



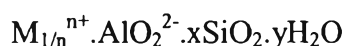
CHAPTER II

LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 General Description of Zeolites

Zeolites are crystalline porous aluminosilicates with three dimensional networks of $[\text{SiO}_4]^{4+}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. The tetrahedra are linked in the corners and share all oxygen atoms. For each aluminum atom in the framework, one charge equivalent from a non-framework cation must balance the charge of the framework. The chemical composition of the zeolite is expressed as:



Where M represents the counterion, n represents the counterion valence, x is generally equal to or greater than 1 since AlO_4 tetrahedral are joined only to SiO_4 tetrahedra, and y indicates the degree of hydration. When a Si atom is substituted with an Al atom, which requires a cation to achieve the charge balance, the exchangeable cations are generally from the group I or group II ions. The framework contains channels and interconnected voids, which are copied by the cations and water molecules. The cations are mobile and may exchange with other cations. The pore diameter is determined by the crystal structure in each zeolite. Pore diameters in known zeolites are between 0.3-1.5 nm [Jansen *et al.*, 1996].

The zeolite used in this work is NaA zeolite, or LTA. Zeolite A has a three-dimensional channel system, which contains equi-dimensional channels intersecting perpendicular to each other. A cubic array of β cages linked by double 4 ring (D4R) units produces an α cage. The free aperture diameter for the α cage is 4.2 Å [Breck, 1974] (see Figure 2.1). Many researches [Jafar *et al.*, 1996, Urtiaga *et al.*, 2003 and Huang *et al.*, 2004,] developed the NaA zeolite for membrane application to sieve out water molecules due to its hydrophilic nature, making the electrostatic

interaction between ionic sites and the water molecule stronger [Szotak *et al.*, 1992]. Vapors, such as water vapor, condense rapidly in the narrow zeolite channels.

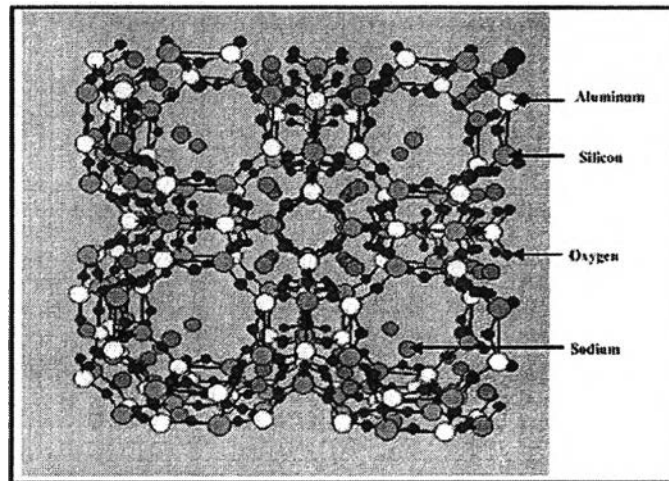


Figure 2.1 Framework structure of zeolite A [Murad *et al.*, 2003].

Zeolite synthesis is carried out under hydrothermal conditions. Usually, there are the two primary steps occurring in crystallization : nucleation of new populations of zeolite crystals, and growth of existing populations of crystals. A schematic representation of the zeolite formation process is shown in Figure 2.2. During NaA zeolite synthesis, an aluminate sol and a silicate solution are mixed together in an alkaline medium to form a milky gel or in some instances, a clear solution. Various cations or anions can be added to the synthesis mixture. Synthesis proceeds at elevated temperature (60-180°C) where the crystal forms a nucleation step. The formation of the zeolite crystal from an amorphous gel or from a solution consists of a series of self-assembly processes involving numerous simultaneous and independent equilibrium and condensation steps [Barre, 1982]. The systematic studies of the processes during the synthesis are complicated, especially because there are no indications for a universal mechanism [Iton *et al.*, 1992 and Feijen *et al.*, 1994]. In the case of the liquid phase ion transportation mechanism, nucleation and crystal growth occur only in the liquid phase [Iton *et al.*, 1992]. The gel phase serves simply as a source of nutrient, dissolving continuously to provide the

complex ions from which the crystal nuclei are formed [Dutta *et al.*, 1994]. Another case is known as the solid hydrogel reconstruction mechanism. Nuclei form directly in the solid gel phase, and crystallization proceeds through depolymerization and rearrangement of the gel network, assisted by hydroxyl ions [Serrano *et al.*, 1996]. It has been also suggested that nucleation and transport of species by surface diffusion and crystallization occur at the liquid-solid interface, where inter-particle contact is maximized and the process of aggregation and coalescence may readily occur [Verduijn *et al.*, 1995].

