Chapter from the book *Advances in Induction and Microwave Heating of Mineral and Organic Materials*
Downloaded from: [http://www.intechopen.com/books/advances-in-induction-and-microwave-heating-of-mineral-and-organic-materials](http://www.intechopen.com/books/advances-in-induction-and-microwave-heating-of-mineral-and-organic-materials)
1. Introduction

Microwaves are electromagnetic waves locating in the electromagnetic spectrum between infrared and radio waves, with wavelengths ranging from as long as one meter to as short as one millimetre, or equivalently, with a frequencies range between 0.3 and 30 GHz. Microwaves consist of an electric and magnetic field, and thus represent electromagnetic energy. This energy can act as a non-ionising radiation that causes molecular motions of charge carriers like ions or electrons and cause also molecules with a permanent dipole moment to follow the alternating field, but do not affect the molecular structure (Bougrin et al, 2005). It has been known for a long time that microwaves can be used to heat materials. In the case of heating solids, the kinetic energy of ions and electrons following the alternating electrical field is transformed into thermal energy. When heating liquids, the orientation polarization of systems of molecules with permanent dipoles like water, methanol or DMF is used. Actually, microwave heating technique has been widely used within the last 50 years not only in the domestic preparation and processing of food, but also in the field of materials synthesis. The classic work of Hippel and co-workers in the early 1950s provided a sound theoretical basis for these technological developments and his group provided an important database of dielectric properties on common substances, foodstuffs and materials (Von Hippel, 1954). Thereafter, Gabriel et al. have summarized the basic theory of underlying microwave dielectric heating and provided a database of dielectric parameters for organic solvents which are used in synthetic organic and inorganic chemistry (Gabriel et al., 1998). Nuchter et al. have given a critical technology overview on reaction engineering in microwave fields (Nuchter et al., 2004).

In the past two decades, microwave heating technique has attracted intense attention from chemists, material scientists and microwave engineers. Microwave heating has currently been employed in many chemical reaction studies, including organic and inorganic syntheses, selective sorption, oxidations/reductions, and polymerizations. Such review articles can be found elsewhere (de la Hoz et al., 2005; Langa et al., 1997; Nuchter, et al., 2003; Rao et al., 1999; Tompsett et al., 2006). The effect of microwave irradiation in chemical reactions is a combination of thermal and non-thermal effects (de la Hoz et al., 2005). Compared with the conventional heating for chemical synthesis, microwave heating has the following advantages (Gabriel et al., 1998): (i) The introduction of microwave energy into a
chemical reaction system remarkably results in much higher heating rates than those which are achieved conventionally in air conditioned ovens. Therefore the synthesis times can be significantly reduced. (ii) The microwave energy is introduced into the chemical reactor remotely without direct contact between the energy source and the reacting chemicals, therefore, leading to a significantly different temperature profile for the reaction and, thus, to an alternative distribution of chemical products from a reaction. (iii) It is possible to achieve selective synthesis of desired materials and to change reaction kinetics and selectivity since chemicals and the containment materials for chemical reactions do not interact equally with microwaves. Specifically the containment materials for a chemical reaction may be chosen in such a way that the microwave energy passes through the walls of the vessel and heats only the reactants. This concept holds true also for addressing droplets of a dipolar solvent in an organic microwaves not-absorbing solvent (reverse microemulsions). (iv) “Hot spots” yielded on local boundaries by reflections and refractions of microwaves and may result in a “super-heating” effect, which can be described best as local overheating and which is comparable to the delayed boiling of overheated liquids under conventional conditions. The advantages outlined above have been exploited extensively during the last 20 years and to date more than 2000 articles have been published to apply microwave heating for chemical synthesis (Figure 1). A special application of microwaves is their use in the crystallization of porous molecular sieve membranes. In this chapter, microwave synthesis of porous molecular sieve membranes was summarized, including recent development and progress in microwave synthesis of porous molecular sieve membranes; combined microwave and conventional heating model; differences between microwave synthesis and conventional hydrothermal synthesis for membrane formation; formation mechanism in the case of microwave synthesis of porous molecular sieve membranes.

Fig. 1. Development of articles in open literatures with microwave heating synthesis.
2. Zeolite and zeolite-like porous molecular sieves

Zeolites are crystalline silicate and aluminosilicates microporous materials that possess three dimensional frameworks built from SiO$_4$ and AlO$_4$ tetrahedral units linked through oxygen atoms with periodic arrangements of cages and uniform channels of nanometer dimensions (Figure 2) (Baerlocher & McCusker, http://www.iza-structure.org/databases). Since the size of the pore aperture of zeolites is comparable to molecular dimensions (typically between 3 and 10 Å), zeolites can function as “molecular sieves”, excluding molecules larger than their pore windows. So far, over 190 molecular sieve structures were registered to the Structure Commission of the International Zeolite Association (IZA) since the Swedish mineralogist Cronstedt discovered the first natural zeolite stilbite (STI) in 1756. Among those, only about 17 are of commercial interest and produced synthetically, i.e. AEL, AFY, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TON, and RHO (Maesen, 2007). Zeolites have been widely used in the chemical industry as catalysts, ion exchangers, and adsorbents due to their uniform pore structure and high thermal stability. The total value of zeolites used in petroleum refining as catalysts and in detergents as water softeners is estimated at $350 billion per year.

Based on the pioneering work of Barrer and Milton on the synthesis of zeolites (Barrer, 1948; Barrer et al., 1953; Barrer, 1981; Breeck et al., 1956), hydrothermal synthesis has become the basic route for zeolite synthesis. Zeolites are usually synthesized under hydrothermal conditions from reactive gels in alkaline media in an air-conditioned oven at temperature of 50 ~ 200 °C for days in a closed system. In the last ten years, microwave heating has been widely used in many chemical reactions, such as organic and inorganic synthesis, oxidation-reductions, and polymerizations, so in the fields of zeolite synthesis. The first report of the microwave synthesis of zeolites was given in an US patent by Mobil Oil Corp. in 1988 for the synthesis of zeolites LTA (NaA) and MFI (ZSM-5) (Chu et al., 1998). The crystallization was found to be significantly accelerated by the exposure of synthesis gels to microwave radiation. Thereafter, microwave heating synthesis has been applied for the synthesis of a number of zeolites, including zeolite A (LTA) (Panzarella et al., 2007; Slangan et al., 1997 (a)), faujasite (FAU) (Panzarella et al., 2007; Srinivasan & Grutzeck, 1999), analcime (ANA) and Gobbinsite (GIS) (Sathupunya et al., 2002), beta (BEA) (Panzarella et al., 2007), ZSM-5 (MFI) (Phiriyawirut et al., 2003; Somani et al., 2003), silicalite-1 (MFI) (Hu et al., 2009), AlPO$_4$-5 (AFI) (Girnus et al. 1995), VPI-5 (VFI) (Carmona et al., 1997), and cloverite (CLO) (Park & Komarneni, 2006). The number of publications of microwave heating synthesis of zeolite increases year by year. The microwave synthesis of zeolites and mesoporous materials was reviewed by Cundy (Cundy 1998) and by Tompsett et al. (Tompsett et al., 2006). Microwave heating synthesis turns out to be much faster, cleaner and more energy efficient than the conventional heating. The possible influences of microwave heating on the synthesis of zeolites were outlined in a previous review (Cundy 1998), mainly including: (i) Uniform heating of the synthetic mixture; (ii) Increase of the reaction rate; and (iii) Changing the association between species within the synthetic mixture. The specific reactions might be enhanced in a microwave field or by the absorption of microwave energy of reactants, intermediate species, and/or products.

For the crystallization of some zeolite structures like types LTA and FAU (zeolites X and Y), temperatures lower than 100 °C are usually applied. In these cases open glass vessels can be used in a microwave oven. However, most zeolites are crystallized at temperatures higher than 100 °C and usually stainless steel autoclaves with a Teflon insert are used. However,
since steel is not transparent for microwaves, full-Teflon or full-ceramic autoclaves have to be used. Several companies offer research-microwave ovens operating at a frequency of 2.45 GHz. This is the world-wide standard frequency for the dipolar heating of water which also allows the efficient heating of other dipolar solvents like methanol or DMF.

![Diagram of framework types of zeolites](image)

Fig. 2. Framework type of some commercial zeolite (Baerlocher & McCusker, http://www.iza-structure.org/databases).

### 3. Microwave synthesis of zeolite and zeolite-like porous molecular sieve membranes

Apart from the use of zeolites as powders, supported zeolite layers are of interest for many potential applications owing to their excellent properties such as uniform pore structure, high thermal stability and high mechanical strength. In the last 25 years, many research efforts have been focused on the preparation of supported zeolite layers due to their potential applications as separators (Lai et al., 2003), reactors (Casanave et al., 1995), sensors (Yu et al., 2007), and electrical insulators (Wang et al., 2001). A great deal of progress in the synthesis of zeolite membrane has been made during the last 25 years, over 2500 articles have been published (Figure 3). To date, MFI (van de Graaf et al., 1998), DDR (Tomita et al., 2004), LTA (Aoki et al., 1998; Huang et al., 2010; Huang & Caro, 2010), FAU (Kusakabe et al., 1997), SOD (Xu et al., 2004), CHA (Carreon et al., 2008), FER and MOR (Nishiyama et al., 1997), BEA (Sirikittikul et al., 2009), and AFI (Guan et al., 2003) membranes, have been prepared on different types of supports for liquid or gas separation. The first industrial application of zeolite membranes is the dewatering of bio-ethanol by using LTA zeolite.
membrane (Morigami et al., 2001; Sato et al., 2008). The significant progresses achieved in the rapidly growing field of supported zeolite membranes are outlined by a large number of review articles (Bein 1996; Caro et al., 2000; Caro & Noack, 2008; Lin, 2001; Tavolaro & Drioli, 1999).

Several synthesis strategies have been developed to prepare supported zeolite membranes/layers, including in-situ hydrothermal synthesis (Yan et al., 1995), secondary (seeded) growth synthesis (Lovallo et al., 1996; Lai & Gavalas, 1998), vapor phase transport synthesis (Nishiyama et al., 1996) and dry gel conversion (Ma et al., 2001). The in-situ hydrothermal synthesis is the best-studied method, in which the surface of the porous supports directly contact with the zeolite precursor solution and keep the system under controlled conditions in order to nucleate and grow a thin continuous zeolite film on the support surface. The process is relatively simple but the characteristics and quality of the obtained membrane are very sensitive to procedures and conditions. It is usually difficult to prepare high quality zeolite membrane by in-situ hydrothermal synthesis directly (Chau et al., 2000; Huang et al., 2007). The secondary growth method is now considered as one of the most attractive and flexible approaches for the formation of high quality zeolite membranes, exhibiting many advantages, such as better control over membrane microstructure (thickness, orientation) and enhancement of the membrane reproducibility (Xomeritakis et al., 1999).

