제올라이트막과 제올라이트/고분자 복합막의 전망과 도전

정해권

Texas A&M 대학교 화학공학과
(2010년 8월 27일 접수)

Zeolite and Zeolite/Polymer Composite Membranes: Promises and Challenges

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(Received August 27, 2010)

최근 에너지 효율이 높은 공정기술의 수요가 증가하면서 분리막을 이용한 기체분리가 많은 연구자들의 관심을 모으고 있다. 현재 분리막에 의한 기체 분리 시장은 고분자막이 독점하고 있으며 탄화수소와 같은 응축기체 분리시장이 훨씬 큼에도 불구하고 주로 비응축 기체분리에 제한되고 있다. 이는 고분자 재료의 물성에 한계가 있기 때문이다. 제올라이트막이나 제올라이트/고분자 복합막이 제올라이트의 우수한 분리력과 화학적/열적 특성으로 인해 고분자막의 한계를 극복할 수 있는 대안이 될 수 있다. 이번 총설에서는 이러한 기체분리를 위한 제올라이트막과 제올라이트/고분자 복합막에 대해 간략히 소개하고자 한다.

Recently membrane-based gas separation has attracted a great deal of research interests due to the growing demands on greener technologies. Current membrane-based gas separation is dominant by polymer membranes and limited mostly to non-condensable gases even though condensable gases such hydrocarbon isomers are much more attractive. This is primarily due to the limitations of polymer materials. Zeolites and their composites with polymer can offer alternative to current polymeric membranes owing to their superior separation and chemical/thermal properties. This review is intended to provide a brief overview on zeolite and zeolite/polymer composite membranes for gas separation applications.

*Keywords: zeolites, composites, membranes, gas separations*

1. Introduction

In spite of the maturity of the Petrochemical and Commodity Chemicals Industries there are still tremendous needs for improving a variety of technologically relevant separations[1]. Traditional separation methods, such as distillation and/or condensation, are highly energy intensive. If global commodity chemical production grows by a factor of six as projected for the year 2040 and the existing separations infrastructure is simply scaled up to meet that demand, Koros estimates that separations in 2040 will then consume 350 Q/y, which is 90% of the world's total energy use in 2005[2]. A scale-up of the current separations infrastructure is clearly not sustainable; new technologies are needed. In this vein membrane-based separations offer great potential in terms of their energy consumption and often smaller (and greener) footprint.

Current membrane markets are currently dominated by polymeric materials. However, despite the ability to produce robust membranes at

relatively low cost, wider implementation of this technology is hindered by intrinsic permeability and selectivity limitations of the polymeric materials as well as their thermal and chemical instability, as illustrated by the so called Robeson plot (see Figure 1)[3]. Therefore, there is a great need to develop membranes with new materials and processes. Zeolite membranes and zeolite/polymer composite membranes (i.e., mixed matrix membranes) are examples of those efforts to address the challenges that polymer membranes face. As can be seen in Figure 1, pure zeolitic SAPO-34 membrane[4] shows superior performance in CO_2/CH_4 separation as compared to polymer membranes. It is important to note that zeolite and zeolite/polymer composite membranes can be viable for certain applications such as separation of isomers.

Over the last couple of decades, zeolites have attracted a great deal of research interest as new materials for membranes[5-7]. This is primarily due to their rigid pores in the scale of molecular dimension which enable precise separation of molecules based on small disparity in size (see Figure 2). In addition, zeolites are well known for their thermal, chemical, and mechanical stabilities, thereby finding potential

