Effect of the Membrane Quality on Gas Permeation and Chemical Vapor Deposition Modification of MFI-Type Zeolite Membranes

Xuefeng Zhu, Haibing Wang, and Y. S. Lin*

Chemical Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona 85287

Chemical vapor deposition (CVD) with methyldiethoxysilane (MDES) for MFI zeolitic pore size reduction is an effective way to improve the H_2/CO_2 separation factor of zeolite membranes. However, only good membranes with few intercrystalline defects are able to show considerable improvement in H_2/CO_2 separation factor through CVD modification. It is unreliable to evaluate the membrane quality on the basis of the H_2/SF_6 or N_2/SF_6 ideal separation factor because the SF_6 adsorption-induced crystal swelling causes shrinkage of the intercrystalline defects in the MFI zeolite membranes. In this study, the quality of MFI zeolite membranes was evaluated on the basis of their performance in separating equimolar H_2/CO_2 mixture gas at room temperature. High-quality membranes are more selective to CO_2 molecules rather than H_2 at room temperature due to the adsorption of CO_2 into the zeolitic pores and blocking of the pore channels for H_2 diffusion. The effectiveness of the quality evaluation method was confirmed by on-stream CVD modification of MFI zeolite membranes with different initial H_2/CO_2 separation factors/ideal separation factors at room temperature. Experimental results showed that only those membranes with low H_2/CO_2 separation factor at room temperature (good membranes) showed improvement in H_2/CO_2 separation factor through CVD modification. For the CVD modified zeolite membrane with good initial quality, the permeance of H_2 is lower than that of He with an activated diffusion behavior for small gas molecules in the modified zeolitic pores.

1. Introduction

Inorganic membrane separation technology has attracted considerable attention because it offers an effective separation alternative to the current high energy cost separation techniques, such as distillation and cryogenic separation.[1,2] Because of the small pore size as well as excellent thermal and chemical stabilities in harsh environments, MFI zeolite membranes (including ZSM-5 and silicalite membranes) have been widely studied for their potential applications in separation of some important industrial gases and organic isomers. There are two different kinds of zeolitic pore channels in MFI zeolites, i.e., a straight channel along the *b*-direction with circular openings of 0.54 nm × 0.56 nm and a sinusoidal channel along the *a*-direction with elliptical openings of 0.51 nm × 0.55 nm. The pore size of MFI zeolites is on the same order of magnitude as the kinetic diameters of many molecules, which makes MFI zeolite membranes effective in separating some gas mixtures and organic isomers, such as H_2/C_4H_{10} mixture gas, butane isomers, and xylene isomers, based on the size exclusion and shape selectivity.[3-5] However, MFI zeolite membranes are ineffective in separation of gas mixtures composed of some small gas molecules, such as H_2 and CO_2 mixture gas, because MFI zeolitic pores are much larger than the sizes of the light gas molecules.

It was reported that single gas diffusion behavior in zeolites can be predicted by a gas translational diffusion model proposed by Xiao and Wei based on the relative size of the gas molecule to the zeolitic pore size and gas molecular loading in the microporous materials.[6] In this model, it is assumed that gas molecules inside the zeolitic pores retain their gaseous characteristics, although the movement of molecules from one site to another is restricted and an energy barrier imposed by the zeolitic pore channels has to be overcome. On the basis of this assumption, the diffusion behavior of some nonadsorbing gases, such as H_2, He, CO, and CO_2 at high temperatures, can be described by this model. The diffusion activation energy can be estimated by considering the difference in Lennard-Jones potentials between a molecule located at an intersection and a molecule located in a channel. The transition from a Knudsen diffusion mode to an activated diffusion mode depends on the ratio of the kinetic diameter of a gas molecule to the diameter of the zeolitic pore, λ (d_k/d_p). Generally, gas transport through MFI zeolite membranes follows a Knudsen-type diffusion mode when λ (d_k/d_p) is less than 0.6, while it follows an activated diffusion behavior when λ (d_k/d_p) is higher than 0.8. Between 0.6 and 0.8, the permeation of small gas molecules through zeolite membranes is controlled by both the Knudsen-type diffusion and activated diffusion.

On the basis of the above theory, it is expected that diffusion of some small gas molecules, such as He (d_k = 0.26 nm) and H_2 (d_k = 0.289 nm) in MFI zeolitic pores follows a Knudsen-type diffusion mode, and the gas permeance through MFI zeolite membranes is expected to decrease with an increase of temperature. The Knudsen-type diffusion behavior of some small gas molecules in MFI zeolite membranes were observed experimentally,[7,8] although some contradictory results showing an activated diffusion behavior were also reported.[9-12] For example, Lovallo et al.[10] reported that the H_2 permeance increases with temperature with an activation energy as high as 16 kJ/mol. These contradictory results suggest that an extensive investigation needs be done to understand the permeation behavior of small gas molecules through MFI zeolite membranes.

Although it is difficult to obtain a high H_2/CO_2 separation factor for MFI zeolite membranes according to the gas translational diffusion model proposed by Xiao and Wei,[6] it is implied that decreasing the zeolitic pore size is an effective way to realize a significant improvement of the H_2/CO_2 separation factor of MFI zeolite membranes. Chemical vapor deposition

(CVD) of amorphous silica onto the zeolite membranes using silanes or silicate esters as the precursor is usually utilized to eliminate the intercrystalline defects and narrow the zeolitic pores of MFI membranes.[13−16] Nomura et al.[13] used a counter diffusion CVD technique to modify silicalite membranes through introducing tetraethyl orthosilicate (TEOS) to the membrane side and O_3 oxidant to the other side of the membrane at 200 °C. The experimental results indicated that intercrystalline defects in zeolite membranes were narrowed or even eliminated due to the reaction of TEOS with O_3 in the intercrystalline defects and subsequent deposition of amorphous silica in the defects. The zeolitic pores were intact after the counter diffusion CVD modification, since TEOS molecules are too large to diffuse into zeolitic pores. The silicalite membrane which was CVD modified for 8 h showed an n-butane/isobutane selectivity of 87.8 at room temperature, while the ideal separation factor of He over N_2 still remained around Knudsen selectivity.

