Tubular MFI Zeolite Membranes Made by In-Situ Crystallization

Kazemzadeh, Akram; Bayati, Behruz; Kalantari, Neda; Babaluo, Ali Akbar*[+]

Nanostructure Materials Research Center (NMRC),Chemical Engineering Department,
Sahand University of Technology, Tabriz, I.R. IRAN

ABSTRACT: *Polycrystalline MFI zeolite membranes were prepared on α-alumina tubular support by hydrothermal treatments at 413 K. The synthesized zeolite membranes were characterized by XRD, SEM and single gas permeation. The influence of hydrothermal treatment steps and the calcination time on the zeolite layer formation were investigated. MFI zeolite membrane prepared by four subsequent hydrothermal treatments and calcined at 673K for 30 h had optimum quality from morphological and crystalline point of view. The grown MFI zeolite layer was uniform with about 20 µm thickness and well-intergrown zeolite crystals.*

KEY WORDS: *MFI zeolite, Membrane, In-situ crystallization, Calcination time, Hydrothermal treatment steps.*

INTRODUCTION

Zeolites are crystalline aluminosilicates with pore sizes between 0.3 and 1.3 nm. Zeolite membranes are polycrystalline films of these materials grown on porous supports that provide mechanical stability. Due to unique properties of zeolites such as their pore size in the range of molecular dimensions and their high chemical and thermal stability, zeolite membranes have high potential to perform many industrially important separations [1]. MFI-type zeolite possesses well-defined micropores, the size of which is 0.50–0.55 nm. Unique specification of MFI zeolite such as suitable pore size, good selectivity, thermal stability, chemical resistance and high lifetime makes this type of zeolite a suitable candidate for memberane applications. Due to these properties, MFI zeolite can be used in separation of hydrocarbons such as n-C_4H_{10} and i-C_4H_{10} [2-4]. During the last few years the various numbers of papers on the preparation of MFI-type zeolite membranes has strongly increased [5]. MFI zeolite structure, including ZSM-5 and alumina-free analog silicalite, has a tow-dimensional pore system consisting of sinusoidal channels running in the {1 0 0} direction and intersecting straight channels running along the {0 1 0} direction [6]. In the separation of linear and nonlinear hydrocarbons, porous structure of MFI zeolite membranes permits the linear molecules to enter in sinusoidal or straight channels easier and faster, but it does not permit the branched hydrocarbons to enter the channels easily [7].

To prepare a zeolite membrane, however, the crystals must grow in an interlocking fashion to form a continuous layer free of nonzeolitic transmembrane pathways. This layer must be thin to provide good permeance, and yet mechanically durable; hence, it must be grown on some porous support element, e.g., a flat plate or tube.

---

* To whom correspondence should be addressed.

\+ E-mail: a.babaluo@sut.ac.ir

1021-9986/12/2/ 8/$/2.80

In-situ crystallization is the most common preparation method of zeolite membranes [8-11]. This method involves crystallization of a zeolite layer onto a porous support from the zeolite precursor gel which is in contact with the support in an autoclave. After the specified reaction time, the autoclave was removed from the oven and quenched with water. After cooling, the support was washed thoroughly with water and dried at identified temperature and time. Subsequent to hydrothermal synthesis and drying, it was calcined to free the zeolite from the trapped organic and its decomposition products. MFI zeolite can be synthesized with Si/Al ratio in the range 5-∞ [12]. For the crystallization of highly siliceous MFI, organic template molecules (such as TPAOH, TPABr, etc.) are added to the synthesis mixture. These molecules are trapped in the pores of the as-synthesized material. In order to make the pores accessible to guest molecules, the organic templates are removed by thermal decomposition at high temperature, a process denoted "calcination". Several studies have shown that cracks tend to form in the zeolite membranes during calcination due to the thermal stress, which is caused by the difference in thermal expansion between zeolite layer and support and/or by changing in lattice parameters of zeolite crystals as a consequence of the removal of templates The MFI structure experiences a strong contraction during template removal, which occurs in the approximate temperature range 300-500 ºC [13-14]. The calcination of zeolite membranes is usually performed for several hours at 400–500 ºC with a slow heating rate from ambient to the calcination temperature. The intensity of some diffraction peaks is highly affected by the template molecules occluded in the as-synthesized structure. As the molecules are removed, the intensity of those peaks changes. The most spectacular change can be observed for the low-angle peaks (1 0 1 / 0 1 1 at $2\theta=7.95^\circ$, 2 0 0 / 0 2 0 at $2\theta=8.9^\circ$). The agreement between TPA occupancy and the intensity of the low angle peaks during heating indicates a dependency between template occupancy and peak intensity [6].

