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Joaquín Coronas[a]; Jesús Santamaría[a]
[a] Department of Chemical and Environmental Engineering, University of Zaragoza Faculty of Science, Zaragoza, Spain

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SEPARATIONS USING ZEOLITE MEMBRANES

Joaquín Coronas and Jesús Santamaría*
Department of Chemical and Environmental Engineering
University of Zaragoza
Faculty of Science. 50009 Zaragoza. Spain

ABSTRACT

This overview describes some of the main features of the use of zeolite membranes for separation applications. Four different types of separations are considered: separation of non-adsorbing compounds, of organic molecules, of permanent gases from vapors, and of water (or polar molecules) from organic (or non-polar) species. Several factors, such as the limiting pore size and pore size distribution, surface diffusion, capillary condensation, shape selectivity and molecular sieving, contribute to the separations observed. However, in most of the high selectivity separations reported in the literature, preferential adsorption is the dominant characteristic. In this case, the adsorption of one component in the mixture is stronger and this blocks or hinders the passage of the other components through the membrane pores.

Keywords: zeolite membrane, separation

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*corresponding author
Phone: +34 976 761153
Fax: +34 976 762142
Email: iqcatal@posta.unizar.es

www.dekker.com

INTRODUCTION

The term *zeolites*, designates a variety of crystalline, hydrated aluminosilicates with a framework structure, which have been used for a long time as detergent builders (in view of their ion-exchange properties), adsorbents and catalysts. However, since the early 1990s, an intensive research effort has been under way, aimed to the synthesis of zeolite membranes and to the development of separation applications. The driving forces for this activity have been varied:

- Because of their membrane character, zeolite membranes hold the potential of separations at a relatively low energy cost, a highly popular attribute at a time when energy conservation is firmly established as one of the top priorities for the industry as a whole. Also, because of their inorganic nature, zeolite membranes can be expected to withstand more severe separation conditions (in terms of pH, temperature, pressure drop, etc.) than their polymeric counterparts.

- Another factor is related to the specific characteristics of zeolites: because the pores of these materials are approximately of the same size as small molecules, we can view zeolite membranes as a special kind of microporous inorganic membranes in which the pore diameter has been tuned to the molecular size. This enables zeolite membranes to carry out separations (e.g., the separation of isomers or of compounds with similar molecular weight) that are out of reach for common membranes with Knudsen selectivity, and compete with traditional separation methods (e.g., distillation) in other fields (such as the separation of azeotropic mixtures or of mixtures of components with close boiling temperatures).

Many reviews deal with synthesis and properties of zeolites [e.g., 1-5] and inorganic membranes [6-13], and a few are also available on zeolite membranes and their applications [14-16]. Zeolite membranes have been used for the separation of mixtures containing non-adsorbing molecules [e.g., 17-19], different organic compounds [19-25], permanent gases and vapors [26-28] and water/organic (or polar/non-polar) [29-35] mixtures. Several factors, such as differences in kinetic diameters, adsorption strengths and polarities of components, were invoked to explain the separations observed.

Zeolite membranes: statement of the problem

Ideally, the formation of a zeolite membrane requires the development of a continuous, defect-free, nearly bi-dimensional layer of zeolite crystals, so that only transport through the zeolite pores takes place. This statement represents a significant challenge to the present state-of-the-art in preparation techniques. Self-standing zeolite layers larger than a few square centimeters are difficult to form, and the resulting structures are handled with difficulty because of their fragility. Therefore, the usual procedure consists in depositing zeolite crystals onto a previously existing porous support (alumina, stainless steel, porous glass, etc.), which confers the necessary resistance and allows the development of more extensive structures.

If a structure that is reasonably defect-free (that is, few defects are present, and these are only somewhat larger than the zeolite pores) is obtained, the resulting zeolite membrane can run separations that could not be achieved by the isolated zeolite crystals. A major difference is the fact that with a zeolite membrane it is possible to operate at steady state, i.e., feeding continuously the mixture to be separated and withdrawing continuously the product streams. This is not possible with isolated zeolite particles, which become progressively saturated with adsorbate. It could be argued that some process configurations with zeolite particles are able to provide an exit stream with constant composition, e.g., several fixed bed adsorbers in parallel (operation/regeneration/stand by), or a fluidized bed with continuous addition and removal of zeolitic material. However, in all of these systems the zeolite material must be regenerated, often involving pressure and/or temperature cycling, something that can be avoided with a zeolite membrane.

Furthermore, the existence of the above mentioned continuous zeolite structure introduces qualitative as well as quantitative changes in the system. Very different conditions (total pressure, composition, temperature) may prevail at either side of the zeolitic barrier, which is often only a few microns thick. This can be used to attain separations that would not be possible in an adsorber with discrete zeolite crystals. Thus, for instance, in the higher pressure (retentate) side of the membrane, the concentration of the permeating component could be high enough to block the passage of other molecules via mechanisms such as preferential adsorption in zeolitic pores, or capillary condensation in intercrystalline microdefects. As will be discussed below, this sometimes leads to separations that are at odds with the widespread perception of zeolites as molecular sieves: the larger molecule permeates and the smaller one is retained.

In spite of its relatively short history, numerous works have already been published in the area of synthesis and application of zeolitic membranes. Rather than attempting a thorough review of the existing literature, this work deals with some general concepts, and then concentrates on examples that illustrate the application of zeolite membranes to different kinds of separations. The last section discusses the research needs and prospects of development for the near future.

Membrane preparation and characterization

Although in early works zeolite membranes were prepared by *ex situ* methods as zeolite-filled membranes [36-43], zeolite membranes are commonly prepared by *in situ* hydrothermal synthesis on porous (alumina, stainless steel) supports. The most widely used preparation method involves liquid-phase hydrothermal synthesis, in which the porous support is immersed into the zeolite precursor gel, and the membrane is synthesized under autogenous pressure. Alternatively, the so-called vapor phase transport preparation [44,45] is a kind of dry gel conversion method where vapors containing amines and water are employed to zeolitize silica or silica-alumina layers previously deposited onto the support. This has been used to prepare ZSM-5 [44,46], ZSM-35 [44], ferrierite [46-48], mordenite [46,48,49] and analcime [46] flat membranes.

Among the membranes prepared by the liquid phase method (see also the references in Table I) are MFI-type zeolite [21,22,26-28,50-56], zeolite A [18,31,57-60], zeolite Y [32,61], mordenite/ZSM-5/chabazite [35,62] and zeolite P [63], prepared on either flat (the most common case) or tubular supports. The liquid phase hydrothermal synthesis method has also been used to prepare zeolite-related materials such as AlPO-5 [64], SAPO-34 [65] and MCM-41 [66].

Regarding the distribution of the zeolite on the support, it is necessary to distinguish between two types of membranes which will be termed A and B respectively in the remainder of this review:

- In *type A* membranes, the zeolite is preferentially deposited inside the porous structure of the support.
- In *type B* membranes most of the zeolite material exists as a thin layer on top of the porous support.

As will be shown below, both types of membranes often exhibit a different separation behavior.

The number of synthesis cycles to be used depends on the particular zeolite and on the preparation conditions. Thus for instance, Vroon et al. [67] used two consecutive hydrothermal treatments with different synthesis temperatures (371-459 K), to prepare zeolite MFI membranes on α-alumina supports. They concluded that their membranes prepared in a single hydrothermal synthesis had defects because of lack of connectivity between the individual particles, i.e., one synthesis was not enough to achieve sufficient crystal intergrowth. On the other hand, zeolite membranes obtained by three or more hydrothermal treatments became too thick and cracked during the removal of the template. Elimination of the template was also pointed out by den Exter et al. [68] as the step where cracks were formed on oriented silicalite films. These authors suggested that the membrane was subjected to less overall stress when the crystals were randomly oriented in the layer.

More often than not, the synthesis of supported zeolite membranes has been carried out following trial and error procedures. To obtain a new type of zeolite membrane, the starting point would be the immersion of the support in a synthesis gel with a composition similar to that reported for the synthesis of the same zeolite as individual crystals. After synthesis the membrane would be subjected to characterization (mainly XRD and permeation measurements), and, depending on the results obtained, the synthesis would be repeated under different conditions: different gel composition, synthesis time, method of wetting the support, rotation of the autoclave, etc. The presence of the support introduces a number of new factors that make synthesis more difficult to reproduce. Among these are the following:

- The mechanism of nucleation changes because the surface of the support provides nucleation sites that are not present in homogeneous synthesis.
- The support itself may dissolve in the synthesis gel and change its composition, as has been evidenced in some attempts to obtain silicalite on alumina supports; the dissolution of the support sometimes led to ZSM-5 rather than silicalite membranes.

TABLE 1

Some examples of zeolite membranes and their performances

Zeolitic Structure	Support	Thickness [μm]	N_2 Permeance·10^7 [mol/(m^2·s·Pa)]	Mixture Separations	Reference
MFI (ZSM-5)	glass plate or pipe	39-46	-	-	Dong et al. (1992)
MFI (silicalite)	clay or stainless steel discs	50-80	0.3 (294 K)	H_2/CH_4; n-C_4/CH_4, i-C_4	Geus et al. (1992, 1993)
MFI (silicalite)	Teflon slab	250	-	n-C_6/2,2-DMB	Tsikoyiannis and Haag (1992)
MFI (silicalite)	ceramic disc	5	1.3-4.4 (293 K)	-	Jia et al. (1993)
MFI (silicalite)	γ-alumina tube	10	16 (298 K)	CH_3OH/H_2	Jia et al. (1994)
MFI (ZSM-5)	α-alumina tube	12-20	0.5 (298 K)	CO_2/N_2	Masuda et al. (1994,1998)
MFI (silicalite)	alumina or stainless steel	400-500	-	EtOH, acetic acid/H_2O; MeOH/MTBE	Sano et al. (1994a, 1994b,

	discs				1995)
MFI (silicalite)	γ-alumina tube	-	-	H_2/SF_6, i-C_4	Bai et al. (1995)
MFI (silicalite)	stainless steel disc	40	-	C_2H_6/C_2H_4; C_3H_8/C_3H_6	Kapteijn et al. (1995)
MFI (ZSM-5)	α-alumina disc	10	0.3 (303 K)	-	Yan et al. (1995a, 1995b)
MFI (silicalite)	stainless steel disc	50-60	1.5 (300 K)[a]	n-C_4/H_2, i-C_4; CO_2/H_2; CH_4/i-C_8	Bakker et al. (1996)
MFI (silicalite)	anodic alumina	30	-	-	Chiou et al. (1996)
MFI (silicalite)	γ-alumina tube	-	-	n-C_8, n-C_7, n-C_6/i-C_8; n-C_7, n-C_6, n-C_5/benzene; n-C_7/toluene; n-C_6/2,2-DMB, 3-MP, cyclohexane; n-C_8/n-C_6/i-C_6; n-C_7/n-C_6/i-C_8;	Funke et al. (1996a, 1996b, 1997)

