Novel Membranes for Efficient CO$_2$ Separation

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Outline

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CO$_2$ separation
Zeolite Membranes for CO$_2$ separation
Zeolitic Imidazolate Frameworks

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Synthesis
Homogeneous and Heterogeneous growth

III. ZIF-8 membranes
Synthesis
Separation performance (CO$_2$/CH$_4$)

IV. Conclusions
CO₂ – environmental and energy concern

Environmental

- main component of greenhouse gas

- World energy-related CO₂ emissions rise from 29.7 billion metric tons in 2007 to 42.4 billion metric tons in 2040.

- 390 ppm by volume in atmosphere

Energy

- significant impurity in many natural gas wells
- reduces the energy content of the gas, and it is acidic and corrosive in the presence of water
CO₂ separation techniques

- Absorption and Adsorption
- Low temperature distillation
- Membranes
- Mineralization And biomineralization

Advantages of membranes
- no moving parts
- low energy consumption
- easy to scale up
- no chemical additives
- simple design and operation
- hybrid processing
- no phase changes

Amine adsorption:
- pollution prone
- high energy consumption
- chemical-involved
- phase changes
- complex equipments

Membrane separation is promising environmentally and economically
CO₂ separation by zeolite membranes

Zeolites are crystalline materials with unimodal pore sizes, highly attractive for the separation of CO₂ from light gases due to:
- Molecular sieving mechanism
- Competitive CO₂ adsorption

SAPO-34 membranes effectively separate \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) mixtures


SAPO-34 membranes separate more effectively \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) gas mixtures than polymeric membranes
The need for novel membranes......

The development of superior performance membranes for gas mixture separations requires *novel materials with fundamentally different structural, compositional, adsorption and transport properties* than those of polymers and zeolites.

Zeolitic imidazolate frameworks (ZIFs) are novel type of crystalline porous materials with highly desirable properties, such as uniform micropores, high surface areas, and exceptional thermal and chemical stability.

ZIFs are appealing materials for CO$_2$ separation applications due to:

- 1. Chemical stability in the presence of water and some hydrocarbons
- 2. Exceptional uptake capacities for CO$_2$
- 3. Open porous framework structure with large accessible pore volumes
- 4. Pore sizes in the range of the kinetic diameter of several relevant gas molecules
Zeolite imidazolate framework - 8

**Relevant ZIF-8 properties:**

- It has small apertures of 0.34 nm
- Highly porous open framework structure
- High CO$_2$ adsorption capacity
- Large accessible pore volume with fully exposed edges

**CO$_2$ separation due to:**

- Small pore apertures (molecular sieving)
- High CO$_2$ adsorption (competitive adsorption)

Room temperature synthesis of ZIF-8 crystals

Zinc sources: Nitrate, acetate, carbonate, chloride, phosphate
Solvents: Methanol, DMF, hexanol, ethanol
Control over crystal size

TEM images and diffraction patterns demonstrate that ZIF-8 crystallinity and particle size increase with time.
ZIF-8 Kinetics of transformation

Avrami’s model:
\[
\ln(-\ln [1 - y(t)]) = \ln K + n \ln t
\]

\(t = \) synthesis time, \(y(t) = \) ZIF-8 relative crystallinity as a function of time
\(k = \) scale constant, \(n = \) Avrami’s constant

ZIF-8 Growth from solid surfaces

ZIF-8 crystals grown directly from the solid liquid interface

M.A.Carreon et al. under review (October 2011)
ZIF-8 membrane synthesis

ZIF-8 membranes were prepared via *in-situ* crystallization on porous alumina or stainless steel supports.
ZIF-8 seeds for membrane preparation

a. XRD pattern
(SOD structure, BCC)
b. Diffraction pattern
(in agreement with XRD)
c. TEM image
(~55 nm crystals)
d. HRTEM image
(lattice fringes (222) plane)
e. N₂ ads-des isotherms
(1072 m²/g; 0.53 cc/g; Type I)
f. CO₂/CH₄ ads isotherms
(CO₂/CH₄ adsorption capacity~ 14)
ZIF-8 membranes

Continuous ZIF-8 membranes prepared on alumina tubular porous supports via in-situ crystallization employing secondary seeded approach.
Separation performance for CO₂/CH₄ mixtures

CO₂/ CH₄ separation properties at a permeate pressure of 99.5 KPa and pressure drop of 40 KPa

