Synthesis, Characterization and Vapor Permeation Performance of B-ZSM-5 Membranes

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ABSTRACT

In the present work, B-ZSM-5 zeolite membranes were synthesized on porous tubular α-alumina supports by several subsequence in situ crystallization hydrothermal treatments. The TiO_2- Bohmite and ɣ- alumina intermediate layers were applied to improve the lattice matching between zeolite layer and the support. The uniform membrane intermediate layers with low permeation resistance were prepared on the alumina support surface. The N_2 permeance of the intermediate layers and support showed that after the modification of the support surface with ɣ-alumina the Knudsen diffusion can be the dominant mechanism.

Selectivity of binary mixture of normal pentane (n-C_5) and iso-pentane (i-C_5) through B-ZSM-5 zeolite membrane was investigated as a function of feed pressure, temperature and sweep gas flowrate in vapor permeation membrane process using the concentration gradient method. The selectivity results depend strongly on the measurement conditions. The obtained results showed that rising sweep gas flowrate from 5ml/min to 15 ml/min, feed pressure from 1.05 bar to 1.3 bar and decreasing temperature from 200°C to 150°C increased the driving force for n-C_5 transfer across the membrane. The selectivity of n-C_5/i-C_5 8.2 was obtained at 150°C for sweep gas flow of 5 ml/min and 10.4 for sweep gas flow of 10ml/min.

1. Introduction

Membrane separation is a promising technology compared to the conventional separation processes. It has the potential to reduce operating and capital cost, minimize unit operations and lower energy consumption. Inorganic membranes in gas separation applications have attracted considerable attention in recent years due to their good separation performance, high stability at elevated temperatures and resistance in corrosive environment [1]. In recent decades, much attention has been drawn into inorganic zeolite membranes because they can be utilized under harsh conditions where organic polymer membranes cannot be applied [2]. Hydroisomerization of light paraffins is the most important process in the oil refinery which has been widely studied [3]. Branched hydrocarbons are preferred over linear isomers as ingredients in gasoline because of their higher octane number. Catalytic isomerization has been used to convert linear hydrocarbons to branched structures. However, the product of isomerization is a thermodynamic equilibrium mixture of linear and branched hydrocarbons, and the separation of linear hydrocarbons from their branched isomers is essential. In fact, high selectivity for linear alkanes over branched isomers through MFI membranes has been reported by several researchers [4,5]. Zeolite membranes have been shown to be effective for separating C_4–C_6 isomers [6] but only a limited number of publications that deal with the separation of pentane isomers have been reported. In 2005, Noack et al. [7] reported the synthesis of MFI type zeolite membrane with deferent Si/Al ratios on metallic and ceramic supports. They investigated the separation of n-C_5 from pentane isomers and found that the permeation results depended strongly on the measurement conditions such as the pressure differences across the membrane and the calcination temperature. They increased the n/i-pentane separation factors to 14.5 with decreasing Al-content. In 2007, Arruebo et al. [8] synthesized MFI membranes on stainless-steel tubular supports for the separation of n-pentane/isoprene mixtures. The reported Single gas and mixture permeation results indicated that *n*-pentane/isoprene separation is determined by size selectivity; the linear alkane diffuses faster than the branched diene. Moreover, the *n*-pentane permeances are lower for the mixture than for a single component because the slower-diffusing isoprene decreases the *n*-pentane diffusion rate.

In the same line, the separation of normal pentane from a light gasoline isomerate through a MFI zeolite composite membrane was investigated by Baudot et al. [9]. They discovered that increasing the total hydrocarbon pressure at the upstream side of the membrane led apparently to an increased sorption of the slowest compounds (branched paraffins), which in turn slowed down the diffusion of the fastest species (linear paraffins) across the selective zeolite layer. They observed Maximal permeate flux, close to 2 kg/m2.h at 250°C - 2 bar total hydrocarbon pressure. In 2013, Bayati et al. [10] synthesized a B-ZSM-5 zeolite membrane layer supported on a porous tubular alumina support for the separation of n-C_5 from the mixture of n-C_5 and 2-MB. They concluded that the performance of membrane in concentration gradient method was higher than the total pressure drop method.

In this work, using the hydrothermal technique a new support surface modification in nanometric structure was applied for the synthesis of B-ZSM-5 zeolite membranes based on the α-Al_2O_3 tubular supports. To remove the mismatching problem of zeolite layer with α-Al_2O_3 substrate and obtain uniform zeolite layers with high permeability, the support surface was modified via dip-coating as a simple and low cost method by dipping in colloidal suspension of TiO_2-Bohmite and ɣ-Alumina sol as reported in our previous work for silica membranes [11]. To the best of our knowledge, B-ZSM-5 membrane layer was synthesized on this type of modified supports for the first time. The effects of some key operating parameters such as the feed pressure, temperature and sweep gas flowrate on n-C_5 and i-C_5 separation were also investigated.

