

On-stream modification of MFI zeolite membranes for enhancing hydrogen separation at high temperature

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Abstract

α -Alumina-supported MFI zeolite membranes were modified by on-stream catalytic thermal cracking of methyl-diethoxysilane (MDES) molecules inside the zeolitic channels during the separation of H_2/CO_2 gas mixture at 450 °C and atmospheric pressure. The MDES vapor was carried by the H_2/CO_2 feed gas and the effect of modification was monitored continuously through online analysis of the permeate stream. The modified membrane exhibited a significant increase in H_2 selectivity over CO_2 with a moderate decrease in H_2 permeance. At 450 °C, the modified MFI membrane obtained a H_2/CO_2 permselectivity of 17.5 with H_2 single gas permeance of $1.86 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ as compared to a permselectivity of 2.78 and permeance of $2.75 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for the membrane before modification. The modified membrane also showed good performance and stability in separation of H_2/CO_2 gas mixture containing up to 28.4% water vapor at 450 °C and atmospheric pressure.

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1. Introduction

High temperature gas separation membranes may play an important role in future cost-effective production of hydrogen (H_2) from catalytic reforming of coal, natural gas, and biomass for use in fuel cells and emerging clean power systems. The economic viability of inorganic membranes for H_2 purification depends on the H_2 flux and selectivity as well as the membrane life time. In general, mesoporous inorganic membranes have very high flux but low H_2 selectivity as limited by Knudsen factor at high temperature. On the contrary, dense inorganic membranes such as precious metal alloy, proton conductive ceramic, and metal-ceramic composite membranes, provide nearly perfect H_2 selectivity but the hydrogen fluxes of dense ceramic membranes are very low while the metallic membranes are expensive and vulnerable to contamination by impurities commonly existing in reforming gases. Microporous

inorganic membranes, particularly zeolite and amorphous silica membranes have been actively researched in recent years because of their potential to achieve high flux and high selectivity in high temperature H_2 separation. The molecular sieve amorphous silica membranes have been demonstrated to have excellent H_2 selectivity over small molecule gases such as CO_2 , CO , N_2 , and CH_4 [1]. However, the thermal instability of microporous silica membranes in humid conditions still remains a major concern. Highly siliceous microporous zeolite membranes possess excellent hydrothermal stability and chemical resistance because of their crystalline nature which makes them very attractive for use in high temperature H_2 separation from catalytic reforming streams [2].

At high temperatures (e.g. >400 °C), where adsorption of small molecules like H_2 , CO_2 , and light hydrocarbons is negligible in zeolites, H_2 separation through zeolite membranes relies primarily on molecular sieve effect and/or competitive diffusion mechanisms [3]. For H_2 and CO_2 , which have close molecular sizes of 0.28 nm and 0.33 nm, respectively, it is difficult to make a membrane with uni-

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form pore size in between the two to realize size exclusion effect. Nevertheless, a high selectivity of H_2 over CO_2 may be obtained when the zeolite pore dimension approaches the size of H_2 to achieve predominant configurational (activated) diffusion mechanism [4]. However, studies on zeolite membranes for high temperature (e.g. $>300^\circ\text{C}$) H_2 separation from small gases like CO_2 have been limited so far.

Membranes of small pore zeolites such as DDR and SAPO-34, which have effective pore sizes of about 0.40 nm and 0.38 nm, respectively, were therefore anticipated to offer good separation for small gases such as H_2 , CO_2 , and N_2 . However, microdefects, mainly nanometer-scale intercrystalline pores and boundaries, may cause serious loss of separation selectivity in such small pore zeolite membranes [5,6]. Tomita et al. [5] reported that, on DDR membranes, H_2 and CO_2 single gas permeance decreased when temperature increased from 28°C to 100°C while the membranes were CO_2 permselective at these temperatures. Hong et al. [6] reported a transition of CO_2 -selective permeation to H_2 -selective permeation for an equimolar H_2/CO_2 gas mixture on SAPO-34 membrane when temperature increased from 25 to 275°C . However, the H_2/CO_2 separation factor at 275°C was only about 2. Such low H_2/CO_2 selectivities may be attributed to the effects of CO_2 adsorption at the relatively low operating temperatures and the existence of microdefects in the polycrystalline membranes. Furthermore, the H_2 permeance in both the DDR and SAPO-34 membranes were quite low ($<5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) because of the large mass transport resistance posed by the small pore size and relatively large membrane thickness (3–5 μm).

