DOI: 10.1002/anie.200604910

Zeolite Membranes

Hierarchical Nanomanufacturing: From Shaped Zeolite Nanoparticles to High-Performance Separation Membranes

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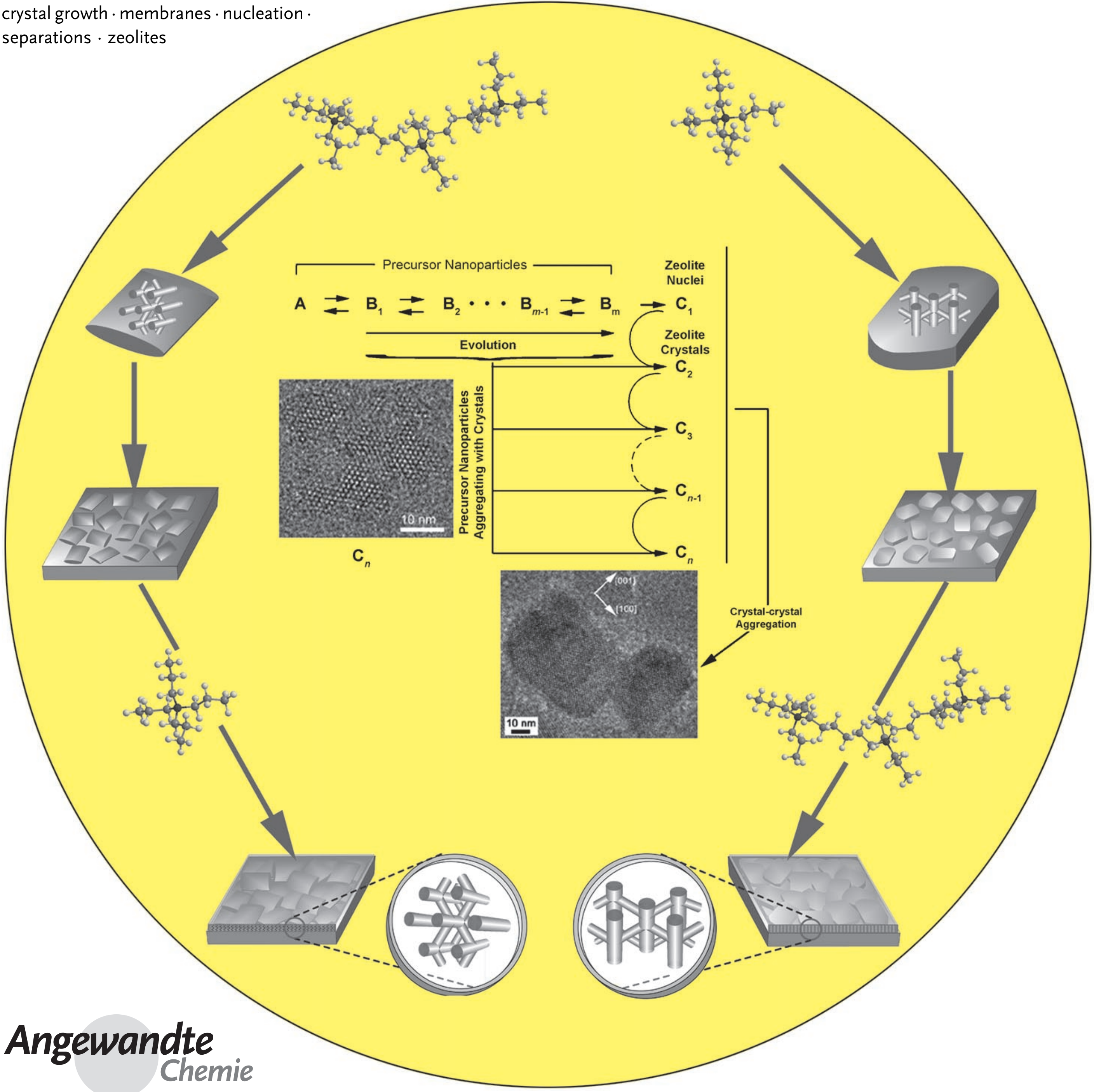
Keywords:
crystal growth · membranes · nucleation · separations · zeolites



Angewandte Chemie

Despite more than a decade of intense research on the high-resolution selectivity of thin zeolite films as alternatives to energy-intensive industrial separations, membranes consisting of intergrown, oriented zeolite crystals have fallen short of gaining wide commercial application. Factors including poor performance, high cost, and difficulties in scale up have contributed to this, and have also stunted their application in other niche markets. Until recently, rational design of these materials was limited because of the elusive mechanism of zeolite growth, and forced more empirical approaches. New understanding of zeolite growth along with recent advances in the molecular engineering of crystal microstructure and morphology, assembly of crystal monolayers, and synthesis of ordered films constitute a strong foundation for meeting stringent industrial demands in the future. Together with new processing capabilities, such a foundation should make it possible to synthesize commercially viable zeolite membranes through hierarchical approaches. Such advances open exciting prospects beyond the realm of separations for assembly of novel and complex functional materials including molecular sensors, mechanically stable dielectrics, and novel reaction-diffusion devices.

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1. Introduction

Zeolites are crystalline materials with compositions and nanoporous structures that can be fine-tuned for catalysis, adsorption, and ion exchange.[1] Interest in separations by zeolite membranes is driven by the pressing need for energy conservation, since they can serve as continuous and less energy-intensive alternatives to current processes of distillation, crystallization, and others.[2–12] In addition, the possibility exists for simultaneously harnessing the well-known and widely exploited shape-selective catalytic properties of zeolitic materials and selective separations for implementation in catalytic membrane reactors.[6,13–20] Zeolite films have also been targeted for other potential applications including chemical sensors,[2,12,21] ion-exchange electrodes,[22] insulating layers in microprocessors,[23–25] and light-harvesting devices.[26]

The earliest reports of zeolitic membrane devices appeared in the early 1940s in regard to ion-selective sensing applications.[27–29] In these and other early studies, zeolitic membranes were fabricated by brute-force pressing of zeolite powders into compact disks or by the impractical use of single crystals of natural zeolites. Since the 1950s, the growing availability of synthetic zeolite crystals has led to numerous composite membranes, synthesized by incorporating the crystals into polymer membrane matrices.[22,30–43] This approach holds considerable merit and is pursued intensively today,[43–49] with the aim of improving the performance in applications that are compatible with polymeric or sol–gel[50] materials.

