Synthesis and Properties of Zeolitic Membranes

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I. INTRODUCTION

Zeolite-based separations involve pressure swing or temperature swing adsorption. These are unsteady-state processes which rely on cycles of preferential adsorption (of one component over the other) and subsequent desorption. Replacement of a swing adsorption process with a steady-state process is arguably advantageous for several reasons, including lower operating costs and reduced energy consumption. Over the last decade, much attention has been focused on the development of continuous zeolite-based separations processes. For such purposes, the natural configuration of the zeolite material is in the form of a thin film or membrane supported on, or deposited in, a porous substrate. A well-fabricated zeolite membrane would be expected to behave as a continuous separation device, with reasonably high selectivity and flux. Many separations that are currently carried out using distillation, crystallization, and other conventional processes can be carried out with a much less energy-intensive zeolite membrane-based separation process. The widely exploited catalytic properties of zeolitic materials also imply the possibility of catalytic membrane reactor processes, combining selective catalysis with selective separations.

The above reasons account in part for the large amount of research effort on zeolite membranes over the last decade. At the same time, zeolite membranes have been pursued for other potential applications in the fields of sensor technology and electrochemistry. Zeolite materials can be used as selective sensing materials due to their high selectivity and low diffusion resistance for certain molecules over other molecules. Similarly, their affinity for charge-balancing metal cations makes them suitable for use as ion-exchange electrodes. In these cases also, a thin zeolite membrane is the most favored configuration that has minimal diffusion resistance and high selectivity. In this chapter, recent developments in the field of zeolite membrane synthesis will be reviewed in detail.

The earliest application of zeolitic membrane devices (1940s) appears to have been as ion-selective electrodes (1–3). These devices mainly employed zeolites such as NaA, NaX, and NaCaA. In these studies, zeolitic membranes were fabricated by pressing zeolite

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powders into thin disks. In the 1950s, 1960s, and later, zeolitic membranes were synthesized by dispersing the zeolite crystals in polymer membrane matrices (4–6). In this case, the adhesion of the zeolite particles to the polymer matrix was usually promoted by dispersing the zeolite in the monomer, followed by polymerization to a plastic phase. The best-known example of a zeolite-polymer composite membrane is that of the silicalite-silicone (polydimethylsiloxane) rubber composite membranes (7–11). Due to the hydrophobic nature of silicalite (a pure silica zeolite), these membranes could be used for pervaporative alcohol (C1–C3)/water separations with a binary selectivity factor ($\alpha$) as high as 50 (8). Zeolite-polymer composite membranes have seen continuing interest to the present day (12–18), although they will not be discussed further here.

In 1987, a method was patented (19) for the synthesis of polycrystalline zeolite membranes supported on a substrate. Most work in the last decade has been focused on zeolite membranes supported on ceramic, glass, or metal substrates. In some cases, composite supports such as TiO2-coated stainless steel have also been used. The macro-porous (i.e., having low diffusion resistance) support provides mechanical stability whereas the thin zeolite layer is intended to perform selective separations. Clearly, the basic requirement for the effectiveness of such a process is the existence of a continuous, largely defect-free zeolite layer on the support surface. Continuity of the polycrystalline zeolite layer results from closely interlocked (intergrown) crystals. This ensures that a large fraction of the total flux from the membrane surface originates from the zeolite nanopores, and not from intercrystalline porosity or defects such as pinholes and cracks.

The first step in the synthesis of a noncomposite zeolitic membrane is to identify a zeolite material that is expected to possess the ability to perform a particular kind of separation. This information is usually derived from adsorption and diffusivity data obtained using powder samples or single crystals, and indicates an estimated level of permeability and selectivity that can be achieved with the zeolite under consideration. Second, it is desirable to have literature information on the synthetic chemistry of the zeolite, i.e., the temperature conditions required for hydrothermal synthesis, and the required reactants. These include a silica source and an alkaline hydroxide (NaOH, KOH). An organic structure-directing agent (SDA) and an alumina source are also often used. Using this preliminary information, one attempts to synthesize by trial-and-error methods a thin, continuous zeolite layer over the surface of a support. The films can then be characterized by a number of techniques, including X-ray diffraction (XRD; to determine crystallinity and crystal orientation in the membrane), scanning electron microscopy (SEM; to examine the morphology of the membrane surface and cross-section, and to detect membrane defects), and electron probe microanalysis (to microscopically determine the membrane composition).

Zeolitic membrane synthesis techniques occurring in the recent literature can be broadly classified into two types. The first category is referred to as the “in situ” membrane growth technique. In this technique, the support surface is put in direct contact with the alkaline solution containing the zeolite precursors, and then subjected to hydrothermal conditions (usually temperatures of 350–473 K and autogenous pressure). Under the appropriate conditions, nucleation of zeolite crystals occurs on the support, followed by their growth to form a continuous zeolite layer over the support. At the same time, reaction events occurring in solution can lead to deposition of nuclei and crystals on the surface, followed by their incorporation into the membrane. Several variants of the in situ process have been reported. One such case, called the vapor phase transport method, involves deposition of an amorphous aluminosilicate gel layer on the support, and the diffusion of water and the organic SDA into this layer from a vapor phase to transform the gel layer into a crystalline zeolite layer under hydrothermal conditions.
The second category is referred to as the secondary (or seeded) growth technique. See Fig. 1 for a schematic representation of this method, in which zeolite nucleation is largely decoupled from zeolite growth by predepositing a seed layer of small (typically $\sim 100$ nm or smaller) zeolite crystals on the support surface. For this purpose, several surface seeding techniques are currently in use and will be reviewed in a following section. The seeded surface is then exposed to hydrothermal growth conditions whereupon the seed crystals grow into a continuous film. As will be discussed below, this method may offer greater flexibility in controlling the orientation of the zeolite crystals and the microstructure of the

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**Fig. 1** (a) Schematic of the secondary (or seeded) growth technique. (b) Events taking place during hydrothermal treatment and in the presence of precursor seeds. (From Ref. 20.)
zeolite membrane because it decouples the nucleation and the growth steps. As a result, the orientation and morphology of the membrane can be manipulated in principle by changing the morphology and orientation of the deposited seed layer, followed by secondary growth under the appropriate conditions. Figure 1b summarizes the events occurring upon hydrothermal growth of zeolite membranes (20). Irrespective of the synthesis technique used, the thickness of the zeolite layer can obviously be controlled by changes in the synthesis conditions. Less obvious is the control of membrane morphology and orientation by varying the reactant concentrations and reaction conditions. Changes in morphology and crystallographic orientation of the membrane affect the degree of crystal intergrowth. For example, a membrane in which the crystals have a relatively high in-plane growth rate will have a higher degree of crystal intergrowth than a membrane whose crystals have a high out-of-plane growth rate.

The flux and selectivity (both single-component and mixture) of the synthesized membranes are measured using permeation cell devices of various types (21). These allow contact of the feed on one side of the membrane, with the concentrations of the permeate being measured on the other side by GC or other analytical techniques. If an organic SDA is occluded in the pores of the zeolite framework, the membranes must first be calcined by heating to high temperatures (typically higher than 650 K) to decompose and remove the organic species. The membranes can be in either a disk or tube geometry, and can be oriented in two ways, with the zeolite layer facing either the feed side (the commonly used arrangement) or the permeate side. Permeation measurements are most often carried out either by the pressure drop or the Wicke-Kallenbach method (21). In the former method, a pressure gradient provides the driving force for permeation by either pressurizing the feed or evacuating the permeate side. The pressure drop configuration can be operated in either a steady-state mode (with continuous removal of the permeate by vacuum) or a batch mode (where the permeate side is a closed chamber that is initially evacuated and allowed to build up pressure as the permeate diffuses in). In the Wicke-Kallenbach mode, a concentration gradient is imposed by using a sweep gas to remove the permeate. The latter arrangement is useful for both single-component and multicomponent measurements. This type of permeation cell consists of two small chambers that are segregated from each other by sealing the zeolite membrane between them. Each chamber has a gas inlet and outlet. The feed entering one chamber is partially absorbed by the membrane, the remainder leaving the outlet as retentate. The permeate side is usually flushed with an inert sweep gas such as helium or argon. The outlet of the permeate side therefore consists of a mixture of sweep gas and the permeate from the membrane. This can be analyzed by a gas chromatograph to determine the composition of the permeate gas. If the volume flow rate of the permeate stream is also measured, the fluxes of each component can easily be calculated. The entire assembly can be placed in a heating oven to control the temperature.

Efforts to quantitatively understand and predict the transport properties of zeolitic membranes have been an integral part of zeolite membrane research. The simplest description of transport in zeolites is provided by Fick’s law, which relates the permeation flux of a species through the zeolite layer to its concentration gradient, using a proportionality constant called the Fick diffusivity. The boundary conditions are derived by assuming thermodynamic equilibrium at the feed–zeolite and zeolite–permeate interfaces, so that an adsorption isotherm can be used to calculate the adsorbed concentrations at the interfaces. However, transport measurements showed quite early (22) that the Fick diffusivity of a species permeating through a zeolite was unfortunately not a constant but could vary in a complicated manner as a function of the partial pressure. Theories based on temperature-activated site hopping mechanisms for molecules adsorbed in zeolites were developed
(23,24), which could explain the concentration dependence of the Fick diffusivity by hypothesizing different types of kinetic expressions for site-to-site jumps of the permeating species. However, the most general description of multicomponent transport in zeolites is the Maxwell-Stefan formulation (25–28). In the Maxwell-Stefan equations, the multicomponent fluxes are related to the chemical potential gradients, which replace the concentration gradients of Fick’s law as the driving forces for transport. When these expressions are cast in the form of Fick’s law, it is found that the Fick diffusivity is a complicated function of the concentration and is a product of two contributions. The first contribution is from purely kinetic effects and can be interpreted as an intrinsic diffusivity for site hopping. The second contribution is a thermodynamic correction factor and accounts for nonideality in the relation between the chemical potential in the Maxwell-Stefan equations and the concentration in Fick’s law. This factor is derived from the equilibrium adsorption isotherm of the species in the zeolite. For the multicomponent mixture, the Maxwell-Stefan equations are in matrix form, containing a diffusivity matrix. Each diagonal element of the diffusivity matrix describes the diffusion of molecules of a particular species in the zeolite, whereas the off-diagonal terms can be interpreted as describing counterexchange of molecules of two different species adsorbed on neighboring sites. The Maxwell-Stefan model can be solved (either analytically or numerically) for several frequently encountered situations, such as single-component diffusion, binary diffusion, single-file diffusion (wherein the zeolite pores are too small to allow counterexchange of molecules), as well as the general case of multicomponent permeation. The theory has provided a good description for most of the steady-state and transient permeation behavior observed in zeolites. In the case of zeolite membranes, the theory works well when transport occurs predominantly through the zeolite and not through defects or intercrystalline porosity, and when the degrees of freedom of the zeolite lattice can be neglected (i.e., when a rigid lattice is assumed). Section II of this review discusses several examples where nonzeolitic porosity as well as lattice flexibility can be important in transport through zeolite membranes. It may also be mentioned that apart from the activation barriers for site hopping in the zeolite framework, other types of transport resistances may also exist at the zeolite surface. For sufficiently thin zeolite films, there may be a significant surface resistance contribution arising from a large energy barrier for desorption of molecules at the zeolite surface as they exit the zeolite. Mathematical descriptions of this effect can be found in Refs. 29 and 30, and some calculations for surface resistance–influenced permeation in silicalite zeolite membranes are available in Ref. 31. Details of the study of transport in zeolites are discussed in other chapters of this volume.

In Sec. II, the synthesis of different types of zeolitic membranes by in situ crystallization and secondary growth will be discussed. In this section, we also include the synthesis of membranes of nanoporous aluminophosphates, metal-substituted zeolites, and microporous tetrahedral-octahedral mixed-oxide materials. In Sec. III, we review different methods used for seeding of surfaces with zeolite crystals, a process of great importance for growing zeolite membranes suitable for technological applications. The concluding Sec. IV contains a discussion of other emerging applications of zeolitic films.

II. ZEOLITE MEMBRANES BY IN SITU AND SECONDARY GROWTH

Only a few zeolite types have so far been fabricated into membranes. The most widely studied zeolite is MFI (ZSM-5 or the pure silica analog silicalite-1). Other zeolite structures that have been formed into membrane devices are zeolite A, faujasite (X and Y forms), mordenite, ferrierite, MEL, and zeolite P. In addition, aluminophosphate
membranes have also been synthesized from the SAPO-34 and SAPO-5 frameworks. We provide below a review of the membrane synthesis and characterization research on the major zeolite types used so far.

A. Zeolite A Membranes by In Situ and Seeded Growth Techniques

It is appropriate to begin with a discussion on zeolite A membranes, since these were the first zeolite membranes to be commercialized (by Mitsui Corporation) for pervaporation and vapor permeation applications. Zeolite A (zeolite framework atlas code LTA) is an aluminosilicate zeolite that has been widely used in ion exchange applications. This is a small-pore zeolite with pores smaller than 5 Å in effective dimension. The pore dimension can be controlled by means of ion exchange. Due to the presence of aluminum in the framework, charge-balancing cations are required. The most common form used in membrane preparation is the sodium form, called NaA. Since this zeolite is hydrophilic, it has potential for selectively permeating water from water/organic liquid mixtures. For this purpose, NaA membranes were synthesized on the surfaces of porous tubular supports of alumina, mullite, or cristobalite (32–34). The use of tubular supports is arguably more suited to industrial applications than are flat surfaces such as disks. The zeolite NaA membranes were fabricated using a seeded growth technique. Seed crystals of zeolite A were coated on the substrate surface by mechanical dispersion (rubbing). This type of seeding procedure has been used before in other types of film growth processes, such as diamond films. Hydrothermal synthesis was then carried out using a gel phase prepared from sodium silicate, aluminum hydroxide, and deionized water. The synthesis temperature was 373 K and the time about 3 h. No organic SDA is used in the preparation of these membranes, which are 10–30 μm in thickness. Electron probe microanalysis (EPMA) showed three distinct compositional regions in the cross-section, namely, the support, the zeolite membrane, and a middle layer between the membrane and the support having composition intermediate between that of the substrate and the zeolite. X-ray diffraction indicated no preferred orientation of the crystals in the membrane.

A recent report (34) examined the sequence of events that lead to the formation of these zeolite NaA membranes (Fig. 2). The membrane crystallization is preceded by the formation of a gel layer over the seed coating, which subsequently transforms into a zeolite layer. At growth times greater than about 3 h, zeolite P crystals began to grow on the zeolite A layer, reducing the pervaporation performance of the membranes. These membranes were found to have high selectivities for water over ethanol in various mixtures (20–95% ethanol). Very high water selectivity (about 45,000) was found for a feed containing 10% water by mass. The water flux was of the order of 2 kg m⁻² h⁻¹ and increased with increasing feed temperature between 300 and 400 K. A more detailed experimental study (35) of pervaporation of alcohol–water mixtures in NaA membranes has also been carried out. The flux of water was found to remain independent of the alcohol in the mixture (methanol or ethanol), a fact that was also true for other mixtures such as acetone–water and ethyl acetate–water. This is consistent with the high preferential adsorption capacity of the zeolite for water molecules. It was suggested that water forms a mobile, capillary-condensed phase in the zeolite pores, thus blocking entry of the organic molecules. However, small but finite amounts of organic components always found in the permeate indicate their possible diffusion through nonzeolitic (intercrystalline) pathways such as grain boundaries and occasional pinholes, microcracks, and other defects.

It may be concluded from the studies described above that zeolite A membranes are advantageous over polymeric membranes for the dehydration of organic mixtures by
Fig. 2  SEM images of the (a) surface and (b) cross-section of the seeded support tube, and (c–f) surface of zeolite NaA membranes after 1, 2, 3, and 6 h, respectively, of the synthesis. (From Ref. 34.)
pervaporation. These advantages include the following: (a) high flux and selectivity, (b) higher temperature stability, and (c) absence of swelling (and subsequent loss of structural integrity) upon contact with water/organic mixtures. However, zeolite A membranes suffer from limited acid stability. This shortcoming precludes their use in separations involving acidic mixtures or in membrane reactors for reactions that take place in acidic environments.

