Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production

Jerry Y.S. Lin, Henk Verweij,

Peter Smirniotis and Junhang Dong

University of Cincinnati
Arizona State University

Project PD8

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Overview

Timeline

- Project start date:
  July 1, 2005
- Project end date:
  June 30, 2009
- Percent complete: **45%**

Barriers

Barrier addressed: Cost reduction of distributed hydrogen production from natural gas and renewable liquids through improvement of reforming and separation efficiencies

Budget

- Total project funding
  - DOE **$1,999,727**
  - Contractor: **$501,310**
- Funding received in FY07: **$592,165**
- Funding for FY08: **$467,066**
- Funding delayed in FY07, FY08

Partners

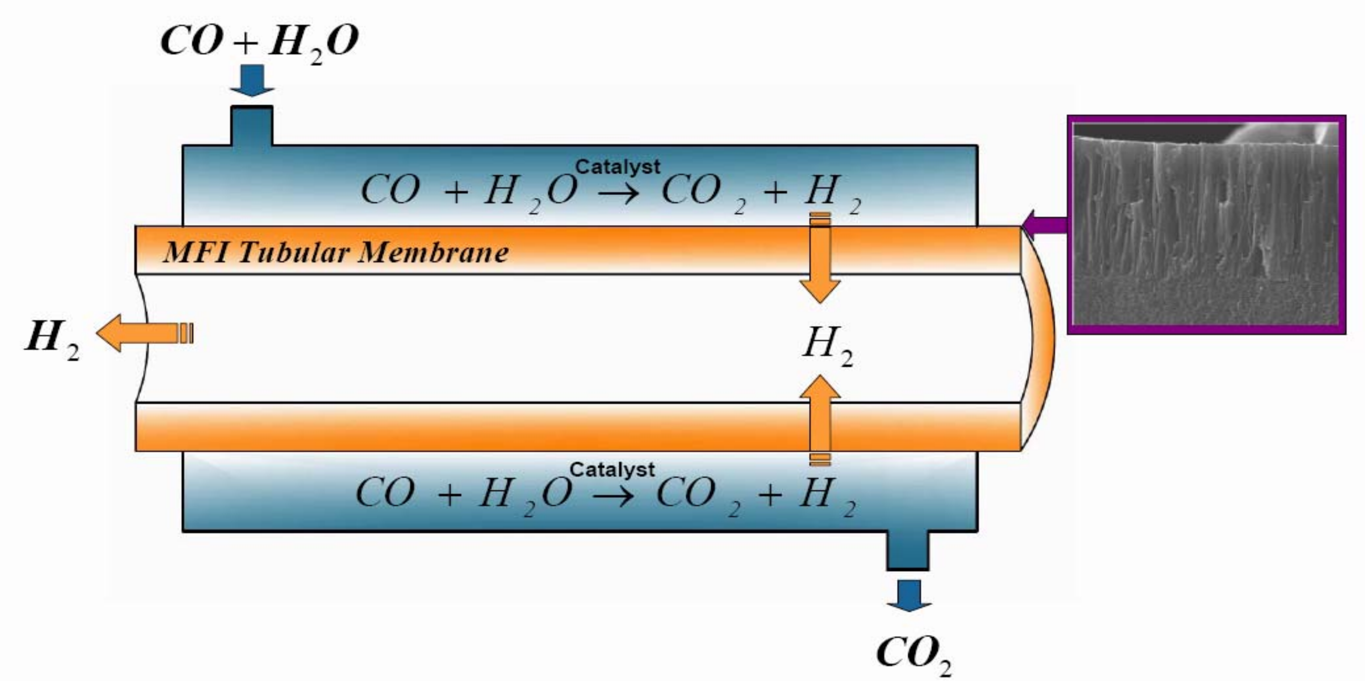
- University of Cincinnati
- Arizona State University
- Ohio State University

Objectives

Fundamental study for the development of chemically and thermally stable zeolite membrane reactor for water-gas-shift reaction for hydrogen production

- *Synthesis and Characterization of Chemically and Thermally Stable Silicalite Membranes*
- *Experimental and Theoretical Study on Gas Permeation and Separation Properties of the Silicalite Membranes*
- *Hydrothermal Synthesis of Tubular Silicalite Membranes and Gas Separation Study*
- *Experimental and Modeling Study of Membrane Reactor for Water-Gas-Shift Reaction*