The performance and processing challenges of both pure molecular sieve and composite membranes are detailed in Table 1. The zeolite-composite, or mixed-matrix, approach relies on the appropriate matching of the properties of the polymeric or inorganic amorphous matrix with the zeolite properties to harvest some fraction of the molecular sieve performance.[51] A recent patent issued by Chevron[52] explores this technology (in this case of MFI particles in a polymeric matrix), but performance is limited, at least in part, by the incorporation of large particles with no preferential orientation. The possibility to control particle morphology and microstructure (platelike particles) as discussed later in this Review, however, raises exciting possibilities for functional nanocomposites of the future.

On the other hand, an all molecular sieve membrane technology—by offering molecular sieve properties uncompromised by the presence of the matrix—would enable their use at a wide range of operating conditions including high temperatures, high pressures, and in reactive environments, while allowing for membrane regeneration by aggressive treatments. In 1987, a patent[3] described polycrystalline zeolite membranes supported on an inorganic porous substrate, and spawned intense research that has led to the establishment of reliable laboratory-scale fabrication procedures and the demonstration of good separation performance by the membranes. Zeolite membranes have in general been prepared from zeolite A,[53–63] faujasite (X and Y forms),[64–71] mordenite,[69,72–74] ferrierite,[75,76] MEL,[77] zeolite P,[78] chabazite,[79] SAPO-34,[80–84] DDR,[85] and a few other zeolites.[86] In addition, aluminophosphate membranes[79,84,87,88] as well as mixed tetrahedral-octahedral oxide membranes (ETS-4 and ETS-10) have also been synthesized.[63,89–92]

Sol–gel films templated with tetrapropylammonium (TPA) salts exist as alternatives to zeolitic membranes. Despite yielding good selectivity for the separation of *o*- and *p*-xylene, and enjoying simple one-step synthesis,[93] the relatively low flux through these films—attributed to the nonuniformity of the pores in the amorphous materials—serves as a potentially significant drawback. Furthermore,

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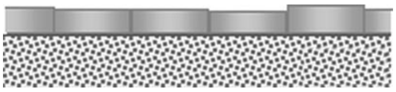
Table 1: Overview of the currently pursued membrane technologies and their respective challenges.

	Film type	Makeup	Performance compromisers	Processing
molecular sieve films		intergrowth of molecular sieve particles	defects	challenging
nanocomposite films		low- and high-loading of molecular sieve particles in matrix	matrix; material mismatch	potentially easier

while admittedly more complicated, the hierarchical (multistep) procedure for the synthesis of zeolite films provides more opportunities for tailoring properties to improve performance.

The first commercially available zeolite membranes appeared more than a decade ago and targeted small-scale distributed applications, that is, requiring modules with membranes having an area of about 10 m^2.[54] Since then, despite significant research effort, commercialization progress has been stagnant, hampered by insufficient performance, high cost, and difficulties in scale up. It has become evident that zeolite membrane technology for large-scale processes depends on reliable manufacturing that can generate thousands of square meters of membrane area while achieving essential film characteristics: film continuity with low defect density, appropriate pore orientation, and membrane thickness well below the micrometer range.

Despite the lull in commercial progress, recent research has yielded a number of breakthroughs that have provided more fundamental insight into the seemingly elusive mechanisms of zeolite growth, means for rational manipulation of particle morphology, and directed assembly of continuous films. These serve as the basis for renewed optimism over the possibility to rationally design and tailor inorganic films to surmount the challenges plaguing the current technology and improve the viability of molecular sieve films for commercial applications. The recent fundamental understanding of zeolite growth should provide a strong foundation for hierarchical control of film morphology starting at the molecuar level. At progressively larger scales, the development of reliable particle deposition techniques and the identification of organic cations that can simultaneously act as crystal structure directing agents and crystal shape modifiers, raise prospects for crystal-engineering-based approaches that stand to yield unprecedented control over the microstructure. Such control, the lack of which has been a significant drawback of other membrane-fabrication methods,[94,95] is expected to enable the synthesis of membranes with superior performance. The aim of this Review, therefore, is to highlight such recent advances in zeolite film technology. Through clarification and critical discussion of the current state-of-the-art, we aim to induce a concerted drive toward the commercial viability of molecular sieve membranes.

The current state-of-the-art regarding the formation of zeolite films on a laboratory scale is based upon the technique of secondary seeded growth, whereby nucleation can be effectively decoupled from film growth in a hierarchical method capable of satisfying many of the stringent requirements mentioned above. In its idealized embodiment (Figure 1), this technique for film fabrication relies on the assembly of preformed, precisely shaped micro- or nanoparticles to form closely packed monolayers, followed by epitaxial growth to yield continuous films. More specifically, it consists of three subprocesses: 1) synthesis of a colloidal suspension of appropriately shaped zeolite particles, 2) deposition of the particles on a porous support to form an oriented seed monolayer, and 3) secondary and, if needed, tertiary treatment of the particles comprising the seed

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Mark A. Snyder earned a BS in Chemical Engineering from Lehigh University in 2000, and a PhD from the Department of Chemical Engineering at the University of Delaware in 2006, working with Prof. D. G. Vlachos. His PhD research focused on multiscale modeling and confocal characterization of zeolite membranes. He received the AIChE Separations Division Graduate Student Award in the area of membranes in 2005. In 2006 he joined the Tsapatsis research group as a Postdoctoral Fellow, where he continues to pursue research into novel inorganic materials.

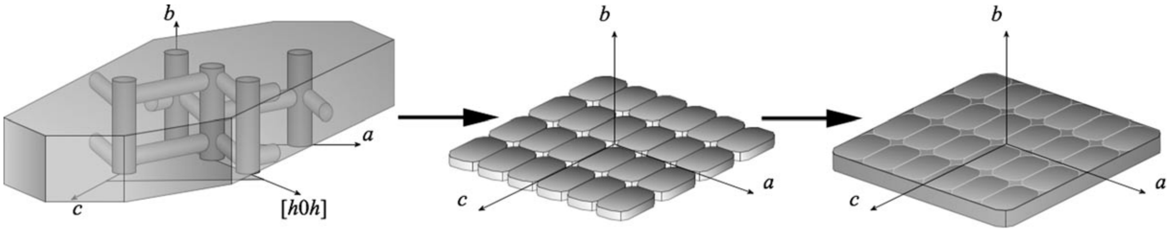

Figure 1. Schematic representation of thin-film processing using molecular sieve particles (left) as building blocks to form crystal monolayers (middle) and oriented, intergrown films (right); shown here in an idealized view without out-of-plane particles. A schematic representation of the MFI structure with intersecting straight (along the *b*-axis) and sinusoidal or zig-zag (along the *a*-axis) channels is shown within the crystal on the left.

monolayer to form a continuous film with aligned nanopores. This process requires precisely sized and shaped zeolite nanoparticles to be used as building blocks in reactive or physical nanoparticle-deposition processes. Ongoing research looks to answer many of these new and difficult questions.

