



CHAPTER I INTRODUCTION

Zeolites are microporous crystalline materials, mostly used as catalysts, ion-exchangers, and adsorbents. They are known as “molecular sieves” due to their pore structure, prohibiting the entrance of larger molecules and allowing only the passage of smaller ones [Chiang *et al.*, 2001]. Generally, zeolites can be classified into small, medium, large, and ultra-large pore materials. Small pore structures have apertures consisting six, eight, or nine tetrahedra (6-, 8-, 9- membered rings); medium pore frameworks have 10-membered rings; large pore zeolites have 12-membered rings; and ultra-large structures have 14-, 18-, or 20- membered rings. Pore diameters in known zeeolites are between approximately 0.3 and 1.5 mm [Meier *et al.*, 1996].

Zeolites are classified according to their framework symmetry with an identification code of three letters used by the International Zeolite Association (IZA). For instance, the MFI-type includes synthetic species with varying chemical composition (silicalite 1 and ZSM 5). Silicalite 1 is a pure silica analogue of ZSM 5, containing only small amounts of or no aluminum at all, whereas ZSM 5 has a $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio of 5-100 [Szotak, 1992]. Faujasite zeolites (zeolite X and Y), which belong to the FAU group, have equidimensional channels intersecting perpendicular to each other. The eight interconnected truncated octahedra (β cages) link tetrahedrally through a double six ring (D6R) in an arrangement like carbon atoms in a diamond. The cavity diameter is 13 °A in each unit cell. A difference between zeolite X and Y is that the Si/Al ratio is 1-1.5 and 1.5-3, respectively [Breck, 1974]. Zeolite NaA, a dimensional channel system, contains equidimensional channels intersecting perpendicular to each other. A cubic array of β -cages linked by double 4 ring (D4R) units produce an α cages. The free aperture diameter for the α cages is 4.2 °A [Breck, 1974]. The frameworks of faujasite zeolite and zeolite A contain more aluminum than ZSM 5. They are thus more hydrophilic than ZSM 5.

Today, the hydrohilic characteristics of NaA zeolite is being applied to separation membranes. To obtain a resonable flux, the zeolite membrane must be thin and the size of the crystal is a significant factor that affects the performance.

Thin zeolite films applied for membrane separation can be prepared by using synthesis conditions allowing for the formation of small and uniform crystals to obtain faster diffusion and higher surface area [Jansen *et al.*, 1996]. Several synthesis strategies and methods have been developed, such as in-situ hydrothermal synthesis [Sano *et al.*, 1994; Yan *et al.*, 1995; Kondo *et al.*, 1997 and Sterte *et al.*, 1997], secondary growth [Lavello *et al.*, 1996; Lai *et al.*, 1998; and Boudreau *et al.*, 1999], dry gel conversion, vapor phase transport [Dong *et al.*, 1990], microwave synthesis [Xu *et al.*, 2000 and Motuzas *et al.*, 2006] and electrophoretic technique [Seike *et al.*, 2002 and Mohammadi *et al.*, 2002].

In-situ hydrothermal synthesis is the best studied method, in which the porous support is immersed into the synthesis solution and then the membrane is formed by direct crystallization. However, in this method, the quality of as-synthesized membrane significantly depends on the support surface [Valchev *et al.*, 1995]. It is usually difficult to prepare high quality membrane by in-situ hydrothermal synthesis directly.

The secondary growth method has many advantages, such as better control over membrane microstructure (thickness, orientation) and high producibility [Huang *et al.*, 2004 and Boudreau *et al.*, 1999]. Seeding of the support has been shown to be an effective technique for the promotion of nucleation of crystals on the support surface [Kita *et al.*, 1995; Aoki *et al.*, 1998; and Kumakiri *et al.*, 1999]. Seeding can be done by several methods, such as rubbing [Kusakabe *et al.*, 1974], treating the support with a cationic polymer before deposition of crystal seeds [Boudreau *et al.*, 1999 and Hedlund *et al.*, 1999], dip coating [Mintova *et al.*, 1998; Xomeritakis *et al.*, 2000; Liet *et al.*, 2000; and Okamoto *et al.*, 2001] and vacuum seeding [Wong *et al.*, 1999 and Shan *et al.*, 2004]. All of these methods have been reported to enhance the formation of continuous membranes. However, each presents distinct advantages and disadvantages.

Microwave synthesis has many advantages, including a very short synthesis time, uniform and small crystal sizes, and broad synthesis composition. Zeolite membranes, such as LTA, sodalite, FAU, MFI, SAPO-5, and AlPO_4^{-5} , have been synthesized by the microwave synthesis method. However, it is not easy to prepare a high performance zeolite membrane by use of microwave synthesis. Recently, it was

also proved that in-situ aging is necessary for the microwave synthesis of a NaA zeolite membrane without seeding.

More recently, the so-called dry gel conversion method (DGM) has been developed, with two different routes: stream-assisted crystallization (SAC) and the vapor phase in the parent gel (VPD). VPD refers to the conversion of a dry amorphous precursor into a fully crystalline material via contact with an organic-water mixture vapor, and SAC via contact with just a water vapor phase. Membranes can be synthesized by either of these methods.

Another technique, electrophoresis deposition, is found to be a simple and effective technique for thin film preparation [Wong *et al.*, 1999 and Shan *et al.*, 2004]. The charged particles can migrate to the support surface homogeneously and rapidly under the action of an applied electric field, resulting in uniform and dense membranes [Huang *et al.*, 2007].

The focus of this present work is to synthesize small size and uniform NaA zeolite and to use it as the seed for secondary growth of membrane synthesis. Recently, Wongkasemjit's group [Piriyawirut *et al.*, 2003; Sathupanya *et al.*, 2004; and Phonthamachai *et al.*, 2004] has developed a novel method to produce uniform zeolites using synthetic silatrane and alumatrane as precursors via sol-gel process and microwave techniques. During NaA zeolite synthesis, the crystal size of the zeolite is determined by two competing phenomena occurring during synthesis, –nucleation and crystal growth. The higher the nucleation rate that occurred, the smaller the crystal that was obtained. There are several parameters involved in the establishment of relative rates of nucleation and crystal growth. Significant parameters, such as seeding technique, time, temperature, aging the reaction mixture etc., may effect the relative rate of nucleation and crystal growth [Renzo *et al.*, 1998]. Moreover, NaA zeolite is produced from those atrane precursors to compare with the direct method in which silica and alumina are used as starting materials.

Finally, NaA zeolite membranes were prepared by the aid of seeding technique using microwave or electrophoretic techniques. Several effects on membrane morphology, thickness, and performance were investigated. The performance of the synthesized membranes relative to those effects is also studied using the pervaporation technique.