2. Experimental method
2.1. Materials and Chemicals

The homemade tubular α-Al_2O_3 supports with 12 mm diameter, 4 mm thickness, and 75 mm length and average porosity of 47.2% were prepared by gel casting method [12]. Before the support surface modification, the supports were cleaned in acetone by an ultrasonic regenerator for 10 min and then dried at 40 °C for 12 h. The chemicals used in this study included, tetraethyl orthosilicate (TEOS, (Si-OC_2H_5)$_4$, 98% Merck Co.) as silica source, tetrapropyl ammonium hydroxide (TPAOH, $C_{12}H_{28}$N.OH, 40% solution in water, Merck) as template, boric acid (H_3BO_3, Merck Co.) as the boron source, sodium hydroxide (NaOH, Merck) as alkali source, TiO_2 (300 nm, Degussa) and Bohmite (Merck Co.) powder as sources of intermediate layer, polyethylene glycol (PEG 6000, Merck Co.) as polymeric binder and aluminum-tri-sec-butylate (97%, Merck Co.) as the source of ɣ-alumina.

2.2. Intermediate Layers Fabrication
2.2.1. TiO_2-Bohmite sub-layers preparation

The first sub-layer was prepared by sol–gel dip-coating technique, involving two subsequent dip-coating steps. Stable suspension was prepared by dissolving of 5 wt. % (based on ceramic powder) of polyethylene glycol with molecular weight of 6000 g/mol in deionized water. Suitable amount of TiO_2 and Boehmite powders were added into the prepared solution with mass fraction of 70/30, respectively. Then, the 0.1N solution of sodium hydroxide was added to increase the range of pH till 9-10. Intermediate layers were obtained by dipping the support in the prepared suspension for 30s and the falling and rising up rate of 60 mm/min. The support was dried at ambient temperature and was sintered at 700–1000°C for 3 h in an electric furnace. Due to the presence of the polymeric binder, the heating rate had to be carefully controlled to avoid buildup formation of the surface cracks. For this aim, heating rate of 0.1°C/min was used for the sintering stage.

2.2.2. ɣ-alumina intermediate layers preparation

ɣ-alumina sol was prepared by adding aluminum-tri-sec-butylate drop-wise to the deionized water, in which about 1.5 l of water per mole alkoxide was added at 80 °C under vigorous stirring. Next, the nitric acid, 0.07mol HNO3 per mole alkoxide, was added to decrease the range of pH till 3-4. The resulting

colloidal suspension was kept under heating until most of the butanol was evaporated. The PEG solution was made by dissolving PEG (1 wt. % of sol) in deionized water and then adding it to sol. After this step, sol was refluxed for 16 h to form a stable ɣ-Alumina sol. The dip-coating process was performed at room temperature. The support speed and dip-time were 60 mm/min and 10 s, respectively. After the dipping step, the membranes were dried at 40 °C. Subsequently, the ɣ-alumina layer was formed by calcining at 600 °C for 3 h in atmospheric condition with a heating and cooling rate of 0.1°C/min. The whole processes of dipping, drying and calcining were repeated 2 times.

2.2.3. Synthesis and characterization of B-ZSM-5 Zeolite layer

B-ZSM-5 membranes were prepared by direct hydrothermal synthesis on $\alpha-Al_2O_3$ support. Zeolite layers were prepared from a synthesis solution with the composition of 4.44 TPAOH: 19.46 SiO_2: 1.55B(OH)$_3$: 500 H_2O. The synthesis mixture was prepared by dissolving tetrapropyl ammonium hydroxide in deionized water. Then, boric acid was added by stirring at room temperature. A determined amount, TEOS was added into the prepared solution in one step drop-by-drop, with vigorous stirring for 1.5h at room temperature until a clear solution was obtained. Then, the synthesis solution was poured into Teflon lined stainless steel autoclave. The supports were immersed in synthesis gel overnight at room temperature prior to the synthesis and then the autoclave was heated up to 453K and maintained at that temperature under autogenous pressure for 24h. After that, the membrane was taken out and washed with deionized water until the pH of the solution became neutral and dried at 373k for 3h. Then, the membrane was calcined in air at 753K for 6h with heating and cooling rates of 0.1 °C/min. The synthesis was repeated until an uncalcined membrane had a N_2 permeance of below 1×10^{-10} mol m^{-2}s^{-1}Pa^{-1} (298 K). The surface morphology and cross-section of the membranes were characterized using SEM. The SEM images were obtained on CamScan MV2300. The membrane composition was analyzed by EDX Line Scan analysis.

