Zeolitic Imidazolate Framework-8 Membrane for H_2/CO_2 Separation: Experimental and Modeling

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Abstract. In this work, ZIF-8 membrane synthesized through solvent evaporation secondary seeded growth was tested for single gas permeation and binary gases separation of H_2 and CO_2. Subsequently, a modified mathematical modeling combining the effects of membrane and support layers was applied to represent the gas transport properties of ZIF-8 membrane. Results showed that, the membrane has exhibited H_2/CO_2 ideal selectivity of 5.83 and separation factor of 3.28 at 100 kPa and 303 K. Besides, the experimental results were fitted well with the simulated results by demonstrating means absolute error (MAE) values ranged from 1.13 % to 3.88 % for single gas permeation and 10.81 % to 21.22 % for binary gases separation. Based on the simulated data, most of the H_2 and CO_2 gas molecules have transported through the molecular pores of membrane layer, which was up to 70 %. Thus, the gas transport of the gases is mainly dominated by adsorption and diffusion across the membrane.

1. Introduction

H_2 has been well known as a carbon-free fuel [1], which can be used as an alternative energy source [2]. Separation of H_2 from CO_2 is important for steam reforming gas purification in order to obtain high purity of H_2 [3]. Meanwhile, membrane-based separation has become an alternative and attractive technology for gases separation due to its low energy consumption and compact design [4]. It involves relatively low cost if compared to conventional separation methods [5-7]. In addition, membrane based separation process is relatively simple with no moving parts and easy to be operated and controlled [8]. Therefore, rapid market growth for membrane system is reported, which is around 8 % to 10 % per year [9]. Besides, at present, large scale membrane systems have been installed for industrial application in United States and European countries [10], with as many as 100 membrane systems installed in the refineries for various gases separation processes [11]. Based on the various types of membranes for gas separation, polymeric [12, 13], inorganic [14, 15], mixed-matrix [16, 17] and organic-inorganic hybrid, such as metal organic framework (MOFs) [18-20], are most widely reported.

   Metal organic framework (MOF) membrane has emerged as a potential application for gas separation attributed to their exceptionally high surface area, adsorption affinity, tailored porosity and frameworks [19, 21]. It is a relatively new type of nanostructured membranes, composing of metal clusters and organic linkers [22-23]. In comparison with MOFs membranes, ZIF-8 membranes exhibit

relatively higher stability due to the strong bonding between metal cations and imidazolate anions [24]. In spite of the promising performance in gas separation, ZIF-8 membrane has shown advantages over the other types of ZIFs membranes with excellent chemical resistance, high thermal and hydrothermal stability [25]. Furthermore, in H_2/CO_2 gas separation, ZIF-8 membrane has shown higher performance over zeolite membranes, such as SAPO-34 [26], DDR [27] and FAU [38]. This is mainly because of the larger pore sizes of zeolite (larger than 3.6 Å), which can hardly separate small gaseous molecules of H_2 and CO_2 with the kinetic diameters of 2.9 Å and 3.3 Å, respectively [29].

Apart from that, the gas transport properties of the porous membrane can be affected by several factors, such as the gas diffusivity of the membrane layer, intercrystalline pores presented and mass transfer resistant of the support layer [30]. To date, the Maxwell-Stefan model has been widely used to study the intrinsic gas diffusivity through the membrane layers [30-31]. Meanwhile, the mass transport resistance caused by the support layer or intercrystalline pores in the membrane can be demonstrated through Binary-Friction model [32]. Overall, the combination of these factors has significantly affected the gas permeation and separation performance of the membrane. However, thus far, the gas transport properties of ZIF-8 membrane in gas separation of H_2/CO_2 are still scarcely reported. Therefore, in this study, ZIF-8 membrane was tested for H_2/CO_2 single gas permeation and binary gases separation. Subsequently, the gas transport properties of the membrane were studied by combining Maxwell-Stefan model and Binary Friction model.