Highly siliceous MFI zeolite, i.e. silicalite and ZSM-5, membranes with zeolitic pore size of $\sim 0.56 \text{ nm}$ offer high permeance of H_2 and excellent hydrothermal and chemical stabilities [2]. However, the H_2 selectivity over CO_2 and other small gases was found to be low at high temperatures because transport of small molecules in zeolites of relatively large pores may be primarily governed by Knudsen-type diffusion mechanism. Based on kinetic theory, Xiao and Wei [4] concluded that, in MFI zeolites, a transition from Knudsen to configurational diffusion mechanism occurs when the ratio of molecular size to zeolite pore size (λ) reaches 0.6–0.8 at 27°C . The transitional value of λ increases with increasing temperature. The λ values of H_2 and CO_2 for MFI zeolites are 0.5 and 0.59, respectively. Thus, a small reduction of the MFI zeolite pore size is expected to cause a dramatic enhancement of H_2/CO_2 separation selectivity. Also, the nanometer-scale intercrystalline pores and grain boundaries exist inevitably in the polycrystalline membranes [7,8]. These non-zeolitic pores can severely reduce the membrane selectivity especially when the separation relies on molecular sieving or size and shape selectivity [9–11]. Theoretical models have been proposed to account for the effect of non-zeolitic pores on mass transport through zeolite membranes [12–15]. By taking into account the activated diffusion, Knudsen diffusion, and viscous flow in the zeolitic and intercrystalline pores,

the dual-pore models [13–16] correctly represented the significant effect of intercrystalline pores in MFI zeolite membranes on small gas permeation. Therefore, to enhance the selectivity for H_2 separation from small molecule gases, the MFI membranes must be modified to reduce the intracrystalline pore size as well as to minimize the non-selective intercrystalline pores.

Masuda et al. [17] modified ZSM-5 zeolite membranes by catalytic cracking of silane molecules (e.g. methyl-diethoxysilane and MDES) pre-adsorbed at the active sites such as acid sites and metal cations in the zeolite structure. By calcining the cracked species in air, mono SiO_2 units formed in the zeolite channels that reduced the effective size of the pores. After modification, the H_2 separation factor for H_2/N_2 mixture increased by more than 50 times at 110°C but the H_2 permeance was reduced by an order of magnitude from $\sim 2.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $\sim 2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. Hong et al. [6] employed a similar silylation method to modify B-ZSM-5 membranes using MDES. The modified membrane exhibited a H_2 separation factor of 47 for equimolar H_2/CO_2 gas mixture at 400°C which was higher than that obtained on the unmodified membrane by an order of magnitude. However, the H_2 permeance on their modified membranes also decreased by an order of magnitude as compared to that on the untreated membrane. In the works of both groups, the severe decreases in H_2 permeance might be caused by excessive deposition of SiO_2 inside zeolitic pores along the entire membrane thickness (3–5 μm) and possible closure of zeolite pores by deposition at the external surface as the silane precursor was pre-adsorbed to saturation level in vapor or liquid phase [6,17].

The above modifications of MFI membranes by silylation inside the zeolitic channels showed the potential for tuning the pore size to enhance H_2 separation from small gases at high temperatures. Also, if the modifying species are deposited at active sites inside the zeolite channels, the modified membranes may have better stability in high temperature humid atmospheres than molecular sieve silica membranes or membranes modified by silica deposition on the external surfaces. However, the modification process must be better controlled to avoid excessive deposition that causes unacceptable loss in gas permeability. In this work, we use an on-stream MDES vapor deposition approach to modify α -alumina-supported MFI membranes during the permeation of H_2/CO_2 gas mixture at 450°C . The membrane modification effect is continuously monitored through online measurement of the H_2/CO_2 separation results that allows great control of the modification process.

2. Experimental

2.1. MFI zeolite membrane preparation

Disc-shaped substrates (2 mm-thick and 25 mm in diameter) were made from Alcoa SG16 α -alumina powders by dry pressing and sintering process. The substrate had a

porosity of 25–30% and average pore size of $\sim 0.1 \mu\text{m}$. The substrates are polished by 600 mesh SiC sandpapers and the disc edges were sealed with glass coatings. The active membrane area was 2.54 cm^2 . The MFI zeolite membranes were synthesized by in situ crystallization method. The detailed synthesis procedure can be found in previous publications [7,9]. The precursor was prepared by dissolving 5 g fumed silica powders (99.8%, Aldrich) in a solution containing 25 ml of 1 M tetrapropylammonium hydroxide (TPAOH) solution (Aldrich) and 0.35 g NaOH (99.998%, Aldrich) at 80°C . After aging for 4 h, the precursor was filtered and then transferred into a Teflon-lined autoclave in which the substrate was placed on the bottom facing upward. Hydrothermal synthesis was performed at 180°C for 4 h. The synthesized membranes were washed, dried, and then calcined in air at 450°C for 8 h. General membrane characterizations were conducted by X-ray diffraction (XRD) to verify the zeolite structure and scanning electron microscopy (SEM) to observe the membrane morphology and estimate its thickness.

