

Synthesis and Applications of Molecular Sieve Layers and Membranes[†]

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Strategies for the preparation of zeolite molecular sieve membranes and layers on different substrates are reviewed. Membranes (and continuous thin films) have been synthesized with ZSM-5 (MFI) type molecular sieves and other zeolites, either as free-standing specimens, grown on various supports according to several schemes, or embedded in polymer matrices. The membranes have been studied for molecule-selective separations and for catalytic reactions. Layers of presynthesized molecular sieves have been deposited by means of sol-gel matrixes and other bonding agents, molecular attachment layers, and via sputtering or laser ablation techniques. The resulting nanoporous layers have been applied in highly selective sensors, for the alignment of NLO chromophores and for molecular separations. Finally, oriented molecular sieve layers have been grown on self-assembled organic mono- and multilayers presenting phosphonate groups at the interface. Mixed phosphonate/alkyl films show profound effects on the surface crystallization of metallophosphate molecular sieves. MFI type zeolites have also been grown through the vapor phase on alkylammonium-modified gold substrates.

1. Introduction

A zeolite molecular sieve could be called an archetype nanostructure. Consider a crystalline object offering highly regular, ordered cages and channels of nanometer scale, with a choice of one-dimensional tunnels, two-dimensional intersecting pores, and finally three-dimensional connected networks, similar to the architectures found in large buildings. In the 1940s, Barrer¹ and co-workers successfully prepared the first synthetic zeolites. Zeolites are typically defined as crystalline, porous tectoaluminosilicates (or other metal oxides), where oxygen bridges two tetrahedrally coordinated framework atoms.^{2,3} More than 90 different framework topologies⁴ and many more compositions are known, with pore sizes ranging from about 0.3 to 3 nm, resulting in a vast range of different sorption properties, and internal surface properties ranging from hydrophilic to hydrophobic and from basic to acidic (Figure 1). The unique properties of zeolite materials have led to major applications in hydrocarbon conversion, size/shape selective heterogeneous catalysis, and gas separation processes.^{5,6} Other molecular sieve framework types continue to be discovered and will be included in this review where appropriate.

Zeolite-based nanostructured materials offer the potential to organize matter and to manipulate molecules with high spatial precision at the nanometer level.

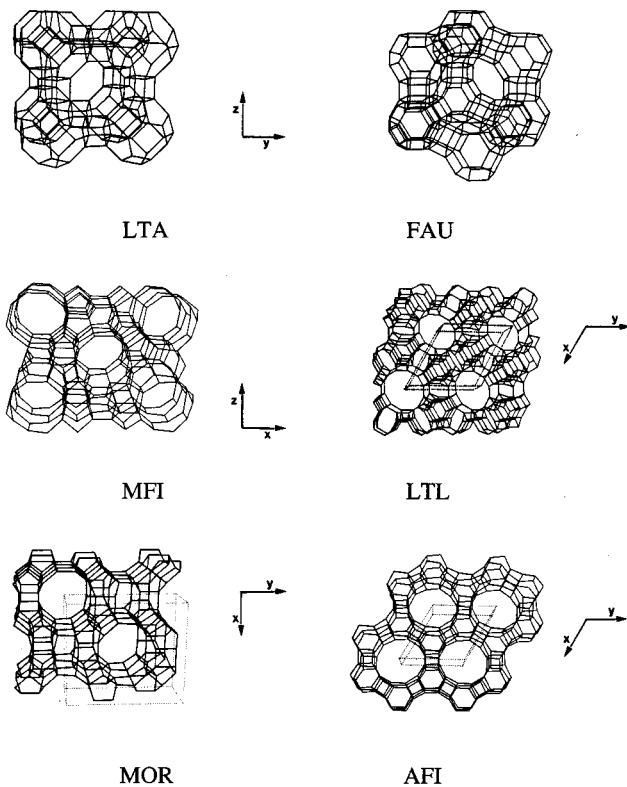


Figure 1. Zeolite structures. LTA, zeolite A (pore size 4.1 Å for the Na^+ form); FAU, zeolite X or Y (faujasite structures with different Si/Al ratios, pore size 7.4 Å); MFI, ZSM-5 (aluminosilicate) or silicalite 1 (pure silica form) (pore sizes 5.3×5.6 and 5.1×5.5 Å); LTL, zeolite L (pore size 7.1 Å); MOR, mordenite (main pore size 6.5×7.0 Å); AFI, AlPO_4 -5 (an aluminophosphate, pore size 7.3 Å). Lines represent oxygen bridges, nodes represent tetrahedral framework atoms such as Si or Al. After ref 4.

[†] Dedicated to Professor Galen D. Stucky on the occasion of his 60th birthday.

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(1) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*, Academic Press: London, 1982.

(2) Breck, D. W. *Zeolite Molecular Sieves*; Krieger: Malabar, FL, 1984.

(3) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, 4, 756.

(4) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 3rd ed.; Butterworth-Heinemann: London, 1992.

(5) Newsam, J. M. *Science* **1986**, 231, 1093.

(6) Thomas, J. M. *Angew. Chem.* **1988**, 100, 1735; *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1673–91.

While the “traditional” uses of zeolites include gas separation and a great variety of catalytic transformations, more recent efforts have also focused on the

construction (and stabilization) of unusual forms of matter such as quantum-size semiconductor clusters, magnetic particles, and alignment of nonlinear optical chromophores.^{7,8} Furthermore, as discussed in this review, the shape selectivity of these structures for molecular sorption and diffusion has inspired the creation of highly selective separation membranes and chemical sensors. Even the release of active agents such as antifungal compounds from zeolite films has been proposed.⁹

Several of the above applications greatly benefit from a planar (layer or film) form of the molecular sieve material. Because it is rather difficult to grow large, thin zeolite single crystals at the present time (but see for example ref 10), significant efforts have focused on the preparation of molecular sieve layers, thin films, and membranes. This review is devoted to the synthesis and applications of such zeolite nanostructures. For the purpose of this paper, we define a film as a continuous, dense intergrown phase, while a layer represents a discontinuous assembly of crystals on a substrate. Membranes are films on a porous substrate (or other assemblies such as free-standing zeolite films or rubber-embedded zeolite crystals) that separate two spaces and can perform chemical separations. As we will show below, both forms, layers and films/membranes, can be useful in different applications.

We can distinguish several different approaches for the design of zeolitic layers and films, as illustrated in Figure 2. Method I involves the deposition or embedding of preformed crystals on a substrate.

For the growth of zeolite layers/films, method II uses the transport of colloidal or polymeric, amorphous aluminosilicate (or other precursor) material to a substrate, thus providing favorable supersaturated conditions for nucleation and growth under hydrothermal conditions in the vicinity of the surface. In some cases, the substrate is partially consumed during synthesis; the substrate supplies the nutrient for the molecular sieve material.

Method III involves direct nucleation on the substrate surface from solution (or from a gel film), followed by growth. Because the synthesis mechanism is often unknown, a distinction between methods II and III is sometimes difficult. As discussed below, a high degree of control in such systems has been achieved in the oriented growth of metal phosphate sieves on organophosphonate layers.

2. Molecular Sieve Films and Membranes

This section will first discuss representative reports on the growth of free-standing zeolite films, followed by films on organic, metallic, and ceramic supports. Applications of molecular sieve films and membranes in separations and catalytic reactions are treated in sec-

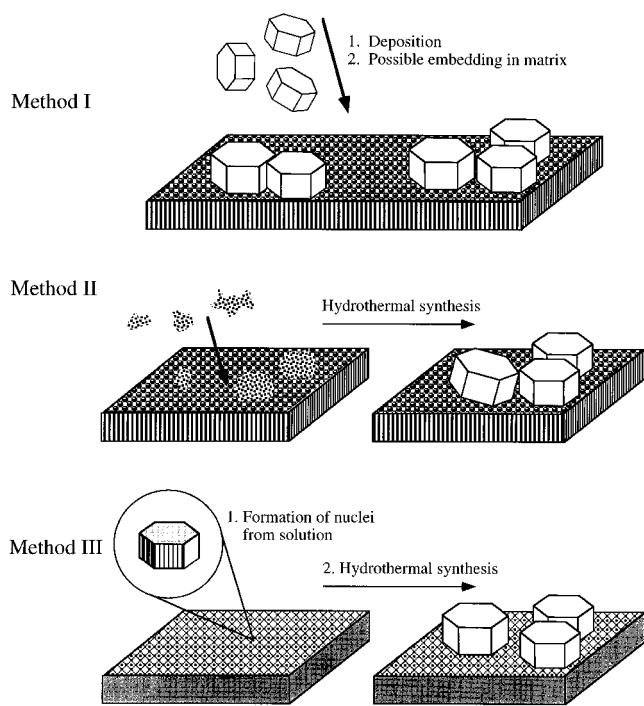


Figure 2. Methods for the design of zeolite layers and films (see text for discussion).

tions 2.2.1 and 2.2.2. Finally, pervaporation of liquid mixtures through polymer-embedded zeolite membranes is covered in section 2.2.3.

2.1. Growth of Molecular Sieve Films and Membranes. *2.1.1. Free-Standing Zeolite Films.* For applications such as gas-separation membranes, free-standing zeolite films could be of interest, and a few examples have been reported. Some zeolites can be grown on Teflon surfaces and removed from the substrates after crystallization. For example, clear synthesis solutions with a high water content ($\text{H}_2\text{O}/\text{SiO}_2 \geq 70$) have been used for the growth of ZSM-5 films on Teflon (30–100 μm thick, 5–10 μm ZSM-5 crystals).¹¹ Steaming of these films at 170 °C for longer than 96 h led to further ZSM-5 crystal growth. The side of the film in contact with the Teflon surface showed a higher Si/Al ratio than the side in contact with solution.¹²

Films of ZSM-5 (20 μm crystals) and gmelinite (one crystal thick, c axes about normal to the substrate) have been grown on polymer substrates (PTFE [poly(tetrafluoroethylene)] and polysulfonated styrene).¹³ The films could be removed from the polymer but were brittle when dried. The gmelinite film was prepared at 90–95 °C for 100 h using Dabco polymer as templating agent, while the ZSM-5 was made using tetrapropylammonium bromide (TPABr) or hexanediamine (the Dabco polymer was formed from 1,4-diazabicyclo[2.2.2]-octane (Dabco) and 1,4-dibromobutane). The authors suggest that the positively charged Dabco polymer attaches to the substrates during synthesis.

Similarly, pure zeolite membranes (20–250 μm thick) consisting of a continuous intergrowth of 10–100 μm ZSM-5 crystals have been prepared at 180 °C (for 0.3–9

(7) Ozin, G. A.; Kuperman, A.; Stein, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 359–76.

(8) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *247*, 669–78.

(9) Microbicidal and antifungal coatings containing zeolite-supported metals and organic antifungal agents such as benzimidazoles were claimed. For example, silver-containing zeolite A loaded with (4-thiazolyl)benzimidazole was reported to show improved inhibitory activity compared to the individual components. Terauchi, S.; Takei, Y.; Sasaki, M.; Shimazu, T.; Tanimoto, T.; Matsuo, R.; Tsurumoto, J.; Makino, J.; Hayashi, Y.; Inui, A. *Japan Kokai Tokkyo Koho*, **06**, 256, 689, Sept 13, 1994; CA 122:49090.

(10) Kuperman, A.; Nadimi, S.; Oliver, S.; Ozin, G. A.; Garces, J. M.; Olken, M. M. *Nature* **1993**, *365*, 239.

(11) (a) Sano, T.; Kiyozumi, Y.; Mizukami, F.; Takaya, H.; Mouri, T.; Watanabe, M. *Zeolites* **1992**, *12*, 131–4. (b) Sano, T.; Kiyozumi, Y.; Kawamura, M.; Mizukami, F.; Takaya, H.; Mouri, T.; Inaoka, W.; Toida, Y.; Watanabe, M.; Toyoda, K. *Zeolites* **1991**, *11*, 842–5.

(12) Sano, T.; Mizukami, F.; Takaya, H.; Mouri, T.; Watanabe, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 146–54.

(13) Anderson, M. W.; Pachis, K. S.; Shi, J.; Carr, S. W. *J. Mater. Chem.* **1992**, *2*, 255–6.

days)¹⁴ on substrates including Teflon, silver, stainless steel, and Vycor glass. The pure films were obtained by mechanical removal from the Teflon and silver substrates (from the latter by wetting with acetone). Permeability ratios as high as 17.2 ($P_{\text{tot}} = 1 \text{ atm}$ on both sides, at 49 °C) for *n*-hexane vs 2,2-dimethylbutane were measured for the pure ZSM-5 membrane, indicating that no significant transecting macroporosity was present (permeability, in units of $\text{cm}^2 \text{ s}^{-1}$, is defined as the ratio of the steady-state flux to the external concentration gradient, where the flux is equal to permeate concentration times flow rate, normalized to the geometric membrane area).

The preparation of self-supporting films of zeolite NaA (ca. 7 μm thick) was also reported. Various substrates (polyethylene, Teflon, glass) have been reacted with a homogeneous, clear synthesis mix at 50–60 °C for 1–2 days¹⁵ (ratio of $\text{H}_2\text{O}/\text{SiO}_2 = 200$). The authors discuss four different ways the membrane could form on the surface. The zeolites crystallized partially on the substrate surfaces and could be peeled off, resulting in a self-supporting agglomerate film of zeolite crystallites. These films could be advantageous because no organic template needs to be removed at high temperatures.

2.1.2. Zeolite Films on Organic Polymer Supports. The fragility of free-standing zeolite films has motivated the development of supported membranes. The design of separation membranes benefits from thin molecular sieve films because the permeability increases.

In addition to the polymer supports mentioned above, an alternative “support” for zeolite film growth (ZSM-5 and silicalite) is a sacrificial substrate (cellulose mouldings such as filter paper) that promotes growth (at 170 °C).¹⁶ The cellulose could be removed by burning at 500 °C, but the zeolite film retained its shape comprised of 5–30 μm crystals intergrown to a film of 500 μm thickness. It is not surprising that the resulting films have macroscopic defects. This approach was also explored for ZSM-11 and SAPO-5 (SAPO = silicoaluminophosphate). Mercury porosimetry showed the presence of large pores in the range of 10 μm .¹⁷

In an effort to achieve the formation of silicoaluminophosphate (SAPO-*n*) films, the hydrothermal synthesis of polycrystalline SAPO-5 film from $\text{Al}(\text{OCHMe}_2)_3$, H_3PO_4 , $\text{HOCH}_2\text{CH}_2\text{NET}_2$, and colloidal silica or $(\text{EtO})_4\text{Si}$ (preferred) on a Teflon slab in an autoclave was described.¹⁸ Similarly, the growth of polycrystalline SAPO-*n* films on Teflon slabs has been studied. SAPO-5, -11, -17, -34, and -41 films were obtained, but only a small fraction of the hydrogel was converted to a film. It was suggested that initially SAPO-*n* crystals with low Si concentration ($\text{AlPO}-n$) were formed on the substrate.¹⁹

Carbon membranes (in the form of hollow fibers) constitute a novel type of support for zeolite layers. The carbon materials were made by pyrolysis of poly-

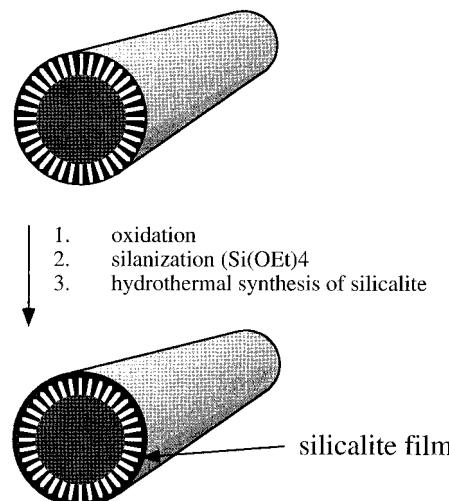


Figure 3. Hollow-fiber carbon zeolite membranes (after ref 20).

