

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Ethanol is an alcohol-based alternative fuel produced by fermenting and distilling starch crops that have been converted to simple sugars. Ethanol is the most common use to enhance octane number and oxygenates value and improves the emissions quality of gasoline. In most areas of the world, 99.5% pure ethanol and unleaded gasoline are mixed at the ratio of 1:9, also called "gasohol". Since ethanol is a renewable fuel and is produced from starch crops, it is an ideally alternative fuel in Thailand.

Commercially, anhydrous ethanol is produced using 2 techniques. Firstly, a simple distillation is used to distil a 12 wt% ethanol to a 94.6 wt% ethanol concentration. At this point, ethanol forms an azeotropic mixture of 94.6/5.4 with water. To obtain anhydrous ethanol, the last 5.4 wt% of water in the azeotropic mixture is removed by azeotropic distillation using benzene or cyclohexane as entrainer. Azeotropic distillation is a very energy intensive technique. However, it is used commercially because it is the only known technology in practice. Removing the last 5.4 wt% of water from the azeotropic mixture by adsorption is another alternative technique. Unfortunately, adsorption process requires even higher energy compared to azeotropic distillation. Membrane pervaporation is the latest ethanol separation technique developed. Commercial application using membrane pervaporation is not yet well accepted. Low water/ethanol membrane selectivity and too slow of water permeation rate, called "flux", through the membrane are believed to be a reason of the unattractive commercial ethanol separation practice. More recently, breakthrough in zeolite membrane is reported for ethanol separation. A selectivity of more than a thousand with very high water flux was reported using zeolite membrane pervaporation (Zah *et al.*, 2006).

Pervaporation is one of the attractive means for the dehydration of water/organic mixtures, especially when an azeotrope is involved. It may also be used for dehydrating chemicals that might be heat sensitive. Pervaporation is a membrane separation process where the separation is based on the different affinity of the components for the membrane. A vacuum is kept on the permeate side of the

membrane while the feed side of the membrane is kept at atmospheric or elevated pressure so a pressure difference is created over the membrane which is the driving force for the pervaporation process. The components that permeate through the membrane evaporate while passing through the membrane because the partial pressure of the permeating components on the permeate side is kept lower than the equilibrium vapour pressure.

Pervaporation has several advantages over traditional distillation. Those are:

1. Reduction of energy demand because only a fraction of the liquid that needs to be separated is vaporized,
2. Simple equipment since only a small vacuum pump is needed to create a driving force and
3. Lower capital cost. (Hoof *et al.*, 2006)

Polymeric pervaporation (PV) membrane has also been widely studied. The major emphasis is on new polymeric materials, modeling of component transport through dense polymers and process design of commercial membrane modules. However, most polymeric membranes fail to give an optimal performance over a broad spectrum of solvents and concentration ranges, in terms of flux and selectivity (Dutta *et al.*, 1996).

Polymeric membranes are not generally suitable for application involving harsh chemicals like unsymmetrical dimethylhydrazine (UDMH) due to their chemical instability. However, a recent development of chemical and temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of thermal, chemical and mechanical instability of hydrophilic polymeric membrane (Jafar *et al.*, 1997).

Synthetic zeolites have a highly crystalline ordered structure and hence offer the unique advantage of narrow pore size distribution. Also, due to their inorganic nature, these materials possess higher resistance to a variety of solvents and stability at elevated temperatures. These distinctive properties, which are very critical for many membrane applications, make the use of zeolite membranes more attractive than polymeric membranes. The zeolite membranes could be potentially used in many pharmaceutical applications, which are typically low-volume processes

and may contain harsh solvents like dimethylformamide, tetrahydrofuran, etc., and inorganic salts (Shah *et al.*, 2000).

Hydrophilic zeolite membrane has been found to be suitable for dehydrating water/organic mixtures by pervaporation, and zeolite A is often the material of choice due to its high Al content and small pore size. Zeolite A membranes provide high selectivity (up to 10000) and high fluxes for the separation of alcohol/water mixture (Gallego-Lizon *et al.*, 2002), and by now, zeolite NaA membranes are commercially available (Morigami, Y. *et al.*, 2001). The pore size of NaA zeolite is 0.41 nm, i.e., smaller than that of the MFI zeolite (~0.55 nm). The small pore size of NaA zeolite makes the separation of small molecules by difference in size possible. The molecular kinetic diameters of short-chain alkanes are close to or larger than the pore size of NaA zeolite (Zimmerman *et al.*, 1997).