Apart from pervaporative applications, zeolite membranes have been studied as candidates for performing gas separations. In the case of zeolite A membranes, their permeation properties for gases like He, H₂, CO₂, O₂, N₂, CH₄, and C₃H₈ have been reported (34,35). Under gas permeation conditions, the zeolite NaA membranes in Refs. 34 and 35 were found to be impermeable to gases unless completely dried. Evidently the presence of water in the hydrophilic NaA framework leads to this impermeability. The gas permeation properties of the dehydrated membranes were found to be dominated by Knudsen diffusion, and not by configurational diffusion through the zeolite pores. However, a different report (36) has claimed selectivities for gas molecules somewhat larger than their Knudsen values, in the case of single-component permeation. The ideal (single-component) H₂/N₂ and H₂/CO₂ selectivities were about 10. These are above the Knudsen values (<5), suggesting that the membrane possessed molecular sieving properties. The binary selectivities were somewhat lower but still above the Knudsen values. However, the study also indicated poor reproducibility of the membrane characteristics—only one out of three synthesized membrane samples had molecular sieving properties, whereas the others exhibited only Knudsen selectivity. The poor reproducibility was attributed to the lack of control over the intercrystalline porosity. Based on the experimental results and the assumption of a model involving both zeolitic and nonzeolitic pores, it was estimated that the total contribution of the hydrogen flux from Knudsen diffusion varied from 10% to 30% for the membrane samples investigated. For larger molecules that enter the zeolite framework less easily, the fraction of Knudsen flux would be still higher. Another study (37) reports more extensive binary gas permeation experiments with zeolite A membranes. In the case of He/n-C₄H₁₀ and H₂/n-C₄H₁₀ permeation, the binary fluxes were the same as the single-component fluxes. Based on these observations, it was suggested that the smaller molecules (He and H₂) permeated through the zeolitic pores whereas the n-C₄H₁₀ molecules permeated mainly through the larger, nonzeolitic pores. However, the reported binary He/n-C₄H₁₀ and H₂/n-C₄H₁₀ selectivities were about 6, close to the Knudsen selectivity (5.4). It therefore appears difficult to deduce that the H₂ and He permeate through the zeolite pores. The fluxes of larger molecules such as O₂ and C₂H₆ are reduced from their single-component values, and it was suggested that these molecules experience competition with the n-C₄H₁₀ molecules for transport through the nonzeolitic pores. However, the selectivities are again close to Knudsen values.

When n-C₄H₁₀ is replaced with H₂O, the binary permeation behavior changes dramatically. Water permeates much faster than all other permeants irrespective of their size, probably due to the hydrophilic nature of the zeolite membrane. In most of the mixtures, water permeated at least two orders of magnitude faster than the second component, except in the case of O₂ and CO₂. For these systems the water selectivity was somewhat lower, an effect that may arise from the affinity of water for these gas molecules. Two other reports (38,39) claim high H₂/n-C₄H₁₀ selectivities for zeolite NaA membranes grown by the secondary growth technique on α-alumina supports. The secondary growth was carried out in three stages in an attempt to improve the quality of the membrane. Preliminary results reported in Ref. 38 indicated a high H₂/n-C₄H₁₀ selectivity of about 100 using a single membrane sample, but more extensive permeation
measurements reported in Ref. 39 indicated a lower selectivity of about 20 for typical
membrane samples. To date, research on gas permeation properties of zeolite A mem-
branes has not established their suitability for performing gas separations. The main
reason for this is the difficulty in preventing the nonzeolitic porosity, arising from the
necessity of dehydrating the membranes prior to gas permeation.

A recent study has reported the synthesis of NaA membranes on seeded supports in
contact with a clear solution (40). This was achieved by increasing the alkali (NaOH)
content of the reaction mixture, thus solubilizing the silica and alumina species, which
would form a gel at the lower pH used in previous studies. This synthesis also resulted in
the formation of membranes with similar pervaporation and gas permeation properties as
previously reported. However, these authors have made a more detailed study on the
events occurring during the growth of zeolite NaA membranes. Other zeolite phases (such
as hydroxysodalite and zeolite X) are found to form on the support as the synthesis time
proceeds. A sequence of events occurring in the seeded growth of NaA membranes from
clear solutions has been proposed (40,41). In agreement with previous studies, the initial
step was the formation of a gel layer on the seeded support surface, followed by nucleation
and growth of NaA crystals. As time passes, the zeolite A crystals begin to dissolve,
leading to the formation of other zeolites that are then incorporated in the membrane.
This is supported by the observed decreases in the intensities of the NaA XRD peaks upon
increasing the synthesis time beyond 3 h, as well as the appearance of peaks assigned to
other zeolite materials. In the absence of the seed layer, no continuous NaA membrane
could be formed on the support surface, which was covered with a discontinuous layer
comprising several zeolite types. Therefore, it appears that the presence of the NaA seed
layer promotes the formation of zeolite A, which is a metastable phase competing with
other phases of similar (or higher) stability under the given growth conditions.

A few reports have addressed the above problem of byproduct formation in the
synthesis of zeolite A membranes by adopting alternative synthesis routes. One study
reports the delaying of the zeolite A transformation into other phases by application of a
temperature gradient between the support and the reaction solution (42). In particular, the
unseeded porous stainless steel support was directly heated to temperatures above 415 K
using a resistance heater, whereas the reaction solution was kept at around 315 K by
immersing the reaction autoclave in a water bath. A highly crystalline and apparently
continuous (by SEM) membrane of pure zeolite A was formed on the support with
synthesis times varying from 12 to 72 h. However, no permeation properties were reported
for these membranes. Another report has described the formation of a zeolite A membrane
on an unseeded polytetrafluoroethylene (PTFE) surface heated by a plate heater (43). This
synthesis was carried out in a static reaction solution as well as a circulated reaction
solution. The resulting membrane was composed of large crystals, 30–60 μm in size.
However, the static solution growth yielded the usual cubic crystal shape, whereas the
circulated solution growth yielded a membrane containing crystals with a globular
morphology. Also, the membranes synthesized by the static method using long synthesis
times (greater than 12 h) had deposits of dense phases such as chabazite and gmelinite,
whereas the circulated solution yielded only zeolite A. While the formation of a zeolite A
membrane is preceded by the formation of an amorphous gel over the surface, the
byproducts nucleated in the solution phase and deposited on the surface at long synthesis
times. The above studies have yielded interesting information on the sequence of events
occurring during the crystallization of zeolite A membranes under various conditions.
However, the relationships between the membrane structures obtained, and their perme-
ation properties, remain to be investigated.

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In general, the effect of preferred orientation of crystals on molecular transport through zeolite membranes is expected to be significant due to the highly anisotropic pore networks found in many zeolites. Preferred orientation of the crystals can affect not only the diffusion rates through the zeolite layer, but also the density and morphology of the intercrystalline pores. In the case of zeolite A, the effect of preferred orientation on intrinsic diffusion rates through the zeolite is expected to be negligible, since the zeolite possesses a cubic crystal structure and has an isotropic pore network with equal diffusion coefficients in all crystal directions. Highly oriented zeolite A films have been synthesized on nonporous glass supports (44) as well as on porous alumina supports (45). While the films synthesized on nonporous glass substrates are not applicable as separations devices, their synthesis illustrates some of the important techniques used for deposition of zeolite seed layers on surfaces, as discussed in a following section. Both the seed layer as well as the resulting zeolite A film after secondary growth are highly oriented, with the \( \{h00\} \) reflections showing high intensity and other reflections being virtually absent. The oriented zeolite A membranes grown on porous alumina supports had high selectivity for water over ethanol in pervaporation experiments.

This summary of the synthesis efforts directed to zeolite A membranes indicates that most of the membranes synthesized by seeded growth show similar morphological and permeation properties. The high pervaporation selectivities shown by both highly oriented and nonoriented zeolite A membranes indicates the independence of permeation properties on crystal orientation, as expected if the cubic zeolite A framework is considered. While these membranes are highly selective for water in pervaporation processes (leading to their current commercial application), their effectiveness in gas permeation was reduced by the presence of intercrystalline porosity. This intercrystalline porosity may be a result of the synthesis conditions (in which case it possibly can be avoided by manipulating the synthesis conditions), or it may be a result of cracking and framework shrinkage during dehydration of the zeolite prior to performance of gas permeation studies (in which case it is more difficult to suppress). Another possible explanation for the poor gas permeation properties of zeolite A is the formation of dense amorphous material on the surface of the zeolite A crystals during drying of the membrane prior to gas permeation. The formation of amorphous material on the zeolite surface may render the zeolite crystals inaccessible to the diffusing species, so that they permeate mainly through the intercrystalline pores which only have Knudsen selectivity. In a recent study (46) of the nucleation and growth of zeolite A in the presence of tetramethylammonium (TMA) cations, it was suggested based on transmission electron microscopy (TEM) images that at certain stages of crystal growth, crystalline zeolite A cores become surrounded by an amorphous gel that is consumed by crystallization as time passes. If such a growth mechanism dominates all synthesis of zeolite A crystals, it is possible that the zeolite A membranes reported in various studies incorporate an amorphous coating. This coating should be converted to crystalline zeolite A by some method before application of the membranes for separations. The formation of crystalline byproduct phases can also hinder the synthesis of pure zeolite A membranes with good molecular sieving properties. However, some new synthesis approaches have succeeded in eliminating this difficulty by suppressing the nucleation events occurring in the solution (where the byproduct phases appear to start forming) and promoting the zeolite condensation reactions at the zeolite A membrane surface.

### B. Zeolite MFI Membranes by In Situ Growth Techniques

The largest amount of work has been done on membranes with the framework topology of MFI (also known as ZSM-5 or its pure silica form, silicalite-1). This is due to two factors
(a) this zeolite has among the most extensive literature regarding synthesis, and (b) its medium-sized pore network leads to the possibility of performing hydrocarbon separations. The crystallization of a selective MFI membrane was first reported in 1992 (47). In this case, the in situ growth of a high-silica MFI membrane was demonstrated on several nonporous surfaces such as Teflon, silver, and stainless steel, as well as on a porous Vycor glass disk. The as-synthesized membranes could be easily removed from the Teflon and silver surfaces but not from stainless steel and Vycor. The synthesis medium was a gel formed by mixing colloidal silica, sodium hydroxide, water, and tetrapropylammonium bromide (TPABr) as the SDA. Since the neutral bromide salt of the TPA cation is used, sodium hydroxide must be added to provide an alkaline medium. Alternatively, tetrapropylammonium hydroxide (TPAOH) can be used as an SDA, in which case addition of a second alkali is not necessary. XRD and SEM revealed a dense, intergrown layer of high-silica MFI crystals on the support surfaces. These membranes were synthesized over several days and were quite thick (up to 25 μm). Unlike the zeolite A membranes, the MFI membranes must be calcined to remove the SDA and open the zeolitic porosity for adsorption and diffusion of permeants. After calcination, the membranes reported in Ref. 47 were found to be selective (α = 17) for n-hexane over dimethylbutane during vapor permeation, indicating shape-selective separation by the zeolite layer. The membranes used for these permeation studies were self-supported membranes removed from the silver surface on which they were grown and were sealed in a permeation cell with epoxy resin.

Between 1992 and 1996, several reports investigated the application of MFI membranes in pervaporation processes. High-silica MFI is hydrophobic, and ZSM-5 can be synthesized with varying degrees of hydrophilicity by changing the aluminum content. High-silica MFI membranes would therefore exhibit the opposite behavior to zeolite A membranes, i.e., they would selectively permeate organics from an organics/water mixture. Hence, the pervaporative separation of ethanol from an ethanol/water mixture was investigated (48). The synthesis was carried out by the in situ method on porous stainless steel or porous alumina disks with pore diameters of 0.5–2 μm. TPABr was used as the SDA and the reaction proceeded from a gel medium for 48 h at 443 K, leading to the formation of a continuous layer of zeolite crystals, 10–25 μm thick as measured by SEM. It was also found that the size and degree of intergrowth of the crystals was highest near the membrane surface and lowest near the membrane–support interface. Characterization by XRD revealed no preferred orientation of the crystals. The membrane samples were detached from the stainless steel surface and were characterized by mercury porosimetry to investigate the presence of defects and pores larger than those of the zeolite. Results showed a single sharp peak in the region of 500 nm, which was attributed to the presence of pores between the zeolite crystals in the region near the membrane–support interface, where the crystals are not well intergrown. However, since these large pores disappear near the membrane surface due to closure of the growing zeolite layer, it was suggested that the membranes can be used in separations. These membranes were tested for defects and cracks by ethanol/water permeation experiments prior to calcination. The ethanol concentration in the feed was 5%. Very low ethanol fluxes (~10^{-3} kg m^{-2} s^{-1}) were measured and water was found to permeate slightly faster than ethanol. This indicates that the membrane was essentially defect-free before calcination and that the observed permeation was through the intercrystalline grain boundaries. The latter are presumably more hydrophilic than the pores inside the zeolite crystals due to surface hydroxyl groups in the grain boundary regions. After calcination, the membranes permeated ethanol with a high selectivity (~60) and with flux ~1 kg m^{-2} s^{-1} (i.e., an increase of three orders of magnitude from the uncalcined membrane). This separation performance was attributed to the high hydrophobic properties of high-silica MFI, which
adsorbs ethanol selectively from the ethanol/water mixture. Another report using essentially the same synthesis examined the separation of acetic acid from acetic acid/water mixtures with acetic acid being the minor component (~15%) in the feed (49). The membranes selectively permeated acetic acid with a flux \( \sim 0.1 \text{ kg m}^{-2} \text{s}^{-1} \) and selectivity \( \sim 10 \). The lower selectivity and flux of acetic acid as compared with ethanol are attributable to the more hydrophobic nature of ethanol over acetic acid.

A slightly different synthesis technique for MFI membranes on the surface of \( \alpha \)-alumina substrates was reported in Refs. 50 and 51. An in situ growth technique was developed that involved contact of the support surface with a synthesis gel. The membranes showed a modest \( n\text{-C}_{4}\text{H}_{10}/i\text{-C}_{4}\text{H}_{10} \) selectivity of \(~6\). In Ref. 52, this technique was improved to produce selective MFI membranes. High-silica MFI membranes were prepared on porous tubular supports of alumina (pore size \(~5\) nm) and stainless steel (pore size \(~500\) nm). A synthesis gel was prepared from fumed silica, TPABr, NaOH, and water, and was aged for at least 24 h. The porous supports were then filled with the gel and capped with Teflon before hydrothermal treatment in a Teflon-lined autoclave at 453 K.

The procedure was repeated twice to form a continuous silicalite membrane on the inner surface of the supports. These membranes preferentially permeated methanol from its binary mixtures with water (with the organic content being 3.5–16.5%). The membranes synthesized on stainless steel supports had higher methanol flux (\(~1.0 \text{ kg m}^{-2} \text{s}^{-1}\)) and selectivity (\(~14\)) than those grown on alumina supports (flux \(~0.5 \text{ kg m}^{-2} \text{s}^{-1}\) and selectivity \(~2.5\)). This is probably because the MFI membranes grown on porous alumina surfaces suffer from incorporation of aluminum into the crystals. This may happen because of dissolution of alumina into the gel and subsequent incorporation into the zeolite crystals. The presence of aluminum increases the hydrophilicity of the membranes, thus lowering their performance in organics/water separations. The membranes grown on stainless steel had very high selectivity (\(\sim 225\)) for acetone from a feed mixture of 0.8% acetone/99.2% water. The membranes did not permeate acetic acid preferentially from acetic acid/water mixtures at several concentrations. These results are consistent with the increasing order of hydrophobicity of the permeants as acetic acid < methanol < acetone. The permeation of acetone appears to be enhanced by its higher adsorption strength, which compensates for its lower diffusivity in silicalite. This study also compared the performance of silicalite membranes (in methanol separation) with those of polyvinyl alcohol (PVA) membranes and polybutadiene (PBD) membranes. The supported silicalite membranes gave total fluxes comparable to (or higher than) the polymeric membranes. However, the advantage of the silicalite membranes lies in their higher selectivity when compared to those of the polymeric membranes. A similar behavior has been reported (53) for methyl ethyl ketone (MEK)/water mixtures. MEK fluxes between 0.05 and 0.3 kg m\(^{-2}\) s\(^{-1}\) were obtained along with high selectivities (i.e., 60–140) for feed concentrations containing up to 15% MEK in aqueous solution.