(acrylonitrile) precursors, and layers of ZSM-5, silicalite-1 [the pure SiO_2 form of ZSM-5], and mordenite were deposited using different growth techniques.²⁰ Silicalite-1 films (ca. 1 μm thick) were formed on the untreated carbon membranes under hydrothermal conditions at 120 °C. However, good adhesion and growth of ZSM-5 and mordenite films was only achieved when the carbon membranes were oxidized, followed by adsorption of tetraethoxysilane and heat treatment, prior to hydrothermal synthesis (Figure 3).

2.1.3. Zeolite Films on Metals. Membranes composed of a continuous intergrowth (10–100 μm) of molecular sieve crystals (e.g., ZSM-5) have been synthesized hydrothermally at 180 °C on various substrates including silver, steel, and glass.^{14,21}

A detailed study of surface crystallization shows that continuous layers (up to 1 cm^2) can be formed with the MFI structure (silicalite-1 and ZSM-5) on many supports, including metals, Si, cordierite, mullite, and quartz.²² Adjustment of synthesis conditions can serve to control the orientation of the crystals to a certain degree: At low temperature and low silicon concentrations, the long axes of the MFI crystals grow normal to the support. On the other hand, at high concentrations a thin gel layer forms that controls crystal growth such that the crystals must grow with their long axes parallel to the substrate (Figure 4). This orientation is favorable for membrane applications. The orientation is rather insensitive to the nature of the substrate and the crystallization is not epitaxial. Gmelinite and NaA layers have also been grown on several of the above substrates. On quartz, partial dissolution of the substrate was suggested to occur. Zeolite films have also been grown on alloy surfaces.²³ Layers of zeolite NaY have been crystallized on different metal substrates, particularly on copper (and Ag, Pt, Ti, Mo, Fe, Sn).^{24,25}

(14) Tsikoiannis, J. G.; Haag, W. O. *Zeolites* **1992**, *12*, 126–30.
(15) Myatt, G. J.; Budd, P. M.; Price, C.; Carr, S. W. *J. Mater. Chem.* **1992**, *2*, 1103–4.

(16) Sano, T.; Kiyozumi, Y.; Maeda, K.; Toba, M.; Niwa, S.; Mizukami, F. *J. Mater. Chem.* **1992**, *2*, 141–2.

(17) Sano, T.; Kiyozumi, Y.; Maeda, K.; Toba, M.; Niwa, S.; Mizukami, F. *Proc. Int. Zeolite Conf.*, 9th, 1993, Meeting Date 1992; Von Ballmoos, R., Higgins, J. B., Treacy, M. M. M. J., Eds.; Butterworth-Heinemann: Boston, MA; Vol. 1, pp 239–46.

(18) Sano, T.; Kiyozumi, Y.; Maeda, K.; Toba, M.; Niwa, S.; Mizukami, F.; Mukoyoshi, I.; Shoji, H. *J. Mol. Catal.* **1992**, *77*, L19–L26.

(19) Kiyozumi, Y.; Mukoyoshi, I.; Sano, T.; Mizukami, F. *Nippon Kagaku Kaishi* **1992**, 877–80; CA 117:153865.

(20) Smith, S. P. J.; Linkov, V. M.; Sanderson, R. D.; Petrik, L. F.; O'Connor, C. T.; Keiser, K. *Microporous Mater.* **1995**, *4*, 385–90.

(21) (a) Haag, W. O.; Tsikoiannis, J. G. U.S. Patent 5,019,263 A, 1991. (b) Dessau, R. M.; Grasselli, R. K.; Lago, R. M.; Tsikoiannis, J. G. U.S. Patent 5,316,661, 1994; CA 121:159729.

(22) Jansen, J. C.; Kashchiev, D.; Erdem-Senatalar, A. *Stud. Surf. Sci. Catal. (Adv. Zeolite Sci. Appl.)*, **1994**, *85*, 215–50.

(23) Xu, W.; Li, J.; Dong, J. *Adv. Mater.* **1991**, *3*, 442.

(24) Davis, S. P.; Borgstedt, E. V. R.; Suib, S. L. *Chem. Mater.* **1990**, *2*, 712.

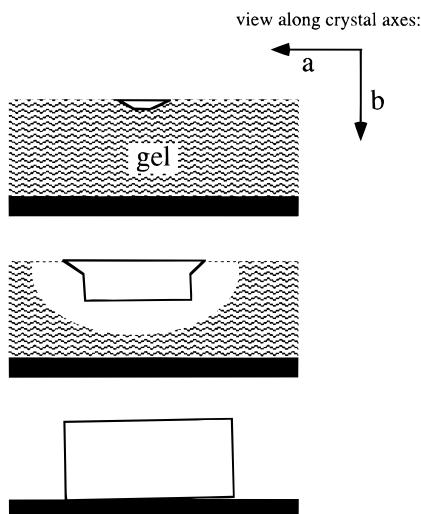


Figure 4. Proposed growth mechanism for MFI-type zeolite films (after ref 22).

It was found that zeolite deposited only on the top sides of horizontal substrates. On tilted substrates a thicker layer was formed at increased depth of immersion in the hydrothermal solution. The zeolite Y layers showed the ion-exchange behavior and porosity of the parent zeolite, and several indications suggest that the crystals grow directly on the metal, resulting in mechanically stable films.

In a related study, the effect of the structural properties of copper and other metal substrates on zeolite Y, silicalite-1 and A film growth kinetics has been explored. It was found that the zeolite film morphology, crystal size, and thickness depend on the surface properties of the substrate and the nature of the metal.²⁶ On substrates of pure metals and alloys having low surface tension, no dense films are formed. In contrast, plastically deformed metal surfaces supported the growth of rather dense films. Porous metals can also serve as supports for crystallizing attached zeolite layers (1–70 μm) by immersing them one or several times into a zeolite synthesis gel under hydrothermal conditions.²⁷

As discussed above (see ref 22), the crystallization of zeolites on different supports sometimes produces rather oriented crystals and/or crystalline intergrowth, in particular with silicalite/ZSM-5 type (MFI) materials.²⁸ The controlling factor is the nucleation/crystallization in the synthesis gel, not so much the nature of the support. A gel layer is formed on the support and converted into the zeolite film, thus favoring alignment of the resulting crystals with the surface. The latter study was focused on the growth of silicalite-1 on Si and quartz substrates. It was found that a SAW (surface acoustic wave; see also section 3.2) device modified with a dried suspension of silicalite-1 showed response to the presence of CO_2 .

(25) Creasy, K. E.; Deng, Y. P.; Park, J.; Borgstedt, E. V. R.; Davis, S. P.; Suib, S. L.; Shaw, B. R. *Mater. Res. Soc. Symp. Proc.* **1991**, 233, 157–67.

(26) (a) Valtchev, V.; Mintova, S.; Konstantinov, L. *Zeolites* **1995**, 15, 679–83. (b) Valtchev, V.; Mintova, S.; Konstantinov, L. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1995**, 40, 279–80. (c) Valtchev, V.; Mintova, S. *Zeolites* **1995**, 15, 171–5.

(27) (a) Barri, S. A. I.; Bratton, G. J.; De Villiers Naylor, T. Eur. Patent Appl. EP 481660 A1, 1992. (b) Barri, S. A. I.; Bratton, G. J.; De Villiers Naylor, T.; Tomkinson, J. D. Eur. Patent Appl. EP 481659 A1, 1992. (c) Bratton, G. J.; De Villiers Naylor, T. Eur. Patent Appl. EP 481658 A1, 1992.

(28) Koegler, J. H.; Zandbergen, H. W.; Harteveld, J. L. N.; Nieuwenhuizen, M. S.; Jansen, J. C.; van Bekkum, H. *Stud. Surf. Sci. Catal.* **1994**, 84, 307–14.

2.1.4. Zeolite Films on Ceramic and Metal Oxide Supports. The growth of zeolite films on ceramic and metal oxide supports has been achieved with synthetic methods similar to those discussed above for metal supports. Basically, a substrate is immersed into an appropriate synthesis mixture and subjected to hydrothermal treatment. Thus, porous ceramic (clay) supports have been used for the growth of continuous, polycrystalline ZSM-5 (MFI) zeolite films by immersing them into zeolite synthesis mixtures under hydrothermal conditions at 180 °C.²⁹ The films are stable to 400 °C and present 50–80 μm crystals on the clay surface. The synthesis conditions can be adjusted such that aluminum leaches from the support resulting in the growth of large analcime crystals. As-synthesized, template-containing MFI clay films are gastight. The composite membrane withstands mechanical stress (up to 4 bar) and exposure to water and methanol. Gas permeation experiments showed that selectivities are influenced not only by diffusivity differences but also by differences in sorption and by reduced mobility of weakly sorbed (faster moving) molecules caused by the slower moving species. In a related study, the effect of calcination on crack formation in large MFI crystals containing the tetrapropylammonium ion was examined.³⁰ The authors arrived at safe protocols for the calcination of membranes made from polycrystalline MFI type membranes synthesized *in situ* on the support.

A certain level of synthetic control over the orientation of the supported MFI films can be achieved by changing the synthesis conditions. In particular, the presence or absence of a continuous gel layer controls if the zeolite crystals are either laterally or axially oriented with respect to the substrate (see discussion in section 2.1.3).³¹ MFI films (200–500 μm thick) can also be grown on Si(001) substrates.^{31b} At certain concentration ranges with tetrapropylammonium (TPA) template, a continuous gel layer formed and was converted into the MFI crystals with lateral orientation relative to the substrate. However, when a mixture of TPA and sodium ions was used, gel spheres formed on the substrate leading to random crystal orientations.

A recent detailed study by Yan et al. has addressed the relationship between the synthesis conditions and resulting morphology of films of silicalite 1 (pure-silica ZSM-5) on fused silica glass.³² The authors found that at the early stages of the reaction a porous gel layer condenses on the substrate, within which the oriented (*b* axis normal to the substrate plane) zeolite crystals grow as mediated by the organic structure-directing agent tetrapropylammonium bromide (TPABr). Additional, less oriented zeolite layers were grown on top of the first crystal layer. IR data suggested that the TPA is located at the gel–solution interface. The authors propose that the orientation of the first layer is due to the strong tendency to grow the (010) faces of the crystals on the substrate surface (compare with the proposed mechanism shown in Figure 4). The size of

(29) Geus, E. R.; Den Exter, M. J.; Van Bekkum, H. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 3101–9.

(30) Geus, E. R.; van Bekkum, H. *Zeolites* **1995**, 15, 333–41.

(31) (a) Jansen, J. C.; Nugroho, W.; Bekkum, H. v.; Proc. Int. Zeolite Conf., 9th Meeting Date 1992; Von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: Boston, MA; 1992; Vol. 1, pp 247–54. (b) Jansen, J. C.; van Rosmalen, G. M. *J. Cryst. Growth* **1993**, 128, 1150–6.

(32) Yan, Y.; Chaudhari, S. R.; Sarkar, A. *Chem. Mater.* **1996**, 8, 473–9.

the individual crystals constituting the films could be controlled between ca. 0.5 and 30 μm by varying the synthesis conditions. In another study, a dense ZSM-5 layer was synthesized on the outer surface of an alumina ceramic filter, using Na_2SiO_3 as the silica source.³³

Films of ZSM-5 (MFI) were also crystallized by Davis et al. on porous α -alumina from a clear solution (details in section 2.2.1 and refs 59 and 60). The formation of different zeolites on porous glass and other supports was claimed.³⁴ A method using hydrothermal synthesis conditions and oligomeric silica species was employed to synthesize silicalite membranes within a macroporous α -alumina support.³⁵ Similarly, the formation of silicalite-1 films on α -alumina supports was studied as a function of pH of the synthesis medium. In high alkalinity gel medium, the zeolite film does not grow until homogeneous nucleation is observed, and the resulting films do not adhere strongly to the support. In contrast, strongly adhering, dense films have been obtained from low-alkalinity sol media with heterogeneous nucleation and crystallization.³⁶

A related approach is to pass orthosilicate solutions through the pores of silica substrates, concentrate them in the pores, treat with aluminum compounds and tetraalkylammonium salts to form an aluminosilicate hydrogel, and crystallize zeolites in the pores by reacting with aqueous alkali.³⁷ Reportedly, this procedure permits control of the pore diameter of the resulting membranes.

Remarkably, some of the volatile reagents for the hydrothermal film synthesis, for example amines, can also be transported through the gas phase such that a "vapor phase" synthesis of zeolite ZSM-5 and ZSM-35 is achieved.³⁸ For example, solutions of aluminum sulfate, Na silicate and NaOH were mixed to form a gel that was washed and deposited on a porous support in an autoclave. Vapors of ethylene diamine, triethylamine and water were allowed to react with the gel at 180–200 °C for several days to give ZSM-5 membranes (Figure 5). ZSM-35 was formed from boroaluminosilicate gels and $\text{PrNH}_2/\text{H}_2\text{O}$ vapors. The pure zeolite membranes are reported to be gas tight before calcination, suggesting the absence of cracks.

A similar vapor-transport technique was used to synthesize a thin ferrierite layer on an alumina plate.³⁹ A precursor aluminosilicate gel was deposited on the plate and treated with vapors of a templating agent (for 3 days in the presence of Et_3N , ethylenediamine, and steam at 175 °C). Permeation rates of H_2 , He, CH_4 , O_2 , N_2 , and CO_2 suggested a compact structure of the ferrierite layer. The selectivity of nitrogen relative to oxygen was higher than that in the Knudsen region.⁴⁰

The same authors have shown that a polycrystalline, defect-free membrane of mordenite can also be formed

(33) Masuda, T.; Sato, A.; Hara, H.; Kouno, M.; Hashimoto, K. *Appl. Catal. A* **1994**, *111*, 143–50.

(34) Suzuki, H. U.S. Patent 4,699,892, Oct 1987.

(35) Uzio, D.; Peureux, J.; Giroir-Fendler, A.; Dalmon, J. A.; Ramsay, J. D. F. *Stud. Surf. Sci. Catal.* **1994**, *87*, 411–18.

