Study on the Separation of H$_2$ from CO$_2$ Using a ZIF-8 Membrane by Molecular Simulation and Maxwell-Stefan Model

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Abstract: The purification of H$_2$-rich streams using membranes represents an important separation process, particularly important in the viewpoint of pre-combustion CO$_2$ capture. In this study, the separation of H$_2$ from a mixture containing H$_2$ and CO$_2$ using a zeolitic imidazolate framework (ZIF)-8 membrane is proposed from a theoretical point of view. For this purpose, the adsorption and diffusion coefficients of H$_2$ and CO$_2$ were considered by molecular simulation. The adsorption of these gases followed the Langmuir model, and the diffusion coefficient of H$_2$ was much higher than that of CO$_2$. Then, using the Maxwell–Stefan model, the H$_2$ and CO$_2$ permeances and H$_2$/CO$_2$ permselectivities in the H$_2$–CO$_2$ mixtures were evaluated. Despite the fact that adsorption of CO$_2$ was higher than H$_2$, owing to the simultaneous interference of adsorption and diffusion processes in the membrane, H$_2$ permeation was more pronounced than CO$_2$. The modeling results showed that, for a ZIF-8 membrane, the H$_2$/CO$_2$ permselectivity for the H$_2$–CO$_2$ binary mixture 80/20 ranges between 28 and 32 at ambient temperature.

Keywords: ZIF-8 membrane; H$_2$ separation; H$_2$/CO$_2$ permselectivity

1. Introduction

Energy has become one of the major concerns in the world due to the growing oil price and the concomitant depletion of fossil fuels, involving the need for greener processes and the use of renewable sources. Therefore, the search for renewable energy has attracted the attention of the scientific community [1,2]. In particular, H$_2$ is seen as a pollution-free energy carrier, possessing high energy density and heat content 3 to 4 times higher than coal and natural gas. This simple element is currently used in chemical industries, particularly in methanol and ammonia production, food processing, and metallurgy, and for heating and electric power generation, in industrial boilers [3–6]. Unfortunately, H$_2$ is not naturally available as a pure gas on the Earth and, at this time, approximately 90% of the total H$_2$ production comes from non-renewable sources such as natural gas and coal, responsible for consistent greenhouse gas emissions [1,6]. Currently, H$_2$ is produced predominantly by the natural gas steam reforming reaction in conventional reformers, followed by the water–gas shift (WGS) reaction, which provides a H$_2$-rich stream containing also CO$_2$ and other impurities [7]. Afterwards, these impurities must be removed in order to obtain high purity H$_2$ for applications and downstream processes [6].
Pressure swing adsorption (PSA) as well as cryogenic and membrane separations have been considered effective methods to purify H₂ from other gases such as CO₂ \[8,9\]. In the framework of H₂ purification by membrane technology and among the various types of membrane solutions, zeolite membranes possess special properties such as physical stability, appropriate chemical resistance, etc. \[10\]. Metal–organic frameworks (MOFs), as a new family of microporous membrane materials, are organized by a network of transition metal cations or clusters bonded by organic ligands \[11\]. Hence, MOFs have become interesting membrane materials, useful in applications such as gas separation, catalysis, and product storage, due to their feasibility in altering pore size and adsorption affinities by functionalizing the linked molecules as well as the porosity and functional groups \[12,13\]. Zeolitic imidazolate frameworks (ZIFs) are an important class of materials that can be categorized as MOFs. ZIF membranes include ZIF-7, ZIF-8, ZIF-22, ZIF-90, ZIF-95, and ZIF-100, which show interesting performance in gas separation applications \[14–16\]. In particular, the separation performances of propylene/propane mixtures were investigated through a ZIF-8 membrane fabricated by a facile hydrothermal seeded growth method by Pan et al. \[14\]. They found that the ZIF-8 membrane had significant separation performance for a wide range of propylene/propane binary mixtures, showing high thermal and long-term stability, and high reproducibility. Lai et al. \[15\] studied the permeation of CO₂/CH₄ through a ZIF-8 membrane based on a combination of generalized Maxwell–Stefan, viscous flow, and Knudsen diffusion models, considering the gas diffusivity, support resistance, and intercrystalline pores of the membrane layer. They found that the simulated results and the experimental gas permeation data were well fitted and consistent with the physical characterizations, including scanning electron microscopy (SEM) and X-ray diffraction (XRD). Furthermore, the transport and diffusivities of hydrocarbons in ZIF-8 as a function of temperature were studied using molecular simulation methods via dynamically corrected transition state theory (dcTST) \[16\]. A comparison of the determined diffusivity results with experimental data demonstrated considerable agreement for all the molecules. Chokbunpiam et al. \[17\] evaluated the adsorption, diffusion, and permeation of the guest molecules in the C₂H₆/ZIF-8 system and the influence of the diffusing C₂H₆ molecules in the ZIF-8 membrane by molecular dynamic simulation. They found that two effects simultaneously include the decrease in window size of the ZIF-8 membrane at higher C₂H₆ loadings, while exerting forces within the cavity by the guest molecules at higher loadings, pressing a given probe molecule toward the window and leading to a weak self-diffusivity dependence on the concentration of guest molecules.