2. Siliceous ZSM-5

While applications for membrane technology have been envisaged for a range of zeolites, the structure-type MFI (also known as ZSM-5) has garnered much interest as a model zeolite system for the development of a generalized membrane manufacturing process. Furthermore, MFI itself bears many potential applications. As such, we focus this Review on this zeolite structure type, more particularly on its purely siliceous form termed silicalite-1 or siliceous ZSM-5.

MFI is one of the most widely studied zeolite structure types since it has a channel system with pore openings approximately the same sizes as many industrially important organic molecules (Figure 1). Numerous studies on zeolite membranes focus on the structure-type MFI, which has selective separation capabilities reported for hydrocarbon isomers,[8,96–120] organic/water,[121–124] and other permeate gas mixtures.

For example, MFI zeolite membranes are ideally suited for the separation of xylene isomers since the pore size of the MFI framework (ca. 6 Å) should allow preferential permeation of *p*-xylene (kinetic diameter ca. 5.8 Å) while excluding the bulkier *o*- and *m*-xylene (kinetic diameters ca. 6.8 Å). The separation of xylene isomers is important in the petrochemical industry since they are widely used as industrial solvents and precursors.[12,125] This demand drives a yearly production of 22 million tons[126] through the catalytic reforming of naphtha, disproportionation of toluene, transalkylation of toluene with C_9 aromatic compounds, and as a by-product of steam cracking of hydrocarbon feeds (pyrolysis gasoline).[127,128] Current separation technology is limited to energy-intensive operations such as fractional crystallization, adsorption in a simulated moving bed, and distillation, which make separations based on zeolite membranes an economically attractive alternative.

Furthermore, an industrial standard for producing high-purity *p*-xylene involves catalytic isomerization with product recycle because of thermodynamic equilibrium (24.8% *p*-, 53.4% *m*-, and 21.8% *o*-xylene at 377 °C)[129] limitations. As such, an unprecedented opportunity exists for an MFI membrane reactor capable of selective removal of *p*-xylene during the reaction to shift the equilibrium and overcome thermodynamic limitations of the isomerization to attain higher yields of *p*-xylene, all within a compact unit design.

Numerous other examples for potential applications of MFI films can be cited, some of which are currently pursued for commercial purposes.[130–132] They include the separation of linear from branched hydrocarbons to enhance the yield and selectivity of hydroisomerization[133] and oligomerization.[134] Later in this Review, we highlight the performance of state-of-the art MFI membranes for the separation of xylene isomers and linear from branched hydrocarbons as a means for benchmarking the quality and separation capabilities of the current membrane technology, and to critically assess the potential for their implementation in the designs of membrane reactors.

MFI, because of its multidimensional channel network, generally allows manipulation of the separation performance through control of the characteristics of the membrane microstructure (thickness, grain boundary structure, orientation, etc.). This possibility expands the potential applications of MFI membranes beyond the separations described above to include applications such as low-k dielectric films in new microelectronic devices,[25] chemical sensors,[135,136] and others.

3. MFI Synthesis from Homogeneous Sols

The ability to rationally design zeolites in a hierarchical manner for specific applications and their adaptation for commercial purposes requires, at the most basic level, a fundamental understanding of the mechanisms driving their nucleation and growth. The elucidation of such mechanisms, however, has proven to be far from facile, and has fueled intensive research for more than a decade. This pursuit of fundamental insight into the nucleation, crystallization, and growth of zeolites represents a resurgence of a very active past research area. As such, a brief review is warranted to provide a historical perspective and highlight similarities with the silicalite-1 system.

3.1. Nucleation and Growth: Historical and Current Perspectives

Classical theories revolve around the coarsening of colloidal crystals nucleated from supersaturated solutions by molecular deposition from monomeric and oligomeric species. This type of growth, commonly termed Ostwald ripening, is based on the increasing stability of particles with size, and results in the growth of larger, more stable particles at the expense of the dissolution of smaller, less stable particles.

Growth by aggregation was also a recognized mechanism in the past that received significant attention, and motivated attempts to differentiate degrees of order and disorder in particulate systems. The result is a range of terminologies to describe the hierarchy of structures spanning from polycrystalline mosaic crystals to ordered tactoids[137–140] (for example, clay, nacre[141,142]), colloidal crystals, or mesocrystals.[143,144] Recognizing the potential confusion involved in differentiating degrees of order and disorder in particulate systems, Kohlschutter[145] coined the term somatoids to generally describe the continuum of structures leading from molecular precursors to crystalline end products.

From the often confusing terminology have arisen two closely related theories, one by Kolthoff and another by Iler, that have important significance for understanding and interpreting the nucleation and growth of silicalite-1. In particular, Kolthoff[146–153] proposed a lesser known, but complementary mechanism to that of Ostwald ripening in which crystal "perfection" occurs through transfer of matter between adjacent crystal faces of disparate stability rather than between particles of disparate size. The concomitant "self-digestion" of particles eliminates crystal defects while reducing the total surface area and maintaining the particle size. Kolthoff ripening can account for perfection in the particle shape when particles are formed by aggregation.

Iler[154] has coupled the ideas of Kolthoff ripening and the classic notion of curvature (surface) dependent solubility as a means for rationalizing the stability and coalescence of aggregated particles, specifically silica, in solution. In Ref. [154] (p. 50), Iler argues that because of its extremely small negative radius of curvature, the crevice formed at the point where two colloidal particles aggregate in solution has a very low solubility. Species then dissolve from the more soluble (that is, concave) surfaces of the particles and preferentially deposit in the crevice, thereby creating a neck joining adjacent particles. Iler[154] has pointed out that a consequence of the suppressed neck solubility and the generally large size of the aggregates leads to aggregate stability exceeding that of the individual particles from which it is formed.