(36) Cheng, M. J.; Yang, W.-S.; Li, X.-S.; Yang, Y.-S.; Xu, Y.-D.; Lin, L.-W. *Ciuhua Xuebao* **1995**, *16*, 89–90; CA 123:123995.

(37) Toda, Fujio; Ko, Shiko; Ishikawa, Akira. Jpn. Kokai Tokkyo Koho JP 04200729 A2, 1992, Heisei, CA 118:698.

(38) Dong, J.; Dou, T.; Zhao, X.; Gao, L. *J. Chem. Soc., Chem. Commun.* **1992**, 1056–8.

(39) Matsukata, M.; Nishiyama, N.; Ueyama, K. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1183–90.

(40) Matsukata, M.; Nishiyama, N.; Ueyama, K. *J. Chem. Soc., Chem. Commun.* **1994**, 339–40.

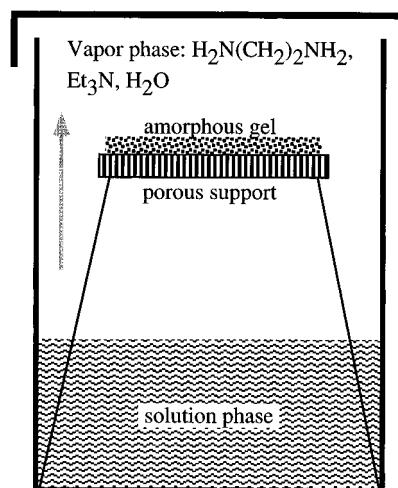


Figure 5. Vapor-phase synthesis of ZSM-5 (after ref 38).

by the vapor-phase transport on a porous alumina plate. The separation of benzene and *p*-xylene was studied, and the high separation factor in pervaporation experiments (>160) suggested zeolite shape selectivity in the membrane.⁴¹

An early patent describes the growth of zeolite X, Y, A and others on inorganic oxides including glasses, silicas, aluminas, aluminosilicates, and other substrates.⁴² The substrates were immersed in synthesis mixtures for the different zeolites.

Similarly, repeated hydrothermal synthesis has been used to deposit an A-type zeolite film on a porous alumina ceramic substrate. The preferred sources for the zeolite framework were Na_2SiO_3 and $\text{Al}(\text{OH})_3$, respectively.^{43a} Membranes of zeolite A have also been prepared on Si/SiO_2 , quartz glass, and quartz fiber filters.^{43b} The liquid phase separated from the reactant hydrogel was used for the membrane synthesis of crystalline, tight membranes on the former two substrates, although the synthesis conditions led to corrosion of the silicon plate. Multifold syntheses using seed crystals produced tight membranes on the quartz fiber filter.

One disadvantage of the direct crystallization of molecular sieves on supports can be the need for calcination in order to remove the organic template (if present). Temperatures up to 500 °C are applied, and the thermal stress can lead to partial destruction of the tight films. The deposition of preformed, calcined zeolites can therefore present an attractive alternative because the thermal stress on the sample can be greatly reduced (see section 3).

2.2. Separations with Molecular Sieve Membranes. Separations play a major role in industrial processing. For example, gases such as nitrogen, oxygen, ethylene, or carbon dioxide are used at a large scale and must be isolated from mixtures. Of several separation techniques, membrane separations are often the fastest and most energy effective. Due to the limited stability of organic membranes at high temperature or when exposed to oxidizing agents or ionizing radiation, there are many opportunities in the development of stable inorganic membranes.^{44,45}

(41) Nishiyama, N.; Ueyama, K.; Matsukata, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1967–8.

(42) Albers, E. W.; Edwards, G. C. U.S. Patent 3,730,910, 1973.

(43) (a) Masuda, T.; Hara, H.; Kouno, M.; Kinoshita, H.; Hashimoto, K. *Microporous Mater.* **1995**, *3*, 565–71. (b) Yamazaki, S.; Tsutsumi, K. *Microporous Mater.* **1995**, *4*, 205–12.

In addition to the molecular sieve membranes discussed below, there are other concepts being evaluated for the design of thermally stable, inorganic systems. Amorphous membranes based on sol-gel chemistry and/or deposition of colloidal oxides on a mesoporous support have the advantage of facile fabrication, but since the pore size depends on particle packing or the extent of polymer interpenetration and collapse, the porosity is often characterized by a broad distribution of pore diameters which limits chemical selectivity. For example, γ -alumina separation layers have been obtained with pore-size distributions around 2.5 nm.⁴⁶ Alternatively, a sol can be made by destabilization of colloidal solutions.⁴⁷ Titania and zirconia membranes with ultrafiltration characteristics have been made based on similar techniques, for example, from polymeric and particulate sols (hydrolyzed in alcohol or water, respectively) derived from the corresponding metal alkoxides.⁴⁸

Recent advances in the development of highly selective sol-gel membranes described by Brinker et al., have led to more narrow pore size distributions in the microporous range.⁴⁹ Detailed analysis of gas transport through sol-gel derived microporous silica membranes (on mesoporous alumina) showed that separation factors for H_2/CH_4 and $\text{H}_2/\text{isobutane}$ of 30 and 200 at 200 °C could be obtained.⁵⁰ The activation parameters of the activated transport were analyzed, and the calculated activation energies for micropore diffusion suggested that the pores are smaller than those of zeolite 4A. A different means of forming microporous thin films is, for example, by deposition of amorphous hydrogenated carbon films deposited by dc magnetron discharge decomposition of acetylene. Quartz crystal microbalance studies showed molecular sieve effects in these films.⁵¹

Crystalline molecular sieves such as zeolites offer the ultimate definition in pore dimensions and channel structure. Provided that continuous membranes can be prepared, molecular sieve membranes have several advantages, including (i) the uniformity of the pore sizes provides very high selectivity, (ii) straight channels enable fast diffusion, (iii) the systems have excellent environmental stability, (iv) and the intrazeolite surface may be modified to enhance adsorptive and diffusional selectivity for certain species.

One of the most challenging problems is to completely exclude pinhole and other leaks from the membranes, particularly under conditions of severe thermal cycling. As discussed in the following, several examples of highly selective, supported zeolite membranes have now been reported.

2.2.1. Separations with Supported and Free-Standing Zeolite Membranes. Membranes of MFI-type zeolites on

- (44) Hsieh, H. P. *Catal. Rev.-Sci. Eng.* **1991**, *33*, 1.
 (45) Armor, J. N. *Appl. Catal.* **1989**, *49*, 1-25.
 (46) (a) Keizer, K.; Uhlhorn, R. J. R.; Van Uren, R. J.; Burggraaf, A. J. *J. Membr. Sci.* **1988**, *39*, 285. (b) Hsieh, H. P.; Bhave, R. R.; Fleming, H. L. *J. Membr. Sci.* **1988**, *39*, 221.
 (47) Larbot, A.; Farbre, J. P.; Guizard, C.; Cot, L. *J. Membr. Sci.* **1988**, *39*, 203.
 (48) (a) Anderson, M. A.; Gieselmann, M. J.; Xu, Q. *J. Membr. Sci.* **1988**, *39*, 243. (b) Larbot, A.; Farbre, J. P.; Guizard, C.; Cot, L.; Gillot, J. *J. Am. Ceram. Soc.* **1989**, *72*, 257.
 (49) (a) Prakash, S. S.; Brinker, C. J.; Hurd, A. J.; Rao, S. M. *Nature* **1995**, *374*, 439. (b) Raman, N. K.; Brinker, C. J. *J. Membr. Sci.* **1995**, *190*, 264.
 (50) de Lange, R. S. A.; Keizer, K.; Burggraaf, A. J. *J. Membr. Sci.* **1995**, *104*, 81-100.
 (51) Yin, Y.; Collins, R. E. *Carbon* **1993**, *31*, 1333-6.

steel have recently attracted considerable attention, probably due to the ease of forming stable and gastight porous supports for the molecular sieving layer.

For example, continuous silicalite layers have been grown on a porous stainless steel support in a high-temperature membrane reactor.⁵² Permeation experiments applying the Wicke-Kallenbach method (concentration gradient as the driving force for permeation, feed and permeate in flows of carrier gases) were performed. At room temperature and high feed pressures, large differences in steady-state permeation (over 2 orders of magnitude) were found, leading to the following sequence: methane ~ krypton > ethane > argon > *n*-butane > neon > CFC-12 (CF_2Cl_2) >> isobutane. At higher temperatures, only the permeability of the first two remained similar while that of all other compounds increased significantly. In binary mixtures, strongly absorbing molecules such as *n*-butane reduced the permeability of weakly adsorbing species such as methane, resulting in high selectivities for the former. The sorbates behaved independently in the Henry region. The presence of some larger pores was concluded from the limited transport observed for 2,2,4-trimethylpentane (which is larger than the zeolite pores). In similar experiments with silicalite on porous steel (Figure 6), the sequence of pure gas permeabilities at room temperature and 0.3 bar partial pressure difference was methane > *n*-butane > isobutane. The lower permeability of isobutane was attributed to the greater bulkiness of the molecule. Again the presence of the butane isomers reduced the permeability of methane by 2 orders of magnitude. At higher temperatures, this effect was reduced as a result of the decreased adsorption of the butanes.⁵³

Pervaporation of liquids was also successful with the MFI/steel membranes. For example, a silicalite-on-steel system provided a separation factor of 60 for the separation of ethanol from water (from a 5% alcohol solution at 30 °C). This membrane showed crystal intergrowth in three dimensions and high thermal stability during calcination, and the permselectivity was attributed to the preferential sorption of ethanol into the silicalite phase.^{54,55} Silane coupling agents have been used to modify similar membrane surfaces, resulting in improved ethanol transport through the membrane.⁵⁶ The same group has also studied the pervaporation of methanol/methyl *tert*-butyl ether (MTBE) through silicalite/steel membranes.⁵⁷ A high selectivity for methanol was observed. Finally, the pervaporation of acetic acid/water mixtures was studied with silicalite/steel membranes, and preferred permeation of acetic acid was observed.⁵⁸

Intensive recent efforts have also focused on separations with MFI-type membranes on **ceramic** supports.

- (52) Bakker, W. J. W.; Zheng, G.; Kapteijn, F.; Makkee, M.; Moulijn, J. A.; Precis. Process Technol. [Int. Conf.], 1st, Meeting Date 1992, Weijnen, M. P. C., Drinkenburg, A. A. H., Eds.; Kluwer: Dordrecht, Netherlands, 1993 pp 425-36.
 (53) Geus, E. R.; van Bekkum, H.; Bakker, W. J. W.; Moulijn, J. A. *Microporous Mater.* **1993**, *1*, 131-47.
 (54) Sano, T.; Yanagishta, H.; Kiyozumi, Y.; Kitamoto, D.; Mizukami, F. *Chem. Lett.* **1992**, 2413-14.
 (55) Sano, T.; Yanagishta, H.; Kiyozumi, Y.; Mizukami, F.; Haraya, K. *J. Membr. Sci.* **1994**, *95*, 221-8.
 (56) Sano, T.; Hasegawa, M.; Ejiri, S.; Kawakami, Y.; Yanagishta, H. *Microporous Mater.* **1995**, *5*, 179-84.
 (57) Sano, T.; Hasegawa, M.; Kawakami, Y.; Yanagishta, H. *J. Membr. Sci.* **1995**, *107*, 193-6.
 (58) Sano, T.; Ejiri, S.; Hasegawa, M.; Kawakami, Y.; Enomoto, N.; Tamai, Y.; Yanagishta, H. *Chem. Lett.* **1995**, 153-4.

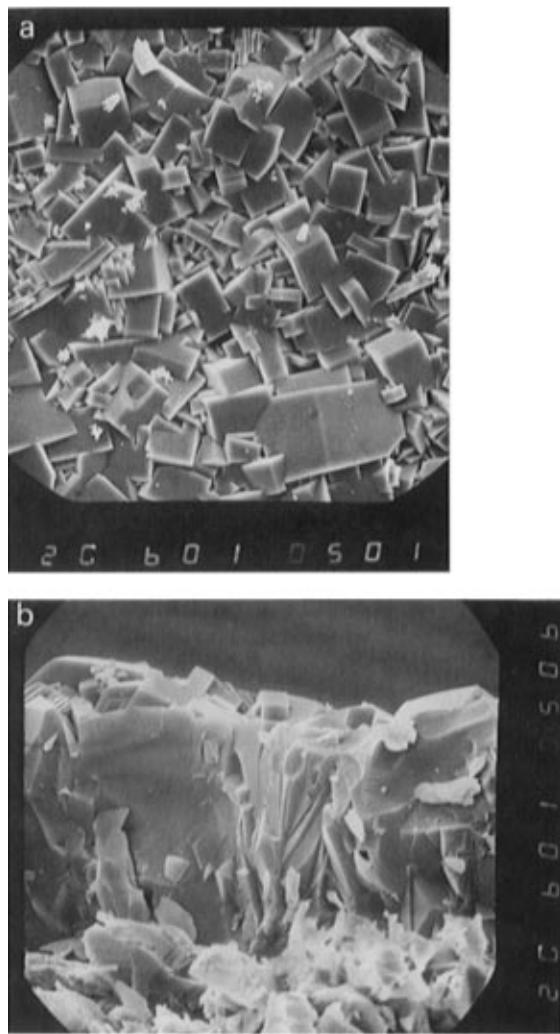


Figure 6. Continuous MFI layer on steel: (a) top view; (b) side view. Magnification: 600 \times . Reproduced with permission from ref 53.

Porous alumina has been the most popular support for these purposes.

A hydrothermal synthesis (at 175 °C) from clear solution was recently used for the preparation of ZSM-5 membranes on (horizontally held) porous supports of α -alumina. The membranes formed at the bottom faces of the support, close to the air–liquid interface, were composed of highly intergrown crystals and had a thickness of about 10 μm . The membranes had good permeation selectivity for *n*-butane/isobutane (with a pure gas flux ratio of 18 at 30 °C) and hydrogen/isobutane (with a ratio of 140), and the larger molecule triisopropylbenzene was effectively excluded from permeation, as expected for a defect-free membrane with ZSM-5 channels.^{59,60} At 185 °C, the flux ratio for *n*-butane/isobutane reached 31. Other zeolite membranes on a ceramic substrate have been prepared by *in situ* synthesis.⁶¹ Permeation selectivities reached 6.2 for *n*-butane over isobutane.

In related work, an alumina membrane tube covered with a 5 nm pore diameter γ -alumina layer has been used for the synthesis of a silicalite film.⁶² Single gas

permeances and separations of mixed gases such as hydrogen/isobutane or hydrogen/SF₆ were determined. With the silicalite membrane (in comparison with an uncoated alumina membrane), transport appeared to be governed by sorption and molecular sieving, and was found to be activated with activation energies at the order of 9–16 kJ/mol. For hydrogen/isobutane, the ratio of single permeances was as high as 1100 at 25 °C, while this ratio was 136 for H₂/SF₆. Separation selectivities at higher temperatures exceeded Knudsen selectivities; for example, the permeance ratio for H₂/SF₆ was 12.8 at 310 °C.

