Molecular Sieve Membranes Made in Thin Sheet Form

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ABSTRACT

A new molecular sieve membrane technology is introduced in this presentation from fundamental designs to performance characteristics. The membrane is prepared by growing the molecular sieve membrane directly on a thin porous metal sheet support. Comprehensive stress modeling analysis of this membrane design suggests that if the membrane layer is controlled thin enough, there would not be any cracks and defects occurring on the membrane. Experimental preparation is illustrated by growing a few commonly-used molecular sieve frameworks, including A-type, MFI-type, and Faujasite-type zeolites as well as a hydrophobic metal-organic framework. The molecular separation characteristics is illustrated with water-selective molecular sieve membranes for dehumidification of humid air and for dehdydration of alcohol-water mixtures. The thin membrane shows exceptional permeance and selectivity. 50µm-thin 20cmx20cm membrane sheets of consistent quality are produced at high throughput. The membrane sheets can be packaged as compact membrane modules for dehumidification of large volume of processing fluids. The membrane sheet and modules are lauchned as ThinSieve™ products by Molecule Works Inc.

Keywords: molecular sieve, zeolite, membrane, sheet, thin sheet

1 BACKGROUND

Molecular sieve materials are well known for their molecular sieving functions, i.e., distinguishing individual molecules based on slight difference in size, shape, and/or weight. Molecular sieve membranes can be used to conduct molecular separation and/or reactions in the thermodynamically most efficient way. Thus, zeolite membranes have drawn a worldwide interest since the mid-1990s. Various separation process concepts in energy conversion and environmental areas have been studied in the literature (1-4). However, significant industrial applications of the zeolite membrane are not yet prevalent.

One major challenge is fabricating zeolite membranes of high surface area packing density at a cost competitive to existing separation means[4]. Most studies around zeolite membranes involve using support structures in a tubular form (10-30 mm diameter) or in a disk form (0.5- 3 mm thickness). The support is typically made of porous ceramics or sintered metals. Preparation of zeolite membranes on monoliths (5-6) and on capillary ceramic tubes (7) has also been explored.

A new membrane product is reported in this work to make the molecular sieve membrane be mechanically robust and provide membrane surface area packing density comparable to polymeric membrane plates or sheets.

2 PRODUCT DESIGN AND EXAMPLES

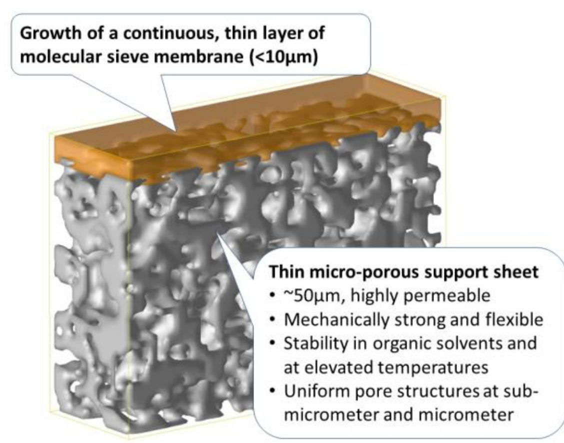

Figure 1: Design of thin molecular sieve membrane sheet.

The design concept of thin molecular sieve membrane sheets is depicted in Figure 1 (8). Molecular sieve materials, such as zeolite, metal organic framework, and carbon, are typically too weak to be prepared as a self-supported thin film. A robust porous support sheet is needed. In this work, 50µm-thin porous metal sheets of surface pore sizes ranged from 0.1 to 2.0µm are used. This kind of metal sheet is prepared by Molecule Works Inc. based on its proprietary process (9) and is recently lauched as a ThinSieve™ metal sheet product. This support provides a unique set of properties for growth of high performance molecular sieve membranes, which include uniform surface pore sizes at sub and micro-meter level, high permeability, chemical and thermal stability, and mechanical rigidity and strength. The molecular sieve and metal support are two different kinds of materials. Cracks and delamination can readily occur if the membrane is not prepared properly. Extensive stress modeling analysis suggests that those defects can be eliminated by preparing the membrane layer thin enough (8).