2.3. Vapor Permeation measurements

The set up for pentane vapor permeation is schematically depicted in Figure1. The liquid feed was pumped into the system by syringe pump (Fanavaran Nano- Meghyas, model SP.1000) that allowed slow and constant flow rates. The feed liquid was vaporized while passing through the heated line. To avoid any condensation and ensure proper partial pressure throughout the set-up, all the lines were heated and maintained at 373 K with heating tape. The permeate side of membrane was swept with N_2 stream. Sweep gas flow rates were controlled by mass flow controllers. The membrane was sealed in a homemade stainless steel module by viton orings, and module was placed in the heating zoon. The differential pressure across the membrane was controlled by a differential pressure gauge. Feed, permeate and retentate streams were diverted to a gas chromatograph (Teif Gostar) equipped with a flame ionization detector and a capillary column (Cat. No. TR-110222, Serial .No. p2085307, TRB-1, Tecknokroma, l: 25 m, ID: 0.25) for analysis.

The vapor permeance of a given pentane isomers mixture was computed as the quotient between the corresponding flux and the mean partial pressure

difference between the feed/retentate and the permeate.The n-C_5/i-C_5 selectivity ($S_{n/i}$) was defined as the enrichment factor of one component to another in the permeate, as compared to the feed composition ratio in the separation of pentane mixtures (Eq. (1))

$$S_{n/i} = \frac{(Y_n / Y_i)_{permeate}}{(X_n / X_i)_{feed}}$$

(1)

Where X_n and X_i and Y_n and Y_i are the molar fractions of species n and i in the retentate and permeate streams, respectively. In our case, n represents n-C_5 while i represents i-C_5.
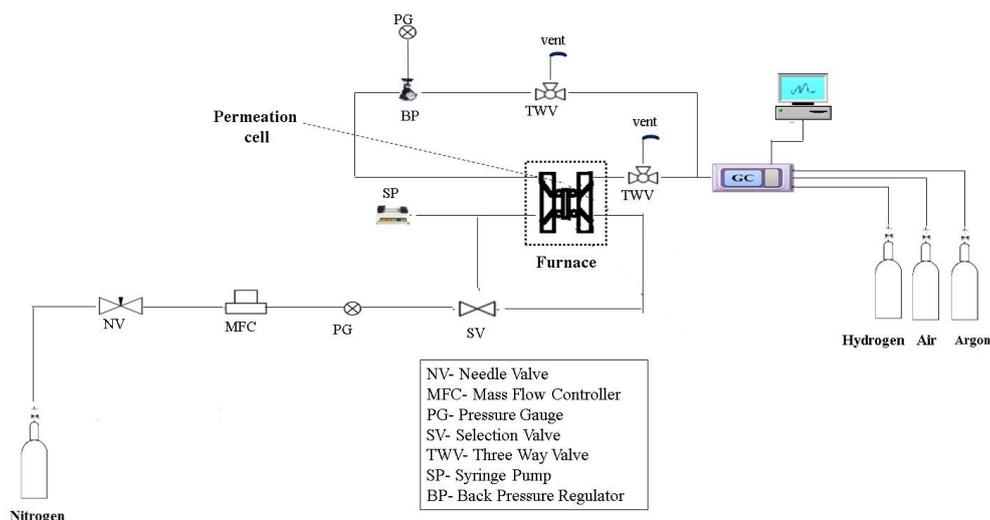
Figure1. Process flow diagram of the experimental setup for the gas permeation experiments