Zeolite Membrane Reactor for Water-Gas Shift Reaction



- Water-gas-shift reaction at one temperature (about 400ºC)
- Two product streams: pure H_2 and pure CO_2

Zeolite Membrane Requirements:

- Operated in 350-550ºC
- Chemically stable in H_2S, thermally stable at ~400ºC
- Hydrogen permeance ~ $5x10^{-7}$ mol/m^2.s.Pa
- Hydrogen selectivity ~ 50

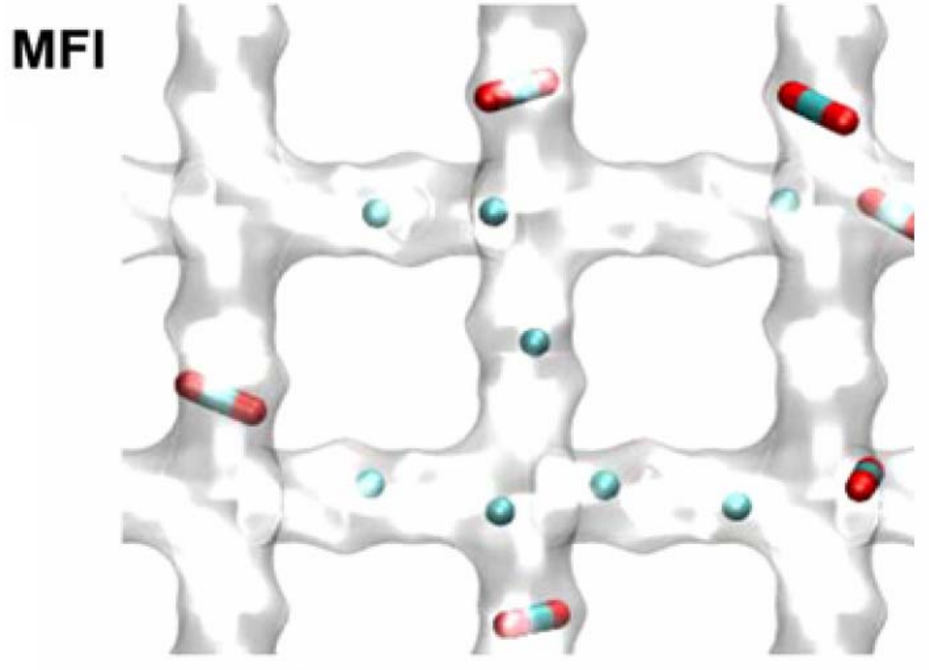
Plan and Approach

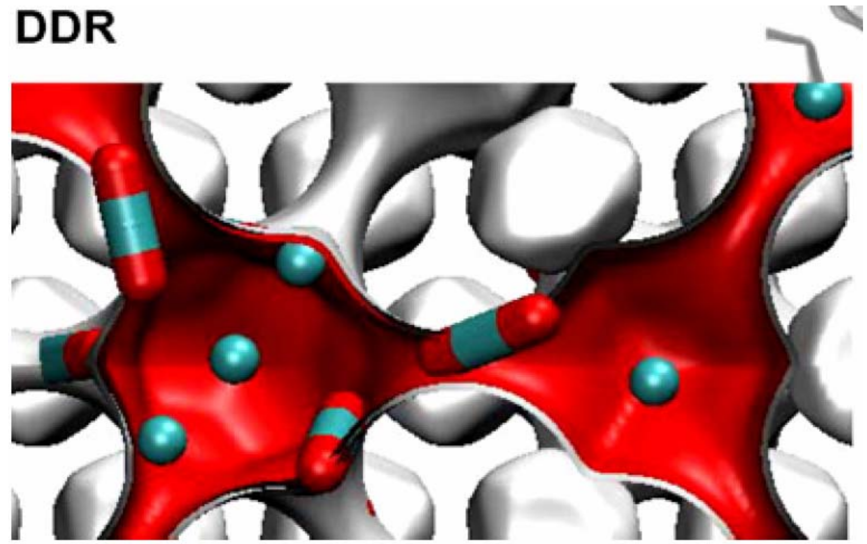
- **Task A- Synthesis and modification of silicalite membranes (90% complete)**
- **Task B-** Separation and stability study (Phase II)
- **Task C Fabrication of tubular support and membrane module (80% complete)**
- **Task D-** Hydrothermal synthesis and CVD modification of tubular silicalite membranes (Phase II)
- **Task E- Microwave synthesis of silicalite membranes (70%)**
- **Task F- Water-gas-shift reaction catalyst and reaction kinetics (50%)**
- **Task G-** Membrane reactor modeling and experiments (Phase II)