Masuda et al.[14] reported that the zeolitic pore size can be reduced from 0.56 to 0.36−0.47 nm through catalytic cracking deposition of methyldiethoxysilane (MDES), a silane source with a kinetic diameter smaller than the zeolitic pore size, into MFI zeolite pores to form a mono-SiO_2 layer. First, silane precursor molecules were preadsorbed chemically onto the active sites including acid sites and metal cations within the zeolite framework at 300 °C. After that, the adsorbed silane molecules were deposited on the active sites as a form of mono-SiO_2 layer by calcining the treated membrane in air at 500 °C. The H_2/N_2 separation factor increased from 1.5−4.5 for the fresh membrane to 90−140 for the modified membrane with a 90% reduction in H_2 permeance. This method was also adopted by Hong et al.[15] to modify B-ZSM-5 membranes, and a 1 order of magnitude decrease in H_2 permeance was observed though a H_2/CO_2 separation factor of 47 was obtained. Recently, Gu et al.[16] improved this modification technique through on-stream monitoring of the gas permeance and H_2/CO_2 separation factor. This on-stream CVD modification method enables prompt termination of CVD modification when the H_2/CO_2 separation factor is stabilized. This was done to avoid excessive deposition of MDES that may lead to more decrease of H_2 and CO_2 permeances without further improvement of the H_2/CO_2 separation factor. The modified MFI zeolite membrane showed a significant increase in H_2 selectivity over CO_2 with only a moderate decrease in H_2 permeance. For example, the H_2/CO_2 separation factor increased from 2.78 for the fresh membrane to 17.5 for the CVD modified membrane, while the H_2 single gas permeance decreased from 2.75×10^{-7} to 1.86×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, which was only a reduction of 32.4%.

Because there are many steps involved in the MFI zeolite membrane synthesis and it is difficult to control each step precisely, the reproducibility of zeolite membrane synthesis is generally poor. It is quite common that membranes synthesized in the same batch exhibit very different initial qualities. For this reason, it is important to develop a reliable method for membrane quality evaluation so that only good quality membranes are selected for extensive gas permeation test and subsequent CVD modification. However, it was reported that H_2/SF_6 and N_2/SF_6 ideal separation factors are invalid for evaluating the quality of MFI zeolite membranes due to the SF_6 adsorption induced crystal swelling.[17,18]

The objective of this work is to evaluate the quality of MFI zeolite membranes on the basis of the H_2/CO_2 separation factor at room temperature. Since MFI zeolitic pores adsorb preferentially CO_2 molecules at room temperature without causing crystal structure change, high-quality membranes with few

intercrystalline defects are more selective to CO_2 at room temperature. MFI zeolite membranes with different H_2/CO_2 separation factors at room temperature were CVD modified subsequently for improvement of the H_2/CO_2 separation factor to confirm the effectiveness of this method for membrane quality evaluation. The permeation and diffusion properties of some small gas molecules, such as He, H_2, and CO_2 (SF_6 for comparison) through unmodified and CVD modified membranes were investigated in a wide temperature range with consideration of gas molecular weight and size.

2. Experimental Section

2.1. Preparation of MFI Zeolite Membranes. α-Alumina porous supports made of alumina powder (Alcoa, A-16) with a thickness of 2 mm and a diameter of 20 mm (average pore diameter, ∼0.2 μm; porosity, ∼45%) were used as the substrates for the synthesis of MFI zeolite membranes.[7] Before the membrane synthesis, both surfaces of α-alumina porous supports were polished consecutively with no. 500, no. 800, and no. 1200 SiC polishing papers. The polished porous supports were then washed and dried. To obtain a good sealing system for gas permeation and separation experiments, the side edge of the α-alumina porous supports was glazed with a dense glass at 1150 °C for about 15 min. Since the α-alumina porous supports were prepared by sintering at 1150 °C for about 30 h and a stable pore structure was obtained, the additional sintering at 1150 °C for 15 min to glaze a dense glass layer did not change the pore structure of the porous supports. MFI zeolite membranes were grown onto the surface of α-alumina porous supports by an in situ crystallization method according to the procedure reported in the literature.[16,19,20] The synthesis solution was prepared by dissolving 4.0 g of fumed silica (99.99%, Aldrich) into a solution containing 20 mL of 1 M TPAOH (Aldrich) solution and 0.28 g of NaOH (>97%, Aldrich) at 80 °C under vigorous stirring. The resultant solution was aged at room temperature for at least 4 h under magnetic stirring. The clear solution was filtered before being transferred into a Teflon-lined autoclave in which three glazed α-alumina porous supports were put horizontally. The autoclave was then placed in an oven at 180 °C for 4 h to allow the growth of zeolite membranes onto the surface of α-alumina porous supports. After hydro-thermal synthesis, the autoclave was cooled in the oven to room temperature. The synthesized membranes were washed with distilled water for several times, then dried, and calcined at 550 °C in air for 8 h to remove the template.