3. Results and discussion

Figure2 (a) is the X-ray diffraction pattern of the α-alumina substrate. This figure clearly shows four strong peaks at 2θ=25.5, 35, 37.7, and 43.3, respectively. The strength and position of peaks are consistent with those of α-alumina, and also the crystal surfaces (012), (104), (110) and (113). The morphology of the alumina support is shown in Figure 2 (b), confirming uniform pore size distribution with average pore size of less than 1μm.
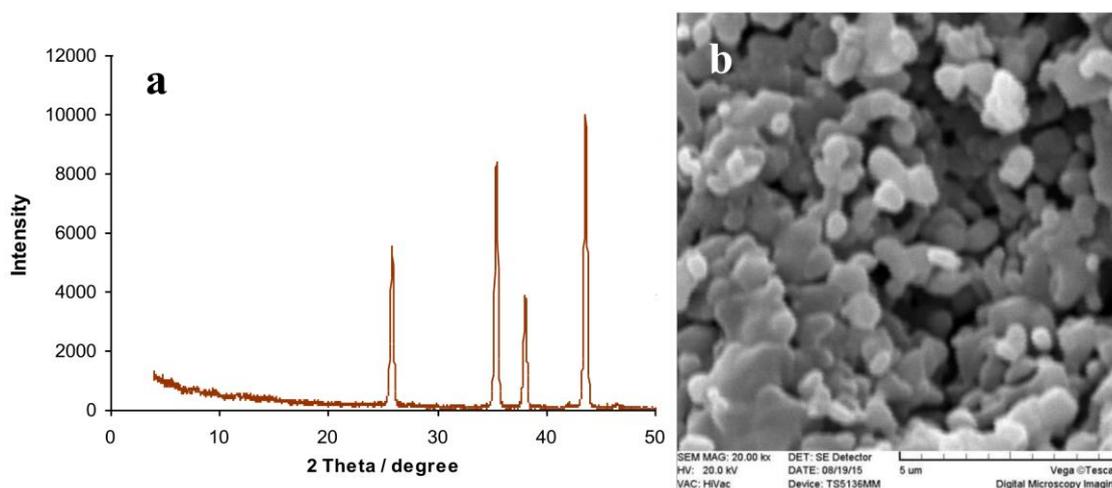

Figure 2. X-ray diffraction pattern and SEM image of the α-alumina substrate surface

In the preparation of zeolite membranes, the quality of the support is very effective on the zeolite layer integrity. The surface roughness and homogeneity of the support determines not only the integrity of the membrane layer, but also the minimal thickness of the membrane layer for the complete surface coverage. The use of thin intermediate layers is an attractive alternative which can be used to generate a smooth surface to improve the chemical adhesion of the zeolite layer to the support, to limit the effect of differential thermal expansion coefficients, and finally to limit the diffusion of the zeolite sol in the support pores. SEM images of the intermediates layers are shown in Figure 3. A typical SEM top view image of the ɣ-alumina layer after calcination is shown in Figure 3. (b). A much smoother mesoporous ɣ-Alumina layer was obtained on the top of the support. Besides providing a smooth surface, the intermediate layers also act as a barrier for avoiding zeolite deposit formation in the interior of the support. Figure 3 (a) is a cross-section image of the modified support. It shows that on the whole the uniform intermediate layers with thickness of about 5μm were formed.
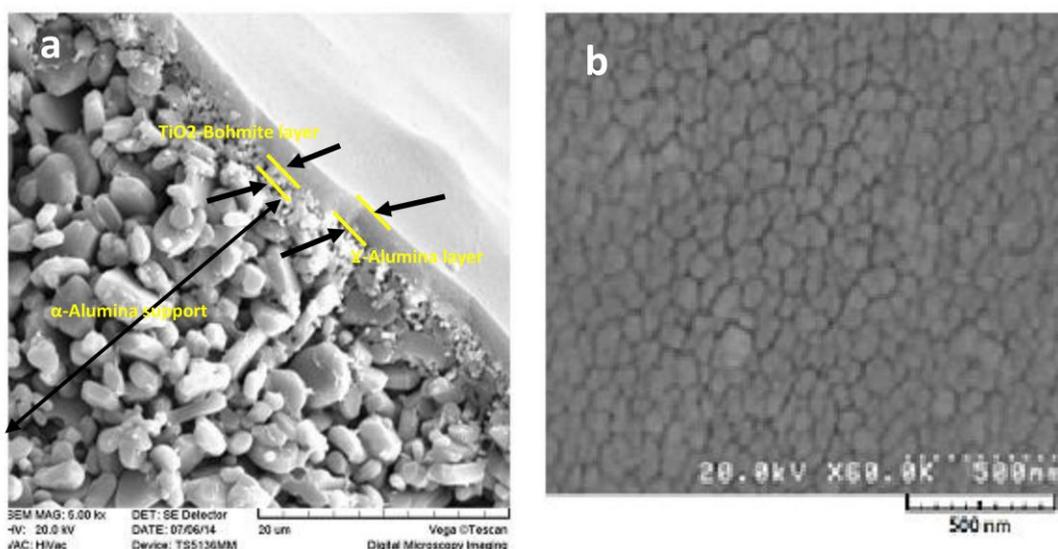

Figure 3. SEM images of cross-section (a) and surface (b) of intermediate layers on substrate surface

Figure 4 shows the XRD pattern of synthesized B-ZSM-5 membrane by XRD analysis of its surface after the calcination. The XRD pattern of membrane is a combination of the diffraction patterns of alumina support, TiO_2-Bohmite and ɣ-alumina intermediate layers and B-ZSM-5 zeolite layer.