In this work, MFI-type zeolite membranes were prepared from a synthesis solution containing organic template molecules on α-Al_2O_3 support by in-situ crystallization with different subsequent hydrothermal treatment steps. The influence of the calcination time as a key factor on crystallinity and morphology of the synthesized MFI zeolite membrane was also investigated. Considering the important role of zeolite layers number to obtain the minimum defect-free thickness, the effect of the number of hydrothermal treatment steps on the transport properties was studied.

EXPERIMENTAL SECTION

Materials

Porous α-alumina tubes (70 mm long, 12 mm OD, 9 mm ID, average pore diameter 570 nm, open porosity: 47 vol%) was used as supports for the preparation of zeolite membranes which were prepared by gel casting as a novel forming method in our laboratory [15]. Other materials used in this study were tetraethyl orthosilicate (TEOS; 98%, ACROS ORGANICS) as SiO_2 source, sodium hydroxide (NaOH: 98%, MERCK) as alkali source, tetrapropylammonium bromide (TPABr; >99%, MERCK) as organic template and deionized water.

Membranes preparation

A synthesis solution was prepared by mixing TetraEthyl OrthoSilicate (TEOS), TetraPropylAmmonium Bromide (TPABr), NaOH and deionized water. The composition of the solution was 1 SiO_2:0.05 Na_2O:0.10 TPABr: 80 H_2O on a molar basis. The zeolite synthesis solution was stirred for 1 h at room temperature. The hydrothermal treatments to grow zeolite membranes on the support were performed in a stainless steel autoclave including teflon holder. The dry supports were positioned on the bottom of the empty autoclave and the zeolite synthesis solution was carefully poured into the autoclave along the supports. The autoclave was closed and heated under autogenous pressure at 413K for 24 h to form a silicalite-1 layer on the support. The vessel was then quenched by water, and the zeolite/α-alumina composite membrane was recovered. After washing with deionized water for several times, the membrane was rinsed into deionized water for 1 h to remove excess materials, and then was dried in air at 333K for 12 h. The MFI zeolite membranes were prepared by 1-4 subsequent hydrothermal treatment steps. After of each step, permeability of membrane was measured by N_2. Finally the membrane was calcined in air at 673K for different times to remove the template

Membrane characterization

The crystallographic properties of the supported MFI membranes were examined with a TW3710 Philips

X’Pert Diffraktometer X-ray diffractometer using CuKα_1 radiation (λ=1.54 Å) operating at 40 kV and 50 mA. The thickness of the membrane layer and the morphology of its external surface were determined by scanning electron microscopy (SEM, LEO 440I, 3×10^5, LEO, UK).

Gas permeation experiments

Single gas permeation measurement was carried out to evaluate the quality and performance of the membranes. Measurements of H_2, N_2 and pentane permeation were made at 318, 346 and 373K and at different pressure differences up to 0.1 MPa. Permeance was measured using the stainless steel permeator. The synthesized silicalite-1 membranes were sealed in a permeation module with the zeolite membrane facing the high-pressure side. Feed gas flows along outside of the membrane and permeated gas flow rate were measured on inner side of the membrane at pressure 1 bar. Pressure differences across the membrane were obtained by varying pressure on the upstream side and keeping the downstream pressure constant at 1 bar. Pressure in shell side of the membrane module was monitored via a pressure gauge.

