Lassinantti, M.; Jareman, F.; Hedlund, J.; Creaser, D.; Sterte, J. *Catal. Today* **2001,** *67* (1-3), 109-119.

21. Bernal, M. P.; Coronas, J.; Menéndez, M.; Santamaría, J. *Microporous Mesoporous Mater.* **2003,** *60* (1-3), 99-110.

22. Hedlund, J.; Noack, M.; Kolsch, P.; Creaser, D.; Caro, J.; Sterte, J. *J. Membr. Sci.* **1999,** *159* (1-2), 263-273.

23. (a) Lai, Z. P.; Tsapatsis, M.; Nicolich, J. R., *Adv. Funct. Mater.* **2004,** *14* (7), 716-729; (b) Gump, C. J.; Tuan, V. A.; Noble, R. D.; Falconer, J. L., Aromatic permeation through crystalline molecular sieve membranes. *Ind. Eng. Chem. Res.* **2001,** *40* (2), 565-577.

24. Ciavarella, P.; Moueddeb, H.; Miachon, S.; Fiaty, K.; Dalmon, J. A. *Catal. Today* **2000,** *56* (1-3), 253-264.

25. Gardner, T. Q.; Martinek, J. G.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **2007,** *304* (1-2), 112-117.

26. Sato, K.; Sugimoto, K.; Nakane, T. *J. Membr. Sci.* **2008,** *319*, 244-255.

27. (a) Lai, Z. P.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003,** *300* (5618), 456-460; (b) Choi, J.; Ghosh, S.; Lai, Z. P.; Tsapatsis, M. *Angew. Chem. Int. Ed.* **2006,** *45* (7), 1154-1158.

28. Geus, E. R.; Denexter, M. J.; Vanbekkum, H. *J. Chem. Soc. Faraday T.* **1992,** *88* (20), 3101-3109.

29. Au, L. T. Y.; Mui, W. Y.; Lau, P. S.; Ariso, C. T.; Yeung, K. L., *Micropor. Mesopor. Mater.* **2001,** *47* (2-3), 203-216.

30. Yoo, W. C.; Stoeger, J. A.; Lee, P. S.; Tsapatsis, M.; Stein, A. *Angew Chem. Int. Ed.* **2010,** *49* (46), 8699-8703.

31. Yamazaki, S.; Tsutsumi, K. *Microporous Mater.* **1995,** *4* (2-3), 205-212.

32. Clet, G.; Jansen, J. C.; van Bekkum, H., S. *Chem. Mater.* **1999,** *11* (7), 1696-1702.

33. Huang, A. S.; Liang, F. Y.; Steinbach, F.; Caro, J. *J.Membr. Sci.* **2010,** *350* (1-2), 5-9.

34. Huang, A. S.; Caro, J. *Chem. Mater.* **2010,** *22* (15), 4353-4355.

35. Kumakiri, I.; Yamaguchi, T.; Nakao, S. *Ind. Eng. Chem. Res.* **1999,** *38* (12), 4682-4688.

36. Ha, K.; Lee, Y. J.; Lee, H. J.; Yoon, K. B. *Adv. Mater.* **2000,** *12* (15), 1114-+.

37. Aguado, S.; Gascon, J.; Farrusseng, D.; Jansen, J. C.; Kapteijn, F. *Microporous Mesoporous Mater.* **2011,** *146* (1-3), 69-75.

38. Chiu, W. V.; Park, I. S.; Shqau, K.; White, J. C.; Schillo, M. C.; Ho, W. S. W.; Dutta, P. K.; Verweij, H. *J. Membr. Sci.* **2011,** *377* (1–2), 182-190.

39. Nomura, M.; Yamaguchi, T.; Nakao, S. *Ind. Eng. Chem.y Res.* **1997,** *36* (10), 4217-4223.

40. Hong, Z.; Zhang, C.; Gu, X. H.; Jin, W. Q.; Xu, N. P. *J. Membr. Sci.* **2011,** *366* (1-2), 427-435.

41. (a) Ockwig, N. W.; Nenoff, T. M. *Chem. Rev.* **2007,** *107* (10), 4078-4110; (b) Tsapatsis, M. *Science* **2011,** *334* (6057), 767-768.

42. Louis, B.; Reuse, P.; Kiwi-Minsker, L.; Renken, A. *Appl. Catal. A-Gen.* **2001,** *210* (1-2), 103-109.

43. Mateo, E.; Lahoz, R.; De La Fuente, G. F.; Paniagua, A.; Coronas, J.; Santamaria, J. *Chem. Mater.* **2004,** *16* (24), 4847-4850.

44. Camblor, M. A.; Corell, C.; Corma, A.; DiazCabanas, M. J.; Nicolopoulos, S.; GonzalezCalbet, J. M.; ValletRegi, M. *Chem. Mater.* **1996,** *8* (10), 2415.

45. Choi, M.; Na, K.; Kim, J.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. *Nature* **2009,** *461* (7261), 246-U120.

46. Varoon, K.; Zhang, X. Y.; Elyassi, B.; Brewer, D. D.; Gettel, M.; Kumar, S.; Lee, J. A.; Maheshwari, S.; Mittal, A.; Sung, C. Y.; Cococcioni, M.; Francis, L. F.; McCormick, A. V.; Mkhoyan, K. A.; Tsapatsis, M. *Science* **2011,** *333* (6052), 72-75.