In Figure 5, the surface and cross-section morphology of B-ZSM-5 membrane can be seen clearly. According to Figure 5 (a), membrane can be roughly divided into four parts: the macroporous support (A), TiO_2- Bohmite intermediate layer (B), ɣ-alumina mesoporous layer (C) and B-ZSM-5 zeolite layer (D). Figure 5 (b) shows dense coverage of B-ZSM-5 crystals on the alumina and Figure5 (a) displays a good coupling between the ɣ -alumina intermediate layer and ZSM-5 top layer.
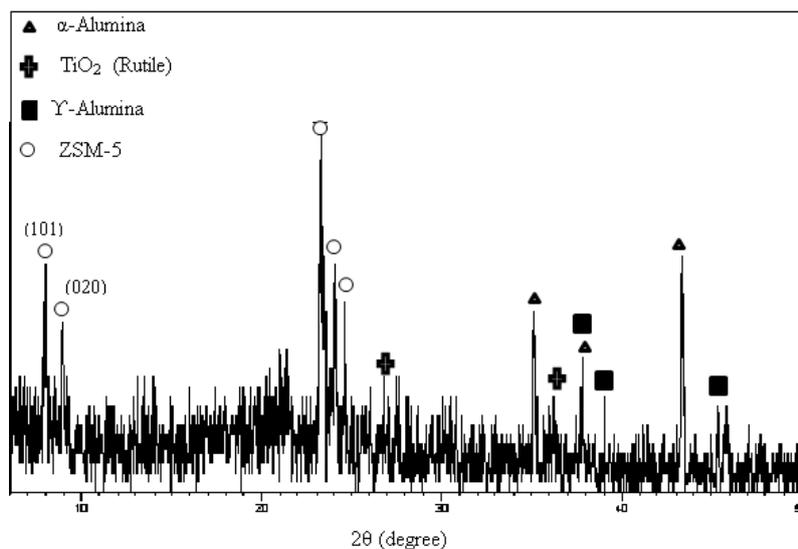
Figure 4. XRD pattern of B-ZSM-5 membrane on modified α-Alumina support surface
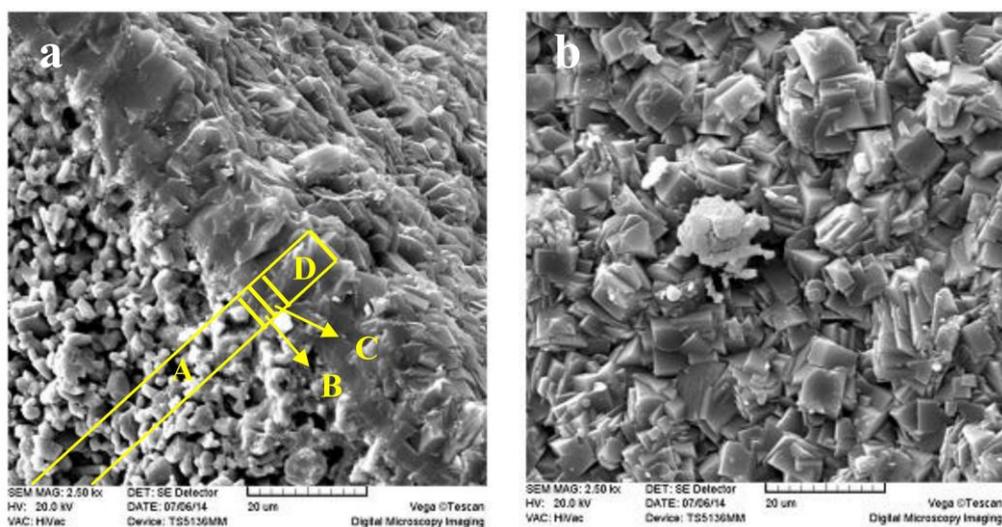

Figure 5. SEM images of B-ZSM-5 membrane; cross-section (a) and top view (b)