The synthesis of silicalite membranes on tubular mullite supports has been reported (54) with the objective of producing zeolite membranes with high enough performance to be commercially viable for pervaporative separation of ethanol/water mixtures. Mullite was chosen since it is much cheaper than \( \alpha \)-alumina supports. The supports were seeded by rubbing them with silicalite crystals in a method similar to that discussed earlier for making zeolite A membranes. The crystallization time (8 h) was claimed to be shorter than all other published reports. The resulting membranes showed high ethanol flux (\(>1.5 \text{ kg m}^{-2} \text{h}^{-1}\)) and selectivity (\(>55\)) from a 10% ethanol feed, and are therefore potentially applicable in a pervaporative process for removing ethanol from water. As with zeolite A, MFI membranes appear to be attractive for pervaporative separations. In
contrast with hydrophilic zeolite A membranes, which can remove water from water/organic mixtures, hydrophobic MFI membranes would be useful for removing organics from these mixtures.

The gas (or vapor) permeation behavior of MFI membranes has received a great deal of attention in recent years, both for the purposes of obtaining potentially commercial separations and for understanding the permeation behavior of molecules through zeolitic membranes. A synthesis method for growing high-silica MFI membranes on the outer surface of a tubular porous alumina support was reported in Ref. 55. The SDA was a mixture of TPABr and TPAOH. No other alkali (such as NaOH) was used. The growth temperature was around 453 K with synthesis times of the order of 24 h. The resulting membrane appeared to have morphology similar to those reported earlier, with randomly oriented, intergrowth crystals forming a layer \( \sim 40 \mu m \) thick on the support surface. These membranes were selective for \( n-C_4H_{10} \) over \( i-C_4H_{10} \); however, the selectivity was said to vary significantly (\( \sim 10–50 \)) between different membrane samples and depending on the permeation temperature. More detailed characterization of these membranes was reported in Ref. 56. Although the membrane was synthesized on the outer surface of the support, the inner surface also showed evidence of zeolite growth. However, the thickness of the zeolite layer on the inner surface was considerably less than on the outer surface, indicating that there was insufficient supply of reactants on the inner side of the support. In this study, the authors reported a reproducible selectivity of about 10 for \( n-C_4H_{10} \) over \( i-C_4H_{10} \). Furthermore, the temperature dependence of the fluxes led to the same value of the apparent activation energy for both species (\( \sim 11 \text{ kJ/mol} \)). For lighter molecules, such as \( N_2 \) and \( CO_2 \), the apparent activation energy was negative (i.e., the fluxes decreased with increasing temperature). These results indicate the role of both zeolitic and nonzeolitic porosity (defects and grain boundaries) in determining the permeation characteristics of the membranes.

A detailed study of butane isomer gas permeation behavior in a silicalite membrane was reported in (57). These membranes were synthesized on porous stainless steel supports and composed of a thin top layer with pore size \( \sim 50 \mu m \) and a thicker bottom layer with pore size \( \sim 200 \mu m \). The reaction proceeded at 353 K from a solution containing only silica, TPAOH, and water. The membrane thickness as observed by SEM was about 50 \( \mu m \) and the crystals in the membrane were randomly oriented. The gas permeation experiments reported in this study (and in most other work on permeation through zeolitic membranes) were carried out in a Wicke-Kallenbach cell.

As mentioned earlier, many aspects of permeation in zeolitic materials can be understood within the framework of the Maxwell-Stefan description of transport in such materials (25–28). In the case of single-component permeation, the flux of \( n-C_4H_{10} \) shows a temperature maximum (at about 420 K) in the temperature range 300–600 K, whereas the single-component flux of \( i-C_4H_{10} \) increases monotonically in this temperature range. This result illustrates the combined role of adsorption and diffusion in determining the temperature dependence of the flux. At low temperatures, strong adsorption occurs (fractional coverage \( \sim 1 \)), with the diffusive flux being determined by the activation energy for the molecule to jump from one adsorption site to the next inside the zeolite framework. For smaller molecules such as \( n-C_4H_{10} \), the activation energy is small (\( \sim 10 \text{ kJ/mol} \)) and also lower than its heat of adsorption in silicalite (58). At low temperatures, the flux increases with increasing temperature due to the increased mobility of the molecules. However, as the temperature increases further, the occupancy of the molecules decreases considerably (due to the high heat of adsorption) in a manner that cannot be compensated by the increase of the diffusivity with increasing temperature. As a result, the flux begins to
decrease. For a bulkier molecule, such as \( i-C_4H_{10} \), the activation energy (~30 kJ/mol) is larger than the heat of adsorption, and the occupancy decreases quite slowly in the temperature range studied. Hence, the flux of this species does not exhibit a temperature maximum in the range that was examined. During binary permeation, high (~60) selectivities were obtained for \( n-C_4H_{10} \) over \( i-C_4H_{10} \) (with an equimolar feed mixture). This cannot be explained only by adsorption selectivity since the adsorption of \( n-C_4H_{10} \) in silicalite is only slightly stronger than that of \( i-C_4H_{10} \).

The observed selectivity is clearly due to the large difference in diffusivities between the two isomers, as is also seen from the single-component permeation results. Although the \( n-C_4H_{10} \) molecules are hindered by the bulkier \( i-C_4H_{10} \) molecules, they are able to bypass the \( i-C_4H_{10} \) molecules due to the three-dimensionally connected pore network of silicalite. On the other hand, single-component \( i-C_4H_{10}/n-C_4H_{10} \) selectivities > 1 have also been reported (59–62). Most of these experiments were done in the pressure drop mode with the permeate side being near atmospheric pressure and the feed side being pressurized above atmospheric. Under these conditions the surface coverage of the more strongly adsorbing \( n-C_4H_{10} \) is high on both ends of the membrane, yielding a small concentration gradient. On the other hand, \( i-C_4H_{10} \) has a steeper dependence of the surface coverage on the partial pressure and therefore has a higher concentration gradient across the membrane. Although the diffusivity of the linear isomer is higher, the branched isomer can permeate faster owing to its higher concentration gradient.

Subsequent to some of the earlier studies described above, several groups published reports investigating mainly the transport and separation properties of MFI membranes. The membranes were made using established methods, predominantly by the route of in situ crystallization. ZSM-5 membranes made by in situ growth have been characterized as a function of calcination temperature (63), which affects the degree of removal of the SDA from the zeolite pores and thus provides some insight on the relative rates of transport through the zeolitic and nonzeolitic porosity. In Ref. 63, the ZSM-5 membrane was calcined at increasingly higher temperatures between 500 and 750 K; each calcination step was carried out for a fixed time of 4 h. The characterization was performed by measuring the room-temperature single-component fluxes of \( N_2 \) and SF\(_6\) after calcination. The membranes remained impermeable to both gases when the calcination temperature was below 523 K. Above this temperature, both gases permeate through the membrane, which has high selectivity (> 150 for calcination temperatures above 700 K) for \( N_2 \). It is well known that SF\(_6\) adsors more strongly in MFI than \( N_2 \) according to extensive adsorption measurements (64,65). In silicalite, its loading was found to be about 10 times that of \( N_2 \) at room temperature and atmospheric pressure, whereas in ZSM-5 (Si/Al ~ 30) its loading was about 3 times higher under the same conditions. Hence, the observed permeation behavior is due to the faster diffusion of \( N_2 \) in the membrane. The effect of permeation temperature was also studied. For a membrane calcined at 573 K, the SF\(_6\) flux did not increase significantly upon increasing the permeation temperature from 300 K to 473 K. However, when the membrane was calcined at 673 K and 753 K, large increases in SF\(_6\) flux were observed on increasing the permeation temperature. It was concluded that at least two types of pores were opened when the membrane was calcined. First the TPA template is removed from the non-zeolitic pores (which are mainly assigned to the grain boundaries between crystals) that are larger than the zeolite pores and are not particularly shape or size selective for \( N_2 \) or SF\(_6\). Therefore, these pores have a lower activation energy for permeation. At higher calcination temperatures, the TPA is evicted from the zeolite pores and highly activated permeation through the zeolite pores becomes the dominant mechanism of transport.
authors use the term *parallel transport pathways* to refer to the two types of permeation. While it is clear that the two pathways for transport are interconnected inside the membrane, the concept of parallel transport pathways serves as a first approximation for modeling transport through the membrane.

As mentioned earlier, MFI membranes are potentially attractive for performing hydrocarbon separations in the petrochemical industry. In this regard, the permeation behavior of alkanes (C₁–C₈) in MFI membranes has been studied by several authors. The preparation of a “defect-free” silicalite layer on porous α-alumina disks has been reported (66). The membrane was composed of randomly oriented crystals and was about 5 µm thick. The synthesis temperature was 393 K for about 16 h. These membranes showed high binary selectivity (~50) at room temperature for \( n-C_4H_{10} \) over \( i-C_4H_{10} \), indicating that the presence of defects had been minimized. The selectivity decreases to about 10 at 473 K, indicating that both sorption and diffusion effects are responsible for the observed behavior. The membrane showed very high selectivities (>600 at room temperature and >2000 at 473 K) for \( n \)-hexane over 2,2-dimethylbutane. In this case, the selectivity is attributed to pure molecular sieving (size exclusion), in which the bulky isomer 2,2-DMB is completely excluded from entering the zeolite pores even though it may have favorable adsorption sites inside the zeolite network.

In Ref. 67, ZSM-5 membranes have been used to study the separation of hexane isomers. These membranes were synthesized on stainless steel supports by in situ growth from a gel containing silica, alumina, TPAOH, and water. They were found to have high mixture selectivity (100–1000) for \( n \)-hexane over its branched isomer, 2,2-dimethylbutane (DMB), in vapor permeation experiments (Fig. 3). The flux of \( n \)-hexane showed a weak maximum on increasing the permeation temperature. This is explained by the competing effects of adsorption and diffusion as explained earlier. However, DMB permeates very slowly at low permeation temperatures but shows a sharp increase in the flux beyond

\[ \text{Fig. 3} \quad \text{Permeances of } n\text{-hexane and 2,2-dimethylbutane for pervaporation through a stainless steel-supported H-ZSM-5 membrane as a function of temperature for a 50:50 mixture. The vapor permeances are also included for comparison. (From Ref. 67.)} \]
It was suggested that this behavior was caused either by expansion of the zeolite pores at elevated temperatures or by opening of the nonzeolitic porosity at higher temperatures. These effects may also be responsible for maintaining the $n$-hexane permeation at higher temperatures, resulting only in a weak temperature maximum. The same membranes were also tested in pervaporation experiments with a 50:50 feed mixture. In this case the results were somewhat different. Although the selectivity for $n$-hexane was still good (~50), the permeance of $n$-hexane was almost an order of magnitude lower than for vapor permeation from a saturated 50:50 vapor. At the same time, the DMB permeance was almost an order of magnitude higher than in the vapor permeation case. The fluxes were also much more insensitive to temperature increases than the vapor permeation case. It was proposed that the permeance of $n$-hexane was higher in vapor permeation than in pervaporation because the molecules saturate the zeolite at low pressures. An increase in the pressure driving force leads to only a small increase in the flux, leading to a decrease in the permeance, which is calculated in units of (flux/driving force). However, in the case of DMB, the coverage was said to be higher in pervaporation so that it diffuses faster than in vapor permeation. However, this does not explain the insensitivity of the permeance to the temperature during pervaporation, as seen in Fig. 3. This temperature insensitivity suggests that adsorption and activated diffusion in the zeolite channels may not control the permeation characteristics of the MFI membranes exposed to liquid feeds for pervaporation. It is possible that in pervaporation there is a significant entropic barrier to the entry of molecules into the zeolite pores from the bulk liquid phase. This entropic resistance may be quite different in the vapor and liquid phases for a linear alkane like $n$-hexane, whereas it may not be so for a more “spherical” molecule like DMB. If $n$-hexane finds it difficult to enter the zeolite pores in the liquid phase, this may well increase the accessibility of the zeolite pores to DMB, which then permeates faster in pervaporation than in vapor permeation. A study (68) of the $n$-hexane/2,3-DMB mixture was also carried out using a ZSM-5 membrane grown on a flat porous alumina substrate by the vapor phase transport method (which is discussed in more detail later in this chapter). High selectivities (>200) for $n$-hexane were reported. This work reported transient data on permeation of binary $n$-hexane/DMB mixtures. It was found that the flux of $n$-hexane passed through a maximum with increasing time, before decreasing and stabilizing at a steady value (in about 48 h). The DMB flux increased slowly to steady state in about 48 h. This can be explained by initial fast penetration of $n$-hexane into the zeolite followed by increased blocking of the zeolite pores as 2,3-DMB also permeates.

Vapor permeation data have been reported (69) for several hydrocarbons including $n$-alkanes (C5-C9), branched alkanes, aromatic and saturated cyclic hydrocarbons in high-silica MFI membranes. The membranes were synthesized on the inside of porous alumina tubes as described earlier. They displayed high selectivity for $n$-alkanes from a mixture with branched and cyclic hydrocarbons. However, the single-component selectivities were low, indicating that molecular sieving was not responsible for the observed mixture selectivity. The selectivity for $n$-alkanes is due to their higher adsorption in the zeolite, thus blocking the pores and preventing bulkier molecules from entering the membrane. For example, the addition of $n$-hexane to a pure benzene feed results in a decrease of the benzene permeance by a factor of 180, whereas the hexane permeance remained almost unchanged. Similarly, addition of $n$-hexane to cyclohexane reduced the permeance of cyclohexane by a factor of 84, while the permeance of $n$-hexane itself was reduced only by a factor of 2. The highest selectivities were obtained at various temperatures depending on the specific mixture. However, mixtures of branched and cyclic hydrocarbons (like i-octane/benzene) could not be separated. This is probably due to their
similar adsorption characteristics in silicalite. Vapor permeation results for the separation of $n$-octane from $i$-octane have also been reported (70). The silicalite membranes used for this study were synthesized on the inner surface of porous $\alpha$-alumina tubes. During single-component permeation, $i$-octane permeated slightly faster than $n$-octane through the membranes between temperatures of 380 and 520 K. However, this behavior could be inverted by adding a large fraction of $n$-hexane diluent, thus creating a ternary feed stream of 91.8\% $n$-hexane/4.1\% $n$-octane/4.1\% $i$-octane. It this case, $n$-hexane decreased the flux of $n$-octane only by a factor of 4 (from the pure component flux) but decreased the $i$-octane flux by a factor of more than 100 such that the $n$-octane/$i$-octane selectivity was as high as 40 at a temperature of 406 K.

The studies described thus far were carried out using organic mixtures of one or two components. However, high-silica MFI membranes grown on porous $\alpha$-alumina disks have recently been reported to be selective for hydrocarbon mixtures over hydrogen from a simulated refinery gas (a multicomponent hydrocarbon-hydrogen stream) (71). The feed stream contained 84\% (molar) of hydrogen, the remaining fraction being composed of C$_1$–C$_4$ hydrocarbons. The permeation experiments were conducted in Wicke-Kallenbach mode using helium as a sweep gas. With the feed at atmospheric pressure and room temperature, the hydrocarbon mixture permeated through the membrane whereas no hydrogen could be detected in the permeate stream. This is attributed to the blockage of the zeolite pores by the strongly adsorbing hydrocarbons, which prevent the weakly adsorbing hydrogen from entering the zeolite framework. At the same time, $i$-butane was also absent in the permeate stream; this can be explained in terms of weak adsorption and slow diffusion of $i$-butane in the zeolite pores. At higher temperatures ($\sim$ 770 K) the membrane permeated hydrogen selectively over the hydrocarbons. At high temperatures, adsorption of the feed components become quite small, so that the selectivity is determined by the diffusivities of the components. Hydrogen diffuses faster in silicalite than the other components of the feed mixture. A simplified model for permeation was also reported, by treating the multicomponent stream as a binary stream composed of a hydrogen component and a lumped hydrocarbon component. The hydrocarbon parameters in the model (apparent activation energy, intrinsic diffusion coefficient, and heat of adsorption) were not estimated independently but rather were fitted from the experimental data.