Oswald's rule is used to explain the transformations of zeolite. Upon the mixing of the reagents for zeolite synthesis, the system is in a disordered state with a higher entropy than its ordered counterpart, the crystallized zeolite structure. For crystalline systems that can exist in several different polymorphic forms, the form with the highest entropy will develop from the highly disordered synthetic mixture. Many desired zeolites are in metastable phases, and recrystallization to other more stable structures can be observed under certain conditions with prolonged reaction time [Szotak, 1992].

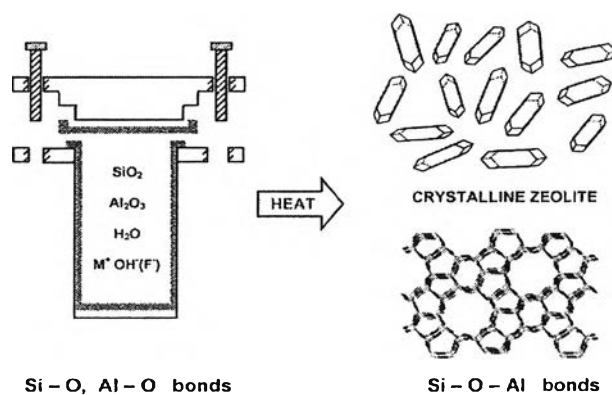


Figure 2.2 Simplified zeolite synthesis scheme [Cundy *et al.*, 2005].

2.1.2 Factors Influencing Zeolite Formation

There are many factors influencing zeolite formation, such as the composition of reaction mixture, mineralizer, temperature, and time. The silica alumina source and seeding are also considered.

a) Composition of reaction mixture

Every zeolite has a specific molar composition range often represented graphically in a ternary compositional phase diagram (Na_2O , Al_2O_3 and SiO_2). On the other hand, each structure will also impose constraints on the amount of Al it can incorporate. High silica molecular sieves, such as ZSM-5, can be synthesized over a wide range of Si/Al ratios (Si/Al from 7 to infinity) [Verduijn *et al.*, 1995].

a) Mineralizer

A mineralizer is a species which enables the formation of a more stable solid phase from a less stable solid phase via dissolution and crystallization. Supersaturation can be reached by dissolution and these soluble species are then available for nucleation and crystal growth [Szotak, 1992]. In most cases, hydroxyl ions act as mineralizing agents. Indeed, OH^- increases the solubility of silica by depolymerizing amorphous silica particles. Oligomeric species are then present in solution. Condensation of the aluminosilicate species, facilitated by the presence of OH^- , occurs and leads to the appearance of the first crystals. In general, high pH values increase crystal growth rates and shorten the nucleation period. Hydroxyl ion concentration can also influence crystal morphology, crystal size, and final zeolite structure.

c) Temperature

Temperature can alter the zeolite structure, as well as the induction period and crystal growth kinetics. The activation energies of zeolite synthesis are quite significant. As the temperature increases, the solubilities of the aluminate and silicate species increase, causing a shift in the concentration of the liquid phase, resulting in the formation of another phase [Szotak, 1992].

d) Time

Time, as a parameter, can be optimized in the synthesis of many zeolites. In the systems that produce only one zeolitic phase, optimizing maximum crystallization over a short span of time is important from a practical stand point and

is accomplished by applying knowledge of the contribution of the many components in the synthesis mixture to minimize the crystallization time. Increasing the temperature or hydroxide component of the reaction mixture and the addition of inorganic and organic cations can all be applied to minimizing the crystallization time [Szotak, 1992].

e) Silica-alumina sources

Nucleation and growth kinetics can depend on the dissolution of solid reagents and on the formation of the alumino-silicate precursor. Kuhl found that crystallization of some structures was dependent on the degree of pre-polymerization of the silica source. Round found that the source of reagents (silica and alumina) used in the synthesis of zeolite A affects the gel rheology, the kinetics of gel chemistry, and the activity at the crystal surface, producing a different crystal morphology [Round *et al.*, 1997]. Mintova and Valchev investigated the colloidal distribution of silicalite-1 synthesis mixtures containing different silica sources which influence the zeolite product [Mintova *et al.*, 2002]. Impurities in the silica and alumina source were likely to influence the crystallization kinetics and framework composition.

f) Seeding

Seeding is a technique in which the saturated system is inoculated with small particles of the material to be crystallized. Using this technique, the nucleation stage is bypassed and the induction period is eliminated [Feigen *et al.*, 1999]. Upon adding the seeds, mass is deposited upon them to grow and give rise to secondary nuclei, and hence a new crop of crystal occurs. In the absence of seed crystals, either the reaction gives very low yield or the obtained product is heavily contaminated with impure phases [Cundy *et al.*, 2005].

