Zeolite and Zeolite/Polymer Composite Membranes: Promises and Challenges

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(Received August 27, 2010)

Zeolite and zeolite/polymer composite membranes offer promise for gas separations applications. The focus of this review is on recent developments in zeolite/polymer composite membranes with emphasis on CO\(_2\)/CH\(_4\) separation. It is noted that pure zeolitic membranes are superior to their polymer counterparts, while mixed matrix membranes exhibit a potential breakthrough for the separation of isomeric molecules. This review highlights some of the progress made in the area of zeolite and zeolite/polymer composite membranes, as well as some of the challenges that remain to be overcome.

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 applications in various fields.
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 \([\text{MO}_4]\) (where \(\text{M}\) 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.

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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
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 [SiO$_4$] or [SiO$_4$] and [AlO$_4$], 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 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.
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, \(\sim 0.3\) 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 the form of hollow fibers with selective skin layers whose thickness ranges from 0.1 to 1 \(\mu\)m[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 \(\text{CO}_2/\text{CH}_4\)[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 \(\text{CO}_2/\text{CH}_4\) and permeability of \(\text{CO}_2\) with 40 vol% loading of SAPO-34 in polyethersulfone matrix as shown in Figure 1.
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 decreases 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 1 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 wt% 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,
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.

Acknowledgement

H.-K.J. acknowledges the financial support from the Artie McFerrin Department of Chemical Engineering at Texas A&M University and Texas Engineering Experiment Station through a new faculty startup. H.-K.J. is grateful for financial supports by National Science Foundation (CBET-0930079) and American Chemical Society Petroleum Research Fund (DNI-08-0831).

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