(continued)

TABLE 1. Continued

				n-C_7/benzente/i-C_8	
MFI (silicalite)	γ- or α-alumina tubes		8.8 (303 K)	n-C_4/H_2; n-C_6/2,2-DMB	Giroir-Fendler et al. (1996)
MFI (silicalite)	α-alumina tube	10-50	0.6-4 (300 K)	n/i-C_4	Kusakabe et al. (1996, 1997)
MFI (silicalite)	stainless steel tube	-	-	MeOH, acetone/H_2O	Liu et al. (1996)
MFI (silicalite)	flat silicalite-alumina	0.5-0.75	0.2 (423 K) 1.2 (423 K)^a	CO_2/CH_4; CO_2, O_2/N_2	Lovallo et al. (1996, 1998)
MFI (silicalite)	Stainless steel tube	-	0.02 (298 K)	MEK/H_2O	Smetana et al. (1996)
MFI (silicalite)	α-alumina disc	<5	-	n-C_4/CH_4, i-C_4; n-C_6/2,2-DMB;	Vroon et al. (1996)
MFI (ZSM-5)	γ- or α-alumina tubes	25-30	8.7 (300 K)	n-C_4/H_2, i-C_4; n-C_6/2,2-DMB	Coronas et al. (1997, 1998)
silicalite (ZSM-5)	α-alumina tube	7	0.32-2.3 (300 K)	-	Oh et al. (1997)
MFI (silicalite)	ceramic plate, tube or	-	-	CO_2/N_2	Ando et al. (1998)

	monolith				
MFI (ZSM-5)	Stainless steel tubes	-	-	H_2O, C_3H_8/He; H_2O/CH_4,C_3H_8, n-C_4/He; H_2O/C_3H_8/He	Bernal et al. (1998)
MFI (ZSM-5)	Stainless stell tube	-	1.6 (300 K)	n/i-C_4	Coronas et al. (1998)
MFI (silicalite)	ytria-zirconia-alumina disc	2-3	12 (298 K)	H_2/CH_4; H_2/C_2H_6	Dong et al. (1998)
MFI (silicalite)	α-alumina disc	3	-	H_2/CH_4, CO_2, C_3H_6; n-C_4/CH_4, i-C_4; CH_4/benzene; C_3H_8/C_3H_6; n-C_6/2,2-DMB; benzene/cyclohexane; p/o-xylene	Keizer et al. (1998)
MFI (silicalite)	alumina-silica tube	400	-	EtOH/H_2O	Kondo et al. (1998)
MFI (ZSM-5)	α-alumina tube	10	0.04-0.057	-	Lai and Gavalas (1998)
MFI	Planar	-	-	CO_2/N_2	Mase et al.

(continued)

TABLE 1. Continued

(silicalite)	alumina				(1998)
MFI (ZSM-5)	α-alumina disc	-	-	n/i-C_4	Matsufuji et al. (1998)
MFI (silicalite)	flat stainless steel	400	-	EtOH/H_2O	Nomura et al. (1998)
MFI (silicalite)	γ- or α-alumina tubes	10-30	2.4-8.6 (298 K)	MeOH, EtOH, PrOH/O_2; EtOH/MeOH/O_2; PrOH/MeOH/O_2	Piera et al. (1998a)
MFI (ZSM-5)	γ-alumina or stainless steel tubes	-	1.4-7.5 (298 K)	H_2O/MeOH/O_2; H_2O/PrOH/O_2; H_2O/n-C_4/He	Piera et al. (1998b, 1998c)
MFI (ZSM-5)	γ-alumina tube	-	-	CO_2/CH_4	Poshusta et al. (1998)
MFI (ZSM-5)	alumina tube	-	1.4-4.4 (373 K)	-	Suda et al. (1998)
LTA? (NaA)	glass tube	-	-	H_2O/ButOH, EtOH	Ishikawa et al. (1989)
LTA (NaA)	α-alumina tube	30	-	H_2O/MeOH, EtOH, i-PrOH, acetone, DMF,	Kita et al. (1995,1998a)

				dioxane	
LTA (NaA)	α-alumina tube	5-25	-	-	Masuda et al. (1995)
LTA (NaA)	α-alumina tube	0.4-3.8	0.1 (308 K)	H_2/N_2	Aoki et al. (1998)
LTA (NaA)	α-alumina disc	4.7-5.4	-	H_2O/EtOH	Kumakiri et al. (1998)
FAU (NaY)	α-alumina tube	20-30	-	H_2O/EtOH; MeOH/MTBE, benzene; EtOH/benzene, cyclohexane, ETBE; benzene/n-C_6, cyclohexane	Kita et al. (1997, 1998b)
FAU (NaY)	α-alumina tube	8	0.1-0.3 (303 K)	CO_2/N_2	Kusakabe et al. (1997)
FAU (NaX)	α-alumina tube	20-30	-	H_2O/EtOH; MeOH/MTBE, benzene	Kita et al. (1998b)
FAU (NaY)	α-alumina disc	2.5-6.7	-	-	Kumakiri et al. (1998)

(continued)

TABLE 1. Continued

MOR (mordenite)	alumina disc	10-20	9 (303 K)	benzene/p-xylene	Nishiyama et al. (1995, 1996, 1997a)
MOR (mordenite)	α-alumina tube	-	-	H_2O, C_3H_6/He; H_2O/CH_4,C_3H_6, n-C_4/He; H_2O/C_3H_6/He	Bernal et al. (1998)
MOR (mordenite)	α-alumina tube	-	2.5-8.0 (298 K)	H_2O/MeOH/O_2; H_2O/EtOH/O_2; H_2O/PrOH/O_2; H_2O/n-C_4/He	Piera et al. (1998b, 1998c)
MOR (mordenite)	α-alumina tube	10	2.5-3 (298 K)	H_2O/PrOH/O_2	Salomón et al. (1998)
FER (ZSM-35)	glass plate or pipe	89	-	-	Dong et al. (1992)
FER (ferrierite)	alumina disc	40	0.02 (303 K)	cyclohexane/benzene; benzene/p-xylene; p-xylene/o-xylene	Nishiyama et al. (1997a, 1997b)
KFI (P)	α-alumina disc	5-15	5.7 (298 K)[a]	-	Dong y Lin (1998)

[a] H_2 permeance instead of that of N_2.

> Because the support can selectively restrict the diffusion of the gel components, synthesis inside the support pores may take place with a composition different from that of the bulk liquid. Additionally, this imposes spatial constraints on crystal growth.

Several avenues are being explored to improve the control over the characteristics of the membranes prepared by hydrothermal synthesis. Among these are: i) seeding the support with crystals of the zeolite to be synthesized, in order to control nucleation [31,61,69]; ii) when type B membranes are sought, diffusion barriers can be used to limit the penetration of precursor species in the support pores [70]; iii) in order to obtain type A membranes, the synthesis gel can be infiltrated into the support pores using pressure or vacuum [71]; iv) the reactants can be segregated at either side of the porous support [72,73]; this procedure is useful to stop the synthesis once the formation of a thin crystal barrier takes place; v) post-synthesis processing can be used to improve the membranes; this includes ion exchange [74,75], CVD [76], ALCVD [77], vapor or liquid phase silylation [78] and coking treatments [79].

However, the most successful approach to control membrane formation involves segregation of the processes of crystal nucleation and growth. Unlike the direct synthesis procedures just discussed, the first step in this method includes only nucleation and initial crystal growth, which are usually carried out as a homogeneous synthesis (in the absence of the porous support), yielding colloidal zeolite crystals. These can now be used as seeds, deposited on the support and brought into contact with a solution containing the necessary nutrients for growth [80-82]. Because the concentration needed for secondary growth is lower than that required for nucleation, further nucleation is strongly decreased and almost all of the crystal growth takes place over the existing crystal seeds. By controlling the composition and concentration of the secondary growth solution, the crystallization of undesired zeolite phases and the dissolution of the support can be avoided, and the rate and direction of crystal growth can, to a certain extent, be controlled.

Independent control of the nucleation and growth stages can also be used to obtain an oriented zeolite layer [80,81]. Oriented channel structures are interesting not only for membranes, but also for size-selective chemical sensors [15]. Several authors have reported the occasional orientation of zeolite films [e.g., 20]; however, only recently a variety of oriented zeolite structures has been purposedly fabricated, among these zeolite L [83], MFI zeolite [80,84-89], zeolite A [90-91] and zeolite UTD-1 [92].

Figures 1a and 1b show, respectively, cross sections of oriented and non-oriented membranes. An oriented zeolite film could be advantageous because of two reasons: first, the number of intercrystalline defects can be reduced if the crystals grow uniformly in the same direction. In this case, by supplying the nutrients from the growth side of the membrane, the rate of growth and the membrane thickness can be controlled accurately (Chau et al. [82] claimed control of the thickness of their oriented MFI membranes to within 0.1 μm). Thus, membranes with a thickness of only a few hundred nanometers can be produced in contrast with the thick membranes with high intercrystalline porosity that are often the result of direct synthesis methods. Second, greater permeabilities could in principle be expected when crystal orientation is controlled in such a way that the main channels are aligned in the direction of flow. Lewis et al [93] fabricated a single crystal ferrierite membrane, and were able to measure independently transport through the 8- and 10-membered ring channel systems. In this case, relatively low permeances were obtained, since both channel systems were aligned in parallel to the large crystal faces; however the experiment served as an elegant demonstration of the fine tuning capabilities of oriented structures with regards to permeation.

Tubular or flat supports?