47. (a) Jia, M. D.; Peinemann, K. V.; Behling, R. D. *J. Membr. Sci.* **1993,** *82* (1-2), 15-26; (b) Jia, M. D.; Chen, B. S.; Noble, R. D.; Falconer, J. L. *J. Membr. Sci.* **1994,** *90* (1-2), 1-10; (c) Funke, H. H.; Kovalchick, M. G.; Falconer, J. L.; Noble, R. D., *Ind. Eng. Chem. Res.* **1996,** *35* (5), 1575-1582; (d) Algieri, C.; Bernardo, P.; Golemme, G.; Barbieri, G.; Drioli, E., *J. Membr. Sci.* **2003,** *222* (1-2), 181-190; (e) Jareman, F.; Hedlund, J. *Microporous Mesoporous Mater.* **2005,** *83* (1-3), 326-332.

48. Rezai, S. A. S.; Lindmark, J.; Andersson, C.; Jareman, F.; Möller, K.; Hedlund, J. *Microporous Mesoporous Mater.* **2008,** *108* (1-3), 136-142.

49. Ravishankar, R.; Kirschhock, C. E. A.; Knops-Gerrits, P. P.; Feijen, E. J. P.; Grobet, P. J.; Vanoppen, P.; De Schryver, F. C.; Miehe, G.; Fuess, H.; Schoeman, B. J.; Jacobs, P. A.; Martens, J. A. *J. Phys. Chem. B* **1999,** *103* (24), 4960-4964.

50. Corma, A.; Diaz-Cabanas, M. J. *Microporous Mesoporous Mater.* **2006,** *89* (1-3), 39-46.

51. Tiscornia, I.; Valencia, S.; Corma, A.; Téllez, C.; Coronas, J.; Santamaría, J. *Microporous Mesoporous Mater.* **2008,** *110* (2-3), 303-309.

52. (a) Heng, S.; Lau, P. P. S.; Yeung, K. L.; Djafer, M.; Schrotter, J. C. *J. Membr. Sci.* **2004,** *243* (1-2), 69-78; (b) Kuhn, J.; Gascon, J.; Gross, J.; Kapteijn, F. *Microporous Mesoporous Mater.* **2009,** *120* (1-2), 12-18.

53. (a)

a C. W. Jones, K. Tsuji, T. Takewaki, L. W. Beck, M. E. Davis, *Microporous and Mesoporous Materials* **2001**, *48*, 57-64.

b B. Gautier, M. Smaihi, *New Journal of Chemistry* **2004**, *28*, 457-461.

54. c H. Lee, S. I. Zones, M. E. Davis, *J. Phys. Chem. B* **2005**, *109*, 2187-2191.

55. Maloncy, M. L.; Maschmeyer, T.; Jansen, J. C. *Chem. Eng. J.* **2005,** *106* (3), 187-195.

56. Hao, J.; Rice, P. A.; Stern, S. A. *J. Membr. Sci.* **2008,** *320* (1-2), 108-122.

57. Caro, J. *Adsorption* **2005,** *11*, 215-227.

58. Morigami, Y.; Kondo, M.; Abe, J.; Kita, H.; Okamoto, K. *Sep. Purif. Technol.* **2001,** *25* (1-3), 251-260.

59. Yu, C.; Zhong, C.; Liu, Y.; Gu, X.; Yang, G.; Xing, W.; Xu, N. *Chem. Eng. Res. Des.* **2011,** *doi: 10.1016/j.cherd.2011.12.003*.

60. Yu, C.; Liu, Y.; Chen, G.; Gu, X.; Xing, W. *Chin.J. Chem. Eng.* **2011,** *19* (6), 904-910.

61. Wee, S.-L.; Tye, C.-T.; Bhatia, S. *Sep. Purif. Technol.* **2008,** *63*, 500-516.

62. Gallego-Lizón, T.; Edwards, E.; Lobiundo, G.; Santos, L. F. d. *J. Membr. Sci.* **2002,** *197*, 309-319.

63. Sato, K.; Sugimoto, K.; Kyotani, T.; Shimotsuma, N. 2010 AIChE Annual Meeting, 10AlChE, Salt Lake City, UT, 2010.

64. *Kühni AG, Unit Operation Process Equipment (http://www.kuhni.ch/pages/uope.html).*

65. Maus, E. Sulzer Chemtech: 2012.
66. Aizawa, M.; Fujita, S.; Takaki, Y.; Yano, K.; Shimizu, T.; Asari, T.; Yano, J.; T, Y.; Sawamura, K.; Shinoya, K. 2010 AIChE Annual Meeting, 10AIChE, Salt Lake City, UT, 2010.
67. Sato, K.; Aoki, K.; Sugimoto, K.; Izumi, K.; Inoue, S.; Saito, J.; Ikeda, S.; Nakane, T. *Microporous Mesoporous Mater.* **2008,** *115*, 184-188.
68. Hoof, V. V.; Dotremont, C.; Buekenhoudt, A. *Sep. Purif. Technol.* **2006,** *48*, 304-309.
69. (a) Liu, Y.; Yang, Z.; Yu, C.; Gu, X.; Xu, N. *Microporous Mesoporous Mater.* **2011,** *143*, 348-356; (b) Yang, Z.; Liu, Y.; Yu, C.; Gu, X. *J. Membr. Sci.* **2012,** *392-393*, 18-28.
70. Ge, Q.; Shao, J.; Wang, Z.; Yan, Y. *Microporous Mesoporous Mater.* **2012,** *151*, 303-310.

