

HIGHLY SELECTIVE H₂ SEPARATION ZEOLITE MEMBRANES FOR COAL GASIFICATION MEMBRANE REACTOR APPLICATIONS

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ABSTRACT

It is desirable to develop inorganic zeolite membranes that are capable of highly selective H₂ separation from other light gases (CO₂, CH₄, CO). Zeolite membranes are thermally, chemically and mechanically stable, and have tunable molecular sieving and catalytic ability. These unique properties make zeolite membrane an excellent candidate for use in catalytic membrane reactor applications related to coal conversion and gasification, which need high temperature and high pressure range separation in chemically challenging environment where existing technologies are inefficient or unable to operate.

In an effort to develop zeolite membranes more suitable for H₂ separation, various types of zeolite membranes were modified. The aim of the modification is to tune the size of zeolite pores and/or to decrease the number of defects within as-synthesized zeolite membranes. The modification attempts include silylation on Al-ZSM-5, B-ZSM-5 and SAPO-34 membranes, and ion exchange of SAPO-34 membranes. Results show that silylation on B-ZSM-5 membranes with low Si/B ratio give the best hydrogen separation membranes in terms of H₂ separation selectivity and high temperature stability. For one B-ZSM-5 membrane after silylation, the H₂/CO₂ separation selectivity at 473 K increased from 1.4 to 37, whereas the H₂/CH₄ separation selectivity increased from 1.6 to 33. However, silylation decreased H₂ permeances more than one order of magnitude in the B-ZSM-5 membrane. The H₂ permeance and H₂/CO₂ and H₂/CH₄ separation selectivities increased with temperature. At 673 K, the H₂ permeance was 1.0×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹, and the H₂/CO₂ separation selectivity was 47.

This is the second annual technical progress report for the university coal research program supported by U.S. DOE NETL (Contract No. DE-FG26-02NT41536). This report summarizes program accomplishments up to December 2004. The report includes an introduction summarizing the research objectives and tasks; it also provides a summary of program activities and accomplishments covering progress in various zeolite membrane synthesis and modification. Possible future work is proposed as well.

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1. INTRODUCTION

Hydrogen, as a clean energy source, is in increasing demand in industry. Hydrogen can be produced from coal conversion and gasification process where coal is converted into synthesis gas. Depending on the particular gasification process, the synthesis gas produced also contains carbon dioxide, methane, carbon monoxide, hydrogen sulfide, water, and other gases. Hydrogen recovery from coal gasification products requires an efficient separation process to purify the gas economically. Traditional separation methods, such as absorption, adsorption and distillation require pressure swings and changes in temperature. They are energy intensive and too expensive to purify dilute H₂. On the other hand, membrane processes are considered to be one of the most promising technologies for generation of pure hydrogen, taking advantage of continuous low energy operation.

Inorganic zeolite membranes have the ability to operate the separation at or near the processing conditions for H₂ production. They can tolerate high temperatures, high pressure-drops and chemically challenging environments. A zeolite layer can be fabricated onto a tubular support, providing high surface to volume ratio, scale up in modular form and the ability to continuously separate. Moreover, zeolites have catalytic properties, which make it possible to integrate reaction and separation into one unit. However, currently used zeolite membranes have not been successful for H₂ separation. This is mainly because the as-synthesized zeolite membranes either have zeolite pores too big for separating H₂ from other light gases or have many non-zeolite pores bigger than the zeolite pores, so called defects. Zeolite membranes with smaller pores should have the potential to effectively separate H₂ from other light gases, if they are made defect-free.

Zeolites are microporous crystalline aluminosilicates, with a uniform pore size distribution in the molecular size range. To selectively separate H₂ from other light gases (CO, CO₂, CH₄), the zeolite membrane will have to discriminate between molecules that are approximately 0.3-0.4 nm in size and 0.1 nm or less in size difference. To accomplish this sieving, we can either synthesize small pore zeolite membranes that have pores in this size range, or post-treat existing zeolite membranes to systematically reduce the pore size and/or the number of defects so as to create good-quality zeolite membranes with desirable pore diameters suitable for hydrogen separation.

Among various types of zeolite membranes synthesized to date, ten-member ring MFI structure (silicalite-1 and ZSM-5) is the most extensively studied case. MFI type membranes have straight, circular channels of 0.54×0.56 nm running perpendicular to sinusoidal, elliptical channels of 0.51×0.54 nm, and are suitable for separations of several industrially important organic molecules. Light gas including H₂ separations, however, are often dominated by competitive adsorption, rather than size exclusion because the MFI pore size is much bigger than the size of light gases. The as-synthesized MFI membranes are sometimes selective towards CO₂ and CH₄, although H₂ is the smallest molecule because the adsorption of CO₂ and CH₄ is stronger than that of H₂, especially at low temperatures. Small pore zeolite membranes have been synthesized, which include zeolite A, SAPO-34, ETS-4, SSZ-13 and sodalite membranes. Our group has successfully synthesized SAPO-34 membranes, which have 8-member ring chabazite structure with pore size of 0.38 nm. The membranes showed high CO₂/CH₄ selectivities at low temperature range, but still have bigger non-zeolite defects in the structure.

In this report, we used two different methods to post-treat as-synthesized zeolite membranes to alter their zeolite pore size and defects size: silylation and ion exchange. In the silylation reaction, methyltriethoxysilane (MTES) was firstly chemisorbed onto the acid sites within the zeolite membrane, then catalytically cracked on sites and oxidized. As a result, additional silicon atoms were added to the original zeolite structures, and the effective pore opening size of the defects and/or zeolite pores was decreased. In the ion exchange reaction, part of H⁺ ions in the zeolite membranes was replaced by Cu²⁺ or K⁺. As a result, zeolite adsorption and/or diffusion properties changed, causing changes of the membrane permeation and separation properties. The effects of initial membrane properties and the modification parameters were studied in detail.