ZSM-5 membranes prepared by the vapor phase transport (VPT) method have also been tested in hydrocarbon separations (72). The membranes were grown on the surface of porous $\alpha$-alumina disks. The parent aluminosilicate sol was made using silica, alumina, sodium hydroxide, and water, with an Si/Al ratio of 500. The alumina support was treated with colloidal silica to prevent dissolution of the alumina surface during synthesis. The treated support was dipped into the parent sol for 24 h, after which one side of the support was evacuated to allow penetration of the sol into the alumina pores. The infiltrated support was dried and placed in the middle of an autoclave. A mixture of ethylenediamine, triethylamine, and water was poured at the bottom of the autoclave. Crystallization was performed at 453 K for 4 days, during which the organic template mixture vaporized, penetrated the support, and led to the crystallization of ZSM-5 inside the support. Large crystals of ZSM-5 were also formed on the top of the support. The calcined membranes were checked for compactness by measuring the flux of 1,3,5-triisopropylbenzene (TIPB), which is larger than the zeolite pores. No permeation of TIPB was detected, indicating that the membrane was defect-free. The membranes had good binary selectivity (\textgreek{>\hspace{1em}} 50) for $n$-butane over $i$-butane in the temperature range 300–380 K. As expected, the binary selectivity was always higher than the ideal (single component) selectivity. These membranes were also tested for pervaporative separation of xylene isomers. For a 50:50
mixture of \( p \)- and \( m \)-xylene, the flux of \( p \)-xylene increased initially but then passed through a maximum before dropping down below the \( m \)-xylene flux, which increased monotonically until steady state was reached. To explain this behavior, it was proposed that in this case both components adsorb strongly in the zeolite. However, \( p \)-xylene initially permeates faster because of its smaller kinetic diameter and is then blocked by the increasing amount of slowly permeating \( m \)-xylene in the membrane. In another experiment, the membrane was allowed to reach steady state with a pure \( m \)-xylene feed, which was then switched to a ternary \( p-/m-/o-xylene \) feed. In this case, the \( m \) and \( o \) isomers completely blocked the \( p \) isomer. This behavior in xylene isomer separations is different from that reported for other MFI membranes, as discussed later. The VPT synthesis of an MFI membrane on the surface of a porous borosilicate glass disk has also been reported (73). The membranes are found to contain boron (dissolved into the zeolite from the glass support) and were about 15 \( \mu \)m thick. They showed some (non-Knudsen) selectivity for \( N_2 \) over \( O_2 \); however, no other permeation data were reported.

As pointed out in Ref. 74, one difficulty with the VPT technique is the necessity of depositing a gel layer on the support. Gel layers are prone to cracking and peeling during drying after the deposition process. In Ref. 74, a method similar to the VPT method was described that does not require the deposition of a gel layer. In this case, a porous alumina support disk was first coated with a dense silica layer, which acts as a diffusion barrier to prevent reactants from penetrating into the support during membrane growth. On top of this layer, a thin coating of zeolite was deposited by settling of small (60–150 nm) zeolite particles from an unstable suspension. The support was then treated under conditions similar to those in VPT; however, no organic template was used. This led to the formation of a thin and continuous zeolite layer on the support. The membranes were shown to be reproducible as well as free of pinholes (since the measured permeances of several permanent gases were pressure independent and therefore do not have any contribution from Poiseuille flow through pinholes). This is an attractive technique that combines seeded growth with the VPT method in the presence of a diffusion barrier. However, no additional permeation data were reported, and it is unknown how the permeation properties of these membranes compare with those of other MFI membranes.

The use of diffusion barriers to improve MFI membrane properties was in fact reported in an earlier work (75). As mentioned above, a diffusion barrier is needed to prevent the penetration of the reactants (silica, template, and water) into the pores, where they may form a siliceous semicrystalline or amorphous deposit. This leads to lower fluxes and lower selectivities. In Ref. 75, a diffusion barrier was constructed by dipping the porous alumina support in furfuryl alcohol, and then polymerizing it inside the alumina pores by heating to 363 K. The polymer was subsequently carbonized by heating the support to 873 K under an inert atmosphere. The carbonized layer was then burned off the support surface, leaving the diffusion barrier in place inside the pores of the substrate. MFI membranes were grown on the treated supports by in situ crystallization with synthesis conditions developed earlier by the same group (76,77), leading to the formation of well-intergrown zeolite layers. The calcined membranes showed high flux and high selectivity for \( n \)-butane over \( i \)-butane, which was attributed to the absence of a siliceous deposit inside the pores. The effectiveness of the diffusion barrier was verified by comparative XRD and electron probe microanalysis of barrier-treated and untreated membranes having identical thicknesses of the top zeolite layer. These analyses indicated a significantly thinner siliceous layer inside the support for the barrier-treated membrane.
C. Zeolite MFI Membranes by Secondary Growth Techniques

The secondary (or seeded) growth method has recently been shown to be effective in the synthesis of MFI membranes with different features from the membranes obtained by in situ growth (20, 78–86). The membranes made by secondary growth can exhibit distinct microstructure as compared to membranes grown by the in situ technique. The synthesis of thin (submicrometer) MFI membranes was reported in Ref. 78. Unsupported silicalite/alumina composite films were fabricated by mixing suspensions of boehmite (a polymorph of alumina) and of silicalite nanocrystals (~100 nm). The mixed suspension was poured into a casting dish and allowed to dry, giving a film 1–2 mm in thickness. Films fabricated by this method were mechanically stable after calcination due to the presence of boehmite, which acts as a binder. The unsupported films were exposed to secondary growth conditions using a reactant solution containing silica, TPAOH, and water. Secondary growth of the silicalite seed crystals at a temperature of 403 K led to the formation of a predominantly [h01] oriented zeolite film on the surface of the composite layer. Hence, the straight and sinusoidal channels of the MFI framework are oriented roughly parallel to the membrane surface. The membranes had high ideal selectivity (~60) for H\textsubscript{2} over N\textsubscript{2}. The secondary growth technique was extended in Refs. 20 and 80 to prepare oriented MFI membranes on nonporous glass and porous alumina substrates. The seed layers were deposited by dip coating the substrates with an aqueous suspension of small silicalite crystals. Hydrothermal growth at 448 K led to the formation of highly [00l] out-of-plane-oriented films. The films have a columnar microstructure (Fig. 4) with a random in-plane orientation (as shown by X-ray pole figure analysis). These films could be grown as thick as 100 μm. The c direction is the direction of fastest growth in silicalite.

Fig. 4 SEM image of the cross-section of a [00l]-oriented MFI film prepared by secondary growth. (From Ref. 20.)
crystals. Seed crystals which are approximately $c$ oriented will show the fastest out-of-plane growth and will prevail over crystals that do not have their $c$ axes perpendicular to the support plane. This leads to the columnar microstructure observed in Fig. 4. The crystals appear well packed but have intercrystalline nanoporosity (grain boundaries) since the rate of growth in the substrate plane is expected to be small in comparison with the out-of-plane rate of growth. Single-gas and mixed-gas permeation data were reported for the membranes synthesized on porous alumina substrates. The membranes showed similar behavior in both single-gas and binary permeation, indicating the presence of a molecular sieving zeolitic layer. Selectivities of up to 20 were obtained for $\text{CO}_2/\text{N}_2$ and up to 8 for $\text{CO}_2/\text{CH}_4$. The temperature dependences appeared to indicate that both adsorption and diffusion effects were important in determining the selectivity through the molecular sieving zeolite layer.

More detailed characterization of the silicalite membranes prepared by secondary growth has been reported in Ref. 20, where this technique was used to manipulate the orientation of the zeolite membrane. In particular, membranes synthesized at a temperature of 413 K were strongly $\{h0h\}$ out-of-plane oriented, whereas those synthesized at 448 K were strongly $\{00l\}$ out-of-plane oriented. Topographical mapping of the membrane surfaces by surface force microscopy (SFM) revealed a rough surface for the $\{00l\}$-oriented membranes, whereas the $\{h0h\}$-oriented membranes had a comparatively smooth surface formed by the $\{h0h\}$ crystal planes oriented at angles smaller than $5^\circ$ to the film surface. These distinctive microstructures of MFI membranes made by secondary growth result from competitive (“evolutionary”) growth of crystals from the randomly oriented seed layers. This competitive growth can be simulated using empirical growth rate parameters for various crystal faces of MFI. The cross-sectional (i.e., two-dimensional) microstructure of an MFI film resulting from the competitive growth of crystals from a substrate has been simulated using a particle tracking technique (79). The method involves the definition of a number of particle vertices on the substrate, where each vertex represents a crystallographic edge of one of the seed crystals. The motion of these vertices by crystal growth outward from the substrate is then tracked by integrating the equations of motion for each particle using predefined growth velocities for each crystal face. The model allows for intersection of two vertices (at a grain boundary), leading to the burial of the intersecting vertices and the creation of a new vertex with a different direction of propagation. The resulting microstructures closely resemble the experimental results and can be varied by changing the relative growth velocities of the crystal faces. It follows that the orientation of zeolite membranes can be changed by manipulating the morphology of the zeolite crystals. In this respect, the systematic variation of the shape of zeolite crystals is highly desirable so as to achieve different preferred orientations.

The $\{00l\}$ oriented membranes synthesized on porous alumina disks were tested in binary permeation of the butane isomers. The samples tested had high (50–90), reproducible selectivities for $n$-butane over $i$-butane at room temperature, with fluxes comparable to those reported by other groups using in situ growth methods. The membranes were thermally stable, as shown by the absence of any significant changes in the permeation behavior upon temperature cycling between 300 and 523 K. The behavior of the binary butane fluxes has also been investigated as a function of the silicalite membrane thickness (81), which was varied by changing the synthesis time and the number of secondary growth steps. Membranes with thickness ranging from 1 to 32 $\mu$m were prepared. It was found that even a 1-$\mu$m-thick zeolite film reduced the $n$-butane flux by a factor of 10 (compared to the flux through the bare support) with a binary
n-butane/i-butane selectivity of ~15. With increasing membrane thickness, the flux of i-
butane continues to drop significantly, whereas the flux of n-butane drops much more
slowly. This behavior is consistent with the saturation of both the zeolitic and nonzeolitic
poles of the membrane by strong adsorption of n-butane, so that the concentration
gradient is insensitive to the thickness of the membrane. On the other hand, the i-butane
flux is a stronger function of membrane thickness due to the decrease in the concentration
gradient with increasing membrane thickness. The results of this study also suggest that a
thin (submicrometer), defect-free zeolite layer can give excellent selectivities and high
fluxes, and that growing the membranes thicker is only necessary to close defects in
the membranes.

MFI membranes prepared on alumina substrates by secondary growth have been
investigated for their potential in separating close-boiling hydrocarbon mixtures such as
xylene isomers (81–83). This is an important separation since the isomers of xylene are
widely used as industrial solvents and as precursors in the petrochemical industry. The
separation of xylene isomers can be carried out by energy-intensive operations such as
fractional crystallization, adsorption in a simulated moving bed, and distillation. Zeolite
MFI membranes are good candidates for performing this separation, since the pore size
of the MFI framework (~6 Å) should allow permeation of p-xylene (kinetic diameter
~5.8 Å) while excluding the bulkier o- and m-xylene (kinetic diameters ~6.8 Å). In
fact, this effect is exploited in Mobil’s ZSM-5 catalyst for production of xylene isomers.
In Ref. 81, a transient study of the permeation of xylene isomers (p-xylene and o-
xylene) through [00l]-out-of-plane–oriented membranes was reported. In this experi-
ment, the membrane was allowed to reach steady state at 373 K with a feed of p-xylene
in helium (partial pressure of p-xylene = 0.86 kPa). This stream was then switched to a
binary p-/o-xylene stream (0.43 kPa/0.32 kPa). The p-xylene flux quickly stabilized to
about half its single-component value (due to the decreased partial pressure of this
component in the binary stream), whereas the o-xylene flux increased slowly until the p-/ o-xylene selectivity was about 2. On further switching the feed to a pure o-xylene feed
(0.64 kPa), the o-xylene flux declined to very low values. On reintroducing the binary
feed, the o-xylene flux increased again. Therefore, it appears that the presence of p-
xylene increased the flux of o-xylene. Although structural phase transitions in the
silicalite/p-xylene system are well known, they occur at higher partial pressure and are
not expected to be of significance at the low xylene partial pressures that were used in
this study. Hence, it was proposed that p-xylene molecules induce local distortions in
the flexible MFI zeolite lattice, which increased the mobility of the o-xylene molecules.
As a result, the membranes were not selective for p-xylene except in very dilute binary
feeds (82), in which case selectivities up to 18 could be obtained. The increase in
selectivity upon dilution of the feed with helium is also consistent with a diminished role
of p-xylene molecules in increasing the mobility of o-xylene molecules. A more complete
picture of the permeation behavior of xylene isomers in [00l]-oriented silicalite
membranes has been provided recently (83). The single-component and binary vapor
permeation behavior was investigated as a function of partial pressure up to high
pressures of 20 kPa and in a temperature range of 300–343 K. The flux of p-xylene
through the membranes obeys a strictly linear partial pressure dependence at low and
moderate partial pressures, and experiences a sudden rise at high partial pressures (near
the saturation vapor pressure of p-xylene at each temperature studied). This behavior is
seen in both single-component and binary permeation. On the other hand, the o-xylene
flux is low in single-component permeation and saturates as the partial pressure is
increased. Due to the comparatively large (and linearly increasing) flux of p-xylene
under similar conditions, high ideal selectivities can be obtained (up to 100). However, at high partial pressures \(o\)-xylene also displays a sudden rise in the flux. During binary permeation, \(o\)-xylene permeates at the same rate as \(p\)-xylene and its flux also varies linearly with partial pressure. Therefore, the Maxwell-Stefan description of transport appears to break down completely in this case. The linearly increasing flux of \(p\)-xylene is due to the ability of the \(p\)-xylene molecules to induce distortions in the MFI lattice. While this does not greatly increase its mobility in the zeolite lattice, it results in stress deformation of the membrane surface, with the result that the intercrystalline porosity becomes more accessible to both isomers. However, \(o\)-xylene does not induce the same effect in the zeolite. At high partial pressures, both molecules undergo capillary condensation in the intercrystalline pores (as well as in any defects, such as pinholes), so that the flux increases abruptly. This type of behavior is different from that reported in Ref. 84, where it was found that in a binary mixture both isomers permeated at the same rate equivalent to the slower isomer (i.e., \(o\)-xylene). This was attributed to single-file diffusion in the zeolite pores. Since the two isomers cannot pass each other in the zeolite pores, the faster isomer is forced to permeate at the same rate as the slower one. This behavior is consistent with the absence of a significant role of the intercrystalline porosity. The membranes used in Ref. 84 were grown by the in situ method and were randomly oriented with a different microstructure from those used in Refs. 81–83. Therefore, differences in membrane orientation and microstructure can have a significant effect on the permeation behavior, especially in molecules that interact strongly with the zeolite framework. A more recent study (88) reports results that can be interpreted to be in agreement with the mechanism proposed in Ref. 82. In this study, it was also found that higher partial pressures of \(p\)-xylene led to increases in the \(o\)-xylene permeation rate, and this effect was attributed to the distortion of the zeolite framework due to adsorption of \(p\)-xylene.