71.
d Lai, L.; Shao, J.; Ge, Q.; Wang, Z.; Yan, Y., The preparation of zeolite NaA membranes on the inner surface of hollow fiber supports. Journal of Membrane Science 2012, 409-410, 318-328.

72. .
e Ge, Q.; Wang, Z.; Yan, Y., High-performance zeolite NaA membranes on polymer-zeolite composite hollow fiber supports. J. Am. Chem. Soc. 2009, 131 (47), 17056-17057.

73. .
f Jang, K.-S.; Kim, H.-J.; Johnson, J. R.; Kim, W.-g.; Koros, W. J., Chem. Mater. 2012, 23, 3025-3028.

74. Meindserma, G. W.; Haan, A. B. *Desalination* **2002,** *149*, 29-34.
75. Matsukata, M. *Inorganic, Polymeric and Composite Membranes: Structure, Function and Other Correlations*, 2011; p 175.
76. Kuhn, J.; Yajima, K.; Tomita, T.; Gross, J.; Kapteijn, F. *J. Membr. Sci.* **2008,** *321* (2), 344-349.
77. Coronas, J.; Santamaria, J. *Top.Catal.* **2004,** *29* (1-2), 29-44.
78. van den Bergh, J.; Gucuyener, C.; Gascon, J.; Kapteijn, F. *Chem. Eng. J.* **2011,** *166* (1), 368-377.
79. (a) van de Graaf, J. M.; Zwiep, M.; Kapteijn, F.; Moulijn, J. A. *Appl. Catal.A-Gen.* **1999,** *178* (2), 225-241; (b) Dittmeyer, R.; Svajda, K.; Reif, M. *Top.Catal.* **2004,** *29* (1-2), 3-27.
80. Li, L.; Liu, N.; McPherson, B.; Lee, R. *Desalination* **2008,** *228*, 217-225.
81. Khajavi, S.; Jansen, J. C.; Kapteijn, F. *J. Membr. Sci.* **2010,** *356* (1‚Äì2), 1-6.
82. Lin, C. C. H.; Dambrowitz, K. A.; Kuznicki, S. M., *Can. J. Chem. Eng.* **2012,** *90* (2), 207-216.
83. Tsapatsis, M. *Science* **2011,** *334*, 767-768.
84. Shi, Y.; Li, X.; Hu, J.; Lu, J.; Ma, Y.; Zhang, Y.; Tang, Y. *J. Mater. Chem.* **2011,** *21*, 16223-16230.
85. Ruthven, D. M. *Chem-Ing-Tech.* **2011,** *83* (1-2), 44-52.
86. Arruebo, M.; Coronas, J.; Menendez, M.; Santamaria, J. *Sep. Purif. Technol.* **2001,** *25* (1-3), 275-286.

87. (a) Himeno, S.; Tomita, T.; Suzuki, K.; Nakayama, K.; Yajima, K.; Yoshida, S. *Ind.Eng. Chem. Res.* **2007,** *46* (21), 6989-6997; (b) van den Bergh, J.; Zhu, W.; Gascon, J.; Moulijn, J. A.; Kapteijn, F. *J. Membr. Sci.* **2008,** *316* (1-2), 35-45; (c) van den Bergh, J.; Tihaya, A.; Kapteijn, F. *Microporous Mesoporous Mater.* **2010,** *132* (1-2), 137-147.

88. Li, S.; Carreon, M. A.; Zhang, Y.; Funke, H. H.; Noble, R. D.; Falconer, J. L. *J. Membr. Sci.* **2011,** *352* (1-2), 7-13.

89. Maple, M. J.; Williams, C. D. *Microporous Mesoporous Mater.* **2008,** *111* (1-3), 627-631.

90. (a) Lew, C. M.; Yan, Y. S., *From Zeolites to Porous Mof Materials: The 40th Anniversary of International Zeolite Conference, Proceedings of the 15th International Zeolite Conference*, 2007; Vol. 170, pp 1502-1507; (b) Beving, D. E.; McDonnell, A. M. P.; Yang, W. S.; Yan, Y. S. *J. Electrochem. Soc.* **2006,** *153* (8), B325-B329; (c) Hunt, H. K.; Lew, C. M.; Sun, M. W.; Yan, Y. S.; Davis, M. E. *Microporous Mesoporous Mater.* **2010,** *130* (1-3), 49-55.

91. Cai, R.; Yan, Y. S. *Corrosion* **2008,** *64* (3), 271-278.

92. Liu, J.; Aguilar, G.; Munoz, R.; Yan, Y. S. *AIChE J.* **2008,** *54* (3), 779-790.

93. (a) O'Neill, C.; Beving, D. E.; Chen, W.; Yan, Y. S. *AIChE J.* **2006,** *52* (3), 1157-1161; (b) McDonnell, A. M. P.; Beving, D.; Wang, A. J.; Chen, W.; Yan, Y. S. *Adv. Funct. Mater.* **2005,** *15* (2), 336-340; (c) Beving, D. E.; O'Neill, C. R.; Yan, Y. S. *Microporous Mesoporous Mater.* **2008,** *108* (1-3), 77-85.

