CHAPTER II
LITERATURE REVIEW

2.1 Membrane Technology for Gas Separation

In the last few years, many researchers developed effective methods to separate the impurities in the natural gases. Ongoing research is being conducted to develop new membrane materials and improve the gas separation efficiency, making membrane gas separation commercially competitive with existing separation technologies. Gas separation membranes are now applied to a wide range of industrial processes.

Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate. Two characteristics of membrane performance require high permeability and selectivity that is the asymmetric membrane. Asymmetric membranes which are suitable for gas separation should have thin and dense skin layers support by thick porous sub-layers (Abedini and Nezhadmoghadam, 2010). Membrane structures are classified using cross section microstructures, as shown in Figure 2.1.
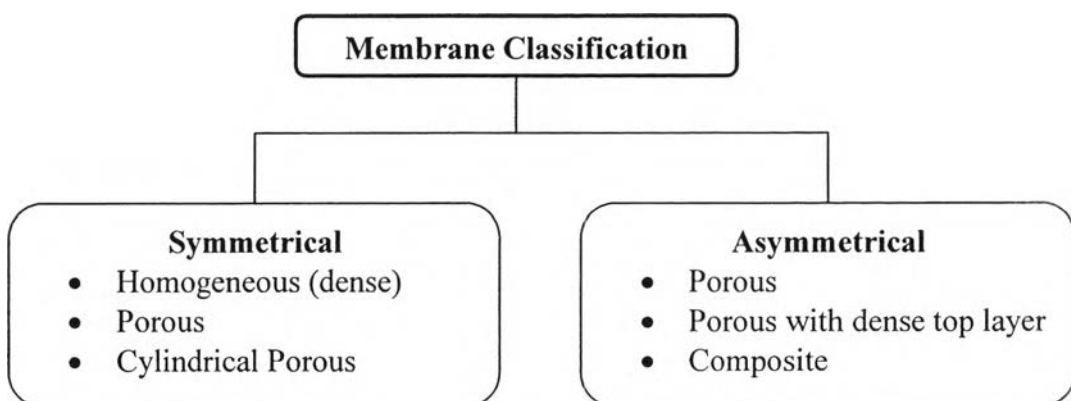

Figure 2.1 Membrane classification.

2.1.1 Mechanisms for Gas Separation

For membrane separation, five possible mechanisms are found (Scholes *et al.*, 2008), namely, Knudson diffusion, molecular sieving, solution-diffusion separation, surface diffusion and capillary condensation, of which the first three are schematically represented in Figure 2.2.
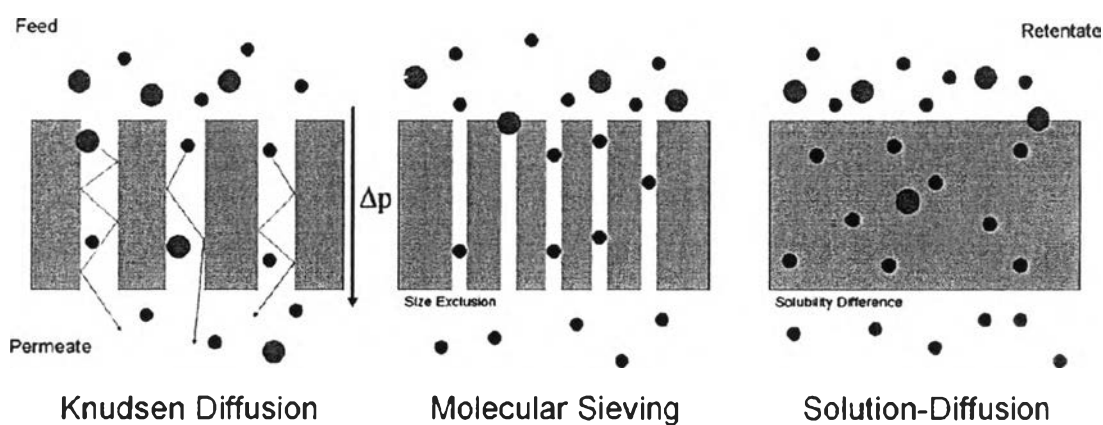

Figure 2.2 Examples of possible mechanisms for membrane gas separation.

Molecular sieving and solution-diffusion are the main mechanisms for nearly all gas separating membranes. For molecular sieving mechanism, membranes must have pore diameters that are in between those of the gas molecules to be separated. If the membrane has pore sizes between the diameter of the smaller and the larger gas molecules, then only the smaller molecule can permeate and a very high separation would be achieved. Moreover, the pore size and porosity of membranes are important for efficiency. If the pore size decreases, the membrane porosity is expected to decrease, resulting in a lower gas flow through the membrane.