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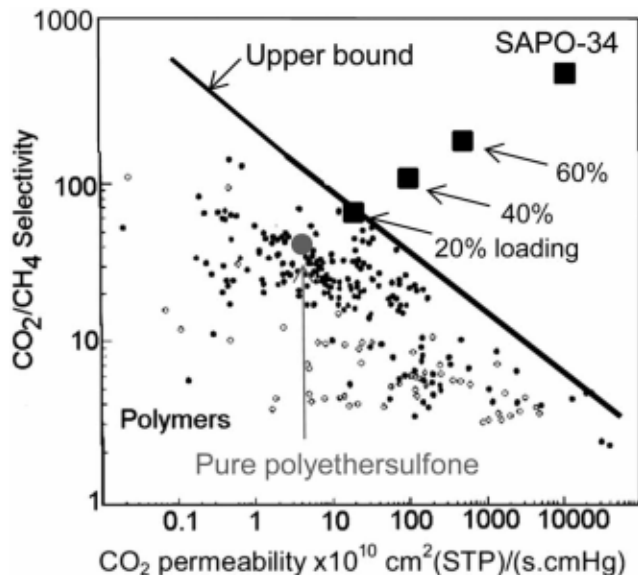
Figure 1. Limitations of polymeric membranes. The solid line shows the Robeson's upper bound[3] beyond which no polymeric materials available. SAPO-34 shows superior permselectivity well above the upper bound. Performance is predicted from the Maxwell model.

applications under harsh environments. However, significant challenges still remain, including high cost mainly associated with manufacturing processes.

Though pure zeolite membranes, if realized at a reasonable cost, can be revolutionary in gas separation, it will likely take years before being commercialized. It is, therefore, desirable to take an evolutionary step to bridge the current polymer membranes and more futuristic zeolite membranes. One such approach is to add highly selective zeolite particles into continuous polymer phases[8,9]. These zeolite/polymer composite membranes, also called mixed matrix membranes, have advantages of both zeolite and polymer. The main idea is to improve the performance of polymer membranes by adding small amount of zeolites (see Figure 2). Since there are only small amount of zeolite incorporated, all the advantages that polymer membranes have over inorganic membranes still hold. One of the most significant advantages of polymer is the processibility of polymer which is an ability to make hollow fibers with a continuous process.

This review is intended to provide a brief overview on zeolite and zeolite/polymer composite membranes for gas separation applications. Some of the promises and challenges in the development of zeolite and composite membranes are presented.

2. Zeolite Membranes

Zeolites are crystalline aluminosilicates consisting of [MO_4] (where M represents metal such as Si or Al) tetrahedral units that are interconnected to form one, two and three dimensional pore structures (see illustrations in Figure 3)[10,11]. The sizes of pores, cavities, and channels in zeolites are in the range of subnanometer, which is the scale of small molecules as shown in Figure 3.

**Table 1. Examples of Potential Applications for Zeolite Membranes [21]**

Separation	Zeolite membrane	Advantages and limitations
Organic-water mixtures by pervaporation	MFI, zeolite A (zeolite A membranes already commercialized)	Highly selective separation with water (zeolite A) or the organic (MFI) as the selective penetrant
Separation of miscellaneous organic compounds that have close boiling points or are heat-sensitive	MFI, zeolite A, others	Potentially useful for specialty chemicals and natural products
CO_2-CH_4 (natural gas upgrading)	Na-Y	Resistance to plasticization and fouling by higher hydrocarbons[b]
CH_4-higher hydrocarbons (natural gas processing)	MFI	Higher alkances are the selective penetrants: has to be compared with separation by liquefaction
Normal alkanes from branched alkanes: aromatics or cycloalkanes from alkanes: separation of xylenes (petroleum refining and petrochemicals)	MFI	Very high selectivity unattainable with polymeric membranes; separation by distillation difficult
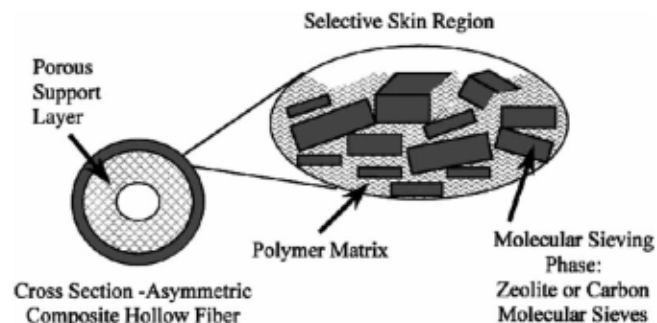
Figure 2. Concept of polymer-zeolite composite membranes (or mixed-matrix membranes). Image was taken from ref 8.

