Inorganic membranes for CO_2/N_2 separation

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Outline

- Introduction/background
- Membrane synthesis
- Mesoporous membranes
- Microporous membranes
- Functionalized membranes
- Membrane performance
- Conclusions

Needs

- Reduce CO_2 emissions from power plants
- Sequestration methods require concentrated CO_2
- Membranes for CO_2/N_2 separation
  - High flux
  - High separation factor
  - Corrosion resistant
  - High temperature operation

Objectives

- Prepare and characterize novel inorganic membranes capable of high separation factors for CO_2/N_2 and high fluxes
- Understand the critical factors in optimizing separation and flux
  - *Membrane microstructure (physical)*
  - *Surface functionality (chemical)*

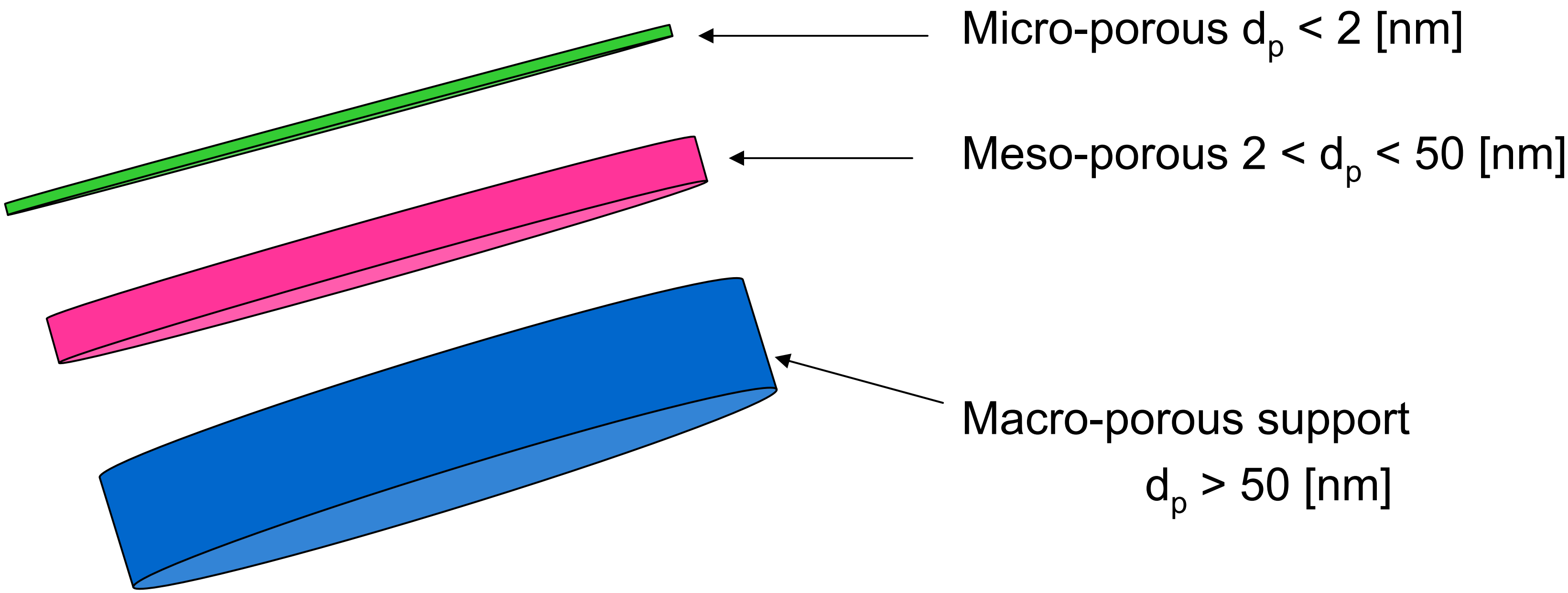
Technical Approach-Microstructure

- Microporous membranes, with pore sizes less than 2nm, offer the best potential for achieving high separation factors
- Generally, there is a trade-off between high separation factors and high flux because high separation requires small pore sizes, and this hinders flux through the membrane

Technical Approach

- In order to achieve high separation and maintain reasonable flux, the microporous membrane needs to be thin
- Membranes are typically fabricated as a series of individual membranes, where the bulk of the resistance is in the microporous layer

CO_2 selective membrane architecture



Gas Transport in Microporous Membranes

- Characterized by a diffusion coefficient according to Fick's first equation

$$J = -D \frac{\partial q}{\partial z}$$

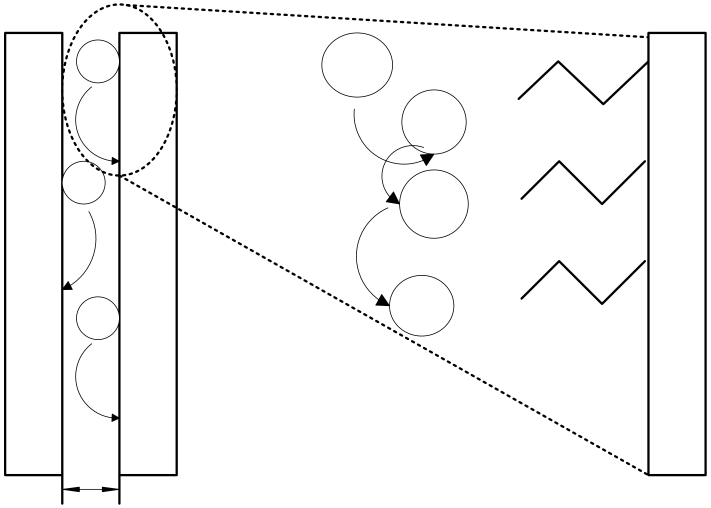
$$q^* = Kp$$

$$J = -KD \frac{\partial p}{\partial z}$$

- *K* is Henry's constant for a linear isotherm

Designing a Membrane for CO_2/N_2 Separation

- Control two processes: diffusion and sorption
  - Pore size and porosity (microstructure)
  - Surface functionalization to enhance selective sorption (chemistry)
- Introduce two novel aspects to this work
  - A method for pore size control below 2 nm
  - A method for functionalizing the pore surface with NH_2 groups, for selective CO_2 sorption



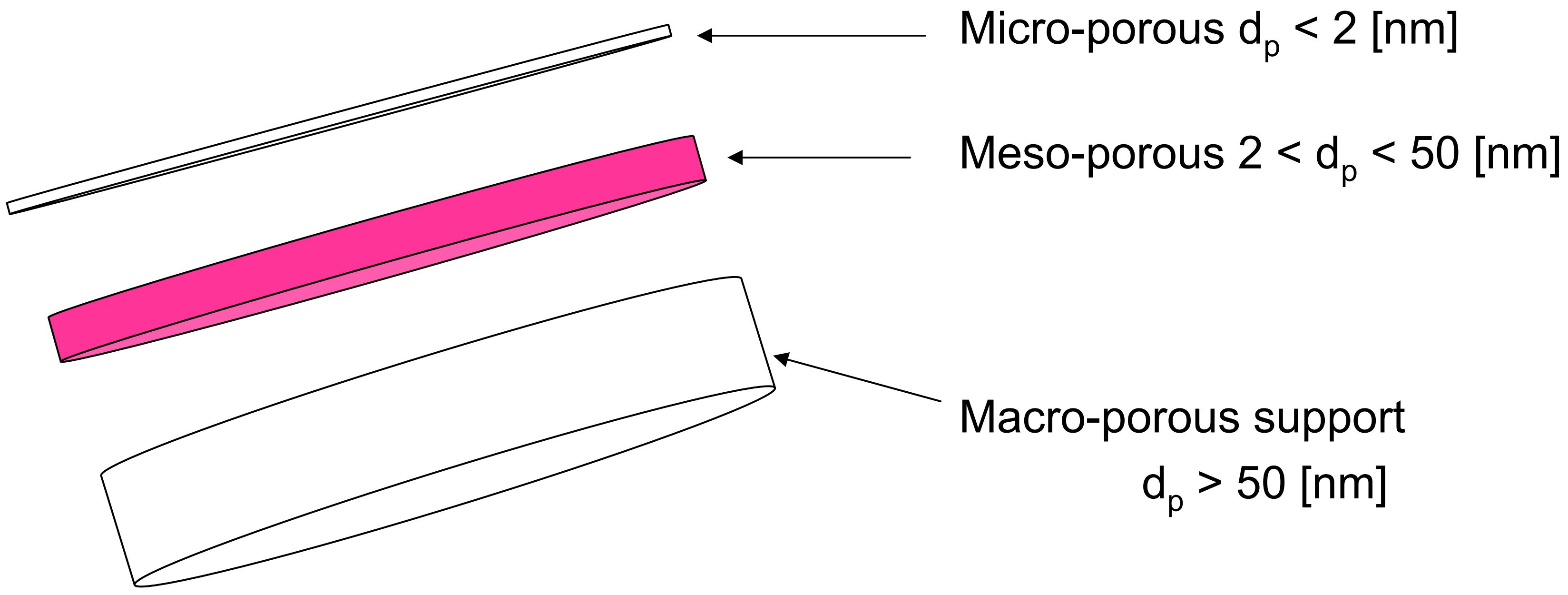
Major Challenges

- Current funded project (year 1)
  - Can functionalizing a silica surface with amino groups enhance CO_2 sorption and selectivity?
  - How does pore size and porosity of functionalized silica membranes impact CO_2 selectivity?