In view of the poor \(p\)-xylene selectivity that is a consequence of the transport mechanism discussed above, efforts to improve the \(p\)-xylene selectivity of MFI membranes are reported in Ref. 85. The selectivity of the thick \([001]\)-oriented membranes used for xylene permeation in Refs. 81–83 could be improved by the use of a ternary \(p\)-xylene/\(o\)-xylene/\(n\)-hexane mixture as a feed. For a feed composition of 0.45/0.35/0.1 kPa, a selectivity of 60 was obtained for \(p\)-xylene at a permeation temperature of 373 K. Apparently, \(n\)-hexane is able to preferentially block \(o\)-xylene from the zeolite and intercrystalline pores. In addition to the membranes described above, thin (~2 \(\mu\)m) \([h0h]\)-oriented membranes were also synthesized with a noncolumnar microstructure that has significantly lower intercrystalline porosity. However, these membranes showed poor selectivity (~2) due to the formation of large cracks during calcination. These microcracks were sealed by dip coating the membrane surface with a surfactant-templated silica sol. After drying, the mesostructured surfactant-silica layer could be easily removed from the membrane surface; however, it remains permanently inside the cracks and acts to seal them. The treated membranes showed high (~75) selectivity for \(p\)-xylene without the addition of \(n\)-hexane in the feed. Thus, it is clear that the MFI crystal is intrinsically selective for \(p\)-xylene over \(o\)-xylene and that the effects of intercrystalline porosity should be minimized to obtain this intrinsic selective behavior. The results of another study (89), wherein the successful separation of xylene isomers with an MFI zeolite membrane is reported, support the above arguments. A self-supporting MFI membrane (previously grown on a Teflon support and thereafter removed) was used in that study to eliminate the deleterious effects of differential thermal expansion between the substrate and the zeolite layer upon calcination. High selectivities for \(p\)-xylene (~250) over \(o\)-xylene and \(m\)-xylene were reported.
There have been some attempts to synthesize MFI membranes without the use of an organic SDA (TPA cations). The absence of the SDA in the pores eliminates the postsynthetic calcination step, thus reducing the possibility of crack formation in the membranes. Also, the elimination of the SDA considerably reduces the cost of preparing a zeolite membrane. One report (90) used the seeded growth technique to prepare SDA-free ZSM-5 membranes on alumina substrates. An aluminosilicate gel was used as the reactant source. The substrate was coated with a positively charged cationic polymer, whereas the seed suspension was negatively charged. As a result, the seeds adsorbed on the porous support due to electrostatic attraction. After secondary growth, a membrane ~1.5 µm thick was obtained. The permeances observed were quite small despite the low thickness of the film, leading to the conclusion that the zeolite pores contained pore blocking species left over from the synthesis. The membranes had poor selectivity (~1) for n-butane over i-butane, but high (~100) selectivity for hydrogen over n-butane. Similar results were reported in Ref. 91 for an SDA-free ZSM-5 membrane synthesized on a porous alumina tube. The butane permeances were very low, suggesting the presence of extraframework material blocking the pores (either inside the zeolite or at the surface). For the same reason, the hydrogen/n-butane selectivities were very high (~10^4). In another recent study (92), compact ZSM-5 membranes were also prepared on alumina supports by secondary growth. Although a pure silica sol was used for synthesis, aluminum was detected in the membranes after calcination. Aluminum was said to have been incorporated into the membrane in two ways: (a) after dissolution from the support during synthesis and (b) by solid-state diffusion from the support into the membrane during calcination at high temperature. The membranes were found to be impermeable to C₃ and C₄ hydrocarbons. The permeation studies through the SDA-free MFI membranes are inconclusive at this time, though it is clear that they show different characteristics from membranes prepared using an SDA.

D. Modifications and Postsynthesis Treatment of MFI Membranes

There have been recent attempts to tune the performance of MFI membranes by varying its chemical composition. This can be done in several ways including changing the Si/Al ratio, substituting Si with other elements (Al, B, Ge, Ti, etc.) in the reaction mixture, or by performing postsynthetic modifications such as ion exchange of ZSM-5 membranes with various metal cations. Thus, Ref. 93 studies the incorporation of B, Al, Fe, and Ge into MFI membranes. These membranes were made by in situ growth on porous stainless steel supports. The synthesis solution also included precursors of the substituting elements (such as aluminum isopropoxide, tetraethylorthogermanate, ferric nitrate, and boric acid). The Si/M (M = Al, Ge, B, Fe) ratio in the synthesized membranes varied from 65 to 200 depending on the substituting element. It was assumed that these elements were in fact incorporated into the framework, though unambiguous evidence for framework incorporation has not been established. The membranes synthesized in the presence of boron (referred to as B-ZSM-5 membranes) had the smallest permeances for permanent gases and butane isomers but also the highest selectivity (~45) for n-butane over i-butane. All of the membranes synthesized in the presence of the above elements had higher butane selectivity than a similar silicalite membrane. In the case of the B-ZSM-5 membrane, the higher selectivity was attributed to the small size of the boron atom when compared to silicon, with the result that the unit cell and the pore size of B-ZSM-5 is significantly smaller than that of silicalite. For the other substituted membranes, the behavior was attributed to differences in adsorption and diffusion.

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characteristics of the molecules in the substituted frameworks as compared to silicalite, as well as to the presence of extraframework material in the pores in the case of Fe$^{3+}$, which, owing to its large size, is expected to be incorporated with difficulty into the framework. It is also a possibility that the change in the synthesis conditions induced by the presence of nonsilicate species may also affect the growth characteristics of the individual zeolite crystals in the membrane, which thereby affect the microstructure and the intercrystalline porosity of the membrane.

The preparation of titanium silicalite (TS) and vanadium silicalite (VS) membranes on porous stainless steel supports has been reported recently (94). In these cases, silicon atoms are partially substituted with tetrahedrally coordinated titanium or vanadium atoms. A secondary growth procedure was used for the membrane growth. The supports were first functionalized by contact with an ethanolic solution of 3-mercaptopropyltrimethoxysilane, whereby the –SH end groups bound to the metallic support. The functionalized supports were then contacted with a silicalite seed suspension during which the zeolite seeds became attached to the functionalized support. The condensation reactions between the organosiloxane moieties on the support surface and the surface hydroxyl groups of the zeolite seeds was completed by drying in an oven. For the secondary growth, tetraethylorthosilicate was used as the silica source and TPAOH was used as the template. Tetraethylorthotitanate or vanadyl sulfate (VOSO$_4$.3H$_2$O) were used as titanium or vanadium sources, respectively, and the Si/Ti and Si/V ratios were varied from 25 to 200. The incorporation of Ti and V into the framework was confirmed by energy-dispersive X-ray (EDX) analysis and Raman spectroscopy. The addition of Ti and V suppressed the growth rate of the membranes. For an Si/M (M = Ti, V) ratio of 100 in the synthesis solution, the membranes were 15–20 µm thick after 48 h of growth, whereas the corresponding pure silicalite membrane was 50 µm thick. Unlike pure silicalite membranes made by secondary growth, the TS and VS membranes synthesized at ~450 K show predominantly [h0l] orientation. The membranes developed cracks upon calcination and so did not exhibit selective behavior.

The effect of ion exchange on the properties of ZSM-5 membranes has also been investigated (95). ZSM-5 membranes were synthesized on porous stainless steel tubes with two Si/Al ratios (25 and 600), exchanged with several cations (H$^+$, Na$^+$, K$^+$, Cs$^+$, Ca$^{2+}$, Ba$^{2+}$) and their permeation properties were measured. The membranes with a high Si/Al ratio (~600) did not show any dependence of gas permeation properties on ion exchange except for i-butane. This was explained as due to the small concentration of ion sites, which is not sufficient to alter the permeation of small molecules significantly. For the membranes with low Si/Al ratios (~25), significant changes were observed in the permeation behavior after ion exchange. Cation sizes are in the order of Cs > K > Ba > Ca > Na > H, whereas the single-gas permeances (He, H$_2$,N$_2$,CO$_2$, butane isomers, and SF$_6$) increased in the order K < Ba < Cs < Na < H. Therefore, with the exception of Cs, the gas permeances increased in the order of decreasing cation size. No explanation was suggested for the apparent anomaly in the permeation behavior through Cs-ZSM-5. Also, the binary butane selectivities were hardly affected by ion exchange.

E. Calcination Effects on Zeolite Membranes

As mentioned earlier, zeolite membranes synthesized with an organic SDA must be treated to remove it from the pores. This is almost always done using calcination (i.e., heating the membrane in air to temperatures > 650 K), and therefore knowledge about the mechanism of SDA decomposition and the effects of calcination on the zeolite crystal is desirable. A
detailed study of the calcination of large MFI (silicalite) single crystals was reported in Refs. 96 and 97. In Ref. 96, the reaction mechanism for the degradation and removal of TPAOH was investigated using in situ optical microscopy and in situ FTIR. Large (>200 μm) single crystals of silicalite were synthesized and embedded on the surface of a silicon wafer using a ceramic adhesive. This wafer was then inserted into an FTIR attachment equipped with a port for optical microscopic observation of the crystals. The spot size of the IR beam was as low as 40 μm, which allows spectra to be obtained from different regions within the single crystal. At room temperature, the FTIR spectra from the center of the crystal included all the C-H stretching and bending vibrations from the TPA cations, as well as the O-H stretching vibrations due to the hydroxyl groups in the structure, which are in chemical equilibrium with the TPA cations. At about 550 K, the hydroxyl absorption band diminishes and the C-H stretching vibrations shift to lower frequencies. The C-H bending vibrations remain unchanged. Between 580 and 610 K, all the C-H bands decrease steadily in intensity and the zeolite is SDA-free at about 650 K. At the same time, optical microscopy indicates that beyond 550 K calcination occurs quite inhomogenously in the crystal, leading to the formation of a brown-colored hourglass-like figure that expands outward in the c direction of the crystal. FTIR spectra taken from areas not exhibiting the coloring indicated that the degradation occurred faster in these areas than in those affected by the coloring. The FTIR spectra are consistent with a Hoffmann elimination mechanism for template degradation, wherein the TPA cations are first degraded to propylamine, along with the formation of propene and water. The propylamine molecules are strongly bound in the crystals, whereas propene and water are removed by transport in the channels. The MFI channels lie in the a and b directions, whereas transport along the c direction involves a tortuous path and therefore transport of propene in the c direction is hindered. This was proposed to account for the brown coloring observed in the crystals, which is due to oligomerization reactions occurring among the propene molecules. The other consequence of the nonuniform calcination is the formation of cracks in the crystals, as reported in Ref. 97. This is due to the nonuniform shrinkage in the unit cell of the crystals as a result of calcination-induced template removal. Based on the experimental results reported in Ref. 97, a low heating rate (<1 K/min) and heating temperatures around 673 K were recommended for calcination of MFI membranes to avoid the formation of cracks. Higher temperatures are not necessary to remove all the TPA from the framework; in fact, they can be detrimental because they increase the disparity in thermal expansion between the membrane layer and the support. Despite these findings, higher calcination temperatures are often used in various reports and the calcined membranes exhibit high selectivities.

An attempt to study the calcination-induced structural changes occurring in ceramic-supported MFI membranes has been reported recently (98). The membranes were made by in situ crystallization on alumina and yttria-zirconia (YZ) supports, with the crystallites in the membrane randomly oriented. The lattice parameters of the MFI were obtained as a function of calcination temperature by temperature-resolved XRD. It was found that the MFI lattice shrinks between 600 and 750 K as the template is removed, and expands on cooling down to room temperature. Based on the observed changes in lattice parameters, hypotheses are made regarding the buildup of in-plane stress in the membrane, which explains the formation of cracks in the membrane. However, the characterization of stress in zeolite membranes, as well as the interpretation of data on structural changes in the membrane, is a difficult task. In Ref. 98, the diffraction measurements were done in a flat-plate geometry where observed changes in the lattice parameters originate only from crystal planes parallel to the membrane surface. Thus, the lattice strain measured is that
occurring in a direction normal to the membrane surface. This gives no information on the in-plane lattice strain. Although the membrane itself may be isotropic due to the random orientation of the crystals, the stresses acting on the membrane are not necessarily isotropic and are probably strongly anisotropic. Also, even if the out-of-plane and in-plane lattice strains were fortuitously identical, very little can be said about the type (tensile or compressive) of the in-plane membrane strains if the corresponding behavior of the unstressed zeolite crystals is unknown under the same calcination conditions. This information is obtained from a determination of the lattice constants of an unstressed MFI single crystal as a function of temperature.

In fact, the diffraction technique has been extensively used to determine residual stress in materials other than zeolites (99). In this method, the flat sample is tilted such that its normal vector makes an angle with the vertical. A particular \((hkl)\) reflection is chosen for analysis and the diffraction peak position of this reflection is measured. Since the \((hkl)\) planes measured at different sample tilt angles are under differing amounts of in-plane and out-of-plane stress, the corresponding strains can be calculated from the tilt angle dependence of the \(d\) spacing. Equations for this purpose are given in Ref. 99. While this method is theoretically applicable to the zeolite membrane, two major complications should be taken into account. First, since the magnitude of lattice strains in MFI is not very large, the measurements must be carried out at very high diffraction angles (>150°) to detect appreciable peak shifts. In the case of zeolites, the high angle reflections have a large overlap and may be difficult to resolve. Also, X-ray scattering intensities are intrinsically weak at high diffraction angles, and neutron diffraction techniques may be more suitable for stress analysis in this case. Second, the technique will likely fail for strongly oriented samples (such as the \([00l]\)-oriented membranes discussed earlier). The method requires sufficient diffraction intensity from a certain \((hkl)\) reflection over a wide range of sample tilt angles, but a strongly oriented film results in the extinction of the diffraction signal since the \((hkl)\) planes in question are available for diffraction only at a specific tilt angle, which is determined by the orientation of the film. In this case, a technique that uses data obtained from many different \((hkl)\) planes measured at their optimal tilt angles is required to extract stress data. Additional work is therefore needed to develop a reliable method for determination of average strains in highly oriented zeolite films from diffraction data.

**F. Characterization of Nanoporosity in MFI Membranes**

The study of transport through zeolitic membranes can be aided by techniques for simulating and characterizing the microstructure and porosity of the membrane. While the structure (and therefore the porosity) of the zeolitic layer can be characterized by diffraction techniques, the characterization of the intercrystalline porosity requires other methods. The technique of fluorescence confocal optical microscopy has been recently used for characterizing the microstructure of MFI membranes (100). This method allows nondestructive characterization of the membrane microstructure at different depths from the substrate (100). A fluorescent dye is adsorbed into the sample and is observed at different depths using a confocal microscope. The dye molecules can penetrate the intercrystalline porosity, which can therefore be observed due to fluorescence from the dye under an optical microscope. Using a confocal lens system, one can observe the microstructure of the membrane at varying depths from the membrane surface and reconstruct a three-dimensional image of the intercrystalline porosity. In this way, the existence of a well-connected intercrystalline porosity in a highly \([00l]\)-oriented MFI membrane is
verified (Fig. 5). On the other hand, the \([h0h]\)-oriented membranes show very little intercrystalline porosity, thus explaining their good separation performance in xylene separation after repair of the microcracks, as described earlier.