Membranes of zeolites have attracted significant research interest due to their thermal and chemical stability, and their high selectivity in certain important separations such as xylene isomers[12-17], CO_2/CH_4 [18,19], and paraffin/olefin[20] separations. Separations by zeolites membranes are based on two mechanisms : kinetic-based separation (molecular sieving) and thermodynamic-based separation (adsorption followed by diffusion). Kinetic-based separation results when the size of the pore apertures is similar to the dimensions of the gas molecules. Even the very critical separation of propane (kinetic diameter~0.43 nm)/ propene (~0.45 nm) is possible in this way. Thermodynamic-based separation results when the adsorption of one species prefer to that of others. Thus very high selectivity is also possible with mixtures of gases when the zeolite pore sizes are significantly larger than the molecules.

Despite their potential, the cost of supports and the laborious steps involved in the preparation process make zeolite membranes much
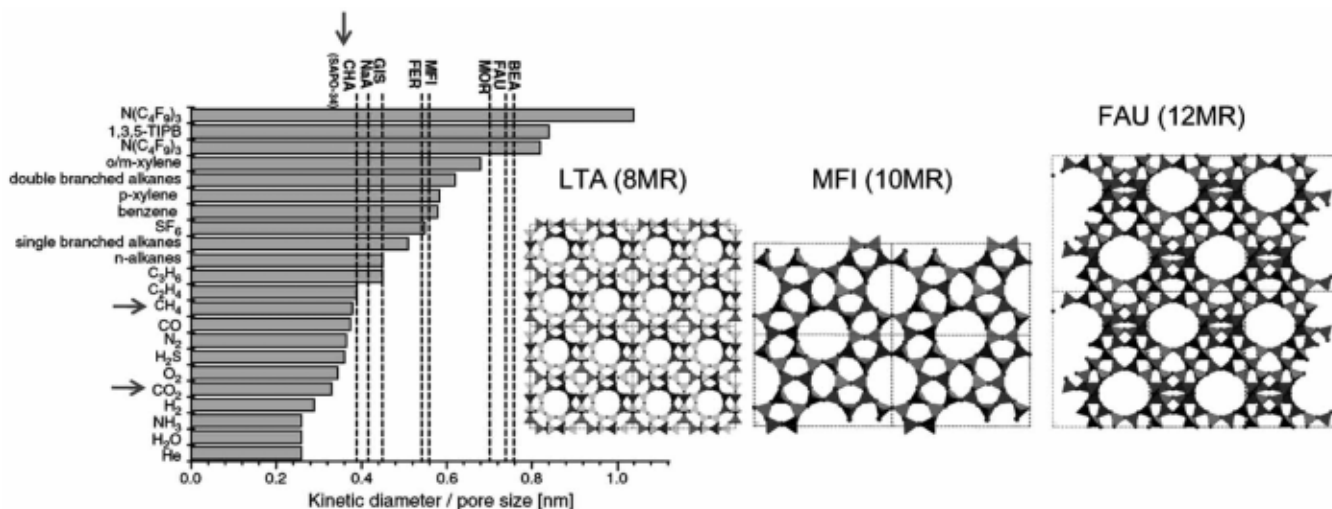
Figure 3. Comparison between the effective pore sizes of different zeolites and the kinetic diameters of gas molecules that are important for separation. Note that the size (0.38 nm) of the aperture of small-pore SAPO-34 with CHA structures is similar to the kinetic diameter of CH₄ (0.38 nm) but larger than that of CO₂ (0.33 nm). Thus, SAPO-34 shows extremely high selectivity of CO₂/CH₄ about 500. The image on the left was taken from ref. 6.

more expensive than the well-established polymeric membranes. Therefore, industrial applications should be considered only for separations where they offer some unique advantages in terms of selectivity, thermal and chemical stability. Mitsui has commercial zeolite A membranes for dehydration of bio-ethanol as shown in Figure 4. More examples of potential applications are listed in Table 1[21].

Due to the simplicity of the synthesis and their potential in the separation of light hydrocarbons (such as p-xylene/o-xylene, n-hexane), MFI membranes (also called silicalite-1 or ZSM-5 when consisting of only [SiO₄] or [SiO₄] and [AlO₄], respectively) on flat or tubular supports, have been most extensively investigated. Therefore, this review will focus on MFI zeolite membranes though other membranes will be mentioned as needed.