94. Bedi, R. S.; Beving, D. E.; Zanello, L. P.; Yan, Y. S. *Acta Biomater.* **2009,** *5* (8), 3265-3271.

95. Johnson, M. C.; Lew, C. M.; Yan, Y. S.; Wang, J. L. *Scripta Mater.* **2008,** *58* (1), 41-44.

96. Chen, G.; Beving, D. E.; Bedi, R. S.; Yan, Y. S.; Walker, S. L. *Langmuir* **2009,** *25* (3), 1620-1626.

97. Cai, R.; Sun, M. W.; Chen, Z. W.; Munoz, R.; O'Neill, C.; Beving, D. E.; Yan, Y. S. *Angew. Chem. Inter. Ed.* **2008,** *47* (3), 525-528.

98. Bourrelly, S.; Moulin, B.; Rivera, A.; Maurin, G.; Devautour-Vino, S.; Serre, C.; Devic, T.; Horcajada, P.; Vimont, A.; Clet, G.; Daturi, M.; Lavalley, J. C.; Loera-Serna, S.; Denoyel, R.; Llewellyn, P. L.; Ferey, G. *J. Am. Chem. Soc.*.

99. Deya, C.; Romagnoli, R.; del Amo, B. *J. Coat. Technol. Res.* **2007,** *4* (2), 167-175.

100. Gademann, K. *Chimia* **2007,** *61* (6), 373-377.

101. (a) Ross, J. *Smithsonian* **1994,** *24* (11), 40-&; (b) Coetser, S. E.; Cloete, T. E., *Crit. Rev. Microbiol.* **2005,** *31* (4), 213-232; (c) Goto, Y. *Water Sci. Technol.* **2002,** *46* (11-12), 45-50.

102. Townsin, R. L. *Biofouling* **2003,** *19*, 9-15.

103. (a) Lalueza, P.; Monzon, M.; Arruebo, M.; Santamaria, J. *Chem. Comm.* **2011,** *47* (2), 680-682; (b) Schulze-Mokuch, D.; Bowman, R. S.; Pillai, S. D.; Guan, H. D. *Ground Water Monit. R.* **2003,** *23* (4), 68-74; (c) Lalueza, P.; Monzon, M.; Arruebo, M.; Santamaria, J. *Mater. Res. Bull.* **2011,** *46* (11), 2070-2076.

104. Edwards-Jones, V. *Lett.Appl. Microbiol.* **2009,** *49* (2), 147-152.

105. Inoue, Y.; Hoshino, M.; Takahashi, H.; Noguchi, T.; Murata, T.; Kanzaki, Y.; Hamashima, H.; Sasatsu, M. *J. Inorg. Biochem.* **2002,** *92* (1), 37-42.

106. (a) Monprasit, P.; Ritvirulh, C.; Sooknoi, T.; Rukchonlatee, S.; Fuongfuchat, A.; Sirikittikul, D. *Polym. Eng.Sci.* **2011,** *51* (7), 1264-1272; (b) Quintavalla, S.; Vicini, L. *Meat Sci.* **2002,** *62* (3), 373-380.

107. Monteiro, D. R.; Gorup, L. F.; Takamiya, A. S.; Ruvollo, A. C.; Camargo, E. R.; Barbosa, D. B. *Int. J. Antimicrob. Agents* **2009,** *34* (2), 103-110.