From the perspective of pre-combustion capture and related zeolite membrane application, the present theoretical study aimed to study the adsorption and diffusion coefficients of H₂ and CO₂ in a ZIF-8 membrane, calculated by using molecular simulations. Then, using the results of molecular simulations and the Maxwell–Stefan model, the membrane permeance of H₂ and CO₂ binary mixtures was also investigated and is discussed below.

2. Materials and Methods

2.1. Molecular Simulation Details

The Materials Studio software (BIOVIA, San Diego, CA, USA) was used for the molecular simulation of adsorption and diffusion of H₂ and CO₂ in a ZIF-8-based membrane. The universal force field was used in all the simulations. The structure of the simulated ZIF-8-based membrane of this study was assumed to consist of a supercell with dimensions of 34 × 34 × 34 Å, as shown in Figure 1. The sorption modulus was used to simulate the adsorption of the components and the Monte Carlo method with periodic boundary conditions was applied to simulate the adsorption on the ZIF-8-based membrane. The cutoff distance in the calculations was 12.5 Å, electrostatic and van der Waals terms were Ewald and atom-based, respectively. The number of calculations was up to a balance of 1,000,000 stages and production steps of about 10⁶. Considering that the driving force for the movement of adsorbed molecules between phases is expressed by their fugacity, the Molecular Dynamics simulation was used to investigate the diffusion of the components in the structure of the
ZIF-8-based membrane. First, 10 molecules of a component were located in a ZIF-8 membrane cell by the sorption module. Then, the system was minimized using the conjugate gradient and steepest descent methods. Molecular Dynamics was carried out 1000 ps NVT at 298 K to reach the equilibrium state. The diffusion coefficients were derived from the linear least-square fits of the plots of the mean square displacement (MSD) of molecules versus time.

![Figure 1. Schematic diagram of the supercell of the ZIF-8 structure.](image)

2.2. Maxwell–Stefan Model

The transport through the ZIF-8-based membranes was demonstrated as adsorption on the external surface, transport into the pores, intercrystalline diffusion, transport out of the pores, and desorption. Different mechanisms may contribute to the selectivity of the ZIF-8 membranes; indeed, in their pores, adsorption equilibrium and diffusion play a major role for some molecules and in particular conditions, whereas for others the molecular sieve effects turn out to be dominant. Considerable progress has been made during the last decade in developing a general theory for describing the diffusion of gaseous mixtures in zeolite membranes, using the Maxwell–Stefan (M–S) formulation [18,19], which is considered an indispensable model for simulating the transient transport across zeolites membranes, to be strongly preferred to other modeling approaches (for example, the simple Fick model) [20–26]. Therefore, it is now widely accepted that, for a proper formulation, it can be applied for describing the gas diffusion in zeolite membranes. It is also generally accepted that the fundamentally correct approach is related to the fluxes (Ni), defined in terms of the cross-sectional area of the membrane, and to the chemical potential gradients (Vμi), by using the M–S equation, shown as Equation (1) below [27]:

\[- \rho \frac{\Theta_i}{RT} \sum_{j=1}^{n} \frac{N_j - \Theta_j N_i}{\Theta_{j,sat} \Theta_{i,sat} D_{ij}} + \frac{N_i}{\Theta_{i,sat} D_i}.\]  