<table>
<thead>
<tr>
<th>Membrane ID</th>
<th>P_{CO₂} \text{ mol/ m}^{2}\cdot\text{s.Pa} \times 10^5</th>
<th>P_{CH₄} \text{ mol/ m}^{2}\cdot\text{s.Pa} \times 10^6</th>
<th>CO₂/CH₄ selectivity</th>
<th>Separation index (π)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>2.43</td>
<td>4.72</td>
<td>5.1</td>
<td>9.9</td>
</tr>
<tr>
<td>Z2</td>
<td>2.19</td>
<td>4.63</td>
<td>4.7</td>
<td>8.0</td>
</tr>
<tr>
<td>Z3</td>
<td>2.11</td>
<td>5.17</td>
<td>4.1</td>
<td>6.5</td>
</tr>
<tr>
<td>Z4</td>
<td>1.69</td>
<td>2.42</td>
<td>7.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

- Unprecedented high CO₂ permeances
- Low CO₂/CH₄ selectivities
- High separation indexes
- Uncoordinated nitrogen atoms in the ZIF-8 may favor its binding with CO₂, resulting in preferential CO₂ adsorption

S.R. Venna, M.A.Carreon, JACS 2010, 132, 76-78
### Separation mechanism

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (0.33 nm)</th>
<th>CH₄ (0.38 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pore size</strong></td>
<td>(0.34 nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>adsorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>diffusion</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CO₂** and **CH₄** molecules are shown with their respective diameters.
## Existing ZIF membranes for gas mixture separations

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Support</th>
<th>Permeance $^b$</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>Asymmetric titania disks</td>
<td>$5 \times 10^{-8}$ (H$_2$)</td>
<td>H$_2$/CH$_4$=11.2</td>
<td><em>JACS</em> 2009, 131,16000</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>Asymmetric alumina disks</td>
<td>$8 \times 10^{-8}$ (H$_2$)</td>
<td>H$_2$/N$_2$=7.7; H$_2$/CH$_4$=5.9</td>
<td><em>Angew. Chem. Int. Ed.</em> 2010, 49, 548</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Porous alumina tubes</td>
<td>$17 \times 10^{-6}$ (CO$_2$)</td>
<td>CO$_2$/CH$_4$=7</td>
<td><em>JACS</em> 2010, 132, 76</td>
</tr>
<tr>
<td>ZIF-69</td>
<td>Porous alumina disks</td>
<td>$3.6 \times 10^{-8}$ (CO$_2$)</td>
<td>CO$_2$/CO=3.5</td>
<td><em>J. Membrane Sci.</em> 2010, 353, 36</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>Asymmetric alumina disks</td>
<td>$4.5 \times 10^{-8}$ (H$_2$)</td>
<td>H$_2$/N$_2$=18; H$_2$/CH$_4$=14 H$_2$/CO$_2$=13.6</td>
<td><em>J. Membrane Sci.</em> 2010, 354, 48</td>
</tr>
<tr>
<td>ZIF-22</td>
<td>Titania and alumina disks</td>
<td>$1.9 \times 10^{-7}$ (H$_2$)</td>
<td>H$_2$/N$_2$=6.4; H$_2$/CH$_4$=5.2 H$_2$/CO$_2$=7.2; H$_2$/O$_2$=6.4</td>
<td><em>Angew. Chem. Int. Ed.</em> 2010, 49, 4958</td>
</tr>
<tr>
<td>ZIF-90</td>
<td>Alumina disks</td>
<td>$2.5 \times 10^{-7}$ (H$_2$)</td>
<td>H$_2$/N$_2$=11.7; H$_2$/CH$_4$=15.3 H$_2$/CO$_2$=7.3; H$_2$/C$_2$H$_4$=62.8</td>
<td><em>JACS</em> 2010, 132, 15562</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>Asymmetric alumina disks</td>
<td>$9 \times 10^{-9}$ (H$_2$)</td>
<td>H$_2$/CO$_2$=8.4</td>
<td><em>Adv. Mater.</em> 2010, 22, 3322</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Alumina disks</td>
<td>$1.75 \times 10^{-7}$ (H$_2$)</td>
<td>H$_2$/CH$_4$=13; H$_2$/N$_2$=11.6 $^c$</td>
<td><em>Langmuir</em> 2010, 26, 14636</td>
</tr>
<tr>
<td>ZIF-90</td>
<td>Alumina disks</td>
<td>$2.1 \times 10^{-7}$ (H$_2$)</td>
<td>H$_2$/N$_2$=15.8; H$_2$/CH$_4$=18.9 H$_2$/CO$_2$=15.3;</td>
<td><em>Angew. Chem. Int. Ed.</em> 2011, 50, 4979</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Asymmetric alumina disks</td>
<td>$1 \times 10^{-7}$ (H$_2$)</td>
<td>H$_2$/CO$_2$=6; H$_2$/CH$_4$=15 H$_2$/C$_2$H$_6$=15; H$_2$/C$_3$H$_6$&gt; 300</td>
<td><em>Chem. Mater.</em> 2011, 23, 2262</td>
</tr>
<tr>
<td>ZIF-69</td>
<td>Porous alumina disks</td>
<td>$1.9 \times 10^{-7}$ (CO$_2$)</td>
<td>CO$_2$/N$_2$=6.3; CO$_2$/CO=5; CO$_2$/CH$_4$=4.6</td>
<td><em>J. Membrane Sci.</em> 2011, 379, 46</td>
</tr>
</tbody>
</table>