108. Abe, Y.; Ishii, M.; Takeuchi, M.; Ueshige, M.; Tanaka, S.; Akagawa, Y. *J. Oral Rehabil.* **2004,** *31* (6), 568-573.
109. Nakane, T.; Gomyo, H.; Sasak, I.; Kimoto, Y.; Hanzawa, N.; Teshima, Y.; Namba, T., *Int. J. Cosmet. Sci.* **2006,** *28*, 10.
110. Zampino, D.; Ferreri, T.; Puglisi, C.; Mancuso, M.; Zaccone, R.; Scaffaro, R.; Bennardo, D. *J. Mater. Sci.* **2011,** *46* (20), 6734-6743.
111. Chen, C. H.; Li, S. Y.; Chiang, A. S. T.; Wu, A. T.; Sun, Y. S. *Sol. Energy Mater. Sol. Cells* **2011,** *95* (7), 1694-1700.
112. (a) Li, Z. J.; Johnson, M. C.; Sun, M. W.; Ryan, E. T.; Earl, D. J.; Maichen, W.; Martin, J. I.; Li, S.; Lew, C. M.; Wang, J.; Deem, M. W.; Davis, M. E.; Yan, Y. S. *Angew. Chem. Int. Ed.* **2006,** *45* (38), 6329-6332; (b) Hunt, H. K.; Lew, C. M.; Sun, M. W.; Yan, Y. S.; Davis, M. E. *Microporous Mesoporous Mater.* **2010,** *128* (1-3), 12-18.
113. Wang, Z. B.; Wang, H. T.; Mitra, A.; Huang, L. M.; Yan, Y. S. *Adv. Mater.* **2001,** *13* (10), 746-749.
114. Maex, K.; Baklanov, M. R.; Shamiryan, D.; Iacopi, F.; Brongersma, S. H.; Yanovitskaya, Z. S., Low dielectric constant materials for microelectronics. *J. Appl. Phys.* **2003,** *93* (11), 8793-8841.
115. Wang, Z. B.; Mitra, A. P.; Wang, H. T.; Huang, L. M.; Yan, Y. S. *Adv. Mater.* **2001,** *13* (19), 1463.
116. Moden, B.; Donohue, J. M.; Cormier, W. E.; Li, H. X. *Top. Catal.* **2010,** *53* (19-20), 1367-1373.
117. Nishiyama, N.; Ichioka, K.; Park, D. H.; Egashira, Y.; Ueyama, K.; Gora, L.; Zhu, W. D.; Kapteijn, F.; Moulijn, J. A. *Ind. Eng.Chem.Res.* **2004,** *43* (5), 1211-1215.
118. Nishiyama, N.; Ichioka, K.; Miyamoto, M.; Egashira, Y.; Ueyama, K.; Gora, L.; Zhu, W. D.; Kapteijn, F.; Moulijn, J. A. *Microporous Mesoporous Mater.* **2005,** *83* (1-3), 244-250.
119. (a) Li, X. G.; Zhang, Y.; Meng, M.; Yang, G. H.; San, X. G.; Takahashi, M.; Tsubaki, N. *J. Membr. Sci.* **2010,** *347* (1-2), 220-227; (b) Li, X. G.; Zhang, Y.; Meng, F. Z.; San, X. G.; Yang, G. H.; Meng, M.; Takahashi, M.; Tsubaki, N. *Top. Catal.* **2010,** *53* (7-10), 608-614.
120. Ren, N.; Yang, Y. H.; Shen, J.; Zhang, Y. H.; Xu, H. L.; Gao, Z.; Tang, Y. *J. Catal.* **2007,** *251* (1), 182-188.
116. Li, X. G.; He, J. J.; Meng, M.; Yoneyama, Y.; Tsubaki, N. *J. Catal.* **2009,** *265* (1), 26-34.
121. (a) Miyamoto, M.; Kamei, T.; Nishiyama, N.; Egashira, Y.; Ueyama, K. *Adv. Mater.* **2005,** *17* (16), 1985; (b) Van Vu, D.; Miyamoto, M.; Nishiyama, N.; Egashira, Y.; Ueyama, K. *J. Catal.* **2006,** *243* (2), 389-394.

122.
g S. Nair, L. A. Villaescusa, M. A. Camblor, M. Tsapatsis, *Chemical Communications* **1999**, 921-922.
----

118. Bouizi, Y.; Diaz, I.; Rouleau, L.; Valtchev, V. P. *Adv. Funct. Mater.* **2005,** *15* (12), 1955-1960.
119. Bouizi, Y.; Rouleau, L.; Valtchev, V. P. *Microporous Mesoporous Mater.* **2006,** *91* (1-3), 70-77.
120. Bouizi, Y.; Rouleau, L.; Valtchev, V. P. *Chem. Mater.* **2006,** *18* (20), 4959-4966.

121. Kinoshita, Y.; Matsubara, I.; Higuchi, T.; Saito, Y. *Chem. Soc. Jpn.* **1959,** *32* (11), 1221-1226.

122. (a) Berlin, A. A.; Matveeva, N. G. *Russ. Chem. Rev.* **1960,** *29* (3), 119-128; (b) Tomic, E. A. *J. Appl. Polym. Sci.* **1965,** *9* (11), 3745; (c) Block, B. P.; Roth, E. S.; Schaumann, C. W.; Simkin, J.; Rose, S. H. *J. Am. Chem. Soc.* **1962,** *84* (16), 3200; (d) Knobloch, F. W.; Rauscher, W. H. *J. Polym. Sci.* **1959,** *38* (133), 261-262; (e) Kubo, M.; Kishita, M.; Kuroda, Y. *J. Polym. Sci.* **1960,** *48* (150), 467-471.

123. (a) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1995,** *117* (19), 5385-5386; (b) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990,** *112* (4), 1546-1554.

124. (a) Kitagawa, S.; Matsuyama, S.; Munakata, M.; Emori, T. *J. Chem. Soc. Dalton Trans.* **1991,** (11), 2869-2874; (b) Kitagawa, S.; Kawata, S.; Nozaka, Y.; Munakata, M. *J. Chem. Soc. Dalton Trans.* **1993,** (9), 1399-1404.

125. Yaghi, O. M.; Li, H. L. *J. Am. Chem. Soc.* **1995,** *117* (41), 10401-10402.

126. Riou, D.; Ferey, G. *J. Mater. Chem.* **1998,** *8* (12), 2733-2735.

127. Low, J. J.; Benin, A. I.; Jakubczak, P.; Abrahamian, J. F.; Faheem, S. A.; Willis, R. R. *J. Am. Chem. Soc.* **2009,** *131* (43), 15834-15842.

128. (a) Couck, S.; Denayer, J. F. M.; Baron, G. V.; Remy, T.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2009,** *131* (18), 6326-6327; (b) Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; van Klink, G. P. M.; Kapteijn, F. *J. Catal.* **2009,** *261* (1), 75-87.

129. Stock, N.; Biswas, S. *Chem. Rev.* **2011**, *doi: 10.1021/cr200304e.*

130. (a) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2011**, doi: 10.1021/cr200190s; (b) van den Bergh, J.; Gücüyener, C.; Pidko, E. A.; Hensen, E. J. M.; Gascon, J.; Kapteijn, F. *Chem. Eur. J.* **2011,** *17* (32), 8832-8840; (c) Stavitski, E.; Pidko, E. A.; Couck, S.; Remy, T.; Hensen, E. J. M.; Weckhuysen, B. M.; Denayer, J.; Gascon, J.; Kapteijn, F. *Langmuir* **2011,** *27* (7), 3970-3976.

131. Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009,** *38* (5), 1294-1314.

132. (a) Corma, A.; Garcia, H.; Xamena, F. X. L. *Chem. Rev.* **2010,** *110* (8), 4606-4655; (b) Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Sai Sankar Gupta, K. B.; Stavitski, E.; van Bekkum, H.; Gascon, J.; Kapteijn, F. *J. Catal.* **2011,** *281* (1), 177-187; (c) Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Lafont, U.; Gascon, J.; Kapteijn, F. *J. Catal.* **2010,** *269* (1), 229-241.

133. Juan-Alcaniz, J.; Gascon, J.; Kapteijn, F. *J. Mater. Chem.* **2012**, *22*, 10102-10118.

134. Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J. S.; Hwang, Y. K.; Marsaud, V.; Bories, P. N.; Cynober, L.; Gil, S.; Ferey, G.; Couvreur, P.; Gref, R. *Nat. Mater.* **2010,** *9* (2), 172-178.

135. (a) Arnold, M.; Kortunov, P.; Jones, D. J.; Nedellec, Y.; Karger, J.; Caro, J., Oriented crystallisation on supports and anisotropic mass transport of the metal-organic framework manganese formate. *Eur. J. Inorg. Chem.* **2007,** *1*, 60-64; (b) Gascon, J.; Aguado, S.; Kapteijn, F. *Microporous Mesoporous Mater.* **2008,** *113* (1-3), 132-138.

136. (a) Hermes, S.; Schroder, F.; Chelmowski, R.; Woll, C.; Fischer, R. A. *J. Am. Chem. Soc.* **2005,** *127* (40), 13744-13745; (b) Hermes, S.; Zacher, D.; Baunemann, A.; Woll, C.; Fischer, R. A. *Chem. Mat.* **2007,** *19* (9), 2168-2173.

137. Ranjan, R.; Tsapatsis, M. *Chem. Mater.* **2009**.

138. (a) Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. *J. Am. Chem. Soc.* **2009,** *131* (44), 16000-16001; (b) Li, Y.-S.; Liang, F.-Y.; Bux, H.; Feldhoff, A.; Yang, W.-S.; Caro, J. *Angew. Chem. Int. Ed.* **2010,** *49* (3), 548-551.

139. Guo, H.; Zhu, G.; Hewitt, I. J.; Qiu, S. *J. Am. Chem. Soc.* **2009,** *131* (5), 1646-1647.

140. Ameloot, R.; Gobechiya, E.; Uji-i, H.; Martens, J. A.; Hofkens, J.; Alaerts, L.; Sels, B. F.; Vos, D. E. D. *Adv. Mater.* **2010,** *22* (24), 2685-2688.

141. Shah, M.; McCarthy, M. C.; Sachdeva, S.; Lee, A. K.; Jeong, H. K. *Ind. Eng. Chem. Res.* **2012,** *51* (5), 2179-2199.

142. Huang, A.; Bux, H.; Steinbach, F.; Caro, J. *Angew. Chem. Int. Ed.* **2010,** *49* (29), 4958-4961.

143. Hu, Y.; Dong, X.; Nan, J.; Jin, W.; Ren, X.; Xu, N.; Lee, Y. M. *Chem. Commun.* **2011,** *47* (2), 737-739.

144. McCarthy, M. C.; Varela-Guerrero, V.; Barnett, G. V.; Jeong, H.-K. *Langmuir* **2010,** *26* (18), 14636-14641.

145. Liu, Y.; Ng, Z.; Khan, E. A.; Jeong, H.-K.; Ching, C.-b.; Lai, Z. *Microporous Mesoporous Mater.* **2009,** *118* (1-3), 296-301.

146. (a) Bux, H.; Chmelik, C.; van Baten, J. M.; Krishna, R.; Caro, J. *Adv. Mater.* **2010,** *22* (42), 4741; (b) Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. *J. Membr. Sci.* **2011,** *369* (1-2), 284-289.

147. (a) Li, Y.; Liang, F.; Bux, H.; Yang, W.; Caro, J. *J. Membr. Sci.* **2010,** *354* (1-2), 48-54; (b) Li, Y.-S.; Bux, H.; Feldhoff, A.; Li, G.-L.; Yang, W.-S.; Caro, J. *Adv. Mater.* **2010,** *22* (30), 3322.

148. Guerrero, V. V.; Yoo, Y.; McCarthy, M. C.; Jeong, H.-K. *J. Mater. Chem.* **2010,** *20* (19), 3938-3943.

149. Huang, A.; Dou, W.; Caro, J. *J. Am. Chem. Soc.* **2010,** *132* (44), 15562-15564.

150. (a) Liu, Y.; Hu, E.; Khan, E. A.; Lai, Z. *J. Membr. Sci.* **2010,** *353* (1-2), 36-40; (b) Liu, Y.; Zeng, G.; Pan, Y.; Lai, Z. *J. Membr. Sci.* **2011,** *379* (1-2), 46-51.