With similar thin silicalite-1 (10 μm) membranes on alumina, great differences in permeance between nitrogen, butanes, methane, methanol and hydrogen have been observed.⁶³ At elevated pressures, methanol was separated from hydrogen and methane, at separation factors of up to 1000 and 190, respectively. The authors suggest that methanol adsorbs and blocks the pores of the silicalite for hydrogen or methane permeation.

The permeation of *n*-butane through a silicalite-1 membrane has been described (in the temperature range between ca. 30 and 360 °C) with the Maxwell–Stefan diffusion model which incorporates occupancy dependency.⁶⁴ The Maxwell–Stefan diffusivity was related to an activated process with an activation energy of about 30 kJ/mol. This formalism was also successfully applied to the permeation of binary mixtures of hydrogen, *n*-butane, and carbon dioxide through silicalite-1 membranes⁶⁵ and other gases (membrane thickness ca. 40 μm).⁶⁶ Alkenes were found to permeate faster than the corresponding alkanes (C₂, C₃). Other authors have confirmed the utility of the Maxwell–Stefan formalism for describing the mass transport in silicalite-1 membranes. For example, at steady state conditions, *n*-butane flux is much higher than that of methane.⁶⁷ In contrast, the Fick formulation fails even at the qualitative level.

Porous sintered glass can also serve as the support for silicalite membranes.⁶⁸ As in many examples discussed above, the as-synthesized membranes were gastight. Permeation studies gave a permeation order (for single gases at 140 °C) of hydrogen > He > nitrogen > isobutene. Selectivity ratios of up to 122 were reported for *n*-hexane/2,2-dimethylbutane, although at the cost of slow permeation (with a membrane of 1 mm thickness at 150 °C). The isomer selectivity was found to depend mainly on membrane thickness and on temperature.

Similar to the studies on MFI/steel membranes discussed above, Geus et al. have also carried out permeation measurements on *in situ* grown MFI type films on macroporous clay-based supports.⁶⁹ With a Wicke–Kallenbach experiment and He carrier gas, the permeation of strongly sorbing gases (butanes) and

(62) Bai, C.; Jia, M.-D.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **1995**, *105*, 79–87.

(63) Jia, M. D.; Chen, B.; Noble, R. D.; Falconer, J. L. *J. Membr. Sci.* **1994**, *90*, 1–10.

(64) Kapteijn, F.; Bakker, W. J. W.; Zheng, G.; Moulijn, J. A. *Microporous Mater.* **1994**, *3*, 227–34.

(65) Kapteijn, F.; Bakker, W. J. W.; van de Graaf, J.; Zheng, G.; Poppe, J.; Moulijn, J. A. *Catal. Today* **1995**, *25*, 213–18.

(66) Kapteijn, F.; Bakker, W. J. W.; Zheng, G.; Poppe, J.; Moulijn, J. A. *Chem. Eng. J.* **1995**, *57*, 145–53.

(67) Krishna, R.; van den Broeke, L. J. P. *Chem. Eng. J.* **1995**, *57*, 155–62.

(68) Meriaudeau, P.; Thangaraj, A.; Naccache, C. *Microporous Mater.* **1995**, *4*, 213–19.

(59) Yan, Y.; Tsapatsis, M.; Gavalas, G. R.; Davis, M. E. *J. Chem. Soc., Chem. Commun.* **1995**, 227–8.

(60) Yan, Y.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652–61.

(61) Jia, M. D.; Peinemann, K. V.; Behling, R. D. *J. Membr. Sci.* **1993**, *82*, 15–26.

weakly sorbing gases (Ne, Ar, methane) was examined. The lower diffusivity of the higher, more strongly sorbing alkanes is apparently compensated by the higher concentration in the zeolite pores, leading to only moderate selectivities in binary mixtures. In those cases, the permeation rate is governed by the slowest moving species. Accordingly, much higher selectivities were observed for sorption within the Henry region at very low intracrystalline concentrations.

The intracrystalline diffusivities of benzene, toluene, and xylene isomers have been determined with a silicalite crystal embedded in epoxy resin. The rate of pressure increase at the outflow side of a pressure gradient was used to obtain diffusivities for the aromatics of about 10^{-13} m²/s.^{70,71}

MFI-type membranes on ceramic supports have also been investigated in pervaporation applications. For example, ZSM-5 on a porous ceramic support (synthesized on a Si(OEt)₄-derived silica interlayer) was used for pervaporation of EtOH/water, and selectivities as high as 15:1 were achieved.⁷² Finally, a zeolite NaA pervaporation membrane has been grown hydrothermally on a cylindrical, porous α -alumina substrate, with crystals 2–4 μ m in size and a membrane thickness of about 30 μ m. Effective dehydration of ethanol was demonstrated.⁷³

Theoretical Models. Barrer has put forward a detailed mathematical model for permeation through porous crystals.⁷⁴ Theoretical concepts of Knudsen, micropore and surface diffusion were evaluated for zeolites, imogolite, and microporous silica, and the potential of these materials for gas-separation membranes was discussed.⁷⁵

A theoretical study of gas diffusion and permeation in molecular sieve membranes shows that for permanent gases, the effect of adsorbed diffusant on total transmembrane flow is insignificant.⁷⁶ However, strongly adsorbing gases can have a profound effect on the flow. The calculated maximum possible permeability coefficients for He through such a molecular sieve membrane exceeded experimental values by a factor of 30 at 30 °C. This difference was attributed to the tortuosity and low porosity of the experimental membrane.

Molecular dynamics simulations of simple Lennard-Jones particles in the channels of silicalite show an unexpected dependence on the diameter of the adsorbate. Once the diameter approaches that of the channel system, the diffusion coefficient exhibits a peak, suggesting implications for many systems involving molecular diffusion.⁷⁷ For example, the authors suggest that one could design zeolites with channels of a particular

(69) Geus, E. R.; Bakker, W. J. W.; Verheijen, P. J. T.; den Exter, M. J.; Moulijn, J. A.; Bekkum, H. v.; Proc. Int. Zeolite Conf., 9th, Meeting Date 1992, Von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: Boston, MA, 1993; Vol. 2, pp 371–8.

(70) Shah, D. B.; Liou, H. Y. *Zeolites* **1994**, *14*, 541–8.

(71) Shah, D. B.; Liou, H. Y. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1347–54.

(72) Fan, S.; Shi, X.; Li, C.; Wang, J. *Water Treat.* **1994**, *9*, 93–100.

(73) Kita, H.; Horii, K.; Ohtoshi, Y.; Tanaka, K.; Okamoto, K.-I. *J. Mater. Sci. Lett.* **1995**, *14*, 206–8.

(74) Barrer, R. M. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1123–30.

(75) Pohl, P. I.; Smith, D. M. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 27–32.

(76) Shelekhin, A. B.; Dixon, A. G.; Ma, Y. H. *AIChE J.* **1995**, *41*, 58–67.

(77) Yashonath, S.; Bandyopadhyay, S. *Chem. Phys. Lett.* **1994**, *228*, 284–8.

diameter in order to maximize the diffusion coefficient of only the adsorbates that fit almost snugly into the channels.

2.2.2. Inorganic Catalytic Membranes and Other Applications. Selective, stable molecular sieve membranes are of great interest for the design of novel catalytic processes.⁴⁵ One can design membranes that act as catalyst or that support catalysts while also separating reactants from products. The membranes can impart selectivity in a reaction by shifting the steady-state concentration of the reactants and products, in order to enhance the concentration of a desired product. For example, a microporous zeolite membrane was studied for the dehydrogenation of isobutane.⁷⁸ An increase in isobutene yields was associated with the continuous removal of hydrogen from the reaction space. In comparison, a mesoporous alumina membrane showed also an increase in isobutene yield, but in the latter case this effect was associated with mixing of reactants, products, and sweep gas.

Oxidative dehydrogenation of propane succeeded with a V–Mg–O catalyst bed enclosed in a zeolite membrane. This membrane acted as an effective gas barrier and resulted in an increased propene yield at low propane/oxygen ratios, with a separate feeding arrangement.⁷⁹ Selective oxidation of cyclohexane to cyclohexanone and cyclohexanol with molecular oxygen using a ZSM-5 membrane on a tubular reactor has been claimed.⁸⁰

Various layers of zeolites on supports have been used for other applications, including NaY and ZSM-5 zeolites on Cu and Pt for size/charge selective electrodes, chromatographic separation media, and oxygen reduction fuel cells.²⁵ For these preparations, the metal surfaces were etched in alkali and HCl prior to zeolite synthesis. Typically, a standard bulk synthesis was quenched before crystallites formed. The resulting sol–gel mixture was filtered, and the etched metal substrates were immersed, followed by hydrothermal reaction.

2.2.3. Polymer-Embedded Zeolites as Pervaporation Membranes. One of the most direct methods of preparing a zeolite-containing membrane is to fill permeable polymeric materials with a high volume fraction of zeolite crystals. While the focus of this review is not on pervaporation, some recent examples of such membranes and their separation performance will be briefly discussed. Pervaporation is a membrane process in which the feed is a liquid mixture and the permeate on the other side of the membrane is removed by a condenser, a vacuum, or a stream of sweep gas. In the following we distinguish different composite membranes according to the host matrix polymer.

(a) *Polydimethylsiloxane (PDMS) matrix:* Silicone rubbers such as PDMS have excellent properties for membrane applications. Permeabilities for many molecules are high, and the material is environmentally stable. PDMS membranes have been filled with hydrophobic zeolites, in particular silicalite with the MFI structure, in order to impart preferred pervaporation for organics such as acetic acid in competition with water.⁸¹

(78) Casanave, D.; Giroir-Fendler, A.; Sanchez, J.; Loutaty, R.; Dalmon, J. A. *Catal. Today* **1995**, *25*, 309–14.

(79) Pantazidis, A.; Dalmon, J. A.; Mirodatos, C. *Catal. Today* **1995**, *25*, 403–8.

(80) Haag, W. O.; Tsikoyiannis, J. G. U.S. Patent 5,110,478 A, 1992; Cont.-in-part of U.S. 5,019,263.

The separation of chlorinated hydrocarbons (VOCs) from water can be achieved with a similar membrane.^{82,83} The sorption in the PDMS matrix is controlled by the hydrophobicity of the compound, while molecular sieving determines the sorption in the silicalite. The zeolite filler makes the membrane sorption capacity less dependent on temperature. The authors suggest that the role of the silicalite filler is primarily that of a reservoir, because the diffusion coefficient in silicalite is orders of magnitude smaller than in the polymer matrix.

Several recent articles have addressed alcohol/water separations with important potential applications in biotechnology and other fields.⁸⁴ The sorption isotherms of alcohols in ZSM-5/silicone rubber membranes showed that the zeolite contributed the largest fraction of the membrane volume.⁸⁵ The incorporation of hydrophilic zeolite Y increased water fluxes, whereas ZSM-5 showed retention of both water and alcohol (C₂-C₄).⁸⁶ It was also observed that zeolite fillers such as Y can be involved in the polymer cross-linking.⁸⁷ The separation performance for alcohol/water separation can be enhanced by steaming and adding electrolytes. The separation factors can reach 30:1 for ethanol vs water.⁸⁸⁻⁹⁰ Other alcohol/water separations (ethanol, 1-propanol, and 2-propanol) and the influence of MFI morphology and composition on selectivity have been studied.⁹¹ The authors found that the Si/Al ratio, cation content, Si-OH defects, and crystallinity of the zeolite phase have an influence of the separation. The silicalite-1 composition (pure SiO₂) showed high selectivity for the pervaporation of the alcohols and particularly for acetone.

(b) *Poly(vinyl alcohol)/zeolite membranes*: Hydrophilic membranes have been prepared by filling poly(vinyl alcohol) with KA, NaA, CaA, and NaX zeolites, and improved selectivity in ethanol/water pervaporation and acetone/water separation (with CaA, KA) was observed. These membranes were applied in catalytic reactions releasing water, i.e., esterification of acetic acid with EtOH, and salicylic acid with methanol. The continuous removal of water from the reaction led to substantial improvements in conversion and reaction time.⁹²

(c) *Epoxy-diacylate/zeolite membranes*: Microporous membranes supporting photochemically grafted epoxy diacrylate composite with 20 wt % of zeolite 13X on a cellulose substrate have been studied.⁹³ The sorption of linear carboxylic acids such as propanoic or *n*-

(81) Netke, S. A.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *J. Membr. Sci.* **1995**, *107*, 23-33.

(82) Dotremont, C.; Brabants, B.; Geeroms, K.; Mewis, J.; Vandecasteele, C. *J. Membr. Sci.* **1995**, *104*, 109-17.

(83) Dotremont, C.; Goethaert, S.; Vandecasteele, C. *Desalination* **1993**, *91*, 177-86.

(84) H. J. C. te Hennepe, D. Bargeman, M. H. V. Mulder, C. A. Smolders, *J. Membr. Sci.* **1987**, *35*, 39.

(85) Bartels-Caspers, C.; Tusel-Langer, E.; Lichtenhaller, R. N. *J. Membr. Sci.* **1992**, *70*, 75-83.

(86) Vankelecom, I. F. J.; Depre, D.; De Beukelaer, S.; Uytterhoeven, J. B. *J. Phys. Chem.* **1995**, *99*, 13193-7.

(87) Vankelecom, I. F. J.; Schepers, E.; Heus, R.; Uytterhoeven, J. B. *J. Phys. Chem.* **1994**, *98*, 12390-6.

(88) Chen, X.; Ping, Z.; Fu, S.; Long, Y. *Gaodeng Xuexiao Huaxue Xuebao* **1993**, *14*, 1190-4; CA **121**:111197.

(89) Ping, Z. H.; Long, Y. C.; Chen, X.; Chen, X. H.; Nguyen, T. Q.; Neel, J. *Recents Prog. Genie Proc.* **1992**, *6*, 395-9; CA **119**:75033.

(90) Chen, X.; Ping, Z.; Ding, Y.; Long, Y. *Yingyong Huaxue* **1994**, *11*, 21-5; CA **121**:85470.

(91) Long, Y. C.; Chen, X.; Ping, Z. H.; Fu, S. K.; Sun, Y. J. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1083-90.

(92) Gao, Y.; Yue, Y.; Li, W. *Zeolites* **1996**, *16*, 70-4.

hexanoic acid into these membranes from aqueous solution is controlled by sorption and ion exchange equilibria.

3. Deposition of Molecular Sieve Layers

3.1. Embedding of Crystals in a Film Matrix. In the previous section we have discussed the growth of rather dense zeolite films and membranes from hydrothermal baths. If successful, these preparations result in gastight membranes that can be used for selective molecular separations. Conceptually, gastight systems can also be prepared via assembly of crystals on a substrate and sealing the gaps between crystals with a dense matrix. However, the unique properties of zeolites can limit the scope of this approach. Primarily, the potential clogging of zeolite pores is a concern. Furthermore, the binder matrix could introduce additional properties such as porosity into the composite, or gaps between binder and zeolite could introduce nonselective diffusion pathways. For example, composite membranes of large ZSM-5 crystals in an alumina matrix have been made by a dip-coating technique.⁹⁴ The crystals were deposited on α -alumina plates, immersed in a glycerol/boehmite (γ -AlOOH) sol, and then calcined at 500 °C. However, the resulting zeolite/ γ -alumina films were not gastight.