Figure 6 shows the EDX line scan from Figure 5 (a). The pronounced maximums of Al signal in region 1 (support) can be seen. Al signal can be observed underneath the Ti peak. From this, we conclude that Al-rich layer is covered by a thin layer of Ti-rich layer (intermediate layers). Ti and Al peaks below the silicon signal are clearly visible. Again, it can be observed that there is Ti and Al-rich layer covered by a thin Si layer in region 3 (zeolite layer). According to the SEM and EDX line scan images of membrane, it is found that intermediate and zeolite layers are composed uniformly on the substrate surface.
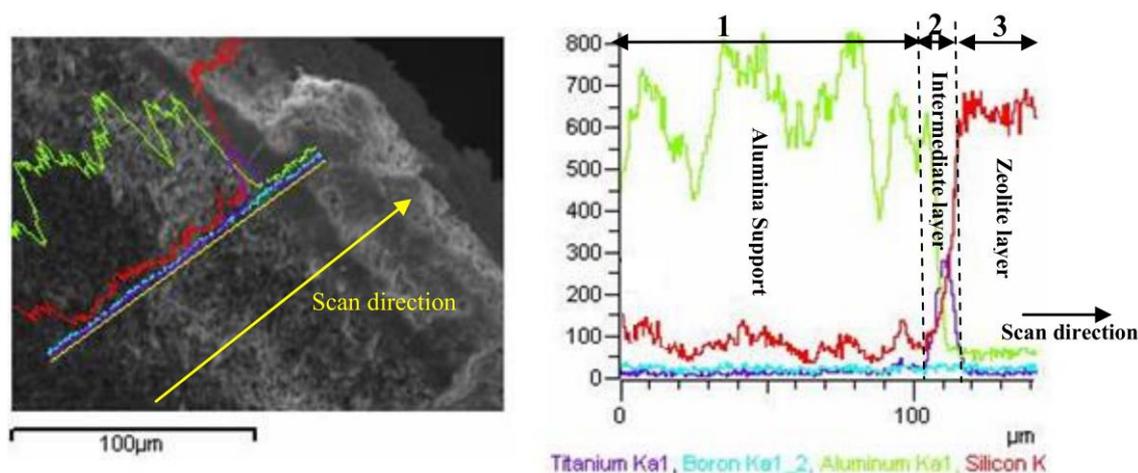
Figure 6. EDX line scan of B-ZSM-5 membrane

To investigate the changes in separation performance caused by intermediate layers on support surface by nitrogen, permeation performance was assessed for TiO_2-Bohmite, ɣ-Alumina and α-Al_2O_3 support. According to Figure7 (a) N_2 permeances for support and surface modification layers increased linearly with mean pressure at constant temperature. The slope of N_2 permeance decreased after modifying the support. N_2 transport through support and TiO_2-Bohmite layer occurred according to the viscous flow mechanism and through meso porous ɣ-Alumina layer followed by viscous flow and Knudsen diffusion. The N_2 permeance in this Figure showed that after the modification of support with ɣ-Alumina the Knudsen diffusion can be the dominant mechanism. Following the hydrothermal synthesis and in order to ensure that the precursor penetrated well in all the pores, the single gas permeation with nitrogen gas was conducted and measured. At this juncture, it is expected that the membrane material should not show N_2 gas permeation because zeolitic pores are occupied by the molecules of the structuring agent (TPAOH). Test of nitrogen permeation conducted at ambient temperature is an indicator that there are no defects in the membrane. To indicate that the precursor penetrates well in the zeolitic pores, the nitrogen flow must be close to zero. It can be observed in Figure7 (b) that N_2 gas permeation was obtained very low after two subsequent hydrothermal steps.
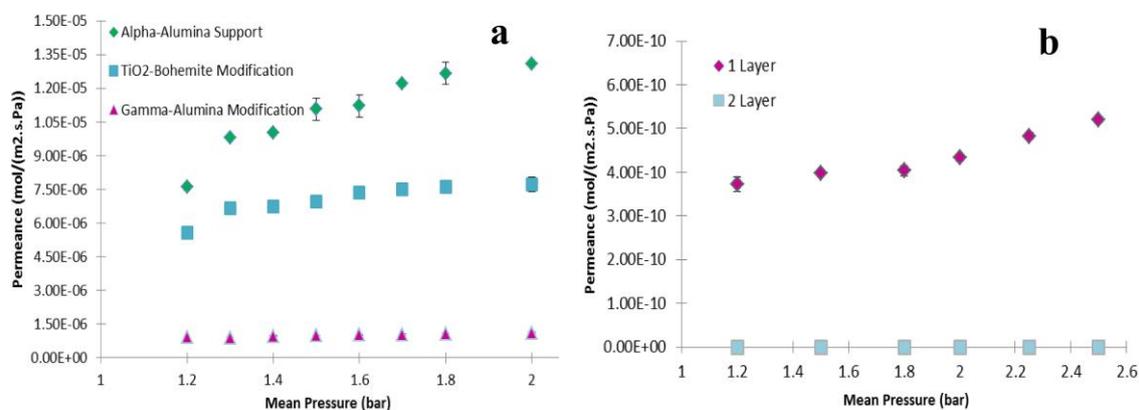
Figure 7. N_2 permeation from support and modified support (a) and B-ZSM-5 membrane before calcination (b)