Phase I Milestones

- Obtain disk-shaped silicalite membranes on the desired intermediate layers with H_2/CO_2 perm-selectivity over 10 and H^2 permeance larger than $1x10^{-7}$ $mol/m^2.s.Pa$ (**Accomplished**)
- Develop methods to fabricate tubular membrane support with desired intermediate layers (**Accomplished**)
- Obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst but with much improved chemical stability SO_2 and H_2S containing WGS reaction stream (**Accomplished**)
- Develop a membrane module and sealing system for tubular membrane reactor that can be operated in the WGS conditions for at least 1 month (**Accomplished**)
- Develop micro-wave synthesis method to prepare tubular silicalite membranes with H_2/CO_2 perm-selectivity over 10 and H_2 permeance larger than $1x10^{-7}$ $mol/m^2.s.Pa$ (**Accomplished**)
- Obtain disk and tubular silicalite membranes with H_2/CO_2 perm-selectivity over 50 and H_2 permeance larger than $5x10^{-7}$ $mol/m^2.s.Pa$ (Partially Accomplished)

Schematic of MFI (Silicalite) and DDR-type Zeolite Structure





Intersecting channels

MFI (Silicalite): 10-T-Ring intersecting channels of 5.1-5.6 A

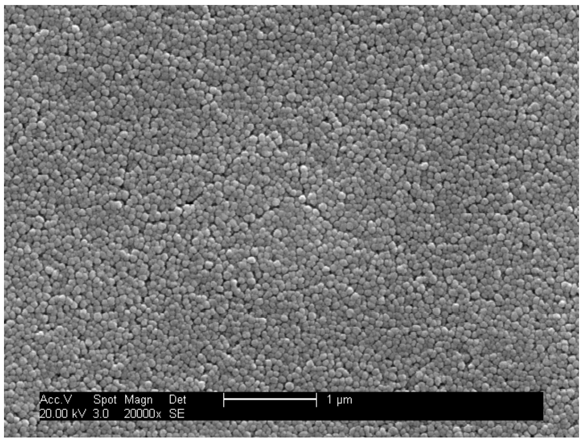
Cages separated by narrow windows

8-T-Ring, Windows of 3.6-4.4 A (studied as a reference)

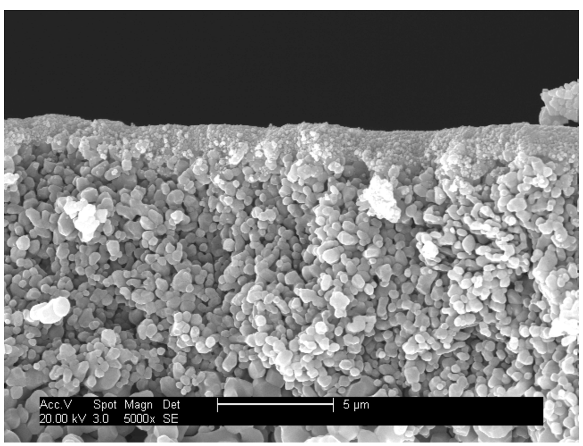
Figures from R. Krishna and J.M. van Baten, (2008)

Technical Progress

- **Secondary growth MFI membrane from organic free solution**
  - ***MFI nanoparticle (<100nm) synthesized by high efficiency microwave heating.***
  - ***MFI nano-crystalline seed layer by slip-casting.***
  - ***High quality MFI membranes by microwave and conventional heating***