2.1.3 NaA Zeolite Membrane Synthesis

Since the mid 1990s, due to their outstanding aspects (e.g. the potential molecular sieving action controlling host-sorbate interactions, and high thermal and chemical stability) extensive efforts have been devoted to the preparation, characterization, and application of zeolite membranes. Much attention has been focused on the development of continuous zeolite-based separation processes. For

such purposes, the preferable configuration of the zeolite material is in the form of a thin film or membrane supported by, or deposited on, a porous substrate [Boudreau *et al.*, 1999; Certin *et al.*, 2001, Lin *et al.*, 2001 and Bon *et al.*, 2003,]. Membrane separation technique is commonly used in a separation unit for either supplementing or replacing other separation techniques, for example, distillation, absorption, extraction and adsorption. The NaA zeolite has been proposed as a good candidate for the dehydration of organic/water mixtures due to its potential for selectively permeating water from water/organic liquid mixtures.

Xu *et al.* (2005) reported that a NaA zeolite membrane can be Synthesized using either a gel or a clear solution synthesis mixture. For the gel synthesis mixture, a thicker gel layer formed on the support surface due to the high viscosity of the gel mixture. Therefore, a thick NaA zeolite formed on the porous support. In regards to the clear solution synthesis mixture, since the viscosity of the clear solution was low, a relative thin gel layer formed on the porous support surface; therefore, So a thin NaA zeolite membrane formed on the porous support from gel and clear solution synthesis mixture as shown in Figure 2.3. In addition, the penetrating of clear solution synthesis mixture in the support pores was deeper than that for the gel synthesis mixture, resulting in higher performance of the obtained NaA zeolite membrane.

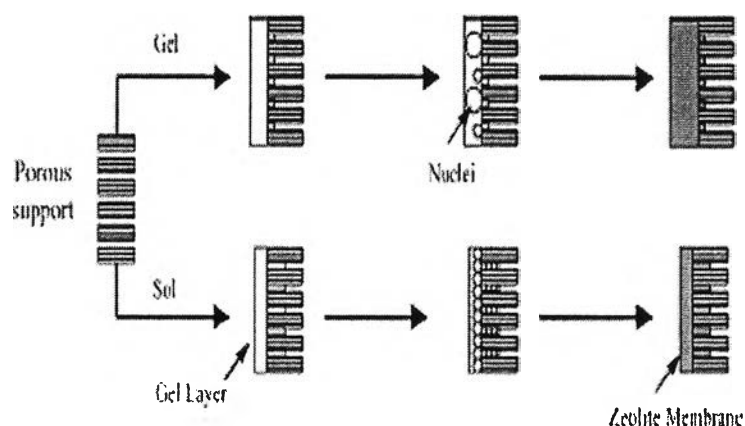


Figure 2.3 Comparison of the formation of NaA zeolite membrane synthesized from gel and clear solution synthesis mixture. [Xu *et al.*, 2005].

NaA zeolite membrane was fabricated using in-situ membrane growth or secondary (seed) growth technique [Nair *et al.*, 1993]. By the in-situ membrane growth technique, the support surface is in direct contact with the alkali solution containing the zeolite precursors, followed by hydrothermal conditions. Under appropriate condition, nucleation of zeolite crystals occurs on the support, followed by their growth to form a continuous layer over the support. For the secondary growth technique, zeolite crystals are deposited on the support surface and then exposed to hydrothermal growth conditions whereupon the seed crystal grows into a continuous film. In the absence of the seed layer, a discontinuous NaA membrane can be formed on the support surface, as detected by a discontinuous layer [Kumakiri *et al.*, 1999 and Xu *et al.*, 2001].

The promotion effect of the nucleation seeds can be explained by the formation mechanism on the porous support, shown in Figure 2.4. The formation of the NaA zeolite membrane on a porous support is a homogeneous process [Jansen *et al.*, 1994]. The clear solution (sol) is initially adsorbed onto the support pores by capillary adsorption and the gel layer formed on the porous support surface. Zeolite nuclei formed in the gel layer or nuclei formed in the bulk synthesis gel move to the support surface by Brownian motion during synthesis. The nuclei grow into zeolite crystals and the zeolite crystals inter-grow eventually to form a membrane. Without the nucleation seed, there are few nuclei formed, due to the low reactivity of the gel layer on the support surface. On the other hand, with coating the nucleation seeds on the support surface, the amount of nuclei on the support surface is increased at the beginning of the synthesis. The formation of NaA zeolite on the support surface is accelerated [Xu *et al.*, 2005].