2.1. Zeolite Membrane Synthesis

A great deal of progress in the science of zeolite membrane synthesis has been made since the first preparation of zeolite membranes by Suzuki in late 80s[22]. Since then there has been exponential growth in papers on the subject and literature[6].

The main difference between zeolite membrane synthesis and zeolite powder synthesis, which is one of the difficulties inherent to the preparation of zeolite membranes, is the presence of an additional parameter, the substrate and the linking of zeolite crystals to that substrate to obtain continuous thin layers of zeolite crystals[21].

There are two most common methods used to produce supported zeolite membranes : 1) *in situ* crystallization in the presence of a substrate such as a porous ceramic and 2) secondary growth process which involves the deposition of colloidal zeolite crystals on a macroporous support followed by hydrothermal synthesis[23]. In *in situ* method (i.e., one-step hydrothermal synthesis method), the porous ceramic support is placed in direct contact with the alkaline precursor solution. Since a piece of alumina or some other support materials is

Figure 4. A-type zeolite membranes for dehydration of bio-ethanol commercialized by Mitsui (www. mitsui.co.jp).

immersed in a synthesis mixture, crystals will generally grow on the solid as well as in the bulk. Whether nucleation takes place more readily on the solid than in the bulk depends on the particular system, especially the surface chemistry of the solid support. Therefore, one of the challenges faced during *in situ* synthesis is to ensure a high nucleation site density on the support, often giving rise to higher film thickness than desired to close all defects. Secondary growth process decouples nucleation and growth steps : i.e., coating the solid with a seed layer and using a relatively dilute solution to reduce bulk crystallization and favor formation of a continuous layer as illustrated in Figure 5. Because of the decoupling, the secondary growth method shows improved control of nucleation site location and density, rendering the nature of substrate less important for membrane growth with growth processing from a layer of the zeolite seed crystals covering the support. In addition, it is easier to control the crystallographic orientation
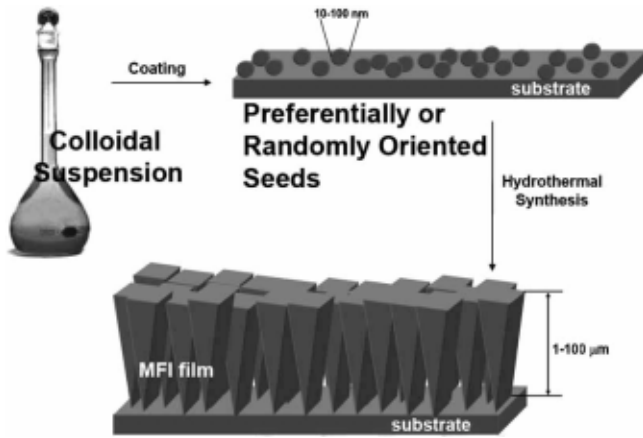
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Figure 5. Schematic illustration of secondary growth (i.e., seeded growth). Illustration is from Prof. Tsapatsis at Minnesota.

using the secondary growth. Since most of zeolites (except cubic systems) are anisotropic in properties, it turns out important to control the orientation of zeolite crystals on substrates for better performance. This point is well illustrated in the breakthrough work done from Tsapatsis group[13,14] as shown in Figure 6. As seen, the membrane performance strongly depends on the out-of-plane orientation of MFI crystals on the substrates. More recently the same group reported another breakthrough showing the substantial enhancement in the performance of *c*-oriented MFI membranes by removing grain boundary defects in the membranes[24].

2.2. Challenges and Outlook of Zeolite Membranes

Despite the recent success achieved in the synthesis of zeolite membranes during the last decade, few reports on the practical application of such membranes exist. In fact, there is only one commercial application so far, zeolite A membranes for dehydration of bio-ethanol (see Figure 4). There are number of challenges that still have to be addressed and/or further explored:

1) The synthesis of membranes with high permeability and selectivity, i.e., oriented, thin layers, i.e., small effective thicknesses are required which must be highly uniform and free of defects.

2) Reproducibility and long-term stability of membrane performance.