Regarding the shape of the support, from the industrial application point of view, tubular membranes are more suitable than plates or discs because tubes are easier to scale up (implemented as multichannel modules) than flat membranes. However, in laboratory-scale synthesis it is usually found that making good quality zeolite membranes on a tubular support is more difficult than on a porous plate. One obvious reason is the fact that the area is usually smaller in flat supports, which decreases the likelihood of defects. In addition, in the direct synthesis method the tubular support is often placed vertically in the autoclave, which is then filled with the synthesis gel. In this case, a clear and homogeneous precursor gel must be used (otherwise segregation may occur, and different parts of the tube would be in contact with different compositions), and the

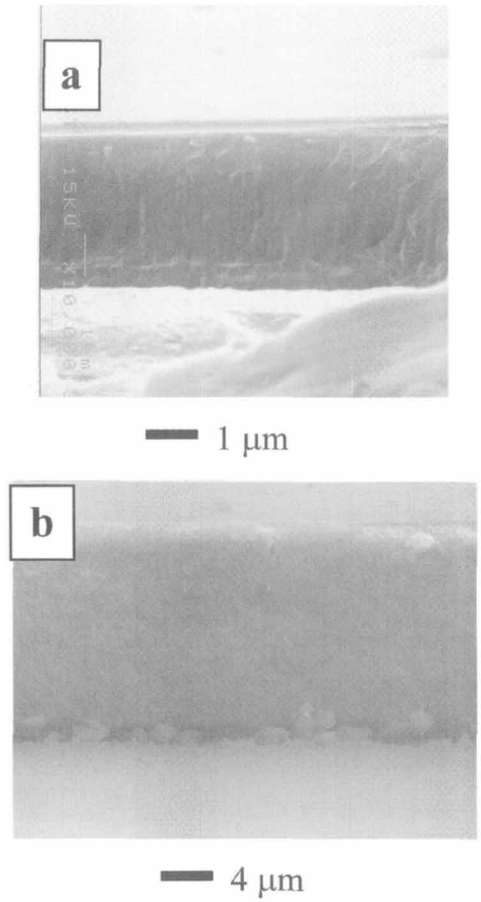

Figure 1. SEM pictures showing cross-sections of silicalite membranes on alumina supports. 1a oriented membrane [82], 1b non-oriented membrane.

amount present must be in sufficient excess to avoid local depletion of the nutrients. Also, with flat supports, the crystal nuclei formed in the bulk of the solution precipitate onto the support, which facilitates the formation of the zeolite layer, something difficult to achieve with vertical support tubes. For this reason, some researchers have kept the tubular support horizontal during the hydrothermal treatment and, in order to achieve a more homogeneous deposition, the autoclave was either rotated around the horizontal axis during synthesis [25,27], or kept fixed and rotated 90° between synthesis [35,62].

The main drawback of this procedure is that, together with crystal nuclei, components of the gel and zeolite crystals formed by homogeneous synthesis can also precipitate onto the support, which may give rise to defects in the zeolite layer.

Membrane characterization

Many of the techniques used to characterize zeolite membranes are also commonly employed in catalyst characterization. Among the most widely used, XRD (X-ray diffraction) is an indispensable tool to identify the type zeolite formed in the synthesis, and to evaluate the type of impurities that are present; XRD pole-figure analysis determines whether the zeolite crystals in the continuous zeolitic layer are oriented. SEM (scanning electron microscopy) can be used to analyze the shape and size of crystals, and their distribution on the support. It can also provide a measurement of membrane thickness and a first impression on the existence of inter-crystalline defects. Surface analyzing techniques such as EPMA (electron-probe microanalysis) or XPS (X-ray Photoelectron Spectroscopy) can be used to measure the Si and Al concentration profiles across the membrane radius.

Specific permeation measurements, either of single gases or of multicomponent mixtures, provide extremely useful information on the effective pore structure of the membrane, and on the existence of inter-crystalline defects. A battery of single-gas permeation experiments using molecules with different kinetic diameters could be used to gauge the effective pore size in defect-free membranes. Alternatively, selective blocking of membrane pores combined with permeation measurements could be used to evaluate defects. Thus, van de Graaf et al. [94] and Lin et al. [95] measured, respectively, krypton and N_2 or SF_6 permeation on membranes calcined at increasingly higher temperatures. Membranes calcined at low temperatures still had their zeolitic pores blocked by the template, and these authors attributed all of the permeation observed below 600-610 K to permeation through microdefects.

Permeation experiments are often complemented by adsorption measurements, which can help to explain the permeation mechanism observed. To this end, temperature-programmed adsorption/desorption experiments are employed, based on weight measurements (thermobalance), or on continuous gas analysis. It is important to ensure that the initial state of the membrane in adsorption experiments is reproducible, i.e., that there is no unwanted material previously adsorbed on the membrane.

Zeolite membranes and their performance in separations

Table 1 lists the characteristics of some zeolite membranes used in the separation of mixtures, together with the main results obtained. MFI (silicalite and ZSM-5) membranes are the most widely studied, although there are also examples of zeolite membranes having LTA, FAU, MOR, FER and KFI structures. Concerning zeolite MFI membranes, the term silicalite is used for the membranes prepared without an aluminum source in the precursor gel. Nevertheless, as mentioned above, the alkaline gels can dissolve the alumina supports, incorporating aluminum into the zeolite. As a result, it seems likely that many of the authors reporting the synthesis of supported silicalite membranes were in fact studying ZSM-5 membranes.

Permeation of individual gases

The permeance of individual gases across a zeolite membrane depends not only on the characteristics of the permeating molecule and the zeolite membrane, as could be expected, but also on the experimental conditions, especially the pressure and temperature. The individual gas permeance that is experimentally observed on a given zeolite membrane can be explained as the result of three simultaneous permeation mechanisms [94]: permeation through defects, activated gaseous diffusion and surface diffusion of adsorbed species. The first of these mechanisms is the main one for molecules whose kinetic diameter is larger than the zeolite pores. In this case, it is likely that Knudsen (mesoporous defects) or viscous (macroporous defects) behavior will be observed, although the balance between both types also depends on the operating pressure and temperature. Permeation through defects can also be important for molecules that are weakly or not at all adsorbed on the zeolite. Thus, as mentioned above, the permeation of krypton through membranes calcined at low temperatures has been used to quantify the flow through intercrystalline defects.

Burggraaf et al [96] studied the permeation of different individual gases between room temperature and 473 K, using a silicalite membrane with a very low concentration of defects. They distinguished four different regimes:

- CH_4 permeated in the Henry sorption regime, where the flux increased linearly with the pressure of the permeating gas at the feed (retentate) side of the membrane.

- Ethane, propane and n-butane permeated in the Langmuir sorption regime. The feed pressure dependence is now non-linear, and maxima in the flux vs. temperature curves can be observed, due to the divergent effects of temperature in the adsorption and diffusion processes, as discussed below.

- Benzene permeated in the saturation regime, where the flux becomes independent of the pressure at the feed side and increases with temperature.

- The size exclusion regime applies to molecules whose kinetic diameters are slightly in excess of the zeolite pore diameter (e.g., 2,2-dimethylbutane).

The relative importance of surface diffusion and activated gaseous diffusion depends strongly on temperature [97]. Figure 2 is a simplified diagram showing the evolution of permeance as a function of temperature [98,99]. Initially (A⇒B), the permeance increases because the increase in temperature enhances the mobility of adsorbed species, even though the amount of physically adsorbed material starts to decrease. Eventually, point B is reached, and from this temperature the decline in occupancy prevails which gives rise to a decrease in permeance (B⇒C). At a sufficiently high temperature (C) the effect of adsorption becomes negligible, and the permeance is controlled by activated transport through micropores, increasing with temperature (C⇒D).

In principle, it could be expected that the permeance of N_2 in $mol/(m^2\cdot s\cdot Pa)$, as a pure non-condensable gas, could give an indication of the effective thickness and density of the zeolitic layer, i.e., of the membrane resistance to the permeation flux. However, as can be seen in Table 1, the N_2 permeance data (in the $0.02\text{-}16\cdot10^{-7}$ $mol/(m^2\cdot s\cdot Pa)$ range, at or near ambient temperature) do not correlate with the thickness reported for the zeolite layer (in the 0.75-500 μm range). This behavior can be explained by taking into account the transport resistance through the support which is often significant [100], and can be vary widely for different membranes, depending on the support thickness and effective pore size. In addition, the presence of the support creates different local concentration conditions at the membrane interfaces, which also affects the separation performance. Finally, depending on the preparation procedure, zeolite crystals can be

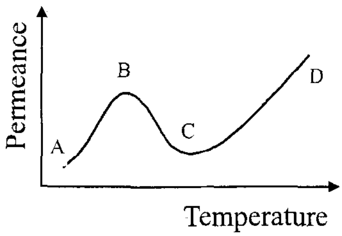

Figure 2. Qualitative diagram showing the dependence of single gas permeance with temperature.

synthesized inside the pores of the support, with a direct effect on the membrane transport properties [27]. Other contributing factors are likely related to the presence of pinholes (due to an imperfect hydrothermal synthesis) and cracks (formed during the calcination and handling of the membranes).

Separation of mixtures

The permeation of mixtures is a more complex phenomenon, and, in general, the behavior that is experimentally observed for mixtures cannot be predicted solely from the permeance of the individual components [27]. As will be shown below, it is often the case that in a binary mixture, the component that permeates faster as a single gas (in general the more weakly adsorbed component) is the one giving the lower permeance in the binary mixture.

Table 1 lists some of the separations of mixtures carried out with zeolite membranes, using gas-phase or pervaporation systems; unless otherwise indicated, in a mixture A/B, A is used to designate the component that permeates preferentially in the mixture. Four groups of separations with different characteristics can be distinguished: separation of mixtures of non adsorbing compounds, of mixtures of adsorbing organic compounds, of permanent gas from vapors and of water or polar molecules from organic compounds. Although the mechanisms of Knudsen diffusion and shape selectivity/molecular sieving may also play a role, the majority of the separations reported with zeolite membranes can be explained in terms of surface diffusion and sometimes capillary condensation.

Kärger and Ruthven [101] explained surface diffusion in zeolites as an additional flux due to diffusion through the adsorbed phase, under conditions where there is significant adsorption on the pore wall. They also pointed out that the conditions under which capillary condensation occurs are also those under which significant surface diffusion may be expected; thus it is often found that both mechanisms coexist on a specific system. It is well known that, due to the effect of surface tension, condensation can occur in small capillaries at partial pressures far removed from those required for condensation as a free liquid. Thus, capillary condensation can easily take place in microporous intercrystalline defects, when these are present in the zeolitic membranes. On the other hand, small condensable molecules such as water or methanol with kinetic diameters of 0.265 nm and 0.39 nm, respectively, are several times smaller than the pores of certain zeolites (e.g., mordenite and zeolite Y have channels of 0.65 x 0.70 nm and 0.74 x 0.74 nm, respectively). In this case, it is possible to visualize the permeating species as a condensed phase in the channels or perhaps in the cages of the zeolite structure, (for example, the framework of zeolite NaA consists of relatively large 1.12 nm diameter cages connected through relatively small channels of 0.41 nm).