The following discussion will show that a number of successful designs have been developed based on embedded crystal membranes and layers. For example, composites can also be made by deposition of a porous interlayer on a macroporous support from calcined silicone rubber or clay, deposition of large ZSM-5 crystals (with dimensions of tens of micrometers or more) of equal size/shape at high coverage, and filling the intercrystalline voids with an impermeable matrix by sol-gel, CVD (chemical vapor deposition), or glazing techniques.^{95,96} Sol-gel processes involving such large zeolite crystals can be subject to cracking. Glaze suspensions are preferred in order to avoid shrinkage and cracking. For example, a lead-boron silicate powder was dip-coated and heated at 550 °C to form a glaze between silicalite crystals on α -alumina. This glaze fills only the large voids but does not cover the zeolite crystals. One limitation of this approach is the large thickness of the resulting film which can be undesirable for membrane separations.

Model permeation studies have been performed with silicalite crystals (ca. 200 × 100 × 350 μ m) embedded in epoxy.⁹⁷ In this system, only small differences were observed for permeabilities of permanent gases and small alkanes at the experimental conditions studied, and it was concluded that the highest selectivities will be realized in the Henry regime where sorption is small, so that permeation is governed by the intrinsic diffu-

(93) Bellobono, I. R.; Selli, E.; Righetto, L.; Missana, T.; Muffato, F.; Pizzala, A.; Taiana, A.; Zeni, M. *Mater. Chem. Phys.* **1991**, *28*, 291-302. See also: Zeni, M.; Bellobono, I. R.; Muffato, F.; Pollissi, A.; Selli, E.; Rastelli, E. *J. Membr. Sci.* **1988**, *36*, 277.

(94) Geus, E. R.; Van Veen, H. M.; Veringa, H. J.; Schoonman, J.; Van Bekkum, H. *Key Eng. Mater.* **1991**, *61*-62 (Inorg. Membr. ICIM2-91), 461-4.

(95) Geus, E. R.; Mulder, A.; Vischjager, D. J.; Schoonman, J.; Van Bekkum, H. *Key Eng. Mater.* **1991**, *61*-62 (Inorg. Membr., ICIM2-91), 57-64.

(96) Geus, E. R.; Schoonman, J.; van Bekkum, H. *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 231-6.

(97) Geus, E. R.; Jansen, A. E.; Jansen, J. C.; Schoonman, J.; Van Bekkum, H. *Stud. Surf. Sci. Catal.* **1991**, *65* (Catal. Adsorpt. Zeolites), 457-66.

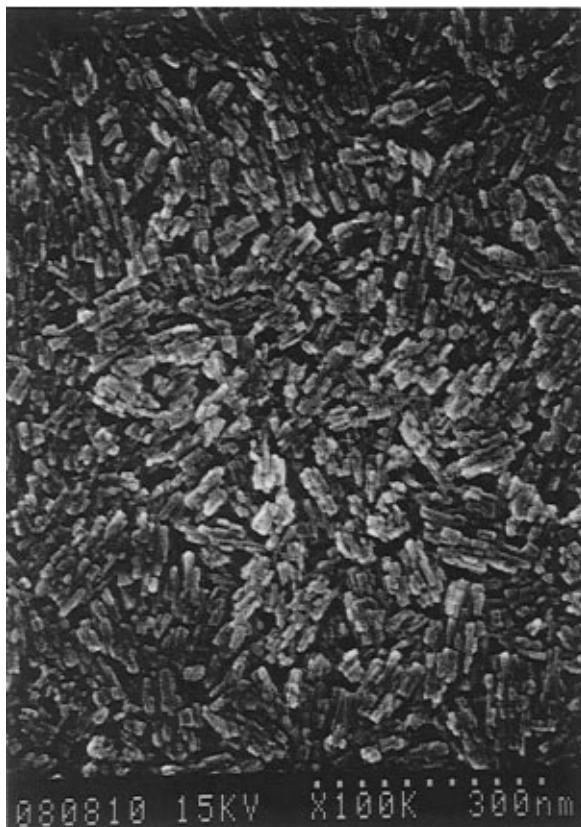


Figure 7. Zeolite L film prepared from a nanocrystal suspension after evaporation of water. Reproduced with permission from ref 100a.

sivity. The authors suggest that the Henry regime should be reached by increasing the temperature in order to ensure high permeabilities. [Related model studies with single crystals sealed with epoxy have been reported: butane diffusion through silicalite⁹⁸ and diffusion of butane and other gases through large single crystals of NaX, with edge lengths of ca. 110 μm .⁹⁹]

Tsapatsis and co-workers have prepared thin films of zeolite L by evaporation from aqueous colloidal suspensions of nanocrystalline zeolite L (Figure 7). These materials (size range <50 nm long, ca. 15 nm diameter) were synthesized from homogeneous potassium aluminosilicate solutions.¹⁰⁰ This synthesis was similar to that from a homogeneous $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system reported by Meng et al.¹⁰¹

Crystals of zeolite NaA have been deposited on glassy carbon electrodes via sedimentation/drying from an aqueous suspension, followed by embedding in a thin polystyrene matrix, and exchange with silver ions.¹⁰² The authors report that 85% of the silver ions in the zeolite can be electrochemically reduced. Cyclic voltammograms show strong dependence on the silver ex-

(98) (a) Hayhurst, D. T.; Paravar, A. R. *Zeolites* **1988**, *8*, 27–29. (b) Paravar, A.; Hayhurst, D. T. *Proc. 6th Int. Zeol. Conf.*; Olson, D., Bisio, A., Eds.; Butterworth: London, 1984; pp 217–224.

(99) Wernick, D. L.; Osterhuber, E. J. *Proc. 6th Int. Zeol. Conf.*; Olson, D., Bisio, A., Eds.; Butterworth: London, 1984; pp 122–130.

(100) (a) Tsapatsis, M.; Lovallo, M.; Okubo, T.; Davis, M. E.; Sadakata, M. *Chem. Mater.* **1995**, *7*, 1734–41. (b) Tsapatsis, M.; Okubo, T.; Lovallo, M.; Davis, M. E. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 21–6.

(101) Meng, X.; Zhang, Y.; Meng, C.; Pang, W. *Proc. Int. Zeolite Conf.*, 9th Meeting date 1992; Von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: Boston, MA, 1993; Vol. 1, pp 297–304.

(102) Li, J.; Calzaferri, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1430

change levels and suggest that several types of silver species are electrochemically active. Zeolite-modified electrodes have been studied by several groups¹⁰³ but are beyond the scope of this review.

The alignment of polar crystals in electric fields followed by embedding in a matrix is discussed in section 3.4.

Zeolite Sol–Gel Composite Films. In contrast to membrane separations, other applications such as **sensors** based on mass changes do not require a gastight film but only a thin layer of sorbent. A tradeoff between signal intensity and equilibration rate as a function of layer thickness can exist if the molecular diffusivities of analytes are small. A number of schemes for the deposition of preformed zeolite crystals on various substrates have been developed.

Layers with molecular sieving properties were formed by embedding microcrystals of zeolite Y and chabazite in a glassy silica matrix.¹⁰⁴ The access of different probe molecules into the zeolitic part of the thin film was examined with *in situ* FTIR techniques and temperature-programmed desorption studies. The resulting films showed molecular sieving properties of the parent zeolite. The inorganic glassy matrix was synthesized via the “sol–gel” process from tetraethylorthosilicate (TEOS). This process uses monomeric metal alkoxides, $\text{M}(\text{OR})_x$, where M is usually a network former, such as Si, B, Al, or Zr, and R is often an alkyl group. In alcoholic solution, the alkoxide groups are removed stepwise by acid- or base-catalyzed hydrolysis reactions and are replaced by hydroxyl groups. Subsequent condensation reactions result in M–O–M bonding with elimination of water or alcohol. The inorganic polymer growth (via M–O–M bonding) can be biased toward extended, weakly branched structures or compact, fully polymerized colloidal particles.^{105–107} A complete spectrum of structures intermediate to these extremes is possible.¹⁰⁸

The composite films were formed by deposition of the zeolite/silicate suspension on the substrate by methods such as dipping or spinning. During deposition, the solvent is evaporated, concentrating the inorganic components on the substrate surface. Condensation causes the silicate film to gel, locking in a particular configuration and orientation of the zeolite crystals. The pore structure of gel-derived films depends on continued condensation and viscous sintering processes at elevated temperatures.^{109,110} The consolidated gel phase can serve as an almost impermeable matrix, such that most of the molecular sorption occurs in the zeolite channels. It can be assumed that mechanisms such as solvent

(103) Rolison, D. R. *Chem. Rev.* **1990**, *90*, 867.

(104) (a) Bein, T.; Brown, K.; Brinker, C. J. *Stud. Surf. Sci. Catal.* **49** (*Zeolites: Facts, Figures, Future*); Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1989; pp 887–896. (b) Bein, T.; Brown, K.; Frye, G. C.; Brinker, C. J. *U.S. 5,151,110*, 1992.

(105) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Ashley, C. S. *J. Non-Cryst. Solids* **1982**, *48*, 47.

(106) Brinker, C. J.; Scherer, G. W. *J. Non-Cryst. Solids* **1985**, *70*, 301.

(107) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non-Cryst. Solids* **1984**, *63*, 45.

(108) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, CA, 1990.

(109) Scherer, G. W.; Brinker, C. J.; Roth, E. P. *J. Non-Cryst. Solids* **1985**, *72*, 369.

(110) Brinker, C. J.; Drotning, W. D.; Scherer, G. W. In *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Elsevier: Amsterdam, 1984; p 25.

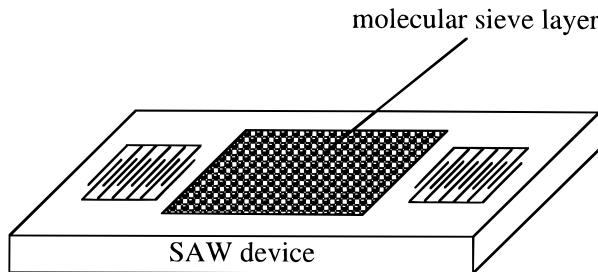


Figure 8. Surface acoustic wave device covered with molecular sieve layer (schematic).

desorption from the zeolite interior during calcination or shrinkage of the thin gel layer serve to keep the gel-covered zeolite pores at least partially open.

In an extension of the above approach, thin film microcomposite coatings with molecular sieving properties were deposited on surface acoustic wave (SAW) devices.¹¹¹ In the SAW device, an alternating voltage applied to an interdigital transducer on a piezoelectric substrate results in an acoustic wave—in the present case a Raleigh surface wave on quartz—whose propagation velocity is a sensitive probe of near-surface mass changes and elastic moduli. SAW devices can be used as highly sensitive piezoelectric balances which respond to small fractions of single-crystal monolayer adsorption; however, the response is nonselective.^{112,113}

The zeolite–silica thin films introduce molecular sieve selectivity for the detection of nanogram quantities on the SAW device. High discrimination ratios between molecules entering the zeolite pore system and those excluded from the molecular sieve sensor were observed (see section 3.2 for an introduction to chemical sensors). Specifically, a glassy silica matrix of ca. 150 nm thickness, embedding crystals of ZSM-5 (pore size ca. 5.4 × 5.6 Å) was coated on the active surface of the device. The resulting structure is depicted schematically in Figure 8. A striking difference in frequency response to different probe molecules is observed. While vapors of methanol (ca. 3.8 Å) and propanol (ca. 4.7 Å) adsorb at significant levels in the film, the response to isoctane (6.2 Å) is minimal. This dramatic difference can be understood if the kinetic diameters of these molecules are compared with the pore openings of the zeolite film.

3.2. Attachment of Crystals to Surfaces—Chemical Sensors. Molecular sieve films are promising candidates for applications in chemical sensors. Chemical sensing is becoming increasingly important in industrial process control, environmental and indoor air-quality monitoring, effluent and auto exhaust control, and medical monitoring. The important advantages of small, inexpensive sensors include the ability to deploy them at many points in the environment, in process streams, and in mobile objects such as cars. The design of stable sensors with molecular selectivity is one of the most difficult challenges in sensor development. The types of sensor transducers developed for chemical sensing include metal oxide gas sensors, CHEMFETs (chemically sensitive field effect transistors), fiber optic devices, ion-selective electrodes, and piezoelectric mass balances such as surface acoustic wave (SAW) devices and quartz crystal microbalances (QCM).^{114–116}

(111) Bein, T.; Brown, K.; Frye, G. C.; Brinker, C. J. *J. Am. Chem. Soc.* **1989**, *111*, 7640–7641.

(112) Ward, M. D.; Buttry, D. A. *Science* **1990**, *249*, 1000–7.

(113) Ricco, A. J.; Frye, G. C.; Martin, S. J. *Langmuir* **1989**, *5*, 273.

Molecular sieve films have excellent characteristics that address many of the requirements for chemical sensors. Well-designed zeolite films or layers have superb shape selectivity, and offer large intraporous volumes that can be used, together with the typical considerable sorption at low partial pressures (type I sorption isotherms)¹¹⁷ to drastically increase sensitivity. Furthermore, zeolites are thermally and chemically stable, particularly in oxidizing environments that would pose problems for organic layers. Accordingly, the design of zeolite-based sensors has been a driving force for the development of stable molecular sieve films and layers. Transducers studied so far for zeolite-based sensors include capacitive devices and piezoelectric acoustic wave devices such as the QCM or the SAW device.

Zeolite Layers Attached through Molecular Coupling Agents. The attachment of zeolite crystals on sensor substrates was achieved by molecular means, i.e., by using bifunctional coupling layers that bind to the substrate as well as to the zeolite crystals. Thus, zeolite crystals were successfully coupled onto the gold electrodes of quartz crystal microbalances (QCM).^{118–120} For example, self-assembled monolayers of thiol–alkoxysilane coupling agents on the gold surface were used as the interfacial layers to promote adhesion of the zeolite crystals to the QCM, and the zeolites could be coated with sol–gel-derived silica to enhance the mechanical stability of the films (Figure 9).

Adsorption of many organic vapors, including small alcohols, chlorinated hydrocarbons, benzene, toluene, as well as water was demonstrated in these films. Dynamic sorption isotherms of organic vapors and nitrogen as well as the transient sorption behavior of organic vapor pulses were studied to characterize the zeolite-coated QCMs. The regular micropores (0.3–0.75 nm) of the QCM-attached zeolite crystals were found to effectively control molecular access into the coatings. Selectivity of the frequency response in excess of 100:1 toward molecules of different size and/or shape (molecular sieving) could be demonstrated. The molecular size selectivity (molecular sieving) of the zeolite films corresponds closely to the behavior expected from the bulk materials. The thin films can adsorb and desorb most vapors within a few seconds to minutes, often at room temperature, while the bulk materials usually require substantial heating (ca. 200–300 °C) to remove the adsorbed vapors.