Major Challenges, con't

- 3-5 Years
  - Optimization of membrane synthesis procedure for CO_2/N_2 separation
  - Process scale-up
  - Understanding the effects of other gases in flue gas on membrane performance and integrity, for example, water and sulfer dioxide
  - Technology transfer

Membrane Synthesis-Mesoporous layer



Mesoporous Membrane Synthesis

- Silica sols were prepared by micellar templating techniques using tetraethylorthosilicate (TEOS)
- Sols were dip-coated onto α-alumina supports and dried at room temperature
- A final firing to remove the surfactant was performed at 500°C

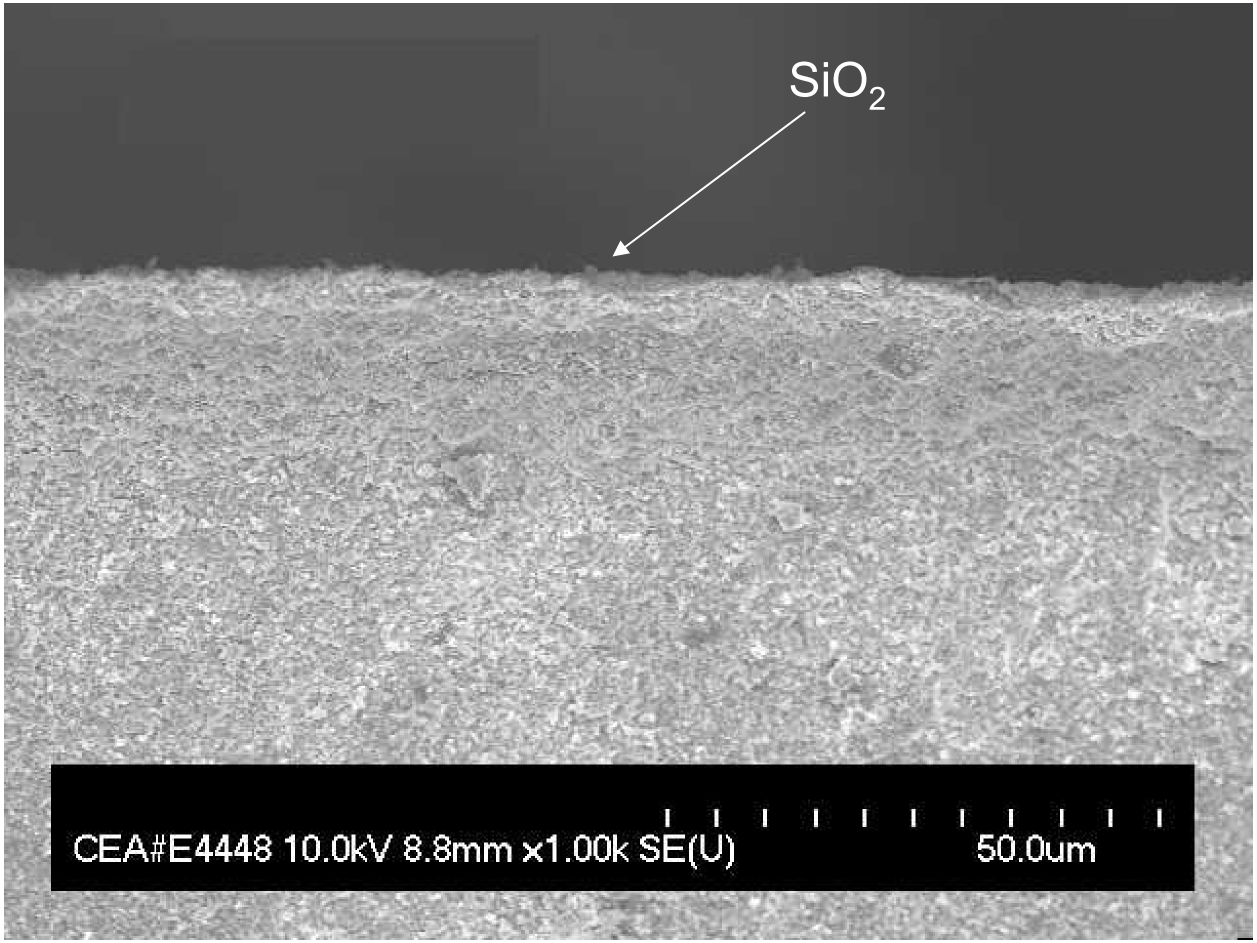
Mesoporous Membrane Characterization

Pore size of powder (prepared by firing the dried dipping sol under identical conditions to the membrane)

- 2.0 nm pore size
- 880 m^2g^{-1} surface area

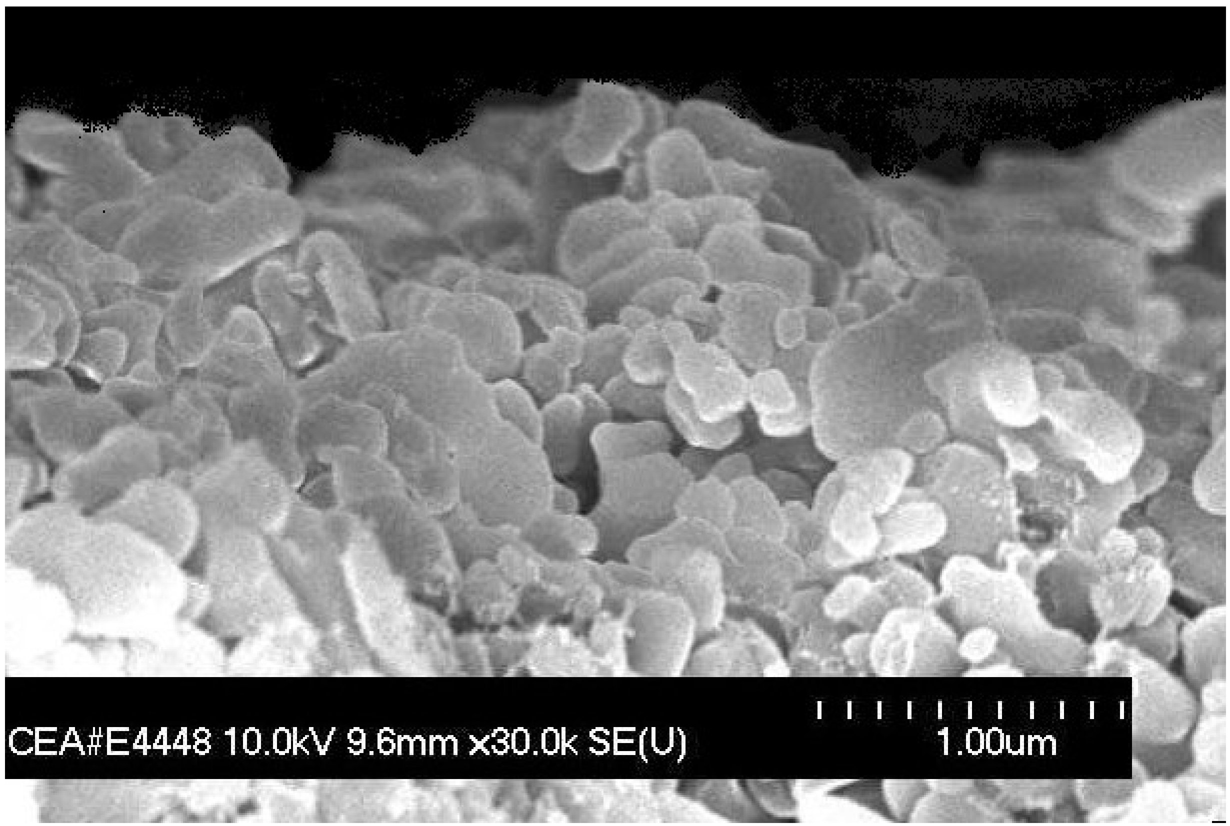
- X-ray diffraction
  - Peaks measured in the 2θ range of 1-7° indicating long range order and a periodicity to the pore structure
  - Peaks were indexed to a simple cubic structure
- Membrane thickness ~ 2μm