While capillary condensation is in principle a non-selective process, there is a wide variation in the strength and specificity of adsorption phenomena, from non-selective physisorption (which is difficult to distinguish from capillary condensation), to highly specific chemisorption. The specificity of the adsorption process can be used to increase the selectivity of a given separation. Thus for instance Morooka and coworkers [75,102] exchanged different cations on faujasite-type membranes to modify the adsorption of CO_2 in the separation of CO_2/N_2 mixtures.

Shape selectivity and molecular sieving become the dominant mechanism in defect-free membranes when the adsorption strength of the potential sorbates on the zeolite membrane decreases sufficiently. This is of interest for the separation of mixtures of non-adsorbing permanent gases, provided that there are significant differences in their molecular sizes. Molecular sieving is also important with adsorbable compounds when these have to be separated at moderate-high temperatures, i.e., above the temperature value at which adsorption effects cease to be significant (which depends on the particular zeolite and on the nature and partial pressure of the permeating compounds).

Good selectivity with defective membranes

A high selectivity has sometimes been used as the sole argument to claim that a defect-free membrane has been synthesized. In fact, as can be deduced from the preceding discussion, high selectivities could be obtained in membranes where defects (i.e., non-zeolitic pores) are present, provided that these are of a sufficiently small magnitude. Two such cases are sketched in Figures 3 and 4. In Figure 3, a binary mixture is flowing on the high pressure side of the membrane. The partial pressure of component A (white circles) is sufficiently high so that capillary condensation occurs in the pores available, which become blocked by A, with little or no permeation of B, even though the pores could be easily permeated by both molecules. The case presented in Figure 4 corresponds to a *type A* membrane (zeolitic material inside the pores of the support), where there are gaps in between zeolite crystals that can be used by both A and B molecules. It is assumed that component A adsorbs preferentially on the zeolite, and is able to use both the zeolite pore network, and the inter-crystalline voids. On the contrary, component B does not enter the zeolite pores (because size exclusion or because these are blocked by A), and has to follow the tortuous path indicated by the dotted line. If the adsorption and desorption processes are fast, the permeation of the molecule that is able to transit the zeolite network will be significantly accelerated, (even though diffusion across the zeolite crystal itself may be slow), leading to a high selectivity.

For a given membrane, modifications in the operating conditions (temperature and partial pressure of the permeating molecules) can substantially change the separation selectivity. This is shown schematically in Figure 5, where the separation of a hypothetical ternary gas mixture with a hydrophilic membrane is considered. The mixture contains molecules with different properties: A and B are small molecules, and C is a large one. A is assumed to be a polar compound that is preferentially adsorbed on the hydrophilic membrane while B is a non-polar permanent gas. Molecular sieving excludes C from penetrating the smallest pores under all conditions, as long as the membrane integrity is preserved. However, C can penetrate the intermediate and larger pores in Figure 5. At low temperatures the adsorption of A is significant, and as a result the smallest pores are blocked to the permeation of B and C. This also holds true for

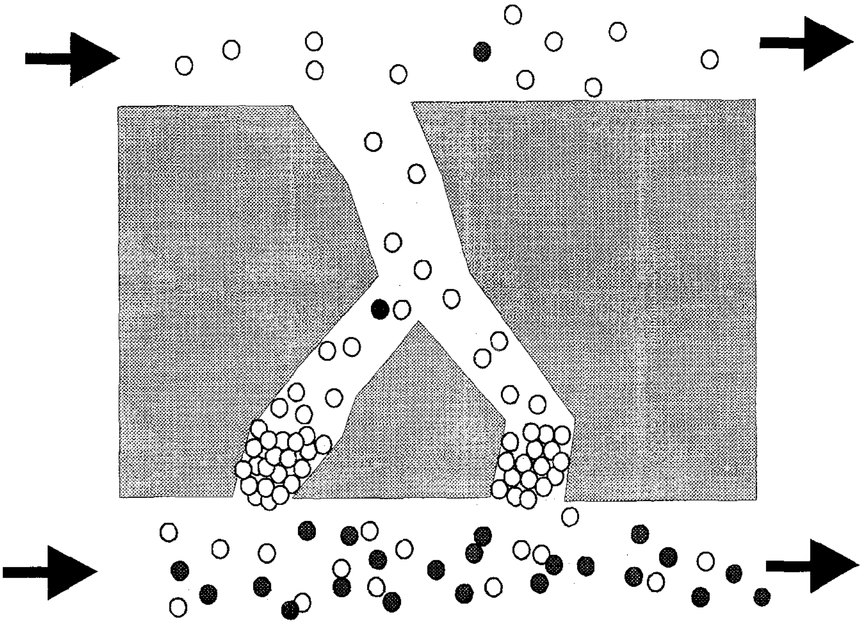

Figure 3. Enhancement of selectivity by capillary condensation.

somewhat higher temperatures if the partial pressure of A is raised accordingly. If the partial pressure of A is further increased and the separation is carried out at a lower temperature the intermediate and larger pores can also be blocked by A through enhanced adsorption and capillary condensation. On the contrary, if the temperature is raised and/or the partial pressure of A decreases, adsorption becomes negligible and the separation selectivity is lost, except for the smaller pores that are still able to exclude C.

Separation of mixtures by molecular sieving

In the ideal molecular sieving regime the interaction of the permeating species with the membrane is minimal, and separation takes place simply because the size or shape of some of the molecules prevents them from entering the membrane pores and/or move across them with substantial velocity. Thus, this broad concept of molecular sieving encompasses not only size exclusion, but also the case when there is a large

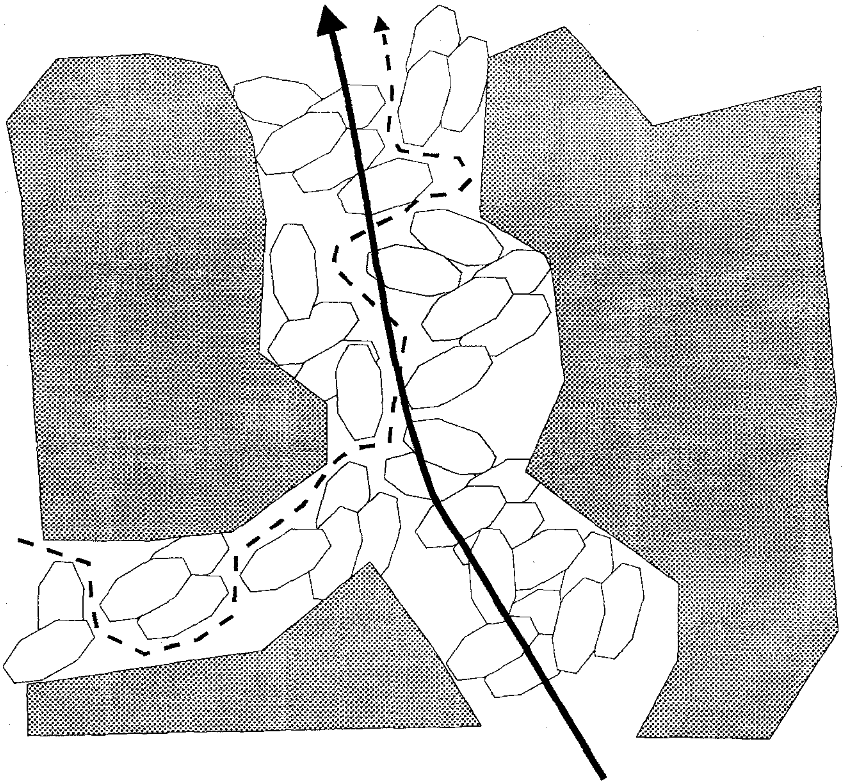

Figure 4. Enhancement of selectivity in a *type A* membrane with intercrystalline voids.

difference between the configurational diffusion rates of the permeating molecules. Concerning this point, not only the size but also the shape of the permeating molecule is important: Xiao and Wei [103] showed that the transition from Knudsen diffusion to configurational diffusion on MFI zeolites at 300 K takes place at a value of λ (ratio of kinetic diameter of the molecule to channel diameter) equal to 0.8 for a value of φ (ratio of Lennard-Jones length constant to kinetic diameter of the molecule) equal to 1; however the value of λ decreased to 0.6 when φ was equal to 1.25. At higher temperatures (500-700 K) the transition takes place at λ values of about 0.8 when φ equals 1.25.

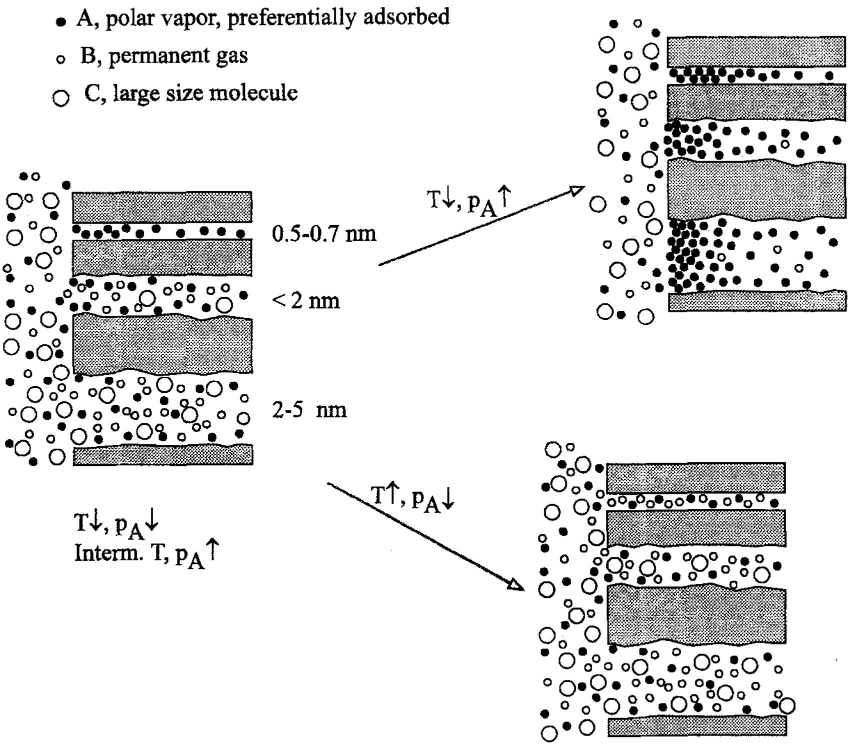

Figure 5. Influence of temperature and partial pressure (hydrophilic membrane, ternary gas mixture).