2. EXPERIMENTAL METHODS

2.1 Zeolite membrane synthesis

Four kinds of 10-member ring MFI membranes were synthesized: Al-ZSM-5, B-ZSM-5 (Si/B=12.5 in the gel), B-ZSM-5 (Si/B=100 in the gel), and silicalite-1. Al-ZSM-5 membranes were synthesized with a standard in-situ crystallization procedure using NaOH in the gel. The membranes were grown on the inner surface of tubular stainless steel supports. The gel composition is 2.0 TPABr : 19.46 SiO₂ : 0.389 Al₂(SO₄)₃ : 500 H₂O : 2.5 NaOH, corresponding to a Si/Al ratio of 25. Sodium silicate was used as the silicon source, aluminum sulfate as the aluminum source, and tetra-propyl ammonium bromide (TPABr) as the template. Since the as-synthesized Al-ZSM-5 membranes were prepared in their Na⁺ form, they need to be converted to their H⁺ form before silylated. The Al-ZSM-5 membranes were ion exchanged to their H⁺ form by a conventional ion exchange technique. The membranes were rotated in 1 M NH₄Cl solution at 368 K for 2 h and then heated to 503 K for 4 h.

Two kinds of boron substituted ZSM-5 (B-ZSM-5) membranes were synthesized with different Si/B ratio in the gel. One kind of B-ZSM-5 membrane was synthesized by secondary growth on the inner surface of tubular α -alumina supports. Silicalite-1 seeds were made from a gel with a molar composition of 9 TPAOH : 24 SiO₂ : 500 H₂O : 96 EtOH, where tetra-propyl ammonium hydroxide (TPAOH) was used as the template, and tetraethoxysilane (TEOS) was used as the silicon source. The seeds were synthesized at 358 K for 3 days. The α -alumina supports were dip-coated three times with a suspension of silicalite-1 seeds (2 wt.% seeds in DI water). The secondary growth gel had a molar composition of 16 TPAOH : 80 SiO₂ : 6.5 B(OH)₃ : 5000 H₂O : 320 EtOH, corresponding to a Si/B ratio of 12.5. In an attempt to minimize penetration into the support, the gel viscosity was increased by adding surfactant cetyltrimethyl ammonium bromide to the gel. Crystallization was carried out at 458 K for 4 h. An additional layer was applied using the same procedure, and the membranes were prepared with two layers. The other kind of B-ZSM-5 membrane was synthesized in-situ from a gel with Si/B ratio of 100. The gel composition was 1.5 TPAOH : 19.5 SiO₂ : 0.195 B(OH)₃ : 438H₂O, where colloidal silica was used as the silicon source and boric acid was used as the boron source. Crystallization was carried out at 458 K for 24 h. Additional layers were applied using the same procedure at 458 K for 48 h, and the membranes were prepared with 4 layers. Silicalite-1 membranes were also prepared in-situ using the gel of 1.5TPAOH: 19.5SiO₂: 438H₂O, and the silicon source was also colloidal silica. The synthesis procedure was the same as for B-ZSM-5 membranes with a Si/B ratio of 100. The silicalite-1 membranes were prepared with 4 layers.

One kind of 8-member ring CHA membrane was prepared: SAPO-34. The SAPO-34 membranes were prepared by in-situ crystallization onto tubular stainless steel supports. The

synthesis gel had a molar composition of 1 Al₂O₃ : 1 P₂O₅: 0.6 SiO₂: 1.07 TEAOH: 56 H₂O, where aluminum isopropoxide was used as the Al source, phosphoric acid as the P source, colloidal silica sol as the Si source, and tetra-ethyl ammonium hydroxide (TEAOH) as template. The hydrothermal synthesis was carried out at 468 K for 20 h. Additional layers were applied using the same procedure, and membranes were prepared with 4 layers.

2.2 Silylation on zeolite membranes

Before silylation, the zeolite membranes were outgassed in N₂ (UHP grade, Airgas) flow at 623 K overnight. The N₂ bubbled through liquid methyldiethoxysilane (97+%, Alfa Aesar) at 297 K and flowed through the inside of the membrane tubes at 623 K for 10 h. For all MFI membranes, their inside were then flushed with N₂, heated to 823 K with a heating rate of 0.6 K/min in air (breathing quality, Airgas) for 4 h, and cooled down in flowing N₂ at a rate of 1.1 K/min. The outgas-silylation-calcination cycle was repeated once. The same silylation procedures were used for SAPO-34 membranes except that the oxidation step was at 663 K and the oxidation time was extended to about 20 h.

2.3 Ion exchange on SAPO-34 membranes

The as-synthesized SAPO-34 membranes have negatively charged framework structure, and H⁺ were present in the extra framework for charge neutralization. The H⁺ ions in the SAPO-34 membranes were exchanged with Cu²⁺ and K⁺ ions. Solutions containing Cu²⁺ or K⁺ ions were prepared by dissolving copper acetate in methanol or potassium acetate in ethanol respectively. The membranes were stirred at 200 rpm in the 0.01 M Cu²⁺ at 328 K for 4 h, or in 0.01 M K⁺ at 348 K for 4 h, and calcined at 673 K for 2-3 h. The same procedure was repeated for complete exchange with the designated ions.