2.2. On-stream membrane modification

Fig. 1 shows the schematic diagram of the experimental apparatus used for membrane modification and gas separation. The zeolite membrane was mounted in a stainless steel cell with the membrane surface facing the feed stream. The membrane cell was placed in a temperature-programmable box furnace. During membrane modification, an equimolar H_2/CO_2 feed gas bubbled through the silane (MDES) saturator at room temperature before entering the membrane cell. The H_2/CO_2 dry gas feed flow rate was 45 (STP) cm^3/min . The downstream of the membrane was swept by helium at a flow rate of 33.5 (STP) cm^3/min . The membrane modification was performed at 450°C and atmospheric pressure because catalytic cracking of MDES at the active sites in MFI zeolites starts to take place at $\sim 430^\circ\text{C}$ [17]. The permeate gas was continuously analyzed by an online gas chromatograph (GC, Agilent, 6890N) equipped with a thermal conductivity detector (TCD) and a Hayesep[®] DB packed column (Alltech). The permeate gas during the silane cracking modification process was also examined by the online GC–mass spectrometer (MS, Agilent, 5975B).

The entire process of modification was monitored. The process started with permeation of the equimolar H_2/CO_2 dry gas mixture at room temperature (23°C) for 90 min. Then, the temperature was raised at a rate of $0.5^\circ\text{C}/\text{min}$ to 450°C where the separation was stabilized for 150 min. The temperature was held at 450°C afterwards and the H_2/CO_2 feed stream was switched to flow through the silane liquid column (saturator) where the feed gas was saturated with MDES vapor at room temperature prior to entering the high temperature membrane cell. The dynamic size of the MDES molecule is $0.4 \text{ nm} \times 0.9 \text{ nm}$ which can readily enter the zeolite pores (diameter $\sim 0.56 \text{ nm}$) because of its linear shape [17]. The feed gas was switched back from the silane saturator to dry feeding route to end the modification when the H_2/CO_2 separation factor reached plateau. Separation of the H_2/CO_2 dry gas continued at 450°C for more than 50 h after the termination of modification.

2.3. Gas permeation and hydrogen separation

The membrane was tested by H_2 and CO_2 single gas permeation in a temperature range of $23\text{--}450^\circ\text{C}$ before and after modification. In the single gas permeation measurements, the feed flow rate was 22.5 (STP) cm^3/min and the downstream He sweep flow rate was 33.5 (STP) cm^3/min . Separation of *p*-xylene/*o*-xylenes (PX/OX) vapor mixtures was also conducted to further evaluate the zeolite pore size reduction by modification. A PX/OX vapor mixture with PX and OX partial pressures of 0.52 kPa and 0.39 kPa, respectively, was carried by He (15 cm^3/min) on the feed side and the permeate side was swept by He flow at 15 cm^3/min . Composition of the xylene permeate stream was analyzed by the online GC equipped with a flammable ionization detector (FID) and a packed column of 5% SP-1200/5% Bentone 34 (Supelco). Separation of H_2/CO_2 gas mixtures was measured at 450°C and total pressure of 101 kPa as a function of the H_2 mole fraction in the feed. The separation of an equimolar H_2/CO_2 mixture was performed at 450°C under conditions with and without the presence of water vapor. In the separation of H_2/CO_2 mixtures, the total feed flow rate was 45 (STP) cm^3/min and the He sweep flow rate was 33.5 (STP) cm^3/min .

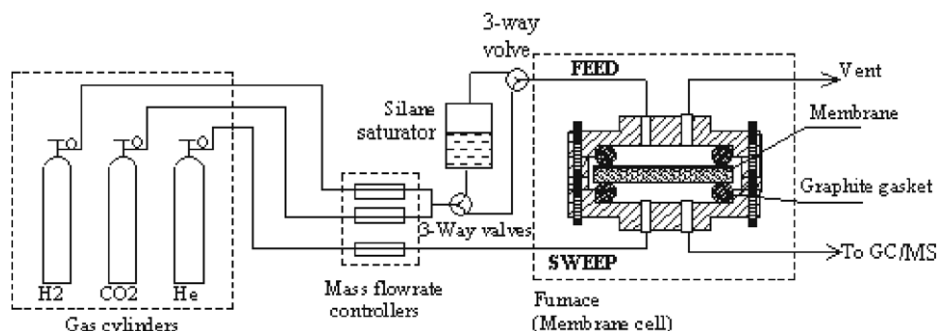


Fig. 1. Schematic diagram of the membrane modification and gas separation apparatus.

The membrane permeance of gas component i (Π_i , $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) is defined as

$$\Pi_i = \frac{Q}{A \cdot t \cdot \Delta P_i} \quad (1)$$

where Q (mol) is the moles of component i permeated through the membrane with an area of A (m^2) over a time period of t (s); and $\Delta P_i = (P_i)_f - (P_i)_p$, where $(P_i)_f$ and $(P_i)_p$ are the partial pressures of i in the feed and permeate sides, respectively. The permselectivity is defined as the ratio of pure gas permeances. The separation factor of component i over j (α_{ij}) is defined by

$$\alpha_{ij} = \frac{(y_i/y_j)}{(x_i/x_j)} \quad (2)$$

where x and y are mole compositions of the feed and permeate gas mixtures, respectively.