![Graph](image_url)

Fig. 3. Development of the articles of zeolite membrane/film in open literatures.

Microwave heating is a fast, simple and energy-efficient method, which could significantly reduce the synthesis time and cost. Microwave heating can also assist in the preparation of zeolite and zeolite-like porous molecular sieve membranes combining with the above synthesis strategies. Like in the case of the crystallization of zeolites powder, full-Teflon or full-ceramic autoclaves and standard microwave ovens operating at 2.45 GHz are used for membrane crystallization. A benefit of microwave heating in membrane preparation is that the autoclave material is transparent for microwaves, hence, the autoclave walls and the reaction system near to the wall remain cool. This effect suppresses heterogeneous...
nucleation at the autoclave wall. In the very beginning of microwave absorption by the liquid solution, steep temperature gradients occur. But usually these gradients are not harmful since the degradation of these temperature gradients with time is faster than the kinetically controlled nucleation. Therefore, volumetric heating produces a homogeneous nucleation and growth as well as fast supersaturation of the reaction mixture. To date, LTA, MFI, FAU, Zeolite T, SOD, AFI, CHA types of zeolite membranes as well as metal-organic frameworks (MOFs) membranes have been successfully synthesized by microwave heating. Usually these molecular sieve membranes are a few µm thick zeolite or MOF layer supported by a macroporous ceramic substrate like alumina, titania or zirconia. Whereas α-Al2O3 supports are transparent for microwaves, a technical TiO2 as mixture of anatase and rutile absorbs microwaves thus influencing nucleation and crystal growth in a liquid layer directly attached to the support. Recently, Li et al. (Li & Yang, 2008) have given a comprehensive review on the microwave synthesis of zeolite membranes, summarizing the development of microwave synthesis of zeolite membranes. After this work, there have been increasing publications on the further developments in the field of microwave synthesis of zeolite membranes. During the last few years, microwave heating synthesis of molecular sieve membranes has extended from zeolite membrane to MOF membranes exploiting the shape-selectivity of membranes in gas separation. In this section, we try to make a comprehensive summary of the development of microwave synthesis of porous molecular sieve membranes.

3.1 LTA zeolite membranes
Zeolite LTA has a cubic unit cell of the composition Na12(Si12O48). The LTA pore size can be fine-tuned by cation exchange, the pore diameters of the K+ (3A), Na+ (4a) and Ca2+ (5A) cation exchanged forms are about 0.3 nm, 0.4 nm and 0.5 nm, respectively. More and more interest has been focused on synthesis and application of zeolite LTA (NaA) membranes due to their strong hydrophilicity in combination with a small pore size of about 0.4 nm for NaA (Kita et al., 1995; Kondo et al., 1997). Actually, among the molecular sieve membranes only the zeolite LTA membrane is produced so far on an industrial scale for the dewatering of bio-ethanol (Morigami et al., 2001; Sato et al., 2008). Probably due to the relative simple composition of the synthesis solution/gel (templates-free) and the relatively low crystallization temperature (usually <100 °C), LTA zeolite membranes have been widely studied by microwave synthesis.

Microwave heating was firstly applied by Han et al. to prepare LTA zeolite membranes in 1999 (Han et al., 1999). It is found that microwave heating markedly accelerated the crystallization rate and reduced the synthesis time from several hours to 20 min. However, no gas permeation or separation results were reported. An LTA zeolite membrane prepared by using microwave heating with separation performance was reported by Xu et al. in 2000 (Xu et al., 2000). It is proposed that the fast microwave synthesis can reduce the crystallization time to form thin and high-permeance LTA zeolite membrane, as illustrated in Figure 4. Results show that microwave heating is an effective method for the synthesis of high-permeance zeolite membranes. The synthesis time of the LTA zeolite membrane prepared by microwave heating was 8 ~ 12 times shorter than that of conventional heating. While the permeances of the zeolite membrane synthesized by microwave heating was four times higher than that of the zeolite membrane synthesized by conventional heating with comparable selectivity. However, the permeation of n-C4H10 that has a larger kinetic
diameter than LTA zeolite pore size indicates that the as-synthesized LTA zeolite membranes had some intergrowth defects. It is found that the permeance and selectivity of zeolite LTA zeolite membranes prepared by microwave heating could be improved through chemical modification of the macroporous alumina support surface with a thin mesoporous top layer to prevent the penetration of the reagent into the support (Chen et al., 2005). The H₂ permeance was about 5~16 times higher than that reported previously with a H₂/C₃H₈ selectivity of 14.7.

Fig. 4. Comparison of synthesis model of zeolite membrane prepared by microwave heating and conventional heating (Xu et al., 2000).

The previous studies indicated that in microwave heating synthesis the coating on the support surface with seed crystals was usually indispensable to promote the growth of LTA zeolite membranes to avoid the formation of foreign phases (Chen et al., 2003; Xu et al., 2001). A recent study in Yang’s group in the utilization of microwave heating further supported the above results. They have developed a new strategy called “in-situ aging-microwave synthesis” method (Li et al., 2006). In the first-stage synthesis, the support is contacted with a clear synthesis solution and then in-situ aged to form germ nuclei on the support surface. In the second-stage synthesis, the consequential crystallization under fast and homogeneous microwave heating was carried out for the nucleation and crystals growth on the support surface. The “in-situ aging” stage in which germ nuclei produce was found to be necessary for the subsequent successful microwave synthesis. In this way, a much higher nucleation rate favored by microwave heating greatly enhanced the number of nuclei on the support surface. Therefore, LTA zeolite crystals could well intergrow in a short time to form high quality LTA zeolite membranes with a H₂/N₂ selectivity of 5.6.

Despite much progress in the preparation of LTA zeolite membranes, usually the separation factors for H₂ from such binary mixtures like H₂/N₂, H₂/O₂, H₂/CO₂ and H₂/CH₄ were found to be still close to the value of Knudsen diffusion (Aoki et al., 1998; Kondo et al., 1997). Therefore, the synthesis of LTA membranes with molecular sieving properties is still a challenge. Recently, we reported a novel synthesis strategy for the seeding-free preparation of dense LTA zeolite membranes by using 3-aminopropyltriethoxysilane (APTES) as covalent linker between zeolite membrane and porous Al₂O₃ support (Huang et al., 2010). As shown in Figure 5, APTES acts as a “bridge” between the zeolite layer and the support surface thus anchoring the LTA crystals, facilitating the formation of dense LTA zeolite
membrane displaying good molecular sieving performance. Making use of the function of APTES, we prepare the LTA zeolite membrane on APTES modified alumina support via microwave heating. After crystallization for 30 min at 90 °C under microwave irradiation, a dense and thin LTA zeolite membrane with a thickness of about 2.5 µm can be formed (Figure 6). Comparing with our previous report on LTA zeolite membrane on APTES modified alumina support via conventional heating, the H2 permeances can increase 2~3 times with a similar H2/N2 selectivity.

Fig. 5. Illustration of preparation of LTA membrane by using 3-aminopropyltriethoxysilane as covalent linker between the LTA zeolite layer and alumina support (Huang et al., 2010).

Fig. 6. (a) Top view and cross-section of SEM images of LTA zeolite membrane prepared with microwave heating on APTES-modified Al2O3 support.

3.2 MFI (Silicalite-1 and ZSM-5) zeolite membrane
MFI type (including Al-free silicalite-1 and its Al-containing analogue ZSM-5) zeolite membranes have been widely studied in hydrocarbon separations due to its ease crystallization as well as high thermal and chemical stabilities (Arruebo et al., 2006; Coronas et al., 1998; Funke et al., 1996). However, the studies of microwave heating synthesis of MFI zeolite membranes are rather few. This is mainly due to the fact that MFI zeolite membranes are usually prepared at a relatively high temperature of 180 °C (Lin et al., 2001) and the organic structure-directing agent TPA+ used to prepare MFI zeolite tends to degrade under microwave irradiation (Arafat et al., 1993). The first study of microwave heating synthesis of silicalite-1 zeolite membranes was reported by Koegler et al. (Koegler et al., 1997). With microwave heating, a better control is
possible over the temperature-time profile to obtain films containing 100 nm silicate-1 crystals on a silicon support. Madhusoodana et al. prepared MFI films on cordierite honeycomb substrates and alumina disks, involving the microwave heating to form a thin zeolite layer with nano-sized seeds and subsequent hydrothermal treatment to crystallize MFI zeolite films (Madhusoodana et al., 2006). It was found that the amount of zeolite layer formed on substrates by 10 min of microwave heating followed by 12 h of hydrothermal treatment was equivalent to that formed in 24 h by conventional hydrothermal treatment. The BET surface area of these samples was more than double that of samples made by conventional hydrothermal synthesis. In combination with secondary growth and microwave heating, Motuzas et al. prepared oriented silicalite-1 zeolite membranes on alumina supports (Motuzas et al., 2006), with the aim to investigate the morphology, thickness, homogeneity, crystal preferential orientation (CPO) and single gas permeation properties of the silicalite-1 membranes in correlation with the synthesis parameters. Thereafter, they have developed an ultra-rapid and reproducible synthesis method for preparation of thin and high quality (101) preferred orientation MFI membranes by coupling the microwave heating synthesis with a rapid template removal method in ozone (Motuzas et al., 2007). Tang et al. recently reported microwave synthesis of MFI-type zeolite membranes by secondary growth of nanocrystalline silicalite seed layers in pure inorganic precursors (Tang et al., 2009). The as-synthesized MFI membranes showed a rather high H$_2$/SF$_6$ selectivity of 1700 and H$_2$ permeance of 3x10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 23 ºC. Very recently, Sebastian et al. prepared MFI zeolite membranes on ceramic capillaries for pervaporation application under microwave heating with a high membrane surface area-to-volume ratio (Sebastian et al., 2010).