The active NaA layer is responsible for the high separation factors achieved with solvent mixtures. The structure of zeolite A is shown in Fig. 2.1. As can be seen from the figure, the aluminosilicate framework of zeolite A is generated by placing truncated octahedrons (β -cage) at eight corners of a cube, and each edge of the cube is formed by joining two β -cages by a D4R linkage. Each β -cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a larger cavity known as the α -cage enclosing a free diameter of 1.14 nm. There are two interconnecting, three-dimensional channels in zeolite A: (i) connected α -cages, 1.14 nm in diameter, separated by 0.42 nm apertures, (ii) β -cages, alternating with the α -cages separated by 0.22 nm apertures (Breck *et al.*, 1974). Thus, molecules smaller than 0.42 nm in diameter can diffuse easily through the micropores of the zeolite. Also, the position of sodium ions in the unit cells is important since these ions act as the sites for water sorption and transport through the membrane. For a typical zeolite, a unit cell having the composition of $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$, eight (out of 12) sodium ions are located inside the α -cage and four ions are located in the β -cage (Gallego-Lizon, T. *et al.*, 2002). The transport of the solvent species (mainly water) through the zeolite matrix comprises of three steps: (i) strong adsorption of the species in the zeolite cage, (ii) surface diffusion of the species from cage to cage and (iii) vaporization of species on permeate side. Normally, any physical adsorption process includes both van der Waals dispersion-repulsion forces and electrostatic forces comprising of polarization,

dipole, and quadrupole interactions. However, since the zeolites have an ionic structure, the electrostatic forces become very large in the adsorption of polar molecules like H_2O . This effect is manifested in the fact that the heat of adsorption of water on zeolitic adsorbents is unusually high (25–30 kcal/mole) (Ruthven *et al.*, 1984).

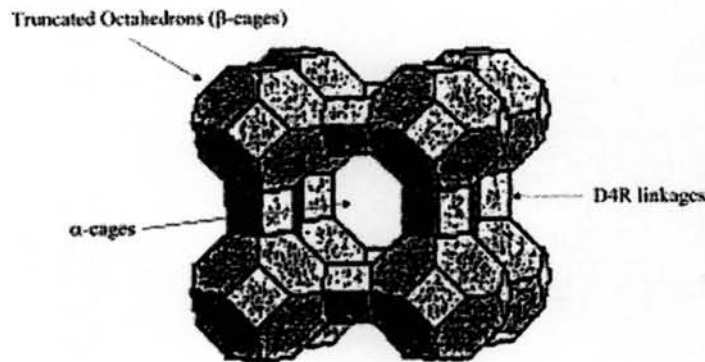


Figure 2.1 Repeating units of zeolite NaA.

NaA zeolite membrane has been traditionally prepared by static discontinuous hydrothermal synthesis using either a milky-like gel or a clear solution onto the surface of a porous support with or without a previous seeding step. The membrane was also successfully synthesized on a porous $\alpha-Al_2O_3$ support from clear solution. When the support was unseeded, the NaA zeolite on the support surface began to transform into other types of zeolites before a continuous NaA zeolite membrane formed (Xu *et al.*, 2001). When the support was seeded, the formation of NaA zeolite on the support was accelerated and the transformation of NaA zeolite was inhibited (Xu *et al.*, 2001). A continuous NaA zeolite membrane can be formed on the seeded support after 2 h of synthesis, but gas permeation results showed that a synthesis time of 3 h produced the best NaA zeolite membrane. When the synthesis time was longer than 4 h, the NaA zeolite on the support surface began to transform into other type of zeolite, and the quality of the NaA zeolite membrane decreased.

The crystallization process is thermally activated and allows a high yield of crystals to be achieved in an acceptable period of time. The crystallization period of zeolite can be subdivided into two steps, namely, the nucleation of a new population of zeolite crystals and the growth of the existing population of crystals. Seeding is a

technique in which a supersaturated system is inoculated with small particles of materials to be crystallized. Using this technique, the nucleation stage is bypassed and the induction period is eliminated (Feigen *et al.*, 1999)

Coating the zeolite seeds on the support surface before hydrothermal synthesis, which is also named secondary growth method, is an effective approach to synthesize a high quality zeolite membrane. It is well known that the presence of seeds on support surface plays an important role in membrane formation (Xu. *et al.*, 2001). Synthesis with seeds gives a better control of the membrane formation process by separating the crystal nucleation and growth with a shortened crystallization time. In addition, the secondary growth method ensures the growth of the zeolite crystal on the supports rather than in the solution and restrains the nucleation transform to other crystals (Gora *et al.*, 1997).