Knudson separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight. Specifically, the diffusion rate for any gas pair is estimated by the inverse ratio of the square root of their molecular weight (Dhingra, 1997).

2.1.2 Polymeric Membranes

Polymeric membrane has been known to limit the permeability and selectivity tradeoff (Zhang *et al.*, 2008) and are generally non-porous (dense), and therefore gas permeation through them is described by the solution-diffusion mechanism (Scholes *et al.*, 2008). This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. The solution-diffusion mechanism is considered to consist of three steps: (1) the absorption or adsorption at the upstream boundary, (2) activated diffusion (solubility) through the membrane, and (3) desorption or evaporation on the other side. These solution-diffusion mechanisms are driven by a difference in thermodynamic activity at the upstream and downstream faces of the membrane as well as the interacting forces between the molecules of the membrane material and permeate molecules. Hence, the separation is not only diffusion dependent, but also reliant on the physical-chemical interaction of the various gas species in the polymer, which determines the amount of gas that can accumulate in the membrane polymeric matrix. The relationship between permeability (P), diffusivity (D), and solubility (S) are shown in equation 2.1:

$$P = DS \tag{2.1}$$

For ideal gases, the permeability is related to the gas permeation rate through the membrane (Q), the surface area of the membrane (A), the thickness of the membrane (l) and the driving force for separation, the pressure difference across the membrane ($\triangle$p):

$$\frac{P}{l} = \frac{Q}{A\Delta p} \tag{2.2}$$

The ideal selectivity (α) of one gas, A, over another gas, B, is defined as:

$$\alpha = \frac{P_A}{P_B} \tag{2.3}$$

2.1.3 Inorganic Membranes

Inorganic membranes are considered for new membrane materials to improve gas separation performance, which have been used widely due to their high permeability and selectivity (Perez *et al.*, 2009). However, their use is still limited for reproducibility problems in the preparation step, as well as lifetime and high cost (Hashemifard *et al.*, 2011).

Nishiyama *et al.* (2000) synthesized an MCM-48 membrane on a porous alumina support in hydrothermal conditions. The permeation of H_2, He, CH_4, O_2, N_2 and CO_2 through the calcined MCM-48 membrane was governed by Knudsen diffusion mechanism. The contribution of viscous flow was not observed in the permeation of H_2. This indicates that there existed no large pinhole in the composite layer of MCM-48/alumina.

Kim *et al.* (2005) investigated for CO_2 separation from N_2 by preparing MCM-48 silica with four different types of amine, such as aminopropyl (monomeric, unhindered), pyrrolidine propyl (monomeric, hindered), polymerized aminopropyl (polymeric, unhindered) groups, and polyethylenimine (PEI) (polymeric, hindered). The monomeric aminopropyl-attached MCM-48 displayed the highest CO_2 adsorption rate at 298 K because of greater accessibility of amine adsorption sites. Aminopropyl-attached MCM-48 samples (APS-MCM-48) also displayed high equilibrium selectivity in adsorptive CO_2/N_2 separation, indicating the promise of these molecularly engineered materials for adsorptive separation of CO_2.

Sakamoto *et al.* (2007) synthesized mesoporous silica membranes on porous alumina supports by both hydrothermal and sol-gel spin-coating methods. Surface modification of the pore walls of mesoporous silica membranes by grafting amino-silane greatly improved the CO_2 perm-selectivity. The amine-modified mesoporous silica membranes showed high CO_2/N_2 separation properties for a mixture of 20% CO_2 and 80% N_2 at 373 K. The CO_2/N_2 selectivities of the membranes prepared using hydrothermal and sol-gel spin-coating methods were 50 and 800, respectively.

2.1.4 Mixed Matrix Membranes (MMMs)

A relatively recent advance that takes advantage of polymeric and inorganic membrane approaches is mixed matrix membranes (MMMs). MMMs are heterogeneous membranes in which inorganic fillers are dispersed in a polymer matrix. A variety of inorganic materials, such as zeolites, carbon molecular sieves, silica, carbon nanotubes, or mesoporous molecular sieves was studied (Kim *et al.*, 2008).

Reid *et al.* (2001) fabricated MMMs from the siliceous MCM-41 molecular sieve as a dispersed phase and polysulfone (PSF) as a continuous phase to enhance the gas permeability. For all gases tested (N_2, O_2, CO_2, CH_4), the permeability increased in proportion to the weight percent of MCM-41 present in the film. At the same time, calculated ideal selectivities remained almost constant irrespective of MCM-41 loading. ATR-FTIR spectroscopy, supported by molecular mechanics calculations, revealed hydrogen-bonding interactions between polysulfone and MCM-41. The increase in permeability, without a loss in selectivity, which is not observed with dense silica or zeolites, suggests that using a mesoporous molecular sieve as the adsorbent additive enhances contact and penetration of the polymer.