2.2. CVD Modification and Gas Permeation of MFI Zeolite Membranes. CVD modification and gas permeation/separation study was conducted on a high-temperature multi-component gas permeation/separation setup described in a previous publication.[8] MFI zeolite membrane was fixed in a stainless steel permeation cell with the membrane layer facing the gas feed side and was sealed by soft graphite seals. The effective membrane area for gas permeation was 1.77 cm^2. The CVD modification was conducted at 450 °C. During the CVD modification process, an equimolar H_2/CO_2 mixture gas with a total flow rate of 45 mL·min^{-1} bubbled through a methyldi-ethoxysilane (MDES) saturator maintained at room temperature and was fed to the feed side of the permeation cell. The permeate side of the membrane was swept by argon gas with a flow rate of 15 mL·min^{-1}. In some CVD modification runs, MDES delivery to the membrane cell for CVD reaction was shut intermittently and either H_2 or CO_2 was sent to the feed side with Ar as the sweep to measure single gas permeance and the ideal separation factor. The gas composition in the permeate

side was analyzed by an online gas chromatograph (GC; Agilent, 6890N) equipped with a thermal conductivity detector (TCD) and a Hayesep DB packed column (Alltech) with a length of 6 m.

The following measures were taken to minimize the effect of the water adsorbed on the gas permeation at room temperature. As soon as the membrane was calcined at 550 °C in air for template removal and cooled to 50 °C, it was loaded into the permeation cell without being exposed to air at room temperature. The membrane was then heated to 300 °C in the permeation cell under the flow of H_2/CO_2 mixture gas and held at this temperature for several hours to remove adsorbed organic impurities and water. After that, the membrane was cooled to room temperature and the permeation measurements were performed from room temperature to high temperatures.

Single gas (He, H_2, CO_2, and SF_6) permeation and H_2/CO_2 mixture gas separation experiments were conducted on membranes before and after CVD modification to study the effect of the CVD modification on gas permeation and separation properties. During the gas permeation and separation experiments, the total gas flow rate on the feed side was also 45 mL·min^{-1}, while the downstream of the zeolite membrane was swept by argon gas with a flow rate of 15 mL·min^{-1}. Both sides of the membrane were kept at atmospheric pressure during the gas permeation and separation process. Gas permeation experiments were conducted in a temperature range of 25−500 °C with a heating/cooling rate of 0.3 °C·min^{-1}. The gas compositions on the feed retentate and permeate sides were analyzed by GC for the calculation of H_2/CO_2 separation factor.

The gas flow rates on the feed side and permeate side were controlled by mass flow controllers and measured by bubble flow meters. The ideal separation factor of gas species i over gas species j, $\alpha_{i/j}^{ideal}$, is defined as the ratio of their single gas permeances; and the separation factor of gas species i over gas species j for gas mixtures, $\alpha_{i/j}^{sep}$, is defined as the ratio of i species composition in the permeate side to that in the feed retentate.

2.3. Characterization of MFI Zeolite Membranes. The crystal structure of the synthesized membranes was characterized by X-ray diffraction (XRD; Bruker AXS-D8, Cu Kα radiation) analysis from 5 to 45° (2θ) with a step size of 0.015° (2θ). The morphology and thickness of the α-alumina supported MFI zeolite membranes were characterized using a scanning electron microscopy (SEM; Philips, XL 30).

3. Results and Discussion

3.1. Gas Permeation Properties of Unmodified Membranes. The microstructure of the in situ synthesized MFI membranes was examined by SEM. It was observed that crack-free, continuous MFI zeolite membranes with a thickness of ~2 μm were formed on the surfaces of α-alumina porous supports. The zeolite crystal size of the MFI membranes was about 0.5 μm, which is similar to that of the in situ synthesized MFI membranes reported by other researchers.[19] X-ray diffraction analysis confirmed that the synthesized zeolite membranes showed a random-oriented MFI crystal structure.

Two membranes were selected to study the effects of the initial membrane quality on the gas permeation and subsequent CVD modification. Single gas permeation property through the unmodified zeolite membrane M1 was studied by measuring the single gas permeances of H_2, He, CO_2, and SF_6 from room temperature to 500 °C, and the results are shown in Figure 1a. The permeances of H_2, He, and CO_2 through this membrane decrease as temperature increases. The results shown in this figure indicate that the diffusion of some nonadsorbing small
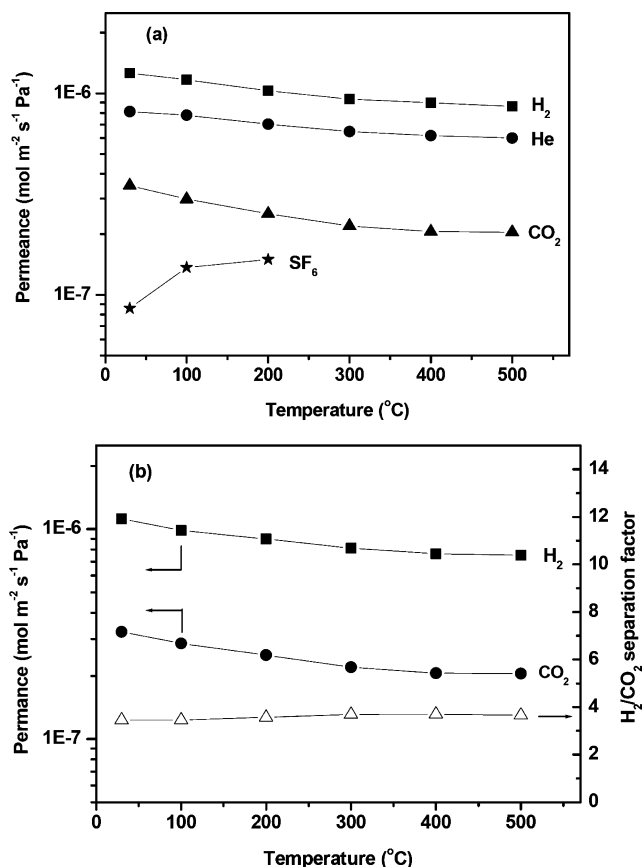

Figure 1. Gas permeation properties of membrane M1 (where, for example, 1E-6 represents 1×10^{-6}): (a) single gas permeation; (b) separation of equimolar H_2/CO_2 mixture gas.