There are two challenging issues related to the synthesis of membrane by the secondary growth method. One is how to prepare colloidal suspension of zeolite particles, and the other is how to coat the seeds onto the support surface. A lot of studies have been reported to prepare stable colloidal suspension (Schoeman *et al.*, 1994), and many methods have been explored to coat the seeds onto the support surface, including dip coating (Xu *et al.*, 2001), rub coating (Kusakabe *et al.*, 1997), spraying coating (Zhang *et al.*, 2001) spinning coating (Mintova *et al.*, 2001) and pulsed laser deposition (Balkus *et al.*, 1998). Although these seeding methods improve membrane synthesis modestly, they had their own limitations. The dip coating is one of the most widely used methods. However, zeolite seeds cannot closely attach to the support surface and the colloidal suspensions easily dribble when the supports are withdrawn from the suspensions. Thus, it is difficult to obtain uniform and continuous seeding layer. In addition, it should repeat coating step several times to obtain seeding layer with good coverage, taking longer time.

The rub coating is the simplest coating method. In the coating process, the zeolite powder is attached on the support surface directly by rubbing zeolite powder. However, the zeolite powder is easily washed down when the synthesis solution is poured into the autoclave. Therefore, it is not easy to synthesize high quality zeolite membranes.

The spraying coating and the spinning coating are effective for coating flat support, but they are unsuitable for tubular support. The pulsed laser deposition method can give well-adhered and highly oriented films, but the method requires rather sophisticated equipment and it is not widely accessible. Recently, M. Tsapatsis and coworkers (Xomeritakis *et al.*, 2000) seeded the supports by changing the value of pH of the solution to match the zeta potentials of the Al_2O_3 support and of the SiO_2 seeds. There are seeded zeolites on the non-porous plane substrates surface by electrostatic forces to prepare thin ZSM-5 layers. Seeding by changing the value of pH of the solution or by electrostatic forces is effective to introduce uniform size zeolite seed to the support surface. However, they are too complicated to operate for large-scale membrane synthesis (Mintova *et al.*, 1998)

Weishen Yang and coworker (2004) explored a new method to coat the seeding layer onto the porous support. Vacuum seeding is another seeding process which is a simple and effective technique for large-scale synthesis of zeolite membrane. In this process, the zeolite seeds are driven onto the support surface under the action of the vacuum force. The water being sucked into the support pore is taken away continuously by the vacuum force. Therefore, the zeolite seeds can be attracted and transport onto the whole support surface homogeneously, forming a smoother and uniform seeding layer. The vacuum seeding method is suitable for both the flat and the tubular supports. In addition, this method does not require sophisticated equipment and is widely accessible. The factors investigated were seed particle size, suspension concentration, coating pressure difference, coating time and pervaporation property (Huang *et al.*, 2004).

Microwave is electromagnetic radiation with wavelengths ranging from 1 m to 1 mm with corresponding frequencies between 300 MHz and 300 GHz. A large part of the microwave spectrum is used for communication purpose and only a restricted number of frequencies are reserved for heating applications. The two most commonly uses are 915 MHz and 2.45 GHz, the last one being the operating frequency of domestic microwave ovens. Microwave irradiation, transferring heat through the surfaces of the materials by convection, conduction and radiation, is more efficient for transferring thermal energy to a volume of material than conventional thermal process (Bonaccorsi *et al.*, 2003).

The microwave hydrothermal was investigated to synthesize NaA zeolite membrane. The results showed that the synthesis time was decreased from 3 h for conventional heating to 15 min (Xu, *et al.*, 2001). It was not only the synthesis time decreased, but also the thickness of membrane reduced to 4 μm thinner than that synthesized by conventional heating. Moreover, the formation mechanism of NaA zeolite membrane on the porous $\alpha\text{-Al}_2\text{O}_3$ support by microwave heating was proposed (Xu *et al.*, 2003).

It is a heterogeneous nucleation process. First, a gel layer formed on the porous support surface, followed by nucleation and crystal growth to form a membrane. The promotion effect of microwave can be divided into two parts: the “thermal effect” and the “microwave effect”. Due to the microwave effect, the water became “active” water, and the dissolution of the gel layer in the support /solution interface was accelerated. At the same time, due to the “thermal effect”, the synthesis mixture was heated up quickly and homogeneously. The fast formation of NaA zeolite membrane was mainly caused by the “microwave effect”, while the formation of a homogeneous and thin NaA zeolite membrane resulted from both the “thermal effect” and the “microwave effect”. Fig. 2.2 shows the comparison of the synthesis model of zeolite membrane between microwave hydrothermal method and conventional method (Xu *et al.*, 2003).