3. Results and discussion

3.1. Monitoring of the membrane modification process

It has been documented in the literature that MFI zeolite membranes synthesized directly on α -alumina substrates by in situ crystallization from aluminum-free precursors are not pure silicalite. The resultant MFI zeolite film contains a small amount of aluminum because of the slight dissolution of alumina surface during hydrothermal crystallization and solid state diffusion of Al^{3+} through the zeolite/alumina interface during high temperature calcination [2,18]. Therefore, a limited number of acid sites and/or cations exist in the zeolite pores which can catalyze MDES cracking to reduce the effective pore size. Through the online monitoring of H_2/CO_2 separation results, the extent of zeolite pore modification by MDES cracking and deposition can be controlled by timely termination of MDES vapor input to achieve high H_2 selectivity while avoiding excessive deposition.

Fig. 2 presents the H_2/CO_2 separation results monitored during the entire modification process. At 23°C , the fresh MFI membrane was selective toward CO_2 with a H_2/CO_2 separation factor of 0.35 and a low H_2 permeance of $5.86 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ because the preferentially adsorbed CO_2 limited the access of H_2 molecules to the zeolite pores. The permeance of H_2 increased and the CO_2 permeance decreased continuously when temperature was raised. The membrane experienced a transition from being CO_2 -selective to H_2 -selective at about 140°C . These results are in principle consistent with the general observations on the temperature dependence of permeation for gas mixtures containing adsorbing and non-adsorbing small molecules which can be well explained by competitive adsorption–diffusion models [3,19–21].

After the H_2/CO_2 gas permeation stabilized at 450°C , the MDES vapor was introduced to the feed stream to start the modification. In the first 5 min after the introduction of MDES vapor, the H_2 and CO_2 permeances were reduced

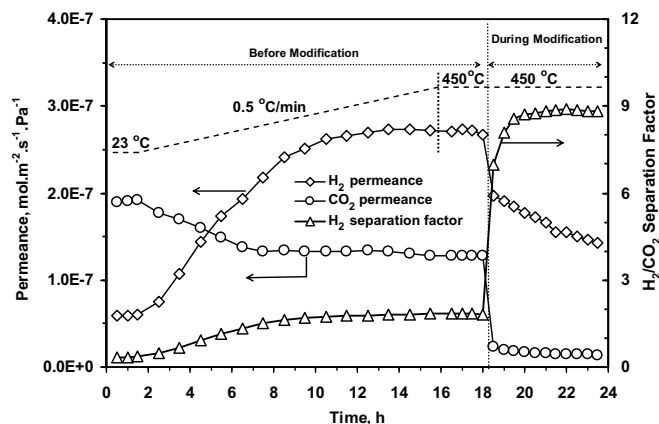


Fig. 2. Permeation of equimolar H_2/CO_2 gas mixture during the process of membrane modification.

rapidly from 2.73×10^{-7} and $1.28 \times 10^{-7} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, respectively, to 1.97×10^{-7} and $2.33 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, respectively, and the H_2/CO_2 separation factor increased sharply from ~ 1.8 to 7.0. The H_2/CO_2 separation factor approached plateau in about an hour. However, the H_2 and CO_2 permeances continued to decrease as the modification process went on, though the decreases of gas permeance were much slower compared to that in the first five minutes. The observation of the quickly stabilizing separation factor with the continuously decreasing permeance suggests that modification of the intracrystalline zeolite pores was nearly completed in less than an hour because of the limited number of active sites in the zeolite structure. Because direct thermal decomposition of MDES on non-catalytic surface is difficult at a relatively low temperature of 450°C , no film deposition could occur at the outer surface of the zeolite membrane where very few catalytic sites existed. However, the MDES molecules, which cannot travel through the modified zeolite pores, may diffuse through the intercrystalline pores to the substrate side. Thus, catalytic cracking and deposition of silane compounds continued at the zeolite (membrane)/alumina (substrate) interface region where high density of acid site exists. The silane cracking and deposition at the membrane/substrate interface reduced the gas permeability without enhancing the selectivity by covering the zeolite external surface on the substrate side. Therefore, in this work, the modification was ended in about 5 h when the H_2/CO_2 separation factor tended to stabilize at about 9.

