



Flow dynamics of gases inside hydrotalcite-silica micropores



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ABSTRACT

Maxwell–Stefan diffusion with single-site Langmuir isotherm was used to model the flow of gas inside micro pores of HT-Silica membrane. Coupled with Van't Hoff and Arrhenius equations, the diffusivity and energy contributed by the surface affinity and gas kinetics were quantified and evaluated. Results indicate that all of the four gases being studied were affected by the surface affinity to a significant extent. The surface affinity contributed 62% of the energy in the adsorption of CO₂, 48% of the energy in the adsorption of CH₄, 48% of the energy in the adsorption of N₂ and 46% of the energy in the adsorption of H₂. This explains the reason for the higher CO₂ permeability despite the fact that the CO₂ gas molecules are heavier than the other gas molecules being compared in the analysis.

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1. Introduction

Hydrotalcite (HT) or hydrotalcite-like compounds, are classified as anionic clays or layered double hydroxides (LDH) [1]. It has been intensively studied recently, as an adsorbent material specifically for CO₂ capture at low and high operating temperature in order to reduce the greenhouse gas emissions from industries [2–5]. HT materials show distinguishing behaviors such as high mechanical strength when operated at high pressure, greater CO₂ adsorption capacity and selectivity at elevated temperatures, and stable CO₂ adsorption capacity when employed in adsorption/desorption cycles in pressure swing adsorption (PSA) either with or without pressure equalization [4–6]. Although synthetic HT material has been exploited in CO₂ adsorption for the last few decades, discussion on HT material in a thin film or in the form of membrane is scarcely found in the literature nor has it been extensively studied [7,8]. This is due to the fabrication of a uniform inorganic membrane assembly is a challenging task and that there exists a trade-off between gas permeability and selectivity when the membrane is applied [9,10]. This trade-off is mainly attributed to the diffusive character of the gas inside the membrane tortuous and meandering pores.

Comparison of results from another approach using a second-order bivariate function derived from an experimental design matrix [11] indicates that unary CO₂ is more effectively diffused along the membrane pore wall than CO₂ in mixed gases. The presence of other gas species in the mixture creates resistance to CO₂ diffusion and adsorption. The dominant transport mechanism inside the HT–silica membrane was found to be affinitive diffusion but ordinary CO₂ and Knudsen diffusions were considered significant only at a low pressure condition [11].

Here, we would like to extend our effort further in quantifying the surface contribution and take a different approach to understand this character by using Maxwell–Stefan diffusion model. Results from this study are then compared with that obtained from the experiment using micro-porous HT membrane fabricated previously [12,13].

2. Modeling

The Maxwell–Stefan diffusion with single-site Langmuir isotherm can be represented by the following function known as the transitory surface occupancies [14]:

$$\frac{\partial \theta}{\partial t} = D_{MS} \frac{\partial}{\partial z} \left[\frac{1}{1 - \theta} \frac{\partial \theta}{\partial z} \right] \quad (1)$$

where, θ is a fractional coverage for Langmuir adsorption and D_{MS} is the Maxwell–Stefan surface diffusivity. The fractional coverage is described as [15]:

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$$\theta = \frac{q}{q_{sat}} = \frac{bp}{1 + bp} \quad (2)$$

where, q is coverage (mol/g HT-silica), q_{sat} is the saturation coverage (mol/g HT-silica), p is the pressure (kPa), and b is an adsorption equilibrium constant (kPa^{-1}).

The steady-state, single and consistent gas flux of the Maxwell-Stefan model in one dimension can be demonstrated as the fractional coverage gradient [16]:

$$J_i^s = -\rho q_{sat} D_{MS} \frac{1}{1 - \theta} \left(\frac{\partial \theta}{\partial z} \right)_{z=\delta} \quad (3)$$

where, J_i^s (mol/m² s) is designated as the single gas flux, where i refers to CO₂, CH₄, N₂ and H₂ gases, ρ is the density of HT-silica (g/m³), D_{MS} is the single component Maxwell-Stefan diffusivity (m²/s), δ is the effective membrane thickness (m). However, Eq. (3) can be rewritten by using Eq. (2), to give [17]:

$$J_i^s = \frac{\rho q_{sat} D_{MS}}{\delta} \ln \left[\frac{1 + bp_{feed}}{1 + bp_{perm}} \right] \quad (4)$$

where, p_{feed} is the feed pressure (kPa) and p_{perm} is the permeate pressure (kPa).