2.4 Membrane Permeation

Single-gas permeance through the membrane was measured in a dead-end stainless steel module at 295 and 473 K. The pressure difference across the membrane was 138 kPa, and the permeate side pressure was 84 kPa. Permeation rates were measured at room temperature using a soap film flowmeter. The estimated permeance error was 2% if the gas permeance was between 10⁻⁵ to 10⁻⁹ mol·m⁻²·s⁻¹·Pa⁻¹. For gas permeance below 10⁻⁹ mol·m⁻²·s⁻¹·Pa⁻¹, the permeance error could be as high as 20%. The lowest measurable flow rate is estimated to be 7×10⁻¹¹ mol·m⁻²·s⁻¹·Pa⁻¹. Ideal selectivity is the ratio of single-gas permeances.

Hexane isomers were separated by vapor permeation in a continuous flow. A syringe pump introduced a 50/50 n-hexane/DMB liquid feed into a preheated helium carrier flow (0.83 mL/s) where the liquid feed vaporized. The total organic feed concentration was maintained at 8%. Both sides of the membrane were at approximately 84 kPa, and a helium sweep gas (0.83 mL/s) was used on the permeate side. Feed, retentate, and permeate flow rates were controlled with mass flow controllers and measured with a soap film flowmeter. The vapor compositions were analyzed on-line by a HP 6890 GC with a flame ionization detector. Log-mean partial pressure differences were used to calculate the permeances. Separation selectivity is defined as the ratio of permeances.

Fifty/fifty gas mixtures of H₂/CO₂, H₂/CH₄, H₂/N₂, and CO₂/CH₄ were separated in a continuous flow system. The permeate pressure was 84 kPa, and the transmembrane pressure drop was 138 kPa. Between 298 and 473 K, silicone O-rings were used to seal the membrane in the module; above 473 K, graphite ferrules were used. Steady state separations at 473 K were compared for these two sealing modes, and the variations in the permeances and selectivities for

the two arrangements were within 2%. Feed, retentate, and permeate flow rates were measured with a soap film flowmeter, and compositions were analyzed on-line by a HP 5890 GC with a thermal conductivity detector. Gas permeances and separation selectivities were calculated in the same way as those for vapor permeation experiments.

3 RESULTS AND DISCUSSION

3.1 Silylation of Al-ZSM-5 membranes

The first type of membrane studied was an Al-ZSM-5 membrane prepared by in situ crystallization. The Al-ZSM-5 membrane (A1) had four layers with Si/Al ratio of 25 in the synthesis gel. Because Al in the zeolite framework is trivalent, the membrane should have plenty of strong acid sites after ion exchanged to its H⁺ form due to its low Si/Al ratio. The single gas permeances of different gases before and after silylation are shown in Fig.1. The reduction of all the gas permeances indicates that the pore size of the membrane has been reduced. The reduction in permeance was most significant for CO₂, which became the slowest permeating molecule among those tested, although its kinetic diameter is smaller than the other gases except H₂. This trend is contrary to the majority of reports on gas transport in MFI zeolite membranes, amongst which some even reported CO₂ permeating fast than H₂ due to its strong adsorption, but in accordance to some literature on small pore zeolite membranes.

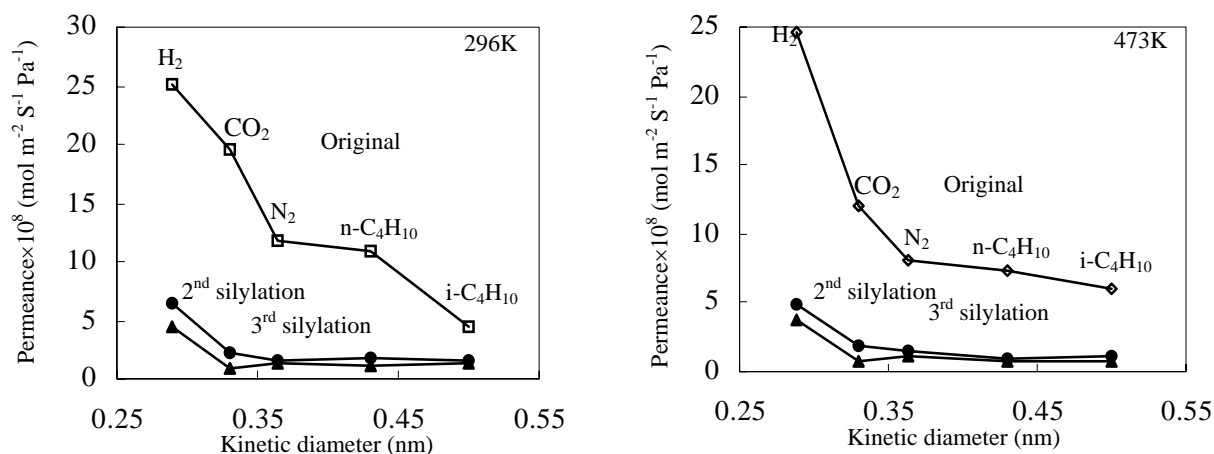


Fig.1 Single gas permeance as a function of kinetic diameter for an Al-ZSM-5 membrane before and after silylation

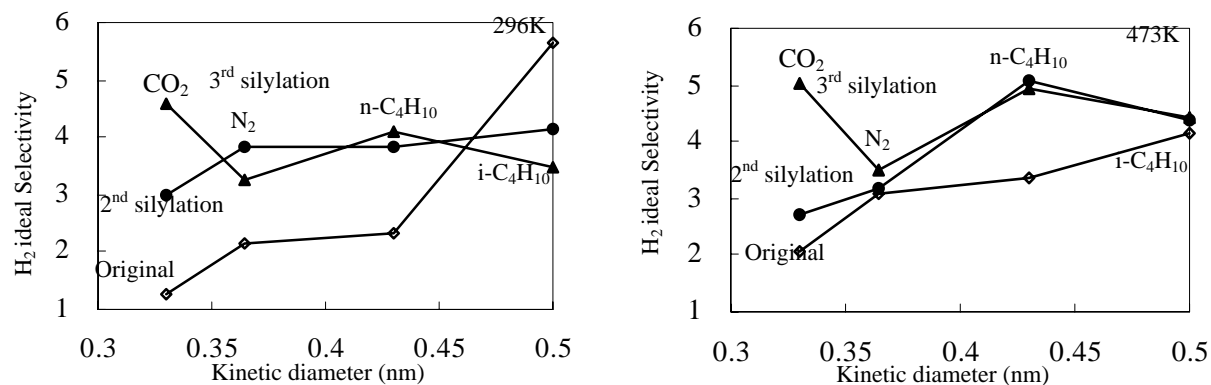


Fig.2 H₂ ideal selectivity for an Al-ZSM-5 zeolite membrane before and after silylation