gas molecules, such as He and H_2, through MFI zeolite membrane follows a Knudsen diffusion behavior. It was reported that CO_2 molecules adsorb into MFI zeolitic pores from room temperature to about 200 °C and the adsorption weakens as temperature increases.[21] At temperatures higher than 200 °C, the adsorption affinity between CO_2 molecules and MFI zeolitic pores is very weak. For this reason, the CO_2 permeance decrease from room temperature to 200 °C for membrane M1 is partly due to the weakening of the adsorption affinity between CO_2 molecules and MFI zeolitic pores, while the decrease of CO_2 with temperature at temperatures higher than 200 °C can be explained by the Knudsen diffusion mechanism. The H_2/SF_6 ideal separation factor of this membrane at room temperature is 15, which is higher than their Knudsen selectivity (8.5). The H_2/CO_2 ideal separation factor gradually increases from 3.7 to 4.3 as temperature increases from room temperature to 450 °C. Figure 1b shows the membrane performance in separating equimolar H_2/CO_2 mixture gas from room temperature to 500 °C. The permeances of H_2 and CO_2 decrease slightly with an increase of temperature; however, the H_2/CO_2 separation factor remains essentially constant around 3.5 from room temperature to 500 °C.

Usually, H_2/SF_6 and N_2/SF_6 ideal separation factors are used to evaluate the quality of MFI zeolite membranes. However, the method was found invalid for this purpose by some researchers.[17,18] Lee et al. found that a B-ZSM-5 membrane having 90% of its helium flux through the relatively small defects at room temperature showed a high H_2/SF_6 ideal separation factor of 260, while another silicalite membrane having only 9% of its helium flux through somewhat large defects showed a H_2/SF_6 ideal separation factor as low as 46.
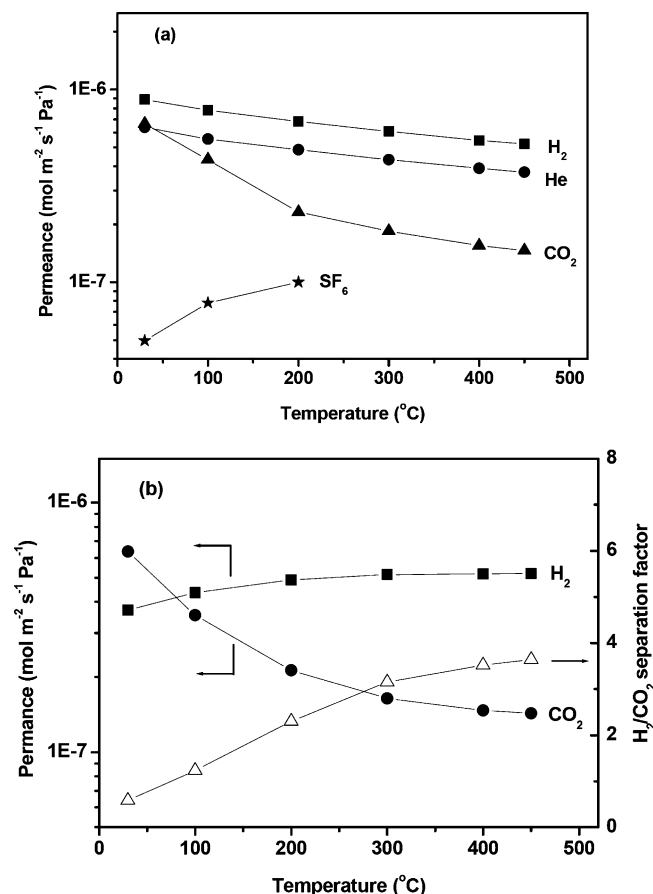
Figure 2. Gas permeation properties of membrane M2 (where, for example, 1E-6 represents 1×10^{-6}): (a) single gas permeation; (b) separation of equimolar H_2/CO_2 mixture gas.

This was ascribed to the fact that the SF_6 adsorption-induced crystal swelling caused significant shrinkage of the relatively small defects and eliminated almost completely the flux through the small defects.[17] However, the flux through the nonselective large defects decreased only slightly by the SF_6-induced crystal swelling. Sebastián and co-workers observed that some MFI membranes with a high N_2/SF_6 ideal separation factor (93.6) showed a lower CO_2/N_2 separation factor (1.13), while a membrane with a low N_2/SF_6 ideal separation factor (6.27) showed a higher CO_2/N_2 separation factor (5.05).[18] According to these experimental observations, it is unreliable to evaluate the membrane quality on the basis of the H_2/SF_6 or N_2/SF_6 ideal separation factors.

To confirm the inadequacy of using H_2/SF_6 ideal separation factor for examining the membrane quality, the gas permeation and separation performance of another membrane (M2) was studied and the results are shown in Figure 2. Single gas permeation properties of this membrane are similar to those of membrane M1; i.e., the permeances of H_2, He, and CO_2 decrease with an increase of temperature, showing a Knudsen-type diffusion behavior for H_2 and He. Compared with the CO_2 single gas permeation behavior of membrane M1, the CO_2 permeance for membrane M2 increases faster as temperature decreases at temperatures below 200 °C. As indicated in Figure 2a, the H_2/SF_6 ideal separation factor for membrane M2 at room temperature is about 18, which is slightly higher than that of M1. However, membrane M2 shows a much lower H_2/CO_2 ideal separation factor (1.33 for M2 compared with 3.7 for M1) at room temperature. Figure 2b shows the performance of membrane M2 in separating equimolar H_2/CO_2 mixture gas from

room temperature to 450 °C. The H_2/CO_2 separation factor for membrane M2 at room temperature is about 0.56, which is also much lower than that of membrane M1 (3.5 for membrane M1). Comparing the H_2/SF_6 ideal separation factor of M2 with that of M1, it is difficult to tell which membrane has a better quality, because the H_2/SF_6 ideal separation factor is similar for membranes M1 and M2. However, membrane M1 and M2 showed quite different H_2/CO_2 ideal separation factor/separation factor at room temperature.