Selective Ethanol Sensor. A chemical microsensor with combined molecular sieve and selective hydrophobic interactions was designed, based on a silicalite layer and a silica binding matrix on the active area of

(114) Seiyama, T. L. *Chemical Sensor Technology*; Kodansha: Tokyo; Elsevier: Amsterdam, 1988; Vol. 1.

(115) Janata, J.; Bezegh, A. *Anal. Chem.* **1988**, *60*, 62R–74R. Janata, J., Huber, R. J., Eds. *Solid State Chemical Sensors*; Academic Press: Orlando, 1985.

(116) Janata, J.; Jasowicz, M.; DeVanay, D. M. *Chemical Sensors. Anal. Chem.* **1994**, *66*, 207R–228R.

(117) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: New York, 1982.

(118) Yan, Y.; Bein, T.; Brown, K.; Forrister, R. M.; Brinker, C. J. *Better Ceramics Through Chemistry V*; Hampden-Smith, M. J., Klemperer, W. G., Brinker, C. J., Eds.; *MRS Symp. Proc.* **1992**, *271*, 435–441.

(119) Yan, Y.; Bein, T. *Synthesis/Characterization and Novel Applications of Molecular Sieve Materials*; Bedard, R. L., Bein, T., Davis, M. E., Garces, J., Maroni, V. A., Stucky, G. D., Eds. *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 175–182.

(120) Yan, Y.; Bein, T. *J. Phys. Chem.* **1992**, *96*, 9387–9393.

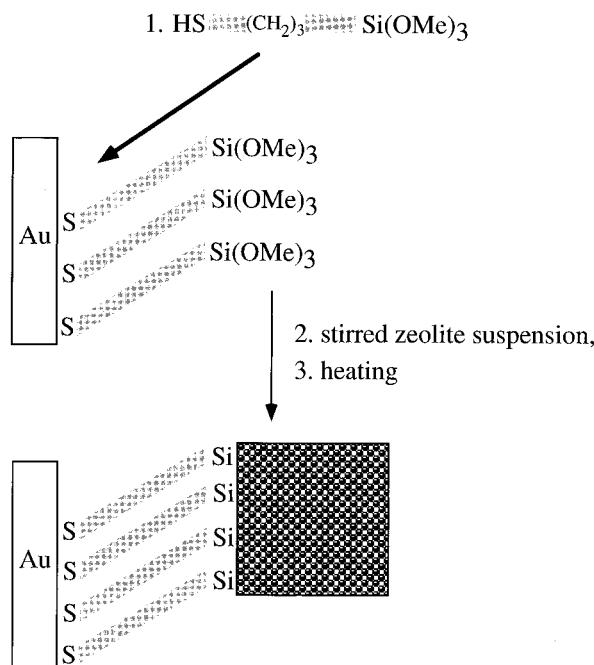


Figure 9. Anchoring of zeolite crystals on a gold surface via thiol alkoxysilane coupling layer.

QCMs.¹²¹ This sensor shows selective responses towards ethanol at low vapor pressures (<1000 ppm). In addition to the high sensitivity and selective size exclusion offered by molecular sieve films, the nature of the chemical surface interactions is important. In the thin silicalite films, interference from water (2.65 Å), which is smaller than ethanol (4.3 Å), was minimized through hydrophobicity of the molecular sieve and the matrix (silica).

Gate Layers. In an extension of the above studies, a surface tailoring technique for the microporous thin films was described, in which organosilane molecules were chemisorbed on the silica overlayer via siloxane linkages, forming a molecular “gate” at the gas–thin film interface.¹²² The permeability of the gate layer controls access of vapors into the zeolite crystals, i.e., the sorption rates and uptake of various molecules. For example, access into thin films of zeolite NaA could be made selective for water while rejecting *n*-hexane.

Tunable Sensors. The gate concept in zeolite films can be extended further, by adjusting the porosity of the zeolite itself. In a recent study, the molecular size selectivity could be controlled between 3 and 5 Å by fast ion exchange.¹²³ The films were formed from molecularly attached zeolite CaA crystals and a silica binding phase on a QCM. The pore openings were controlled by ion exchange with other cations from aqueous solution, such as Na⁺, K⁺, and Rb⁺. Remarkable differences in the nitrogen sorption between the CaA films and the Na, K, and Rb forms are related to the partial closure of the 8-ring windows of the zeolite A structure. As a result, exclusion of progressively smaller molecules from the internal porosity of the film is observed as a function of the cation size and their siting in the crystal structure (Figure 10).

Other Sensors with Microporous Layers. Examples of capacitive devices coated with the proton form

of zeolite Y or with a platinum-containing zeolite Y show the potential of zeolite sensors based on this simple type of transducer.¹²⁴ The voids of interdigitated capacitors were filled with the zeolite that takes the role of dielectric. Sorption of molecules such as *n*-butane, ammonia, or NO led to reproducible changes in capacitance responses. For instance, capacitance increases at the order of one picoFarad (of 175 pF base capacitance at 1000 Hz) were observed for 1% butane in air at 55 °C. With the Pt-loaded zeolite film and at higher temperature (200 °C), greater responses were observed, but these were attributed to the effect of water from combustion of the hydrocarbon.

On the basis of the above concepts, the authors have constructed a combustion gas sensor from a thin-film interdigital capacitor covered with a layer of Pt–Y zeolites.¹²⁵ It was found that the ac impedance changed when exposing the sensor to butane in wet air, but much less with CO or hydrogen in wet air (at 350 °C). The authors associate the observed increasing resistance with the reduced mobility of the zeolite sodium ions when butane is present in the Pt-loaded zeolite cages.

An unusual sensor/dosimeter concept was based on sorption and temporary retention of analytes in polyethylene/zeolite membranes on silver halide optical fibers.¹²⁶ After exposure, analytes such as benzene or dichlorobenzene were detected (with limited sensitivity) on the fiber by IR spectroscopy.

The mesoporous material MCM-41 (or modifications thereof) has been proposed as a selective detecting element for the quantification of physical, chemical, or biological processes in the channel system.¹²⁷ Finally, microporous layered metal phosphonates of the formula Zn(O₃PR) (R = CH₃, C₆H₅) have been deposited on QCM devices, and shape-selective intercalation of amines and ammonia was demonstrated.¹²⁸

3.3. Sputtering and Laser Ablation—Chemical Sensors. Laser ablation from a zeolite target is a potential alternative method for the generation of molecular sieve films on substrates. This method produces high-energy atoms, molecules, ions, and clusters that can deposit on a substrate. There seems to be agreement that much of the material is initially deposited in amorphous form, but the reaction conditions and/or subsequent hydrothermal treatments can recrystallize some of the desired molecular sieve phase. Various synthesis conditions have been used by Balkus and co-workers to form different films containing molecular sieves. Laser ablation (with KrF, 248 nm) of an AlPO₄-H4 target results in the deposition of aluminum orthophosphate or AlPO₄ cristobalite, AlPO₄ tridymite, and amorphous material. At pulse energies of 50–100 mJ and low substrate temperatures, the former two phases were observed, while low laser power density and high substrate temperatures favored the AlPO₄

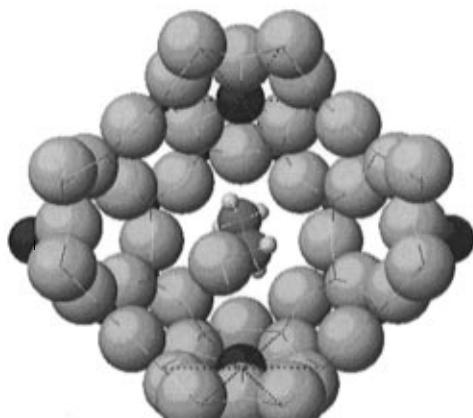
(124) (a) Alberti, K.; Haas, J.; Plog, C.; Fetting, F. *Catal. Today* **1991**, *8*, 509–13. Plog, C.; Haas, J. *Chem.-Ing.-Tech.* **1991**, *63*, 838–9. (b) Alberti, K.; Gubicza, L.; Fetting, F. *Chem.-Ing.-Tech.* **1993**, *65*, 940. (c) Kurzweil, P.; Maunz, W.; Plog, C. *Sens. Actuators B* **1995**, *24–25*, 653–6. (d) Scheibe, C.; Obermeier, E.; Maunz, W.; Plog, C. *Sens. Actuators B* **1995**, *24–25*, 653–6.

(125) Plog, C.; Maunz, W.; Kurzweil, P.; Obermeier, E.; Scheibe, C. *Sens. Actuators, B* **1995**, *B25*, 584–7.

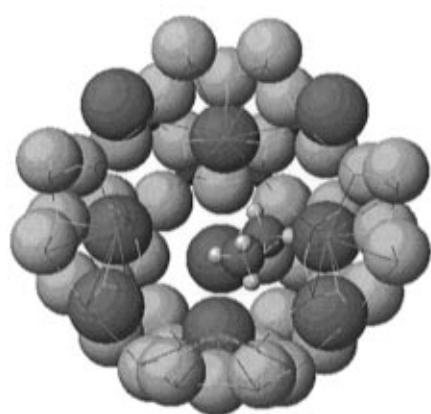
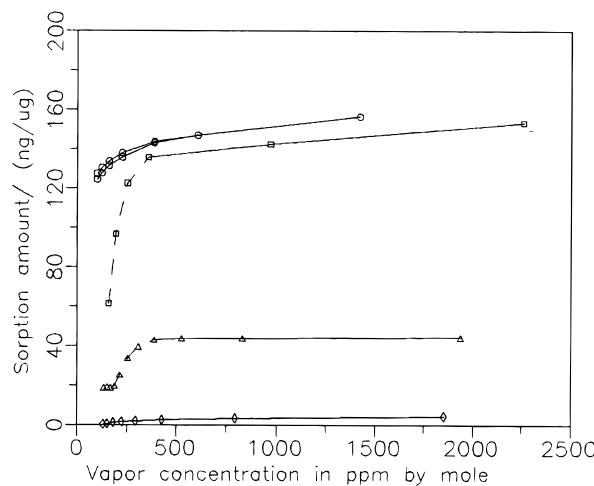
(126) Glatkowski, P.; Druy, M. U.S. Government Report (1992) Order No. PB93-159358 (NTIS), 1992; CA 120:225328.

(127) Olson, D. H.; Stucky, G. D.; Vartuli, J. C. U.S. Patent 5,364,797, Nov. 15, 1994; CA 122:122124.

(128) Aoki, K.; Brousseau, L. C.; Mallouk, T. E. *Sens. Actuators, B* **1993**, *14*, 703–4.



EtOH in CaA



EtOH in KA

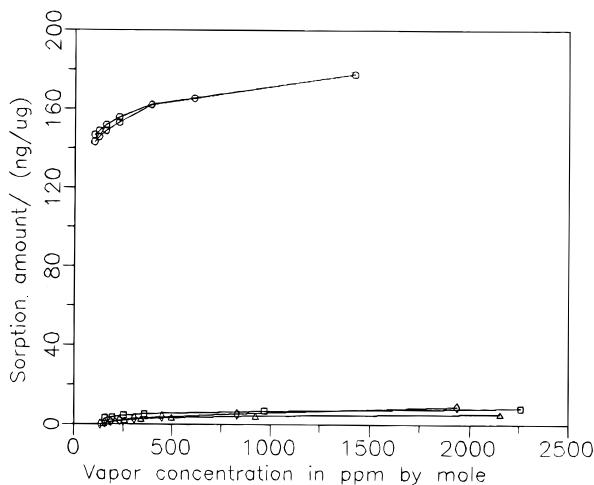


Figure 10. Pore openings (with ethanol molecule) of zeolite A with Ca and K ions, and the associated sorption isotherms on QCM devices for water (○), EtOH (square), *n*-hexane (triangle), and 3-methylpentane (rhombus) (after ref 123).

tridymite phase.¹²⁹ Thin films of aluminophosphate molecular sieves (AlPO₄-5, AlPO₄-H3, and AlPO₄-H1) have been deposited on Ti nitride substrates via ablation of the parent materials with an excimer laser (KrF, 248 nm). The crystallinity of the films was enhanced by hydrothermal posttreatment.¹³⁰ Aluminum phosphate capacitance sensors have been designed based on this deposition principle.^{131,132} The molecular sieve materials used as targets included AlPO₄-H1 (VFI), AlPO₄-H3, AlPO₄-5, and VAPo-5, deposited by laser ablation on titanium nitride coated Si wafers, and subjected to a hydrothermal posttreatment followed by Pd/Au deposition to form the capacitor device. Different molecular selectivities were observed. For instance, CO (kinetic

diameter 3.8 Å) did not result in a capacitance response with AlPO₄-H3 (small pore 3.5 × 3.7 Å) while water did (diameter 2.65 Å). A sensor coated with VFI showed a stronger response for CO₂ over CO, while the reverse was true for the AlPO₄-5 (AFI) molecular sieve film.

Similarly, pulsed laser ablation of mordenite and faujasite targets was used to deposit films on various substrates. The films consisted of an amorphous matrix containing small crystallites, and the matrix appeared to be porous with pore sizes comparable to those of the zeolites.¹³³

Finally, the argon ion beam sputter deposition of zeolite material on gold has been explored.¹³⁴ With HY zeolites as targets, XPS data on thin 10 nm films showed a decrease of the Si/Al ratio with deposition time, to converge at the values of the target material. On the

(129) Balkus, K. J., Jr.; Sottile, L. J.; Riley, S. J.; Gnade, B. E. *Thin Solid Films* **1995**, *260*, 4–9.

(130) Balkus, K. J., Jr.; Riley, S. J.; Gnade, B. E. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 437–42.

(131) Sottile, L. J.; Balkus, Jr., K. J.; Riley, S. J.; Gnade, B. E. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 263.

(132) Balkus, K. J., Jr.; Sottile, L. J.; Nguyen, H.; Riley, S. J.; Gnade, B. E. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 33–8.

(133) Peachey, N. M.; Dye, R. C.; Ries, P. D. *Proc. Int. Conf. Lasers 1995*, Vol. Date 1994, 17th; pp 666–73.

(134) Boszormenyi, I.; Nakayama, T.; McIntyre, B.; Somorjai, G. A. *Catal. Lett.* **1991**, *10*, 343–55.