2. Experimental

The ZIF-8 membrane synthesized in our previous work [33] using solvent evaporation secondary seeded growth was tested for H_2 and CO_2 using a constant pressure method at room temperature. The permeation flow rate was collected via bubble flow meter at the steady-state. For single gas permeation of H_2 and CO_2, the gas was fed at the total pressure difference ranged from 100 kPa to 700 kPa with 200 ml min^{-1} of flow rate. It is noted that, the blank support was tested using single gas permeation prior to the membrane growth for pore size characterization. The permeance of component i, P_i (mol $m^{-2} s^{-1} Pa^{-1}$), was calculated using (1) as follows [34]:

$$P_i = \frac{N_i}{\Delta p}$$

(1)

where N_i is the flux (mol $m^{-2} s^{-1}$) and Δp is the pressure difference (Pa). The membrane area was 6.36 $\times 10^{-5}$ m^2. Then, the ideal selectivity for gas component i and j was determined as the ratio of the respective gas permeance using (2) as follows:

$$\alpha_{i/j} = \frac{P_i}{P_j}$$

(2)

For binary gases separation, the collected gas from the permeate side was analyzed using gas chromatograph (GC, Perkin Elmer, Model 2103) in order to quantify the composition of the gases. The gas permeance for binary gas mixture was determined based on (1), with Δp referred to the partial pressure difference of the respective gas. Meanwhile, the selectivity for the binary mixed gas (α_{mixed}) was calculated based on the ratio of gas permeance also, as shown in (3):

$$\alpha_{mixed} = \frac{\left(\dfrac{N_T \times x_{i,p}}{p_f \times x_{i,f} - p_p \times x_{i,p}}\right)}{\left(\dfrac{N_T \times x_{j,p}}{p_f \times x_{j,f} - p_p \times x_{j,p}}\right)}$$

(3)

where x is the mole fraction, N_T is the total flux (mol m^{-2}s^{-1}), p_f is the pressure at the feed side (Pa) and p_p is the pressure at the permeate side (Pa).

The gas transport properties of the membrane were studied through a general model as shown in (4). The total gas permeance of the membrane (P_T) is calculated by the reciprocal resistance of the membrane layer (P_M) and the support layer (P_S). Meanwhile, for the ZIF-8 membranes synthesized in the present work, intercrystalline pores of the membrane (P_V) and membrane effective area (C) is also considered. The presence of pores or gaps on the membrane which was hardly to be avoided during the membrane synthesis has contributed towards the presence of intercrystalline pores on the membrane. Besides, the area of the membrane involved in the gas permeation might not be the same as the measured membrane area. Therefore, membrane effective area is required to be estimated based on the experimental results. The detailed solution methodologies for both single gas permeation and binary gases separation have been reported in our previous work [35].

$$P_T = \left[\left\{ \frac{1}{(P_M + P_V)C} \right\} + \left(\frac{1}{P_s} \right) \right]^{-1}$$

(4)

3. Results and discussion

Figure 1 exhibits the experimental and simulated H_2 and CO_2 single gas permeation data and ideal selectivities of the ZIF-8 membrane at 303 K. The simulation was performed based on the membrane properties stated in Table 1. It can be observed from Fig. 1 that the simulated data is fitted well with the experimental data with means absolute error (MAE) values ranged from 1.13 % to 3.88 %.
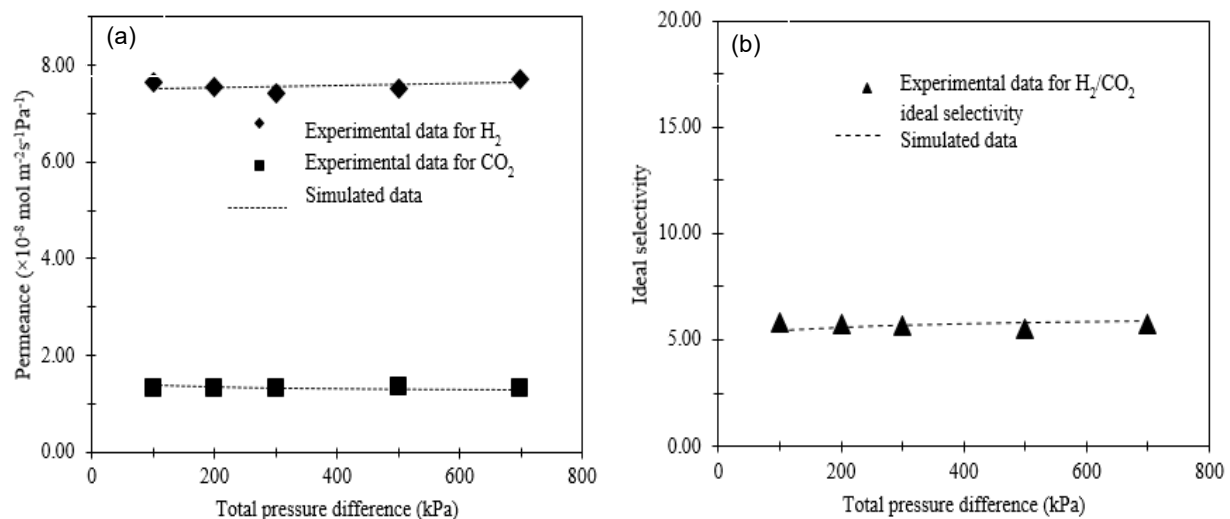