Generally, molecules transport through MFI zeolite membranes via three different pathways, i.e., zeolitic pores (0.55−0.6 nm), intercrystalline defects (0.6−2 nm), and large meso- and macroporous defects (>2 nm).[1] It is well-known that zeolitic pores are more selective to CO_2 molecules at room temperature due to the adsorption of CO_2 molecules into the zeolitic pores and blocking of the diffusion channels for H_2 molecules. However, diffusion of CO_2 through intercrystalline defects may follow approximately Knudsen diffusion behavior even at room temperature. The reason is that although some CO_2 molecules adsorb onto the walls of the intercrystalline defects, the uncovered region of a defect is still large enough to allow CO_2 molecules to transport through it in a Knudsen-type diffusion behavior. For this reason, membranes with poor initial quality may still show a Knudsen-type diffusion behavior for CO_2 at room temperature. The lower H_2/CO_2 ideal separation factor/ separation factor at room temperature for membrane M2 is a strong indication that there are fewer intercrystalline defects in membrane M2 than those in membrane M1. As temperature increases from room temperature to 450 °C, the H_2/CO_2 ideal separation factor for membrane M2 increases to 3.65. At high temperatures, adsorption of H_2 and CO_2 on MFI zeolites is negligible. The permeation of these gases through the zeolitic pores follows a mechanism similar to the Knudsen flow observed for the permeation through the intercrystalline defects. Therefore the H_2/CO_2 separation factor through zeolitic pores is similar to that through intercrystalline defects. For this reason, the H_2/CO_2 separation factor at high temperatures cannot be used to examine the quality of the membrane. According to these experimental observations, the H_2/CO_2 separation factor at room temperature is a better indicator of the membrane quality.

Besides some small gas molecules (such as H_2 and CO_2), xylene isomers and C_6 hydrocarbon isomers were also used to characterize the quality of MFI membranes. However, a MFI zeolite membrane with a high selectivity for C_6 isomers might have a low selectivity for xylene isomers because the MFI crystal structure is not rigid and it may change due to the adsorption of some big molecules.[22,23] It was found that the adsorption of n-hexane molecules in MFI membranes caused an obvious decrease in n-hexane flux through nonzeolitic pores.[17,24] The main disadvantage of these methods is that the strong adsorption of some large molecules in MFI zeolitic pores leads to the expansion of zeolite crystals, which in turn causes shrinkage of the intercrystalline defects. However, some small gas molecules with moderate adsorption strength in MFI zeolitic pores, such as CO_2, would not expand zeolite crystals by adsorption and would not cause shrinkage of intercrystalline defects. It is reported that n-hexane, n-pentane, n-butane, n-propane, and SF_6 molecules swell MFI zeolite crystals through their adsorption into zeolite pores, while no crystal expansion and defect shrinkage is caused by adsorption of CO_2.[17]

Figure 3 gives schematic illustrations of H_2 and CO_2 permeation through MFI zeolite membranes. Since CO_2 molecules could not fill the entire defect gaps by adsorption because
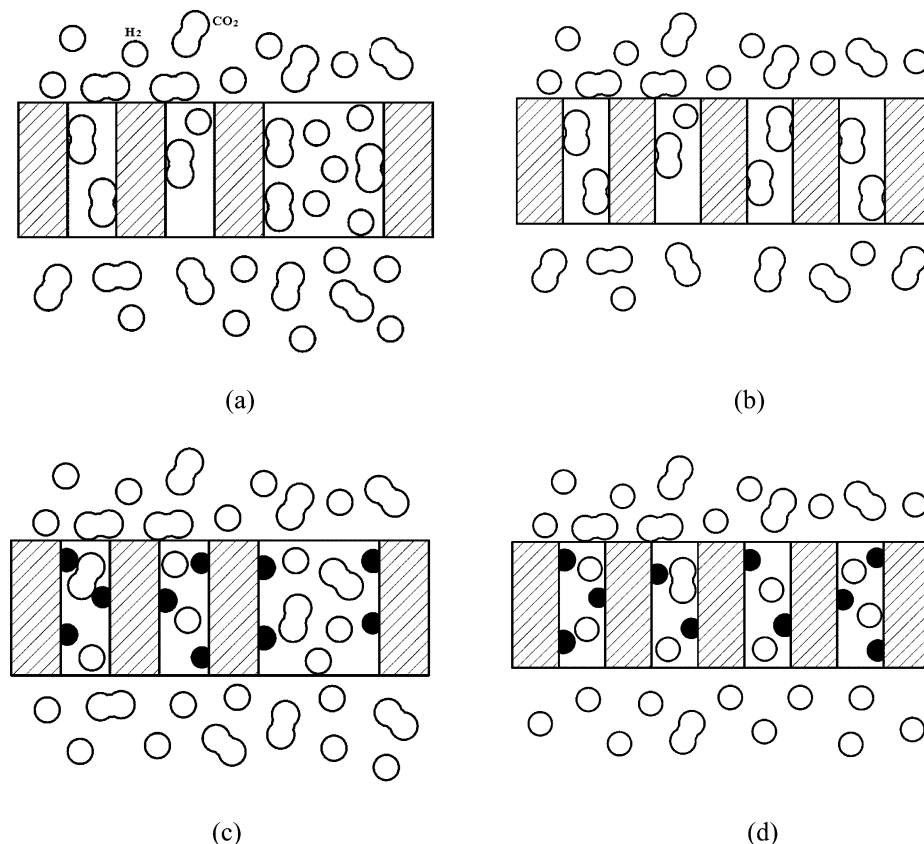
Figure 3. Schematic illustrations of H_2 and CO_2 permeation through the unmodified and CVD modified MFI membranes with different initial qualities: (a) unmodified membrane with relatively bad quality, (b) unmodified membrane with good quality, (c) CVD modified membrane with bad initial quality, and (d) CVD modified membrane with good initial quality.

of the relatively large size of the intercrystalline defects (Figure 3a), membranes with bad initial quality usually show a higher H_2 permeance than that of CO_2 at room temperature. For MFI zeolite membranes with good quality, adsorption of CO_2 molecules in the zeolitic pores blocks the zeolitic pore channels and retards transport of H_2 through the membrane (Figure 3b). On the basis of this analysis, it is clear that membrane performance in separating equimolar H_2/CO_2 mixture at room temperature is a reliable method for evaluation of membrane quality.