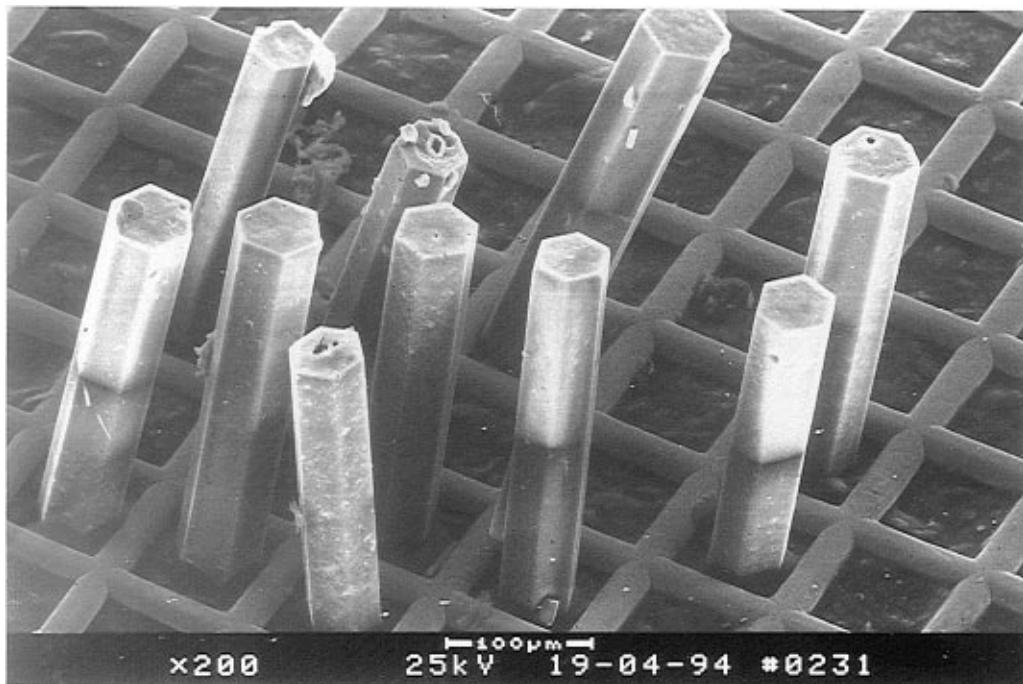


Figure 11. Nickel grid with AlPO₄-5 crystals aligned by electric field. Reproduced with permission from ref 137.

basis of Auger data, it was suggested that no SiO₂/Al₂O₃ segregation occurred in the film. XRD results on 1 μ m thick films indicate that the SiO₂/Al₂O₃ layers are amorphous, although catalytic activity in cumene cracking suggested that some chemical/structural similarity with the target material was retained.

3.4. Embedding and Alignment of Polar Crystals. Certain polar molecular sieves can be aligned in electric fields. The group of Caro has recently developed oriented arrays of polar crystals such as AlPO₄-5 (AFI). This alignment technique has been used for large (50–200 μ m) and smaller (20 μ m) crystals. One important condition for this concept to function is that the crystals are not isometric; often aspect ratios exceed 5. After alignment, the crystals can be permanently locked in position by embedding them in water glass or polymer matrix, or in electrolytically deposited metal. The authors suggest potential applications in (i) molecular sieve membranes, (ii) orientation of guest molecules for spectroscopy, and (iii) materials for frequency doubling (optical second harmonic generation).¹³⁵

Highly uniform crystals of AlPO₄-5 have been prepared via microwave synthesis with the mother liquor from a previous synthesis step, using H₃PO₄, H₂O, Et₃N, Al(OCHMe₂)₃, and HF as gel starting materials.¹³⁶ Furthermore, columnar AlPO₄-5 crystals have been aligned and embedded in nickel (by galvanic deposition) and studied in the permeation of heptane and different aromatic hydrocarbons (Figures 11 and 12).¹³⁷ The molecules with diameters exceeding the aluminophosphate pore diameter were effectively prevented from diffusion.

Silicalite crystals have been embedded in silver or nickel foils by galvanic metal deposition, resulting in

high-temperature membranes (thermally stable up to 380 °C).¹³⁸ Separation of toluene/n-heptane was achieved with a separation factor of about 4. In a different application, the orientation of guest molecules has been studied in AlPO₄-5 crystals that had been aligned in electric fields.¹³⁹ Second harmonic generation with *p*-nitroaniline adsorbed in the aligned crystals was demonstrated.

4. Growth of Oriented Molecular Sieve Films on Organic Molecular Layers

4.1. Self-Assembled Organic Layers as Templates for Crystal Growth. Great demands regarding the synthesis or assembly process of molecular sieve layers or films arise if *oriented* molecular sieve channels are desired. Oriented nanometer channel structures are of considerable interest for size-selective chemical sensors, separation membranes, and other novel devices. In previous sections we have discussed the occasional orientation of MFI-based zeolite films; however, in those cases the orientation appears to be caused by the unique chemistry of the gel–solution interface in the hydrothermal synthesis of this zeolite type and is rather independent of the substrate. In an approach inspired by the feats of biomineralization, we are exploring the growth of oriented molecular sieves on functional organic mono- and multilayers. We reasoned that certain functional organic layers should be capable of assisting in the surface nucleation and growth of molecular sieves. The surface is considered to act as a “template” for crystal growth.

Biomineralization results in complex materials such as bones, shells, and teeth, that are characterized by a remarkable level of molecular control of the particle size, structure, morphology, aggregation, and crystallo-

(135) Caro, J.; Finger, G.; Jahn, E.; Kornatowski, J.; Marlow, F.; Noack, M.; Werner, L.; Zibrowius, B.; *Proc. Int. Zeolite Conf.*, 9th, Meeting Date 1992; Von Ballmoos, R., Higgins, J. B., Treacy, M. M., Eds.; Butterworth-Heinemann: Boston, MA, 1993; Vol. 2, pp 683–91.

(136) Girnus, I.; Pohl, M. M.; Richter-Mendau, J.; Schneider, M.; Noack, M.; Venzke, D.; Caro, J. *Adv. Mater.* **1995**, 7, 711–14.

(137) Noack, M.; Koelsch, P.; Venzke, D.; Toussaint, P.; Caro, J. *Microporous Mater.* **1994**, 3, 201–6.

(138) Koelsch, P.; Venzke, D.; Noack, M.; Toussaint, P.; Caro, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2491–2.

(139) Caro, J.; Finger, G.; Kornatowski, J.; Richter-Mendau, J.; Werner, L.; Zibrowius, B. *Adv. Mater.* **1992**, 4, 273–6.

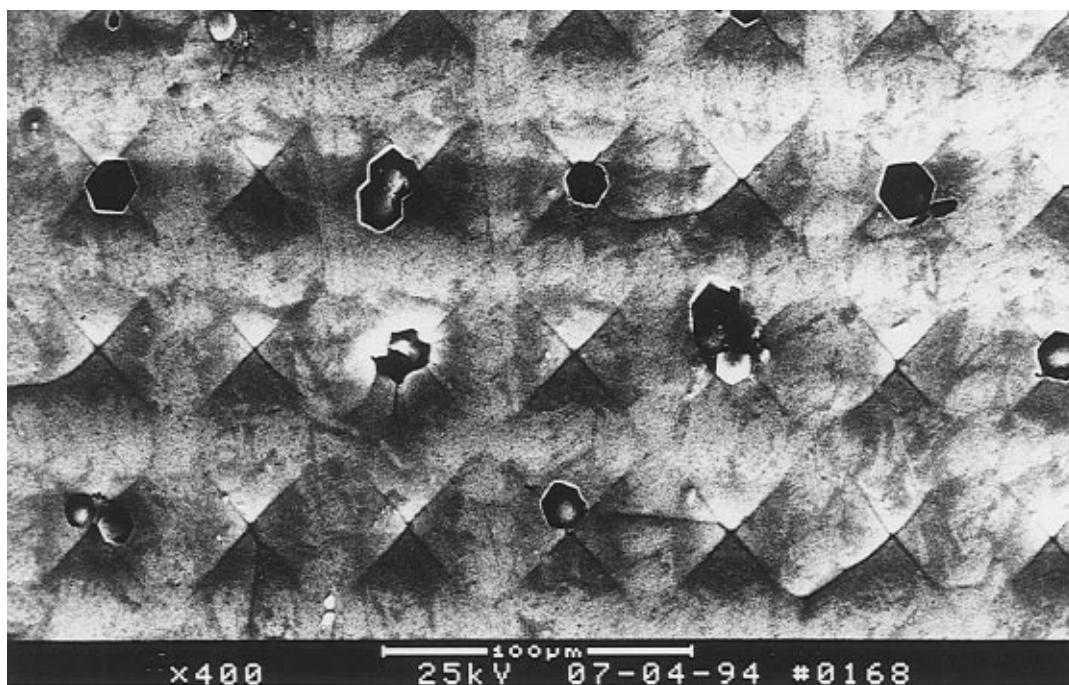


Figure 12. $\text{AlPO}_4\text{-5}$ in nickel membrane, in top view. Reproduced with permission from ref 137.

graphic orientation of the mineral phases.^{140–142} A central principle of biominerization is that the nucleation, growth, and morphology of the inorganic crystals are regulated by processes involving molecular recognition at organized assemblies of organic matrixes.

Recent studies inspired by biominerization have shown that surfactant monolayers can be utilized as substrates on which to grow inorganic and organic crystals and that stereochemical matching between the monolayers and crystal lattices can result in oriented or even epitaxial crystal growth.^{143–145} For example, the epitaxial growth (from (111) basal planes) of PbS on arachidic acid Langmuir layers has been reported.¹⁴⁶ Functionalized interfaces such as sulfonated styrene have been used to grow films of oxides, hydroxides, and sulfides, such as goethite (FeOOH) from aqueous solutions.¹⁴⁷ Depending on the deposition conditions, several of these films can be grown with preferred crystal orientations.

We have recently developed systems that mimic some features of biominerization to grow oriented zeolite molecular sieve films. These systems are based on various self-assembled, organophosphate- or phosphonate-terminated layers. Relevant features of such self-assembled layers will be discussed in the following.

Self-Assembled Functional Layers. Organic thin films have been used in many emerging technological

applications, such as chemical and biochemical sensors, protective layers, patternable materials for microelectronics, and nonlinear optical devices.¹⁴⁸ Among self-assembled monolayers (SAMs),¹⁴⁹ those based on alkanethiols covalently attached to gold have been studied extensively.

In the construction of appropriate functional surfaces for surface crystallization, several criteria must be met, including thermal and chemical stability as well as chemical/structural compatibility with the molecular sieve phase under consideration. Many phosphate molecular sieves are known, and it was expected that the presentation of phosphate or phosphonate groups on a self-assembled organic layer would assist in the nucleation and growth of the microporous solid. Furthermore, an entire family of organophosphonate–metal multilayer films has been developed in recent years, and these films offer greater stability than many single-layer films.¹⁵⁰ These multilayers have been introduced by Mallouk and co-workers, based on analogies with bulk layered metal phosphates.^{151–153}

4.2. Growth of Oriented Metallophosphate Molecular Sieves on Multilayer Organophosphonate Films. Zincophosphate Layers. We have recently discovered that organophosphonate films can promote the growth of oriented molecular sieves, specifically zincophosphate¹⁵⁴ and aluminophosphate crystals (for the latter, see below). Several factors are important for the surface nucleation process of a specific zincophos-

(140) Addadi, L.; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 153.

(141) Lowenstam, H. A.; Weiner, S. *On Biominerization*; Oxford University Press: New York, 1989.

(142) (a) Mann, S. *Nature* **1988**, 332, 119–124. (b) Mann, S. *Nature* **1993**, 365, 499–505.

(143) Fendler, J. H. *Membrane-Mimetic Approach to Advanced Materials*; Springer-Verlag: Berlin, 1994.

(144) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, 7, 607–632.

(145) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, 261, 1286–92.

(146) Zhao, X. K.; Yang, J.; McCormick, L. D.; Fendler, J. H. *J. Phys. Chem.* **1992**, 96, 9933.

(147) Bunker, B. C.; Rieke, P. C.; Tarasevich, B. J.; Campbell, A. A.; Fryxell, G. E.; Graff, G. L.; Song, L.; Lin, J.; Virden, J. W.; McVay, G. L. *Science* **1994**, 264, 48–55.

(148) (a) Swalen, J. D.; Allara, D. L.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, 3, 932. (b) Wegner, G.; *Adv. Mater.* **1991**, 3, 8. (c) Fuchs, H.; Ohst, H.; Prass, W. *Adv. Mater.* **1991**, 3, 10.

(149) Ulman, A. *Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic: Boston, MA, 1991.

(150) Thompson, M. E. *Chem. Mater.* **1994**, 6, 1168–75.

(151) (a) Lee, H.; Kepley, L. J.; Hong, H.-G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, 110, 618–20. (b) Lee, H.; Kepley, L. J.; Hong, H.-G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, 92, 2597.

(152) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, 20, 92–7.

(153) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, 25, 420–7.

(154) Feng, S.; Bein, T. *Nature* **1994**, 368, 834–6.

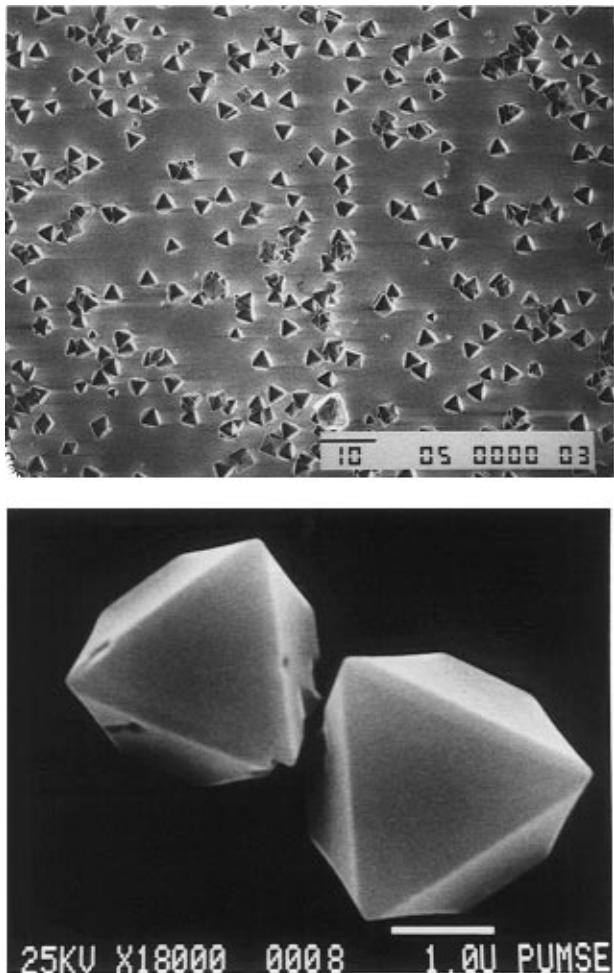


Figure 13. (A, top) Zincophosphate on Zr-phosphonate layer. Reproduced with permission from ref 154. (B, bottom) Zincophosphate on Zr-phosphonate layer (closeup). By Sue Feng, Ph.D. Thesis, Purdue University, 1995.

phate with the faujasite structure, discovered by Stucky and Gier,¹⁵⁵ including the presence of the phosphonate surface, a specific solution templating agent, substrate orientation, gel concentration, and synthesis temperature. The crystals are attached to the surface with one of their triangular (111) faces (Figures 13 and 14).

To elucidate the role of the organic/inorganic interface, we have designed three models with a variety of mixed phosphonate layers on gold surfaces.¹⁵⁶ The first model uses spacer molecules that have a chain length similar to the phosphonate chains but contain "inert" methyl headgroups. In model II, the phosphonate surface acts as a base layer, and a longer alkyl spacer molecule is embedded in the surface. A third model system contains alkylammonium groups separated by shorter alkyl chains. Preliminary results for the latter suggest that the surface attached "template" groups cannot assist in surface crystallization of the zincophosphate.