Anson *et al.* (2004) incorporated micro–mesoporous activated carbons into the acrylonitrile-butadiene-styrene (ABS), and found that the resulting mixed matrix membranes displayed a simultaneous increase of CO_2 permeabilities (40-600%) and CO_2/CH_4 selectivities (10-100%) over the pure ABS performance by increasing the carbon content.

Kim *et al.* (2006) prepared MMMs of mesoporous MCM-48 silica and polysulfone (PSF). From SEM images, MMMs suggest that MCM-48 silica particles adhered well to the PSF matrix and that the MMMs were defect free. Gas permeation tests indicated that the increases in permeability resulted from increases in solubility as well as diffusivity. The increases in transport properties for all tested gases make mesoporous MCM-48 silica an attractive additive for enhancing the gas permeability of MMMs without sacrificing selectivity.

Kim and Marand (2008) prepared MMMs containing mesoporous MCM-41 nanoparticles with ~80 nm particle size. These smaller nanoparticles lead to a high polymer/particle interfacial area and provide an opportunity to fabricate

composites containing up to 40 wt% of molecular sieve in the polymer matrix. With 40 wt% of nano-sized MCM-41 silica, gas permeability of the mixed matrix membranes is shown to increase by up to 300% when compared to the neat polymer. In addition, amine-functionalization of MCM-41 can significantly enhance CO_2/CH_4 selectivity of the membranes.

Zhang *et al.* (2008) reported the Matrimid® membrane containing ZSM-5 crystals and showed an increase in permeability with a decrease in selectivity, suggesting poor contact between the zeolite crystals and polymer. Calcined MCM-48 was also added into Matrimid® and the resulting membrane showed higher permeability and unchanged ideal selectivity, comparing with the pure Matrimid® membrane. These control experiments suggest that the mesopores are important in forming defect-free membranes, while the micropores can provide size and shape selectivity.

Xing and Ho (2009) synthesized both zeolite 5A filled and unfilled crosslinked polyvinyl alcohol/polyethylene glycol (PVA/PEG) blend membranes for CO_2/CH_4 separation. The effects of the zeolite 5A loading, temperature, and feed pressure were investigated for the gas separation performance of both zeolite-filled and unfilled PVA/PEG membranes. It was found that CO_2/CH_4 selectivity decreased as the zeolite 5A content increased, while CO_2 permeability first decreased and then drastically increased. Increasing temperature enhanced CO_2 permeability, but sacrificed their selectivity for both zeolite-filled and unfilled PVA/PEG membranes. As temperature decreased, the unfilled PVA/PEG membranes could perform beyond the Robeson's upper bound. Compared to the unfilled PVA/PEG membrane, the zeolite-filled PVA/PEG membrane showed improvement of performance as feed pressure increased.

Polybenzoxazine can also stabilize the gas transport properties because of its high performance thermosetting resin. Ployangoonsri (2010) synthesized a novel mixed matrix membrane (MMM), ZSM-5-polybenzoxazine. Polybenzoxazine was prepared from bisphenol–A, formaldehyde, and 1,6-hexadiamine. The 1 wt% of zeolite loading showed the highest CO_2 and CH_4 permeability and great CO_2/CH_4 selectivity when compared with those obtained from

higher percent of ZSM-5 loading. However, CO_2 and CH_4 permeability of ZSM-5-polybenzoxazine membranes are lower than the pure polybenzoxazine membrane.

2.2 Polybenzoxazine (PBZ)

Polybenzoxazines have been developed as a novel type of phenolic resin due to the disadvantages of the traditional phenolic resins, viz. brittleness, the need of catalyst for polymerization, formation of voids because of the volatiles formed during the cure, and large volumetric shrinkage upon cure. The volatilization of phenol and formaldehyde into the air during the cure process also causes some health concern.

A series of polybenzoxazines was obtained by the ring-opening polymerization of cyclic monomers, benzoxazines. The monomers are easily prepared from phenols, primary amines, and formaldehyde. The wide variations of raw materials, phenols, and amines, allow considerable molecular-design flexibility for the cyclic monomers. Polymerization proceeds through the ring-opening of the cyclic monomers only by heat treatment without the need of catalyst and without generating by-products or volatiles, and thus excellent dimensional stability is obtained. Polybenzoxazines provide characteristics found in the traditional phenolic resins, such as high heat resistance and flame retardant. They also provide characteristics that are not found in the traditional phenolic resins, such as excellent dimensional stability, low water absorption, and good dielectric properties. So, polybenzoxazine used mostly for electronic materials, matrix resin of polymer composites, and adhesives are expected.