Another form of ageing involves structural changes of metastable particles by phase transformations between amorphous and crystalline phases or between crystalline polymorphs. Crystal growth by nucleation in and growth through transformation of amorphous gel phases has been observed for both inorganic systems (for example, goethite in iron oxide gels[155]) and ones in nature.[156–162] Examples of amorphous-to-crystalline[163,164] and polymorph transformations[165] also exist. In these cases and others, the transformations often yield crystallization centers and nuclei with functionality capable of triggering oriented aggregation. Thus, the onset of aggregation and growth is limited by the rate of such transformations.

3.2. MFI Nucleation and Growth: The Debate

Silicalite-1 nucleation and growth can occur in clear TPA-silica solutions in the presence of precursor nanoparticles. These nanoparticles are spontaneously formed within TPA-silica solutions,[166–170] and, when prepared by hydrolysis with tetraethoxysilane (TEOS) at room temperature, exhibit a core–shell structure consisting generally of a silica-rich core surrounded by a TPA-rich layer.[171] Fully condensed silicalite-1 crystals, with TPA molecules centered at channel intersections, eventually appear in solution. The degree of condensation of the silica core of the precursor nanoparticles is unknown.

For more than a decade, a concerted debate has revolved around the role, or lack thereof, of the nanoparticles in the growth of MFI zeolite crystals. Until recently, classification of their role ranged from spectators to active precursors or even crystalline building units for zeolite growth. Existing theories can be generally categorized according to the mechanism of nucleation and growth resulting from: 1) oligomeric nutrients provided by dissolution of the colloidally stable precursor nanoparticles,[166,167] 2) direct addition of subcolloidal particles to growing zeolite crystals,[172] 3) nanoparticle gelation and subsequent crystalline transformation,[173,174] 4) ageing and oriented aggregation of partially transformed precursor nanoparticles,[175] or 5) self-assembly of crystalline precursor nanoparticles.[176]

Conclusive and noncontradictory evidence of the latter mechanism is lacking.[168,177–180] On the other hand, an undisputed commonality among the former four is the consistent detection of precursor nanoparticles (approximately 3–5 nm in size) in fresh and aged TPA-silica precursor solutions bearing no evidence of silicalite-1 structure.[169–172,181] While the focus of this Review is mainly upon silicalite-1 obtained from clear sols, it is important to recognize that silicalite-1[182] and other zeolites[173,174,183] can result from nucleation in and transformation of amorphous gels, reminiscent of the non-zeolitic systems discussed previously.[163–165]

An additional commonality among the viable mechanisms is the eventual emergence of a population of particles that do bear the crystalline TPA-MFI structure upon hydrothermal or room-temperature ageing of TPA-silica sols. Numerous studies have been carried out in attempts to more clearly elucidate the mechanisms that give rise to the delayed evolution of precursor solutions to a crystalline end product in clear TPA-silica precursor sols.

The delay in the emergence of the bulk crystalline end product serves as strong evidence that zeolite growth is a nucleation-controlled process rather than one of assembly of preexisting particles. Namely, the possibility for the self-assembly of crystalline precursor nanoparticles[176] or even amorphous ones can be reasonably ruled out since such a process would be expected to follow second-order kinetics with respect to the nanoparticle concentration. Such kinetics, however, *cannot* explain the induction period observed in the growth of zeolite crystals.

Early studies suggested two possible explanations for the involvement of precursor particles: either 1) as sources of nutrients, through Ostwald ripening,[166,167] or 2) as active participants in an aggregation and densification growth mechanism.[166,172,184] Despite the evidence for aggregative growth of silicalite-1,[172,184] a definitive understanding of the delayed evolution or so-called "induction period"[185] leading to a crystalline end product has remained elusive until recently. One of the general uncertainties plaguing most studies of zeolite growth is the unclear effect of ex situ characterization (that is, quenching of high-temperature experiments or particle isolation) in light of the temperature-dependence of silica solubility and the dynamics of the precursor particles.

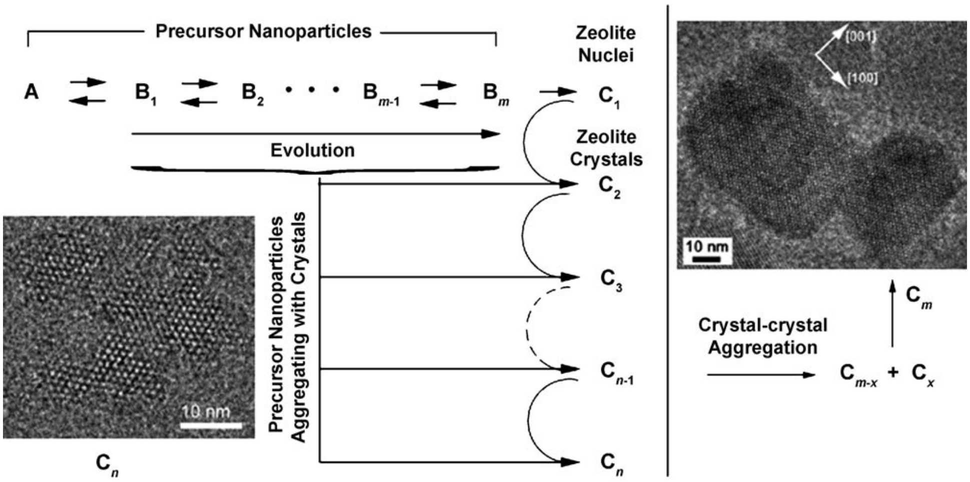

Figure 2. Proposed mechanism by which spontaneously formed precursor nanoparticles evolve towards a capacity for growth by oriented aggregation. The HRTEM images of aggregates of precursor nanoparticles (left) and crystals (right) are shown. The image on the right has been reproduced from Ref. [187].

Motivated by evidence of room-temperature ageing of TPA-silica solutions,[169,185,186] Davis et al.[175] recently carried out room-temperature studies of TPA-silica solutions over a period of more than one year. In that study, the evolution of TPA-silica solutions of three compositions ($x\,SiO_2$:9 TPAOH:8100 H_2O:4x EtOH, $x = 5$, 20, 120) was studied comprehensively by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), cryo-TEM, high-resolution TEM (HRTEM), and atomic-force microscopy (AFM), and a mechanistic model of growth by aggregation was proposed. The formation of precursor nanoparticles in the two most silica-rich solutions, and absence thereof in the solutions with the lowest silica content, suggested monomeric speciation of the majority of the added silica in the latter case. Moreover, in the limiting cases ($x = 5$, 120), only dense silica rather than silicalite-1 was formed after a year.

