Helium Recovery from Natural Gas over Porous Organic Cage Membranes

Keerthana Krishnan
Advisors: Dr. Moises Carreon, Dr. Carolyn Koh
Introduction

- Abundant usage of Helium for various applications
- Almost 30,000 tons per year in the US
- Major source: helium-containing natural gas
- Another major component of natural gas? Methane

Conventional techniques:
- cryogenic distillation
- pressure swing adsorption

Alternative??
- MEMBRANE BASED SEPARATIONS
  - Example: cellulose acetate, Polymeric membranes

How to choose a membrane:
- Permeability
- Selectivity

https:Cryogenic Distillation of Air - Chemical Engineering World
**Material Properties and Functional Applications**

**Material Functionality**
- Gas Storage
- Crystallinity
- Surface Area
- Morphology
- Porosity
- Separations
- Catalysis

**Gas separation:**
- Molecular Sieving
- Adsorption
- Kinetics

**MOFs:** fluctuating permeance
**Polymers:** have poor thermal and chemical stability, plasticization

**Inorganics:** brittleness, low A/V ratio, lower permeabilities

**Carbon Molecular Sieves (CMS):** high cost of synthesizing
Porous Organic Cages

Discreet “dual” porosity

- Uniform micropores
- Chemical and thermal stability
- High BET surface area
- Permanently porous (desolvation)

Polymorphs

- 533 m²/g
- 423-900 m²/g

Song, Q.-L., Cooper, A. I., et al. Advanced Materials 2016, 28 (13), 2629
Hasell, T. Cooper, A. I. Nature Reviews Materials 2016, 1 (9), 14
Applications

- Gas Adsorption and storage
  - High pressure CO$_2$ adsorber
- Stable water adsorber/desorber
- Catalysis supports
- Gas and Pharmaceutical separations
  - SF$_6$ / N$_2$
  - Kr/Xe (Xe selectivity ~20)
  - Olefin paraffin separations
Seed Synthesis

Analyze Morphology (XRD and FESEM)

Support Preparation

Membrane synthesis (solvothermal or microwave)

Checking membrane’s pressure holding ability

Add another membrane layer to support

Gas mixture Calibration

Membrane testing with equimolar gas mixture

Membrane selectivity and single gas permeance calculation
Materials and Methods

Trans-1,2-diaminoclohexane 4:6.5 1,3,5-triformylbenzene

Figure 1: Autoclave for membrane synthesis
Figure 2: Layered membrane in porous alumina support
Figure 3: Permeance testing unit
Chromatograph to evaluate separation performance

Treat at 100°C for 2 hours
Results

Figure 5: X-Ray Diffraction pattern (Left) and SEM image (Right) of CC3 crystals

Figure 6: Cross sectional view (Left) and Top view (Right) of CC3 membrane

Figure 7: Nitrogen Adsorption at 77K over CC3 crystals

Surface Area: 725 m$^2$/g
Results

He Permeance
4.45 x 10^-07 (mol/m²·s·Pa)

Separation Selectivity $\alpha$
10

Diffusion Coefficient: He
4.48 x 10^-09 m²/s

Diffusion Coefficient: CH₄
8.05 x 10^-10 m²/s

Separation Index $\pi$
2.6 x 10^-01 mol/m²·s

Figure 8: Comparison of membrane performance with state-of-the-art membranes for helium-methane separation
Conclusions/Discussion

• Synthesize continuous and defect free CC3 membranes
• Helium Permeability as high as $4.45 \times 10^{-7}$ mol/ (m$^2$ s Pa)
• Separation selectivity as high as 10
• Outperformed the upper limit in the Robeson plot.
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