RESULTS AND DISCUSSION

Hydrothermal treatment steps effect

In Fig. 1, XRD patterns are given for different layers of the uncalcined silicalite zeolite film grown on the support. The XRD pattern of the membrane is a combination of the diffraction patterns of alumina support and MFI zeolite layer. The data in first layer (Fig1a) shows that the membrane consists of randomly crystals of α-alumina (high intensity) and randomly oriented crystals of silicalite-1 (low intensity). With increasing the number of the layers, the peaks of MFI zeolite are predominant and the peaks of α-alumina vanish, which can be attributed to complete formation of MFI zeolite film in the fourth layer on the support.

SEM micrographs of the non-calcined silicalite-1 zeolite membranes surface with two and four hydrothermal synthesis steps have been presented in Fig. 2a and c respectively, confirming the formation of a continuous and defect-free zeolite layer on the outer surface of α-alumina tubular support.

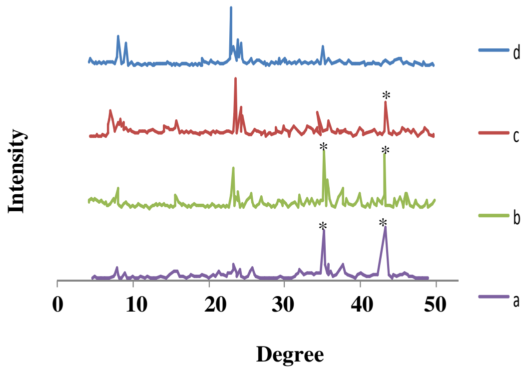

Fig. 1: XRD patterns of the silicalite-1 /α-alumina composite membranes at the first (a); second (b); third (c) and fourth (d) hydrothermally synthesized layers (the peaks originating from the α- alumina support were labeled with "").*

Fig. 2b and d are cross-section of the non-calcined silicalite-1/α-alumina composite membranes. It can be seen that the silicalite-1 thin film with ~ 20µm thickness was formed onto the α-alumina support surface after four synthesis steps. In other words, after four synthesis steps, the surface of α-alumina supports are completely covered with uniform layer of randomly oriented silicalite-1 crystals.

Table 1 shows the single gas (N_2) permeation of MFI zeolite membranes at room temperature as a function of the number of hydrothermal synthesis steps. The single gas permeation was measured after drying the membrane at 333K for 12 h. Single gas permeation data decrease with increasing the number of layers and after the fourth layers, the prepared zeolite membrane is not permeable which can be due to the presence of TPA^+ ions in the zeolite pores. This trend verifies the formation of uniform and defect-free silicalite-1 zeolite layer on the α-alumina support surface, as shown in SEM micrographs.

Calcination time effect

Fig. 3 shows the XRD patterns of the synthesized MFI zeolite membranes with different calcination times. The relative intensity of the characteristic peaks changes with calcination time. Intensity of some reflections increases whereas the intensity of others diminishes as the calcination time increases. The strongest increase intensity is observed at $2\theta = 8.0°$, which is due to {1 0 1} crystal plane. This means that the prepared membranes consist of the [*h* 0 *h*] oriented MFI-type zeolite crystallites as a dominant crystalline phase which is desirable in the synthesis of high performance MFI zeolite membranes. With increasing the calcination time