### 3.3 FAU zeolite membranes

The FAU zeolite (NaX and NaY) membrane, with a pore diameter of 0.74 nm, is suitable for separating large molecules, which cannot be handled effectively by MFI or LTA zeolite membrane (Jeong et al., 2003). Especially, FAU zeolite membrane display high adsorption affinity towards CO$_2$, showing high CO$_2$/N$_2$ permselectivity (Gu et al., 2005). In addition, FAU zeolite membrane was also reported for the dewatering of bio-ethanol due to its hydrophilic character (Li et al., 2002). Most of the FAU zeolite membranes were synthesized by secondary growth method using seeding technique with conventional heating (Lassinantri et al., 2000). Weh et al. made the first attempt to synthesize FAU composite membranes with either conventional heating or microwave heating (Weh et al., 2002). Results of gas permeation suggested that the separation of small gas molecules by the large and heteropolar FAU zeolite membrane was mainly based on differences of adsorption or diffusion rates, rather than on size exclusion like in LTA or MFI zeolite membranes. Thereafter, by applying the so-called “in-situ aging-microwave synthesis” method in a clear solution, Zhu et al. prepared high-quality FAU zeolite membranes with highly preferable water-selectivity in the dehydration of ethanol and isopropanol through pervaporation (Zhu et al., 2009). The method coupled in situ aging at a low temperature under conventional heating and fast crystallization at a relatively high temperature under microwave heating. It was found that an amorphous gel layer containing plenty of pre-nuclei was first formed on the support surface after in-situ aging, which was indispensable to facilitate the nucleation of FAU zeolite and suppress the formation of LTA impure phase. The following rapid crystallization process under microwave heating promoted these pre-nuclei rapidly and simultaneously to develop into crystal nuclei, and then the crystals growth through
Advances in Induction and Microwave Heating of Mineral and Organic Materials

propagation of gel network. Finally, a dense zeolite layer could be obtained without the aid of artificial seeding after the two-stage synthesis.

3.4 Zeolite T membranes
Pervaporation (PV) has gained widespread acceptance in the chemical industry as an effective process and energy-efficient technique for separation of azeotropic or close-boiling liquid mixtures (Feng & Huang, 1997). It has been applied to the dehydration of organic liquids mixtures by using zeolite membranes due to their better chemical and thermal stability than polymeric membranes (Shah et al., 2000). So far, most of the studies on dehydration of organic liquids mixtures by using zeolite membranes have been focused on LTA and FAU zeolite membrane (Kita et al., 1995; Li et al., 2002). LTA zeolite membranes with excellent separation performances for Pervaporation of water/organic liquids are currently commercially available and have been applied for the dehydration of organic solvents in a large scale (Morigami et al., 2001; Sato et al., 2008).

It is well known that, with an increase in Al content in the framework, the hydrophilicity of a zeolite increases, whereas the acid resistance simultaneously decreases because a strong acid leaches Al from the zeolite to decompose its framework structure (Muller et al., 2000). Therefore, LTA and FAU zeolite membranes cannot be applied for dehydration of organic liquids in acidic media. On the other hand, high silicate zeolite membranes such as MFI are stable toward acid, but have poor performance for the dehydration of organic liquids of the hydrophobic character (Sano et al., 1997). Zeolite T with a middle Si/Al ratio of 3-4 is considered to be less hydrophilic but more stable to acid than zeolites LTA and FAU. Thus zeolite T membranes are preferable for the dehydration of organic liquids in acidic media. Zeolite T membranes were successfully prepared by the secondary growth synthesis with conventional heating and displayed the high PV performances for the dehydration of water/organic liquid mixtures even in acidic media (Cui et al., 2004). However, it was reported that there was no selectivity found for the membranes prepared on the unseeded tubes and dense and permselective crystalline layer was formed only on the seeded tubes.

As a simple preparation method, in situ synthesis is favored preparing zeolite membranes at a large scale. Recently, in situ synthesis of zeolite T membranes was developed by Zhou et al. through repeated microwave heating (Zhou et al. 2009 (a)). The obtained membranes displayed high separation performance with H$_2$O/alcohol selectivity higher than 10000 and rather high flux. Thereafter, Zhou et al. reported high-flux αβ-oriented zeolite T membranes by microwave-assisted hydrothermal synthesis method with high reproducibility (Zhou et al. 2009 (b)). When microwave heating was introduced in the synthesis process, the properties of the membranes were significantly improved and the synthesis time was markedly shortened to several hours.

3.5 SOD zeolite membranes
In the strictest sense of the word, sodalite (SOD) is not a zeolite, because it has only 6-ring windows with a small pore size of 2.8 Å$^3$ and thus has very limited sorption capacity. However, its framework density of 17.2 T-atoms per 1000 Å$^3$ is well within the zeolite range. Only small molecules, such as He (2.6 Å), NH$_3$ (2.5 Å) and water (2.65 Å), can enter the pore of SOD. Therefore, SOD zeolite membrane can be expected to display a better performance for the separation of small molecules from larger ones. SOD zeolite membrane can be
prepared by both conventional heating and microwave heating. Khajavi et al. (Khajavi et al., 2007) have investigated the suitability of synthesis of a SOD membrane through conventional heating for water permeation. Julbe et al. (Julbe et al., 2003) have evaluated the potentialities of microwave heating for synthesis of SOD membranes on $\alpha$-Al$_2$O$_3$ asymmetric tubes. It was found that the aluminium leaching from the support lead to a disturbing phenomenon for both the reproducibility and scaling-up of the direct membrane synthesis. This negative influence could be overcome by the pre-seeding/secondary growth method, which allowed synthesizing larger and homogeneous samples with a good reproducibility.

For single gas permeation at 20–165 °C, gas through the SOD/$\alpha$-Al$_2$O$_3$ membrane was essentially governed by adsorption and surface diffusion, yielding a maximum selectivity a He/N$_2$ of 6.2 at 115 °C.

Subsequently, Xu et al. have developed the microwave synthesis of high quality pure SOD zeolite membranes on $\alpha$-Al$_2$O$_3$ supports (Xu et al., 2004). With detailed studied on the influence of microwave synthesis conditions, such as synthesis time and synthesis procedure, on the formation of SOD zeolite membrane, it was found that only 45 min was sufficient to form dense SOD zeolite membranes, which was eight times faster than the conventional heating hydrothermal synthesis. A pure SOD zeolite membrane was easily synthesized by microwave heating, while impure phases such as FAU zeolite, LTA zeolite, were usually found by conventional heating. The pure SOD zeolite membrane prepared by microwave heating displayed good gas separation performance with H$_2$/N$_2$ permselectivity larger than 1000.

### 3.6 AFI zeolite membranes

Aluminophosphate molecular sieves, known as series of AlPO$_4$-n and built from alternating AlO$_4^-$ and PO$_4^{2+}$ tetrahedra with a neutral framework, are useful in a number of applications as catalysts and adsorbent (Wilson et al., 1982). Among them, a well known AlPO$_4$-5 molecular sieve with an AFI type framework has attracted much attention due to its onedimensional 12-membered-ring channels parallel to the c-axis with a pore diameter in micropore region of 0.73 nm (Gupta et al., 1995). The aluminophosphates are usually prepared under conventional hydrothermal heating conditions with a reaction time ranging from several hours to several days (Wan et al., 2000). For the first time, Girnus et al. (Girnus et al., 1995) reported the microwave synthesis of large AlPO$_4$-5 single crystals in 1995. After 60 s of microwave heating, well-shaped hexagonal column-like large AlPO$_4$-5 crystals up to 130 µm in length and 40 µm in thickness could be obtained and were found to be effective for one dimensional molecular sieving membrane. While Mintova et al. (Mintova et al., 1998) prepared nanosized AlPO$_4$-5 molecular sieves and submicron AlPO$_4$-5 films on gold coated quartz crystal microbalances by microwave treatment of aluminophosphate precursors. It was shown that the morphology, orientation, and size of the AlPO$_4$-5 crystals could be controlled by varying the chemical composition of the initial solution and the conditions of microwave treatment of aluminophosphate precursors. The application of microwave heating leads to improved preparation of nanosized molecular sieve crystals and thin AlPO$_4$-5 films in a very short crystallization times.

### 3.7 MOFs and ZIFs membranes

Since the discovery of metal-organic frameworks (MOFs), microporous MOFs have been attracted intense attention due to their potential applications in gas adsorption and storage,
molecular separation, and catalysis (Yaghi et al., 1995; Rosi et al., 2003; Pan et al., 2006; Wu & Lin, 2007). MOFs generally consist of metal-oxygen polyhedra containing divalent (Zn$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$) or trivalent (Al$^{3+}$, Cr$^{3+}$) metal cations interconnected with a variety of organic linker molecules, resulting in tailored nanoporous materials. To date, mainly research efforts have been directed towards the synthesis of novel MOF structures through the assembly of molecular building blocks to construct tailored frameworks with tunable sizes, morphologies, structures, and desired properties (Li et al., 1999; Rowsell & Yagie, 2005). On the other hand, their highly diversified structures and pore size as well as high surface areas and specific adsorption affinities recommend MOFs as fascinating candidates for fabrication of superior molecular sieve membranes for gas separation. The potential of MOFs as membrane material has been well recognized both experimentally and computationally (Keskin & Sholl, 2007; Guo et al., 2009; Venna et al., 2010). A great deal of research effort has been focused on the preparation of supported MOF membranes. However, progress in MOF membranes is rather limited and synthesis of continuous MOF layers as membranes still remains a challenge. One major obstacle to grow MOF films on supports are the organic linkers in MOF materials, which usually do not provide additional linkage groups that can form bonds with OH groups on the surface of the supports. It was rather difficult to prepare continuous MOF membrane layers by a direct solvothermal synthesis route since the heterogeneous nucleation of MOF crystals on supports is very poor. Therefore, chemical modifications (Hermes et al., 2005) and seed coating (Ranjan & Tsapatsis, 2009) of the supports are usually indispensable to direct and control the nucleation and growth of the MOFs layers.

Recently, we have developed a novel synthesis strategy to prepare molecular sieve ZIF-22 membranes through covalent functionalization by using 3-aminopropyltriethoxysilane (APTES) as covalent linkers between the ZIF-22 layer and the titania support (Huang et al, 2010). As shown in Figure 7, in the first step, the porous alumina supports were treated with APTES for introducing the amino groups through a reaction between the ethoxy groups of the APTES and the surface hydroxyls of the Al$_2$O$_3$ support. In the second step, the amino groups of APTES coordinate to the free Zn$^{2+}$ centres and bind the growing nanocrystals directly, leading to building of a “bridge” between the growing ZIF-22 membrane and the ceramic support to promote the nucleation and growth of the ZIF-22 on the support surface. Results strongly indicate that the covalent linkages between the ZIF-22 and the alumina support indeed facilitate the formation of a compact ZIF-22 layer on the APTES modified support. After solvothermal reaction, the polycrystalline ZIF-22 has grown as a compact layer on the APTES-modified TiO$_2$. The scanning electron microscopy (SEM) top view (Fig. 8a) and cross-section (Fig. 8b) show that the ZIF-22 membrane has a thickness of about 40 µm and is well intergrown, no cracks, pinholes or other defects are visible. On the contrary, separate ZIF-22 crystals and crystal islands rather than a continuous layer are formed if the support surface was not treated with APTES before ZIF-22 crystallization. Microwave heating synthesis has been proved to be an effective way for preparation of high quality zeolite membrane in a rather short synthesis time. Rapid production of MOF crystals and films via microwave-assisted solvothermal synthesis has been recently reported (Ni & Masel 2006; Jhung et al., 2007). Yoo et al. made the first attempt to prepare MOF-5 films on carbon-coated anodic aluminium oxide (AAO) support by microwave heating synthesis (Yoo & Jeong, 2008). It was found that there was little MOF-5 deposition on bare AAO, but a coating with well-developed cubic crystallites was formed on amorphous carbon/AAO and a rather continuous film of smaller crystallites on graphite/AAO. The enhancement of
Fig. 7. Scheme of the preparation of a ZIF-22 membrane by using APTES as covalent linker between the ZIF-22 membrane and the titania support (Huang et al, 2010).