In the case of the intermediate silica concentration ($x = 20$), precursor nanoparticles were observed to evolve (initially rapidly) in size (3.8–4.8 nm in diameter) and number over approximately 100 days. Following an extended period (245 days) of aging with a constant particle size and population, a second particle population of a much larger crystal size bearing a silicalite-1 structure emerged. This second population of larger particles grew at an activated rate that was consistent with previous seeded-growth studies.[172] This finding indicates similar rate-limiting steps in the growth at high and room temperatures.

TEM imaging of particles at their early stage of growth revealed poorly formed crystal morphology that was characterized by voids and crystalline domains of a size comparable to the precursor nanoparticles (Figure 2, left). A slight misorientation of the crystalline domains, a signature often attributed to oriented aggregation,[188–190] was also observed. Following these initial stages of crystal growth, more compact crystals appeared, with typical (pill-shaped) morphologies developing after approximately 500 days.

The room-temperature studies carried out by Davis et al.[175] help to clarify and, in some cases more conclusively discount, possible mechanisms that lead to zeolite growth. In particular, the seeded-growth studies in low-silica solutions revealed neither growth nor dissolution of the seed particles. Unseeded studies in the same solutions yielded only dense silica instead of silicalite-1, thus revealing the critical role of precursor nanoparticles and discounting 1) homogeneous nucleation and growth and 2) facile aggregation of nanoparticles as viable mechanisms for the evolution of silicalite-1. At the same time, the failure to produce silicalite-1 in solutions with a high silica content suggests that the mere presence of precursor nanoparticles is an insufficient condition for the growth of silicalite-1.

Insight into the complexity of the nucleation and growth of silicalite-1 comes from the long induction period between the initially rapid evolution of nanoparticles (in terms of size and population) and the emergence of the secondary crystals. This delay in crystallization points to an evolution of the nanoparticle structure with a concomitant increase in the colloidal stability, a slowing of dissolution kinetics, and an increased tendency for aggregation. Such differences between fresh and aged precursor nanoparticles was confirmed by in situ AFM studies[175] that revealed qualitative differences in their affinity for mica surfaces as a function of particle ageing. These AFM studies, coupled with the delay in crystallization, further underscore the likely metastability of the precursor nanoparticles,[191] with transformations akin to those observed for metal hydroxide systems studied by Buyanov et al.[163,164]

In regards to this evolution of the particles, it is necessary to reconsider the stability of nanoparticles. It was proposed that the stability of fresh precursor nanoparticles derives from the surface adsorption of TPA molecules[167] and the higher apparent surface potential of the nanoparticles relative to TPA-silicalite-1.[192] It is conceivable,[193] however, that the evolution of the precursor nanoparticles towards crystallization generally degrades this stability by 1) decreasing the charge and surface stabilization through incorporation of external TPA molecules within the nanoparticle interior and/or 2) partial condensation of the internal structure to a zeolite-like one. Such changes would undoubtedly lead to an increased probability for aggregation, and may ultimately support crystal nucleation.

Based on these experimental results and a mathematical model that quantitatively describes the experimental observations, it has been suggested[175,194] that nucleation and early growth of MFI is driven by the evolution of the distribution of precursor particles toward crystalline structures and nuclei, with growth in early stages occurring by oriented aggregation of partially transformed precursor particles. Figure 2 (left) summarizes the mechanism proposed in Ref. [175] for early stages of growth, according to which precursor nanoparticles (species A), which do not contribute directly to aggregative growth, evolve in their structure (species B_1 through B_m) until a small fraction of them transforms to zeolite nanocrystals with sizes of 5–10 nm (species C_1). Despite their colloidal stability and propensity for growth,[172] the concentration of these zeolite nanocrystals remains low since as soon as they are formed, and before they have the chance to develop to well-faceted (shaped) nanocrystals, they undergo relatively fast aggregative growth by the rapid addition of partially transformed (and thus destabilized with respect to colloidal stability) precursor nanoparticles (species B_1 to B_m) to yield the C_n population of particles.

In this process, the older B particles (higher subscripts m) of the population bear an increasing probability for contributing to such growth by aggregation. The contribution of the noncrystalline B particles to the aggregative growth has been found[195] to be critical for capturing the broad particle distribution observed experimentally. In fact, a simplified mechanism of zeolite growth based solely upon the aggregation of C_1 particles appears incapable of capturing the presence of relatively large crystals at very low yields (particles of ca. 50 nm at less than 5 % yield).[175] While the mechanism proposed in Ref. [175] is consistent with the findings of Ref. [172] in terms of the predicted and measured activation energies for growth, it goes further to address the unresolved issue in that study of why only a portion of the particle population (10^{12} cm^{-3} instead of 10^{17} cm^{-3}) apparently contributes to growth. Namely, the findings of Ref. [175] rationalize this to be a result of the distribution of particle stability rather than particle size, as was conjectured in that study.

TEM images[175,187] of the early stages of crystal growth (see the left image in Figure 2) show signs of oriented aggregation of nanoparticles in inhomogeneous structures bearing slightly misoriented silicalite-1 crystallinity. It is possible that amorphous regions of these crystals either are indistinguishable in the TEM images or that they dissolve during sample preparation by dialysis.[175] Iler's theory[154] on aggregate stability helps rationalize the preservation (stability) of these crystal aggregates in solution. Moreover, the ultimate filling of interstices between crystalline domains at early stages of growth and the later evolution of particle morphology to common pill shapes is reminiscent of perfection by Kolthoff ripening.[148] At the same time, at this latter stage of growth, Ostwald ripening and growth by monomer addition[167] probably becomes an important contributor, especially in light of the increased surface area of the crystals, the increased pH value arising from the formation of silicalite-1, and the reduced nanoparticle concentration. Figure 2 (right) also highlights the possibility for zeolite growth by oriented crystal–crystal aggregation.