The permeance of nonadsorbing or weak adsorbing small gas molecules through MFI zeolite membranes can be described by the following equation:[8]

$$F = \frac{\varphi}{L}\frac{\alpha\beta}{z}\left(\frac{8RT}{\pi M}\right)^{1/2} \exp\left(\frac{-E_d}{RT}\right) \qquad (1)$$

where E_d is the activation energy for diffusion of the gas molecules in zeolitic pores, M is the molecular weight of the permeating gas, α is about 1 nm for diffusion in MFI-type zeolites, and z is the diffusion coordination number (4 for MFI-type zeolites). β is a constant of the gas molecule load in zeolite, which has a maximum or equilibrium value of $\beta = 1/RT$. If the transport of gas molecules through a MFI zeolite membrane is governed by a Knudsen-type diffusion mode, the activation energy, E_d, is equal to zero. Table 1 shows the activation energies for permeation of some small gas molecules, such as H_2 and He, through an unmodified M2 membrane at temperatures above 300 °C. As shown in this table, for the unmodified membrane M2, the permeation activation energies of H_2 and He are very close to zero, showing a Knudsen-type mode of diffusion at temperatures above 300 °C.

Table 1. Permeation Activation Energies of He and H_2 through the Unmodified and Modified Membrane M2 above 300 °C

		permeation activation energy, kJ mol^{-1}	
molecule	kinetic diameter, nm	before CVD	after CVD
He	0.26	1.1 ± 0.3	7.1 ± 0.8
H_2	0.289	0.6 ± 0.2	10.2 ± 0.2

3.2. CVD Modification and Gas Permeation Properties of Modified Membranes. Membranes M1 and M2 with different initial qualities were CVD modified for improvement of H_2/CO_2 separation factor to confirm the effectiveness of the membrane evaluation method. Figure 4 shows the single gas permeation of H_2 and CO_2 during the on-stream CVD modification of membrane M1 at 450 °C. As shown in this figure, H_2
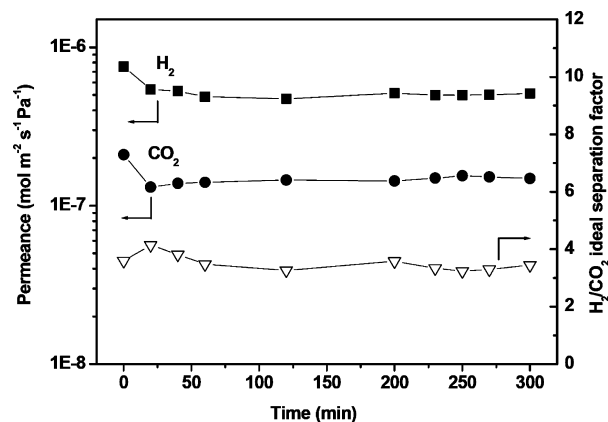

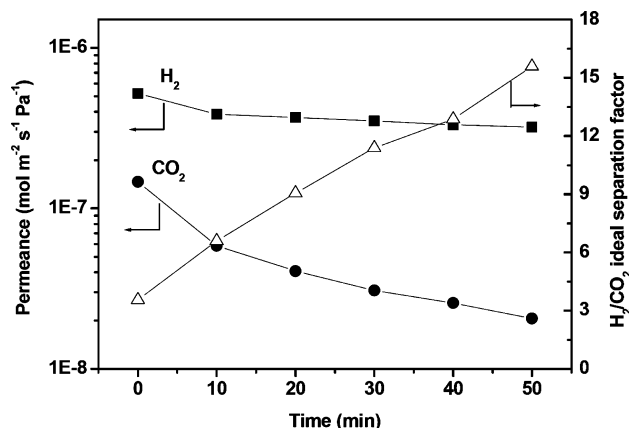**Figure 4.** On-stream CVD modification of membrane M1 at 450 °C (where, for example, 1E-6 represents 1×10^{-6}).

Figure 5. On-stream CVD modification of membrane M2 at 450 °C (where, for example, 1E-6 represents 1×10^{-6}).

Table 2. Correlation between the H_2/CO_2 Separation Factor at Room Temperature and the Corresponding Separation Factor after CVD Modification of in Situ Synthesized MFI Membranes

membrane no.	$\alpha^{sep}_{H_2/CO_2}$ at room temperature	$\alpha^{sep}_{H_2/CO_2}$ at 450 °C after CVD modification
M1	3.5	3.5
M2	0.56	8.2
M3	0.59	6.5
M4	0.67	6.1

was very small compared with the gas permeation through CVD modified zeolitic pores with a higher selectivity. It was reported that even a very small amount of intercrystalline defects can lower significantly the H_2/CO_2 separation factor of the membranes.[25] Hence, it can be concluded that the permeation selectivity can be improved significantly through catalytic cracking deposition of MDES molecules in zeolitic pores only when the membrane has a good initial quality (Figure 3d). Table 2 shows the correlation between the H_2/CO_2 separation factor at room temperature and the corresponding separation factor after CVD modification at 450 °C for four membranes. It is clear that a membrane with a lower H_2/CO_2 separation factor at room temperature shows more improvement in H_2/CO_2 separation factor through CVD modification. This suggests that the H_2/CO_2 separation factor at room temperature is a good indicator for the quality of MFI zeolite membrane levels. The CVD modification results also confirmed that the H_2/CO_2 ideal separation factor and separation factor at room temperature are good indicators of the membrane quality.