The constituents of the permeate stream was analyzed by GC–MS during the early stage of modification period and non-modification regular separation process. Besides the CO_2 , which existed in the feed, H_2O , CO , CH_4 and C_2H_4 , which were not found in the feed gas, were identified by the MS during modification. The H_2O and CO may be generated by the reverse reaction of water gas shift on the catalytic zeolite/alumina surface [6]. The intensity of H_2O peak in the mass spectrum was much higher in the membrane modification period than in the regular H_2/CO_2 dry gas separation process, indicating dehydration of the

MDES cracking species C_2H_5OH and $[C_2H_5O-Si]$ to C_2H_4 [22]. The CH_4 could be a direct product of MDES cracking [23] and/or produced by CO methanation reaction at acid site in the reducing atmosphere. Masuda et al. [17] have confirmed that $Si-CH_3$, $Si-H$, $Si-OC_2H_5$, and Si form from decomposition of the chemisorbed MDES in ZSM-5 zeolites in inert atmosphere or under vacuum at 400–500 °C. They reported that further heating up to 550 °C resulted in deposition of Si bonded to the zeolite framework. In this work, MDES decomposition kinetics in the reducing atmosphere is expected to be similar to the case of inert gas. However, the water generating reactions may facilitate the hydrolysis of $Si-OC_2H_5$ to form $Si-H$ and C_2H_5OH .

The permeation of H_2/CO_2 dry gas mixture was continued at 450 °C for more than 48 h after the modification period. As shown in Fig. 3, where the on-stream time is continued from Fig. 2 to indicate the operation continuity, the H_2 permeance increased while the CO_2 permeance decreased slightly in the initial ~10 h and then stabilized. This is likely due to the film annealing effects and gradual completion of thermal cracking of the deposited species. The H_2/CO_2 separation factor increased accordingly from ~9 to a stabilized value of 10.8 with H_2 permeance of $1.64 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

3.2. Gas/vapor permeation before and after modification

Table 1 shows the results of PX/OX vapor separation at 300 °C on the membrane before and after modification. The fresh membrane exhibited a PX/OX separation factor of 9.1 suggesting a reasonably good membrane quality. After modification, the membrane had virtually no separation for the PX/OX mixture when the permeance values of PX and OX decreased for 139 and 18 times, respectively. This indicates that both the intracrystalline zeolitic pores and nanometer-scale intercrystalline pores were reduced by the modification. Before modification the PX (dynamic

Table 1

Separation of PX/OX vapor mixture at 300 °C on the MFI membrane before and after modification

Membrane	Permeance ($\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)		Separation factor (PX/OX)
	PX	OX	
Before modification	1.67×10^{-8}	2.00×10^{-9}	9.1
After modification	1.20×10^{-10}	1.11×10^{-10}	1.1

size 0.58 nm) permeates primarily through the zeolitic pores and OX (dynamic size 0.68 nm) permeates mainly through the nanometer-scale intercrystalline pores [9].

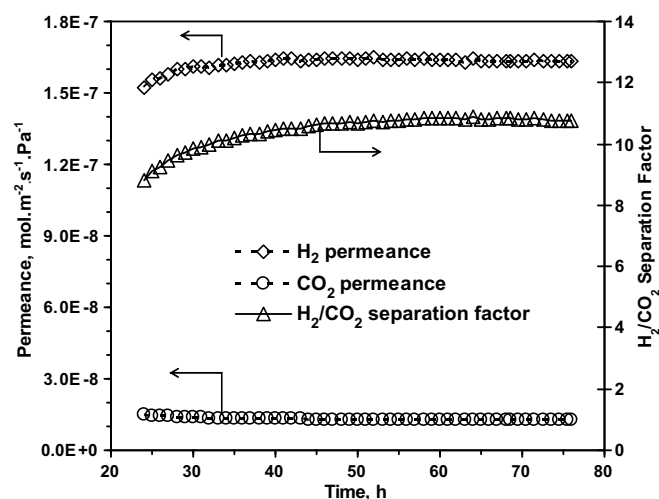


Fig. 3. Equimolar H_2/CO_2 binary gas permeation at 450 °C immediately after modification.