The scalable process is developed by Molecule Works Inc. to grow the membrane structure shown in Figure 1 with known molecular sieve materials. The resulting membrane structures are illustrated with three common zeolite frmeworks in Figure 2. NaA-type zeolite of pore size about 0.5nm is widely used for selective removal of water from mixtures. MFI-type zeolite of pore size about 0.5-0.6nm is widely used for separation and catalytic reactions of intermeidate sizes of molecules. Al-free MFI-type zeolite – silicalite is highly hydrophoblic and provides organic-philic properties that allow selective removal of organics from water mixtures, opposite to the NaA-type membrane. Faujasite-type zeolite of pore sizes ranged from 0.7-0.8nm is widely used for adsorption in the industry and for catalytic processing of large molecules. The lattice framework of a membrane can be confirmed by X-ray diffraciton analysis. Typcially, zeolite crytals of different lattice frameworks exhbit different morphologies as evidenced in Figure 2. It can be seen that the membrane comprises a dense, inter-grown crystal layer. There are no cracks and pinholes. The membrane also exhibits good adhesion to the support after the membrane is subjected to treatment and/or testing at different temperatures.

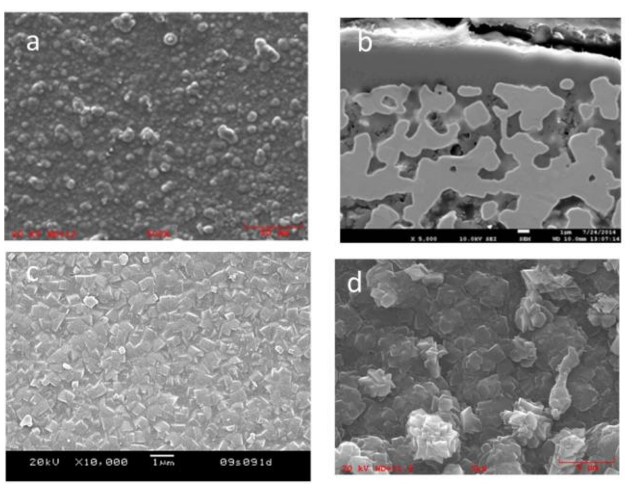

Figure 2: Examples of molecular sieve membranes grown on the thin metal sheet: a = surface texture of NaA-type membrane, b = cross-section of the NaA membrane, c= MFI-type membrane, d= Faujasite-type membrane.

3 MOLECULAR SEPARATION CHARACTERISTICS

The molecular sieving functions of the thin zeolite membrane sheets are illustrated with the NaA-type zeolite membrane for dehydration of water-alcohol mixtures and dehumidification of humid hot air in the following section.

3.1 Dehydration of water-alcohol mixtures

Water flux and water/alcohol separation factor of the NaA-type zeolite membrane in the thin sheet form for dehydraiton of water-alcohol mixtures are shown in Figure 3. The separation tests were conducted over a range temperature with 10 wt % methanol (Fig 3a), ethanol (Fig 3b), iso-propanol (Fig 3c), and n-butanol (Fig 4d) in water. At temperatures below the boiling point, the separation was conducted in pervaporation mode (feed in liquid phase, permeate in vapor phase). At the test temperature above the boiling point, the separation was conducted as gas-phase separation.

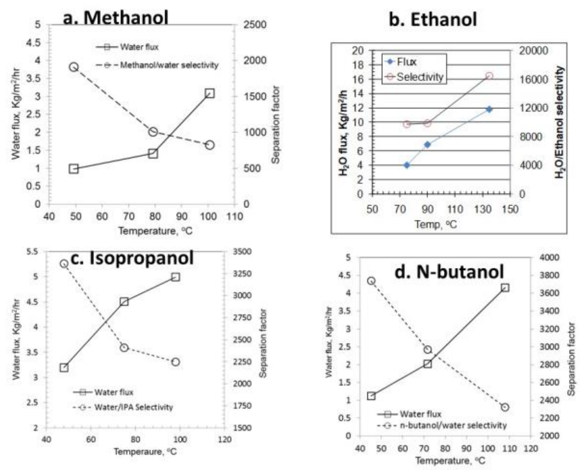

Figure 3: NaA-type zeolite membrane for selective separation of water from water-alcohol mixtures by pervaporation and gas-phase separation.

It is worth to note that due to H_2O-molecular specificity, the membrane shows excellent selectivity toward H_2O over alcohols, and the separation factor is above 500 over the range of the temperature tested. Thus, the membrane separation can be conducted in either pervaporation or gas-separation mode. Water flux increass with temperature, which can be explained by increased diffusivity of water molecules through the zeolite pores. The results show that the membrane is versatile for dehydration of water-miscible mixtures because of its molecular specificity. Particularly for dehydration of ethanol fuel, preliminary process design and economic analysis suggests that energy consumption can be reduced by more than 90% compared to distillation and adsorption processes.