Fig. 8. (a) Top view and (b) cross-section SEM of the ZIF-22 membrane, (c, d) EDXS mapping of the sawn and polished ZIF-22 membrane (colour code: green, Zn; blue, Ti; brown is C from the polymer used for sample preparation) (Huang et al, 2010).
coating coverage on graphite/AAO was attributed to the better absorption of the microwaves. Thereafter, Yoo et al. prepared a MOF-5 seed layers on porous supports under microwaves, and then secondary growth was carried out to form a continuous MOF-5 membrane (Yoo et al., 2009). However, gas permeation results showed that the diffusion of small gas molecules ($\text{H}_2$, $\text{CH}_4$, $\text{N}_2$, and $\text{CO}_2$) through the MOF-5 membrane mainly followed the Knudsen diffusion behavior.

For MOF membranes synthesis, not only the problems with growing a dense polycrystalline layer on porous ceramic or metal supports but also the thermal and chemical stability of the MOFs have to be considered. Among the reported MOFs, zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs based on transition metals (Zn, Co) and imidazolates as linkers, have emerged as a novel type of crystalline porous material for the fabrication of molecular sieve membranes due to their zeolite-like properties such as permanent porosity, uniform pore size, exceptional thermal and chemical stability (Park et al., 2006; Phan et al., 2010). Bux et al. reported ZIF-8 membranes with molecular sieving performance by microwave-assisted synthesis method (Bux et al., 2009). With microwave heating synthesis, a crack-free, dense polycrystalline layer of ZIF-8 with thickness of about 30 µm could be formed on a porous titania support (Figure 9). Energy-dispersive X-ray spectroscopy (EDXS) reveals that there is a sharp transition between the ZIF-8 layer (Zn signal) and the titania support (Ti signal). The ZIF-8 membrane showed a good $\text{H}_2/\text{CH}_4$ selectivity higher than 10 (Figure 10), while a $\text{H}_2/\text{CO}_2$ selectivity close to Knudsen diffusion due to the fact that ZIF-8 is very flexible with pore size of 0.34 nm larger than the kinetic diameter of $\text{CO}_2$ (0.33 nm). For separation of $\text{H}_2$ from $\text{CO}_2$, ZIF-7 membrane (Li et al., 2010), which prepared on a seeded alumina support via microwave heating synthesis, displayed a better separation performance due to a smaller pore size of 0.30 nm, which is just in between the molecular size of $\text{H}_2$ (0.29 nm) and $\text{CO}_2$ (0.33 nm). After secondary growth with microwave irradiation, a well intergrown polycrystalline ZIF-7 layer without any pinholes or cracks was formed on the seeded alumina support (Figure 11a). Owing to the very thin seed layer and rather short secondary growth time by microwave heating, the thickness of ZIF-7 layer is only about 1.5 µm (Figure 11b). EDXS reveals that there is a sharp transition between the ZIF-7 layer (Zn signal) and the alumina support (Al signal) (Figure 11c). As shown in Figure 12, for both single and mixed gas permeation, there is a clear cut-off between $\text{H}_2$ and $\text{CO}_2$. The $\text{H}_2/\text{CO}_2$ ideal selectivity (calculated as the ratio of single gas permeances) and separation factor are 6.7 and 6.5, respectively, which exceed the Knudsen separation factor (~4.7). For the 1:1 binary
mixtures, the $\text{H}_2/\text{N}_2$ and $\text{H}_2/\text{CH}_4$ separation factors are 7.7 and 5.9, respectively (at 200 °C and 1 bar), both are higher than the corresponding Knudsen separation factors (3.7 and 2.8, respectively) (Li et al., 2010).

Fig. 10. Single (squares) and mixed (triangles) gas permeances for a ZIF-8 membrane as function of kinetic diameters (Bux et al., 2009).

Fig. 11. a) Top view and b) cross-section SEM images of the ZIF-7 membrane; c) EDXS-mapping of the ZIF-7 membrane, color code: orange, Zn; cyan, Al (Li et al., 2010).
Fig. 12. Permeances of single gas (circles) and from 1:1 mixtures (squares: \(\text{H}_2/\text{CO}_2\) mixture, rhombus: \(\text{H}_2/\text{N}_2\) mixture, triangles: \(\text{H}_2/\text{CH}_4\) mixture) of the ZIF-7 membrane at 200 ºC as a function of molecular kinetic diameters (Li et al., 2010).

4. Combined microwave and conventional heating modes

In the past ten years, the fast synthesis of porous molecular sieving membranes by microwave heating is relatively well established. However, progress in understanding the mechanism and engineering for the rate enhancement of the syntheses is rather limited and still remains a challenge. The crystallisation of zeotype materials is frequently constrained by limitations at the nucleation stage. Therefore, it is common practice to age reaction mixtures or to add seeds (Cundy et al., 1998), thus leading to a reduction of the induction period and to a promotion of a dominant crystalline phase. In a previous report (Slangen et al., 1997 (b)), the synthesis time of microwave heating of LTA zeolite was reduced as short as 1 min by aging the reaction mixtures for various periods, and it was suggested that the rearrangement of the synthesis mixture to yield nuclei was the bottleneck in the microwave synthesis. Jhuang et al. quantitatively investigated the selectively accelerated stage between nucleation and crystal growth by various heating modes together with microwave irradiation (MW) and conventional electric heating (CE) (Jhuang et al., 2007). It was demonstrated that the microwave irradiation accelerates not only the nucleation but also crystal growth.

For microwave synthesis of molecular sieving membranes, multiple heating modes together with microwave heating (MH) and conventional heating (CH) are usually applied since it is difficult to prepare high performance zeolite membranes by use of microwave synthesis only. Recently, we prepared uniform and dense LTA zeolite membrane by hydrothermal synthesis method together with microwave heating and conventional heating (Huang & Yang, 2007). Two heating models were cooperated to prepare uniform and dense LTA zeolite membrane, as shown in Figure 13. Before conventional heating, the pretreated support was quickly heated to 363 k for 25 min in a microwave oven. After microwave synthesis, the support surface was covered with uniform and small zeolite particles, with crystals sized of
about 2~3 μm, which were used as seeds for further hydrothermal growth. The following hydrothermal growth in an air oven at 363 K for 4 h helps to increase the membrane density, facilitating to form well inter-grown and pure LTA zeolite membrane. In the case of microwave-free hydrothermal synthesis, no dense LTA zeolite membrane could be formed, and impure phases such as cabbage-like spherical crystals as well as octahedral crystals were usually formed among the cubic LTA zeolite crystals (Huang & Yang, 2007).

A different heating model containing conventional heating (CH) and microwave heating (MH) called “in-situ aging-microwave synthesis” was developed to prepare high quality LTA zeolite membrane as shown in Figure 14 (Li et al., 2006). Firstly the support is contacted with a clear synthesis solution and then in-situ aged at 50 °C for 7 h to form germ nuclei on the support surface. And then, the consequential crystallization under fast and homogeneous microwave heating at 90 °C for 25 min was carried out for the nucleation and
growth of LTA zeolite membrane on the support surface. The “in-situ aging” stage to produce germ nuclei was found to be necessary for the subsequent successful microwave synthesis. In this way, a much higher nucleation rate favored by microwave heating greatly enhanced the number of nuclei on the support surface. Therefore, LTA zeolite crystals could well intergrow in a short time to form high quality LTA zeolite membranes. Applying this heating mode, FAU (Zhu et al., 2009) and T (Zhou et al. 2009 (b)) zeolite membrane were successfully synthesized. It should be noted that for both the above heating model, the first stage to produce nuclei as essential seeds for further growth is necessary to form dense membranes.

5. Differences between microwave and conventional hydrothermal synthesis

As shown above, microwave heating can remarkably reduce the synthesis time from days (hours) to hours (minutes). This is probably one of the best advantages of microwave synthesis compared with conventional heating synthesis. In the field of microwave synthesis of porous materials such as zeolites as well as its analogues, it has been well recognized that the microwave heating can effectively control particle size as well as size distribution (Hu et al., 2009), phases (Yoon et al., 2005), and morphology (Phiriyawirut et al., 2003). In the case of zeolite membranes, microwave synthesis also has great effect on the membrane characteristics such as crystals size, morphology and density, which essentially determine the membrane separation performances. According to the fast and homogeneous microwave heating leading to high nucleation rate, uniform and thinner zeolite membranes with higher fluxes/permeances can be obtained (Xu et al., 2000). Differences in crystals morphology of the zeolite membrane between microwave heating and conventional heating are usually observed. As shown in Figures 15 and 16, different to well-shaped cubic crystals of the LTA AlPO₄ and LTA aluminiumsilicate membrane prepared by conventional heating, the crystals of the two membranes prepared by microwave heating display a cone-shaped morphology with more uniform crystals of a smaller size. Different crystals morphology of the LTA zeolite membrane prepared by microwave heating and conventional heating were also reported by Li et al. (Li et al., 2006). The LTA zeolite membrane prepared by conventional heating was composed of well-shaped cubic LTA crystals, while the LTA zeolite membrane prepared by microwave heating consists of spherical grains without well-developed crystal faces. It was also reported that microwave heating synthesis leaded to differences in chemical composition of the zeolite membranes. Weh et al. reported the as-synthesized FAU

Fig. 15. SEM images of LTA AlPO₄ zeolite membrane prepared with (a) microwave heating synthesis (b) conventional heating synthesis.
zeolite membrane prepared by microwave heating had a slightly increased Si/Al ratio (from 1.4 to 1.8) (Weh et al., 2002). For microwave synthesis of LTA zeolite membranes, it was also found that the as-synthesized LTA zeolite membrane had a higher Si/Al ratio of 1.43 (usually 1) (Li et al., 2006).