Mesoporous Membranes

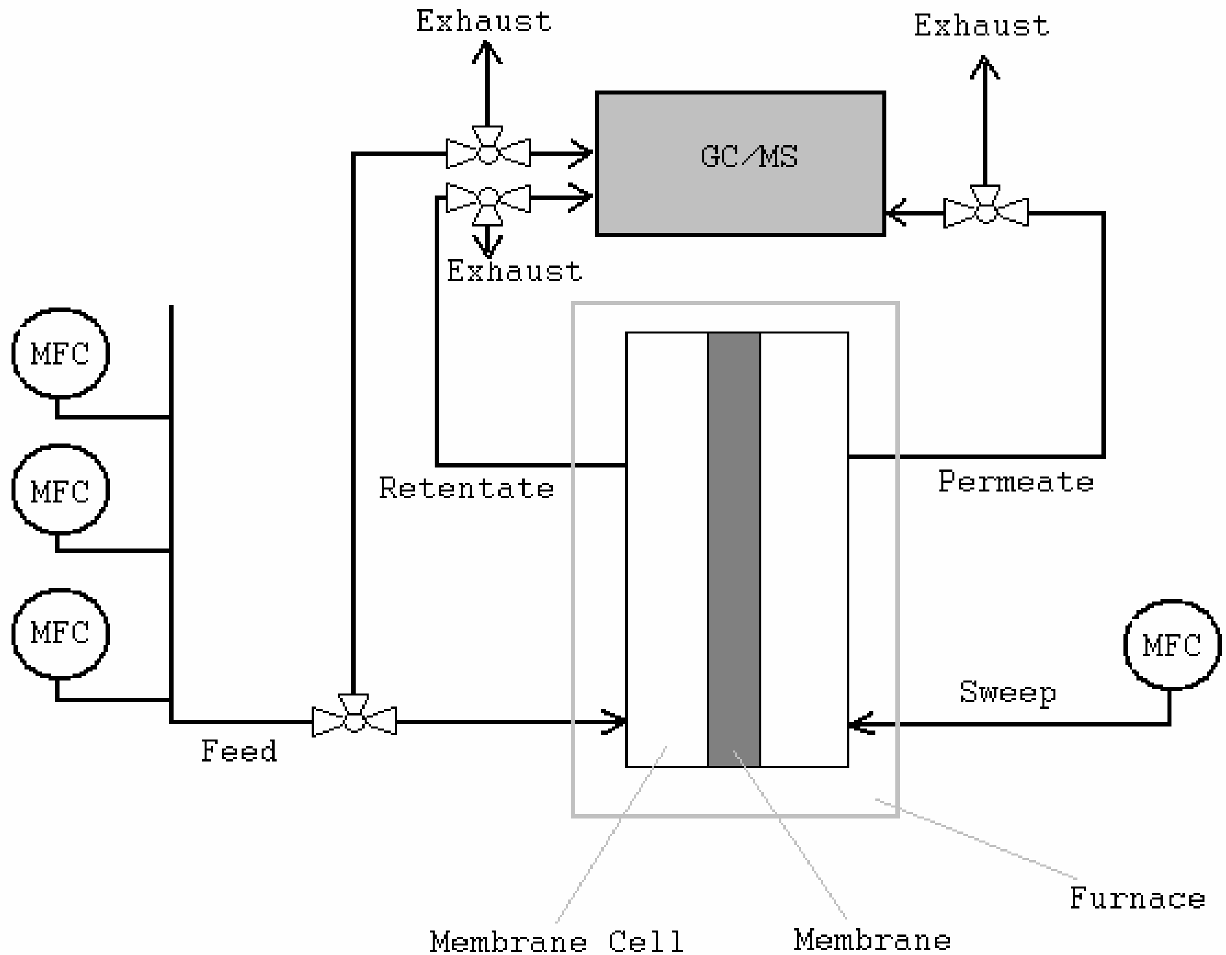


Mesoporous Membranes

Membrane surface



Membrane gas permeation apparatus



Gas Transport in Mesoporous Membranes

- Mesoporous membranes (pore size 2-10 nm) are dominated by Knudsen diffusion

$$Flux \propto \frac{1}{T^{0.5} MW^{0.5}}$$

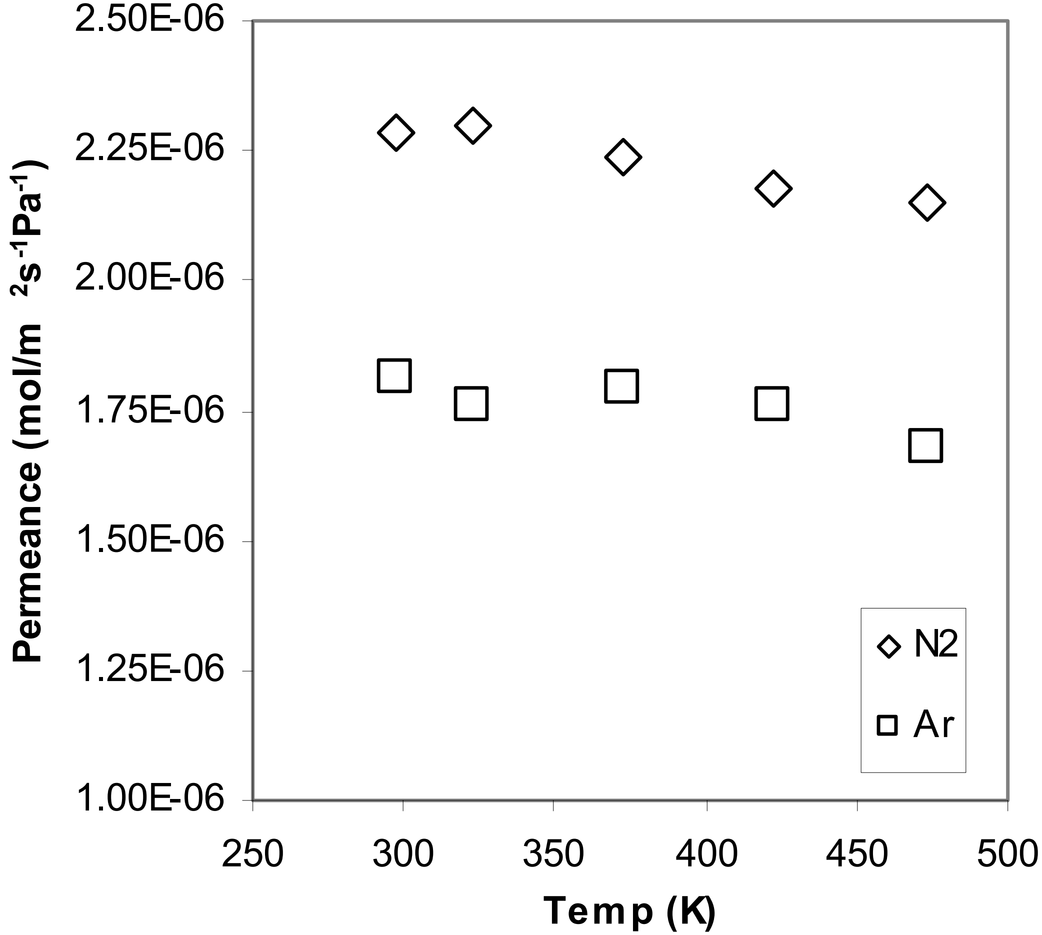
- Separation is based on molecular weight differences