3.2 Dehumidification of air and gas

The molecular-seiving fucntion of the zeolite membrane is further illustrated for dehumidfication of hot humid air. Air dehumidification in hot humid climate is a vey energy-intensive process with today's technologies. Because of large volume of air flow, it is very desirable to sieve water molecule out of the humid air. To this application, both water vapor permeance and water/air selectivity are important. Dehumidification performance of the present thin zeolite membrane sheet is compared to other membrane materials in Figure 4. The zeolite membrane exhibits exceptionally high H_2O permeance and H_2O/air separation factor through continuing innovations. Because of its molecular-sieving separation mechanism, there is not trade-off between the permeance and selectivity, and there is no theoretical limit about the permenace.

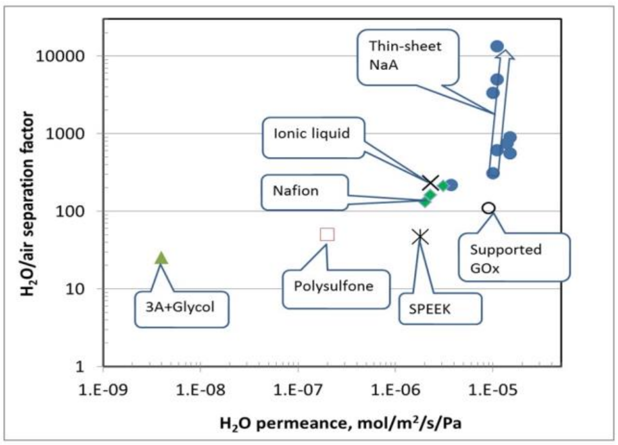

Figure 4: NaA-type zeolite membrane for air dehumidification by gas-phase separation (32°C, 80% relative humidity).

4 MEMBRANE PRODUCT DEVELOPMENT

At the permeance and selectivity level shown in Figure 4, it becomes attractive to develop compact membrane dehumidifiers for removal of moisture from large volume of air or gas. Molecule Works Inc. has developed a scalable process to produce the zeolite membrane sheets at high throughput and also developed a cassette-type membrane module design(10). Figure 5 shows that two 20cm x 20cm zeolite membrane sheets can be packaged into a cassette frame with permeate holes on the side of the frame. As humid air flows over the zeolite membrane surface, water vapor adsorbs on the zeolite pore and diffuses into the interior of the membrane cassette. The permeated water vapor is removed out of the cassette interior from the side holes by pulling vacuum.

A group of the membrane cassettes can be stracked together to form a compact membrane module as shown in Figure 6. The compact membrane module enables dehumidification be comapcted at low air pressure drop. The air pressure drop is a significant consideration to reduce air blower power consumption for dehumidification of large volume air. The compact module also reduces the footprint and space requirements, which are important for building applications. Molecule Works Inc. has launched the ThinSieve^{TM} membrane sheet and module products for applications to air and gas dehumidifcation.

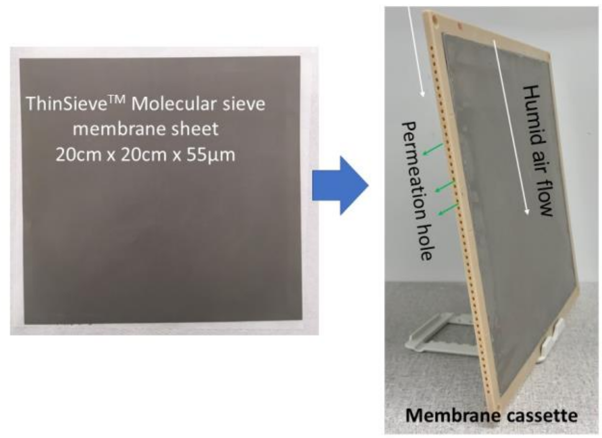

Figure 5: Packaging of two thin membrane sheets into a membrane cassette.

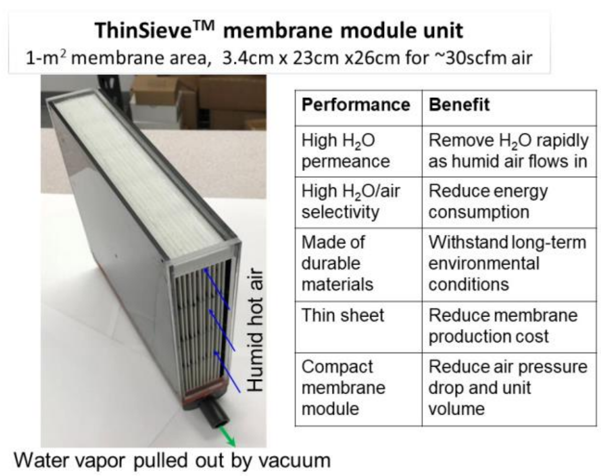

Figure 6: Stacking of the membrane cassettes into a compact module.

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