Probably the most important difference between microwave heating and conventional heating is that of separation performances. Li et al. made a detailed comparison of separation performances of LTA zeolite membrane prepared by microwave heating and conventional heating synthesis (Li et al., 2006). LTA zeolite membrane prepared by in situ aging microwave synthesis displayed an improved permselectivity for the separation of H$_2$/N$_2$ with a selectivity of 5.6 with a high permeance. It was proposed that LTA zeolite membranes prepared by microwave heating containing spherical grains with undefined crystal facets could decrease the inter-crystalline defects, thus leading to the formation of compact defect-free zeolite membranes. The difference in separation performances of LTA zeolite membranes prepared by microwave heating and conventional heating synthesis was also confirmed by pervaporation separation (Li et al., 2007). For the membrane prepared by microwave heating (Figure 17), when the water concentration in the feed (WF) decreased from 9.6 to 0.2 wt.%, the water concentration in the permeate (WP) varied from 100.0 to 90.0

![Fig. 16. SEM images of LTA aluminiumsilicate membrane prepared with (a) microwave heating synthesis (b) conventional heating synthesis.](image)

![Fig. 17. Comparison of pervaporation performances between LTA zeolite membranes synthesized by microwave heating and conventional heating. Wp: the water concentration in permeate (Li et al., 2007).](image)
wt.%, with a permeation flux decreasing approximately linearly from 0.86 to 0.08 kgm\(^{-2}\)h\(^{-1}\). However, for the membrane prepared by conventional heating, the WP decreased rapidly when the WF was smaller 2.0 wt.%. When the WF was 1.0 wt.%, the WP was only 18.0 wt.%, while the permeate flux abnormally increased dramatically. This indicated that the membrane synthesized by conventional heating might have quite a few non-zeolitic defects. When the WF was low, the adsorbed water was not sufficient to block the defects to restrain isopropanol permeation, thus more isopropanol began to pass through the defects, which leaded to a decrease in the WP and to an increase of the permeate flux.

6. Formation mechanism of microwave synthesis of zeolite membranes

A full understanding of the formation mechanisms of zeolite membranes is of great significance to control and optimize membrane growth. Formation of a membrane could outlined in four different ways (Myatt et al., 1992), as shown in Figure 18: (1) production of nuclei and growth of crystals in the bulk solution followed by their attraction to and association with the substrate; (2) production of nuclei in the bulk solution, but diffusion to and accumulation on the substrate before significant growth has occurred; (3) diffusion of amorphous aluminosilicate material to and concentration on the substrate, providing more favorable conditions for nucleation and growth in the vicinity of the surface; (4) production of nuclei on the substrate surface, followed by growth. It is proposed that option (4) in conjunction with either option (2) or (3) was responsible for membrane formation.

Fig. 18. Four possible growth mechanisms of zeolite membrane (Myatt et al., 1992).

Up to now, the molecular understanding of the formation mechanism of zeolite membranes by microwave heating synthesis is still rather limited. In the beginning of the 1990s, good experience in the crystallization of large and phase-pure zeolite crystals was made by using microwave heating synthesis. Pioneering papers reported the successful synthesis of MFI (ZSM-5) and FAU(Y) (Arafat et al., 1993), LTA and FAU(X) (Jansen et al., 1992), AFI (CoAPO-5 (Girnus et al., 1994) and AlPO\(_4\)-5 (Girnus et al., 1995 (a) and (b)). However, there was and is still some mystery about the molecular understanding of microwave heating.
Homogeneous vs. heterogeneous heating: There can be a very high energy input by microwave absorption compared with the classical heating of autoclaves in air conditioned ovens. Microwave absorption takes place exponentially from outside to inside of an autoclave following Lambert Beer Law and leads – at least in a short time scale - to immense temperature gradients. Therefore, the synthesis mixture is heated heterogeneously by the microwaves. However, since the walls of the autoclave must be transparent for microwaves, these walls and a liquid layer near to the wall remain cold and heterogeneous nucleation is avoided.

Freely rotating water molecules: The energy of one OH-bridging bond in water is about 20 kJ/mol (Greenwood & Earnshaw, 1997), i.e. $1.13 \times 10^{-20}$ J per one water molecule. Since statistically every water molecule has about 3.4 OH-bridges, the energy of one OH-bridge is close to $3.3 \times 10^{-20}$ J which is much larger than as the energy of one microwave quantum ($1.6 \times 10^{-24}$ J). Therefore, the existence of freely rotating water molecules as super-solvent seems not to be realistic (Caro & Noack, 2006). The dipolar heating of liquids like water, methanol or DMF is more a flip-flop orientation than a free rotation.

Microwave effect: Probably there is no intrinsic microwave effect leading to a reduction of the nucleation and crystallization time compared to conventional heating if the latter can be done quick enough, e.g. by using induction heating which is based on the mobility of ions in an alternating field and results in a really homogeneous heating (Jansen, 2006). However, there are other microwave effects which originate from the quick energy input and the resulting fast heating rate which brings the zeolite batch quickly to the crystallization temperature and suppresses kinetically the formation of nuclei. Hence, microwave heating can shorten the nucleation period. Furthermore, because of the accelerated heating of the synthesis mixture, the silicate species, due to a kinetic effect, are not in their thermal equilibrium since the heating rate is faster than decomposition rate of the macromolecular silica species. It is assumed, therefore, that the transport and the reactivity of alumina and silica species to precursor building units of a zeolite or MOF crystallization are influenced by microwave heating due to the kinetics of precursor formation, kinetics of nucleation and kinetics of crystal growth.

A remarkable progress in the utilization of microwave heating synthesis of zeolite membranes was achieved by Yang et al. in the last few years who developed the “in situ aging – microwave synthesis” method (AM method) (Li et al., 2006; Zhu et al., 2009; Zhou et al. 2009 (b)). Recently, they proposed the formation mechanism of LTA zeolite membranes by using gravimetric analysis, XRD, SEM, XPS, ATR/FTIR, and gas permeation to characterize the whole formation process of LTA zeolite membranes (Li et al., 2006), as illustrated in Figure 19. In this way, a gel layer containing plenty of pre-nuclei is firstly formed on the support after in situ aging. During the following microwave heating synthesis, these pre-nuclei rapidly and simultaneously develop into crystal nuclei, and then crystal growth, and finally formation of compact LTA zeolite membranes consisting of spherical grains with undefined crystal facets. It is believed that the essential mechanism of zeolite membrane formation in microwave heating is similar to that in conventional heating. Therefore, it can be concluded that the function of microwave irradiation during zeolite membrane formation is mainly derived from its thermal effect. The acceleration effect of microwave synthesis is mainly a result of fast and simultaneous nucleation.
7. Conclusions and outlook

Microwave heating synthesis is a promising method for the facile synthesis of porous molecular sieve membranes. There is an impressive progress in the development of porous molecular sieve membranes by microwave heating synthesis technique during the past decade. The microwave technology is now available to prepare porous molecular sieve membranes with sufficient quality and reliability. More and more molecular sieve membranes with good separation performances have been successfully synthesized under microwave irradiation. The combination of microwave and conventional heating is helpful to promote the nucleation and growth of zeolite membranes thus improving the membrane separation performance. Microwave heating synthesis can remarkably reduce the synthesis time, which will open a door for the production of zeolite membranes at industrial scale. Besides markedly accelerating the rate of membrane preparation, the microwave heating can effectively control the membrane morphology, orientation, composition, and thickness, thus leading to great improvement of separation performances of the zeolite membranes. Often only a few nuclei are formed since the nucleation step of crystallization is usually kinetically controlled. The high energy input causes a quick heating up of the crystallization system. Therefore, microwave heating is especially fruitful for secondary growth of membranes, i.e. in a first step seed crystals are attached to the support surface and in a
second step these seeds grow to continuous layers at low supersaturation by microwave heating since a new homogeneous or heterogeneous nucleation is suppressed. Much effort has been made towards the understanding of the formation mechanism of zeolite membranes under microwave irradiation. Thermal effect and some specific microwave effects are proposed to be responsible for the influences of microwave heating on the synthesis of zeolites membranes. However, further research work is still needed to clarify the formation mechanism of zeolite membranes under microwave irradiation. This needs the interdisciplinary co-operation between material science, physical chemistry and microwave engineering. On the other hand, in situ characterization of the chemical and physical changes during microwave synthesis is required, such as neutron and X-ray scattering, and vibrational (Raman) spectroscopy.

8. References
Aoki, K.; Kusakabe, K. & Morooka, S. (1998). Gas permeation properties of A-type zeolite membrane formed on porous substrate by hydrothermal synthesis. *Journal of Membrane Science*, 141, 2, (April 1998) 197-205, 0376-7388
Arafat, A.; Jansen, J. C.; Ebaid, A. R. & Vanbekkum, H. (1993). Microwave preparation of zeolite-Y and ZSM-5. *Zeolites*, 13, 3, (March 1993) 162-165, 0144-2449
Arruebo, M.; Falconer, J. L. & Noble, R. D. (2006). Separation of binary C-5 and C-6 hydrocarbon mixtures through MFI zeolite membranes. *Journal of Membrane Science*, 269, 1-2, (February 2006) 171-176, 0376-7388
Baerlocher, Ch. & McCusker, L. B. Database of Zeolite Structures, http://www.iza-structure.org/databases.
Barrer, R. M. (1948). Synthesis of a zeolitic mineral with chabazite-like sorptive properties. *Journal of the Chemical Society*, (February 1948) 127-132, 03009246
Barrer, R. M.; Hinds, L. & White, E. A. (1953). The hydrothermal chemistry of silicates. Part III. Reactions of analcime and leucite. *Journal of the Chemical Society*, (May 1953) 1466-1475, 03009246
Barrer, R. M. (1981). Zeolite and their synthesis. *Zeolites*, 1, 3, (October 1981) 130-140, 0144-2449
Bein, T. (1996). Synthesis and applications of molecular sieve layers and membranes. *Chemistry of Materials*, 8, 8, (October 1996) 1636-1653, 0897-4756
Bougrin, K.; Loupy, A. & Soufiaoui, M. (2005). Microwave-assisted solvent-free heterocyclic synthesis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 6, 2-3, (October 2005) 139-167, 1389-5567
Breck, D. W.; Eversole, W. G. & Milton, R. M. (1956). New synthetic crystalline zeolites. *Journal of the American Chemical Society*, 78, 10, (May 1956) 2838-2839, 0002-7863
Bux, H.; Liang, F. Y.; Li, Y. S.; Cravillon, J.; Wiebcke, M. & Caro, J. (2009). Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *Journal of the American Chemical Society*, 131, 44, (November 2009) 16000-16001, 0002-7863
Carmona, J. G.; Clemente, R. R. & Morales, J. G. (1997). Comparative preparation of microporous VPI-5 using conventional and microwave heating techniques. *Zeolite*, 18, 5-6 (May 1997) 340-346, 0144-2449
Caro, J.; Noack, M.; Kolsch, P. & Schafer, R. (2000). Zeolite membranes-state of their development and perspective. *Microporous and Mesoporous Materials*, 38, 1, (July 2000) 3-24, 1387-1811