Figure 1. Experimental and simulated (a) single gas permeances and (b) ideal selectivity at 303 K for H_2 and CO_2 over ZIF-8 membrane.

Referring to figure 1 also, gas permeances of H_2 and CO_2 remain nearly unchanged with the increasing total pressure difference. Although the increase in pressure difference increases the fluxes, this increment is almost similar to the increase in pressure difference. Therefore, the gas permeances remain constant eventhough the flux increases with the total pressure difference. Besides, ideal selectivity of H_2/CO_2 remains almost constant, ranged from 5.72 to 5.82. This is attributed to the constant H_2 and CO_2 permeances when the total pressure differences increase.

Table 1. Structural properties for ZIF-8 membrane.

Properties	Value
Membrane layer	
Thickness (m)	5.0×10^{-5} [a]
Density (kg m^{-3}) [b]	924
q^{sat} for H_2 (mol kg^{-1}) [c] q^{sat} for CO_2 (mol kg^{-1}) [d]	30.000 10.070
K_{H2} (Pa^{-1}) [c] K_{CO2} (Pa^{-1}) [d]	5.000×10^{-8} 1.294×10^{-6}
D_{H2} (m^2 s^{-1}) [e] D_{CO2} (m^2 s^{-1}) [f]	9.5×10^{-9} 2.2×10^{-10}
Support layer	
Thickness (m)	2.0×10^{-3}
Pore radius (m)	5.5×10^{-8}
ε/τ ($\tau = 1$)	2.0×10^{-1}

[a]- Estimated from SEM image [33];

[b]- Obtained from the literature data [36];

[c] - Extrapolated based on the literature data [37];

[d] -Extrapolation based on literature data [38] using Langmuir adsorption model.

[e] -Estimated based on permeation data.

[f] -Retrieved from the literature data [38].

Meanwhile, Table 2 shows the simulated percentages of the gas molecules which transported through the membrane intercrystalline pores (P_V) across ZIF-8 membrane. It can be seen from Table 2 that the percentages of H_2 and CO_2 gases molecules permeate through the membrane intercrystalline pores are lower than 20 % and 35 %, respectively. These results show that most of the H_2 and CO_2 gases permeation is dominated by the surface dependency and diffusivity of the membrane. Nonethless, when the total pressure difference increases, percentage of gas permeated through the intercrystalline pores of the membrane also increases. This result has quantitatively implied that the effect of the intercrystalline pores of the membrane on its gases separation performance becomes more significant at higher total pressure difference.

Table 2. Simulated percentage of gases permeated through membrane intercrystalline pores (Pv) of ZIF-8 membrane at total pressure difference ranged from 100 kPa to 700 kPa at temperature of 303 K.

Total pressure difference (kPa)	Percentage of P_V (%)*	
	H_2	CO_2
100	15.67	21.89
200	16.14	24.14
300	16.60	26.33
400	17.07	28.45
500	17.52	30.49
600	17.98	32.47
700	18.43	34.38