3) Small pore zeolite membranes, ~0.3 nm without inter-crystalline pores for thermodynamic-based separations

4) Scaling-up of membrane modules. Large surface areas

5) Cost of membranes

These challenges are currently under extensive investigations. If these challenges are to be addressed, it is expected to see more industrial applications of zeolite membranes.

3. Zeolite/Polymer Composite Membranes

Gas separations by membranes are currently dominated by polymeric materials. This is primarily owing to the excellent processibility of polymer, thereby the low manufacturing cost of polymer membranes (see Figure 7(b)). State-of-the-art polymer membranes are produced in
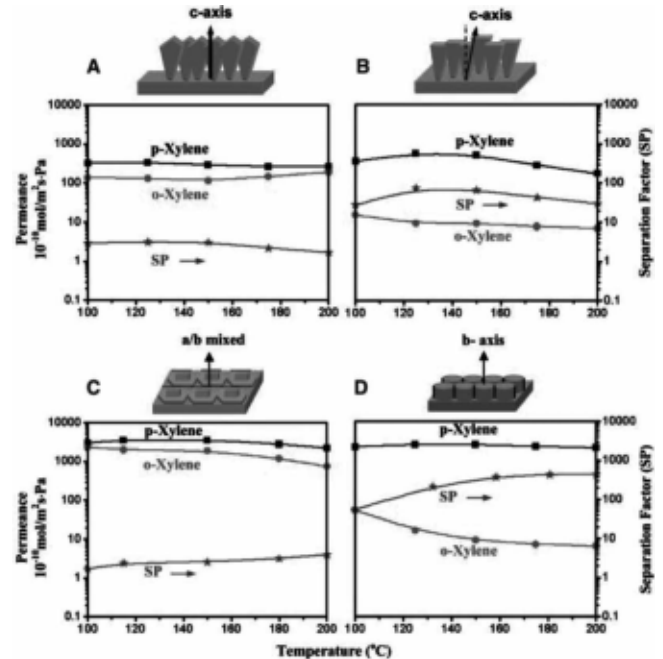

Figure 6. ZSM-5 membrane performance in xylene isomer separation, showing strong dependence on the orientation of the crystals[13].
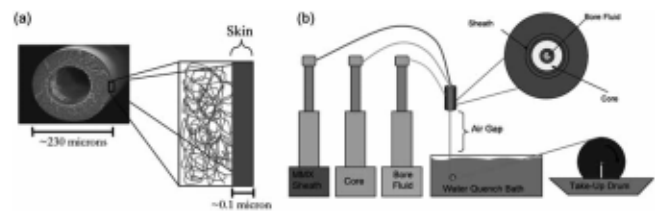

Figure 7. (a) Asymmetric hollow fiber membranes and (b) schematic for hollow fiber spinning set-up. The SEM image on the left is from ref. 24. Illustration for hollow fiber spinning is from Prof. Koros at Georgia Tech.

the form of hollow fibers with selective skin layers whose thickness ranges from 0.1 to 1 μm[25] as illustrated in Figure 7(a).

These thin selective skin layers are of great importance since the permeance of membranes is inversely proportional to the thickness of the layers. However, despite the ability to produce robust membranes with submicrometer thick selective skin layers at relatively low cost, wider implementation of this technology is hindered by intrinsic permeability and selectivity limitations of the polymeric materials. These intrinsic limitations can be seen in Figure 2 as the so called Robeson's upper bound for CO_2/CH_4[3]. On the other hand, highly selective nanoporous materials such as zeolites have shown superior separation properties well beyond the upper bound. Composites of polymers with these highly selective nanoporous materials were thus proposed as new membrane materials as illustrated in Figure 1. The Maxwell's model predicts a two-fold increase in both selectivity of CO_2/CH_4 and permeability of CO_2 with 40 vol% loading of SAPO-34 in polyethersulfone matrix as shown in Figure 1.
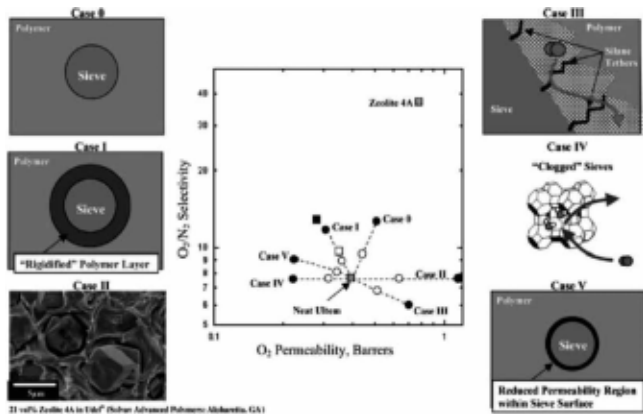
Figure 8. Effect of interfacial regions on the membrane performance taken from ref. 25. Circles represent calculated values : ○ 15 vol% 4A and ● 35 vol% 4A.
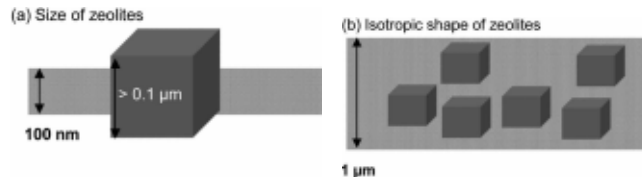