In a separation controlled by molecular sieving adsorption is not important: either the permeating species do not adsorb, or their adsorption is roughly the same, so that adsorption does not favour the permeation of any particular species. Under these conditions, the separation selectivity (ratio of actual permeances in the mixture) should coincide with the ideal selectivity (ratio of single gas permeances).

Bakker et al. [19] made an interesting experimental study of the separation of linear and branched paraffins using silicalite membranes on stainless steel discs. They reported shape selectivity for the n/i-butane mixture, with separation selectivities of 27 at 295 K and 23 at 403 K, and concluded that such a difference in permeation fluxes could not be explained by the relatively small difference in adsorption strength (for silicalite crystals, they found a 1.5 n/i-butane factor at 295 K, and a value close to 1 at 403 K). However, alternative explanations are also possible. Thus, it has already been mentioned that linear and branched alkanes present a different adsorption pattern on silicalite [104,105]: branched alkanes are located predominantly at the intersections of the straight and zigzag channels while linear alkanes are distributed more evenly. Under these circumstances, a relatively small difference in adsorption strength could result in a large difference in permeances. Furthermore, it is not totally clear that the relative adsorption strength obtained with silicalite powder fully translates to the silicalite membrane (where a film of zeolite crystals probably coexists with intercrystalline regions).

Coronas et al. [25,27] observed a maximum in the permeation of butane on *type A* ZSM-5 membranes (see Figure 6), while the maximum did not appear when the membrane was formed as a continuous layer of intergrown ZSM-5 crystals on the inner wall of the support (*type B* membranes). Since a maximum in the temperature-permeance curve is indicative of strong adsorption effects [98,99,106], it could be concluded that n-butane adsorption is weaker on the second type of ZSM-5 membranes. The same authors found that for 5 different ZSM-5 membranes prepared using the same method the maximum n/i-butane separation selectivities were 8.3, 16, 18, 33 and 54 respectively, at temperatures between 365 and 394 K, [25,27], while for all the membranes the ideal separation selectivity (ratio of single gas permeances) was close to 1. These results suggest that i) a relatively small difference in adsorption strength is sometimes sufficient to obtain good separations in good quality membranes; ii) butane isomers are separated on MFI membranes mainly because n-butane prevails in the competitive adsorption with i-butane, even at moderately high temperatures, and iii) it is difficult to reproduce exactly membranes prepared by the direct synthesis method: relatively minor variations in the number and/or size of defects can give rise to large differences in the separation performance obtained.

A more probable case of molecular sieving is the methane/i-octane separation which was also carried out by Bakker et al. [19] who found a separation factor of more than 300. The kinetic diameter of i-octane (0.62 nm) is higher than the silicalite pore size (ca. 0.55 nm), and therefore i-octane cannot enter the silicalite pores while methane can.

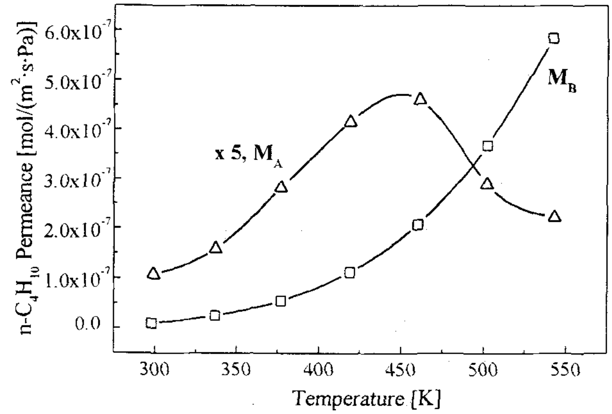

Figure 6. Evolution with temperature of the single gas permeance of n-butane through *type A* and *type B* ZSM-5 membranes as a function of temperature.

The presence of some defects in the silicalite membrane accounts for the fact that absolute separation was not obtained, as would be the case with a perfect silicalite membrane.

The most convincing case of molecular sieving would be the separation of a binary mixture of two non-adsorbing permanent gases. Bai et al. [17] studied the separation of the H_2/SF_6 mixture using a silicalite tubular membrane. SF_6 is a inert molecule that at high temperatures does not adsorb significantly on silicalite. Furthermore, the single gas permeance of SF_6 is small, due to its kinetic diameter of 0.55 nm. Single gas permeances of H_2 and SF_6 at 583 K were $61 \cdot 10^{-7}$ and $6.7 \cdot 10^{-7}$ mol/(m^2·s·Pa), respectively; and the permeances of H_2 and SF_6 measured at the same temperature using the binary mixture were $51 \cdot 10^{-7}$ and $4.0 \cdot 10^{-7}$ mol/(m^2·s·Pa), respectively. The ideal and experimental separation selectivities are therefore close (9.1 and 12.8, respectively, which are comparable values, especially taking into account that a different permeation method was used in the single gas and mixture experiments), indicating that the separation takes place by molecular sieving.

There are other studies in which the molecular sieving mechanism could in principle be invoked, in view of the fact that the molecule with the smaller kinetic diameter (0.289, 0.33, 0.346, 0.364 and 0.38 nm for H_2, CO_2, O_2, N_2 and CH_4, respectively) permeates preferentially. This is the case in the separation of H_2/CH_4 [52], CO_2/CH_4 [80,107], CO_2/N_2 [80,108-110] and O_2/N_2 [80], carried out on zeolite MFI membranes; of CO_2/N_2 on a zeolite NaY membrane [61,75]; and of H_2/N_2 on a zeolite NaA membrane [18]. These separations were achieved at temperatures from 298 to 450 K, in general with low to moderate separation selectivity. However, at least in the case of mixtures containing CO_2, the preferential adsorption of CO_2 on the zeolite must be taken into account and, as already mentioned, this can be enhanced by exchanging with the appropriate cations [75,102,108]. The importance of CO_2 adsorption is underlined by the results of Kusakabe et al. [61] who reported CO_2/N_2 separation selectivities of 50-75 at 303 K and 8-15 and 403 K, respectively on NaY zeolite membranes. In this case, in spite of the large pore size of the NaY zeolite (0.74 nm), a high selectivity was obtained due to the strong adsorption of CO_2 on this zeolite. Finally, regarding the separation of O_2 and N_2, whose adsorptive characteristics on MFI zeolite are very similar, Lovallo et al. [80] pointed out that the separation observed on a 0.5 μm thick oriented MFI membrane could be explained because O_2 may permeate more readily than N_2 by switching between channel networks.

Separation of vapors or of adsorbable organic compounds from non-adsorbing permanent gases

In these mixtures, the vapor or organic compound can either adsorb preferentially on the zeolite or undergo capillary condensation in pores of small diameter, therefore blocking the membrane for the other species in the mixture (i.e., the permanent gas). As shown in Figure 3, even a membrane with a significant number of defects can give a high separation selectivity, provided that these are small enough to be blocked by adsorption or capillary condensation. Thus for instance, when methanol/H_2 [26], alcohol/O_2 [28] (alcohol=methanol, ethanol or propanol) and n-butane/H_2 [21,27] mixtures were separated with zeolite MFI membranes, the flux of permanent gas (H_2 or O_2) was strongly reduced with respect of its single gas permeance value, due to the adsorption or condensation of the other components. A common feature of these separations is that the selectivity towards the blocking molecule decreases with increasing temperature, following the decrease in adsorption and capillary condensation.

The separation of the n-butane/H_2 mixture on zeolite MFI membranes is a good example to illustrate the mechanisms of permeation and the differences between traditional mesoporous membranes and zeolitic membranes. In many cases, the ratio of N_2 or H_2 single gas permeances at room temperature over that of SF_6 [26,27] or n-butane [27,28,35] has been employed to calculate ideal selectivities, and to have an assessment of the quality of a membrane. In the case zeolite MFI membranes, the H_2/n-butane ideal selectivity at room temperature is often high for membranes with a continuous layer of intergrown silicalite or ZSM-5 crystals on the inner wall of tubular supports (e.g., 58 for Bai et al. [17], and 290 for Coronas et al. [27]; both with H_2 permeances of $33\text{-}34\cdot10^{-7}$ mol/($m^2\cdot s\cdot Pa$)); and low, sometimes close to the Knudsen selectivity, when the membranes have zeolite crystals dispersed within the pores of the alumina tubular supports (e.g., 4.3 for Giroir-Fendler et al. [21], and 14 for Coronas et al. [27], both with H_2 permeances in the $1.2\text{-}12\cdot10^{-7}$ mol/($m^2\cdot s\cdot Pa$) range). Other works reported a H_2/n-butane ideal selectivity of 8.3 and 1.7 at 303 and 458 K on a ZSM-5 membrane on a flat alumina support [111], with H_2 permeances of $0.619\cdot10^{-7}$ and $1.01\cdot10^{-7}$ mol/($m^2\cdot s\cdot Pa$), respectively; and a selectivity of 3, with a H_2 permeance of $1.5\cdot10^{-7}$ mol/($m^2\cdot s\cdot Pa$), at about 300 K for a silicalite membrane on a flat stainless steel support [98]. In spite of these relatively low values of the ideal selectivity, many of these membranes performed efficiently in the separation of mixtures, as will be shown below.

In membranes prepared by the direct synthesis method the ideal selectivity usually decreases when the temperature is increased: around 425-450 K all of the above mentioned membranes show smaller H_2/n-butane ideal selectivities, in the 1.3-13 range. However the behavior can be rather different for oriented membranes. Thus, Lovallo and Tsapatsis [84] prepared a preferentially oriented silicalite membrane, 0.75 μm thick, in which the H_2/n-butane ideal selectivity was 36 and 29 at 423 and 458 K, respectively (with H_2 permeances of $0.62\cdot10^{-7}$ and $1.0\cdot10^{-7}$ mol/($m^2\cdot s\cdot Pa$), respectively). This indicates that, even though the membrane was in this case very thin, most of the transport at high temperature still takes place using zeolite pores, while in directly synthesized membranes parallel pathways become available for n-butane transport at high temperature. These parallel pathways are either intercrystalline regions (which are probably more abundant in a membrane with randomly intergrown crystals than in one where oriented growth has

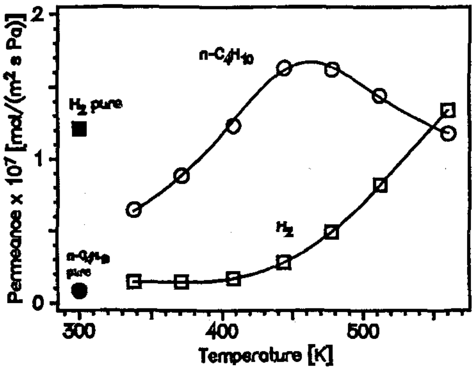

Figure 7. Permeance of H_2 and n-butane in a 50/50 mixture as a function of temperature. *Type A* ZSM-5 membrane ([27], reproduced with permission of the American Institute of Chemical Engineers Copyright © 1997 AIChE J., 43(7), 1797. All rights reserved).

taken place) or non-zeolitic micropores. As temperature increases, thermal stress could lead to enlargement of these pathways [27], or to their unblocking by removal of the adsorbed/condensed species.