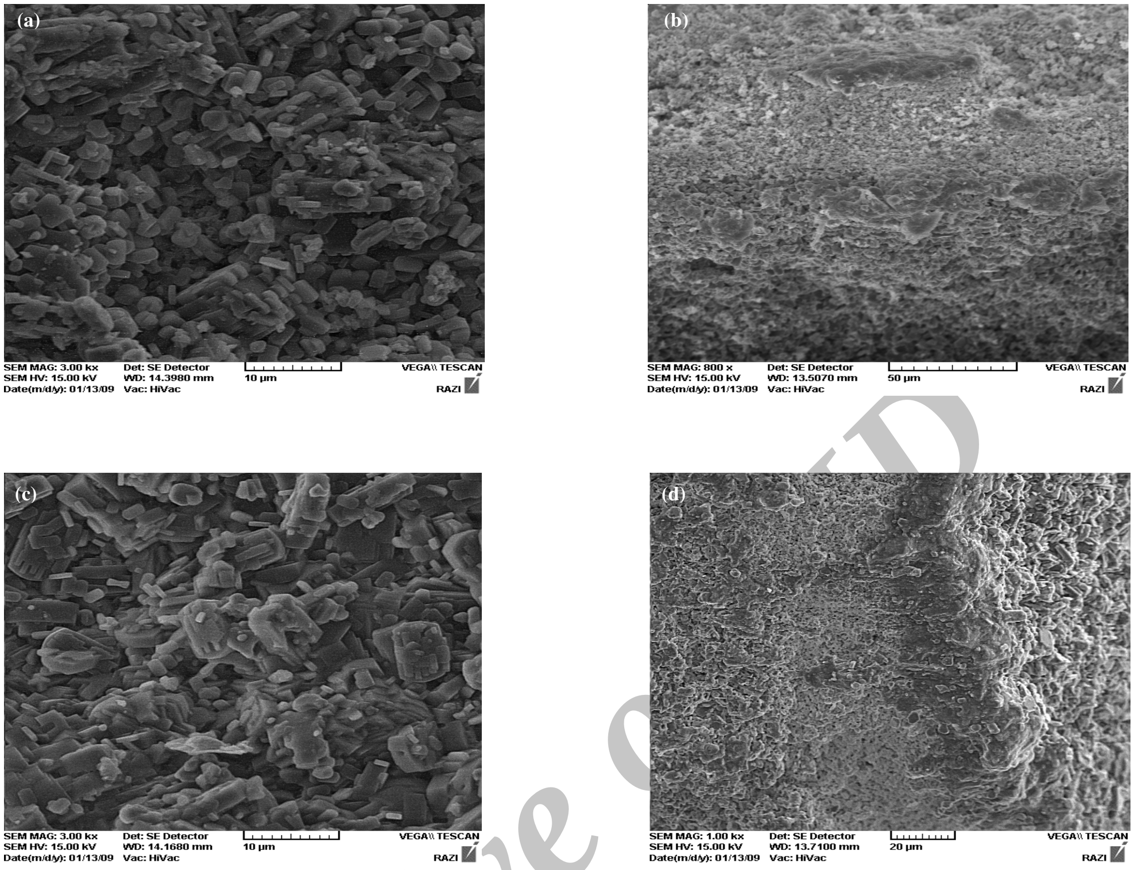

Fig. 2: SEM micrographs of the non-calcined supported MFI zeolite membranes: surface (a) and cross section (b) of the membrane with two and surface (c) and cross section (d) of the membrane with four hydrothermally synthesized layers.

Table 1: Single gas permeation of the non-calcined MFI zeolite membranes at room temperature with different number of hydrothermal synthesis steps.

Multi-layer zeolite membrane	Permeance*10^7 N_2 (mol/m^2.s.Pa)
without zeolite layer (support)	287
The first zeolite layer	197
The second zeolite layer	48.4
The third zeolite layer	6.87
The fourth zeolite layer	0

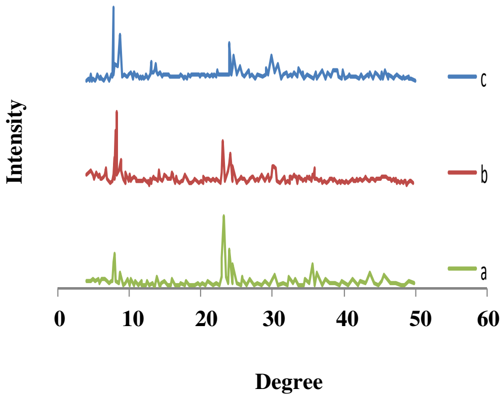

Fig. 3: XRD patterns of the MFI zeolite membranes (with four hydrothermal synthesis steps) calcined at 673K after different calcination times 4h (a), 8 h (b) and 30 h (c).