In Figure 8 (a) and (b), the permeance and selectivity of H_2 and N_2 for B-ZSM-5 membrane after calcination are plotted against the mean pressure. Measurements were carried out at room temperature, atmospheric pressure on the downstream side and no sweep gas. It can be seen that H_2 and N_2 permeation and H_2/N_2 selectivity are approximately constant with the rising of mean pressure. All these suggest that membrane is defect free, although the surface morphology confirmed these results.
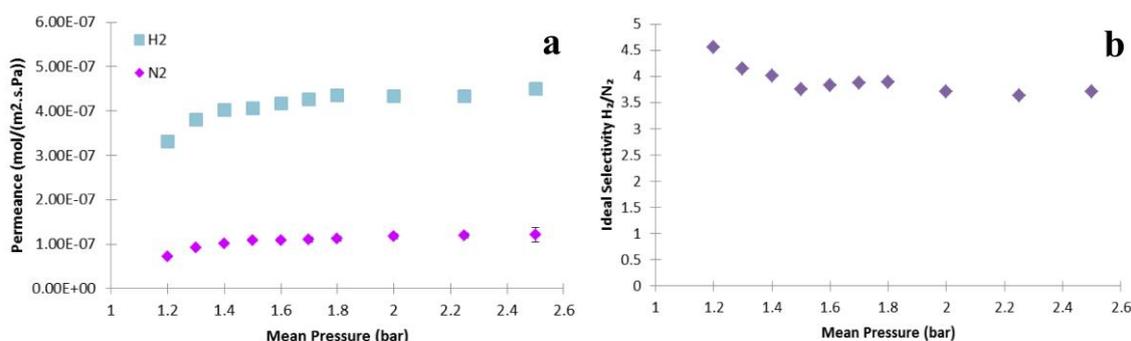

Figure 8. N_2 and H_2 permeation (a) and N_2/H_2 selectivity (b) for B-ZSM-5 membrane\

Feed compositions were 50/50 wt.% $n\text{-}C_5$ and $i\text{-}C_5$. At room tempreture (25°C) the permeate side pressure was maintained at atmospheric pressure for binary permeation experiments. The compositions in feed, permeate and retentate streams were detected by GC analysis. Figure 9 (a) and (b) show the evolution of the $n\text{-}C_5/i\text{-}C_5$ selectivity as a function of temperature and feed pressure at different sweep gas flowrates. As can be seen $n\text{-}C_5/i\text{-}C_5$ selectivity decreased by increasing the temperature caused by the adsorption- diffusion phenomena. Competitive adsorption in zeolitic pores plays a key role in the separation of linear and branched alkans. The selectivity of $n\text{-}C_5/i\text{-}C_5$ at lower temperature was higher because $n\text{-}C_5$ adsorbed amounts are higher than that of $i\text{-}C_5$ at low temperature, and therefore the more strongly adsorbed species can better block adsorption sites.
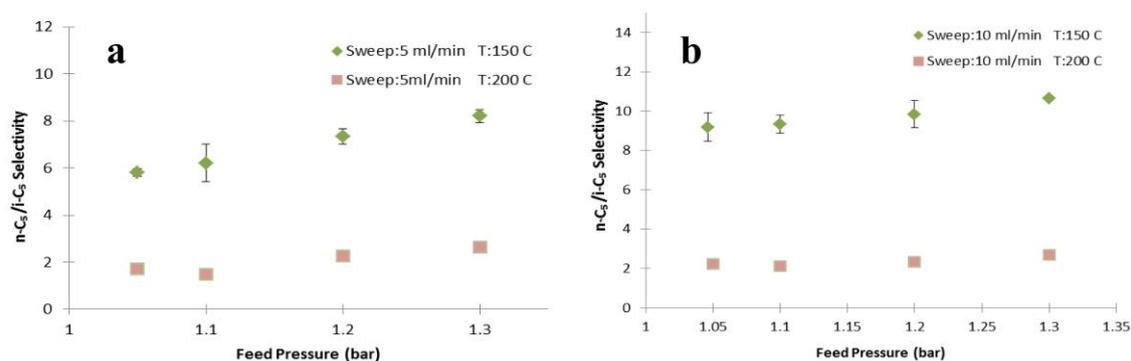

Figure 9. $n\text{-}C_5/i\text{-}C_5$ selectivity vs. feed pressure at sweep gas of 5 ml/min (a) and 10 ml/min (b)