In general, the aggregative growth mechanism discussed above and shown in Figure 2 explains why the highly sought after (that is, for the purposes of large-scale membrane fabrication) well-shaped 5–10-nm zeolite MFI crystals cannot be isolated in substantial yield. Rather, 50-nm-sized poorly developed crystals are obtained even at crystal yields that are a fraction of a percent. Methods for the mass production of small uniformly sized and shaped zeolite nanoparticles are currently being explored as enabling technologies for large-scale fabrication of membranes. We discuss these as part of the future outlook in the conclusion of this Review.

4. Oriented MFI Membranes: State of the Art

The fabrication of MFI membranes involves a hierarchical approach (Figure 1) in which small zeolite particles are designed and used to seed a porous support. Upon secondary and/or tertiary growth, these crystal monolayers are transformed into a continuous film. A clarifying analogy can be drawn between such a technique and a tiling process, in which zeolite seed crystals (analogous to individual tiles) are deposited in a monolayer on a support in a similar fashion to the deposition of tiles on a surface. Secondary and/or tertiary growth then serves to close the gaps between the tiles. Membranes fabricated by this technique are currently the laboratory-scale state-of-the-art, both in terms of control over the microstructure and separation performance.

4.1. Hierarchical Control of Film Microstructure

By using a combination of microstructure design, surface-seeding techniques, and crystal growth in the presence of tailor-made crystal-shape modifiers, synthesis procedures have been developed to create oriented zeolite films by design.

4.1.1. Tile Preparation

The multidimensional pore topology of MFI (Figure 1) provides a rich palate for fabricating films with various pore orientations by crystal design. The schematic representation in Figure 3 illustrates the associated processing steps required for the manipulation and control of the microstructure. Control of the size, shape, morphology, and microstructure of zeolite crystals is possible through variation of the synthesis conditions (namely, composition, temperature, time) as well as appropriate selection of organic cations, generally termed structure-directing agents (SDAs). The SDA commonly employed for the synthesis of MFI is tetrapropylammonium (TPA). Hydrothermal growth in its presence (first arrow, Figure 3) leads to a progressive transformation of the MFI crystal morphology from spherical (left, Figure 3) to the signature coffin-shape (center, Figure 3).

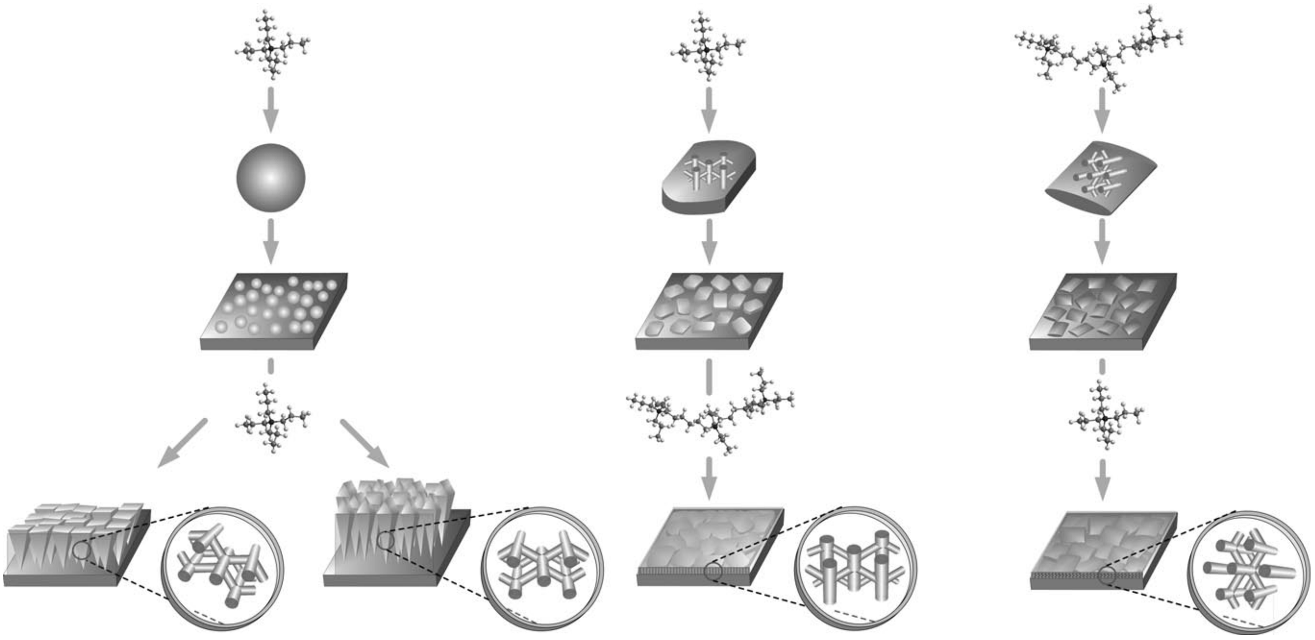

Figure 3. Scenarios of microstructure control by crystal-shape design, deposition, and growth using crystal-shape modifiers including tetrapropylammonium hydroxide (monomer-TPA: TPA) (for example, top left) and bis-1,6-(tripropylammonium)hexamethylene dihydroxide (dimer-TPA: dC6) or bis-*N*,*N*-(tripropylammoniumhexamethylene)-di-*N*,*N*-propylammonium trihydroxide (trimer-TPA: tC6) (for example, top right). Platelike particles (not shown) arise in the presence of the structure-directing agent dC5 ($(C_3H_7)_3N^+(CH_2)_5N^+(C_3H_7)_3$).

Figure 3 highlights the efficient manipulation of the pore orientation that is possible by a crystal-engineering approach involving the development of SDAs that, while templating the same structure (MFI), act as modifiers to generate a range of crystal shapes. Namely, the crystal on the right has zig-zag channels along its short dimension, the crystal in the middle has straight channels of slightly different size (fraction of an Angström) along its short dimension, and the crystal on the left is equiaxed.

Inspired by an earlier study[196] that attributed a change in the MFI crystal morphology to a better fit of $(C_3H_7)_3N^+$-$(CH_2)_6N^+(C_3H_7)_3$ ions (referred to from this point forward for simplicity as dimerC6-TPA and denoted as dC6) as the SDA in the straight (along the *b*-axis) versus the sinusoidal (along the *a*-axis) channels of MFI, we have reported a systematic investigation of the role of diquaternary and triquaternary cations on crystal morphology. Specifically, we studied the use of the diquaternary ammonium cations $(C_3H_7)_3N^+(CH_2)_n$ $N^+(C_3H_7)_3$, where $n = 5, 6, 7$ (denoted as dC5, dC6, and dC7, respectively), as well as the trimerC6 TPA cations[197] (denoted as tC6) as SDAs for the synthesis of silicalite-1 with the objective of altering the crystal shape.