One important feature of the n-butane/H_2 separation in randomly oriented membranes is that the ideal selectivity obtained from the ratio of single gas permeances does not directly correlate with the separation selectivity measured when mixtures are fed to the retentate side of the membrane. For zeolite MFI membranes, while, in general, the H_2/n-butane ideal selectivity at room temperature is higher than 4, the actual H_2/n-butane separation selectivity is under 1. This means that n-butane/H_2, instead of H_2/n-butane, separation selectivity, i.e., the opposite of molecular sieving, is found under such conditions. Figure 7 illustrates this behavior for a ZSM-5 membrane where the H_2/n-butane ideal selectivity was 392 at room temperature. It can be seen that at low to moderate temperatures the permeance of n-butane is higher, due to its adsorption in the pores of the membrane that inhibits H_2 permeance. The membrane gave at maximum n-butane/H_2 separation selectivity of 11 at 370 K. As temperature increases, n-butane desorbs from the ZSM-5 pores and H_2 permeates faster; eventually a temperature is

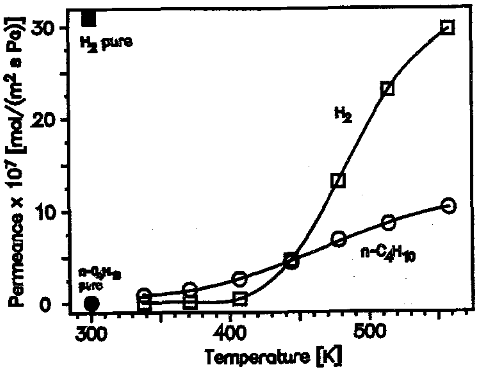

Figure 8. Permeance of H_2 and n-butane in a 50/50 mixture as a function of temperature. *Type B* ZSM-5 membrane ([27], reproduced with permission of the American Institute of Chemical Engineers Copyright © 1997 AIChE J., 43(7), 1797. All rights reserved).

reached (T_{eq}), at which the n-butane and the H_2 permeances are equal; in this case this takes place at 440 K [27]. Similar results were reported with membranes prepared at IRC [21,112]. In this respect, *type A* and *B* membranes also behave differently, with T_{eq} being lower for *type B* membranes. Figure 8 shows that when the zeolite crystals are dispersed within the pores of the supports (*type A* membrane) T_{eq} increases, reaching values of 550 K [27,112] or 530 K [21].

Another evident case of pore blocking by adsorbed organic compounds is that of the separation of alcohols and alcohols/O_2 mixtures using tubular silicalite membranes [28]. In this work, Piera et al. reported a maximum selectivity of 7415 for the ethanol/O_2 separation in an ethanol/methanol/O_2 mixture. Separations were achieved because one of the components in the mixture (the alcohol, and in the case of alcohol mixtures mainly the less polar, higher molecular weight alcohol) adsorbs preferentially, thus hindering the pass of the other components through the zeolite membrane. When the evolution of O_2 permeance versus temperature was analyzed (Figure 9) for different mixtures, it was found that the blockage of the silicalite pores in the membrane was highest

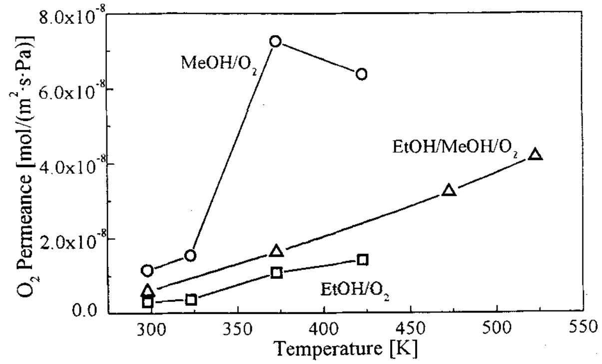

Figure 9. O_2 permeance as a function of temperature at a total pressure of 108 kPa for different feed mixtures: ethanol (2.6 kPa)/O_2, methanol (6.6 kPa)/O_2 and ethanol (1.6 kPa)/ethanol (3.9 kPa)/O_2. Silicalite membrane ([28], reprinted from Journal of Membrane Science, 142, E. Piera, A. Giroir-Fendler, H. Moueddeb, J.A. Dalmon, J. Coronas, M. Menéndez and J. Santamaría, "Separation of alcohols and alcohols/O_2 mixtures using zeolite MFI membranes", 97-109, Copyright (1998), with permission from Elsevier Science).

(corresponding to the lowest O_2 permeance) for ethanol, then for the methanol/ethanol mixture and finally for methanol. This is in agreement with the organophilic character of silicalite, that leads to a stronger adsorption of the less polar alcohol (ethanol), whose adsorption is also stronger because of its larger size. This work also showed that *type A* membranes were more robust than their *type B* counterparts: as the temperature increased *type A* membranes maintained a higher selectivity, while *type B* membranes were more liable to the development of defects in the membrane structure as a consequence of thermal stress.

Separation of mixtures of organic compounds

Most of the separations of organic/organic mixtures reported in the literature can also be explained in terms of competitive adsorption between the permeating compounds. However, predicting the adsorption of mixtures is not straightforward: even relatively similar compounds (e.g., linear and branched paraffin isomers) can show a considerably different adsorption behaviour. Recent molecular simulations of adsorption of paraffins on silicalite (e.g., [105]) show that the linear and branched alkanes tend to occupy different adsorption sites, and the linear alkane is able to "squeeze out" the branched alkane from the silicalite structure.

In general, for a given zeolite membrane, the separation selectivity increases as the difference in the strength of adsorption of the permeating components increase. The separations of n-butane and i-butane [19,20,25,27,113] and of n-hexane and 2,2-dimethylbutane (2,2-DMB) [20-22,27] using zeolite MFI membranes have been widely studied. Both pairs of C_4 and C_6 compounds have the same molecular weight and therefore cannot be separated with mesoporous membranes where transport is governed by Knudsen diffusion. The differences between the kinetic diameters concerned (0.43 nm for n-butane and n-hexane, 0.50 nm for i-butane, and 0.62 nm for 2,2-DMB) are sufficient to warrant significant shape selectivity/molecular sieving effects. However, again the results were different than anticipated; for instance, when a ZSM-5 tubular membrane was used for the separation of a n-hexane/2,2-DMB mixture [25] the ideal selectivity was found to be under 20, but the actual separation was governed by competitive adsorption, and the selectivity was in the order of thousands. Further, a high 2,2-DMB single gas permeance was measured, in spite of the fact that the kinetic diameter of 2,2-DMB is larger than the pore size of the ZSM-5 (ca. 0.55 nn). This strongly suggest that there are microdefects in the membrane that allow the passage of 2,2-DMB as a single gas, though these defects are partially obstructed by adsorbed n-hexane molecules when the permeation of mixtures is carried out.

A similar description fits the separation of butane isomers with zeolite MFI membranes, studied in a recent work [27]. Figure 10 shows that, while at temperatures below 450 K the permeation of i-butane was considerably reduced with respect to its single gas value by the presence of n-butane, the permeation flux of n-butane (the blocking compound) was little affected by i-butane throughout the range of temperature tested. As temperature increases n-butane desorbs, freeing permeation pathways for i-butane. As a result, at the highest temperature tested the permeances were almost equal (including single gas permeances and permeances in the mixture).

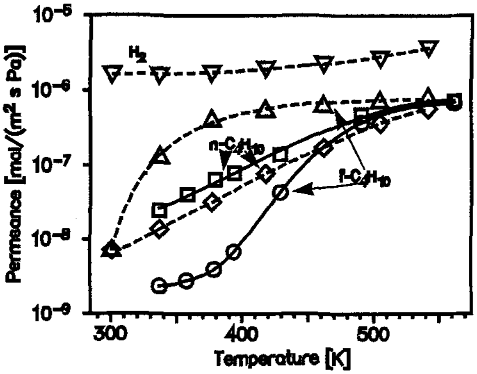

Figure 10. Permeances of n-butane, i-butane and H_2 through a *Type B* ZSM-5 membrane as a function of temperature. Solid lines: permeances for a 50/50 n-butane/i-butane mixture; dashed lines: single gas permeances ([27], reproduced with permission of the American Institute of Chemical Engineers Copyright © 1997 AIChE J., 43(7), 1797. All rights reserved).

It is also important to evaluate the steadiness of membrane operation, especially when adsorption governs the separation mechanism. Coronas et al. [25] carried out the n-hexane/2,2-DMB separation using ZSM-5 membranes [25]. Again, the ideal selectivity at 374 K was 2.1 and 17 for *type B* and *A* membranes respectively. However, much higher selectivities were found in the permeation of mixtures. The initial n-hexane/2,2-DMB selectivity on a *type B* membrane was 2580, which decreased to 500, after 29 h on stream. For a *type A* membrane a smaller decrease, from 79 to 70, was observed after 22 h. This clearly suggest the possibility of some kind of fouling of the membrane (e.g., by water or by other strongly adsorbed impurities of the commercial products), which directly compete with n-hexane adsorption. This was confirmed by performing the separation again, after calcination of the membranes at 753 K for 8 h, which restored the initial values of permeances and separation selectivity.