Caro, J. & Noack, M. (2006). Proceedings of the workshop on zeolite membranes, 9th International Conference on Inorganic Membranes, 13:978-82-14-04026-5, Lillehammer, Norway, June 2006

Caro, J. & Noack, M. (2008). Zeolite membranes– Recent developments and progress. *Microporous and Mesoporous Materials*, 115, 3, (November 2008) 215-233, 1387-1811

Carreon, M. A.; Li, S. G.; Falconer, J. L. & Noble, R. D. (2008). Alumina-supported SAPO-34 membranes for CO₂/CH₄ separation. *Journal of the American Chemical Society*, 130, 16, (April 2008) 5412–5413, 0002-7863

Casanave, D.; Giroir-Fendler, A.; Sanchez, J.; Loutaty, R. & Dalmon, J. A. (1995). Control of transport properties with a microporous membrane reactor to enhance yields in dehydrogenation reactions. *Catalysis Today*, 25, 3-4, (August 1995) 309-314, 0920-5861

Chau, J. L. H.; Tellez, C.; Yeung, K. L. & Ho, K. (2000). The role of surface chemistry in zeolite membrane formation. *Journal of Membrane Science*, 164, 1-2, (January 2000) 257-275, 0376-7388

Chen, X. B.; Yang, W. S.; Liu, J. & Lin, L. W. (2005). Synthesis of zeolite NaA membranes with high permeance under microwave radiation on mesoporous-layer-modified macroporous substrates for gas separation. *Journal of Membrane Science*, 255, 1-2, (September 2005) 201-211, 0376-7388

Cheng, Z. L.; Chao, Z. S. & Wan, H. L. (2003). Synthesis of compact NaA zeolite membrane by microwave heating method, *Chinese Chemical Letters*, 14, 8, (August 2003) 874-876, 1001-8417

Chu, P.; Dwyer, F. G. & Vartuli, J. C. (1998). Crystallization method employing microwave radiation, US Patent, 4778666, (October 1988).

Coronas, J.; Noble, R. D. & Falconer, J. L. (1998). Separations of C-4 and C-6 isomers in ZSM-5 tubular membranes. *Industrial & Engineering Chemistry Research*, 37, 1, (January 1998) 166-176, 0888-5885

Cui, Y.; Kita, H. & Okamoto, K. I. (2004). Zeolite T membrane: preparation, characterization, pervaporation of water/organic liquid mixtures and acid stability. *Journal of Membrane Science*, 236, 1, (June 2004) 17-27, 0376-7388

Cundy, C. S. (1998). Microwave techniques in the synthesis and modification of zeolite catalysts. A review. *Collection of Czechoslovak Chemical Communications*, 63, 11, (November 1998) 1699-1723, 0010-0765

Cundy, C. S.; Plaisted, R. J. & Zhao, J. P. (1998). Remarkable synergy between microwave heating and the addition of seed crystals in zeolite synthesis-a suggestion verified. *Chemical Communications*, 14, (June 1998) 1465-1466, 1359-7345

de la Hoz, A.; Diaz-Ortiz, A. & Moreno, A. (2005). Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chemical Society Reviews*, 34, 2, (2005) 164–178, 0306-0012

Feng, X. S. & Huang, R. Y. M. (1997). Liquid separation by membrane pervaporation: A review. *Industrial & Engineering Chemistry Research*, 36, 4, (April 1997) 1048-1066, 0888-5885
Funke, H. H.; Kovalchick, M. G.; Falconer, J. L. & Noble, R. D. (1996). Separation of hydrocarbon isomer vapors with silicalite zeolite membranes. *Industrial & Engineering Chemistry Research*, 35, 5, (May 1996) 1575-1582, 0888-5885

Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J. & Mingos, D. M. P. (1998). Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews*, 27 (May 1998) 213-223, 0306-0012

Girnus, I.; Hoffmann, K.; Marlow, F.; Caro, J. & Döring, G. (1994). Large CoAPO-5 single crystals: Microwave synthesis and anisotropic optical absorption. *Microporous Materials*, 2, 6, (July 1994) 543-555, 0927-6513

Girnus, I.; Jancke, K.; Vetter, R.; Richter-Mendau, J. & Caro, J. (1995). Large AlPO₄-5 crystals by microwave heating. *Zeolites*, 15, 1, (January 1995) 33-39, 0144-2449

Girnus, I.; Pohl, M. M.; Richtermendau, J.; Schneider, M.; Noack, M.; Venzke, D. & Caro, J. (1995). Synthesis of AlPO₄-5 aluminumphosphate molecular sieve crystals for membrane applications by microwave heating. *Advanced Materials*, 7, 8, (August 1995) 711-714, 0935-9648

Greenwood, N. N. & Earnshaw, A. (1997). *Chemistry of the Elements*, Butterworth-Heinemann, 0-7506-33654, Oxford

Gu, X. H.; Dong, J. H. & Nenoff, T. M. (2005). Synthesis of defect-free FAU-type zeolite membranes and separation for dry and moist CO₂/N₂ mixtures. *Industrial & Engineering Chemistry Research*, 44, 4, (February 2002) 937-944, 0888-5885

Guan, G.; Tanaka, T.; Kusakabe, K.; Sotowa, K. & Morooka, S. (2003). Characterization of AlPO₄-type molecular sieving membranes formed on a porous α-alumina tube. *Journal of Membrane Science*, 214, 2, (April 2003) 191-198, 0376-7388

Guo, H. L.; Zhu, G. S.; Hewitt, I. J. & Qiu, S. L. (2009). “Twin copper source” growth of metal-organic framework membrane: Cu₃(BTC)₂ with high permeability and selectivity for recycling H₂. *Journal of the American Chemical Society*, 131, 5, (February 2009) 1646-1647, 0002-7863

Gupta, V.; Nivarthi, S. S.; McCormick, A. V. & Davis, H. T. (1995). Evidence for single file diffusion of ethane in the molecular sieve AlPO₄-5. *Chemical Physics Letters*, 247, 4-6, (December 1995) 596-600, 0009-2614

Han, Y.; Ma, H.; Qui, S. L. & Xiao, F. S. (1999). Preparation of zeolite A membranes by microwave heating. *Microporous and Mesoporous Materials*, 30, 2-3, (September 1999) 321-326, 1387-1811

Hermes, S.; Schroder, F.; Chelmowski, R.; Woll, C. & Fischer R. A. (2005). Selective nucleation and growth of metal-organic open framework thin films on patterned COOH/CF3-terminated self-assembled monolayers on Au (111). *Journal of the American Chemical Society*, 127, 40, (October 2005) 13744-13745, 0002-7863

Hu, Y. Y.; Liu, C.; Zhang, Y. H.; Ren. N. & Tang. Y. (2009). Microwave-assisted hydrothermal synthesis of nanozeolites with controllable size. *Microporous and Mesoporous Materials*, 119, 1-3, (March 2009) 306-314, 1387-1811

Huang, A. S. & Yang, W. S. (2007). Hydrothermal synthesis of NaA zeolite membrane together with microwave heating and conventional heating. *Materials Letters*, 61, 29, (December 2007) 5129-5132, 0167-577X

Huang, A. S.; Yang, W. & Liu, J. (2007). Synthesis and pervaporation properties of NaA zeolite membranes prepared with vacuum-assisted method. *Separation and Purification Technology*, 56, 2, (August 2007) 158-167, 1383-5866
Huang, A. S.; Liang, F. Y.; Steinbach, F.; Gesing, T. M. & Caro, J. (2010). Neutral and cation-free LTA-type aluminophosphate (AlPO₄) molecular sieve membrane with high hydrogen permselectivity. *Journal of the American Chemical Society*, 132, 7, (February 2010) 2140-2141, 0002-7863

Huang, A. S.; Liang, F. Y.; Steinbach F. & Caro, J. (2010). Preparation and separation properties of LTA membranes by using 3-aminopropytriethoxysilane as covalent linker. *Journal of Membrane Science*, 350, 1-2, (March 2010) 5-9, 0376-7388

Huang, A. S. & Caro, J. (2010). Cationic polymer used to capture zeolite precursor particles for the facile synthesis of oriented zeolite LTA molecular sieve membrane. *Chemistry of Materials*, 22, 15, (August 2010) 4353-4355, 0897-4756

Huang, A. S. Bux, H.; Steinbach, F. & Caro, J. (2010). Molecular-sieve membrane with hydrogen permselectivity: ZIF-22 in LTA topology prepared with 3-aminopropytriethoxysilane as covalent linker. *Angewandte Chemie International Edition*, 49, 29, (2010) 4958-4961, 1433-7851

Jansen, J. C.; Arafat, A.; Barakat, A. K. & Van Bekkum, H. (1992). Microwave techniques in zeolite synthesis, In: *Synthesis of Microporous Materials*, Occelli, M. L. & Robson, H. (Ed.), 507-521, Van Nostrand Reinhold, 0-442-00661-6, New York

Jansen, J. C. (2006). 9th International Conference on Inorganic Membranes. *Proceedings of the workshop on zeolite membranes*, 13:978-82-14-04026-5, Lillehammer, Norway, June 2006

Jeong, B. H.; Hasegawa, Y.; Sotowa, K., I.; Kusakabe, K. & Morooka, S. (2003). Permeation of binary mixtures of benzene and saturated C-4-C-7 hydrocarbons through an FAU-type zeolite membrane. *Journal of Membrane Science*, 213, 1-2, (March 2003) 115-124, 0376-7388

Jhung, S. H.; Lee, J. H.; Yoon, J. W.; Serre, C.; Ferey, G. & Chang, J. S. (2007). Microwave synthesis of chromium terephthalate MIL-101 and its benzene sorption ability. *Advanced Materials*, 19, 1, (January 2007) 121-124, 0935-9648

Jhung, S. H.; Jin, T. H.; Hwang, Y. K. & Chang, J. S. (2007). Microwave effect in the fast synthesis of microporous materials: which stage between nucleation and crystal growth is accelerated by microwave irradiation? *Chemistry - A European Journal*, 13, 16, (September 2007) 14055-14059, 1932-7447

Julbe, A.; Motuzas, J.; Cazevielle, F.; Volle, G. & Guizard, C. (2003). Synthesis of sodalite/alpha Al₂O₃ composite membranes by microwave heating. *Separation and Purification Technology*, 32, 1-3, (July 2003) 139-149, 1383-5866

Keskin, S. & Sholl, D. S. (2007). Screening metal-organic framework materials for membrane-based methane/carbon dioxide separations. *The Journal of Physical Chemistry C*, 111, 38, (September 2007) 14055-14059, 1932-7447

Khajavi, S.; Kapteijn, F. & Jansen, J. C. (2007). Synthesis of thin defect-free hydroxy sodalite membranes: New candidate for activated water permeation. *Journal of Membrane Science*, 299, 1-2, (August 2007) 63-72, 0376-7388