*-Calculated based on $[P_V/(P_V + P_M)]$ x 100%

The physical properties of ZIF-8 membrane shown in Table 1 were used to simulate the results for binary gases separation. Figure 2 shows the simulated and experimental data for binary gases separation of H_2/CO_2 under equimolar feed compositions of mixed gases at temperature of 303 K and total pressure difference ranged from 100 kPa to 700 kPa. The simulated data are matched with the experimental data with MAE values ranged from 10.81 % to 21.22 %. The values obtained are within the acceptable range (< 39%) as reported in the literature [31].
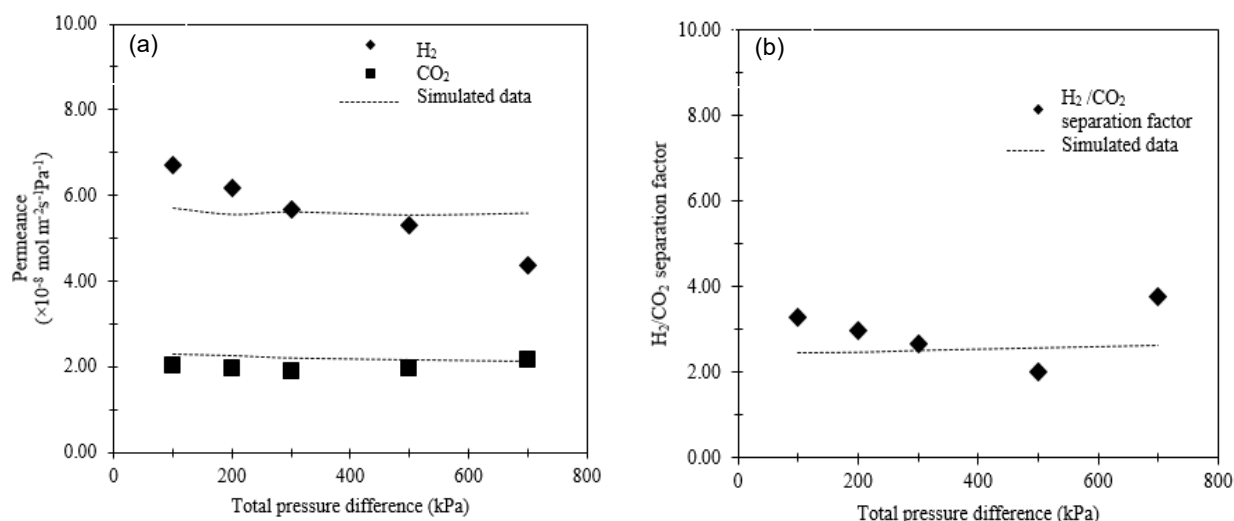

Figure 2. Experimental and simulated (a) binary gas permeances and (b) H_2/CO_2 separation factor for ZIF-8 membrane at equimolar feed composition of mixed gases of H_2/CO_2.

As observed from figure 2 also, H_2 permeances decrease with the increase in pressure difference. This is attributed to the presence of larger molecules, such as CO_2, in the mixed gases, which has created the drag force over H_2 gas molecules [39]. Therefore, the transport of H_2 molecules across the membrane is affected. Meanwhile, CO_2 permeance remains almost constant (varied from 2.05×10^{-8} mol m^{-2} s^{-1} Pa^{-1} to 2.17×10^{-8} mol m^{-2} s^{-1} Pa^{-1}) when the total pressure difference increases. As mentioned earlier, H_2 diffuses faster than CO_2 across the ZIF-8 membrane due to its lighter molar mass and lower viscosity as compared to CO_2 [40]. Therefore, highly mobile H_2 gas molecules will act as the sweeping gas to promote the permeation of CO_2 gas molecules transported through the ZIF-8 membrane [41]. Meanwhile, the kinetic diameter of CO_2 (0.33 nm) is comparable to the pores of ZIF-8 (0.34 nm). Hence, CO_2 molecules can be passed through ZIF-8 pore without much hindrance. Eventually, the CO_2 flux increases linearly with the partial pressure difference and resulted in the constant CO_2 permeance.

4. Conclusion
In conclusion, ZIF-8 membrane synthesized via solvent evaporation seeding method exhibited high quality in the membrane growth by showing H_2/CO_2 ideal selectivity of 5.83 at total pressure difference of 100 kPa and temperature of 303 K. In the binary gases separation, selectivity of 3.28 was obtained for mixed gases of H_2/CO_2 at equimolar feed composition, under total pressure difference of 100 kPa and temperature of 303 K. Besides, the simulated results are fitted well with the experimental results by achieving MAE values less than 21.22 %. Overall, the gas transport properties of ZIF-8 membrane in H_2/CO_2 gas separation have been successfully presented for single gas permeation and binary gases separation.

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