Analogous results on tubular silicalite membranes were obtained by Funke et al. [23,24,114], who demonstrated that n-alkanes, could be separated efficiently from branched and cyclic compounds (n-C_i/benzene, i=5-9; n-heptane/toluene) via adsorption of the n-alkanes, which blocked the pores and were selectively transported across the membrane. It should be noted, however, that longer paraffins were less efficient at blocking benzene: C_8/benzene and C_9/benzene selectivities were not as high as the selectivity for lower alkanes: the maximum selectivity reported in this work was 219 at 363 K, for the separation of n-hexane and benzene. On the other hand, mixtures of branched and branched and cyclic molecules (e.g., 2,2-DMB/3-methylpentane, benzene/i-octane and i-octane/methylcyclohexane) were not separated, probably because they have similar adsorption properties. Also, it was found that adding a second paraffin increased the separation selectivity. Thus, in the separation of n-heptane/n-hexane/i-octane, the presence of n-hexane further decreased the i-octane permeance and as a result the maximum n-heptane/i-octane separation selectivity increased from 59 to 138. This indicates that both n-hexane and n-heptane (with the same kinetic diameters and similar adsorption strengths on silicalite) used the same pathways across the membrane (silicalite pores and microdefects), and both of them cooperate in blocking the permeation of i-octane, which takes place mainly via defects in the silicalite layer. In addition, the authors concluded that permeances are strongly dependent on the type and concentration of the other species present; this implies that permeances of hydrocarbons in mixtures cannot be predicted from the single component permeances. The same authors [115] carried out an unsuccessful attempt to separate the p-xylene/o-xylene, p-xylene/ethylbenzene, m-xylene/ethylbenzene, p-xylene/toluene and p-xylene/toluene/benzene on a silicalite membrane. They explained their lack of selectivity by postulating that the molecule with the slowest permeation rate limits the diffusion and slows the other species down to its own pace in single-file transport through the ca. 0.55 nm zeolite pores of the membrane. This of course means that under the conditions of the experiment none of the permeating molecules has a clear-cut advantage regarding adsorption.

Few examples are available on the separation of organic/organic mixtures using zeolitic membranes without the MFI structure. Among these are the separation by pervaporation of benzene/n-hexane and benzene/cyclohexane using NaY tubular membranes [116]; the separation of benzene/p-xylene using a flat mordenite membrane [49] and the separation of cyclohexane/benzene, p-xylene/o-xylene and benzene/p-xylene mixtures using ferrierite flat membranes [117]. The zeolite NaY membrane yielded maximum benzene/n-hexane and benzene/cyclohexane separation factors of 29 and 45 at 378 K, with fluxes of 0.05 and 0.007 kg/(m^2·h), respectively. The mordenite membrane achieved a benzene/p-xylene factor that exceeded 160 at 295 K (with a total flux of $1.19 \cdot 10^{-4}$ mol/(m^2·s)), which was much greater than the theoretical value of 11.3 predicted from the gas-liquid equilibrium; this was explained as a result of shape selectivity at the mouth of the mordenite pores on the feed side, since benzene and p-xylene cannot pass each other inside the zeolitic pores. Using a ferrierite membrane, Nishiyama et al. [117] found a benzene/p-xylene separation factor of 101, whereas for the cyclohexane/benzene and p-xylene/o-xylene mixtures the separation factors were 1.3 and 3.2, respectively.

Separation of water or polar molecules from organic compounds

These separations are usually carried out by pervaporation (see Table 2) but they have also in been performed with gas phase feeds using silicalite [28] or hydrophilic membranes [35,118,119]. Since silicalite is organophilic, the permeation of the organic or less polar compounds in the mixture will be favored, while the opposite trend (faster permeation of water and/or strongly polar species) is expected with hydrophilic membranes.

Organophilic membranes

As shown in Table 1, silicalite membranes are organophilic zeolite membranes often tested for separations. In most of the separations with silicalite membranes on both ceramic and stainless steel supports, methanol [33], ethanol [30,120,121], acetone [33], acetic acid [122] and MEK (methyl ethyl ketone) [34] were separated by pervaporation from their mixtures with water. The maximum separation factors occurred at temperatures in the 303-323 K range with values of 14, 63, 255 and 146 for methanol, ethanol, acetone and MEK with permeation fluxes in the 0.15-1.3 kg/(m^2·h) range.

Sano et al. [123] carried out the separation of the methanol/MTBE (methyl-tert-butyl ether) mixture using a silicalite membrane on porous stainless steel, and obtained a maximum methanol/MTBE separation factor of ca. 10 at 303 K with a flux of approximately 0.1 kg/(m^2·h). In this case, the opposite, i.e., a MTBE/methanol separation factor higher than 1, could have been expected since MTBE is less polar than

TABLE 2

Separation of A/B mixtures by pervaporation in various zeolite membranes

Membrane	A/B Mixture	Temperature [K]	Feed [A wt%]	Flux [kg/(m^2·h)]	$\alpha_{A/B}$, Separation Factor
silicalite [33]	MeOH/H_2O	305	16.5	1.3	14.3
silicalite [121]	EtOH/H_2O	303	5[a]	0.6	63
silicalite [120]	EtOH/H_2O	303	5	0.15	63
silicalite [124]	EtOH/H_2O	303	4.65	0.6	64
silicalite [33]	acetone/H_2O	305	0.8	0.2	255
silicalite [122]	acetic acid/H_2O	303	15[a]	0.04	2.6
silicalite [34]	MEK/H_2O	307	5	0.32	146
silicalite [123]	MeOH/MTBE	303	50[a]	0.1	9
NaA [31]	H_2O/MeOH	323	5.5	0.23	2500
NaA? [29]	H_2O/EtOH	352	5	0.1	1633
NaA [31]	H_2O/EtOH	348	5.1	1.1	16000
NaA [60]	H_2O/EtOH	303	10	-	10000
NaA [125]	H_2O/EtOH	393	10.09	8.37	47000
NaY [31]	H_2O/EtOH	348	10	1.59	125
NaX [116]	H_2O/EtOH	348	10	0.98	410
NaA [31]	H_2O/acetone	323	5	0.83	6800
NaA [133]	H_2O/i-PrOH	348	10	1.5	5600
NaA [31]	H_2O/DMF	333	10.5	0.95	8700
NaA? [29]	H_2O/ButOH	361	40	0.72	2499
NaA [31]	H_2O/dioxane	333	10	1.87	9300
NaY [32]	MeOH/benzene	323	14	0.62	1400
NaX [116]	MeOH/benzene	323	10	0.57	74
NaY [32]	MeOH/MTBE	323	10	0.32	7600
NaX [116]	MeOH/MTBE	323	10	0.41	71
NaY [32]	EtOH/benzene	323	10	0.15	740
NaY [32]	EtOH/cyclohexane	323	14	0.19	540
NaY [116]	EtOH/ETBE	323	10	0.21	1200
NaY [116]	benzene/n-hexane	378	50	0.05	29
NaY [116]	benzene/cyclohexane	378	50	0.007	45

[a] vol%

methanol. The authors postulated that the separation took place also through the voids between silicalite crystals (size estimated at ca. 1 nm); they also measured the adsorption of the individual components on the whole silicalite membrane (i.e., silicalite crystals plus support), and found that the amount of methanol adsorbed at 303 K was almost 5 times larger than that of MTBE (176 vs. 37 mg/g).

On the other hand, Nomura et al. [124] measured the adsorption of ethanol on a silicalite on a stainless steel membrane prepared by the same procedure of Sano et al. [123], and found that the amount adsorbed was similar to that on silicalite powder; in addition, for the same relative pressure, the amount of ethanol adsorbed was higher than that of water, as expected given the hydrophobicity of the membrane. Finally, the amount of water adsorbed with an ethanol/water mixture, at a given partial pressure of water was lower than that measured using water as a single adsorbable component at the same partial pressure, i.e., the adsorption of water decreased because of the presence of ethanol. All of these findings correspond well with the organophilic character of silicalite. Finally, Sano et al. [78] increased the hydrophobicity of a silicalite membrane using vapor and liquid phase silylation techniques. As a result of the treatment, ethanol/water separation factor measured in pervaporation experiments increased, while the flux decreased.

Hydrophilic membranes

Several zeolite structures with high aluminum contents (MOR, LTA and FAU) have been prepared as hydrophilic membranes (see Table 3). In 1989, Ishikawa et al. [29] reported one of the pioneering works on separation with zeolite membranes. Using a zeolite membrane (probably zeolite NaA although this was not stated) with pores of 0.3-0.5 nm supported on a porous glass tube, they separated water/ethanol and water/butanol mixtures at 352-362 K, with separation factors of 2499 and 1633, and fluxes of 0.1 and 0.719 kg/(m^2·h), respectively. In other cases (see Table 2), high separation factors (several thousands, i.e., real separations) have been achieved by pervaporation through hydrophilic zeolite membranes for mixtures where the most polar species in the mixture (water, methanol or ethanol) was selectively transported.

It is often found that, as the feed concentration of the fastest permeating compound (water, methanol, etc. with hydrophilic membranes and the least polar

TABLE 3

Separation of the water/propanol/O_2 mixture on ZSM-5 and mordenite zeolite membranes. Water and propanol partial pressures in the feed were 2.0-2.7 and 0.3-0.4 kPa, respectively

	Water Permeance	Separation Selectivity	
Membrane	[mol/(m^2·s·Pa)]	H_2O/PrOH	H_2O/O_2
ZSM5	$1.6 \cdot 10^{-7}$	8.2	47
Mordenite	$1.4 \cdot 10^{-7}$	149	4.1

molecule with organophilic membranes) increases, its permeation flux and the separation selectivity also increase. On the other hand, an increase in temperature leads to a higher permeation flux and a lower separation factor. All of this is consistent with a mechanism dominated by adsorption, where an increase in the feed concentration of the permeating compound increases its surface coverage, while a higher temperature decreases it.

In spite of this, in pervaporation experiments it is generally observed that although both concentration and temperature have a direct effect on the permeation flux, the separation factor seems to be mainly governed by concentration. Thus for instance, Kondo et al. [125] reported a water/ethanol separation factor of 46.000 with a flux of 0.772 kg/(m^2·h) on a zeolite NaA membrane at 323 K with 10 wt% water in the feed. When the temperature was raised to 393 K, the total flux increased to 8.37 kg/(m^2·h), while the water/ethanol separation factor was substantially unchanged. However, when the water concentration was reduced to 5% and then to 1% at 323 K the separation factor decreased to 4800 and 500 respectively, with a proportional reduction in the measured water permeation flux (to 0.396 and 0.079 kg/(m^2·h), respectively).