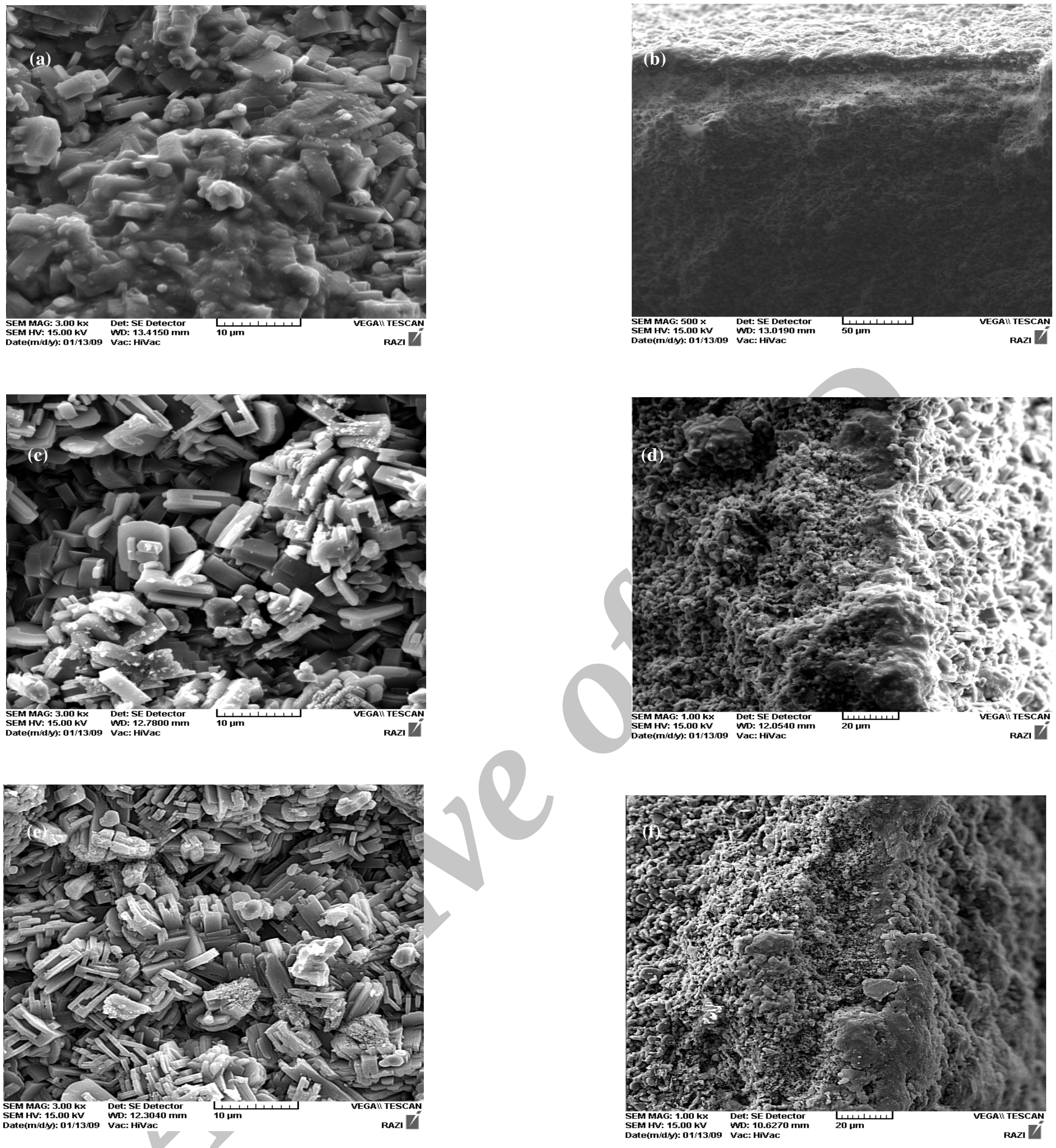

Fig. 4: SEM micrographs of the supported MFI zeolite membrane (with four hydrothermal synthesis steps): surface and cross section of the membranes calcined at 673K after different calcination times 4 h (a,c); 8h (c,d); 30 h (e,f).

and then removing of TPA$^+$ ions, MFI membrane with high crystalline structure was formed which is in good agreement with literature [16].