Permporometry (101–105) is another technique for characterization of zeolite membrane microstructure and quality, and was introduced in Ref. 101 for MFI membranes. This method is based on measuring the permeance of a noncondensible gas such as helium through a membrane whose pores are being progressively filled by increasing the partial pressure of a condensible vapor present in the helium feed stream. Condensible species such as \(n\)-hexane saturate the zeolite MFI pores even at low partial pressures, and the noncondensible gas will permeate exclusively through the intercrystalline pathways. It is assumed that at low partial pressures capillary condensation of \(n\)-hexane in the intercrystalline pores will not occur. Clearly, a membrane with intercrystalline porosity will exhibit some permeation of the noncondensible gas even after the zeolite pores have been blocked by increasing the partial pressure of \(n\)-hexane, whereas a well-intergrown membrane will become impermeable to the noncondensible gas. Depending on the permeation characteristics as a function of vapor pressure of the condensible species, the intercrystalline nanopores can also be distinguished from larger defects such as pinholes and calcination-induced cracks. Permporometry and fluorescence confocal microscopy should be established as standard tests for judging the quality of zeolite membranes.

\[ \text{Fig. 5} \quad \text{Fluorescence confocal optical microscope images of the grain boundaries in an MFI membrane at (a) } z = 0 \mu m, (b) z = 2.5 \mu m, (c) z = 5 \mu m, \text{ and (d) } z = 7.5 \mu m \text{ from the membrane surface. The } x \text{ and } y \text{ coordinates are the same for all sections. (From Ref. 100.)} \]
G. Studies of MFI Membrane Formation

A detailed mechanistic understanding of the nucleation and growth of zeolite crystals is of technological importance in controlling characteristics such as crystal size, crystal morphology, and the orientation of zeolite films. The nucleation and growth mechanism of zeolite MFI has been the most widely studied. It is generally accepted that small “subcolloidal” particles (smaller than 10 nm) exist in solution during the synthesis of MFI. These particles have been studied extensively by small-angle and wide-angle X-ray scattering (SAXS and WAXS) (106–108), and a particle size of 2.8 nm has been proposed (108). With the use of binuclear (1H-29Si MAS) NMR, it was also shown that the subcolloidal particles contain tetrapropylammonium (TPA), as well as silicate species organized into specific oligomeric units (109). A procedure for extraction of the particles from suspension has been proposed (110). Based on NMR data from the extracted particles, it has been suggested (111) that the particles have a slab-like shape with dimensions of $1.3 \times 4.0 \times 4.0$ nm$^3$, though it remains uncertain at this stage whether this particle shape alone uniquely fits all the existing structural and spectroscopic data. Although the existence of these particles is well established, their concentration and structure is still debatable. As a result, their role in the growth of MFI crystals is not firmly established. An MFI crystal may grow by incorporation of the subcolloidal particles, by incorporation of aggregates of subcolloidal particles, or by addition of TPA cations, silicate monomers, and silicate oligomers from the solution (Fig. 6). The subcolloidal particles, their aggregates, and the silicate monomers/oligomers in solution may also be interconverted. In a recent study (112), growth rates measured by dynamic light scattering (DLS) were found to be in good agreement with a model based on the Derjaguin-Landau-

![Fig. 6 Possible mechanisms of silicalite-1 (MFI) crystal growth.](image)
Verwey-Overbeek (DLVO) theory (113,114) of electrostatic and van der Waals interactions between a subcolloidal particle and the zeolite surface on which it may be incorporated. It was then proposed (112) that the addition of the subcolloidal particles can be the rate-limiting step in the growth of silicalite crystals. Although this type of mechanism is not unique to zeolites or to MFI in particular (115), further studies are required to prove or disprove its existence.

Several qualitative investigations have been made regarding the sequence of events that occur during the formation of MFI membranes on substrate surfaces by both in situ and seeded growth techniques. A mechanism was proposed in Ref. 116 for the growth of a film of \(\{0k0\}\)-oriented high-silica MFI crystals on a substrate. In that study, optical microscopy showed that MFI film growth is preceded by the formation of a gel layer on the substrate. Furthermore, it was proposed that nucleation occurs at the interface of the gel and the liquid, which was the only location in which both the silica species and the organic SDA are present in abundance. This was supported by chemical analysis of the gel, which was found to have a very low TPA concentration. Therefore, the growth of the zeolite film takes place from the gel–liquid interface down to the gel–substrate interface, as experimentally observed. This mechanism for conversion of a gel layer into a zeolite film appears to be different from that proposed for the growth of silicalite particles in a clear suspension of subcolloidal particles. In a later report (117), the deposition of a silicalite film on various substrates was observed by optical microscopy. The substrates used were sapphire, borosilicate glass, fused silica, and PFA (polytetrafluoroethylene-perfluoroalkylvinylether). The hydrothermal reaction was carried out at 453 K with an alkali- and aluminum-free reactant solution. The deposition process was observed via in situ optical microscopy. The silicalite crystals deposited on the PFA support were found to be mainly \(\{0k0\}\) oriented and were only weakly attached to the support. Most of these crystals were deposited by settling from solution and moved around on the surface to form a film. The absence of zeolite nucleation on the PFA support is explained by the chemical inertness of this support, and also to its smooth texture (devoid of cracks and scratches), which does not allow attachment of crystals. In the case of the borosilicate glass support, crystals appeared on the surface due to nucleation and settling. Most of the crystals were anchored in either \(\{0k0\}\) or \(\{h00\}\) orientations and continued to grow on the substrate surface. The other two supports showed intermediate behavior between the PFA and the borosilicate supports. In these cases, the crystals moved around on the surface when they were small but became immobile once they grew larger. These results partly corroborate the steps reported in Ref. 117 for membrane formation under in situ growth conditions.

It is interesting to observe that the morphology and orientation of the zeolite crystals reported in Refs. 116 and 117 appear to be independent of the type of substrate used. It follows that for the types of substrates examined in the above studies, the kinetics and energetics of the events occurring at the gel–liquid interface influenced the morphology of the MFI crystals to a greater extent than the events occurring at the gel–substrate interface. The most important surface characteristics of the substrate that could influence zeolite film growth are pore size, surface roughness, and chemical composition. Of these three factors, the chemical composition of the support, if altered to a large enough extent, have the largest influence on crystal nucleation and growth. A study of the effect of support surface chemistry on the growth of a silicalite membrane has been reported in Ref. 118. Porous stainless steel (SS-316L) supports made of \(\sim 10-\mu m\) steel particles were used for the study. The support surface was composed of Fe (in the form of \(Fe_2O_3\)) and Cr, as revealed by EDX analysis. The supports were coated with thin (\(\sim 20 \text{ nm}\)) layers of various
metals (Cr, Fe, Au, Ag) and oxides (alumina, silica, ferric oxide and titania) by sputter coating and reactive sputter coating, respectively. The stainless steel surfaces were also functionalized with organic functional groups using mercapto compounds with hydroxyl, carboxylic acid, or silanol groups. The mercapto group binds to the support, thus anchoring these functionalizing molecules to the support surface. Supports functionalized with mercaptopropyltrimethoxysilane (MP-TMOS) were coated with silicalite seed crystals of \( \sim 120 \) nm. The membranes grown at 398 K on untreated stainless steel supports were typically well intergrown and about 10 \( \mu \)m thick. As for the supports coated with metals, it was found that only the Ag- and Fe-coated supports allowed nucleation of MFI leading to the formation of a well-intergrown membrane. The grain size of the silicalite crystals on the Fe-coated support was much smaller than that in the Ag-coated support, implying that the Fe layer provided a larger density of nucleation sites. However, the Fe surface layer is actually converted to Fe\(_2\)O\(_3\) on exposure to the atmosphere. The Au- and Cr-coated supports did not allow the preparation of a continuous film, instead showing poorly attached deposits of crystals. All of the metal oxide–coated supports allowed the nucleation of crystals, but the grain sizes were larger and the degree of intergrowth lower than those obtained on uncoated supports. The zeolite crystals observed on silica-, alumina-, and titania-coated supports also showed evidence of secondary nucleation of smaller crystals on their surfaces, a feature not observed in the membranes grown on uncoated or metal-coated supports. The membrane formed on the ferric oxide–coated support looked identical to that formed on the Fe-coated support. Membranes formed on supports functionalized with hydroxyl, carboxylic acid, or silanol functional groups were well intergrown with a smaller crystal size and a large number density of crystals (hence a larger density of nucleation sites). Therefore, the functionalized surfaces used in this study favored the nucleation of silicalite crystals.

Examination of the mechanism of formation of MFI membranes on porous alumina supports, which are often used as a substrate for zeolite membranes, was reported in (119). The membranes were made by in situ crystallization. One set of experiments was conducted using a clear reactant solution containing no aluminum. SEM was used to examine the surface of the samples treated hydrothermally for different times. Membrane crystallization was found to be preceded by the formation of a gel layer on the support surface. The thickness of this initial layer was comparable to the thickness of the fully crystallized membrane. Thus, it is probable that the membrane formation occurs by the transformation of the gel layer into a well-intergrown, crystalline membrane. This process may also involve diffusion of the TPA cations from the solution. Experiments carried out using an aluminosilicate reactant solution led to slower formation of a membrane, as evinced by the presence of a gel layer on the support surface for longer times than those observed for aluminum-free reactant solutions. This is probably due to the tendency of even a small amount of aluminate to induce polymer-like gelation. Thus, the presence of aluminum leads to faster formation of the gel layer but increases the time required for transformation of this amorphous gel into zeolite crystals. The aluminosilicate gel also penetrates the pores of the support to a certain extent, but this gel would remain largely amorphous due to the large concentration of alumina inside the pores of the support, which lowers the Si/Al ratio of the gel and delays its crystallization.

A detailed investigation of the effect of the chemical composition of the synthesis solution on the morphology of silicalite films is presented in Ref. 120, especially with respect to the formation of \( \{0k0\}\)-oriented films. Polished, nonporous stainless steel supports were used in the study. In particular, the orientation of the film was found to be dependent on the \( \text{OH}^-/\text{Si (0–1)} \) and the \( \text{Na}^+/\text{TPA}^+ (0–1.6) \) ratios. Variations in these
parameters led to changes in the orientation of the silicalite film, and a two-dimensional map could be prepared showing regions of the composition space where the films were $[h00]$, $[0k0]$, $[00l]$, or randomly oriented. The study suggests the possibility of manipulating zeolite membrane orientation by in situ growth techniques to obtain membranes with particular morphologies. However, the efficacy of these procedures remains to be tested in the case of porous substrates, and the suitability of these membranes for separations is an interesting subject for further work.

On the other hand, the secondary growth technique renders the nature of the substrate less relevant for purposes of membrane growth, since the growth proceeds from a layer of zeolite seed crystals covering the support. However, there should be good adhesion between the seed layer and the support because otherwise the membrane may be quite unstable on heating or on application of mechanical force. Good adhesion can be achieved by using supports like alumina or glass, which form strong bonds with the surface of the zeolite crystals by condensation reactions between hydroxyl groups on the support and on the zeolite. Although organic functional groups can be used to promote adhesion of the seed layer prior to hydrothermal treatment, these compounds will be decomposed during calcination of the membrane. In the secondary growth technique, the problem of manipulating the morphology of the membrane can be approached in one or both of the following ways: (a) depositing a layer of already oriented seed crystals on the support; and (b) developing the appropriate growth conditions to manipulate the relative growth rates of different crystal faces of the deposited crystals. A demonstration of the second approach to manipulating MFI membrane orientation is available in Ref. 121. In that study, a randomly oriented seed layer of MFI nanocrystals (~80 nm in diameter) was deposited on glass substrates (Fig. 7). Highly oriented MFI films with orientations from

![Fig. 7](image_url) Growth of MFI films with controlled out-of-plane orientation.
[001] to [h0h] (Fig. 8) could be grown by varying the synthesis conditions, most notably the temperature. The film orientations could be preserved by repeated secondary growth steps, leading to the ability to form thick (~100 μm) zeolite films on glass substrates. Under different secondary growth conditions, [h00]-out-of-plane–oriented films were prepared (86,87) from randomly oriented seeds. It is also of interest to compare the films made by secondary growth with those made by in situ growth under the same hydrothermal synthesis conditions. This is reported in Refs. 20 and 121. In the case of in situ growth using the same synthesis conditions as for secondary growth, a few crystals were found to be initially nucleated on the glass substrate and as time passes, deposition of zeolite crystals from the solution takes place to yield a nonuniform layer of MFI crystals on the substrate. It was proposed that secondary growth eliminated not only the need for a high nucleation rate on the support but also film growth by incorporation of particles nucleated in solution or on the growing film. This can be understood by the nutrient reduction in the vicinity of the film caused by the uniform film growth throughout the secondary growth process.

There also exists the possibility of manipulating the orientation of the film by depositing a seed layer of crystals with defined morphology and orientation. An attempt was made to synthesize (0k0)-oriented MFI films on silicon substrates by secondary growth (122), using seed crystals with a plate-like morphology having their (0k0) planes parallel to the substrate surface. Since the straight channels of the MFI structure are oriented along the (0k0) direction, membranes with this orientation are attractive because they provide the least diffusion resistance. Also, since the fastest growing [001] direction would now be parallel to the substrate plane, a well-intergrown membrane could be expected to form. Though XRD patterns indicated a high degree of {0k0} orientation in the seed layer, the orientation was preserved for only a limited time during secondary growth, and the membranes switched to an {h00} orientation upon prolonged secondary growth. The reason for this “change” in orientation, or, in other words, the failure to preserve the [0k0]-out-of-plane orientation of the seed layer as the film thickens, can be attributed to several possible causes. One proposal involves

![Fig. 8](image)

Fig. 8 Range of out-of-plane orientations achieved, denoted by gray region, for MFI membranes.
the tendency for twinning in MFI, and another is the misorientation of the seeds during secondary growth. However, it is most likely attributable to the slow growth of MFI crystals along the [0k0] axis. Starting from [0k0]-oriented seeds, because of the slow growth rate along this axis, the nutrient consumption in the vicinity of the seed layer is not fast enough to eliminate nucleation of new crystals either directly or by incorporation from solution. The newly nucleated overlayer is then responsible for the different orientation as the film thickens.

As a result of the slow growth of MFI along the [0k0] axis, it has proven very difficult to grow well-intergrown [0k0]-oriented MFI films by seeded growth. At the same time, the early success of in situ growth on silicon wafers and the more recent extension to aluminum and stainless steel supports has not been followed by similar success on porous supports appropriate for permeation measurements. The preparation of a functional [0k0]-oriented MFI membrane on a porous support remains a challenge.

H. Faujasite Membranes

Several preparations of faujasite (FAU) membranes have been reported. The pore size of this zeolite (~7.4 Å) is considerably larger than that of MFI and zeolite A types; thus, it can be used in applications involving larger molecules. Moreover, small molecules can be separated by this zeolite due to differences in their adsorption characteristics. Faujasite is crystallized as an aluminosilicate framework and is referred to as either type X (Si/Al = 1–1.5) or type Y (Si/Al > 2). The zeolite occludes charge-balancing cations and therefore its properties can be manipulated extensively by ion exchange. A type Y membrane was synthesized in Ref. 123 using seeding methods similar to those used to synthesize zeolite A membranes. In this case, a seed layer of type X crystals was mechanically applied to a tubular porous alumina substrate. A template-free sodium aluminosilicate solution with Si/Al ~ 5 was used for hydrothermal synthesis at 363 K for approximately 24 h. A continuous membrane about 5 μm thick was obtained on the support, and the crystals appeared to be randomly oriented by XRD. The membranes were tested for separation of CO2 from N2 by the Wicke-Kallenbach method. High selectivity (~100) was obtained for CO2 at room temperature. This selectivity decreased to 20 at 375 K, indicating that the separation was due to the preferential adsorption of CO2 in the zeolite lattice. More extensive permeation results on these membranes were reported in Ref. 124 with binary permeation data for mixtures of CO2/N2. The membranes used in this study were of three types: as-synthesized NaY, lithium ion–exchanged LiY, and potassium ion–exchanged KY. Adsorption isotherms measured with powder forms indicated that the order of adsorption capacity for the strongly adsorbing CO2 was in the order LiY > KY > NaY. For weakly adsorbing N2 the order was LiY > NaY > KY. The data were fitted to Langmuir isotherms in all cases and appeared to indicate that the best adsorption selectivity (especially at high partial pressures) was given by the KY-type zeolite. The binary permeation selectivities at 308 K of several membrane samples of the KY type varied between 35 and 67, and were larger than those of NaY samples (i.e., 24–39) and LiY samples (i.e., 6–9). The selectivities decreased with increasing permeation temperature, and the membranes became nonselective at 673K. As stated in Ref. 124, the above data indicate that preferential sorption of CO2 over N2 is responsible for the high selectivity of the membranes near room temperature. Fortunately, this is the relevant temperature for commercial use in these types of separations.

Type Y zeolite membranes were also fabricated for use in pervaporative separations (125). These membranes were grown by the secondary growth method. A seed layer of
type Y crystals was deposited on the support by dip coating from a colloidal suspension. After secondary growth at 373 K for 5 h, a zeolite Y membrane ~20 μm thick was obtained. In pervaporation experiments, the membranes had high selectivity (540–7600) for methanol or ethanol from binary mixtures with other organics such as benzene, MTBE, or cyclohexane. The alcohol flux varied from 0.1 to 0.6 kg m⁻² h⁻¹. The membranes also showed good selectivity (~125) for water from a water/ethanol mixture, although this selectivity is lower than those achieved for some of the zeolite A membranes discussed earlier (~10,000). It is worth noting that although this difference in selectivity is significant from the fundamental standpoint, its practical significance has not been established. Since all the molecules considered are smaller than the pore size of the zeolite, the separation performance was attributed to differences in the adsorption strengths of these molecules. Clearly, there is expected to be an adsorption contribution to the selectivity since the hydrophilic zeolite framework would preferentially adsorb water and alcohols over hydrocarbons and ethers. However, the temperature dependence of the fluxes and selectivities was not reported in this work.