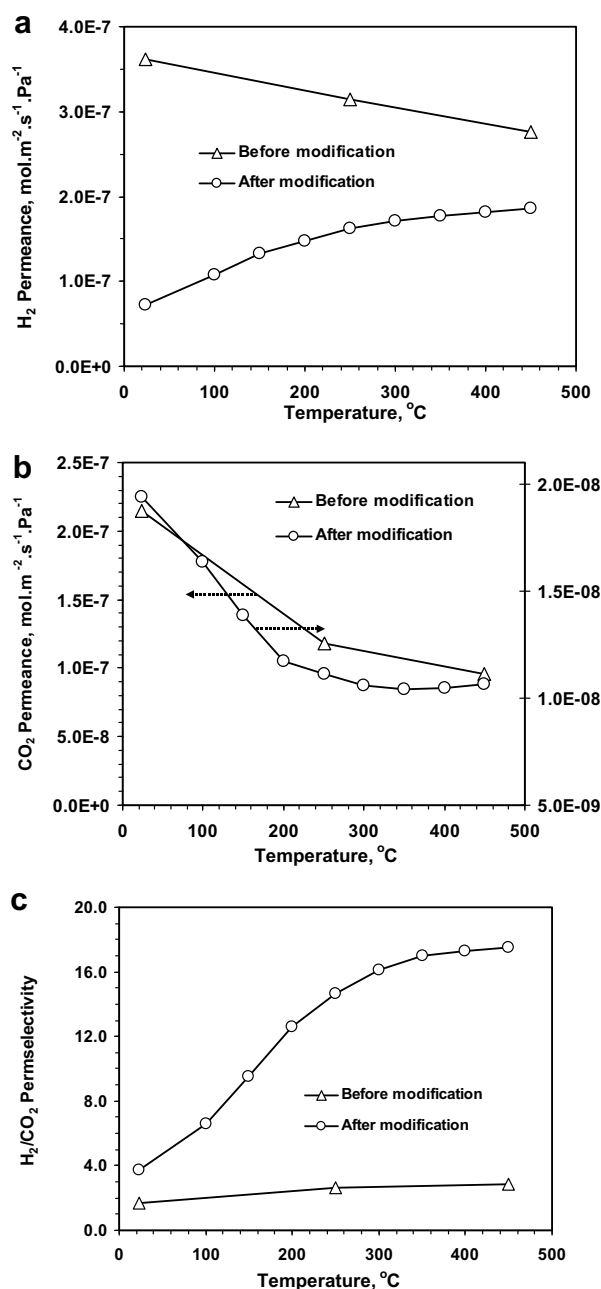


Fig. 4. Single gas permeation as a function of temperature before and after membrane modification: (a) H_2 permeance, (b) CO_2 permeance and (c) H_2/CO_2 permselectivity.

After modification, the zeolitic pores became impermeable to the PX. Therefore both PX and OX permeated through the non-selective intercrystalline pores which were also significantly reduced as indicated by the drastic decrease in OX permeance.

The results of H_2 and CO_2 single gas permeation measured in a temperature range of 23–450 °C are presented in Fig. 4. Before modification, permeance of both H_2 and CO_2 decreased with increasing temperature because Knudsen-type diffusion mechanism dominated the small gas transport in the 0.56 nm zeolitic pores [4]. After modification, the H_2 permeance increased with increasing temperature because the permeation became controlled by activated diffusion in the zeolitic pores of reduced size. The decrease in H_2 permeance caused by the membrane modification was quite moderate (<50%). On the other hand, the CO_2 permeance decreased drastically by an order of magnitude after the modification because the zeolite pore size reduction posed a greater obstacle to the diffusion of the CO_2 molecules which have a dynamic size slightly larger than H_2 . The apparent activation energies for transport of H_2 and CO_2 through the modified membrane were calculated to be 2.1 kJ/mol for H_2 and 18.1 kJ/mol for CO_2 based on the permeance data in the temperature range of 350–450 °C. The H_2/CO_2 permselectivity increased from 2.78 for the fresh membrane to 17.5 for the modified membrane at 450 °C. The H_2/CO_2 permselectivity on the unmodified membrane was lower than the ideal Knudsen factor (4.7) because the counter permeation of the He sweep gas has a much greater impact on the H_2 (smaller than He) permeation than on CO_2 (much bulkier than He) [24].

The CO_2 permeance in the modified membrane exhibited a minimum value at ~350 °C. The total CO_2 permeance was very low in the modified membrane. The CO_2 flow comprised two parts of permeation, including the activated diffusion through the modified zeolitic pores and Knudsen diffusion through the intercrystalline pores. The minimum CO_2 permeance is a result of the temperature-dependent changes in the activated diffusion coefficient, which increases following an exponential function of $1/T$, and the Knudsen diffusion coefficient, which decreases by a linear function of $1/\sqrt{T}$.

3.3. Separation of H_2/CO_2 dry gas mixture

Separation of equimolar H_2/CO_2 dry gas mixture was conducted as a function of temperature. The results are shown in Fig. 5. When temperature increased from 23 to 450 °C, the H_2 permeance increased continuously from $5.89 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $1.64 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ while the CO_2 permeance again showed a minimum at ~350 °C. A qualitative change of H_2/CO_2 selectivity was observed at low temperature on the modified membrane compared to the fresh membrane. At 23 °C the fresh membrane was CO_2 -selective with a H_2/CO_2 separation factor of 0.35 (Fig. 2) because of the preferential adsorp-