151. Venna, S. R.; Carreon, M. A. *J. Am. Chem. Soc.* **2010,** *132* (1), 76.

152. Aguado, S.; Nicolas, C.-H.; Moizan-Basle, V.; Nieto, C.; Amrouche, H.; Bats, N.; Audebrand, N.; Farrusseng, D. *New J. Chem.* **2011,** *35* (1), 41-44.

153. Bux, H.; Feldhoff, A.; Cravillon, J.; Wiebcke, M.; Li, Y.-S.; Caro, J. *Chem. Mater.* **2011,** *23* (8), 2262-2269.

154. Huang, A.; Caro, J. *Angew. Chem. Int. Ed.* **2011,** *50* (21), 4979-4982.

155. Nan, J.; Dong, X.; Wang, W.; Jin, W.; Xu, N. *Langmuir* **2011,** *27* (8), 4309-4312.

156. Yoo, Y.; Varela-Guerrero, V.; Jeong, H.-K. *Langmuir* **2011,** *27* (6), 2652-2657.

157. Zhao, Z.; Ma, X.; Li, Z.; Lin, Y. S. *J. Membr. Sci.* **2011,** *382* (1–2), 82-90.

158. Zou, X.; Zhang, F.; Thomas, S.; Zhu, G.; Valtchev, V.; Mintova, S. *Chem. Eur. J.* **2011,** *17* (43), 12076-83.

159. Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008,** *319* (5865), 939-943.

160. Park, K. S.; Ni, Z.; P., A.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Nat. Acad. Sci.* **2006,** *103* (27), 10186-10191.

161. Bux, H.; Liang, F. Y.; Li, Y. S.; Cravillon, J.; Wiebcke, M.; Caro, J. *J. Am. Chem. Soc.* **2009,** *131* (44), 16000.

162. Bakker, W. J. W.; Kapteijn, F.; Poppe, J.; Moulijn, J. A. *J. Membr. Sci.* **1996,** *117* (1-2), 57-78.

163. Gucuyener, C.; van den Bergh, J.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2010,** *132* (50), 17704-17706.

164. Aguado, S.; Bergeret, G.; Titus, M. P.; Moizan, V.; Nieto-Draghi, C.; Bats, N.; Farrusseng, D. *New J. Chem.* **2011**.

165. Luebbers, M. T.; Wu, T.; Shen, L.; Masel, R. I. *Langmuir* **2010,** *26* (19), 15625-15633.

166. (a) Deckman, H. W.; Kortunov, P.; Ni, Z.; Paur, C. S.; Reyes, S. C.; Zengel, J.; Santiesteban, J. G. EP 2 249 947, 2010; (b) Deckman, H. W.; Kortunov, P.; Ni, Z.; Paur, C. S.; Zengel, J.; Reyes, S. C.; Santiesteban, J. G. EP 2 254 683, 2010.

167. Li, Y.-S.; Liang, F.-Y.; Bux, H.; Feldhoff, A.; Yang, W.-S.; Caro, J. *Angew. Chem. Int. Ed.* **2010,** *49* (3), 548-551.

168. Li, M. Y.; Dinca, M. *J. Am. Chem. Soc.* **2011,** *133* (33), 12926-12929.

169. Basu, S.; Maes, M.; Cano-Odena, A.; Alaerts, L.; De Vos, D. E.; Vankelecom, I. F. J. *J. Membr. Sci.* **2009,** *344* (1-2), 190-198.

170. Vermoortele, F.; Maes, M.; Moghadam, P. Z.; Lennox, M. J.; Ragon, F.; Boulhout, M.; Biswas, S.; Laurier, K. G. M.; Beurroies, I.; Denoyel, R.; Roeffaers, M.; Stock, N.; Duren, T.; Serre, C.; De Vos, D. E. *J. Am. Chem. Soc.* **2011,** *133* (46), 18526-18529.

171. Zhao, Z. X.; Ma, X. L.; Li, Z.; Lin, Y. S. *J. Membr. Sci.* **2011,** *382* (1-2), 82-90.

172. Loeb, S.; Sourirajan, S. *Adv. Chem. Ser.* **1962,** *38*, 117-132.

173. (a) Mahajan, R.; Burns, R.; Schaeffer, M.; Koros, W. J. *J. Appl. Polym. Sci.* **2002,** *86* (4), 881-890; (b) Chung, T.-S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S. *Prog. Polym. Sci.* **2007,** *32* (4), 483-507.

174. Koros, W. J.; Coleman, M. R.; Walker, D. R. B. *Annu. Rev. Mater. Sci.* **1992,** *22*, 47-89.

175. Baker, R. W. *Ind. Eng. Chem. Res.* **2002,** *41* (6), 1393-1411.

176. Spillman, R. W. *Chem. Eng. Prog.* **1989,** *85* (1), 41-62.

177. Aroon, M. A.; Ismail, A. F.; Matsuura, T.; Montazer-Rahmati, M. M. *Sep. Purif. Technol.* **2010,** *75* (3), 229-242.

178. (a) Robeson, L. M. *J. Membr. Sci.* **1991,** *62* (2), 165-185; (b) Robeson, L. M. *J. Membr. Sci.* **2008,** *320* (1-2), 390-400.