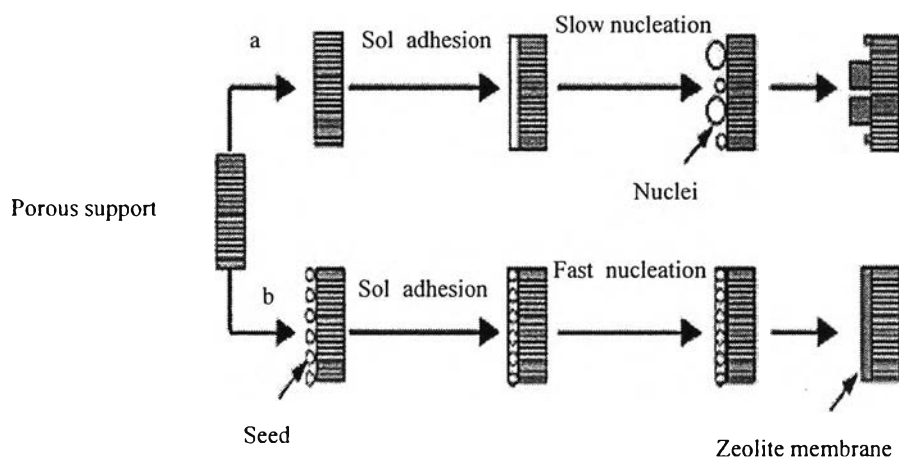


Figure 2.4 Formation mechanisms of NaA zeolite membranes on the $\alpha\text{-Al}_2\text{O}_3$ support without (a) and with (b) the aid of a nucleation seed [Xu *et al.*, 2005].

In the past ten years, the most challenging work in the field of zeolite membranes is to prepare a membrane with high performance, while keeping the separation factor high. Several preparation methods have been developed, such as hydrothermal synthesis [Jia *et al.*, 1993, Kondo *et al.*, 1997 and Zhang *et al.*, 2004,], microwave heating [Xu *et al.*, 2000, 2001 and 2004] and electrophoretic technique. However, microwave synthesis of zeolite has many advantages, viz. much shorter synthesis time, narrow zeolite particle size distribution, and high purity [Xu *et al.*, 2000]. The synthesis was also carried out in either a static or a circulated reaction solution. The static reaction solution provides the usual cubic crystal shape, whereas the circulated one yields crystals with a globular morphology. The formation of a zeolite membrane on a porous support is a heterogeneous nucleation process. In both the microwave and conventional heating techniques, a gel layer is firstly formed on the porous support surface, followed by nucleation and crystal growth to form a membrane [Nakazawa *et al.*, 1998] as shown in Figure 2.5.

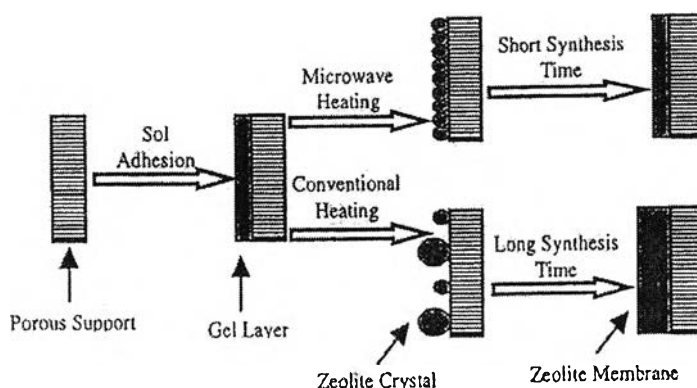


Figure 2.5 Formation mechanism of zeolite membrane prepared by microwave heating and conventional heating [Xu *et al.*, 2000].

In the microwave environment, because of the fast and homogeneous heating and the formation of an active water molecule [Jansen *et al.*, 1992], the gel layer at the support/solution interface dissolves quickly, which results in a rapid and more simultaneous nucleation of zeolite on the support surface than if heating conventionally. Moreover, because of the simultaneous nucleation and homogeneous heating, uniform and small zeolite crystals can be synthesized. As a result, thin zeolite membranes can be formed quickly. In the case of conventional heating, the nuclei are not formed on the support surface simultaneously because of the low dissolution rate of gel and the low heating rate. Thus the zeolite crystals formed are also not uniform in size. In order to form a dense membrane, a long synthesis time will be needed, resulting in a thicker membrane.