(1)

The friction is the result of the interactions between adsorbed molecules and between a molecule and the pore wall. The parameters D_{ij} and D_i are the Maxwell–Stefan surface diffusivities and represent inverse friction factors between molecules and between molecules and pore wall, respectively, whereas \(\Theta_i\) is the molecule loading expressed in molecules per unit cell and \(\Theta_{i,sat}\) is the saturation loading. The interchange coefficient \(D_{ij}\) is calculated as a logarithmic average of the single-component M-S diffusivities, Equation (2):

\[D_{ij} = [D_{ij}]^{\frac{\Theta_i}{\Theta_{j,sat}}} [D_{ij}]^{\frac{\Theta_j}{\Theta_{i,sat}}}.\]  

(2)
The fractional occupancies are defined by Equation (3):
\[ \theta = \frac{q_i}{q_i^{sat}} = \frac{\Theta_i}{\Theta_i^{sat}}, \]  
where \( q_i \) is the molar loading of species \( i \) and \( q_i^{sat} \) is its saturation loading.

The chemical potential gradient may be expressed in terms of the fractional occupancy gradient via thermodynamic correction factors \( \Gamma_{ij} \), defined by Equations (4) and (5):
\[ \frac{\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^{n} \Gamma_{ij} \nabla \theta_j, \]  
\[ \Gamma_{ij} = \theta_i \frac{\partial \ln p_i}{\partial \theta_j}. \]

The adsorption of components in equilibrium with the ZIF-8-based membrane can be described by a Langmuir adsorption isotherm equation (Equation (6):
\[ \Theta = \frac{b \Theta_{sat} P}{1 + bP}, \]
where \( P \) is the pressure (Pa) and \( b \) represents the temperature-dependent sorption strengths (expressed in \( \text{Pa}^{-1} \)) [25].

3. Results and Discussion

Figure 2 shows the simulated adsorption isotherms for \( \text{H}_2 \) and \( \text{CO}_2 \) on zeolite ZIF-8 at 298 K and their comparisons with the experimental isotherms from the literature [28,29]. The agreement between the simulated isotherms and the experimental results coming from the literature of \( \text{H}_2 \) and \( \text{CO}_2 \) adsorption in the entire range of pressure studied in this work is reported in Figure 2a,b. On the one hand, the molecular simulations of \( \text{H}_2 \) adsorption match quite well the experimental results apart from the range of pressures higher than 2500 Pa where a certain disagreement is evident, as is seen in Figure 2a. On the other hand, the molecular simulations of \( \text{CO}_2 \) adsorption match quite well the experimental data from the literature at lower pressures, whereas at higher pressures a clear deviation from the simulated isotherms is evident toward lower loadings, as shown in Figure 2b. This occurs because, at higher pressures, the system is far from the ideal state and the non-ideal terms are not incorporated into the system, with a consequent disagreement. Furthermore, at high pressures, some structural features such as the simulated surface area, pore volume of the adsorbent and force field parameters can have an influence on the agreement within experimental and modeling data. However, both figures indicate the validity of the simulation results using the universal force field.

In Figure 3, simulation results of \( \text{H}_2 \) and \( \text{CO}_2 \) adsorption on the ZIF-8-based membrane were fitted by using a Langmuir model. As shown, there is a good agreement between the former model and the molecular simulation results. In particular, the adsorption of \( \text{H}_2 \) and \( \text{CO}_2 \) on the ZIF-8-based membrane looks like a monolayer adsorption. The model parameters derived from the fitting process are shown in Table 1.