Figure 6 shows the temperature dependence of single gas permeances of He, H_2, and CO_2 through membrane M2 after CVD modification for 120 min (after the selectivity reached the plateau). The CVD modified M2 membrane shown in Figure 6 has a lower H_2 permeance ($\sim 1.5 \times 10^{-7}$ mol/(m²·s·Pa)) and higher H_2/CO_2 ideal separation factor (~ 20) than the M2 with a shorter CVD modification time shown in Figure 5 ($\sim 3 \times 10^{-7}$ mol/(m²·s·Pa)) and 16, respectively, at 450 °C). For the CVD modified M2 membrane shown in Figure 6, the permeances of He and H_2 increase with temperature and He permeance is higher than that of H_2. These results indicated that the diffusion of these small gas molecules through the CVD modified membrane with good initial quality follows an activated diffusion mode due to the narrowed zeolitic pore size. These permeation properties are also consistent with the results of the microporous silica membranes prepared by the sol−gel method[26,27] or CVD methods.[28,29] The results suggest that the CVD modification resulted in the deposition of silica units in
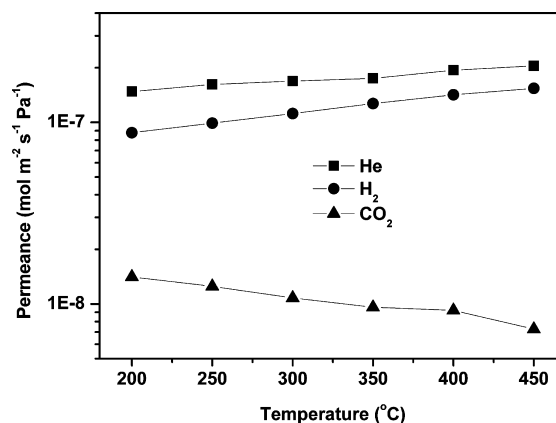
and CO_2 permeances decrease quickly in the initial 10 min and then level off. No obvious improvement of H_2/CO_2 ideal separation factor was observed during the entire CVD modification process. Membrane M2 was also CVD modified under the same condition, and the results are shown in Figure 5. The permeances of H_2 and CO_2 decrease quickly in the initial 10 min; after that, the H_2 and CO_2 permeances decrease slowly. The H_2/CO_2 ideal separation factor was improved from 3.6 for the fresh membrane to 16 for the CVD modified membrane. Compared with membrane M1, the H_2/CO_2 ideal separation factor of membrane M2 was improved significantly by CVD modification due to its better initial quality.

Since MDES has a molecular size smaller than the zeolitic pore size of MFI zeolite membranes, they can diffuse into zeolitic pores and adsorb and deposit selectively onto the acid sites in the zeolitic pores to reduce the zeolitic pore size.[14−16] It was reported by Masuda et al.[14] that thermal decomposition of MDES and homogeneous deposition of the decomposed products occurred in a nonoxidative gas phase at temperatures higher than 750 K. At relatively low temperatures, the nonselective deposition of the decomposed products on the membrane surface can be avoided. Since MDES molecules only adsorb chemically onto the acid sites, the resulting silica can deposit selectively only on the acid sites in the zeolitic pores to reduce the pore size. It should be noted that there are some acid sites on the membrane external surface, and some MDES molecules can adsorb and deposit onto these acid sites. However, due to the small size of the mono-SiO_2 units and the limited number of acid sites on the membrane external surface, the deposited mono-SiO_2 units are not able to cover completely zeolitic pores and the membrane surface. This was confirmed by the results reported by Gu et al.[16] showing absence of the SiO_2 amorphous layer on external surface of the MFI zeolite membrane covered after CVD modification. Although the intercrystalline defects in the MFI zeolite membranes can be narrowed slightly by CVD modification of MDES molecules on the active sites in the defects, it is difficult to reduce the defects down to a certain size, through which diffusion of H_2 and CO_2 becomes activated (Figure 3c). As a result, there was only a moderate decrease in H_2 and CO_2 permeances in the initial 10 min, while no obvious improvement of H_2/CO_2 ideal separation factor was observed for membrane M1 with bad quality.

For membrane M2 with fewer intercrystalline defects, the H_2/CO_2 ideal separation factor was improved by CVD modification since the zeolitic pore size of membrane M2 was reduced by CVD. Although there might have some intercrystalline defects in membrane M2, gas permeation through these defects

Figure 6. Temperature dependence of the single gas permeances of He, H_2, and CO_2 through membrane M2 modified with MDES (where, for example, 1E-7 represents 1×10^{-7}).
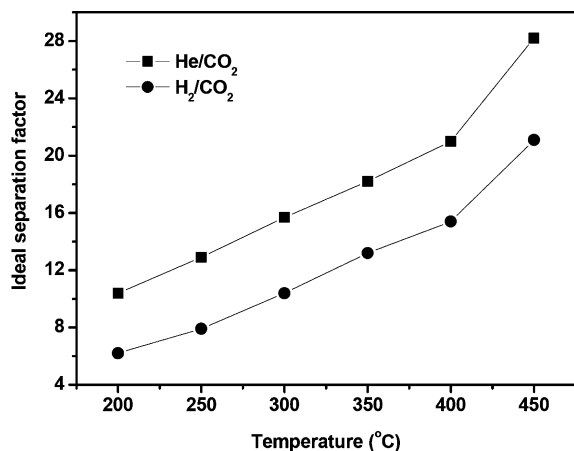
Figure 7. Influence of temperature on the ideal separation factor of He/CO_2 and H_2/CO_2 for membrane M2 modified with MDES.