Figure 9. Schematic of practical challenges of mixed matrix membranes associated with length scales and shapes of fillers: (a) size of zeolites is typically 0.1~1 micron, which is in the same scale of the selective skin layer and (b) zeolites are typically isotropic thus requires large amount of zeolites to enhance the performance of polymer membranes.

3.1. Challenges to Composite Membrane Preparation

Despite their potential to improve polymeric membrane properties, it has been difficult to realize the full promise of the mixed matrix membranes. There are two major challenges : 1) interfaces between zeolites and polymer and 2) mismatch in sizes of zeolite particles and selective skin layers.

3.2. Zeolite/Polymer Interfaces

In general, the properties of composites are greatly influenced by the properties of interfaces. Same is true for zeolite/polymer composite membranes. Koros and co-workers recognized this challenge.

In general, the properties of composites are greatly influenced by the properties of interfaces. Same is true for zeolite/polymer composite membranes. Koros and co-workers recognized this challenge early on and attributed primarily to the difficulty in understanding and controlling the complex nature of the interfaces between organic and inorganic entities[26-30]. The relationship between interfacial structures and membrane performance is well illustrated in Figure 8, presenting six difference model cases. In Case II, there is no bonding between zeolite and polymer, which creates "sieve-in-a-cage" structure. In this case, the permeance increases while the selectivity decreases. In Case III, when there are gaps in the molecular scales, the permeance increases while the selectivity deceases slightly. This is called "leaky". In Case IV, zeolite pores are clogged by polymer chains, thereby showing reduced permeability. In Case V, zeolite pores are partially blocked, thus reducing permeability while still capable of increasing selectivity slightly. In Case I, when zeolite/polymer interfacial bonding is too strong, the free volume of polymer chains decreases, resulting in "matrix rigidification". When this happens, the permeance decreases. In Case 0, the most ideal interface is where the bonding between zeolite and polymer is neither too strong nor too weak. In this case, both the permeance and the selectivity increase. In addition, as more zeolite particles incorporated, the selectivity generally increases while the permeance decreases. Substantial membrane performance improvement can be achieved if one can minimize the "rigidified" interface regions as in Case I thus approaching to Case 0 as shown in Figure 8[26].

To improve the interfaces between zeolite and polymer, there are several strategies developed. For instance, zeolite particles are dispersed in 5~10 w% of priming polymer solutions before incorporating zeolite particles in polymeric solutions. This "priming" process coats thin layers of polymer on the particles, thereby enhancing the interaction between zeolite particles and polymer. "Silanation" is to use silane molecules as a glue to minimize the void at the interfaces and to promote the interfacial bondings. Most recently the Koros group reported a novel strategy to promote adhesion between zeolite and the polymer by introducing nanostructures on the zeolite surface, which showed impressive improvement in the membrane performance[31]. They qualitatively attributed this to the improved interaction at the interface due to entropically promoted adsorption of the polymer chain and subsequent interlocking on the surface nanostructures.