Fig.2 gives the effect of silylation on the H₂ ideal selectivities over other light gases for this Al-ZSM-5 membrane. Except for H₂/iso-butane, all the H₂ ideal selectivities increased after silylation. The H₂/CO₂ ideal selectivity more than doubled, suggesting that silylation is effective for light gas separations. However, big isobutane molecule was still permeating even after the 3rd silylation treatment, illustrating the inability of this method to repair large non-zeolite pores. The n-/iso-butane ideal selectivity of 1.2 at 473K for the fresh membrane also indicates that the Al-ZSM-5 membrane contained a large amount of defects and was not a good quality membrane initially. Membranes with better quality are needed to start the modification.

3.2 Silylation of B-ZSM-5 membranes with Si/B=12.5 in the gel

As ion-exchanged Al-ZSM-5 membrane was not of good quality initially, membranes with better quality (indicated by n-/iso-butane ideal selectivity > 10 or hexane isomer separation selectivity > 100) are needed as a starting membrane for the silylation. Previous results showed that B-ZSM-5 membranes prepared in our laboratory had higher n-/i-butane selectivities than Al-ZSM-5 and silicalite-1 membranes prepared by similar procedures. Boron substitution creates acid sites that should be the adsorption and reaction sites for MDES, just as the Al sites in the Al-ZSM-5 zeolite membranes, although B-ZSM-5 acid sites have lower Brönsted acid strength than Al-ZSM-5 acid sites.

Table 1. Single gas and mixture permeances for alkane isomers at 473 K for B-ZSM-5 membranes (Si/B ratio = 12.5)

Membrane	Butane permeance $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	n-/i-butane ideal selectivity	Hexane permeance $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	n-hexane/DMB separation selectivity
B1	22	7.4	40	11
B2	5.5	22	15	120

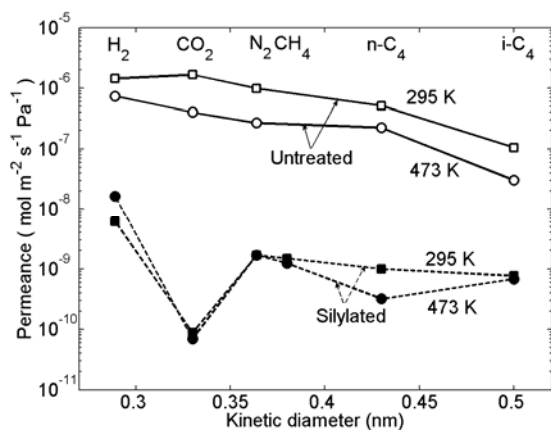


Fig. 3 Single gas permeances before and after silylation for B-ZSM-5 membrane B1 as a function of kinetic diameter at 295 K and 473 K

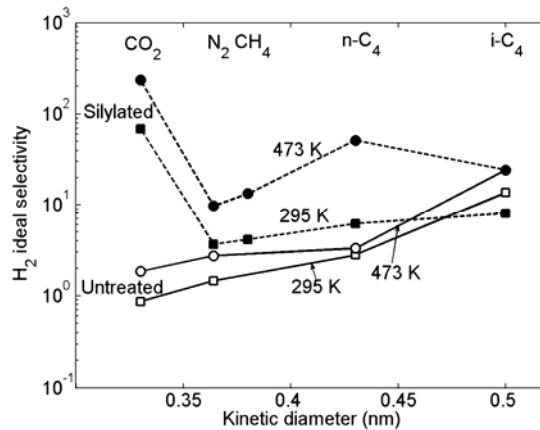


Fig. 4 H₂/gas ideal selectivity before and after silylation for B-ZSM-5 membrane B1 as a function of kinetic diameter at 295 K and 473 K

Two B-ZSM-5 membranes with Si/B ratio of 12.5 (B1, B2) were used. The SEM pictures (not shown here) showed that membranes were approximately 3.5 μ m thick with inverted pyramid shape of the zeolite crystals on top of the support, indicating that the membranes may be c-

oriented. Their n-butane/i-butane ideal selectivities and n-hexane/DMB separation selectivities at 473 K are shown in Table 1. Their high selectivities for C₄ and C₆ isomers indicate good quality membranes. The single gas permeances for membrane B1 generally decreased at both 295 and 473 K as the kinetic diameter increased for the untreated membrane, as shown in Fig. 3. The only exception is CO₂, which permeates faster than H₂ at 295 K. After the membrane was silylated, the permeances of all gases except CO₂ decreased by approximately two orders of magnitude. The CO₂ permeance decreased by approximately four orders of magnitude. Thus, silylation increased the H₂/CO₂ ideal selectivity by a factor of 80 at 295 K, as shown in Fig. 4. The H₂/CO₂ ideal selectivity on the silylated membrane was 230 at 473 K; this is 120 times the selectivity of the untreated membrane. Because the CO₂ permeance was close to the detection limit of the system, the H₂/CO₂ selectivity is less accurate than the other values. The estimated errors for the H₂/CO₂ selectivities are $\pm 30\%$. The H₂/N₂ and H₂/n-butane ideal selectivities also increased, and at 473 K the H₂/n-butane selectivity increased by a factor of 15. Note that at 473 K, i-butane permeated faster than n-butane through the silylated membrane. Thus, the H₂ selectivity relative to the other gases increased for all gases after silylation except for i-butane; the H₂/i-butane selectivity is the same or lower after silylation.