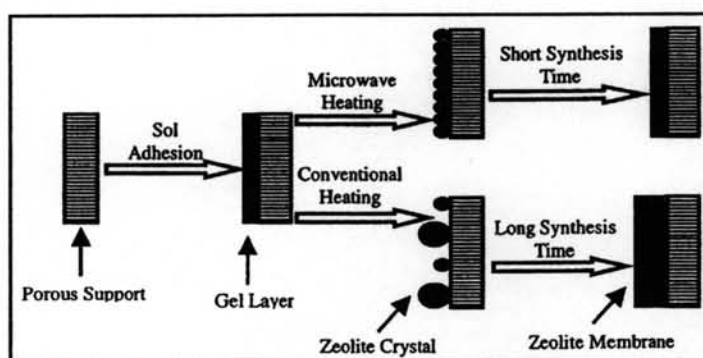


Figure 2.2 Comparative synthesis model of zeolite membrane by microwave hydrothermal and conventional hydrothermal methods.

Edoardo Proverbio and coworkers (2003) demonstrated as to how an adequate tailoring of the microwave energy released to a synthesis mixture can lead to pure zeolite A without particular pre-treatment of the solution. They did the experiment that the density of synthesis mixture was increased. Increasing the crystallization rate and raising pH are the effects of reduction in water content of the synthesis mixture, called dense gel. The total processing time of this experiment was 1h by exposing the reaction mixture to a microwave electromagnetic field under atmospheric pressure (Bonaccorsi *et al.*, 2003).

Slangen and coworkers (1997) found that ageing is a prerequisite for the successful rapid synthesis of NaA by using microwave technique for synthesis, and this is in contrast to the conventional synthesis. During the ageing, mixing on a molecular scale is envisaged to allow the formation of nuclei necessary for the crystallization of NaA. In conventional synthesis, the mixing and formation of nuclei can take place during the slow heating-up, so that no ageing is necessary for a successful synthesis. In sufficient ageing and inadequate stirring cause the formation of impurities in the final product and low crystal yield, so that the limiting factor was identified as a lack of nuclei formation in the synthesis mixture during the short heating time. When the synthesis mixture has been aged sufficiently, the synthesis of NaA can be done in 1 min by microwave heating, leading to small crystals with a relatively homogeneous crystal size distribution. Thus, all the advantages from a few minutes of crystallization in microwave oven are lost, due to the necessity of several ageing hours at room temperature (Zah *et al.*, 2006).

Jaco Zah and co-workers (2006) described the structural membrane development over time that membrane was synthesized by conventional technique. The layer development over time (1.0–4.0 h) was described in terms of morphology, growth rate and elemental composition. For morphology, an initial layer of semicrystalline, hemisphere-shaped grains transform into a fully crystalline layer with cubic morphology at the end of the growth process. The membrane growth for NaA, under the given synthesis condition, proceeded along two distinctive morphological pathways: a homogeneous layer of semicrystalline, hemisphere-shaped grains after 2.0 h, followed by the well-known cubic morphology after 4.0 h. Formation of the first layer type could be explained in terms of the supersaturation of

nutrients in the associated gel material. Transition into the second morphology type coincided with a suggested decrease in nutrient concentrations, while grain crowding within the structural membrane confines probably contributed to this transformation. Moreover, they studied the film thickness over time and found that the increase in layer thickness was not linearly correlated to the full duration of synthesis. For the growth rate, The development of the hemisphere-shaped grains was associated with a period of accelerated growth during the first 2.5 h of synthesis ($3.3 \times 10^{-10} \text{ m s}^{-1}$), followed by a period of slower growth for the formation of the cubic morphology ($1.9 \times 10^{-10} \text{ m s}^{-1}$). Fig. 2.3 shows the film thickness as a function of the synthesis time.

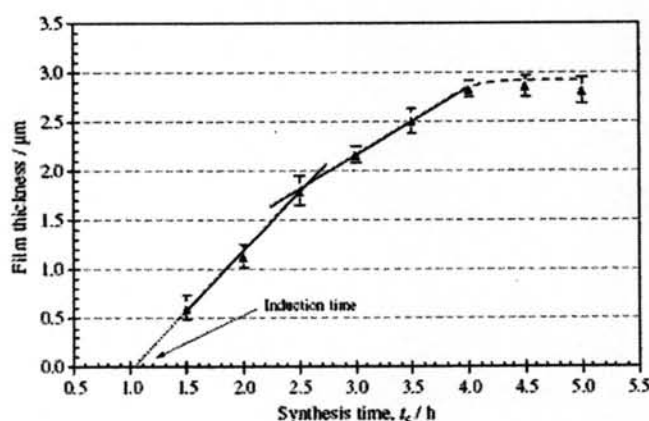


Figure 2.3 Film thickness, averaged from 10 scattered measurements each, as a function of crystallisation time, t_c .