The predominant crystal terminations (complete pentasil chains and incomplete 6MRs) and step heights were observed by HRTEM to be comparable, at least between crystals grown in the presence of TPA and tC6,[198] with the only marked difference being the presence of (001) faces in the former and absence in the latter. The most remarkable difference, however, especially from the standpoint of designing oriented MFI films, is the manipulation and control at the molecular level of the MFI morphology afforded by various SDAs: from plates that are very thin along the *b*-axis (dC5) to plates that are thin along the *a*-axis (tC6).[198,199] Crystals with thin dimensions along the *c*-axis have yet to be prepared, and remain as a persistent challenge in the crystal engineering of MFI.

4.1.2. Tiling a Surface

By using the crystals described in the previous section, it is possible to deposit (second set of arrows from top, Figure 3) a layer of particles on a porous support. This process is analogous to tiling a surface, especially in the case of the platelike particles, where the tiles are placed with their flat side parallel to the surface rather than end on. Consequently, the different morphologies of the crystals depicted in the middle and on the right of Figure 3 lead to deposition with the zig-zag and straight channels, respectively, perpendicular to the support. The equiaxed crystals, illustrated on the left, are randomly oriented upon deposition.

In the state-of-the-art silicalite-1 membranes, a porous support (alumina, stainless steel, etc.)[114] is first coated with a layer of mesoporous silica (pore size 2 nm) by the sol–gel technique developed by Brinker and co-workers.[200] The mesoporous silica layer provides a smooth surface that can be functionalized for the deposition of the tiles. Details of the deposition procedure can be found in Refs. [95,201,202]. Here we briefly mention that a viable seed-deposition method is based on their covalent attachment to the support by use of the coupling reactions developed by Yoon and co-workers.[203] Recent developments allow for this deposition to take place, both from solution and from dry powders, at ambient conditions within minutes (for a review see Refs. [204,205]). Alternative deposition techniques, including Langmuir–

Blodgett desposition[206,207] and convective-evaporation-driven-assembly at the contact line, are also under development.[208] However, the former cannot be easily scaled up, and both suffer from an inability to control the continuous deposition of a monolayer.

4.1.3. *Preserving Microstructure Orientation during Intergrowth of Continuous Films*

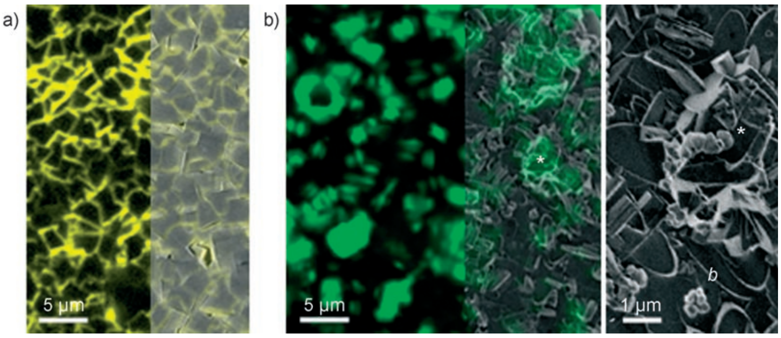

Figure 4. LSCM images of a) *c*-oriented[214] and b) *b*-oriented MFI films. The right parts of (a) and (b) are partially transparent SEM images of the membrane surface to simultaneously view the fluorescing polycrystalline features. The right-most image of (b) is an SEM image of higher magnification that shows the crystal defects (*) associated with the fluorescing features, and the well-intergrown *b*-oriented crystals (labeled "*b*").

The growth of continuous films (third arrow in Figure 3) involves crystal intergrowth or filling of the gaps between the deposited particles. The key for successful secondary growth is to promote in-plane (parallel to the support) growth of the zeolite tiles so as to eliminate gaps and generate a continuous film while minimizing out-of-plane growth and nucleation of misoriented grains. This approach proved difficult, for example, in the case of the hydrothermal treatment of *b*-oriented seed layers in the presence of TPA,[95] which led to the emergence of *a*-oriented twins and eventual *c*-oriented films by van der Drift's evolutionary selection (that is, dominance of the faster growth direction).[11,209,210] In that case, destruction of the initial seed orientation was attributed to the slow consumption of nutrients concomitant with sluggish growth along the *b*-axis.

To achieve the contradicting objectives defined above for preserving the seed orientation, we found that optimization of the secondary growth conditions is required to induce comparable in-plane and out-of-plane growth rates.[95] This is done by selecting an appropriate SDA/shape modifier that may be different from the one employed during the original crystal growth. A continuous and oriented film can then be obtained. The film, depicted in the middle scenario of Figure 3, has the straight pores perpendicular to the substrate, while zigzag pores run perpendicular to the substrate in the scenario on the right. *c*- and *h0h*-oriented films (Figure 3, left) can also be prepared from randomly oriented seeds by taking advantage of the faster growth along that direction.[11]

4.2. *ZSM-5 Thin Film Performance in Separations*

By comparing the separation capabilities of siliceous MFI membranes having different microstructures, it is evident that separation performance is an extremely sensitive function of the preferred orientation,[95,114,211] and not simply a limit of the trade-off between flux and separation that is characteristic of polymeric films.[212] The sensitivity in the case of zeolitic films can be attributed not only to differences in the orientation of intracrystalline pores, but, as suggested by laser scanning confocal microscopy (LSCM) studies,[213,214] to differences in intercrystalline pathways (grain boundary structure) as well.

Figure 4 shows representative LSCM images from within *c*-oriented[214] and *b*-oriented[215] silicalite-1 membranes as well as correlative SEM images of the membrane surface. LSCM has enabled quantitative analysis of membrane polycrystallinity for silicalite-1[214] and other[216] films. The accessibility of the grain boundaries in the *c*-oriented films to dyes larger than the zeolitic pores points to their potentially nonselective nature. The fewer polycrystalline features in *b*-oriented films is striking, with correlative SEM/LSCM studies revealing that the features correspond to grain boundaries between apparent *h0h*- or *c*-oriented crystalline defects. The lack of fluorescence from the periphery of *b*-oriented crystals (similar to that observed in *c*-oriented membranes[213,214]) suggests good intergrowth of those crystals.