Kita, H.; Horii, K.; Ohtoshi, Y.; Tanaka, K. & Okamoto, K. I. (1995), Synthesis of a zeolite NaA membrane for pervaporation of water/organic liquid mixtures. *Journal of Materials Science Letters*, 14, 3, (February 1995) 206-208, 0261-8028

Koegler, J. H.; Arafat, A.; van Bekkum, H. & Jansen, J. C. (1997). Synthesis of films of oriented silicalite-1 crystals using microwave heating. *Studies in Surface Science and Catalysis*, 105, (1997) 2163-2170, 0-444-82344-1
Kondo, M.; Komori, M.; Kita, H. & Okamoto, K. (1997). Tubular-type pervaporation module with zeolite NaA membrane. *Journal of Membrane Science*, 133, 1, (September 2000) 133-141, 0376-7388

Kusakabe, K.; Kuroda, T.; Murata, A. & Morooka, S. (1997). Formation of a Y-Type zeolite membrane on a porous α-alumina tube for gas separation. *Industrial & Engineering Chemistry Research*, 36, 3, (March 1997) 649-655, 0888-5885

Lai, R. & Gavalas, G. R. (1998). Surface seeding in ZSM-5 membrane preparation. *Industrial & Engineering Chemistry Research*, 37, 11, (November 1998) 4275-4283, 0888-5885

Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M. & Vlachos, D. G. (2003). Microstructural optimization of a zeolite membrane for organic vapor separation. *Science*, 300, 5618, (April 2003) 456-460, 0036-8075

Langa, F.; de la Cruz, P.; de la Hoz, A., Diaz-Ortiz, A. & Diez-Barra, E. (1997). Microwave irradiation: more than just a method for accelerating reactions. *Contemporary organic synthesis*, 4, 5, (October 1997) 373-386, 1350-4894

Lassianitti, M.; Hedlund, J. & Sterte, J. (2000). Faujasite-type films synthesized by seeding. *Microporous and Mesoporous Materials*, 38, 1, (July 2000) 25-34, 1387-1811

Li, H.; Eddaoudi, M.; O’Keeffe, M. & Yaghi, O. M. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, 402, 6759, (November 1999) 276-279, 0028-0836

Li, S.; Tuan, V. A.; Falconer, J. L. & Noble, R. D. (2002). X-type zeolite membranes: preparation, characterization, and pervaporation performance. *Microporous and Mesoporous Materials*, 53, 1-3, (June 2002) 59-70, 1387-1811

Li, Y. S.; Chen, H. L.; Liu, J. & Yang, W. S. (2006). Microwave synthesis of LTA zeolite membranes without seeding. *Journal of Membrane Science*, 277, 1-2, (June 2006) 230-239, 0376-7388

Li, Y. S.; Liu, J. & Yang, W. S. (2006). Formation mechanism of microwave synthesized LTA zeolite membranes, *Journal of Membrane Science*, 281, 1-2, (September 2006) 646-657, 0376-7388

Li, Y. S.; Chen, H. L.; Liu, J.; Li, H. B. Yang, W. S. (2007). Pervaporation and vapor permeation dehydration of Fischer-Tropsch mixed-alcohols by LTA zeolite membranes. *Separation and Purification Technology*, 57, 1, (October 2007) 140-146, 1383-5866

Li, Y. S. & Yang, W. S. (2008). Microwave synthesis of zeolite membranes: A review. *Journal of Membrane Science*, 316, 1-2, (May 2008) 3-17, 0376-7388

Li, Y. S.; Liang, F. Y.; Bux, H.; Feldhoff, A.; Yang, W. S. & Caro, J. (2010). Molecular sieve membrane: supported metal-organic framework with high hydrogen selectivity. *Angewandte Chemie International Edition*, 49, 3, (2010) 548-551, 1433-7851

Lidstrom, P.; Tierney, J.; Wathey, B. & Westman, J. (2001). Microwave assisted organic synthesis—a review. *Tetrahedron*, 57, 51, (December 2001) 9225-9283, 0040-4020

Lin, X.; Kita, H. & Okamoto K. (2001). Silicalite membrane preparation, characterization, and separation performance. *Industrial & Engineering Chemistry Research*, 40, 19, (September 2001) 4069-4078, 0888-5885

Lin, Y. S. (2001). Microporous and dense inorganic membranes: current status and prospective. *Separation and Purification Technology*, 25, 1-3, (October 2001) 39-55, 1383-5866
Lovallo, M. C. & Tsapatsis, M. (1996). Preferentially oriented submicron silicalite membranes. *AIChE Journal*, 42, 11, (1996) 3020-3029, 0001-1541.

Ma, Y. H.; Zhou, Y. J.; Poladi, R. & Engwall, E. (2001). The synthesis and characterization of zeolite A membranes. *Separation and Purification Technology*, 25, 1-3, (October 2001) 235-240, 1383-5866

Madhusoodana, C. D.; Das, R. N.; Kameshima, Y. & Okada, K. (2006). Microwave-assisted hydrothermal synthesis of zeolite films on ceramic supports. *Journal of Materials Science*, 41, 5, (March 2006) 1481-1487, 0022-2461

Maesen, T. (2007). The zeolite scene–An Overview, in: *Introduction to zeolite science and practice*, Jiří Čejka, Herman van Bekkum, Avelino Corma and Ferdi Schüth (Ed.), (1-9), Elsevier, 978-0-444-53063-9, Hungary

Mintova, S.; Mo, S. & Bein, T. (1998). Nanosized AlPO₄-5 molecular sieves and ultrathin films prepared by microwave synthesis. *Chemistry of Materials*, 10, 12, (December 1998) 4030-4036, 0897-4756

Morigami, Y.; Kondo, M.; Abe, J., Kita, H. & Okamoto, K. (2001). The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane. *Separation and Purification Technology*, 25, 1-3, (October 2001) 251-260, 1383-5866

Motuzas, J.; Julbe, A.; Noble, R. D.; van der Lee, A. & Beresnevicius, Z. J. (2006). Rapid synthesis of oriented silicalite-1 membranes by microwave-assisted hydrothermal treatment. *Microporous and Mesoporous Materials*, 92, 1-3, (June 2006) 259-269, 1387-1811

Motuzas, J.; Heng, S.; Lau, P. P. S. Z.; Yeung, K. L.; Beresnevicius, Z. J. & Julbe, A. (2007). Ultra-rapid production of MFI membranes by coupling microwave assisted synthesis with either ozone or calcination treatment. *Microporous and Mesoporous Materials*, 99, 1-2, (February 2007) 197-205, 1387-1811

Muller, M.; Harvey, G. & Prins, R. (2000). Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl₄ by H-1, Si-29 and Al-27 MAS NMR. *Microporous and Mesoporous Materials*, 34, 2, (February 2000) 135-147, 1387-1811

Myatt, G. J.; Budd, P. M.; Price, C. & Carr, S. W. (1992). Synthesis of a zeolite NaA membrane. *Journal of Materials Chemistry*, 2, 10, (October 1992) 1103-1104, 0959-9428

Ni, Z. & Masel, R. I. (2006). Rapid production of metal-organic frameworks via microwave-assisted solvothermal synthesis. *Journal of the American Chemical Society*, 128, 38, (September 2006) 12394-12395, 0002-7863

Nikolakis, V.; Xomeritakis, G.; Abibi, A.; Dickson, M.; Tsapatsis, M. & Vlachos, D. G. (2001). Growth of a faujasite-type zeolite membrane and its application in the separation of saturated/unsaturated hydrocarbon mixtures. *Journal of Membrane Science*, 184, 2, (March 2001) 209-219, 0376-7388

Nishiyama, N.; Ueyama, K. & Matsukata, M. (1996). Synthesis of defect-free zeolite-alumina composite membranes by a vapor-phase transport method. *Microporous Materials*, 7, 6, (December 1996) 299-308, 0927-6513

Nishiyama, N.; Ueyama, K. & Matsukata, M. (1997). Gas permeation through zeolite-alumina composite membranes. *AIChE Journal*, 43, 11, (1997) 2724-2730, 0001-1541

Nuchter, M.; Muller, U.; Ondruschka, B.; Tied, A. & Lautenschlager, W. (2003). Microwave-assisted chemical reactions. *Chemical Engineering & Technology*, 26, 12, (December 2003) 1207-1216, 0930-7516
Application of Microwave Heating on the Facile Synthesis of Porous Molecular Sieve Membranes

Nuchter, M.; Ondruschka, B.; Bonrath, W. & Gum, A. (2004). Microwave assisted synthesis—a critical technology overview. *Green Chemistry*, 6, 2, (2004) 128–141, 1463-9262

Pan, L.; Olson, D. H.; Ciemnolonski, L. R.; Heddy, R. & Li, J. (2006). Separation of hydrocarbons with a microporous metal-organic framework. *Angewandte Chemie International Edition*, 45, 4, (2006) 616-619, 1433-7851

Panzarella, B.; Tompsett, G.; Conner, W. C. & Jones, K. (2007). In Situ SAXS/WAXS of zeolite microwave synthesis: NaY, NaA, and Beta zeolites. *Chemphyschem*, 8, 3, (February 2007) 357-369, 1439-4235

Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O’Keeffe, M. & Yaghi, O. M. (2006). Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proceedings of the National Academy of Sciences of the United States of America*, 103, 27, (July 2006) 10186-10191, 0027-8424

Park, M. & Komarneni, S. (2006). Rapid synthesis of AlPO₄-11 and cloverite by microwave-hydrothermal processing. *Microporous and Mesoporous Materials*, 20, 1-3, (February 2006) 39-44, 1387-1811

Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O’Keeffe, M. & Yaghi, O. M. (2010). Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. *Accounts of Chemical Research*, 43, 1, (January 2010) 58-67, 0001-4842

Phiriyawirut, P.; Magaraphan, R.; Jamieson, A. M. & Wongkasemjit, S. (2003). Morphology study of MFI zeolite synthesized directly from silatrane and alumatrane via the sol-gel process and microwave heating. *Microporous and Mesoporous Materials*, 64, 1-3, (October 2003) 83-93, 1387-1811

Ranjan, R. & Tsapatsis, M. (2009). Microporous Metal organic framework membrane on porous support using the seeded growth method. *Chemistry of Materials*, 21, 20, (October 2009) 4920-4924, 0897-4756

Rao, K. J.; Vaidhyanathan, B.; Ganguli, M. & Ramakrishnan, P. A. (1999). Synthesis of inorganic solids using microwaves. *Chemistry of Materials*, 11, 4, (April 1999) 882-895, 0897-4756

Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M. & Yaghi, O. M. (2003). Hydrogen storage in microporous metal-organic frameworks. *Science*, 300, 5622, (May 2003) 1127-1129, 0036-8075