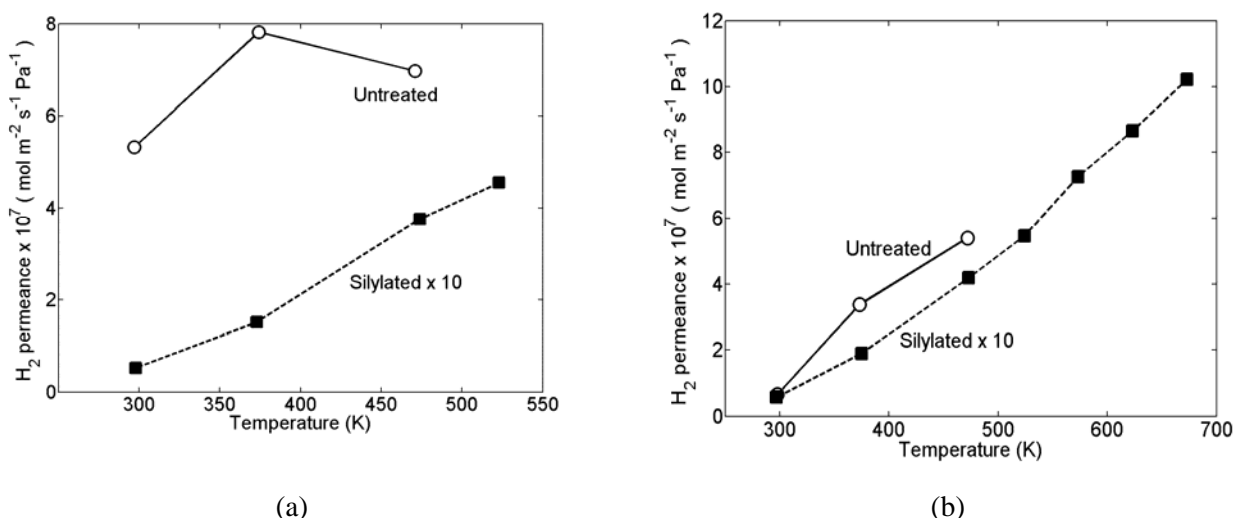


Fig. 5 Hydrogen permeance before and after silylation for B-ZSM-5 membrane B2 as a function of temperature in a 50/50 mixture of (a) H₂/CH₄ and (b) H₂/CO₂

The B-ZSM-5 membrane B2 was used to separate 50/50 mixtures of H₂/CO₂ and H₂/CH₄ before and after silylation. As shown in Fig. 5a, the H₂ permeance in the H₂/CH₄ mixture at low temperature decreased by almost two orders of magnitude after silylation. The H₂ permeance in the H₂/CO₂ mixture was approximately one order of magnitude lower after silylation, as shown in Fig. 5b. For clarity, the H₂ permeances in Fig. 5 were multiplied by ten for the silylated membrane. The decrease was less for the H₂/CH₄ mixture because the H₂ permeance for the original membrane, at least at low temperature, was significantly lower when CO₂ was present than when CH₄ was present. At 473 K, the H₂ permeances in H₂/CH₄ and H₂/CO₂ mixtures were about one order of magnitude lower in the silylated membrane.

Although the H₂ permeances decreased significantly with silylation, the permeances of the other gases decreased more, so that the H₂/CO₂ and H₂/CH₄ separation selectivities increased. The

separation selectivities were more than one order of magnitude higher than the original selectivities, as shown in Fig. 6a,b. Both the H₂/CH₄ and H₂/CO₂ selectivities increased significantly as the temperature increased from 298 K to 523 K, mainly because the H₂ permeance increased with temperature. Above 573 K, H₂ permeance in the H₂/CO₂ mixture continued to increase with temperature (Fig. 5b), but the CO₂ permeance also increased, so the selectivity leveled off (Fig. 6b). The modified membranes were stable, so that when silylated membrane B2 was stored in humid air for two months at room temperature and then heated at 523 K overnight, the permeances and selectivities at 473 K for H₂/CH₄ and H₂/CO₂ mixtures were within 2% of the values in Fig. 5 and Fig. 6. The membrane also operated at 773 K in the presence of hydrogen for 16 h with no degradation.