Such insight underscores the challenge in a priori prediction and control of the performance of polycrystalline films. From the separation data of Figure 5 it is also evident that one cannot identify a single superior microstructure (often naively referred to as defect-free) for all separations. Rather, depending on the separation application, one finds that certain microstructures perform better than others. For example, from the data presented in Figure 5 a it is clear that the best separation performance for xylene isomers is

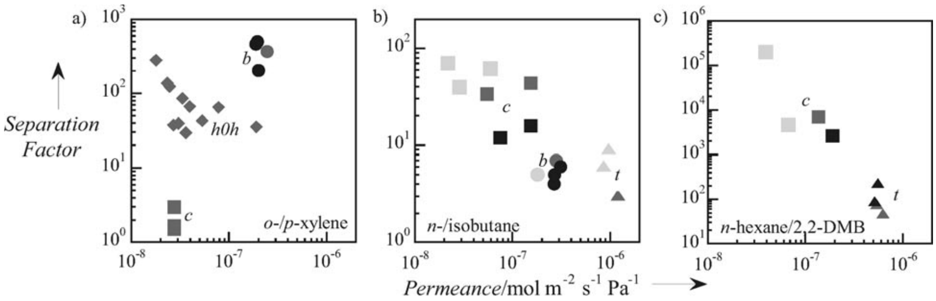

Figure 5. Performance of *c*- (■),[114,211,222,223] *b*- (●),[95,201] *h0h*-oriented (◆),[114] and thin (500 nm) randomly oriented (▲, *t*)[125,224] silicalite-1 membranes for separating the indicated components at temperatures ranging from room temperature to as high as 400 °C (light gray: RT–100 °C, gray: 100–200 °C, black: 200–400 °C. 2.2-DMB: 2,2-dimethylbutane.

obtained from *b*-oriented films, while *c*-oriented films hardly exhibit any selectivity for xylenes. This large disparity in performance for this difficult separation (that is, requiring angström resolution) could be rationalized based upon the drastic differences in the polycrystallinity observed by confocal microscopy of these films under the assumption that the non-zeolitic pathways are nonselective.

This performance, however, is to be contrasted with the separation of linear from branched hydrocarbons (Figure 5b and c) in which *c*-oriented films are superior to *b*-oriented ones. While this opposite trend is counterintuitive in light of the confocal microscopy studies described above, it suggests that a more complex mechanism for separation (for example, selective grain boundaries) must be at play in those systems. Efforts towards understanding the effect of non-zeolitic transport by use of simulations[217,218] have been reported, and recent progress[219] points to important effects of strongly adsorbing components.

The encouraging selectivity in all cases of silicalite-1 membranes (Figure 5) suggests the possibility for utilizing these and other zeolitic films for membrane reactors, with the aim of enhancing the selectivity and yield especially in view of equilibrium limitations, and also reducing the equipment and the energy footprints associated with current processes. Interesting possibilities also exist for improving the reaction selectivity by incorporating zeolitic films as selective coatings for catalyst pellets[220] (see Ref. [221] for a brief review of this technology).

4.3. Other Applications of ZSM-5 Thin Films

Besides separations of molecular mixtures, the finely tuned and oriented pores of MFI films have received attention for applications in the areas of dielectrics and sensing. Their ordered and open-pore structure makes them attractive, ultralow-k alternatives to the current state-of-the-art dense silica insulators widely used in the semiconductor industry.[25] Drawbacks associated with the poor mechanical stability of MFI films,[25] however, have limited their rapid adoption by the industry. As such, future advances in thin-film technology such as those described below could help to pave the way for their commercial application.

Molecular sensing applications have generally been a hot topic of research in the materials community for more than ten years. The selective pores of MFI and the ability to modify it from its purely siliceous to cationic forms makes it an attractive candidate for high-resolution sensing of molecules. Current sensing technology has focused not only on the MFI structure,[225] but also on LTA[225–227] and faujasite[21] in different devices for the detection of molecules ranging from alkanes to alcohols to water.

5. Summary and Outlook

The more fundamental understanding of MFI growth,[175] the ability to rationally manipulate the morphology and microstructure of MFI particles,[221] and the established hierarchical techniques for the design and synthesis of thin films, places the membrane, zeolite, and materials community on the threshold of a breakthrough. Namely, possibilities exist for improving the commercial viability of zeolite films through development of reliable manufacturing techniques that can generate thousands of square meters of membrane area.

Although the demonstration of high selectivity and separation factors in laboratory trials generates excitement regarding the potential of zeolite membranes, for large-scale applications it is imperative that high selectivity is combined with high flux because of the inverse proportionality of the required membrane area to the flux for a certain separation factor. Admittedly, attempts to reduce film thickness have been hampered by the presence of defects (see points marked *t* (thin) in Figure 5), caused by the large size of available seed crystals and the film thickness, which is practically set to about ten times the seed size to fill the typical gaps within seed layers.

As such, a recognized challenge for the future is the development of membrane-processing capabilities that will enable simultaneous reduction of both film thickness and parasitic defects. The successful completion of this task will undoubtedly require high-yielding fabrication of uniform, faceted particles with controlled microstructure, a goal that has become more feasible because of the recent elucidation of mechanisms driving MFI nucleation, growth, and ageing. As such, techniques such as confined synthesis[228–230] and others may enable the mass-production of faceted MFI nanoparticles.

Exciting prospects accompany such designed crystals for the development not only of the thinnest continuous inorganic films employing novel molecular linkages for monolayer assemblies, but also for incorporation in scalable nanocomposites (for example, dC5 directed platelike MFI particles instead of large unoriented particles). In addition, new possibilities exist for the directed assembly and growth of complex and functional materials beyond films for separations, such as molecular sensors, mechanically stable dielectrics, and novel reaction-diffusion devices.[231–234]

Our research on zeolite membranes was supported by the National Science Foundation (CTS-0522518) and the Department of Energy. This work was also supported in part by the MRSEC Program of the NSF under award number DMR-0212302. M.A.S. acknowledges funding from the University of Minnesota Supercomputing Institute for Digital Simulation and Advanced Computation Research Scholarship. We also gratefully acknowledge Professor D. G. Vlachos for allowing access to previously unpublished data, as well as J. Choi and J. A. Lee for designing graphics included in this Review.

Received: December 5, 2006

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