$$\alpha^* = \sqrt{\frac{MW_2}{MW_1}}$$

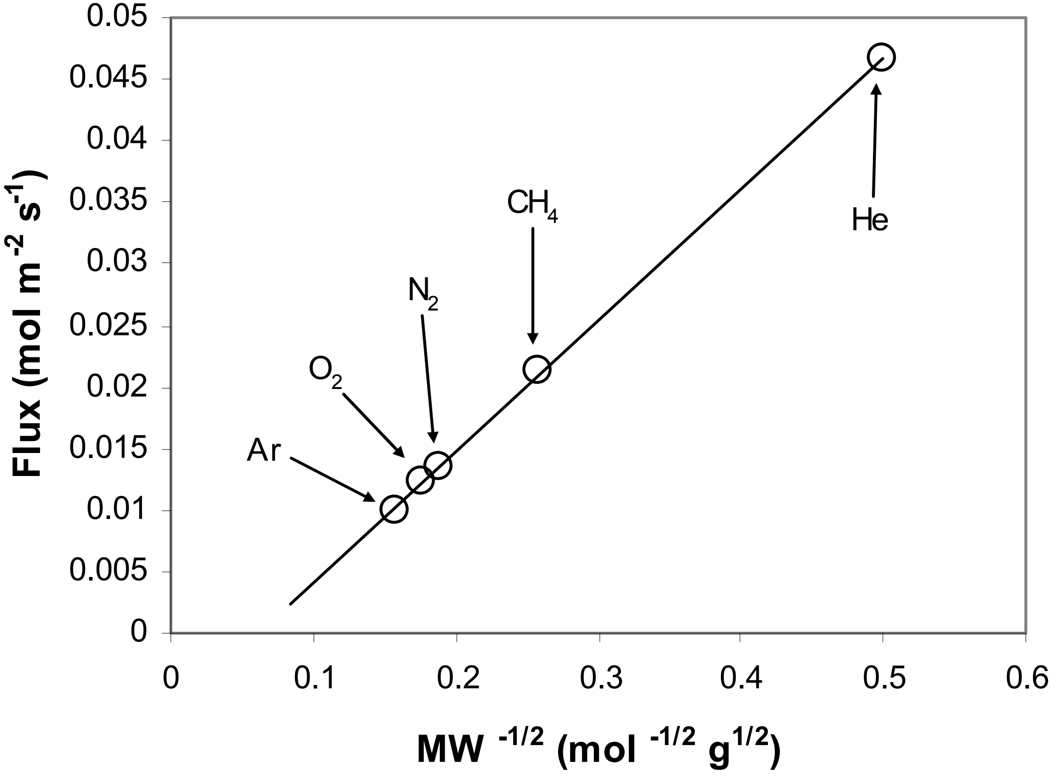
$$MW_2 > MW_1$$

Mesoporous Membrane Characterization

Separation of N_2/Ar corresponds to separation of ~1.2 (ideal Knudsen = 1.19)

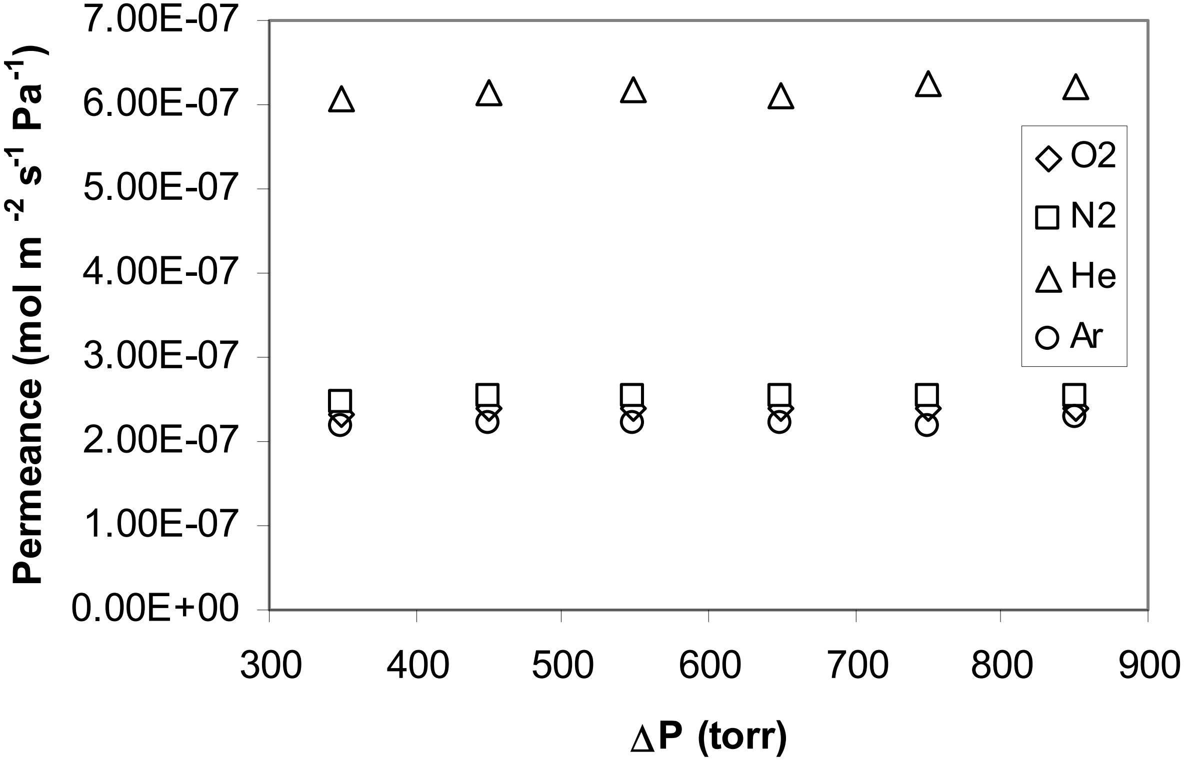


Mesoporous Membrane Characterization



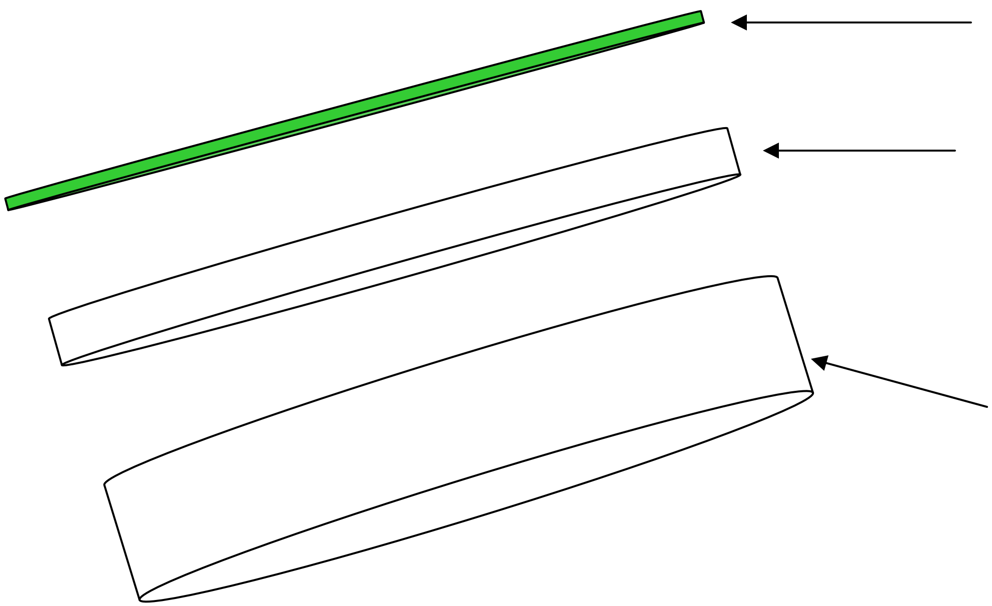
Linear dependence of flux on the inverse square of molecular weight characteristic of Knudsen-dominated diffusion

Mesoporous Membrane Characterization



Permeance is independent of pressure indicating Knudsen-dominated flow and minimal viscous flow which correlates to minimal defects