Localised changes in supersaturation, combined with the possible effects of grain crowding, were offered as feasible explanations for the observed morphology and growth rate tendencies. The elemental composition showed a gradual decrease in the Na/Si ratio with increasing crystallization time (Slangen *et al.*, 1997).

Toraj Mohammadi and coworkers (Mohammadi *et al.*, 2002) synthesized kaolin based zeolite A membrane by electrophoresis. Tubular module of kaolin was prepared by electrophoretic deposition on a cylindrical electrode. Fig.2.4 shows the electrophoretic deposition (EPD) setup.

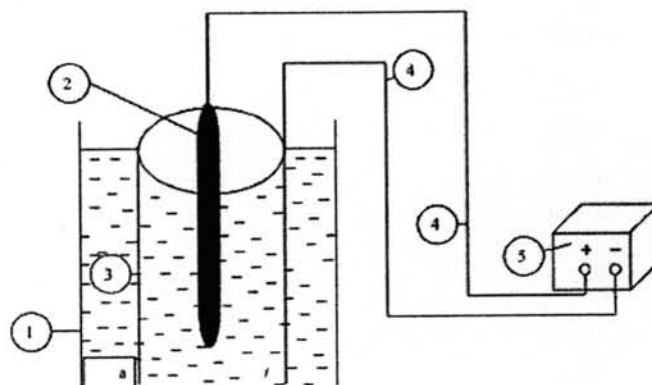


Figure 2.4 EPD setup; 1: container, 2: anode, 3: cathode, 4: wires, 5: power supply.

Voltage and current in electrophoresis method were 10 V and 0.25 A, respectively. Required time for preparation of a module with o.d. = 10 mm (i.d. = 8 mm) was 2 min. The density of suspended clay was 1.5 g/cm^3 . Increasing voltage causes gas generation from anode. Lower voltage needs more time for the module to be prepared with desirable diameter. After preparation, module was removed from anode, dried at 80°C and then calcined at 700°C for 3 h. Finally, it was placed in an autoclave with 14% sodium hydroxide solution. A thin zeolite A membrane was formed on the kaolin tube. Then, the tube was washed with distilled water and dried overnight at 60°C . For drying temperatures of more than 60°C , the membrane was separated from the support. This membrane was used for ethanol/water separation. The highest separating factor of 25.14 was measured using the membrane. From these results, Zeolite A membrane prepared from pure kaolin was cracked due to its water adsorption. A 30% γ -alumina module which was soaked in zeolite solution showed a maximum selectivity of about 25.14 which is not very high, however, its strength was remarkably improved. As mentioned before, some cracks may be introduced during the calcination process.

A. Berenguer-Murcia and coworkers (Berenguer-Murcia *et al.*, 2003) used the electrophoretic deposition method as a seeding method. Continuous, well-intergrown layers of molecular sieve crystals have been grown on porous carbon supports by secondary (seeded) growth carried out by electrophoretic deposition of nanocrystals of silicalite-1 on the carbon support. The seeding was carried out by applying a constant current density between the carbon disc (working as a cathode

i.e., negative charge) and a Pt counter-electrode in the working cell (see Fig. 2.5). At the experimental conditions used, almost no deposition occurs when carbon support is used as an anode. Additionally, no significant deposition happens when the carbon support is put in contact with the suspension in absence of current. Both the time during which the seeding was carried out and the intensity was applied to the circuit were analyzed so as to obtain a homogeneous coating of seeds on the support. A closed silicalite-1 layer was then obtained by applying a standard hydrothermal treatment to the seeded disc. The obtained zeolite layers are defect free and well-intergrown.

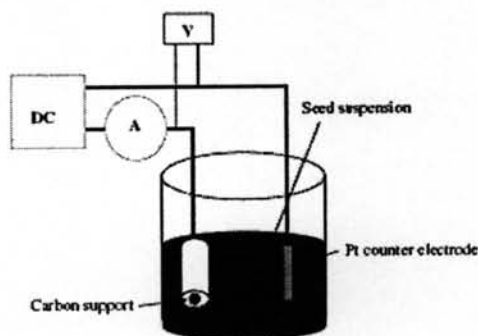


Figure 2.5 Scheme of the set-up used for the EPD of seed crystals on the carbon support.