Fig. 4 shows SEM micrographs of the supported zeolite MFI membranes prepared by four subsequent hydrothermal treatments and calcined at 673 K after different calcination times. Microstructure of the prepared MFI membrane is greatly affected by calcination time. As can be seen, by removing of template ions at high calcinations time, MFI zeolite layers with high inter-crystalline pores can be obtained. This trend was confirmed by single gas permeation results (see Table 2). The obtained results confirm that the zeolite membranes permeance increases with increasing the calcination time

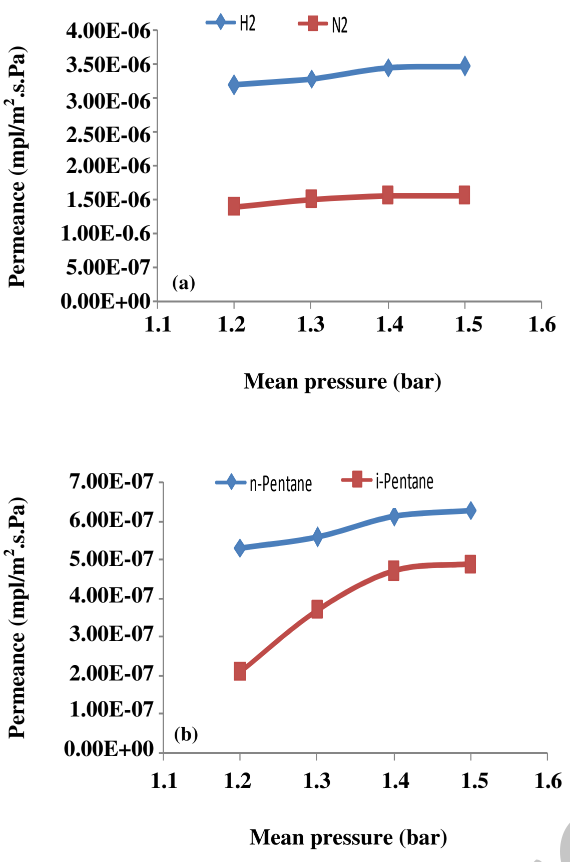

Fig. 5: Single gas permeance a) H_2 and N_2 and b) pentane isomers through MFI zeolite membrane (with four hydrothermal synthesis steps, calcined at 673K for 30h) as a function of mean pressure at 100 ºC.

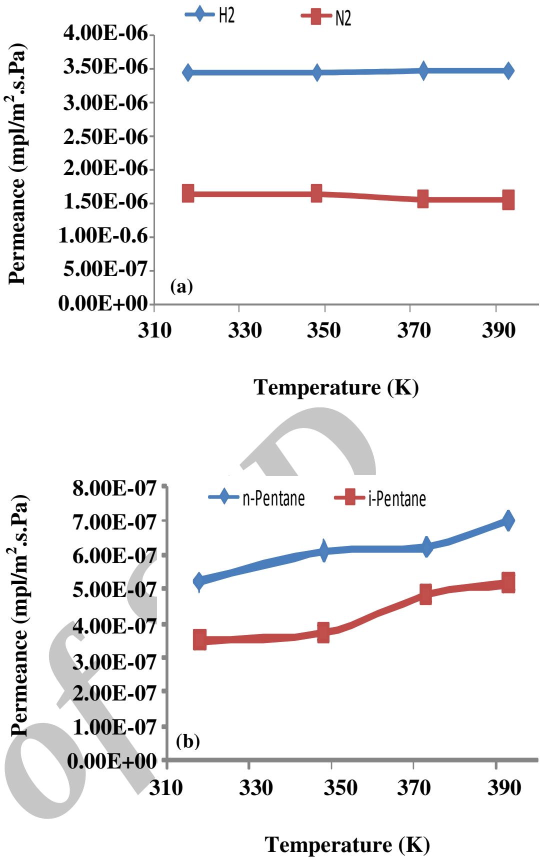

Fig. 6: Single gas permeance a) H_2 and N_2 and b) pentane isomers through MFI zeolite membrane (with four hydrothermal synthesis steps, calcined at 673K for 30h) as a function of temperature at 1 bar.

which can be due to the removing of TPA^+ ions as template. This trend was in good agreement with XRD patterns (Fig.3).