| Component | Langmuir Model | \( R^2 \) | Diffusion Coefficient \( (\text{m}^2/\text{s}) \) |
|-----------|----------------|----------|---------------------------------------------|
|           | This Work      | Literature |                                              |
| \( \text{H}_2 \) | \( \Theta_s = 356; b = 4.02 \times 10^{-5} \) | 0.999     | 2.62 \times 10^{-8} | 2.5 \times 10^{-8} [28] |
| \( \text{CO}_2 \) | \( \Theta_s = 127; b = 1.31 \times 10^{-3} \) | 0.998     | 1.71 \times 10^{-10} | 2.2 \times 10^{-10} [29] |
The chemical potential gradient may be expressed in terms of the partial molar chemical potential and the product rates of the adsorption reaction, with the following expression for the chemical potential gradient, \( \Gamma_{ij} \): 

\[
\Gamma_{ij} = \sum \nu_{ij} \frac{\partial}{\partial n} \mu_i
\]

where \( \nu_{ij} \) denotes the stoichiometry coefficient for the adsorption reaction, and \( \mu_i \) is the partial molar chemical potential. This expression is derived from Equations (4) and (5).

Figure 2. Comparisons between the simulated isotherm adsorption and experimental results from the literature on the ZIF-8-based membrane at 298 K: (a) \( \text{H}_2 \) (experimental results from [26]) and (b) \( \text{CO}_2 \) (experimental results from [27]).

Figure 3. Langmuir model fitting to the molecular simulation results of \( \text{H}_2 \) and \( \text{CO}_2 \) uptake on the ZIF-8-based membrane at 298 K.
MSDs were evaluated from trajectories that are carried out through the periodic boundaries [30]. Figure 4 displays the MSD as a function of time for both H2 and CO2 molecule diffusion in the ZIF-8-based membrane at 298 K and for a set loading of 10 molecules/cell. The relationship between the observed MSD versus time is linear, with a very good approximation, as also observed in other works in the literature [31,32].

![Figure 4](image_url)

**Figure 4.** Mean square displacement (MSD) as a function of time for both H2 and CO2 molecule diffusion in the ZIF-8-based membrane at 298 K and for a set loading of 10 molecules/cell.

This indicates that the normal diffusion occurs at this time scale. The calculated diffusion coefficient at 298 K for a set loading of 10 molecules is equal to $2.62 \times 10^{-9}$ for H2 and $1.71 \times 10^{-10}$ m²·s⁻¹ for CO2, respectively. In both cases, it is calculated as the slope of the plot MSD versus time, as is shown in Figure 4. These values are in good agreement with reported experimental diffusion coefficients in the literature [28,29] (Table 1). Table 2 shows further H2 and CO2 diffusion coefficients at 298 K of other membranes beside the ZIF-8 one of this study.

As shown, in most of the cases reported in the table, H2 and CO2 diffusion coefficients of the ZIF-8 membrane are higher than the other ones from the literature, apart from the H2 diffusion from [34] and the CO2 diffusion from [33].
was reached with the H2 pressures and less 
properties, the Maxwell–Stefan model was adopted for investigating these phenomena. 
The permeance of these components across the ZIF-8 membrane depends on their adsorption and di-
constant trend around 28.

between 28 and 32, although at a pressure higher than 300 kPa the permselectivity value showed a
best result of this theoretical work, Figure 6 shows that the highest simulated H2 at lower pressures, H2
reduced, causing their adsorption decrease in the competition with other molecules. Furthermore,
by increasing the H2 ratio were simulated as a function of pressure at 298 K, as seen in Figure 6. It can be observed that
separation from CO2, particularly at lower pressures, making the ZIF-8-based membrane suitable for H2 
separation from CO2. H2/CO2 membrane selectivities for various H2–CO2 mixtures at different molar 
ratio were simulated as a function of pressure at 298 K, as seen in Figure 6. It can be observed that 
by increasing the H2 concentration, the H2/CO2 selectivity increased as a consequence of a higher 
hydrogen permeation driving force across the membrane. Meanwhile, the CO2 molecule density was 
reduced, causing their adsorption decrease in the competition with other molecules. Furthermore, 
at lower pressures, H2/CO2 permselectivity was higher because CO2 showed lower adsorption at low 
pressures and less effect on permeance; this mode is more favorable for hydrogen selection. As the 
best result of this theoretical work, Figure 6 shows that the highest simulated H2/CO2 permselectivity 
was reached with the H2–CO2 mixture showing a H2/CO2 ratio equal to 80/20, with values ranging 
between 28 and 32, although at a pressure higher than 300 kPa the permselectivity value showed a 
constant trend around 28.