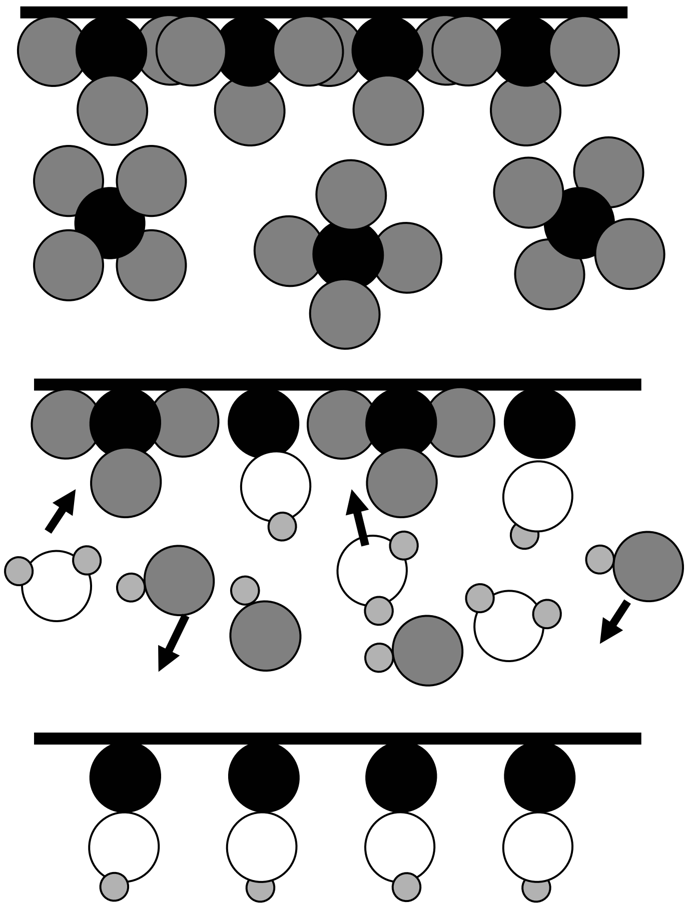
Membrane Synthesis-Microporous layer



Microporous layer synthesis

- Modify the mesoporous layer by depositing a thin layer within the pore structure, reducing pore size
- Use surface-limited chemical vapor deposition reactions, referred to as atomic layer deposition (ALD)
- Catalyze the surface-limited reactions with a tertiary amine base (BCALD)
  - Reduce reaction temperature
  - Reduce reaction times
  - Self-limit pore size reduction
  - Heal minute defects

Atomic Layer Deposition



$SiCl_4$ adsorption

$SiCl + H_2O \rightarrow$
$SiOH + HCl$

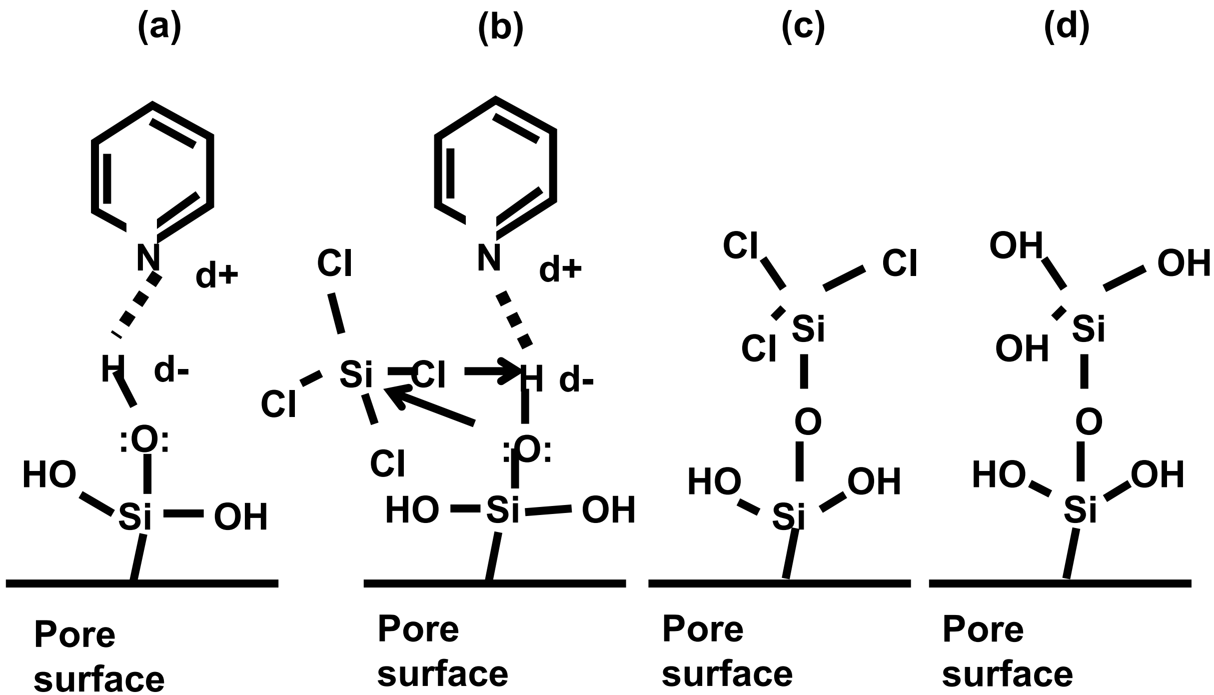
SiOH

- Sequential reactions

$SiCl_4 + SiOH \rightarrow$
$SiOSiCl_3 + HCl$ (A)

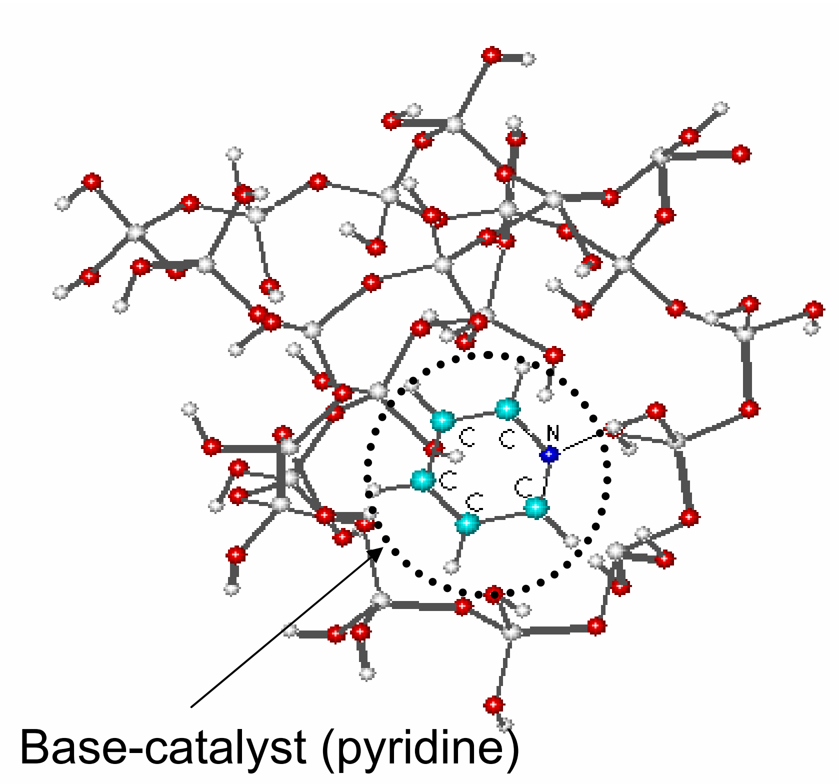
$SiOSiCl_3 + 3H_2O \rightarrow$
$SiOSi(OH)_3 + 3HCl$ (B)

Base-Catalyzed Atomic Layer Deposition (BCALD)



- The addition of a tertiary amine lowers the ALD reaction temperature from 300°C to room temperature.