2.1. Adsorption properties for surface affinity evaluation

The characteristics of the microporous HT-silica membrane are presented in Table 1. The experimental procedure for evaluating the adsorption equilibrium constants (b_i) of a diverse type of permanent gases (CO₂, CH₄, N₂ and H₂) on HT-silica membrane operated at various temperature (303–463 K) has been reported in details previously [12,13]. The adsorption equilibrium constants were selected accordingly in order to attain the best fit in terms of straight-line through the origin, where the experimental single gas flux, (J_i^s) was plotted, against $\ln \left[\frac{1 + bp_{feed}}{1 + bp_{perm}} \right]$ in accordance with the Eq. (4) [14,17]. On the other hand, the adsorption equilibrium constant (b) can be expressed in terms of the entropy and heat of adsorption by Van't Hoff equation [19]:

$$b = \exp \left(\frac{\Delta S}{R} - \frac{\Delta H}{RT} \right) \quad (5)$$

where, ΔS is the entropy of adsorption (J/mol.K), ΔH is the heat of adsorption (J/mol), R is the gas constant (J/mol.K), T is the absolute temperature (K). On the contrary, plotting $\ln(b)$ values of CO₂, CH₄, N₂ and H₂ against ($1/RT$), resulted in a straight line with slope of ($-\Delta H$) and intercept of ($\Delta S/R$), respectively.

2.2. Maxwell-Stefan diffusivity

Maxwell-Stefan diffusivities (D_{MS}) of diverse gas molecules (CO₂, CH₄, N₂ and H₂) were obtained using Eq. (4) by employing the observed single gas flux at various operational temperature and pressure conditions [12,13]. An average D_{MS} value for each gas was evaluated individually, from five set of different D_{MS} attained at five different pressure differences (100–500 kPa) isothermally. In addition, Arrhenius equation was used to calculate the Maxwell-Stefan diffusivity at zero loading (D_{MS0}) and the activation energy (E) of different gas molecules [20], in accordance with Eq. (6):

$$D_{MS} = D_{MS0} \exp \left(\frac{-E}{RT} \right) \quad (6)$$

As a result, Maxwell-Stefan diffusivities (D_{MS}) and the activation energy (E) of diverse gases (CO₂, CH₄, N₂ and H₂) were obtained from the plot of $\ln(D_{MS})$ against ($1/RT$), which forms a straight line with (E) at slope, while $\ln(D_{MS0})$ at the intercept, respectively.

2.3. Gas permeation and separation

The simulated single gas flux (J_i^s), across the HT-silica membrane at different temperature and pressure conditions was calculated by employing Eq. (4), accordingly. However, the simulated single gas permeance, K_i^s (mol/m².s.Pa) was calculated by a fraction between the simulated single gas flux and the pressure difference across the HT-silica membrane, Δp^s (Pa), as shown in Eq. (7), correspondingly.

$$K_i^s = \frac{J_i^s}{\Delta p^s} \quad (7)$$

On the other hand, the simulated permselectivity or ideal selectivity ($\alpha_{i/j}^s$) of the HT-silica membrane can be calculated by using Eq. (8):

$$\alpha_{i/j}^s = \frac{K_i^s}{K_j^s} \quad (8)$$

Table 1
Characteristics of the microporous HT-silica membrane.

Parameters	Value	Reference
Pore size, Å	8.5	[12]
Pore volume, cm ³ g ⁻¹	0.142	[18]
Percentage of microspores, %	52	[18]
N ₂ adsorption type	Type I	[12]
BET surface area, m ² g ⁻¹	298.1	[18]
Tortuosity	2.5	[13]
Porosity	0.3	[13]
Membrane density, g cm ⁻³	2572	[18]
Membrane thickness, nm	200	[12]
CO ₂ adsorption capacity, mg CO ₂ /g sorbent	47.48	[12]
CO ₂ permeance, mol m ⁻² s ⁻¹ Pa ⁻¹	4.7 × 10 ⁻⁷	[18]
H ₂ permeance, mol m ⁻² s ⁻¹ Pa ⁻¹	0.78 × 10 ⁻⁷	[18]
N ₂ permeance, mol m ⁻² s ⁻¹ Pa ⁻¹	1.32 × 10 ⁻⁸	[18]
CH ₄ permeance, mol m ⁻² s ⁻¹ Pa ⁻¹	0.98 × 10 ⁻⁸	[18]

3. Results and discussion

Adsorption equilibrium constant of diverse gas (CO₂, CH₄, N₂ and H₂) by HT-silica membrane at various operational conditions was determined from the plot of gas flux, J_i^s , versus $\ln[(1 + bp_{feed})/(1 + bp_{perm})]$, as depicted in Fig. 1, where the solid straight lines are the best fit to the experimental data. The calculated adsorption equilibrium constants for CO₂, CH₄, N₂ and H₂ gas molecules, at different temperatures are presented in Table 2. The adsorption equilibrium constants for all the gases were observed to decrease with increasing temperature. CO₂ exhibited the highest adsorption equilibrium constant of approximately 0.0003 kPa⁻¹. Strong adsorption affinity of CO₂ gas molecules over the HT material, is considered to be the main reason for higher adsorption equilibrium constant value [21,22]. The reduction in adsorption

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