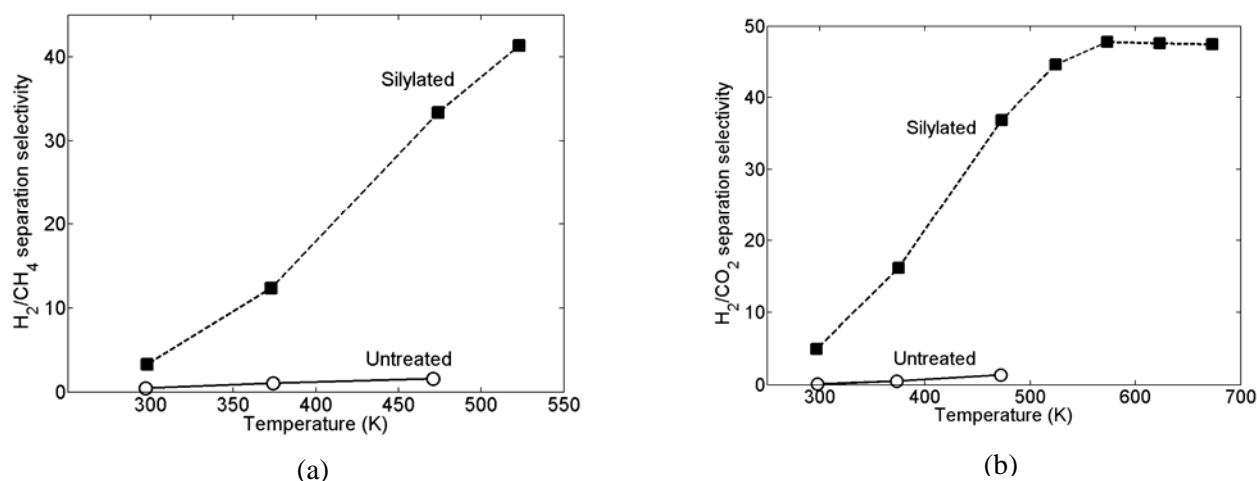


Fig. 6 Separation selectivity before and after silylation for B-ZSM-5 membrane B2 as a function of temperature in a 50/50 mixture of (a) H₂/CH₄ and (b) H₂/CO₂

Table 2. H₂ permeances and separation selectivities of silylated B-ZSM-5 membrane B2 for a H₂/CO₂ mixture at high temperature

Temperature (K)	Percent Conversion	Permeance $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)			Separation selectivity	
		H ₂	CO ₂	CO	H ₂ /CO ₂	H ₂ /CO
723	4 %	10.5	0.23	< 0.2	46	> 48
773	15%	12.5	0.21	0.22	60	57

Above 673 K, the H₂ and CO₂ reacted to form H₂O and CO; the modified B-ZSM-5 membrane catalyzed the reverse water gas shift reaction. Carbon monoxide was observed in the retentate and the permeate, but the GC could not detect water at low concentrations so the following concentrations are on a dry basis. At 723 K, the retentate contained 2% CO, and the CO concentration in the permeate was below 0.2%. The H₂ and CO₂ concentrations in the permeate were 93% and 7% respectively. At 773 K, the retentate contained 8% CO; the permeate contained 92% H₂, 7% CO₂, and 1% CO. Table 2 gives the percent conversion of the water-gas shift reaction, hydrogen permeances, and separation selectivities at 723 and 773 K.

3.3 Silylation of other MFI membranes

To confirm that the silylation reaction using MDES takes place on the acid sites within the zeolite membranes, a B-ZSM-5 membrane with Si/B=100 (B3) and a silicalite-1 membrane were silylated using the same procedure. Membrane B3 has a lower concentration of acid sites than B1

and B2 because less trivalent boron is present in the framework. Silicalite-1 is the all silicon analog of ZSM-5 without any active sites, since no trivalent Al or B is present in the framework. When the B-ZSM-5 membrane with a Si/B ratio of 100 (B3) was silylated, its H₂ permeance only decreased to half its initial value, and the H₂ selectivities relative to N₂, CO₂, and CH₄ only increased about 15% (Table 3). The H₂ permeance and separation selectivities of a silicalite-1 membrane, which does not have acid sites, did not change after silylation. This confirms that acid sites are needed for the silylation reaction with MDES, as the MDES will be pre-adsorbed there. This is also in accordance with the literature result.

Table 3. H₂ permeances and separation selectivities at 523 K before and after silylation of a B-ZSM-5 membrane with Si/B ratio of 100 (membrane B3)

Membrane	H ₂ permeance in mixture $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)			Separation selectivity		
	H ₂ /N ₂	H ₂ /CO ₂	H ₂ /CH ₄	H ₂ /N ₂	H ₂ /CO ₂	H ₂ /CH ₄
Fresh	27	26	29	2.0	1.7	1.4
Silylated	13	13	14	2.3	1.8	1.6

3.4 Silylation of SAPO-34 membranes

Two SAPO-34 membranes (S1, S2) with similar properties were prepared; their gas permeances and selectivities are shown in Table 4. The untreated SAPO-34 membrane S1 selectively separated H₂ from CH₄ (Fig. 7); the highest selectivity was 35, measured at 298 K. The H₂/CH₄ separation selectivity was high for the original SAPO-34 membranes because the SAPO-34 pores are almost the same size as the CH₄ kinetic diameter, which is 0.38 nm. In contrast to B-ZSM-5 membranes, silylation did not decrease H₂ permeances in mixtures for SAPO-34 membranes (Fig. 8 and Table 4). The CH₄ permeance decreased after silylation (Fig. 8), so that the H₂/CH₄ selectivity increased (Fig. 7). For clarity, the CH₄ permeance in Fig. 8 is multiplied by 20. The highest H₂/CH₄ separation selectivity for the silylated SAPO-34 membrane S1 was 59 at 298 K. As temperature increased, the H₂ permeance slightly decreased and the CH₄ permeance slightly increased, so the H₂/CH₄ separation selectivity decreased with temperature. The CH₄ permeance increased more for the silylated membrane. Thus, as shown in Fig. 7 and 8, at 525 K, silylation had no effect on permeance or selectivity. Silylation also increased the CO₂/CH₄ separation selectivity at room temperature, as shown in Table 4. The CO₂ permeance in a CO₂/CH₄ mixture decreased about 30% due to silylation.