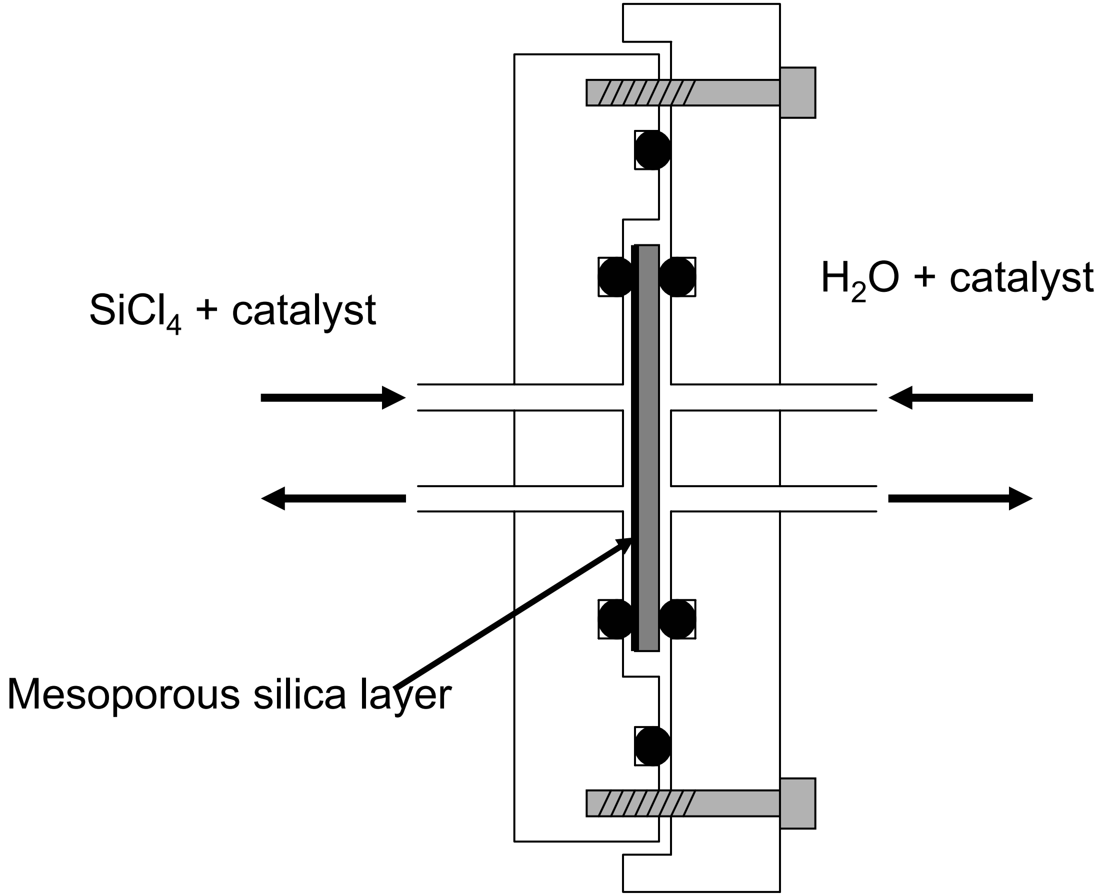
BCALD modification of pore size



Base-catalyst (pyridine) hydrogen bonded within a silica pore

- *Controlled atomic layer-by-layer reduction of pore size via silica deposition*
- *Silica deposition is catalyzed by a tertiary amine (base)*
- *Pore reduction is terminated when the catalyst is excluded from the pore*

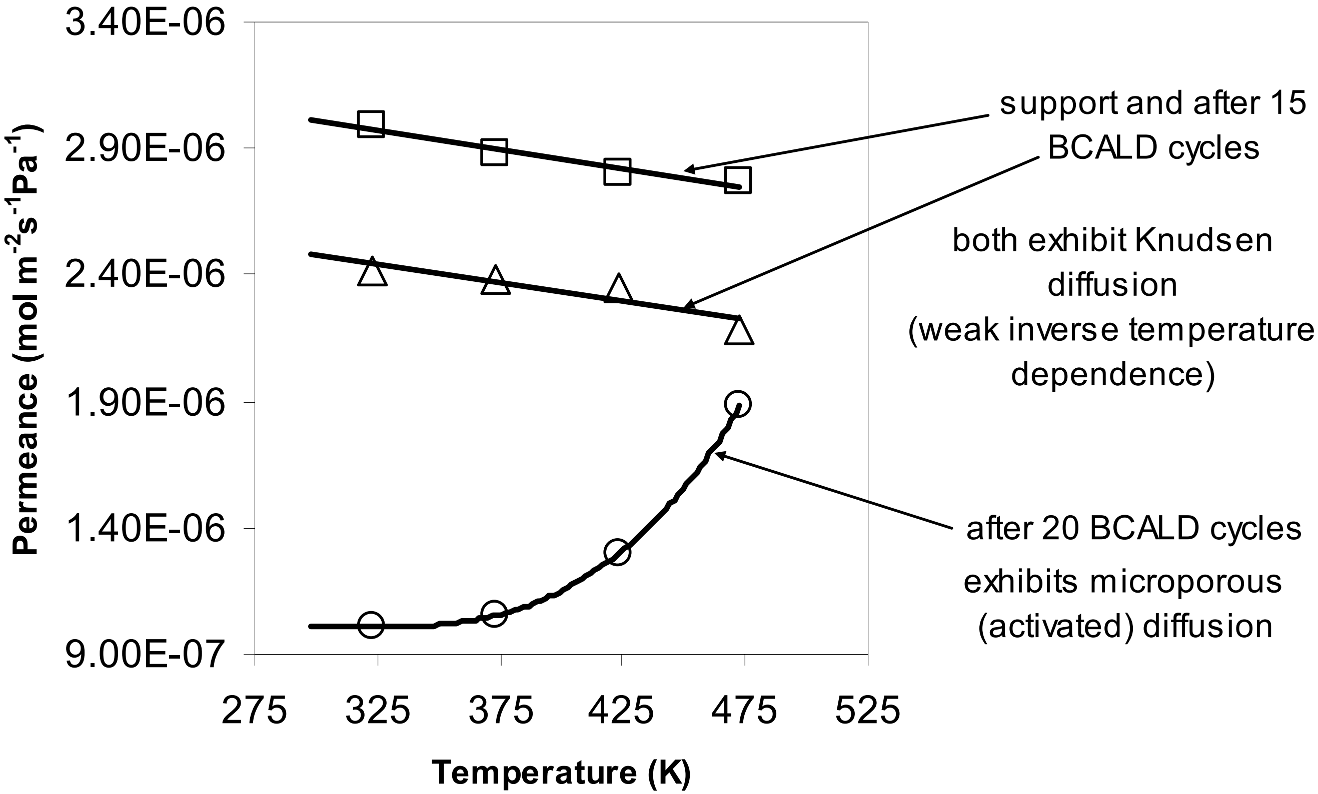
BCALD Reactor



BCALD Reaction Parameters

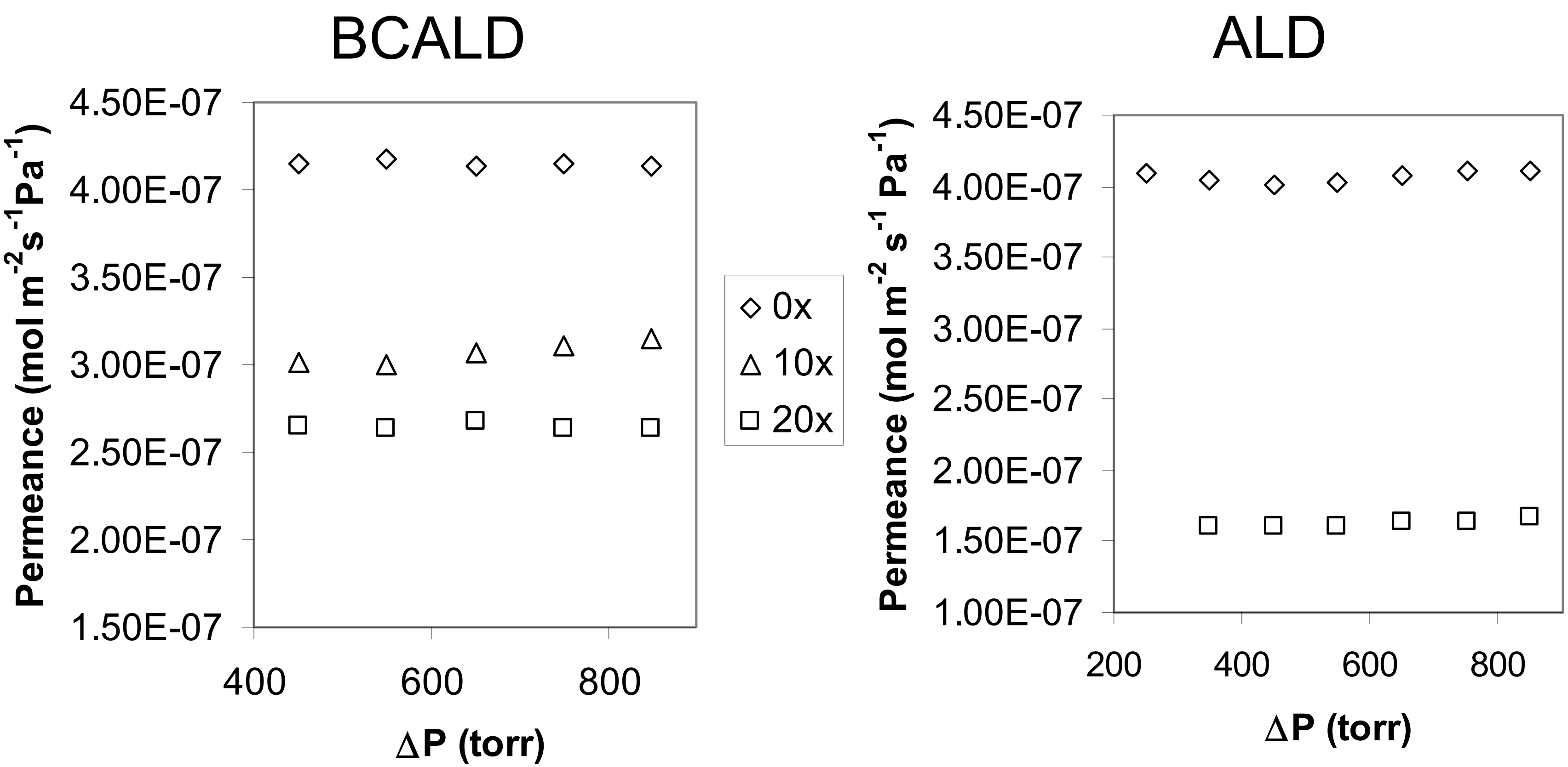
- Reagents: $SiCl_4$, H_2O and Pyridine
- Growth temperature of 70°C (lowered from 300°C)
  - Determined emprically by monitoring the pyridinium chloride salt sublimation
- Process Parameters
  - Reagent flow rate
  - Time of exposure
  - Flush time between exposures
  - Number of reaction cycles
  - Exposing the surface of the membrane vs. the entire membrane