Permeation measurements

Fig. 5 shows single gases permeance as a function of mean pressure at 100 ºC for MFI zeolite membrane prepared by four subsequent hydrothermal treatments and calcined at 673K for 30 h. The permeance of molecules such as H_2 and N_2 exhibits only weak pressure dependence, indicating a relatively defect-free membrane (Fig 5a). However, larger condensable molecules like pentane isomers showed a rather slight increase in permeance, indicating adsorption-diffusion as a dominant mechanism for condensable hydrocarbons (Fig 5b). On the other hand, at low temperatures, adsorption is dominant and the permeation behavior can be described by adsorption followed by surface diffusion mechanisms [17,18].

The single gases permeance as a function of temperature is plotted in Fig. 6. As can be seen, the permeance of H_2 and N_2 (Fig 6a) were nearly constant that shows the adsorption of these molecules are very poor in the synthesized silicalite-1 membrane, but the permeance of larger molecules like pentane isomers (Fig 6b), unlike the small molecules, increases with increasing of temperature that can be due to the effect of temperature on diffusivity of condensable molecules.

The ideal selectivity of H_2/N_2 and H_2/i-pentan binary gas mixtures for MFI zeolite membranes prepared by four subsequent hydrothermal treatments and calcined at 673 K for 30 h, have been presented in Table 3 and Table 4 as a function of mean pressure and temperature.

Table 3: Ideal selectivity of MFI zeolite membrane (with four hydrothermal synthesis steps, calcined at 673K for 30h) at different mean pressures at 100 ºC.

P_m(bar)	H_2/N_2	H_2/n -pentan	H_2/i -pentan
1.2	2.28	6.015	15.2
1.3	2.2	5.9	8.9
1.4	2.21	5.63	7.5
1.5	2.21	5.52	7.1

Table 4: Ideal selectivity of MFI zeolite membrane (with four hydrothermal synthesis steps, calcined at 673K for 30h) at different temperatures at 1 bar.

T(K)	H_2/N_2	H_2/n -pentan	H_2/i-pentan
318	2.09	7.55	10.08
346	2.11	7.52	8.76
373	2.21	5.52	7.1
393	2.25	4.99	6.02

The obtained results confirm that the synthesized MFI membranes have suitable performance in the separation of small molecules from condensable hydrocarbons.

CONCLUSIONS

MFI-type zeolite membranes with uniform structures were prepared on α-Al_2O_3 tubular support by in-situ crystallization method. The effects of hydrothermal synthesis steps and calcination time on the morphology and crystallinity of the synthesized MFI zeolite membranes were investigated. With increasing the number of layers, the intensity of the characteristic peaks of MFI zeolite increases significantly which can be attributed to the formation of a uniform MFI zeolite layer on the support surface. The obtained results confirmed that the calcination time in the synthesis of MFI zeolite membranes is a crucial factor, affecting on the crystallinity, morphology and performance of the final zeolite membranes. The permeance data of the synthesized membranes showed a suitable ideal selectivity for the separation of small gas molecules from condensable hydrocarbons.

Received : Aug. 22, 2009 ; Accepted : July 15, 2011

REFERENCES

[1] Gardner T.Q., Lee J.B., Noble R.D., Falconer J., Adsorption and Diffusion Properties of Butanes in ZSM-5 Zeolite Membranes, *Ind. Eng. Chem. Res.*, **41**, p. 4094 (2002).

[2] Hasegawa Y., Ikeda T., Nagase T., Kiyozumi Y., Hanaoka T., Mizukami F., Preparation and Characterization of Silicalite-1 Membranes Prepared by Secondary Growth of Seeds with Different Crystal sizes, *J. Membr. Sci.*, **280**, p. 397 (2006).

[3] Noack M., lsch P.K., Seefeld V., Toussaint P., Georgi G., Caro J., Influence of the Si/Al-Ratio on the Permeation Propertiesof MFI-Membranes, *Micropor. Mesopor. Mater.*, **79**, p. 329 (2005).