3.3. Zeolite Particle Size and Shape

As stated above, the most important merit of zeolite/polymer composite membranes is to take advantages from both polymer and zeolites, i.e., processibility and selectivity, respectively. When considering commercial applications of composite membranes, it is very important to be able to incorporate highly selective zeolite particles into submicron thick skin layers without sacrificing good properties and processibility of polymer. Although this point is critical for commercial applications of composite membranes, most of academic research fails to address this issue. This is due to two major challenges as illustrated in Figure 9. First, most of zeolite particles investigated as selective phases are in the range of 0.1 to 1 micron in size. This means that it is almost impossible to incorporate these particles into submicron selective skin layers (see Figure 9(a)). Second, zeolite particles are more or less isotropic in morphologies when small (e.g., spheres or cubes). Therefore, it requires a large quantity of particles in order to improve the separation performance of polymer membranes, typically up to 40 wt% (see Figure 9(b)). When incorporating this much of particles, chances are likely that all the good properties of polymer may be compromised.

4. Outlook of Zeolite/Polymer Composite Membranes

Despite the challenges mentioned above, future of composite membranes is promising considering the surge in demands for cleaner and greener technologies. Nevertheless, in order to be commercialized,
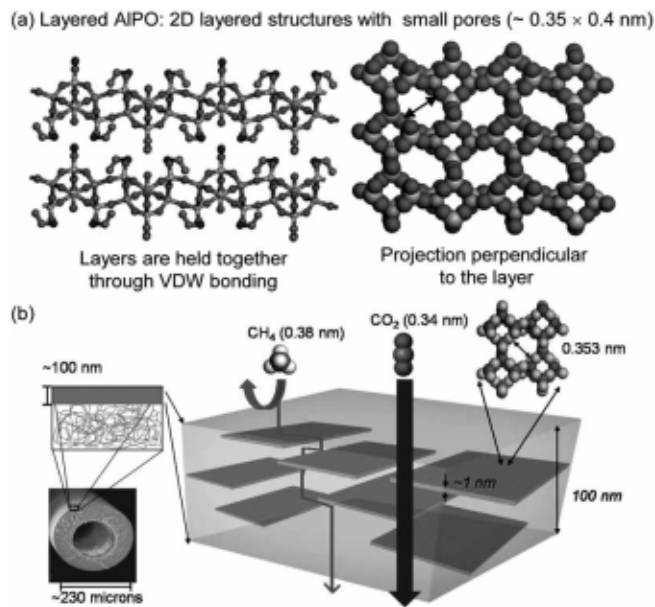
Figure 10. (a) Crystal structure of layered AlPO with pores perpendicular to the layers and (b) schematic of the concept of polymer/layered molecular sieve composite membranes[37].

there need to be several breakthroughs that can address the challenges. Here a few comments are made in regards to how to address these challenges.

1) To obtain the ideal interfaces between zeolite particles and polymer, it is important to understand the interaction between the organic and inorganic phases at their interface, ultimately enabling design of the interface to fully realize the potential for dramatically improved membrane performance by using highly selective phases in a polymer matrix. It has, however, proven very difficult to examine the interfacial region in these membranes in part because of their small volume and also because of the limitations of conventional characterization techniques [9,28]. To address this issue, one can develop model systems such as flat substrates coated with polymers and examine how the dynamics of polymer chains are affected by the chemical/physical properties of the substrate using fluorescent spectroscopy.

2) To address the size and morphology issue of zeolite particles, either plate-like zeolite nanoparticles or porous layered materials (such as AlPO[32-34] and silicates[35,36]) deserves more attentions as illustrated in Figure 10. Jeong *et al.*[37] has reported a proof-of-concept work on the use of porous layered AlPO. Substantial improvement in the performance of polymer membranes was observed with only 10 wt% of the inorganic phase.

5. Summary

While pure zeolite membranes can be revolutionary and deserve more research, evolutionary zeolite/composite membranes can offer an immediate opportunity. Due to the extensive efforts from many researchers around the world, there have been significant breakthroughs in zeolite and zeolite/composite membranes. However, there require

more breakthroughs in order to move from academic research to industrial research. In particular, engineering issues related to the cost of manufacturing should deserve more attention in the years to come.

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