Microporous silica membrane prepared by BCALD



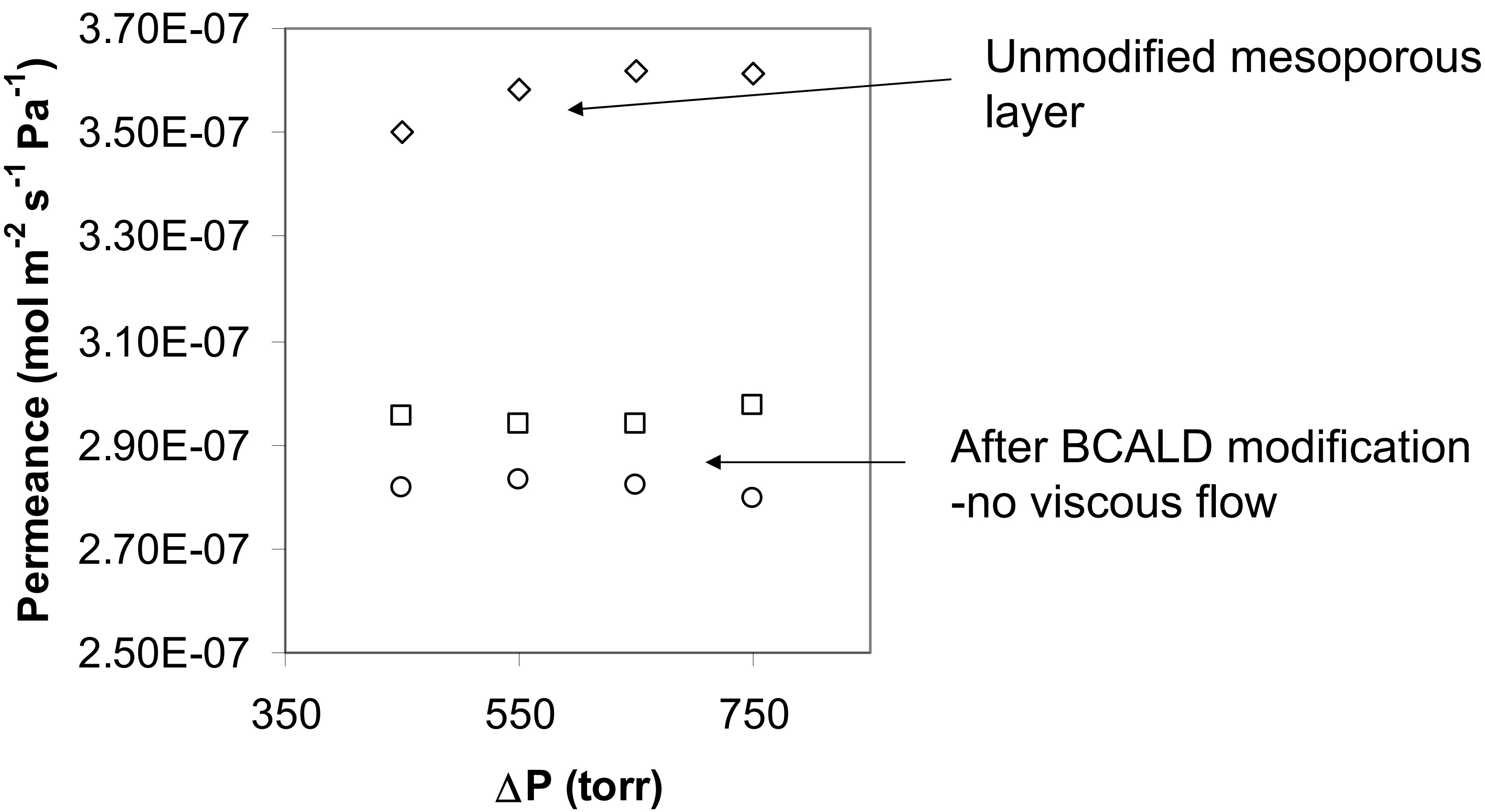
Onset of microporous diffusion achieved

Permeance drop after modification



After 20 reaction cycles, ALD modification is greater indicating a self-limiting reaction using a catalyst

Defect reduction via BCALD modification



Elimination of viscous flow through defects via BCALD modification

Advantages of BCALD

- Lowered reaction temperature
- Self-limiting pore size reduction based on the catalyst size
- Healing of minute cracks and defects

Surface modification

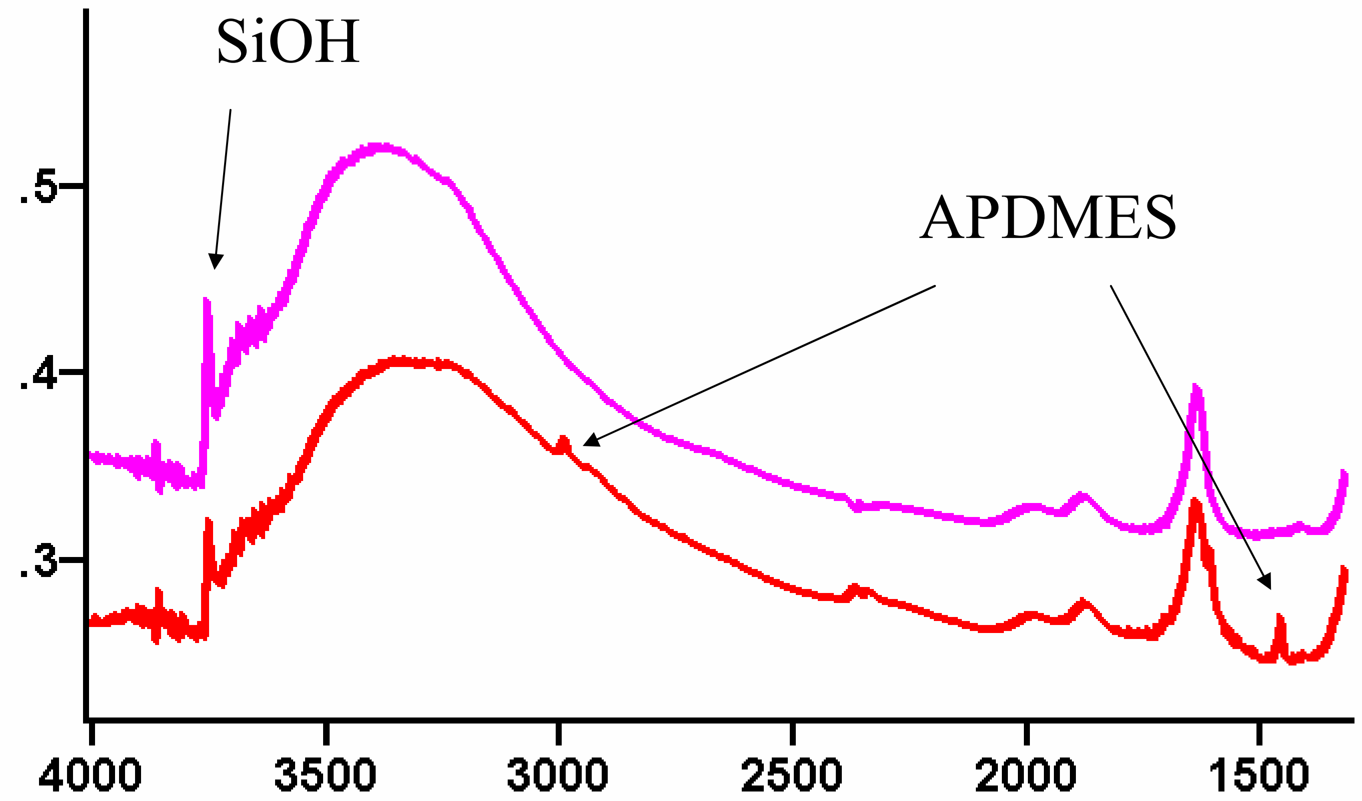
- Attachment of aminopropyl groups via aminopropyldimethylethoxysilane
  - One reactive site, no self-polymerization
  - Attached via gas transport through the membrane

$$\begin{array}{c} CH_3 \\ | \\ H_2N\text{—}(CH_2)_3\text{—}Si\text{—}OCH_2CH_3 \\ | \\ CH_3 \end{array}$$