The fabrication of thin faujasite membranes on porous alumina disks was reported in Ref. 126 using a more sophisticated seeding technique. Colloidal crystals of NaY were synthesized from a clear solution containing sodium hydroxide, alumina, silica, water, and TMAOH. The synthesized crystals were stabilized as a colloidal suspension in water at pH 10.0 (adjusted using a dilute ammonia solution). At this pH, the surfaces of the zeolite crystals are negatively charged. A positive charge was created on the support surface by deposition of a cationic polymer (from a solution) onto the surface. The modified supports were then immersed in the colloidal suspension of zeolite seed crystals that adhered to the support. Secondary growth was carried out with a template-free synthesis solution at 373 K. Thin membranes (~0.1–1 μm) were obtained (Fig. 9) that displayed preferred orientation in the {111} direction. No permeation properties have yet been reported for these membranes.

Faujasite membranes have also been investigated for the separation of saturated/unsaturated hydrocarbon mixtures (127). These membranes were made by secondary growth with a seed layer of ZSM-2 crystals. The seed crystals were synthesized using an aluminosilicate solution containing TMAOH as the template (128). The seed layer was deposited on the support from a colloidal suspension, and the sodium aluminosilicate solution used for secondary growth contained TMAOH. Well-intergrown FAU membranes were obtained as verified by XRD and SEM. Compositional analysis using EPMA indicated an Si/Al ratio of 1–1.5, and a membrane of type NaX. The membranes showed good selectivities for unsaturated hydrocarbons from mixtures such as benzene/cyclohexane (separation factor as high as 160), benzene/n-hexane (145), and toluene/n-heptane (45). The binary permeation behavior for the benzene/cyclohexane system was investigated in detail because of the commercial importance of this separation. Maxwell-Stefan equations were used to model the permeation of benzene and cyclohexane in the FAU membrane. The adsorption and diffusion parameters were taken from the literature and were derived from single-component measurements. While the single-component diffusivities for both species are comparable in magnitude, the separation is mainly due to the greater adsorption strength of the unsaturated hydrocarbon in the zeolite. The model predicts the observed temperature and pressure dependence of the binary fluxes fairly well but does not give good agreement with the experimental results at lower temperatures (<373 K) and pressures (<2 kPa). The discrepancies are probably due to the lack of adequate experimental data on binary adsorption and diffusion of benzene and cyclohexane in the FAU framework.
Apart from the LTA (small pore), MFI (medium pore) and FAU (large pore) zeolite types discussed above, other studies have included synthesis of mordenite (MOR) (129–132), ferrierite (FER) (133–135), MEL (136), zeolite P (GIS) (137), and chabazite (138) type zeolite membranes. A few reports have also dealt with the preparation of nanoporous silicoaluminophosphate (SAPO) membranes. One study (139) reports a synthesis method.

Fig. 9  SEM images of the surfaces and cross-sections of faujasite membranes synthesized on α-alumina wafers for (a, b) 3 h, (c, d) 12 h, and (e, f) 21 h. (From Ref. 126.)

I. Membranes of Other Framework Types

Apart from the LTA (small pore), MFI (medium pore) and FAU (large pore) zeolite types discussed above, other studies have included synthesis of mordenite (MOR) (129–132), ferrierite (FER) (133–135), MEL (136), zeolite P (GIS) (137), and chabazite (138) type zeolite membranes. A few reports have also dealt with the preparation of nanoporous silicoaluminophosphate (SAPO) membranes. One study (139) reports a synthesis method.
for SAPO-34 membranes by in situ growth on tubular alumina supports. This method was based on an earlier report of the crystallization of a SAPO-34 membrane (102); the material is isomorphous to the zeolite chabazite and has a pore size of ~4 Å. The reactant gel had a molar composition of Al₂O₃ P₂O₅ 0.6SiO₂ 1.07TEAOH/56H₂O. The synthesis was carried out for 20 h at 468 K. The calcined membranes were tested in single-component gas permeation experiments using H₂, CO₂, N₂, CH₄, and n-C₄H₁₀. The membranes were found to have a small but significant permeance of n-butane (which is nominally larger than the pore size of the material). This indicated the presence of some noncrystalline porosity in the membranes. The membranes had fairly high ideal selectivity (~25) for H₂ over CH₄ at 298 K, but this selectivity decreased with increasing permeation temperature. The permeance decreased with increasing kinetic diameter of the permeants. Therefore, the SAPO-34 membranes synthesized in the report appear to have molecular sieving characteristics.

Apart from zeolitic and aluminophosphate materials, mixed tetrahedral-octahedral oxide materials also have potential as molecular sieves and catalysts (140). The inclusion of octahedrally coordinated metal species results in the formation of framework types different from those obtained in tetrahedrally coordinated zeolite materials. The nanoporous titanosilicates, such as ETS-4 (141) and ETS-10 (142), form an important class of such materials. The synthesis of an ETS-4 membrane has been reported (45). This titanosilicate material has both 12-membered and 8-membered ring channels. However, owing to faulting in the crystals, the 12-membered large pores are blocked such that the material has molecular sieving properties similar to that of a small-pore zeolite (141). Furthermore, the presence of charge-balancing metal cations renders the material hydrophilic. The ETS-4 membranes reported in Ref. 45 were synthesized on porous titania disks via secondary growth of an ETS-4 seed layer formed on the support by in situ hydrothermal treatment. An alkaline sodium titanosilicate solution was used that contained sodium hydroxide, silica, titania, potassium fluoride, and water (no organic SDA). This is followed by two secondary growth steps leading to the formation of a well-intergrown ETS-4 membrane that is about 5 µm thick. XRD patterns of the membranes indicated a significant degree of [0k0] preferred orientation such that the 8-membered channels are perpendicular to the substrate surface. These membranes were selective for water over ethanol in pervaporation experiments. Their room temperature selectivity at (~340) is comparable to those of NaX and NaY membranes, but two orders of magnitude lower than that of the zeolite A membranes discussed earlier. However, ETS-4 pervaporation membranes have the potential advantage of greater acid stability than membranes of zeolite A and zeolite MFI.

The synthesis and properties of crystalline nanoporous membrane appears to be a still expanding area of research. On one hand, the existence of many different zeolite types with varying properties and the discovery of new nanoporous materials should lead to a continuation in reports of membrane synthesis and new transport and separation properties. On the other hand, there are important general issues to be addressed in the preparation of zeolite membranes. The most important unresolved issue in the area of zeolite membrane research is the commercial viability of zeolite membrane–based separation processes. Although zeolite membranes can be highly selective, their generally low permeation rates often render them uncompetitive for commercial applications. One way of increasing the permeation rate (membrane flux) is to fabricate very thin (submicrometer), defect-free membrane layers such that the flux is increased by at least an order of magnitude from current values while retaining highly selective behavior. For example, in the case of xylene separation, current state-of-the-art micrometer-sized MFI membranes
have permeances corresponding to flux levels at operating conditions that require membrane areas in excess of 20,000 m² per plant (500,000 tons/year). This appears to be a prohibitively large number for this industry’s standards. However, a 10-fold increase in flux will make the technology very feasible and attractive. The increase in flux through MFI films can be achieved either by a 10-fold reduction of film thickness (to 100-nm levels) or by a change in the preferred orientation. For this and other applications, the ultimate objectives for zeolite thin film processing remain (a) to grow a thin, defect-free membrane, and (b) to control its orientation so as to provide the path of least diffusion resistance to the fast-permeating species and/or improve the selectivity. While considering secondary growth techniques for both purposes, it is desirable to have control over the morphology and orientation of the seed crystals, as well as control over the growth rates of different crystal directions during secondary growth. Ideally, the crystals composing the membrane should be oriented such that the permselective molecular sieving channels are perpendicular to the support surface, thus offering the highest fluxes and selectivities. At present, there is inadequate understanding of the growth process of zeolite crystals, and no proven method exists for predicting and manipulating zeolite crystal morphology. As a result, there is no technology that allows the controlled growth of defect-free membranes of a specified orientation for any given zeolite. Fundamental studies of the structure, composition, and dynamics of zeolite surfaces during crystal growth may provide valuable insights for developing methods to control zeolite crystal growth and morphology. This development, when combined with the secondary growth technique and advanced techniques for deposition of defect-free zeolite seed layers (described in Sec. III), can result in submicrometer zeolite membranes suitable for separations and catalytic reaction-separation applications.

III. METHODS FOR DEPOSITION OF ZEOLITIC SEED LAYERS ON SUBSTRATE SURFACES

As stated in the previous section, thin (submicrometer), defect-free zeolite membranes are a well-established goal that will enable commercial applications. The secondary growth technique based on the predeposition of a dense seed layer appears to be a possible method of preparing such membranes. Clearly, the deposition of a defect-free, close-packed seed layer is essential for the subsequent growth of a thin, defect-free membrane with favorable separation properties. The seeding methods reported in the zeolite membrane literature vary in their level of sophistication and quality of results. In this section we discuss the methods used for applying seed layers of zeolite crystals on substrate surfaces.

The synthesis of zeolite A membranes is often carried out by the secondary growth method. In Refs. 32 and 34, the seed layer was generated by simply rubbing the substrate surface with crystals of zeolite A. While this approach appears to generate sufficient crystal nuclei on the substrate surface for growth of a thick membrane with selective properties, it is questionable if it can give satisfactory results for the growth of submicrometer membranes since the seed layer is hardly continuous and uniform. Several reports employ the method of dip coating the substrate in a colloidal suspension of the zeolite crystals (44,79–86). The method involves the synthesis of small (ideally <100 nm) crystals of the zeolite, followed by their stabilization in an aqueous colloidal suspension. Stabilization of the seed crystals is achieved by adjusting the pH of the suspension to a region away from the isoelectric point, so that the crystals carry a (mutually repulsive) surface charge that prevents them from aggregating. The pH is adjusted by using an
alkali, a mineral acid, or by adding the organic template cations. In Ref. 44 for zeolite A and Refs. 79–86 for silicalite, seed layer deposition on the substrate was carried out very simply by bringing the horizontal surface of the polished support disk in contact with the surface of the zeolite suspension (which is placed in a Petri dish), so that the aqueous suspension adhered to the porous support due to surface tension and capillary action. Once contact between the support and the suspension is established, the support is removed tangentially and left to dry with its surface inclined at an angle to the horizontal. During this time the liquid layer flows down the support surface by gravity while the seed crystals precipitate on the surface. This simple method is quite effective for preparing continuous seed layers on porous alumina supports over macroscopic length scales. However, on closer inspection by optical microscopy and SEM, defects such as pinholes and low-density regions are always found. Their effects can be eliminated only if the membranes are grown several micrometers thick. Also, this method does not work as well on nonporous substrates such as glass slides, since the contribution of capillary forces in attaching the crystals to the surface is small. In this case, multiple dip coatings may be necessary to achieve a continuous seed layer on the surface.

It is therefore more desirable to deposit seed layers by creating specific, well-defined attractive interactions between the crystals and the substrate. These interactions may be of a Coulombic, van der Waals, or covalent nature. To create these favorable crystal–substrate interactions, it is necessary to modify the surface composition of the zeolite crystals and/or the substrate. A method for electrostatic deposition of zeolite A seed layers on glass substrates was reported in Ref. 44. A suspension of zeolite A seed crystals was made, and its isoelectric point was determined to be at a pH of 5 (based on measurements of the ζ potential as a function of pH). The suspension was stabilized at a pH of about 9 in which case the particles are negatively charged. Surface modification of the seed crystals was carried out by reacting them with 3-aminopropyltrimethoxysilane (AP-TMOS) under an inert atmosphere. After the reaction was completed (~ 1 h), the particles were redispersed at neutral pH. Since the free end of this organosiloxane molecule contains an amino group (with a pKₐ of ~ 10.7) and the amino group is protonated at neutral pH, the modified zeolite particles have a positive surface charge at this pH. This was confirmed by a ζ potential measurement that gave a value of +43 mV at pH 7. Hence, two types of suspensions (unmodified and modified) were prepared with the seed crystals being negatively and positively charged, respectively. Two types of substrates were also used: an ordinary glass substrate and a modified silicon substrate. These were first cleaned with alkaline and acidic hydrogen peroxide solutions and then reacted with AP-TMOS dissolved in toluene. Following this, a monolayer of sodium poly(styrene)sulfonate was applied to the surface to give it a negative charge. The negatively charged substrate could be converted to a positively charged one by further application of a layer of polyallylamine. Deposition of the seed layers on the glass substrate was carried out by dip coating with a slow withdrawal rate (~ 1 cm/h). The immersion-modified silicon substrates were immersed in the zeolite suspensions for seed layer deposition. The dip-coated glass slides showed well-ordered closely packed zeolite A crystals (Fig. 10a) over large areas of the substrate. However, continuous coverage could not be obtained over the entire substrate with a single dip coating; multiple cycles were required. On the other hand, the electrostatic deposition on modified silicon substrates resulted in a dense, continuous coverage of oriented zeolite A particles on the surface (Fig. 10b). Only one coating was required to achieve high coverage of the entire substrate. These seed layers could be grown into a continuous zeolite film on the substrate surface by using the
Fig. 10 (a) Highly ordered region of a zeolite A precursor film obtained by dip coating of a glass slide. (b) Zeolite A precursor film obtained by electrostatic deposition on a modified silicon substrate. (From Ref. 44.)
secondary growth technique. Similar techniques for electrostatic deposition of MFI (143) seed layers have been reported.

Covalent linkages can also be used to assemble zeolite crystals to substrate surfaces. In this case, the zeolite and the substrate surfaces are functionalized with molecules that can react to form covalent bonds, thus strongly bonding the zeolite crystals to the substrate surface. A variety of functionalizing molecules can be used, which may lead to different characteristics of the assembled zeolite layers. Due to the strong and specific covalent interaction between the substrate and the surface, a monolayer of zeolite crystals can be assembled on a substrate. Multilayers deposited by sedimentation adhere only loosely to the covalently bonded zeolite monolayer below them and can be removed mechanically (e.g., by ultrasonication). In Ref. 144, the deposition of zeolite A, ZSM-5, and SAPO-34 monolayers on glass substrates by covalent linkage was reported. Fairly large crystals (~1 μm) were used. The hydroxyl groups on the zeolite surfaces were functionalized with 3-aminopropytriethoxysilane (AP-TEOS), whereas the hydroxyl groups on the glass surface were reacted with 3-(2,3-epoxypropoxy)propyltrimethoxysilane. All reactions are carried out in anhydrous organic media under an inert atmosphere. The functionalized glass surface is then contacted with a toluene suspension of the functionalized crystals whereupon the epoxide functional groups on the glass surface react with the amine groups of the zeolite surface, thus anchoring the zeolite crystals in a monolayer on the surface. Areas with excellent surface coverage are obtained, with the ZSM-5 crystals having \{0k0\} orientation and the zeolite A crystals having \{h00\} orientation. However, low-magnification SEM showed a high density of defects (uncovered areas). It was argued that because this scheme depends on the close proximity (on the molecular level) between the zeolite crystal surface and the substrate surface, the failure to achieve complete coverage may be due to the limited number of possible linkages between the amine and epoxide groups, arising from the large roughness of both surfaces. To enhance the bonding of the crystals to the substrate, a modification of the scheme of Ref. 144 was reported in Ref. 145. In this modification both the zeolite and the substrate are functionalized with epoxide groups while a polymer acts as a linker between the two surfaces. The polymeric linker in this case contains a large number of pendant amine groups and is also flexible on the molecular scale. As a result, there is a high concentration of covalent linkages between the linker and the surfaces of both the zeolite and the substrate. In this study, polyethyleneimine was found to be a good linker, leading to the deposition of strongly attached zeolite A monolayers on flat glass plates and on the cylindrical surfaces of glass fibers. The monolayers were resistant to sonication for prolonged periods (~1 h), indicating that the crystals, the polymer, and the substrate were covalently linked.