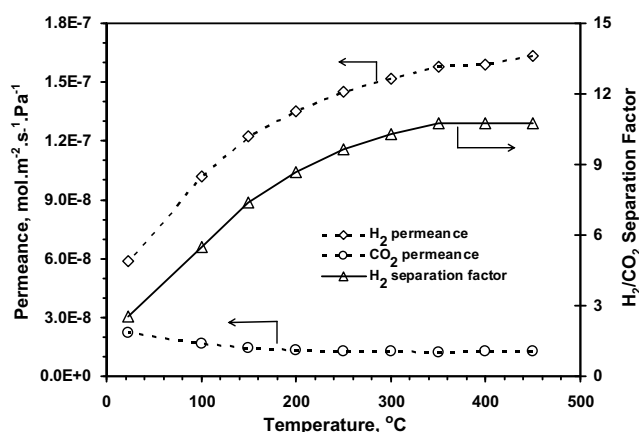


Fig. 5. Separation of an equimolar H_2/CO_2 dry gas mixture on the modified membrane as a function of temperature.

tion of CO_2 . The membrane became H_2 -selective after modification even at 23 °C where a H_2/CO_2 separation factor of 2.56 was obtained. This indicates that the modified membrane possess certain size-selectivity between H_2 and CO_2 . Compared to the fresh membrane, the modified membrane only had a moderate loss of 40% in H_2 permeance when the H_2/CO_2 separation factor increased from ~1.85 to 10.8 at 450 °C.

Experiments were also conducted to measure the separation of H_2/CO_2 gas mixture at 450 °C as a function of H_2 mole fraction in the feed at a total feed pressure of 101 kPa. The results are presented in Fig. 6. The CO_2 permeance was nearly unchanged in the entire tested range of H_2 mole composition in the feed. The H_2 permeance, however, increased from $1.40 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $2.30 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ when the H_2 feed composition increased from 4% to 93% and the H_2/CO_2 separation factor enhanced accordingly from ~10.8 to 14.6. This observation can be explained by taking into account the influence of sweep gas counter permeation. It was reported by van de Graaf et al. [24] that, when raising the feed pressure while maintaining the sweep pressure, the permeance

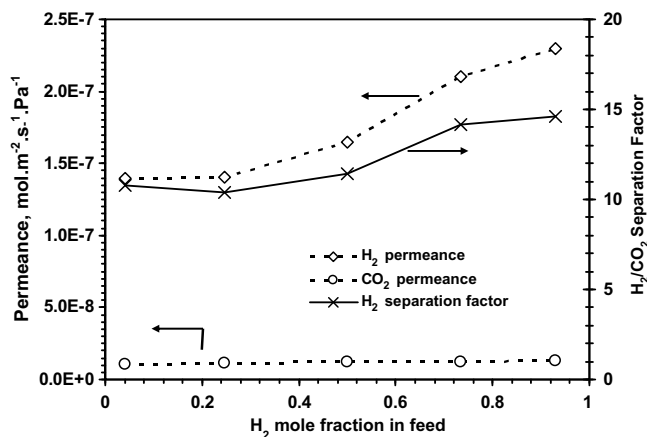


Fig. 6. H_2/CO_2 separation on the modified membrane as a function of H_2 mole fraction at 450 °C and 101 kPa.

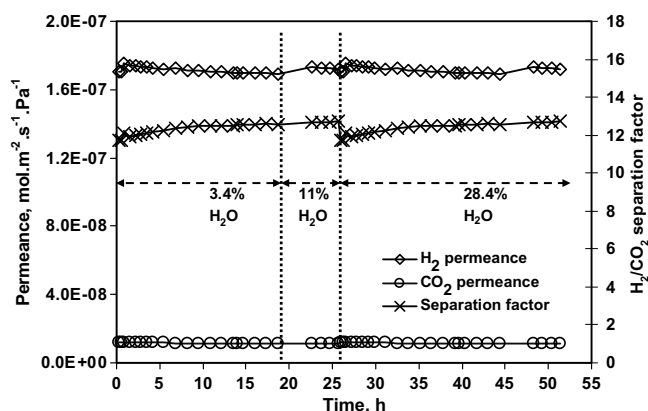


Fig. 7. Separation of H_2/CO_2 humid gas mixture on the modified membrane.

of feed gas increased and the counter permeance of sweep gas decreases. In the current case, under constant total pressure, raising the H_2 feed composition increased the H_2 partial pressure in the feed and thus enhanced the H_2 permeance. On the other hand, CO_2 permeance was hardly affected by changing composition as its permeation is much less influenced by the sweep He because of its much larger molecular mass than the He.