APDMES

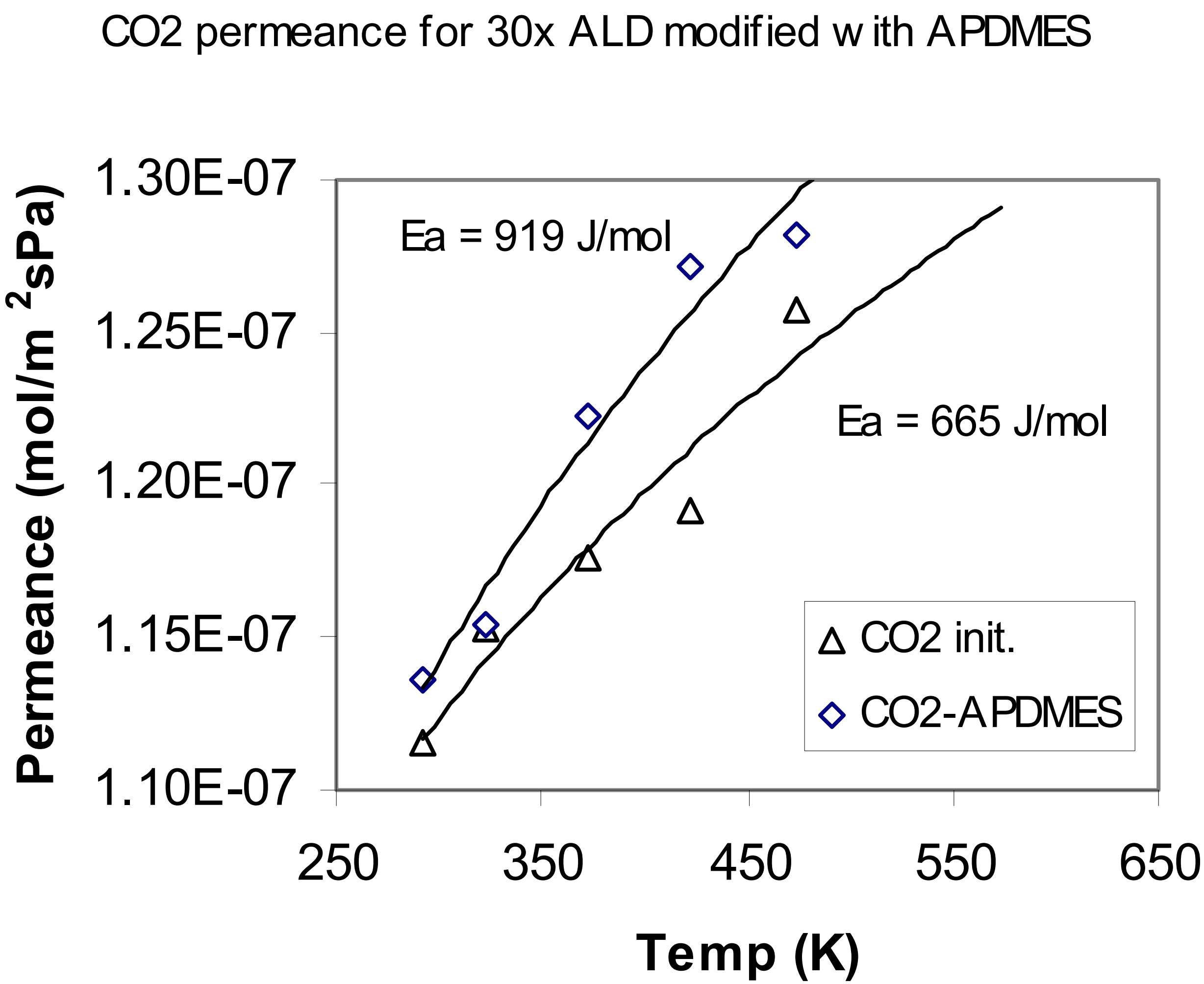
- *Attach to all available OH sites vs. thick silane layer on the surface?*

FTIR Spectroscopy of powders modified by APDMES

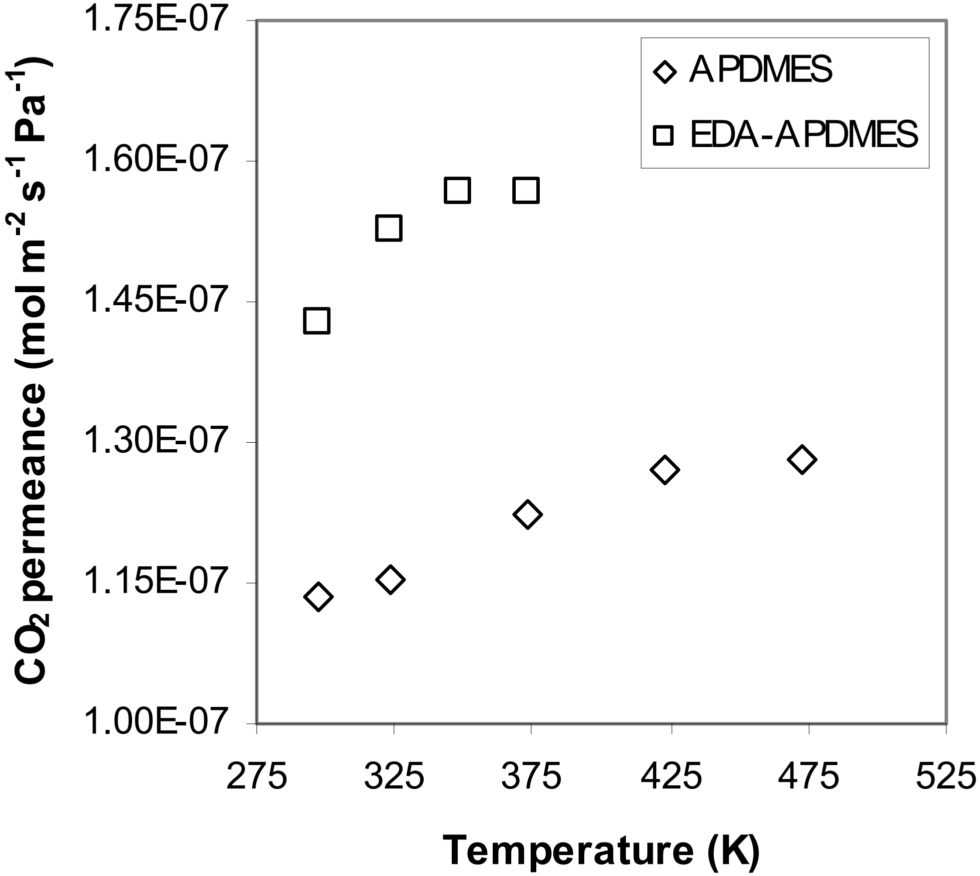


Confirmation of attached aminopropyl groups using FTIR spectroscopy

CO_2 Permeance Increase with NH_2 terminated pores



CO_2 Permeance for Amine functionalized membranes



Ethylene diamine co-reacted with APDMES increases CO_2 permeance

Conclusions

- CO_2 permeance increases with amine functionality
- Chemistry of amine termination affects CO_2 permeance
- BCALD is successful in modifying membranes
  - Lower temperature
  - Self-limiting pore size
- Separation not yet achieved
- Pore sizes still too large to achieve blocking of N_2

Future work

- Understand the functionalization-
  - were pores completely functionalized?
  - are all sites active?
- Deposit microporous silica membranes via dip-coating
- Functionalize membranes
- Gas transport characterization

Acknowledgements

- Ben McCool, Ph.D. Student
- Nick Hill, technician
- Professor Doug Ruthven, University of Maine
- DOE grant DE-FG26-02NT41548