As already mentioned, water/organic mixtures can also be separated in the gas phase. Piera et al. [28] used a composite hydrophilic membrane (mordenite/ZSM-5/chabazite) on a tubular α-alumina support for the gas phase separation of water/alcohol/O_2 ternary mixtures. Figures 11 and 12 show their results as a function of temperature. As expected, because of the high hydrophilicity of this membrane, water was selectively adsorbed, hindering the passage of methanol and O_2. The separation was

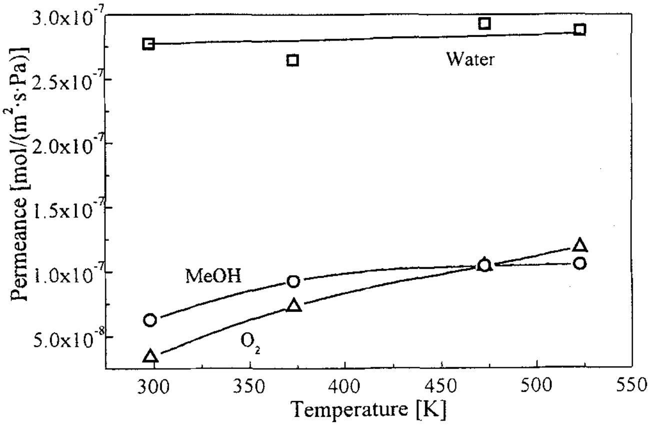

Figure 11. Water, methanol and O_2 permeances through a mordenite/ZSM-5/chabazite membrane as a function of temperature. Feed: water/methanol/O_2 mixture at a total pressure of 101.3 kPa (water and methanol partial pressures were 2.0 and 1.5 kPa, respectively, with the remainder being air) ([35], reprinted from Journal of Membrane Science, 149, E. Piera, M.A. Salomón, J. Coronas, M. Menéndez and J. Santamaría, "Synthesis, characterization and separation properties of a composite mordenite/ZSM-5/chabazite hydrophilic membrane", 99-114, Copyright (1998), with permission from Elsevier Science).

more efficient at the lowest temperatures tested; as the temperature was increased from 298 to 523 K water adsorption decreased, leading to a considerable increase of the methanol and O_2 permeances. This caused a decrease in the water/methanol and water/O_2 selectivities (Figure 12). However, even at the highest temperature tested (525 K) the water/methanol selectivity was still above 2.5, i.e., twice the Knudsen selectivity.

It is interesting to compare the separation selectivity achieved with molecules of the same family, with different polarity and adsorption properties. Piera et al. [28] changed the alcohol from methanol to ethanol and propanol in mixtures with water, over the same mordenite/ZSM-5/chabazite hydrophilic membrane. In order to minimize the differences in the contribution of capillary condensation with each alcohol, a similar

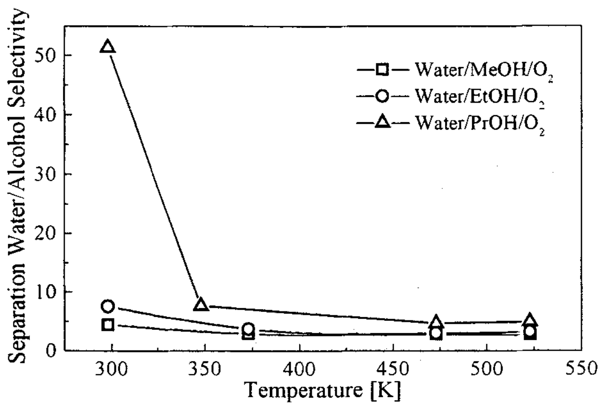

Figure 12. Water/alcohol separation selectivities through a mordenite/ZSM-5/chabazite membrane as a function of temperature. Feed: water/alcohol/O_2 mixture at a total pressure of 101.3 kPa. The water partial pressure in the feed was always 2.0 kPa, while the alcohol partial pressure was 1.5, 0.6 and 0.3 kPa, in experiments carried out with methanol, ethanol and propanol respectively ([35], reprinted from Journal of Membrane Science, 149, E. Piera, M.A. Salomón, J. Coronas, M. Menéndez and J. Santamaría, "Synthesis, characterization and separation properties of a composite mordenite/ZSM-5/chabazite hydrophilic membrane", 99-114, Copyright (1998), with permission from Elsevier Science).

relative pressure was maintained for each of the alcohols throughout the range of temperatures studied. Again, for all the mixtures tested, water permeated faster than the corresponding alcohol, with water/alcohol selectivity increasing in the order methanol<ethanol<propanol (Figure 12). Also, the highest water/alcohol selectivities were found at the lowest temperature tested (298 K): 4.4, 7.5 and 51 for methanol, ethanol and propanol, respectively. As temperature increased, the preferential adsorption of water became less important, and the water/alcohol selectivity decreased, being similar for the three alcohols. The permeance of the different alcohols followed the order propanol<ethanol<methanol. The contributing factors are the molecular size and the polarity of the permeating molecule, and in both cases the permeation of methanol is

favoured. In the same work [28], it was found that the permeation of O_2 was practically independent of the alcohol present in the mixture. A possible explanation is related to the fact that water and oxygen, with kinetic diameters of 0.27 and 0.35 nm, respectively, could use the channels of chabazite or even the small channels of mordenite, which are not trafficable for the alcohols. In this way, a change in the alcohol has a reduced effect on the permeance of oxygen. On the other hand, it seemed that water directly competes with oxygen for these permeation channels, which was confirmed in separate experiments with varying water partial pressures where a change in the water partial pressure from 1.5 to 2.0 kPa decreased the O_2 permeance by approximately 22%.

The hydrophilic character of a zeolitic membrane can be regulated by changing the Si/Al ratio. Figure 13 compares the results obtained with a mordenite membrane (maximum Si/Al atomic ratio= 11 at the outer surface) and a ZSM5 membrane (Si/Al atomic ratio= 32) in the separation of a water/methanol/O_2 mixture. For the most hydrophilic membrane (mordenite) the water/propanol separation selectivity was 149, while it was only 8.2 on the ZSM-5 membrane. Analogous results were obtained in the gas phase separation of water/n-butane/He [118] and water/propane/He [119] ternary mixtures using zeolite MFI and mordenite/ZSM5/chabazite tubular membranes. Water/n-butane and water/He selectivities as high as 8.3 and 7.6, respectively, were obtained at 298 K. In this case, in addition to preferential water adsorption, capillary condensation and molecular sieving also played a role in the water/hydrocarbon and water/He separations observed.

Final remarks

Throughout this work, it has been shown that most of the successful separations reported can be qualitatively explained, with preferential adsorption often being the determining factor. Nevertheless, many difficulties remain, and we are far from fully understanding the development of zeolite membranes or controlling their performance. On the contrary, this is an emerging area of enormous potential, whose investigation has barely begun. In particular, an intense research effort is needed on the following topics:

i) Extend the preparation procedures of zeolite membranes to another zeolite structures different from the common MFI, LTA, FAU or MOR, in order to

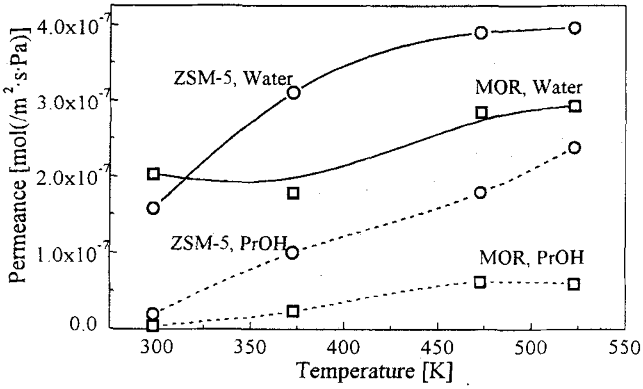

Figure 13. Water and propanol permeances through a mordenite/ZSM-5/chabazite and ZSM-5 membranes as a function of temperature. Feed: water/propanol/O_2, total pressure 101.3 kPa. The water and propanol partial pressures in the feed were respectively 2.0 and 0.3 kPa for the composite membrane, and 2.6 and 0.4 kPa for ZSM-5 membrane ([35], reprinted from Journal of Membrane Science, 149, E. Piera, M.A. Salomón, J. Coronas, M. Menéndez and J. Santamaría, “Synthesis, characterization and separation properties of a composite mordenite/ZSM-5/chabazite hydrophilic membrane”, 99-114, Copyright (1998), with permission from Elsevier Science).

tackle new problems in the separation of mixtures. The preparation of defect-free, small-pore zeolites (KA, chabazite, etc.) should allow molecular sieving separations of gas mixtures such as N_2/CO_2, H_2/CO_2, N_2/O_2, etc.

ii) Improve control over the synthesis of zeolite membranes, mainly by separating and fine-tuning the nucleation and growth processes. This should lead to a reduction of the thickness of the zeolite membranes (and a higher permeability), without increasing the defect density. Some scarcely explored avenues include a better control of the temperature during the heating and cooling periods, and the preservation of a constant composition of the gel in contact with the membrane, perhaps with continuous flow of the synthesis solution.

iii) It is also necessary to reproducibly modify zeolite membranes. This is already being investigated as a means to repair membranes (e.g., by plugging defects) or improve their quality; other areas include the modification of the pore size of zeolites, and of its adsorption properties (e.g., via cation exchange). In this respect the potential for modification is large (e.g., exchanging Na^+ with Ca^{2+} produces a change of 3 orders of magnitude in the diffusivity [126]).

iv) Develop alternative methods to fabricate dense layers of oriented zeolite crystals. It is important to be able to make these on top of commercially available tubular supports, whose roughness is often considerable. If the zeolite crystals are grown inside the support pores, a better control is needed of the depth at which the synthesis takes place.

v) Develop reactor applications for zeolite membranes. It has recently been shown [127] that the use of flow-through catalytic microporous membranes can lead to significant improvements in selectivity by suppressing overreaction. Also, membranes are frequently proposed as a means to increase conversion by equilibrium displacement using selective product removal. The main challenge regarding the use of membranes in this area is related to the fact that the separation selectivity disappears at the high temperatures (e.g., 500-900 K) where many reactions take place. However, there are examples of industrially important processes such as isomerization and metathesis reactions [128] or MTBE synthesis [129], where the low reaction temperature allowed the use of a membrane for selective product separation.

vi) A broad modelling approach is needed where realistic membrane systems are considered. This will contemplate the separation of mixtures in membranes with different types of pores (zeolitic pores, defects or intercrystalline pores, effect of the support). Also, since in many cases the separation is due to competitive adsorption phenomena, it is necessary to undertake modelling of adsorption and transport processes in the presence of multicomponent mixtures.

vii) Develop methods for implementation of zeolite membranes at a larger scale. Since the common tubular or flat supports usually employed until now have a low permeation area per unit volume, multitubular modules seem to be the best option for industrial separations. As higher temperature applications are considered, significant developments in sealing and manifolding will be needed. This will probably limit the industrial use of zeolite membranes to those synthesized on stainless steel supports.

viii) The binary, and sometimes ternary, mixtures separated until now with zeolite membranes are mainly academic systems. It would be interesting to tackle real and industrially important separations, with a higher number of components and in the presence of impurities.

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