Recently, the electrophoretic technique was effective for the preparation of thin films [Wong *et al.*, 1999 and Keneko *et al.*, 2002]. The charged particles can migrate to the support surface homogeneously and rapidly under the action of an applied electric field, consequently forming uniform and dense films in a short time, as shown in Figure 2.6. During hydrothermal synthesis, zeolite particles were orderly driven to the support surface for membrane preparation due to better controlling of the homogeneous nucleation.

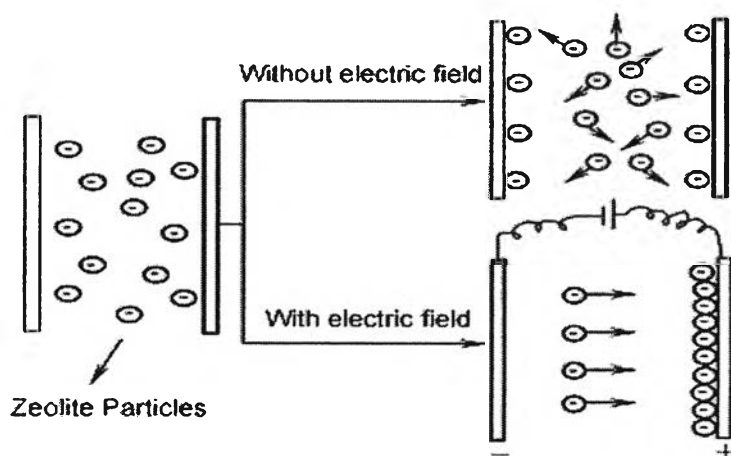


Figure 2.6 Formation mechanism of a zeolite membrane prepared in an electric field [Huang *et al.*, 2006].

In general, zeolite membranes are formed when crystals grow on surface and interlock to give a coherent layer. For applications in separation processes, the membrane must be free of any defects which could provide alternative transport pathways to the zeolite pores [Jafar *et al.*, 1996]. According to well-defined properties for separation purposes, controlling the thickness and texture of coatings is a significant task to determine the performance of the system. Thin and continuous zeolite films are required for some applications, especially those related to membrane separation. The film should be as thin as possible for optimal performance, and free of any pinholes. Orientation of the crystals on the surface is also important because preferred orientation of crystals on the zeolite membrane affect not only the diffusion rates through the zeolite layer, but also the density and morphology of the inter-crystalline pores [Li *et al.*, 2003]. The performance of zeolite membranes and sensors is also influenced by the orientation of zeolite crystals constituting the film. The orientation will affect the diffusion path through the membrane and adsorption kinetics of a sensor consisting of a support zeolite film [Hedlund *et al.*, 1997].

NaA zeolite membranes were prepared by different routes, such as microwaving, autoclaving and the electrophoretic technique, in Wongkasemjit's group. The whole synthesis procedure is illustrated in Figure 2.7.