[4] Xomeritakis G., Gouzinis A., Nair S., Okubo T., He M., Overney R.M., Tsapatsis M., Growth, Microstructure, and Permeation Properties of Supported Zeolite (MFI) Films and Membranes Prepared by Secondary Growth, *Chem. Eng. Sci.,* **54**, p. 3521 (1999).

[5] Vroon Z.A.E.P., Keizer K., Burggraaf A.J., Verweij H., Preparation and Characterization of Thin Zeolite MFI Membranes on Porous Supports, *J. Membr. Sci.,***144**, p. 65 (1998).

[6] Gualtieri M.L., Gualtieri A.F., Hedlund J., The Influence of Heating Rate on Template Removal in Silicalite-1: An in Situ HT-XRPD Study, *Micropor. Mesopor. Mater.,* **89**, p. 1 (2006).

[7] Duval J.M., Folkers B., Mulder M.H.V., Desgrandchamps, G. and Smolders, C.A., Adsorbent Filled Membranes for Gas Separation. Part 1. Improvement of the Gas Separation Properties of Polymeric Membranes by Incorporation of Microporous Adsorbent, *J. Membr. Sci.*, **80**, p. 189 (1993).

[8] Bayati B., Babaluo A.A., Ahmadiyan P., Synthesis and Seeding Time Effect on the Inter-Crystalline Structure of Hydroxy-Sodalite Zeolite Membranes by Single Gas (H_2 and N_2) Permeation, *Iran. J. Chem. Chem. Eng.,* **29**, p. 1 (2009).

[9] Yan Y., Davis M.E., Gavalas G.R., Preparation of Zeolite ZSM-5 Membranes by In-Situ Crystallization on Porous α-Al_20_3, *Ind. Eng. Chem. Res.*, **34**, p. 1652 (1995).

[10] Raileanu M., Popa M., Moreno J.M.C., Stanciu L., Bordeianu, L. and Zaharescu, M., Preparation and Characterization of Alumina Supported Silicalite Membranes by Sol-Gel Hydrothermal Method, *J. Membr. Sci.*, **210**, p. 197 (2002).

[11] Cheng Y., Wang L., Li J., Yang, Y., Sun X., Preparation and Characterization of Nanosized ZSM-5 Zeolites in the Absence of Organic Template, *Mater. Lett.*, **59**, p. 3427 (2005).

[12] Szostak R., "Handbook of Molecular Sieves", Van Nostrand Reinhold, New York, (1992).

[13] Geus E.R., Van Bekkum H., Calcination of Large MFI-Type Single Crystals, Part 2. Crack Formation and Thermomechanical Properties in View of the Preparation of Zeolite Membranes*, Zeolites,* **15**, p. 333 (1995).

[14] Dong J., Lin Y.S., Hu M.Z., Peascoe R.A., Payzant E.A., Template-Removal-Associated Microstructural Development of Porous-Ceramic-Supported MFI Zeolite Membranes, *Micropor. Mesopor. Mater.*, **34**, p. 241 (2000).

[15] Bayati B., Babaluo A.A., Manufacturing Porous Support of Ceramic Membranes and Debinding Behavior in Gel-Casting Method, *11th National Iranian Chemical Engineering Congress*, 28-30 Nonember 2006, Chemical Engineering Department, Tarbiat Modares University, Iran.

[16] Gualtieri M.L., Gualtieri A.F., Hedlund J., The Influence of Heating rate on Template Removal in Silicalite-1: an in Situ HT-XRPD Study, *Micropor. Mesopor. Mater.*, **89**, p. 1 (2005).

[17] Barrer R.M., Porous Crystal Membranes*, J. Chem. Soc. Faraday Trans.*, **86**, p. 1123 (1990).

[18] Bakker W.J.W., Kapteijn F., Poppe J., Moulijn A., Permeation Characteristics of a Metal-Supported Silicalite-1 Zeolite Membrane*, J. Memb. Sci.*, **117**, p. 57 (1996)