Rowsell, J. L. C. & Yaghi, O. M. (2005). Strategies for hydrogen storage in metal-organic frameworks. *Angewandte Chemie International Edition*, 44, 30, (2005) 4670-4679, 1433-7851

Sano, T.; Ejiri, S.; Yamada, K.; Kawakami, Y. & Yanagishita, H. (1997). Separation of acetic acid-water mixtures by pervaporation through silicalite membrane. *Journal of Membrane Science*, 123, 2, (January 1997) 225-233, 0376-7388

Sathupunya, M, Gulari, E, & Wongkasemjit S. (2002). ANA and GIS zeolite synthesis directly from aluminatr and silatr via the sol-gel process and microwave technique. *Journal of the European Ceramic Society*, 22, 13, (December 2002) 2305-2314, 0955-2219

Sato, K.; Aoki, K.; Sugimoto, K.; Izumi, K.; Inoue, S.; Saito, J.; Ikeda, S. & Nakane, T. (2008). Dehydrating performance of commercial LTA zeolite membranes and application to fuel grade bio-ethanol production by hybrid distillation/vapor permeation process. *Microporous and Mesoporous Materials*, 115, 1-2, (October 2008) 184-188, 1387-1811
Sebastian, V.; Mallada, R.; Coronas, J.; Julbe, A.; Terpstra, R. A. & Dirrix, R. W. J. (2010). Microwave-assisted hydrothermal rapid synthesis of capillary MFI-type zeolite-ceramic membranes for pervaporation application. *Journal of Membrane Science*, 355, 1-2, (June 2010) 28-35, 0376-7388

Shah, D.; Kissick, K.; Ghorphade, A.; Hannah, R. & Bhattacharyya, D. (2000). Pervaporation of alcohol-water and dimethylformamide-water mixtures using hydrophilic zeolite NaA membranes: mechanisms and experimental results. *Journal of Membrane Science*, 179, 1-2, (November 2000) 185-205, 0376-7388

Sirikittikul, D.; Fuongfuchat, A. & Booncharoen, W. (2009). Chemical modification of zeolite beta surface and its effect on gas permeation of mixed matrix membrane. *Polymers for Advanced Technologies*, 20, 10, (October 2009) 802-810, 1042-7147

Slangan, P. M.; Jansen, J. C. & van Bekkum, H. (1997). (a) Induction heating: A novel tool for zeolite synthesis. *Zeolites*, 18, 1, (January 1997) 63-66, 0144-2449; (b) The effect of ageing on the microwave synthesis of zeolite NaA. *Microporous Materials*, 9, 5-6, (May 1997) 259-265, 0927-6513

Somani, O. G.; Choudhari, A. L.; Rao B. S. & Mirajkar, S. P. (2003). Enhancement of crystallization rate by microwave radiation: synthesis of ZSM-5. *Materials Chemistry and Physics*, 82, 3, (December 2003) 538-545, 0254-0584

Srinivasan, A. & Grutzeck, M. W. (1999). The adsorption of SO$_2$ by zeolites synthesized from fly ash. *Environmental Science & Technology*, 33, 9, (May 1999) 1464-1469, 0013-936X

Tang, Z.; Kim, S. J.; Gu, X. H. & Dong, J. H. (2009). Microwave synthesis of MFI-type zeolite membranes by seeded secondary growth without the use of organic structure directing agents. *Microporous and Mesoporous Materials*, 118, 1-3, (February 2009) 224-231, 1387-1811

Tavolaro, A. & Drioli, E. (1999). Zeolite membranes. *Advanced Materials*, 11, 12, (August 1999) 975-996, 0935-9648

Tomita, T.; Nakayama, K. & Sakai, H. (2004). Gas separation characteristics of DDR type zeolite membrane. *Microporous and Mesoporous Materials*, 68, 1-3, (March 2004) 71-75, 1387-1811

Tompsett, G. A.; Conner, W. C. & Yngvesson, K. S. (2006). Microwave synthesis of nanoporous materials. *Chemphyschem*, 7, 2, (February 2006) 296-319, 1439-4235

van de Graaf, J. M.; van der Bijl, E.; Stol, A.; Kapteijn, F. & Moulijn, J. A. (1998). Effect of operating conditions and membrane quality on the separation performance of composite silicalite-1 membranes. *Industrial & Engineering Chemistry Research*, 37, 10, (October 1998) 4071-4083, 0888-5885

Venna, S. R. & Carreon, M. A. (2010). Highly permeable zeolite imidazolate framework-8 membranes for CO$_2$/CH$_4$ separation. *Journal of the American Chemical Society*, 132, 1, (January 2010) 76-78, 0002-7863

Von Hippel, A. R. (1954). *Dielectric and Waves*, Technology Press of MIT and John Wiley, New York

Wan, Y.; Williams, C. D.; Duke, C. V. A. & Cox, J. J. (2000). Systematic studies on the effect of water content on the synthesis, crystallisation, conversion and morphology of AlPO$_4$-5 molecular sieve. *Journal of Materials Chemistry*, 10, 12, (2000) 2857-2862, 0959-9428
Wang, Z. B.; Mitra, A. P.; Wang, H. T.; Huang, L. M. & Yan, Y. S. (2001). Pure silica zeolite films as low-k dielectrics by spin-on of nanoparticle suspensions. *Advanced Materials*, 13, 19, (October 2001) 1463-1466, 0935-9648

Weh, K.; Noack, M.; Sieber, I. & Caro, J. (2002). Permeation of single gases and gas mixtures through faujasite-type molecular sieve membranes. *Microporous and Mesoporous Materials*, 54, 1-2, (July 2002) 27-36, 1387-1811

Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R. & Flanigen, E. M. (1982). Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids. *Journal of the American Chemical Society*, 104, 4, (1982) 1146-1147, 0002-7863

Wu, C. D. & Lin, W. B. (2007). Heterogeneous asymmetric catalysis with homochiral metal-organic frameworks: Network-structure-dependent catalytic activity. *Angewandte Chemie International Edition*, 46, 7, (2007) 1075-1078, 1433-7851

Xomeritakis, G.; Gouzinis, A.; Nair, S.; Okubo, T.; He, M. Y.; Overney, R. M. & Tsapatsis, M. (1999). Growth, microstructure, and permeation properties of supported zeolite (MFI) films and membranes prepared by secondary growth. *Chemical Engineering Science*, 54, 15-16, (August 1999) 3521-3531, 0009-2509

Xu, X. C.; Yang, W. S.; Liu, J. & Lin, L.W. (2000). Synthesis of a high-permeance NaA zeolite membrane by microwave heating. *Advanced Materials*, 12, 3, (February 2000) 195-198, 0935-9648

Xu, X. C.; Yang, W. S.; Liu, J. & Lin, L.W. (2001). Synthesis of NaA zeolite membrane by microwave heating. *Separation and Purification Technology*, 25, 1-3, (October 2001) 241-249, 1383-5866

Xu, X. C.; Bao, Y.; Song, C. S.; Yang, W. S.; Liu, J. & Lin, L. W. (2004). Microwave-assisted hydrothermal synthesis of hydroxy-sodalite zeolite membrane. *Microporous and Mesoporous Materials*, 75, 3, (November 2004) 173-181, 1387-1811

Yaghi, O. M.; Li, G. & Li, H. (1995). Selective binding and removal of guests in a microporous metal-organic framework. *Nature*, 378, 6558, (December 1995) 703-706, 0028-0836

Yan, Y. S.; Davis, M. E. & Gavalas, G. R. (1995). Preparation of zeolite ZSM-5 membranes by in situ crystallization on porous \(\alpha\)-Al\(_2\)O\(_3\). *Industrial & Engineering Chemistry Research*, 34, 5, (May1995) 1152-1631, 0888-5885

Yoo, Y. & Jeong, H. K. (2008). Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition. *Chemical Communications*, 21, (June 2008) 2441-2443, 1359-7345

Yoo, Y.; Lai, Z. P. & Jeong, H. K. (2009). Fabrication of MOF-5 membranes using microwave-induced rapid seeding and solvothermal secondary growth. *Microporous and Mesoporous Materials*, 123, 1-3, (June 2009) 100-106, 1387-1811

Yoon, J. W.; Jhung, S. H.; Kim, Y. H.; Park, S. E. & Chang, J. S. (2005). Selective crystallization of SAPO-5 and SAPO-34 molecular sieves in alkaline condition: Effect of heating method. *Bulletin of the Korean Chemical Society*, 26, 4, (April 2005) 558-562, 0253-2964

Yu, M.; Falconer, J. L.; Amundsen, T. J.; Hong, M. & Noble, R. D. (2007). A controllable nanometer-sized valve. *Advanced Materials*, 19, 19, (October 2007) 3032-3036, 0935-9648

Zhou, H.; Li, Y. S.; Zhu, G. Q.; Liu, J. & Yang, W. S. (2009). (a) Preparation of zeolite T membranes by microwave-assisted in situ nucleation and secondary growth.
Materials Letters, 63, 2, (January 2009) 255-257, 0167-577X; (b) Microwave-assisted hydrothermal synthesis of a&b-oriented zeolite T membranes and their pervaporation properties. Separation and Purification Technology, 65, 2, (February 2009) 164-172, 1383-5866

Zhu, G. Q.; Li, Y. S.; Zhou, H.; Liu, J. & Yang, W. S. (2009). Microwave synthesis of high performance FAU-type zeolite membranes: Optimization, characterization and pervaporation dehydration of alcohols. Journal of Membrane Science, 337, 1-2, (July 2009) 47-54, 0376-7388
Advances in Induction and Microwave Heating of Mineral and Organic Materials
Edited by Prof. Stanisław Grundas

ISBN 978-953-307-522-8
Hard cover, 752 pages
Publisher InTech
Published online 14, February, 2011
Published in print edition February, 2011

The book offers comprehensive coverage of the broad range of scientific knowledge in the fields of advances in induction and microwave heating of mineral and organic materials. Beginning with industry application in many areas of practical application to mineral materials and ending with raw materials of agriculture origin the authors, specialists in different scientific area, present their results in the two sections: Section 1-Induction and Microwave Heating of Mineral Materials, and Section 2-Microwave Heating of Organic Materials.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Aisheng Huang and Jürgen Caro (2011). Application of Microwave Heating on the Facile Synthesis of Porous Molecular Sieve Membranes, Advances in Induction and Microwave Heating of Mineral and Organic Materials, Prof. Stanisław Grundas (Ed.), ISBN: 978-953-307-522-8, InTech, Available from: http://www.intechopen.com/books/advances-in-induction-and-microwave-heating-of-mineral-and-organic-materials/application-of-microwave-heating-on-the-facile-synthesis-of-porous-molecular-sieve-membranes