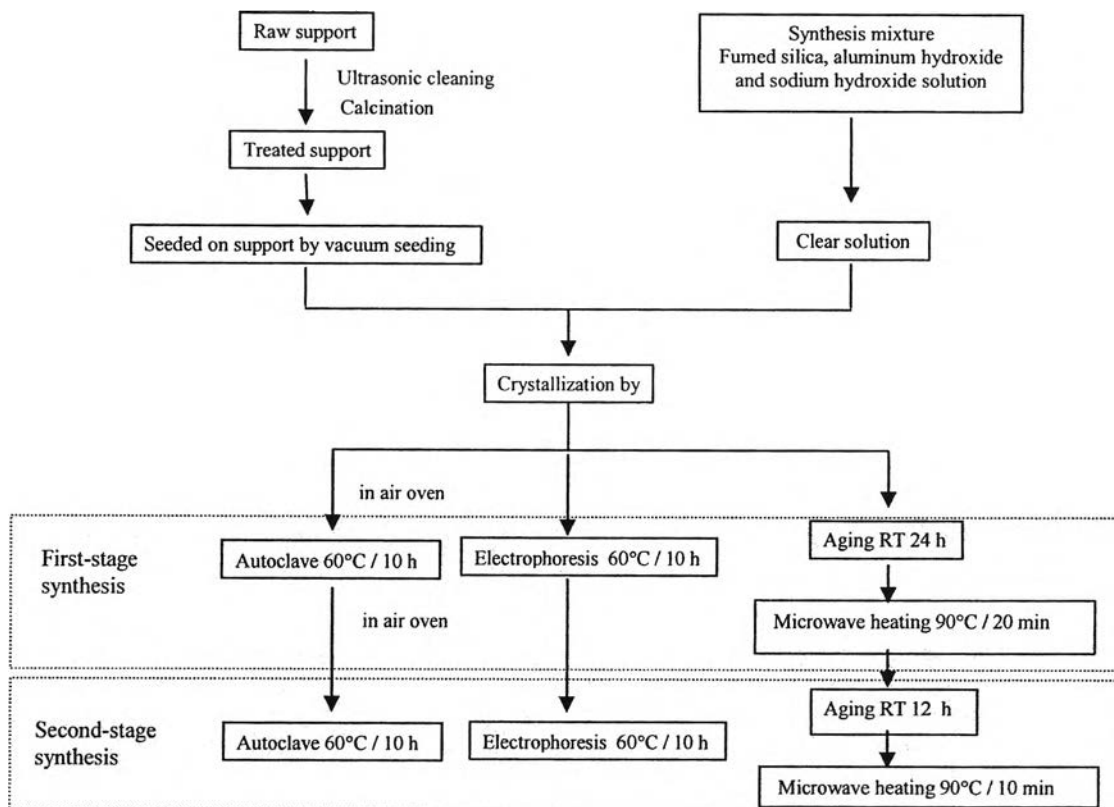


Figure 2.7 Illustration of the different routes for NaA zeolite synthesis.

2.1.4 Pervaporation

Pervaporation, a contraction of the term permeation and evaporation, allows for the separation of some mixtures that are difficult to separate by distillation, extraction, and sorption. The feed is liquid and the vapor exits the membrane from the permeate side, as shown in Figure 2.8. The vapor is enriched in the preferentially permeating component and is condensed for future processing [Fleming *et al.*, 1992]. Only a fraction of the mixture is vaporized during pervaporation, and a lower temperature than that required in distillation is usually used. Pervaporation has advantages in separation azeotropes, close-boiling mixtures, and thermally sensitive compounds, and in removing species present in low concentrations. It has been applied to the dehydration of organic liquid (ethanol, isopropanol (IPA) or ethylene glycol, etc.).

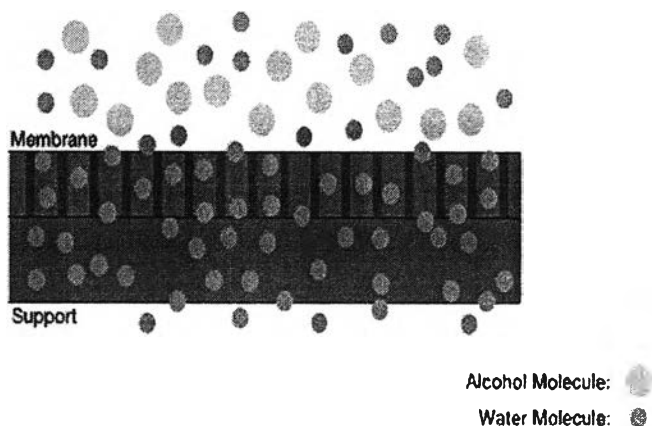


Figure 2.8 Diagram of pervaporation across a membrane.

Transportation across non-porous membranes in pervaporation is generally considered to follow the well-known solution-diffusion model [Fleming *et al.*, 1992]. The efficiency of membrane separation is defined in terms of separation factor and flux, which are important factors in practical applications. Pervaporation fluxes in lab-scale studied are usually measured by weighing the amount of permeate collected in a liquid trap during a given time period, as given in equation 2.1. Fluxes are typically reported in units of $\text{kg/m}^2\cdot\text{h}$ because they are the units used in industrial separations. Molar fluxes in $\text{mol/m}^2\cdot\text{h}$, however, are more useful for comparing the permeation of components with different molecular weights. For comparison, a $\text{kg/m}^2\cdot\text{h}$ water flux is the same as $55 \text{ mol/m}^2\cdot\text{h}$ [Bowen *et al.*, 2004]. Gas chromatography is usually used to measure permeate concentrations. Separation performance in pervaporation is generally reported by separation factors (α), as given in equation 2.2.

$$F = \frac{w}{\zeta \Delta t A} \quad (2.1)$$

w = weight (g)

ζ = density (g/ ml)

t = permeation time (h)

A = membrane area (cm^2)

$$\alpha = \frac{Y_w/Y_o}{X_w/X_o} \quad (2.2)$$

Y_w/Y_o = the weight ratio of water to organic liquid in the permeate

X_w/X_o = the weight ratio of water to organic liquid in the feed

Okamoto *et al.*, 2001 investigated the dehydration of several organic compounds by pervaporation through NaA zeolite membranes. The results in Table 1 show high separation factors and fluxes using the same NaA zeolite membrane to dehydrate methanol, ethanol, 1-propanol, 2-propanol, acetone, dioxane, and dimethyl formamide. Typically, zeolite membranes with lower Si/Al ratios have higher separation factors for organic dehydration [Bowen *et al.*, 2004].