Figure 10 plots the effect of sweep gas flowrate on membrane performance in the separation of $n\text{-}C_5$ and $i\text{-}C_5$ mixtures. The measurements were made at different sweep gas flowrates where the total organic concentration in the feed was held constant. As expected, the separation factor

was significantly higher at the high sweep flowrate (10cm^3/min). This trend should be ascribed to the reduction of n-C_5 permeate partial pressure as the sweep gas flow rate increases. This might contribute to a decrease of n-C_5 surface coverage at the membrane/ permeate surface and an increase of n-C_5 driving force across the membrane.
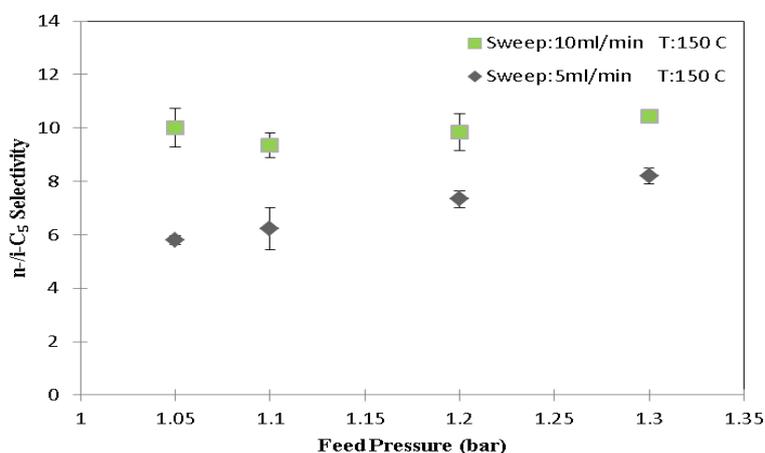

Figure 10. n-C_5/i-C_5 selectivity vs. feed pressure at 150 °C

According to the literature [10], the performance of membrane in concentration gradient method was higher than the total pressure drop method. Therefore, concentration gradient method was used as a separation method in this work. The framework symmetry of MFI zeolites is strongly related to the nature and amount of guest molecules adsorbed in the channel network. In Figs. 9 and 10 the membrane selectivity to n-C_5 increases by an increase in the feed pressure. At lower feed pressures the adsorption of n-C_5 and i-C_5 is close together but at higher feed pressures selective adsorption of n-C_5 on MFI blocks is higher than that of i-C_5. It seems that at higher feed pressures, i-C_5 are replaced by normal pentane at the membrane/ feed surface and consequently the selectivity of n-C_5 to i-C_5 is improved.

4. Conclusion

In this study, B-ZSM-5 zeolite membrane was successfully prepared on α-alumina support. For a better matching between the support surface and the zeolite layer, thin TiO_2- Boehmite and ɣ -alumina layers were applied as intermediate layers. The N_2 permeance of intermediate layers and support showed that after the modification of support with ɣ-alumina, the Knudsen diffusion can be the dominant mechanism. High n-C_5/i-C_5 selectivities were obtained at the lower temperature used in this study due to the selective adsorption. The reason is that the n-C_5 adsorbed amounts are higher than that of i-C_5 at the low temperature, and therefore the more strongly adsorbed species can better block the adsorption sites. At lower feed pressures the adsorption of n-C_5 and i-C_5 is close together but at higher feed pressures the selective adsorption of n-C_5 on MFI blocks is higher than i-C_5. n-C_5/i-C_5 selectivity increases from 8.3 at sweep gas of 5 ml/min to 11 at sweep gas of 10 ml/min due to the decrease of the n-C_5 surface coverage at the membrane/

permeate surface and the increase of the n-C$_5$ driving force across the membrane at high sweep gas flowrate.

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سنتز، مشخصه یابی و عملکرد غشاءهای B-ZSM-5
در عبوردهی گازها

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چکیده	مشخصات مقاله
در این تحقیق، غشاهای زئولیتی B-ZSM-5 روی پایههای متخلخل آلفا آلومینا به روش هیدروترمال درجا سنتز شدند. لایههای میانی برای سنتز لایهٔ زئولیتی مناسب بر روی پایه به کار گرفته شدند. انتخابگری مخلوط دو جزیی نرمال پنتان ($n-C_5$) و ایزو پنتان ($i-C_5$) از میان غشاء زئولیتی B-ZSM-5 در دماها و فشارهای مختلف خوراک و جریانهای مختلف گاز جاروب کننده بررسی شد. برای این منظور از فرایند عبوردهی در فاز گاز با روش گردایان غلظتی استفاده گردید. نتایج نشان داد که انتخابگری غشاء به شدت به شرایط اندازهگیری وابسته بوده طوری که با افزایش شدت جریان گاز جاروب کننده و فشار خوراک و کاهش دما نیروی محرکه انتقال $n-C_5$ و به تبع آن انتخابگری افزایش مییابد.	

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