Table 4. Gas permeances and separation selectivities at 298 K on SAPO-34 membranes before and after silylation

Membrane		H ₂ permeance $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	H ₂ /CH ₄ selectivity	CO ₂ permeance $\times 10^8$ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	CO ₂ /CH ₄ selectivity
S1	Fresh	4.7	35	10	73
	Silylated	4.8	59	7.7	110
S2	Fresh	3.4	20	10	68
	Silylated	3.5	30	6.4	87

The SAPO-34 membranes had much lower selectivities for H₂/CO₂ and H₂/N₂ mixtures than for H₂/CH₄ mixtures, but the selectivities increased with temperature, as shown in Fig. 9. Silylation did not change the H₂/CO₂ separation selectivity, and it increased the H₂/N₂ separation selectivity by less than 15%. Similar to the H₂ permeance in the H₂/CH₄ mixture, the H₂ permeances in H₂/CO₂ and H₂/N₂ mixtures did not change after silylation. Similar H₂/CH₄ and

H₂/CO₂ separation performance with temperature (not shown here) was seen for membrane S2 before and after silylation.

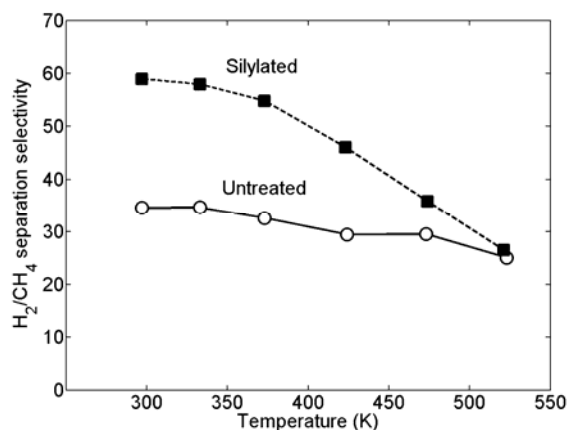


Fig. 7 H₂/CH₄ separation selectivity before and after silylation for SAPO-34 membrane S1 as a function of temperature in a 50/50 mixture of H₂/CH₄

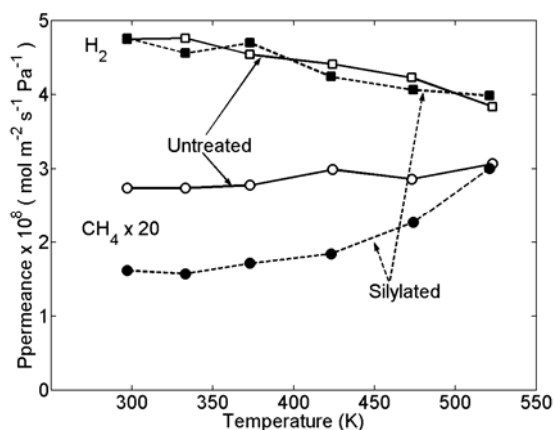


Fig. 8 H₂ and CH₄ permeances before and after silylation for SAPO-34 membrane S1 as a function of temperature in a 50/50 mixture of H₂/CH₄

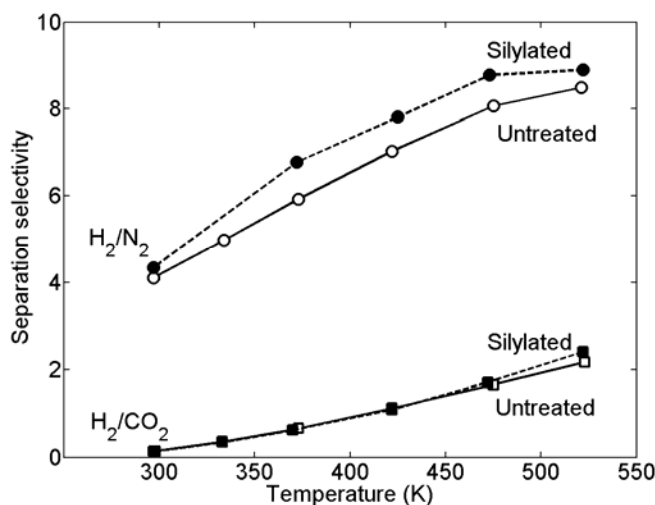


Fig. 9 Separation selectivity before and after silylation for SAPO-34 membrane S1 as a function of temperature in 50/50 mixture of H₂/CO₂ and H₂/N₂

3.5 Ion-exchange of SAPO-34 membranes

Two SAPO-34 membranes (S3, S4) were ion exchanged from the H⁺ form to the metal form. Membrane S3 was exchanged with Cu²⁺ ion and membrane S4 with K⁺ ion. The hydrogen permeance in H₂/CH₄ mixture was almost not affected by exchange with Cu²⁺ ion, and the H₂/CH₄ selectivity increased about 25% (Fig. 10). As for S4, however, the K⁺ ion exchange decreased both its hydrogen permeance and H₂/CH₄ separation selectivity in the binary mixture (Fig. 11). Therefore, the ion exchange of SAPO-34 membranes is not an efficient method for improving their hydrogen separation performance (as of Cu²⁺ exchange) or maybe even partially blocked the zeolite channel (as of K⁺ exchange). Interestingly, both the Cu²⁺ and K⁺ exchange increased the CO₂/CH₄ separation selectivity of the SAPO-34 membranes accompanied by a slight decrease in

CO₂ permeance (Table 5). This maybe because the CO₂ and CH₄ adsorption properties on the zeolite membranes were altered by ion exchange.