Table 2.1 Typical pervaporation performance of NaA zeolite membranes with membrane (thickness 30 μm) on Al_2O_3 substrate. [Okamoto *et al.*,2001]

Organic liquid	Mixture (H₂O wt%)	Temperature (K)	Total flux (kg/m².h)	Separation factor
Ethanol	10.3	348	2.15	10,000
Ethanol	5.1	348	1.10	16,000
Methanol	10.2	323	0.57	21,000
Methanol	5.5	323	0.23	2500
1 Propanol	10	348	1.91	18,000
2 Propanol	10	348	1.76	10,000
Acetone	10.1	323	0.91	5,600
Acetone	5.0	323	0.83	6,800
DMF	10.5	333	0.95	8,700
Dioxane	10.0	333	1.87	9,300

2.2 Background and Literature Review

Zeolite A, discovered by Milton in 1956 [Breck *et al.*,1956 and Rao *et al.*, 1999], is a microporous crystalline material used mostly as a catalyst, an ion-exchanger, and as an absorbent. It is known as a “molecular sieve” due to its pore structure. Zeolites are crystallized by hydrothermal conditions, often using a high temperature and pressure. The product is obtained in the form of a powder. A common procedure is to mix the components, transfer the mixture (synthetic gel) to the autoclave and heat the autoclave for a certain time. Numerous research works have by now appeared using the microwave synthesis of zeolite because of the highly shortened synthesis time compared to the conventional heating method [Piriyawirut *et al.*, 2003, Sathupanya *et al.*, 2004 and Phonthamachai *et al.*, 2004]. The reduction of time is a consequence of two main effects: a relatively fast dissolution of the gel and rapid homogeneous heating of the system mixture which leads to the more abundant nucleation [Bon *et al.*, 2003].

Slangen *et al.* (1997) studied the effect of aging the reaction mixture during NaA zeolite synthesis. It was found that the aging is a prerequisite for the successful rapid synthesis of NaA. During the aging, mixing on a molecular scale is envisaged to allow the formation of nuclei necessary for crystallizing NaA. Under conventional synthesis methods, the slow heating allows the formation of a sufficient number of nuclei for a successful synthesis, and crystal growth becomes the limiting factor. The crystal growth rate can be accelerated by raising the temperature [Miese *et al.*, 1973].

Sathupanya *et al.* (2003) synthesized NaA (1 μm crystal size zeolite) via the sol-gel process and microwave technique using silatrane and alumatrane as precursor with the composition $\text{SiO}_2:\text{Al}_2\text{O}_3:10\text{Na}_2\text{O}:410\text{H}_2\text{O}$. They found that the increasing of Na_2O concentration strongly affects the particle size and particle size distribution. Small crystallite size is obtained from a high $\text{Na}_2\text{O}:\text{SiO}_2$ ratio (10:1) while a low $\text{SiO}_2:\text{Na}_2\text{O}$ ratio (1:3) gives large crystallite sizes ($\sim 4.5 \mu\text{m}$). Moreover, an increase of water ratio also affects the crystal size. As the water ratio increases, larger crystallites with a high degree of irregularity are formed [Breck, 1974].

Bonaccorsi *et al.* (2003) synthesized pure NaA zeolite from a dense gel by microwaving technique within a total time of 1 h. The strong effect associated with microwave has been used to synthesize dense gels, obtained by a progressive reduction of the water amount in the initial formulation below conventional limits. A water decrease allows a high yield of product. The crystal size of zeolite is determined by relative rates of two competing phenomena occurring during synthesis; namely, nucleation and crystal growth. Varying the parameters may lead to a change in the size of crystals. For example, the rates of both nucleation and growth are known to decrease as temperature is lowered [Feoklistva *et al.*, 1989 and Mintova *et al.*, 1992].

Seeding is another factor affecting zeolite synthesis. It is long been known that adding seeds to a zeolite synthesis mixture accelerates the crystallization rate. Edelman *et al.* (1988) showed several different crystallization phenomena, such as polycrystalline breeding, surface nucleation, and particle agglomeration occurring in different seeded zeolite systems. They concluded that the circumstances exist where surface nucleation of polycrystalline breeding can occur. Acceleration of the

crystallization rate is due to the formation of new nuclei on the seed crystal surfaces. Subsequent growth of these new crystallites, of the same phase or a new phase, results in a dramatic increase of crystal surface. The amorphous gel is responsible for seed crystal agglomeration; it would appear that facilitated growth of seed mass does occur. It is doubtful that the presence of seeds facilitates the nucleation of new crystals, except in some special cases, but quite likely seed crystal growth in the vicinity of the gel is facilitated.