Other covalent linkers such as fullerene-containing molecules have also been used as reported in Ref. 146. In this case, zeolite A or ZSM-5 crystals and the glass substrate were functionalized with amine, and fullerene was used as the covalent linker. Dense and apparently defect-free monolayers of oriented zeolite crystals were formed on the support. The study also investigated the possible mechanism for the monolayer deposition by means of SEM imaging of the glass surface at various stages of deposition. The results are shown in Fig. 11. At low coverages, there are a large number of isolated crystals on the surface. With increasing coverage, the crystals appear to migrate on the surface, leading to the formation of circular areas of low crystal density bounded by areas of high crystal density. Further deposition appears to occur toward the centers of these empty circles, and they shrink in area until the entire surface is covered with crystals. This mechanism is believed to be due to the slow chemical reaction between the fullerene linker and the
zeolite/substrate surface, which allows the crystals to migrate before becoming firmly anchored to the surface. Zeolite monolayers have also been formed on surfaces such as porous silica and porous alumina by using 3-halopropylsilyl reagents as covalent linkers (147). In this case, the hydroxyl groups of the zeolite surface and the substrate were directly reacted with the linking molecule.

The above techniques have been recently extended to carry out selective deposition of zeolitic layers on patterned surfaces by combining them with well-known techniques of surface micropatterning such as photolithography and microcontact printing (148,149). Figure 12 illustrates the principle of photopatterning followed by zeolite deposition. A glass substrate was treated with 3-iodopropyltrimethoxysilane in order to impart iodide functionality (150). The surface then was exposed to ultraviolet radiation

Fig. 11  SEM images showing various spots on a glass plate with different coverages of zeolite A crystals at magnifications of 3 (A), 4 (B), 1.5 (C), 3 (D), and 6 K (E, F). (From Ref. 146.)
through a patterned mask such that the functional groups in the areas not shielded by
the mask undergo photochemical reaction, oxidizing these areas to a hydroxyl function-
ality. Zeolite crystals can then be attached to either the exposed or unexposed areas
depending on the surface functionality of the zeolite crystals, as indicated in Fig. 12.

A process called pulsed laser ablation has also been used for depositing zeolite seed
layers (152–156). Recent work using this technique has resulted in the preparation of
oriented UTD-1 membranes (155). In the laser ablation process, a high-intensity laser
beam strikes the zeolite target, which is in the form of a pressed pellet. This generates a
plume of zeolite fragments ablated by the laser, which can be deposited on an appropri-
ately positioned substrate. This layer can then be hydrothermally treated to grow a
membrane (152,155). In fact, laser ablation followed by hydrothermal treatment was one
of the first demonstrations of the seeded growth technique. The particle size and thickness
of the deposited layer can be controlled by varying the laser energy and the time of

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In this method, the zeolite material becomes amorphous when ablated by the laser beam and the deposited seed layers often have weak or no XRD intensities. However, it is speculated that sufficient zeolite nuclei exist in the ablated layer to allow growth of a zeolitic membrane. The method is also useful for coating three-dimensional objects of various shapes. In Ref. 156, the coating of small spherical glass beads with thin layers of UTD-1 is reported, and the results are illustrated in Fig. 14. The technique is most attractive when used for coating small areas and irregular shapes, and would be rather expensive and laborious to use for coating macroscopic areas in a membrane separation module.

In conclusion, significant progress has been made toward depositing both porous and nonporous defect-free zeolite layers on various types of substrates. Functionalization approaches that attempt to tune the interactions between the substrate surface and zeolite crystals in suspension appear to offer a good starting point for such a development. There exist potential problems with these techniques. First, due to the inherent roughness of most porous supports, it is difficult to deposit a thin, defect-free layer of zeolite seed crystals that can be grown into a thin (submicrometer) membrane with molecular sieving properties. However, smooth porous surfaces for deposition of zeolite seed layers can
possibly be created by first depositing a thin mesoporous (157) or microporous (158) silica film on the support. Second, organic molecules are used to link the zeolite and the support. These linkages would likely be destroyed during calcination at high temperatures and yield mechanically unstable membranes.

IV. EMERGING APPLICATIONS FOR ZEOLITE MEMBRANES

In addition to their traditional uses as catalysts, ion-exchange materials, and selective sorbents, zeolites have been investigated for other applications that exploit their unique structural features. In this concluding section, we briefly review some of these developments. Although much of the work described in this section does not involve the fabrication of a well-intergrown zeolite membrane, the applications discussed below are likely to be eventually realized in the form of zeolite membrane/thin-film devices.

A. Zeolites as Ionic Conductors

Zeolites can occlude charge-balancing cations adsorbed within their pore spaces. A sizable concentration of charge-balancing cations (commonly protons and alkali metal cations) exists in aluminosilicate zeolites due to the presence of aluminum atoms that give the framework a net negative charge. The concentration of the cations can be varied by changing the Si/Al ratio in the framework, and different types of cations can be introduced by ion exchange. Other ionic species such as hydroxyl ions (formed due to
silanol defects in the framework) and hydronium ions (formed by the coordination of protons with water molecules adsorbed in the pore space) can also exist in the zeolite pores. In addition, the microporous channels provide diffusion paths for cations between neighboring adsorption sites. Thus, zeolites satisfy the basic requirements for an ionic conductor, implying their possible use as solid electrolytes in batteries, fuel cells, chemical sensors, etc.

The ion conduction properties of zeolites are quantified by impedance spectroscopy. In this technique, the zeolite is usually pressed into a pellet or a disk, and the complex impedance of the sample is measured over a wide frequency range (usually 10 Hz–10 MHz) to measure the characteristic frequency responses and to extract ac conductivity ($\sigma$) values. The ac conductivity is written as the sum of two terms, i.e., the dc conductivity and the dispersive (frequency dependent) term (159). The latter term frequently has a power law dependence on the frequency. The dc conductivity represents the transport of charge carriers over long distances, whereas the dispersive term is due to local relaxations of the charge carriers. Effective activation energies for ion conduction can also be measured by temperature-dependent conductivity measurements. The activation energy is extracted from the Arrhenius dependence of the product $\sigma T$, as given by the Nernst-Einstein law. This technique is illustrated in Ref. 160, which reports a systematic study of alkali metal (Li, Na, K, Rb) ion conduction through the synthetic forms of the zeolites offretite, cancrinite, and zeolite A. The activation energies for the cations were found to lie between 50 and 110 kJ/mol, and the conductivities were in the range $10^{-3}$–$10^{-6} \Omega^{-1} \text{cm}^{-1}$. The highest conductivity ($\sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$) and lowest activation energy was observed for Na-offretite, and in general the sodium-containing zeolites exhibited higher conductivities than those containing lithium, potassium, or rubidium ions. It was suggested that the ion conductivity behavior observed in zeolites is influenced by three major factors: (a) the electrostatic attraction (adsorption potential) between the cations and the zeolite framework, (b) the intercationic repulsions, and (c) the site-hopping diffusion barriers experienced by the cations. The conductivities of the above zeolites were also compared with other solid electrolytes such as ZrO$_2$/Y$_2$O$_3$, AgI, and Na-β-alumina. The ionic conductivities of the zeolite samples were found to be rather low in comparison with other solid electrolytes, and the need for improvement of the conductivity by at least two orders of magnitude ($\sim 10^{-1} \Omega^{-1} \text{cm}^{-1}$) was suggested. A more recent study (161) reports the ionic conduction behavior of hydrated zeolite XA (X=Li, Na, K) at pressures up to 5 GPa. In agreement with Ref. 160, NaA possesses higher conductivity than the other forms. It was also observed that the conductivity passed through a maximum at around 2 GPa, and then dropped sharply as the zeolites became amorphous at very high pressures. This behavior is anomalous since the conductivity of ionic conductors generally decreases with increasing pressure (162) due to a shrinkage in the unit cell volume and stronger cation–framework interactions. It was speculated that this behavior is due to increased interaction between the cations and water molecules, an increase in protonic conduction, or an increase in cation mobility with pressure.

Ion conduction in medium pore zeolites has also been investigated. In Ref. 163, the conductivity of X-ZSM-5 (X=Li, Na, K, Rb) is studied as a function of the Si/Al ratio. Samples with low Si/Al ratios ($\sim 25$) had higher conductivities (up to $10^{-3} \Omega^{-1} \text{cm}^{-1}$). This can be explained by the increase in the concentration of charge-balancing cations as the Si/Al ratio is lowered. Na-ZSM-5 exhibited the highest conductivity of all the ion-exchanged forms. Also, the conductivities appeared to rise steeply as the Si/Al ratio was lowered, indicating that very high conductivities could be obtained from ZSM-5 samples having Si/Al < 20. In addition, adsorption of $n$-butane increased the conductivity of Na-ZSM-5 by as
much as 60%. This is presumably due to a favorable effect of butane adsorption on the locations or mobilities of the cations in ZSM-5.

Most studies on ion conduction in zeolites use pressed disks or pellets of zeolite powders, where the quantity measured is an effective (average) conductivity arising from a large number of randomly oriented zeolite crystals. However, zeolite crystal structures are often quite anisotropic with ion conduction channels running in specific directions, and therefore a directional dependence of ionic conductivity is expected. Recently, the ionic conductivity of a single crystal of ferrierite was measured (164). This zeolite had an Si/Al ratio of 9 and an Na/Al ratio of 0.6, with 10-membered channels in the $[001]$ direction and 8-membered channels in the $[0k0]$ direction. Cation transport along both directions was found to be activated, with the activation energy for transport in the narrow 8-membered channels higher than that for transport through the 10-membered channels. However, the conductivities were rather low at near $10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 873 K.

The ionic conductivity of large-pore zeolites such as faujasite is generally of the same order of magnitude as those of small-pore and medium-pore zeolites. As mentioned in Sec. II, faujasite is synthesized in two forms: X (Si/Al < 1.5) and Y (Si/Al > 2). This zeolite also occludes a considerable amount of water in addition to the charge-balancing cations. The cations are located in several sites, either in the sodalite cages or in the supercage formed by linking together the sodalite cages (163). The dc conductivity of zeolite NaX was found to pass through a minimum as a function of the degree of dehydration of the framework (165). The dc conductivities of the fully hydrated and the completely dehydrated NaX were similar. These results were explained by the hypothesis that the dc conductivity is mainly due to weakly bound cations in the supercages. When the temperature is increased, the mobility of these cations is reduced due to the removal of water molecules coordinated with these cations. The presence of water molecules is known to modify the potential barriers for site hopping of cations (166). At higher temperatures water molecules also begin to leave the coordination spheres of cations in other coordination sites, and these cations then move into the supercages resulting in an increased concentration of charge carriers and an increase in the dc conductivity. A similar result was obtained for zeolite NaY (167,168). The mechanisms for conduction in both zeolites were suggested to be similar, but since the two zeolites contain different concentrations of exchangeable cations the values of the conductivities and activation energies differed as a function of the degree of dehydration and the temperature. NaX generally has a higher conductivity, probably owing to its higher concentration of charge carriers. In addition, the sodium forms of these zeolites are more conductive than the protonated forms (169). This has been explained on the basis of strong binding of the protons to the framework oxygen atoms, thus reducing proton mobility in the zeolite. In general, proton conductivities of dehydrated zeolites are quite low ($\sim 10^{-7} \Omega^{-1} \text{cm}^{-1}$) for the reasons mentioned above. However, the conduction of protons can be assisted by the presence of sorbed species such as water (170) and ammonia (171), or by $\gamma$ irradiation (172,173). In Ref. 170, it is reported that compressed pellets of H-ZSM-5 crystals show increases of several orders of magnitude in conductivity after being immersed in water. However, it is not clear whether the increase in conductivity is due to an increased transport rate of protons through the zeolite channels or due to the formation of a continuous water phase in the intercrystalline pore space. The effect of ammonia on the proton conductivity of the large pore zeolite H-beta is also reported in Ref. 171. It was found that ammonia adsorption increased the proton conductivity of H-beta by a Grotthuss mechanism, wherein the ammonia molecules lower the activation energy for
site hopping of protons by the formation of an intermediate NH$_4^+$ cation. Indeed, the temperature dependence of the conductivity revealed a decrease of about 60 kJ/mol in the activation energy of proton conduction, upon adsorption of ammonia from a water vapor phase containing 25 ppm of ammonia. The conductivity increase was highly dependent on ammonia content, suggesting that this phenomenon may be applicable to the development of an ammonia sensor with high sensitivity in the ppm range.

While the literature on ion conduction in zeolites is now fairly extensive, it is apparent that no substantial increases in the ionic conductivity of zeolites have been achieved. Although the intrinsic conductivity of these materials may be limited by their structure, the ionic current (flux) can, in principle, be increased by production of thin (submicrometer), defect-free zeolite films that would have a considerably lower electrical resistance than the compressed pellets and disks used in previous studies. Hence, the development of thin zeolite membranes with appropriate microstructure and orientation is also of importance in exploiting the electrical properties of cation-containing zeolites.

B. Zeolites as Nanostructured Hosts and Dielectrics

Due to their precisely defined nanoscopic void spaces, zeolites are desirable host materials for the formation of nanostructures such as nanowires, nanotubes, and nanoclusters. The long-range periodicity of the zeolite pores and the available techniques for synthesizing defect-free single crystals of zeolite materials leads to the possibility of fabricating large, defect-free arrays of nanostructured materials inside their pore spaces. This is a formidable task, but demonstrations of the possibilities in this area of research have appeared in the literature from time to time. Two decades ago, the incorporation of metals such as lead, thallium, mercury, and selenium into the channels of mordenite single crystals was reported (174,175). In particular, isolated chains of selenium could be formed in the zeolite host and were detected by electron microscopy (176). Likewise, the incorporation of potassium metal (from its vapor phase) into zeolite L (177) has been found to increase the conductivity of the zeolite by five orders of magnitude (178) from that expected by ionic conduction of protons. Thus, the presence of electron-conducting potassium nanostructures in the zeolite is inferred. In Ref. 179, the formation of ferromagnetic cobalt nanoparticles (~15 nm) in zeolite NaX was reported based on a method originally outlined in Ref. 180. The nanoparticles were formed by occlusion of cobalt nitrate into the pores by heating a mixture of the salt and the zeolite followed by reduction to metallic cobalt under hydrogen. The observed nanoparticle size is much too large to be incorporated in the zeolite channels, and in fact the zeolite lattice is destroyed in the regions occupied by the magnetic particles. Other types of nanoparticles (such as Pt, Pd, Cu, Fe, Au, Ag, Ni, ZnS, and CdS) have also been synthesized in the pores of zeolitic materials (181–185). The synthesis of monodisperse (in diameter) carbon nanotubes in the pore space of the microporous aluminophosphate framework AlPO$_4$-5 (186) opens up possibilities for fabricating highly ordered arrays of carbon nanotube structures in order to exploit their unique electronic properties. Thin, oriented zeolite films can form an ideal host for incorporation of these types of nanostructured materials. For this type of application, in-plane as well as out-of-plane preferred orientation of the zeolite crystals is desirable. The first demonstration of such a film (Fig. 15) has been achieved by heteroepitaxial growth on cancrinite (CAN) crystals on a single crystal of sodalite (SOD) (187).

Zeolite thin films have also been investigated recently for application as insulating spacers in microprocessors (188,189). Ideally, a dense solid with a dielectric constant close
to 1 is required, but few solids have dielectric constants lower than 2. Porous inorganic materials such as zeolites have been theoretically predicted to have dielectric constants lower than 2, and they are moreover chemically inert and thermally stable. In Ref. 188, a thin (250–500 nm) silicalite film was synthesized by in situ crystallization on a silicon wafer. Its dielectric constant was measured at 2.7 using an impedance analyzer following deposition of aluminum electrodes on the film, which increased to about 3.5 after exposure to moist air. As is well known, submicrometer zeolite films made by current methods have a large number of defects and intercrystalline nanopores, which act to increase the measured dielectric constant by virtue of adsorption of high dielectric constant species such as water. Similar results were obtained (189) for films made by spin coating of silicalite nanoparticles from a suspension. However, a dramatic improvement was seen after the spin-coated film surface was made hydrophobic by silylation with chlorotrimethylsilane. After long exposure times in air, the film still had a low dielectric constant of 2.2. This is a promising result that may lead to the application of zeolitic thin films in the microprocessor industry.

REFERENCES


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