Crystallization experiments show that the mixed film composition of model I systems has a dramatic effect on the zincophosphate crystal growth. The overall trend is an increase in zincophosphate crystal surface density as the fraction of phosphonate groups at the interface increases. We observe a threshold surface concentration of phosphonate groups that must be exceeded to start

A. Condensation of zeolite nuclei with the organophosphonate film

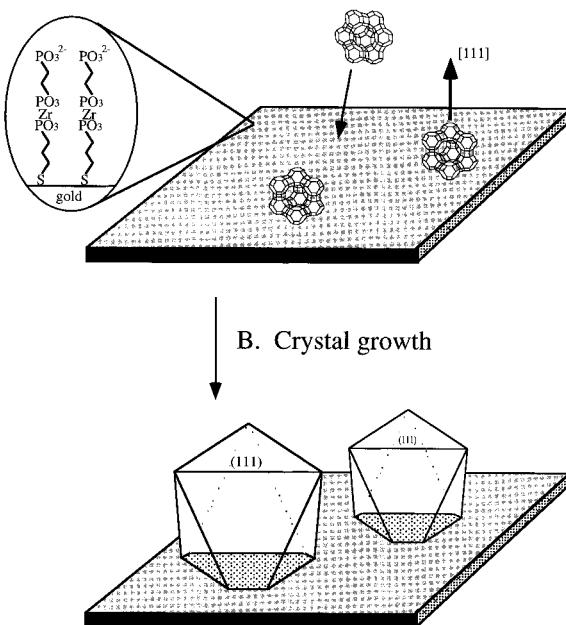


Figure 14. Growth of zincophosphate molecular sieves on organophosphonate film (schematic) (after ref 154).

significant surface crystal growth. On all but the highly concentrated phosphonate films, the zincophosphate crystals are also less oriented than on the 100% phosphonate surface. The array of phosphonate groups appears to act as a template for molecular sieve surface crystallization.

The findings strongly suggest that large domains do not form in the model I mixed films with compounds H₂O₃P-(CH₂)₁₀-PO₃H₂ and H₂O₃P-O-(CH₂)₁₁-CH₃, because if large domains had formed, the nuclei would have a probability of surface attachment that is linearly related to the surface fraction of phosphonate domains, and they should always have a similar orientation.

In contrast to the observations regarding model I, model II systems with the long spacer molecules do *not* favor surface crystallization, even if the phosphonate-to-spacer ratio is as large as 1:1. In this case, the space between the longer, bent-down methylene chains is probably too small for nuclei to penetrate into the voids and reach the "buried" phosphonate headgroups to initiate the crystal growth. However, as the phosphonate functional group density is increased beyond 80% in the mixture, apparently there are enough phosphonate sites to induce surface growth. A high density of oriented crystals is then formed on the substrate. Again these findings support the notion of statistically distributed functional groups and a strong correlation between exposed phosphonate group density and surface crystallization.

Growth of Vertical Aluminophosphate Crystals on Multilayer Organophosphonate Films. The examples of surface-induced zincophosphate crystal growth on organophosphonate-modified Au substrates discussed in the previous section illustrate the potential of molecular preorganization and templating in controlling molecular sieve growth. This approach was extended to the construction of oriented aluminophosphate crystals on zirconium phosphonate (ZrP) precoated Au

(155) Gier, T.; Stucky, G. D. *Nature* **1991**, *349*, 508-10.

(156) Feng, S.; Bein, T., to be published.

surfaces.¹⁵⁷ The AlPO₄-5 framework is essentially constructed of cylinders of uniform cross section (7.3 Å). In addition, AlPO₄-5 also exhibits excellent thermal stability.^{158,159} As mentioned in section 3.4, oriented aluminophosphate molecular sieve crystals could offer interesting applications, such as host materials for nonlinear optical chromophores or molecular sieve membranes. To induce surface nucleation and oriented growth of AlPO₄-5 crystals, organophosphonate layers cross-linked with Zr(IV) were assembled on gold, and the modified substrate was immersed into a hydrothermal bath containing reagents for the molecular sieve synthesis. Reflection-absorption infrared (RAIR) studies demonstrate the stability of the phosphonate layers under hydrothermal conditions. The striking thermal stability of the ZrP film (up to 180 °C under slightly acidic conditions, pH = 3) is very likely related to the stability of its solid analogues featuring strongly bonded Zr phosphate networks.⁵

For the purpose of surface crystallization, the AlPO₄-5 crystals were synthesized hydrothermally from boehmite (AlOOH), orthophosphoric acid (H₃PO₄), 1,4-diazabicyclo[2.2.2]octane (Dabco), and water in Teflon-lined autoclaves without stirring under autogeneous pressure at 180 °C. The molar composition of the gel was 1 Al₂O₃·1P₂O₅·3.2Dabco·*d*H₂O. The water content *d* was adjusted from 60 to 600, and the reaction time was 8–12 h.

The ZrP trilayer films promote the growth of aluminophosphate molecular sieves from the hydrothermal synthesis mixtures (as shown in Figure 15). Different crystal morphologies form with different water content (*d*) in the synthesis mixture. Specifically, the electron micrographs show that (i) the aspect ratio increases with the water content, (ii) when *d* = 300, almost all of the crystals orient with their *c* axis perpendicular to the surface; and when *d* = 400 and 600, the majority of the crystals show *c*-axis preferred orientation with tilted angles. Spherical aggregates were obtained at 150 °C and lower water content (*d* = 60).

These observations are consistent with the report by Finger et al.,¹⁶⁰ who found in bulk synthesis that increasing the water content in the AlPO₄-5 synthesis gel favors the growth along the *c* axis and that the minimum water content at which single hexagonal prisms can be formed was about 100.

It appears quite unlikely that individual ions could assemble an oriented structure as complex as AlPO₄-5 on the substrate without epitaxial control, and we propose that small, ring-shaped subunits assemble on the substrate to start the growth (see Figure 16). The oriented AlPO₄-5 structures could be used in applications such as catalytic membranes with true molecular selectivity, or in the controlled access of molecules of preselected size to a sensor surface.

4.3. Growth of Other Molecular Sieves on Organic Layers.

A recent report by Schüth and co-

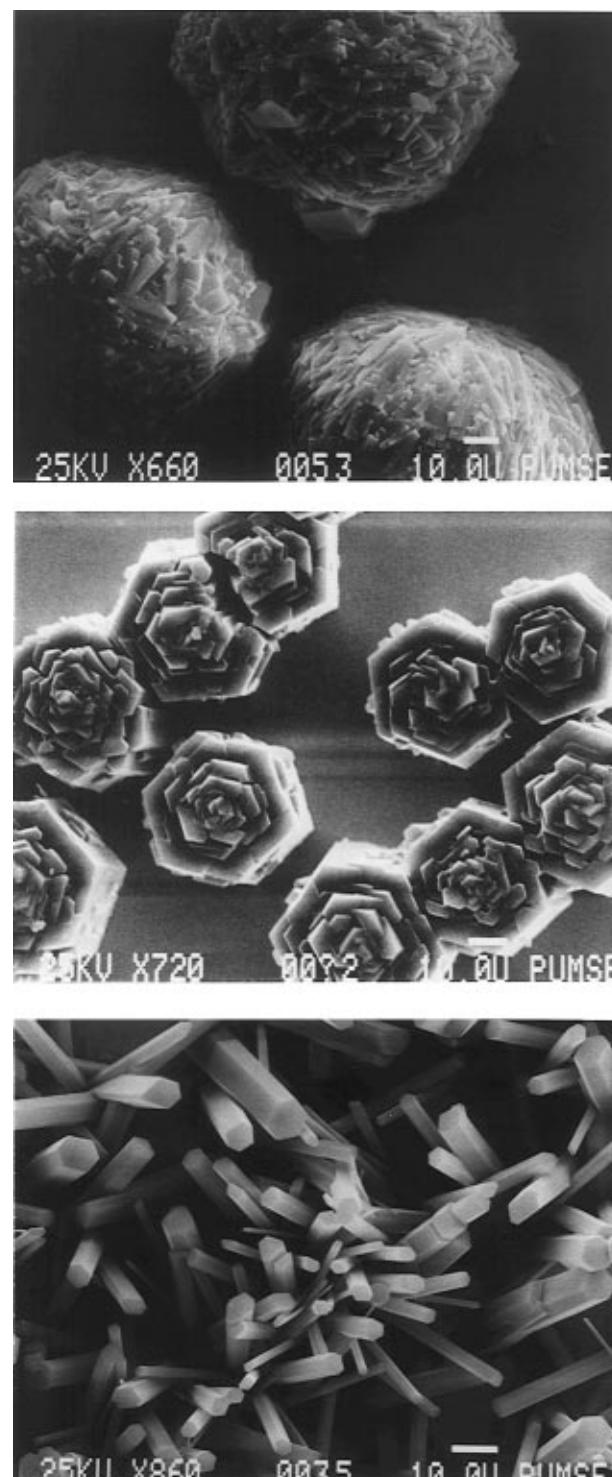


Figure 15. Growth of aluminophosphate molecular sieves on organophosphonate film (scanning electron micrographs). (A, top) Water content *d* = 60, temperature *T* = 150 °C. By Sue Feng, Ph.D. Thesis, Purdue University, 1995. (B, middle) *d* = 300, *T* = 180 °C. (C, bottom) *d* = 600, *T* = 180 °C. Reproduced with permission from ref 157.

workers extends the concept of surface-assisted growth from the liquid phase to the vapor phase. The vapor transport was achieved by using solid amorphous silica mixed with NH₄F which apparently forms volatile SiF₄ and small amounts of water.¹⁶¹ Tri-*n*-propylammonium groups were deposited on a gold substrate through a thiol linker. The surface functionality was expected to

(157) Feng, S.; Bein, T. *Science* **1994**, *265*, 1839–1841.

(158) (a) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigan, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146–7. (b) Wilson, S. T.; Lok, B. M.; Flanigan, E. M. U.S. Patent 4,310,440, 1982. (c) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Flanigan, E. M. *Proceedings of the Sixth International Zeolite Conference*, 1983, Reno, NV; Butterworth: Guildford, 1984; pp 97–109.

(159) Bennett, J. M.; Cohen, J. P.; Flanigan, E. M.; Pluth, J. J.; Smith, J. V. *ACS Symp. Ser.* **1983**, *218*, 109.

(160) Finger, G.; Mendau, J. R.; Bulow, M.; Kornatowski, J. *Zeolites* **1991**, *11*, 443.

(161) Althoff, R.; Unger, K.; Schüth, F. *Microporous Mater.* **1994**, *2*, 557–562.

A. Nuclei of the aluminophosphate attach to the stable phosphonate film

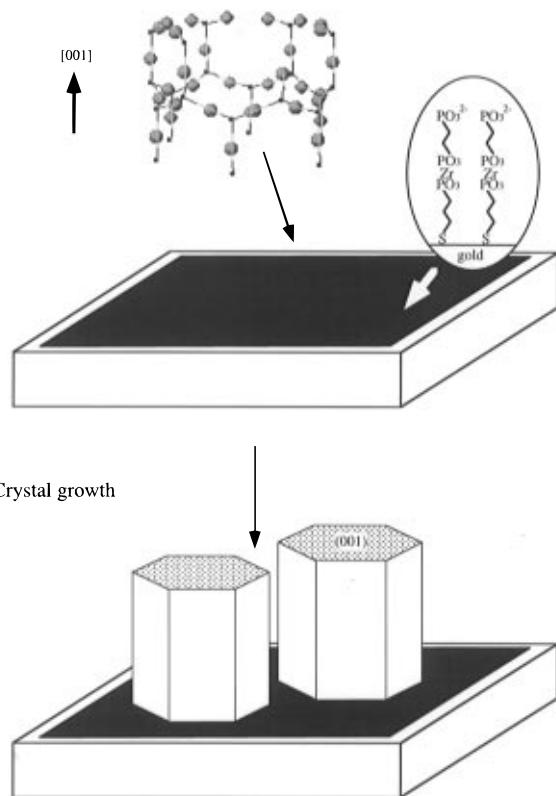


Figure 16. Growth of aluminophosphate molecular sieves on organophosphonate film (schematic). After ref 157.

simulate the tetra-*n*-propylammonium template used for ZSM-5 type (MFI) synthesis, thus assisting in the surface growth of these zeolites. Using the vapor-phase synthesis method, growth of MFI type zeolites was indeed observed on the surface.¹⁶²

The reactants deliver enough material to the separate substrate such that zeolite growth can occur. Given the absence of a commensurate lattice of surface propylammonium groups and the facile growth of MFI on many substrates, it might be possible that the surface growth was controlled by wetting of the precursors rather than by incorporation of the alkylammonium groups into the growing crystals. This concept shows promise for novel deposition methods, for example, in the design of zeolite arrays on surfaces, and for applications such as catalytic membranes, sensors, or optical coatings.

Finally, we note that nanochannel materials can also be made in very different ways, for example by forming nanochannel etched glass bundles¹⁶³ or preparing thin

(162) Althoff, R.; Sellegren, B.; Zibrowius, B.; Unger, K.; Schüth, F. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1995**, 40, 240–2.

metallic replicas of the latter.¹⁶⁴ Details regarding these and other interesting design strategies for nanometer channel structures are beyond the scope of this review.

5. Conclusions

In conclusion, we have demonstrated the great variety of synthetic approaches toward the design of molecular sieve layers and membranes. The following issues will be likely to play a role in future research in this area.

In the field of inorganic separation membranes, there is a trend to reduce the thickness of dense, gastight membranes in order to increase permeability, while not increasing defect densities that would compromise the molecular selectivity. Furthermore, more work is warranted in the effort to create dense membranes from zeolites other than ZSM-5 and a few other recent examples. This requires a greater understanding of the nucleation and growth of zeolite materials at interfaces in general. Continuing work on zeolite growth on functional organic monolayers is aimed at addressing some of the issues involved.

Catalytic membranes are just beginning to emerge as a new application of zeolite membranes. Provided the permeability is acceptable, there appears to be great potential in catalytic applications. Polymer-embedded zeolites, operating as pervaporation membranes, will also play a role in this context, because (i) the preparation is simple, and (ii) permselectivities can be controlled by both matrix and zeolite material.

Finally, among novel applications of zeolite films and layers, chemical sensors have received considerable attention. Issues such as film stability, compatibility with sensor transducers, and novel transduction concepts will very likely play a role in future research. Other demonstrated or potential applications of zeolite films include solar energy conversion, zeolite electrodes, electron relays, zeolite batteries, zeolite fast ion conductors, intrazeolite semiconductors, and zeolite imaging and data storage materials. It is a wide field waiting to be explored.

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(163) Tonucci, R. J.; et al. *Science* **1992**, 258, 783.

(164) Pearson, D. H.; Tonucci, R. J. *Science* **1995**, 270, 68–70.