Fundamental studies of mass transport through zeolite membranes for CO$_2$/CH$_4$ separation

Mojtaba Sinaei Nobandegani

2021-12-02
Upgrading Biogas

- Main Components: CH\textsubscript{4} (35-70%) and CO\textsubscript{2} (30-60%)

- Required grid and fuel specification: upgrade to at least 96% CH\textsubscript{4}

- Membranes are promising alternatives for conventional methods
Zeolite

- Ceramic inorganic materials (Natural and Synthetical)
- 3D porous structure
  (Composed tetrahedra interlinked Al and Si with oxygen)

- Si/Al ratio in tailoring physical and chemical properties

- CO$_2$ molecule: 0.33 nm
- Window size: 0.37 nm
- CH$_4$ molecule: 0.38 nm
• Ultra-thin CHA membrane (disc) with Si/Al ratio of 80 was synthesized:

General Equation for Mass Transfer:
\[ J = k (C_2 - C_1) \]

Fick’s Law:
\[ J = \frac{D}{L} (C_2 - C_1) \]

From Literature

Membrane properties

\[ J = \alpha^f (C_{eq}^f - C_b^f) \epsilon \]

\[ J = \alpha^p (C_b^p - C_{eq}^p) \epsilon \]

\[ J = \alpha^f \alpha^p D \frac{(C_{eq}^f - C_{eq}^p)}{D \alpha^f + L \alpha^f \alpha^p + D \alpha^p} \epsilon \]

\[ C_b^p \epsilon \]

are obtained from adsorption data
• CHA crystals with 3 different Si/Al ratio was synthesized

![Si-CHA](image1.png) ![CHA77](image2.png) ![CHA45](image3.png)

• Adsorption data were measured (ASAP 2020Plus) and modelled by Toth model

\[ C = \frac{C_{sat}bP}{[1 + (bP)^t]^{1/t}} \]
\[ C = \frac{C_{sat} b P}{[1 + (bP)^t]}^{1/t} \]

\[ \ln b = \frac{-\Delta H_{ads.}}{RT} + \frac{\Delta S_{ads.}}{R} \]
Surface permeabilities are estimated by fitting the model to the experimental data.

\[
J = \frac{\alpha_f \alpha_p D (C_{eq}^f - C_{eq}^p)}{D \alpha_f + L \alpha_f \alpha_p + D \alpha_p} \varepsilon
\]
Membrane showed high selectivity in CO$_2$/CH$_4$ separation:

- **Permeance Selectivity** = \( \frac{\pi_{CO_2}}{\pi_{CH_4}} \)
- **Adsorption Selectivity** = \( \frac{\theta_{CO_2}}{\theta_{CH_4}} \)
- **\( \alpha \) - Selectivity** = \( \frac{\alpha_{CO_2}}{\alpha_{CH_4}} \)
1. Mass transport in nanoporous materials, e.g., ultra-thin membranes are controlled by surface barriers.

2. The surface barrier was a surface diffusion process at the pore mouth with higher activation energy than the diffusion process within the pores.

3. The highly selective mass transport in the membrane was mostly a result of a selective surface barrier and, to a lesser extent, a result of adsorption selectivity.

4. Based on the proposed model and membrane performance, zeolite membrane processes can be designed in order to upgrade biogas into biomethane in industrial scale.
Acknowledgement