3.4. Separation of H_2/CO_2 gas mixture containing water vapor

The effect of water vapor in the H_2/CO_2 feed stream on the membrane separation performance was tested at 450°C . The steam concentration was increased from 3.5% to 11% and then to 28.4% without interrupting the operation. The membrane was stable in a tested period of more than 50 h as shown in Fig. 7. The addition of water vapor to the feed stream caused a slight decrease in CO_2 permeance by $\sim 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ or $\sim 8\%$ of the permeance under dry condition. Such a small reduction of CO_2 permeance may be attributed to the reversible water gas shift reaction, which consumed a small amount of CO_2 during permeation, as well as that the small water molecules (0.30 nm) further limited the probability for CO_2 to enter the pores. On the contrary, the presence of water vapor caused a slight increase in the H_2 permeance by $\sim 7 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ or $\sim 4\%$ of the permeance in dry condition. A possible reason for this small increase of H_2 permeance is the water-associated reaction and condensation of siliceous species deposited at the membrane external surface [23], especially at the zeolite/alumina interface, which opens up the covered zeolite pores.

4. Conclusions

The results of this research demonstrated that the on-stream silane vapor deposition via catalytic thermal cracking in the zeolite pores was an effective method for

modifying zeolite membranes to enhance high temperature separation of small molecule gases. The on-stream operation allows continuous monitoring of the modification results that provides excellent controllability to achieve the optimal level of deposition/modification. The modification of MFI membranes using MDES as precursor was successful for enhancing H_2/CO_2 separation at high temperature up to 450°C . The modified membrane with silicon compounds deposited inside the zeolite channels appeared to be stable in humid condition at 450°C within a testing period of more than 50 h. Because of the ability to control the modification process via online monitoring of the separation results, excessive deposition can be avoided to retain a high permeance when enhancing the separation factor. At 450°C , the MFI membrane modified in this work achieved an increase of H_2/CO_2 permselectivity from 2.78 to 17.5 while the pure H_2 permeance decreased only moderately from $2.75 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $1.86 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The membrane modification approach developed in this work may be also useful as an on-stream repairing method for zeolite membranes during high temperature gas separation processes.

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References

- [1] H. Verweij, Y.S. Lin, J. Dong, MRS Bull. 31 (2006) 756.
- [2] M. Kanezashi, J. O'Brien, Y.S. Lin, J. Membr. Sci. 286 (2006) 213.
- [3] J. Dong, Y.S. Lin, W. Liu, AIChE J. 46 (2000) 1957.
- [4] J. Xiao, J. Wei, Chem. Eng. Sci. 47 (1992) 1123.
- [5] T. Tomita, K. Nakayama, H. Sakai, Micropor. Mesopor. Mater. 68 (2004) 71.
- [6] M. Hong, J.L. Falconer, R.D. Noble, Ind. Eng. Chem. Res. 44 (2005) 4035.
- [7] J. Dong, Y.S. Lin, M.Z. Hu, R.A. Peascoe, E.A. Payzant, Micropor. Mesopor. Mater. 34 (2000) 241.
- [8] G. Bonilla, M. Tsapatsis, D.G. Vlachos, G. Xomeritakis, J. Membr. Sci. 182 (2001) 103.
- [9] X. Gu, J. Dong, T.M. Nenoff, D.E. Ozokwelu, J. Membr. Sci. 280 (2006) 624.
- [10] Y.S. Yan, M.E. Davis, G.R. Gavalas, J. Membr. Sci. 123 (1997) 95.
- [11] M. Nomura, T. Yamaguchi, S. Nakao, Ind. Eng. Chem. Res. 36 (1997) 4217.
- [12] J.M. van de Graaf, F. Kapteijn, J.A. Moulijn, Chem. Eng. Sci. 54 (1999) 1081.
- [13] S. Sommer, T. Melin, F. Falconer, R.D. Noble, J. Membr. Sci. 224 (2004) 51.
- [14] F. Jareman, J. Hedlund, D. Creaser, J. Sterte, J. Membr. Sci. 236 (2004) 81.
- [15] F. Jareman, J. Hedlund, Micropor. Mesopor. Mater. 82 (2005) 201.
- [16] F. Jareman, J. Hedlund, Micropor. Mesopor. Mater. 83 (2005) 326.
- [17] T. Masuda, N. Fukumoto, M. Kitamura, Micropor. Mesopor. Mater. 48 (2001) 239.
- [18] K. Wegner, J. Dong, Y.S. Lin, J. Membr. Sci. 158 (1999) 17.
- [19] X. Gu, J. Dong, T.M. Nenoff, Ind. Eng. Chem. Res. 44 (2005) 937.
- [20] J.M. van de Graaf, F. Kapteijn, J.A. Moulijn, AIChE J. 45 (1999) 497.

- [21] W.J.W. Bakker, F. Kapteijn, J. Poppe, J.A. Moulijn, *J. Membr. Sci.* 117 (1996) 57.
- [22] M. Niwa, S. Kato, T. Hattori, Y. Murakami, *J. Chem. Soc. Faraday Trans. 1* (1984) 3135.
- [23] C.T. O'Connor, K.P. Moller, H. Manstein, *CatTech.* 5 (2001) 172.
- [24] J.M. van de Graaf, F. Kapteijn, J.A. Moulijn, *J. Membr. Sci.* 144 (1998) 87.