$^a$Listed by chronological publication dates; $^b$ (mol/m$^2 \cdot$ s $\cdot$ Pa); $^c$ pure gas measurements
Conclusions

1. We have demonstrated the synthesis of *ZIF-8 crystals with controlled particle size*. These crystals serve as “seeds” for membrane growth.

2. ZIF-8 crystals have been prepared via *homogeneous and heterogeneous nucleation*.

3. We have presented one of the first examples of the preparation of *continuous and reproducible ZIF-8 membranes* for a functional gas separation application.

4. The membranes displayed *unprecedented high CO₂ permeances* and relatively high separation indexes for CO₂/CH₄ mixtures.

5. ZIF membranes are *novel and promising for CO₂ separation* from light gases.
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ACS-PRF (49202-DNI5)
Separation performance parameters

For an economic separation: \( \frac{\text{CO}_2}{\text{N}_2} > 70 \), \( \text{PCO}_2 = > 3 \times 10^{-7} \ \text{mol/m}^2\text{sPa} \)

For \( \frac{\text{CO}_2}{\text{CH}_4} > 60 \), \( \text{PCO}_2 = > 3 \times 10^{-7} \ \text{mol/m}^2\text{sPa} \) (at 1000 psia)

\[
\text{Selectivity} = \alpha_{\text{CO}_2/\text{CH}_4} = \frac{J_{\text{CO}_2}}{J_{\text{CH}_4}} = \frac{\text{CO}_2 \text{ Permeance}}{\text{CH}_4 \text{ Permeance}}
\]

The pressure is log mean pressure is calculated using

\[
\Delta P_{\ln,i} = \frac{(P_{f,i} x_{f,i} - P_{p,i} x_{p,i}) - (P_{r,i} x_{r,i} - P_{p,i} x_{p,i})}{\ln \left[ \frac{(P_{f,i} x_{f,i} - P_{p,i} x_{p,i})}{(P_{r,i} x_{r,i} - P_{p,i} x_{p,i})} \right]}
\]

Permeance of \( \text{CO}_2 = J_{\text{CO}_2} = \frac{\text{amount of carbon dioxide permeated}}{\text{Pressure} \cdot \text{area of the membrane} \cdot \text{time}} \)
SAPO-34 membranes successfully prepared in 25 cm stainless steel supports

Membrane module

SAPO-34 membranes for the separation of CO₂ from natural gas have been developed close to commercial demonstration stage.

S. Li, M.A. Carreon, et al. *Journal of Membrane Science* 2010, 352, 7
Conversion of CO$_2$ to chemicals

Carbon dioxide as a feedstock for conversion to *fuels* and *chemicals*

\[ \text{Epoxide} \quad \begin{array}{c} \text{R} \\ \text{O} \end{array} \quad + \quad \text{CO}_2 \quad \xrightarrow{\text{Bio-MOF}} \quad \begin{array}{c} \text{Cyclic carbonate} \\ \text{R} \quad \text{O} \quad \text{O} \end{array} \]

$\text{R}=\text{CH}_2\text{Cl, CH}_3, \text{C}_6\text{H}_5, \text{C}_4\text{H}_9$

Cyclic Carbonates and Polycarbonates as well as Carbamates and polycarbamates are important raw materials for: the manufacture of a variety of polymers (e.g., polyurethanes) used in foams, coatings, adhesives, plastics and fibers. They are also used as herbicides, fungicides and pesticides in agrochemical industry.
Designing CO$_2$ selective MOF membranes

Optimize the main factors affecting the overall separation performance of the membranes:

1. Synthesis routes to prepare crystals with different sizes and morphologies
2. Surface chemistry control: functionalization of MOF crystals with basic pendant functionalities or use of BioMOFs (which have already as part of their structures these basic functionalities: adenine, aspartame, and other basic biomolecules).
3. Effect of seeding techniques to improve membrane intergrowth: physical vs chemical approach.
4. Interaction between membrane and support (nature of the support: composition and textural properties).
5. Effective control over membrane thickness
Bio-MOF-1

- 3-D permanently porous framework
- Zn(II)-Adeninate columns composed of octahedral cages
- Cage consists of 8 \( \text{Zn}^{2+} \) cations with 4 adeninate linkers
- Columns interconnect with biphenyldicarboxylate
- Surface area: 1700 m\(^2\)/g