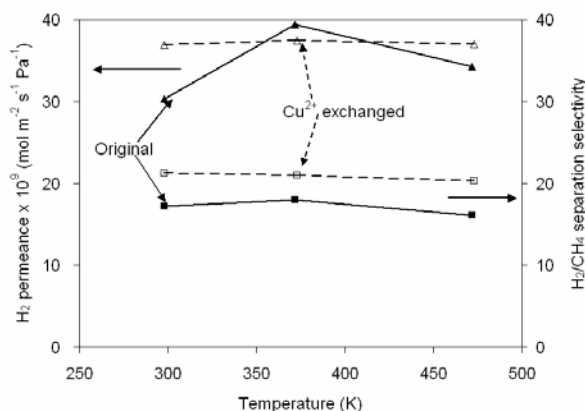


Fig. 10 H₂ permeance and separation selectivity before and after Cu²⁺ exchange for SAPO-34 membrane S3 as a function of temperature in 50/50 mixture of H₂/CH₄

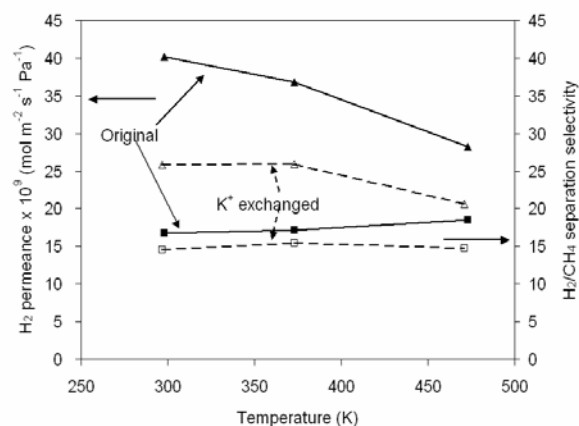


Fig. 11 H₂ permeance and separation selectivity before and after K⁺ exchange for SAPO-34 membrane S4 as a function of temperature in 50/50 mixture of H₂/CH₄

Table 5. Gas permeances and separation selectivities at 298 K on SAPO-34 membranes before and after ion exchange

	Membrane	H ₂ permeance × 10 ⁸ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	H ₂ /CH ₄ selectivity	CO ₂ permeance × 10 ⁸ (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	CO ₂ /CH ₄ selectivity
S3	Fresh	3.0	17	8.9	49
	Cu ²⁺ exchanged	3.7	21	7.8	69
S4	Fresh	4.0	17	1.0	40
	K ⁺ exchanged	2.9	14	5.3	64

4. CONCLUSIONS

For medium pore MFI membranes, silylation using catalytic cracking of methyl-diethoxysilane decreased their effective zeolite pore size and increased their H₂ separation selectivities, but H₂ permeance decreased more than an order of magnitude. The effect of silylation depends heavily on the number of acid sites within the structure, but not the strength of the acid sites. The best H₂ separation results were obtained on silylated B-ZSM-5 membranes with Si/B ratio of 12.5. Both the H₂ permeance and H₂/CO₂ and H₂/CH₄ separation selectivities significantly increased with temperature up to 773 K. The highest H₂/CO₂ and H₂/CH₄ separation selectivities were 48 and 41, respectively. The highest H₂ permeance during separations was 1 × 10⁻⁷ mol·m⁻²·s⁻¹·Pa⁻¹.

For small pore CHA type SAPO-34 membranes, methyl-diethoxysilane did not fit into SAPO-34 zeolite pores, but it partially blocked non-zeolite pores and increased H₂/CH₄ and CO₂/CH₄ separation selectivity while the H₂ permeance was unchanged. The highest H₂/CH₄ separation selectivity for a SAPO membrane was 59 at 298 K. Ion exchanges of SAPO-34 membranes from H⁺ form to Cu²⁺ or K⁺ form were not efficient methods for improving the H₂

separation performance. Both silylation and ion exchange significantly increased the CO₂/CH₄ separation selectivities on SAPO-34 membranes.

5. FUTURE WORK

The silylated B-ZSM-5 membranes (Si/B=12.5) could effectively separate H₂ from other light gases. However, H₂ permeance decreased more than an order of magnitude. Our B-ZSM-5 membranes were about 3.5 μm thick, with initial H₂ permeance about $5 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. Thinner MFI membranes (silicalite-1) with a thickness of 0.5 μm have been reported in literature that have H₂ permeances as high as $2.2 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at room temperature, but their membranes do not have acid sites. Our first proposed future work is to synthesize thinner MFI membranes with large number acid sites in the structure that should have high initial H₂ permeance. Silylating such membranes might yield H₂-selective membranes with higher permeances than obtained in the current study, and that might have potential for commercial application. Another approach to increase the H₂ permeance through the silylated membranes would be masking the bulk zeolite channel during the silylation. As a result of the masking, only the channel entrance part will be reduced, with the bulk zeolite channels intact. Therefore, only the upper part of zeolite channel has the reduced size and act as a thin effective separating layer of the membrane, and the transport resistance should be much less than if the whole zeolite channel size is reduced.

As the silylation procedure on zeolite membranes shows promise for H₂ separation, the underlying mechanisms will be investigated. Gas adsorption isotherms on zeolite powders before and after silylation will enable us to study the adsorption, diffusion and structure changes of the zeolite pores. Membranes with different initial gas transport properties but with similar number of acid sites will be silylated. This will tell us about the role of the non-zeolite transport pathways and what is the dominant transport mechanism. The silylation procedure will be optimized based on the knowledge obtained.

Although the modified MFI membranes showed promising H₂ separation properties, small pore (0.3-0.4 nm) zeolite membranes that directly separate H₂ without the need for further modification is highly desirable. Therefore, a more interesting and challenging task is to synthesize these small pore zeolite membranes by modifying their powder preparation procedures.

Currently, selectivities and permeation rates were measured in binary mixtures of H₂/CO₂, H₂/CH₄ and H₂/N₂ at 138 kPa and 298-773 K. More realistic separation conditions will be explored for highly selective H₂ separation zeolite membranes, which include separation of syngas mixtures in the presence of water at elevated pressures from 100 - 2000 kPa.