179. Moore, T. T. PhD thesis. The University of Texas, Austin, TX, 2004.

180. Vu, D. Q.; Koros, W. J.; Miller, S. J. *Membr. Sci.* **2003,** *211* (2), 335-348.

181. Erucar, I.; Keskin, S. *Ind. Eng. Chem. Res.* **2011,** *50* (22), 12606-12616.

182. (a) Chung, T. S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S. *Prog. Polym. Sci.* **2007,** *32* (4), 483-507; (b) Goh, P. S.; Ismail, A. F.; Sanip, S. M.; Ng, B. C.; Aziz, M. *Sep. Purif. Technol.* **2011,** *81* (3), 243-264; (c) Cong, H. L.; Radosz, M.; Towler, B. F.; Shen, Y. Q. *Sep.Purif. Technol.* **2007,** *55* (3), 281-291; (d) Bernardo, P.; Drioli, E.; Golemme, G. *Ind. Eng. Chem. Res.* **2009,** *48* (10), 4638-4663.

183. Zimmerman, C. M.; Singh, A.; Koros, W. J. *J. Membr. Sci.* **1997,** *137* (1-2), 145-154.

184. (a) Mahajan, R.; Koros, W. J. *Ind. Eng. Chem. Res.* **2000,** *39* (8), 2692-2696; (b) Reid, B. D.; Ruiz-Trevino, A.; Musselman, I. H.; Balkus, K. J.; Ferraris, J. P. *Chem. Mater.* **2001,** *13* (7), 2366-2373.

185. (a) Mahajan, R.; Burns, R.; Schaeffer, M.; Koros, W. J. *J. Appl. Polym. Sci.* **2002,** *86* (4), 881-890; (b) Mahajan, R.; Vu, D. Q.; Koros, W. J. *J. Chin. Inst. Chem.l Eng.* **2002,** *33* (1), 77-86; (c) Zimmerman, C. M.; Mahajan, R.; Koros, W. J. *Abstr. Paper. Am. Chem. Society* **1997,** *214*, 270.

186. (a) Gur, T. M. *J. Membr. Sci.* **1994,** *93* (3), 283-289; (b) Husain, S.; Koros, W. J. *J. Membr. Sci.* **2007,** *288* (1-2), 195-207; (c) Zornoza, B.; Tellez, C.; Coronas, J. *J. Membr. Sci.* **2011,** *368* (1-2), 100-109.

187. (a) Galve, A.; Sieffert, D.; Vispe, E.; Tellez, C.; Coronas, J.; Staudt, C. particles. *J. Membr. Sci.* **2011,** *370* (1-2), 131-140; (b) Rubio, C.; Casado, C.; Gorgojo, P.; Etayo, F.; Uriel, S.; Téllez, C.; Coronas, J. *Eur. J. Inorg. Chem.* **2010**, 159-163.

188. Zornoza, B.; Irusta, S.; Tellez, C.; Coronas, J. *Langmuir* **2009,** *25* (10), 5903-5909.

189. (a) Duval, J. M.; Folkers, B.; Mulder, M. H. V.; Desgrandchamps, G.; Smolders, C. A. *J. Membr. Sci.* **1993,** *80* (1-3), 189-198; (b) Vu, D. Q.; Koros, W. J.; Miller, S. J. *J. Membr. Sci.* **2003,** *211* (2), 311-334.
190. Choi, J. H.; Jegal, J.; Kim, W. N. *J. Membr. Sci.* **2006,** *284* (1-2), 406-415.
191. Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. J. *Science* **2002,** *296* (5567), 519-522.
192. Yehia, H.; Pisklak, T. J.; Ferraris, J. P.; Balkus, K. J.; Musselman, I. H. *Abstr. Paper Am. Chem. Soc.* **2004,** *227,* U351-U351.
193. (a) Zornoza, B.; Martinez-Joaristi, A.; Serra-Crespo, P.; Tellez, C.; Coronas, J.; Gascon, J.; Kapteijn, F. *Chem. Commun.* **2011,** *47* (33), 9522-9524; (b) Bae, T.-H.; Lee, J. S.; Qiu, W.; Koros, W. J.; Jones, C. W.; Nair, S. *Angew. Chem. Int. Ed.* **2010,** *49* (51), 9863-9866.
194. Zornoza, B.; Tellez, C.; Coronas, J.; Gascon, J.; Kapteijn, F. *Microporous Mesoporous Mater.* **2012,** *doi:10.1016/j.micromeso.2012.03.01.*
195. (a) Moore, T. T.; Mahajan, R.; Vu, D. Q.; Koros, W. J. *AIChE J.* **2004,** *50* (2), 311-321; (b) Pal, R. *J. Colloid Interface Sci.* **2008,** *317* (1), 191-198.
196. Ho, M. T.; Allinson, G.; Wiley, D. E. *Desalination* **2006,** *192* (1-3), 288-295.
197. Caro, J.; Noack, M. *Stud. Surf. Sci. Catal.* **2004,** *154,* 80-93.
198. Kesting, R. E.; Fritzsche, A. K., *Polymeric Gas Separation Membranes*. John Wiley and Sons, Inc. ed.; New York, 1993.
199. Ekiner, O. M.; Kulkarni, S. S. U.S. Patent 6663805, 2004.
200. Wang, D. L.; Teo, W. K.; Li, K. *J. Membr. Sci.* **2002,** *204* (1-2), 247-256.
201. Koros, W. J.; Fleming, G. K. *J. Membr. Sci.* **1993,** *83* (1), 1-80.

TOC graphic

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