| DH2 [m²/s] | DCO₂ [m²/s] | Membrane       | Ref.          |
|------------|-------------|----------------|--------------|
| 2.62 × 10⁻⁸ | 1.71 × 10⁻¹⁰ | ZIF-8          | This work    |
| 1.73 × 10⁻⁸ | 5.22 × 10⁻¹⁰ | Silicalite     | [33]         |
| 5.06 × 10⁻⁸ | 1.45 × 10⁻¹⁰ | Silicalite     | [34]         |
| 1.33 × 10⁻⁹ | 8.82 × 10⁻¹¹ | DDR zeolite    | [35]         |
| 5.01 × 10⁻⁹ | 1.58 × 10⁻¹¹ | DDR zeolite    | [36]         |
| 5.79 × 10⁻¹⁰ | 4.12 × 10⁻¹¹ | NaY zeolite    | [37]         |
| 1.27 × 10⁻⁹ | 1.23 × 10⁻¹⁰ | SAPO-34        | [38]         |

The molecular simulation results of the adsorption and diffusion of H2 and CO2 in the ZIF-8-based 
membrane showed that the latter adsorption was much higher than that of H2. On the other hand, 
the H2 diffusion coefficient in the ZIF-8-based membrane was much higher than that of CO2. Since the 
permeance of these components across the ZIF-8 membrane depends on their adsorption and diffusion 
properties, the Maxwell–Stefan model was adopted for investigating these phenomena.

In Figure 5, the permeances of H2 and CO2 as a binary mixture (H2/CO2 molar ratio = 70/30) 
are shown at a temperature of 298K and different pressures. It is observable that H2 permeance is 
higher than CO2, particularly at lower pressures, making the ZIF-8-based membrane suitable for H2 
separation from CO2. H2/CO2 membrane selectivities for various H2–CO2 mixtures at different molar 
ratio were simulated as a function of pressure at 298 K, as seen in Figure 6. It can be observed that 
by increasing the H2 concentration, the H2/CO2 selectivity increased as a consequence of a higher 
hydrogen permeation driving force across the membrane. Meanwhile, the CO2 molecule density was 
reduced, causing their adsorption decrease in the competition with other molecules. Furthermore, 
at lower pressures, H2/CO2 permselectivity was higher because CO2 showed lower adsorption at low 
pressures and less effect on permeance; this mode is more favorable for hydrogen selection. As the 
best result of this theoretical work, Figure 6 shows that the highest simulated H2/CO2 permselectivity 
was reached with the H2–CO2 mixture showing a H2/CO2 ratio equal to 80/20, with values ranging 
between 28 and 32, although at a pressure higher than 300 kPa the permselectivity value showed a 
constant trend around 28.

**Figure 5.** Permeance of H2 and CO2 in a binary mixture H2/CO2 = 70/30 for the ZIF-8-based membrane 
at 298 K and as a function of pressure.
Figure 5. Permeance of H$_2$ and CO$_2$ in a binary mixture H$_2$/CO$_2$ = 70/30 for the ZIF-8-based membrane at 298 K and as a function of pressure.

Figure 6. H$_2$/CO$_2$ selectivity of the ZIF-8 membrane for the binary H$_2$–CO$_2$ mixture at 298 K and different H$_2$/CO$_2$ molar ratios.

4. Conclusions

The separation of H$_2$ from CO$_2$ was theoretically investigated by using a ZIF-8 membrane. The adsorption and diffusion contributions of H$_2$ and CO$_2$ were studied by using molecular simulations. The ZIF-8-based membrane showed a strong tendency to adsorb CO$_2$, whereas the H$_2$ diffusion coefficient was much higher than that of CO$_2$. By combining the molecular simulation results with the Maxwell–Stefan model, the theoretical results demonstrated that the ZIF-8 membrane possesses a H$_2$/CO$_2$ permselectivity higher than 30 at relatively lower pressure (below 300 kPa), while it decreases raising the pressure. This effect is due to the progressively reduced CO$_2$ adsorption contribution at lower pressure. However, this trend was theoretically confirmed in all the H$_2$–CO$_2$ binary mixtures considered in this work.

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**Sample Availability:** Samples of the compounds are not available from the authors.

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