Dutta *et al.* (1994) studied the interaction between zeolite Y seed and amorphous aluminosilicate gel influencing zeolite synthesis. The results indicated that the seed crystals modify the crystallization process if they are in physical contact with the gel, but do not influence it if they are kept separate via the membrane. Crystal growth occurs by incorporation of a solution-mediated nutrient.

Since the beginning of the 1980s, the development of zeolite membranes has attracted the attention of many research groups [Kondo *et al.*, 1997, Xu *et al.*, 2000 and 2001]. A zeolite membrane has the advantage of potentially sieving out molecules in a continuous process. For example, a hydrophilic zeolite membrane derived from NaA was commercialized for alcohol dehydration and solvent dewatering. Zeolite membrane is the most commonly synthesized on porous supports of alumina, on steel, on silicon wafer or on glass slides. Zeolites are crystallized by the hydrothermal treatment of a clear solution or synthesis gel containing a silica source, an alumina source, and an alkali source (alkali hydroxide or/and organic bases). The composition of the synthesis mixture, the temperature during synthesis, and the synthesis duration are the main parameters determining which zeolite phase will be formed [Nair *et al.*, 1993].

Xu *et al.* (2001) synthesized a NaA zeolite membrane using microwave heating. Compared with the conventional hydrothermal technique, microwave synthesis has the advantage of very short time, broad composition, and high purity due to the fast homogeneous nucleation and the easy dissolution of the gel [Jansen *et al.*, 1992]. They report that the synthesis time of the NaA zeolite membrane by microwave is 8-12 times shorter than by conventional hydrothermal synthesis.

Xu *et al.* (2005) synthesized a NaA zeolite membrane on an α alumina tube with the aid of nucleation seeding from a gel synthesis mixture. They found that

synthesis conditions, e.g. synthetic times, synthesis stages, and nucleation seeds affected the formation and permeation properties of the NaA zeolite membrane. Nucleation seeds played a critical role in the formation of the continuous NaA zeolite membrane. The best NaA zeolite membrane was obtained from a three stage synthesis with a 24 h synthesis time in an autoclave by a synthesis mixture of $3\text{Na}_2\text{O}:2\text{SiO}_2:\text{Al}_2\text{O}_3:200\text{H}_2\text{O}$ and with the aid of nucleation seeding. They also reported that the clear solution provided a thin layer of NaA zeolite membrane with high performance. The reason for this is that the viscosity of the clear solution is relatively low, causing a higher amount of the synthesis mixture to be adsorbed into the support pore than the gel synthesis mixture.

Huang *et al.* (2006) fabricated uniform and dense NaA zeolite membranes on an $\alpha\text{-Al}_2\text{O}_3$ support by electrophoretic technique. They found that the negatively charged zeolite particles could migrate to the support surface homogeneously and rapidly under the action of an applied electric field. High quality NaA zeolite membranes can be prepared in a short time. The applied potential had a great effect on membrane morphology, membrane thickness, and separation performance.

Among the many synthesis routes, the secondary growth technique, based on the pre-deposition of the dense seed layer, is essential for subsequently crystallizing to form a thin, defect free membrane with favorable separation properties.

Boudreau *et al.* (1999) prepared a NaA zeolite membrane on a silicon wafer substrate. Modification of the external surfaces of zeolite particles by silylation reaction produces particles that contain a positive charge. This suspension of the positively charged particles can be used for the preparation of adsorbed layers of charged particles on the oppositely-charged substrate by electrostatic attraction. The deposition process leads to a high coverage of the substrate with well-adhered particles. They also reported that the seeded layers were subjected to secondary growth in order to prepare continuous inter-grown films. The inter-grown films have predominately [h00] out-of-plane orientation. After extending secondary growth treatment, a population of [hhh] grain appears on the surface of the re-grown films.

Huang *et al.* (2004) applied the vacuum seeding technique to coat the seeds on the surface of the alumina support before hydrothermal synthesis. In this technique, a pressure difference was created between the two sides of the support wall. Water

flowed into the support pore and was removed by vacuum force, resulting in zeolite A being coated on the support. They found that the seed particle size, suspension concentration, coating pressure difference and coating time have great effects on the seed layer and properties of the as-synthesized NaA zeolite membrane.