Figure 8. Permeation of equimolar H_2/CO_2 mixture gas through membrane M2 modified with MDES.

the zeolitic pores and decrease of the effective pore size of MFI zeolite membranes. The permeation activation energies for H_2 and He for the CVD modified membrane M2 are compared with those for the unmodified membrane in Table 1. The heavier He molecule with smaller kinetic diameter ($d_k = 0.26$ nm) has a lower permeation activation energy, while the lighter H_2 molecule with a larger kinetic diameter ($d_k = 0.289$ nm) has a higher permeation activation energy. The results for the CVD modified membrane M2 suggests that the ratio of He kinetic diameter to the zeolitic pore size of the modified membrane (d_k/d_p) is higher than 0.8 on the basis of the theory developed by Xiao and Wei.[6] Masuda et al.[14] estimated that the zeolitic pore size of a modified MFI zeolite membrane was in the range of 0.36−0.47 nm.

Compared with the single gas permeation results of unmodified membrane shown in Figure 2a, it is clear that the H_2/CO_2 ideal separation factor of membrane M2 was improved significantly after CVD modification (Figure 6). The H_2 and He single gas diffusion mode changed from the Knudsen diffusion mechanism for the unmodified membrane M2 to the activated diffusion mode for the modified membrane M2. As shown in eq 1 and also as reported by Tang et al.,[30,31] the improvement in H_2/CO_2 ideal separation factor through CVD modification can be attributed to both the diffusion mode change of small single gas molecules through the modified membranes and the change of the gas molecular loading in the modified zeolite membranes. Tang et al.[30] reported that the H_2 molecular loading is doubled in a modified zeolite membrane while the CO_2 molecular loading in the modified zeolite membrane decreased greatly after CVD modification. Figure 7 shows the influence of temperature on the ideal separation factors of He/CO_2 and H_2/CO_2 for the CVD modified membrane M2. The ideal separation factors increase with temperature due to the increase of He and H_2 permeances and the decrease of CO_2 permeance with temperature.

Since the adsorption of CO_2 molecules in the zeolitic pores becomes stronger for the CVD modified membrane at room temperature due to the reduced zeolitic pore size, it is necessary to study the performance of the CVD modified membrane M2 in separating an equimolar H_2/CO_2 mixture gas. Figure 8 shows the performance of the CVD modified membrane M2 in separation of equimolar H_2/CO_2 mixture gas from room temperature to 450 °C. It is shown in this figure that the H_2/CO_2 separation factor at 40 °C is 0.52 which is a little smaller than that of the unmodified membrane. This result indicated that the modified membrane is more selective to CO_2 at low temperatures
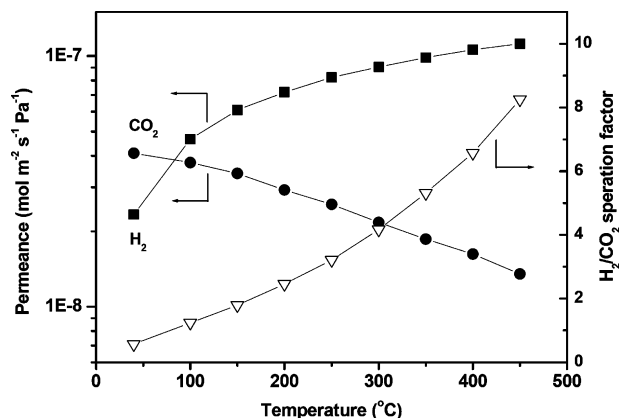
due to the stronger adsorption between the modified zeolitic pores and CO_2 molecules. The H_2 permeance increases from 0.22×10^{-7} to 1.1×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} when temperature increases from 40 to 450 °C, while CO_2 permeance decreases from 0.42×10^{-7} to 0.13×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} during the ramping process. The H_2/CO_2 separation factor for the CVD modified membrane M2 at 450 °C is about 8.2, much lower than its ideal separation factor at 450 °C (see Figure 7). For unmodified MFI zeolite membranes the mixture H_2/CO_2 separation factor is similar to the ideal gas separation factor at high temperatures (>300 °C), as show in Figure 2 and reported previously.[8] The results given in Figures 7 and 8 clearly show the CVD modified MFI zeolite membrane has stronger adsorption affinity for CO_2 than the unmodified one, even at high temperatures. Thus the presence of CO_2 hinders diffusion of H_2, lowering the separation factor for the mixture.

4. Conclusions

Transport of nonadsorbing small gas molecules through unmodified MFI zeolite membranes is governed by a Knudsen-type diffusion mode. The H_2/CO_2 ideal separation factor and separation factor at room temperature are better indicators than H_2/SF_6 and N_2/SF_6 ideal separation factors for evaluation of membrane quality. Membranes with good initial quality are CO_2 selective with a low H_2/CO_2 ideal separation factor or separation factor at room temperature due to the adsorptive diffusion of CO_2 molecules in zeolitic pores, which blocks diffusion channels for H_2 permeation. However, membranes with bad initial quality exhibit a higher H_2/CO_2 ideal separation factor or separation factor at room temperature since the diffusion of small gas molecules through intercrystalline defects follows a Knudsen-type diffusion mode even at room temperature. On-stream CVD modification with MDES is effective in improving H_2/CO_2 separation factor only for membranes with good initial quality. The permeation behavior of some small gas molecules, such as He and H_2, for the MFI zeolite membranes changed from a Knudsen-type diffusion mode to an activated diffusion mode after CVD modification due to the reduced zeolitic pore size.

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