However, there are some shortcomings for polybenzoxazines. The cured materials are brittleness due to the short molecular weight of the network structure; a relatively high temperature needed for the ring-opening polymerization, and difficultly in processing into thin film from the typical monomers because most monomers are powder (Takeichi *et al.*, 2005).

Polybenzoxazine precursors have been obtained from various aromatic/ aliphatic amines, mono/diphenols, and formaldehyde (Allen and Ishida, 2006; Takeichi *et al.*, 2005). One approach was to synthesize polybenzoxazine from a low

molecular weight monomer, using monofunctional amine, phenol, and formaldehyde, as reactants (Takeichi *et al.*, 2005). However, polybenzoxazines obtained via this approach usually suffered from brittleness.

To develop the toughness of polybenzoxazines by addition of a flexible component, Allen and Ishida (2006) switched multi-functionality of the benzoxazines to the amine portion of the structure. The limitations of the bisphenolic linkage can be eliminated, and less brittle materials can be specifically designed at the molecular level by incorporating a flexible di-functional amine as the central core. All of these properties, such as room temperature modulus, glass transition temperature, crosslink density, thermal degradation temperature, and char yield, of the polybenzoxazines exhibit strong dependence on the amine chain length. These aliphatic amine-based polybenzoxazines are found to be much more flexible than the bisphenol-type polybenzoxazines.

Another method was the preparation of polybenzoxazine from high molecular weight oligomers from diamine, bisphenol-A, and formaldehyde. The properties of the polybenzoxazines derived from these high molecular weight oligomers, especially brittleness, have been greatly improved when compared with cured films from the typical low molecular weight precursors (Pakkethati *et al.*, 2011). This enables polybenzoxazine to be an excellent candidate for flexible membrane applications to improve the membrane selectivity and permeability. Maintaining a good flexibility of matrix was reported to produce favorable interaction with the molecular sieves (Mahajan *et al.*, 2002).

High molecular weight polybenzoxazine precursors have also been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. The precursors were obtained as soluble white powder. The ratio of the ring-closed and the ring-opened benzoxazine structures in the high molecular weight precursor was estimated from ^{1}H NMR spectrum and also from the exotherm of DSC, showing that the ratio of the ring-closed benzoxazine structure was 77–98%. The toughness of the crosslinked polybenzoxazine films from the high molecular weight precursors was greatly enhanced, compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine

exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass transition temperature of the polybenzoxazines derived from the high molecular weight precursors were as high as 238-260°C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability (Takeichi *et al.*, 2005).

2.3 MCM-48

A new family of ordered mesoporous molecular sieves designated as M41S was discovered by Mobil (Beck *et al.*, 1992). The M41S family includes members having uniform pore structures of hexagonal (MCM-41), cubic (MCM-48), and lamellar (MCM-50) symmetry. The cubic MCM-48 indexed in the space group of *Ia3d* is the most interesting in term of catalytic activity because it has a three-dimensional pore structure which reduces the diffusion limitations and avoids the pore-blocking of the catalysts. The characteristic properties of MCM-48 are high surface area and a narrow pore-size distribution (Longloilert *et al.*, 2011). As an adsorbent, catalyst, catalyst support, and template for the synthesis of advanced nanostructures, MCM-48 may be a more potential candidate than MCM-41 and MCM-50. However, the preparation of MCM-48 requires relatively extended reaction time and more rigorous synthesis conditions, since the MCM-48 phase is often an intermediate during the transformation from a hexagonal phase or disordered surfactant/silica mesophase to a lamellar phase. Especially, it is difficult to synthesize MCM-48 with good long-range ordering structure. Therefore, most researchers have mainly focused on MCM-41 (Kim and Marand, 2008; Reid *et al.*, 2001) and tried to find the method for improvement of long-range ordering of mesoporous materials.

Shao *et al.* (2005) reported the long-range structural ordering and hydrothermal stability improved only when adding NaF at the early stage of hydrolysis and polymerization of silicate. Longloilert *et al.* (2011) synthesized the high-quality cubic MCM-48 using a new silica source, known as silatrane, and cetyltrimethylammonium bromide (CTAB) as the structure-directing agent via sol-

gel process. The effects of synthesis parameters; crystallization temperature, crystallization time, surfactant concentration, quantity of NaOH, and silica source, on the product structure were investigated. Optimally, this product is synthesized from samples crystallized at 140°C for 16 h with a CTAB/SiO$_2$ ratio of 0.3 and NaOH/SiO$_2$ ratio of 0.5. The XRD result exhibits a well-resolved pattern, corresponding to the *Ia3d* space group of MCM-48. The BET surface area of this product is as high as 1,300 m^2/g with a narrow pore-size distribution of 2.86 nm. The SEM images also show the truncated octahedral shape and well-ordered pore system of MCM-48 particles.