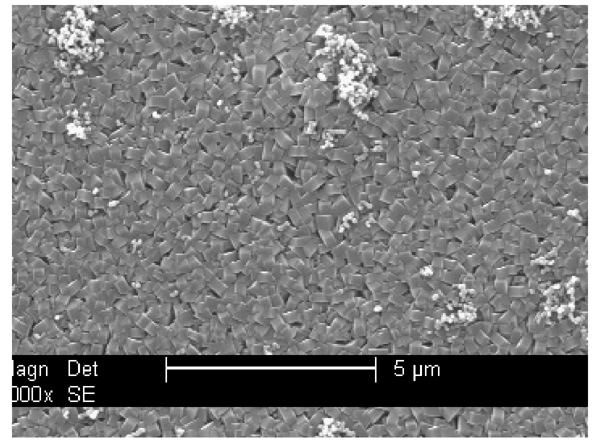


Nano-particle Seed layer

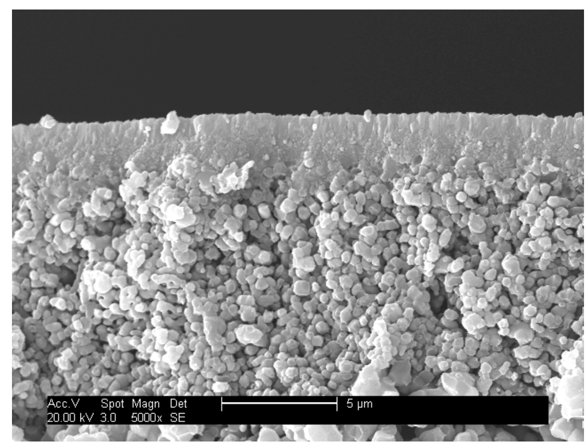


Secondary growth:
Si/Al ratio:
∞ ~ 80

Microwave synthesis time ~3 hr at 180°C

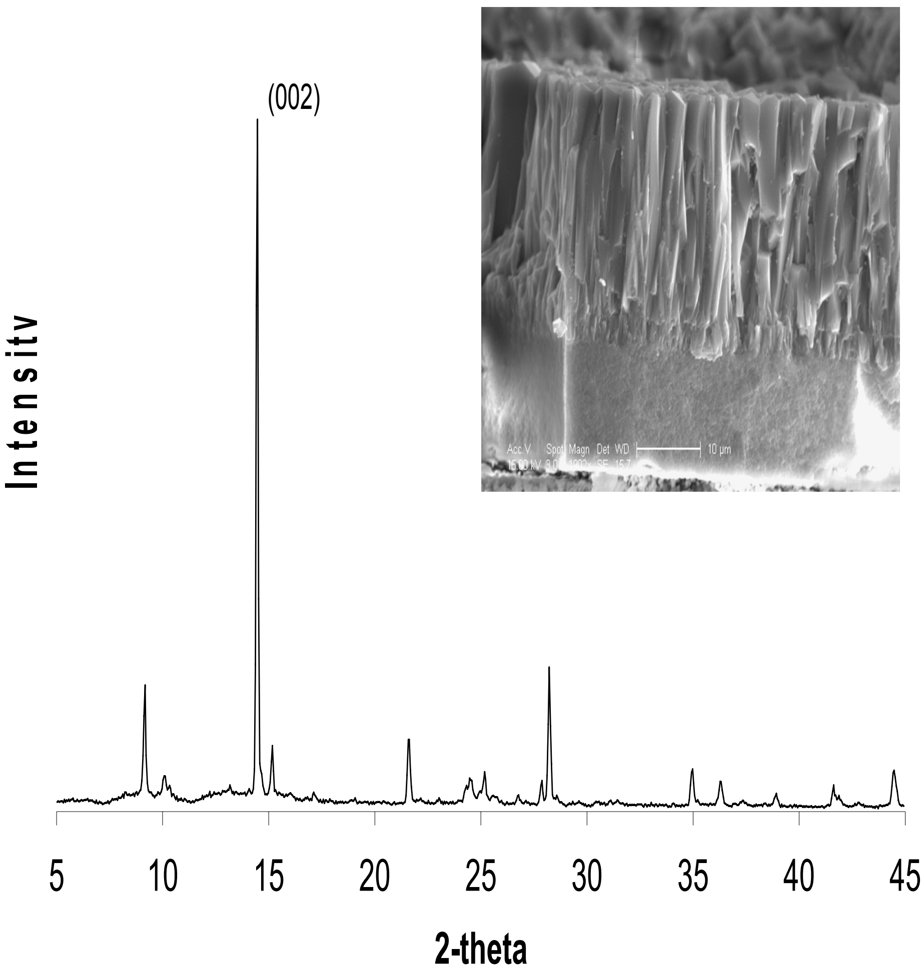


MFI membrane

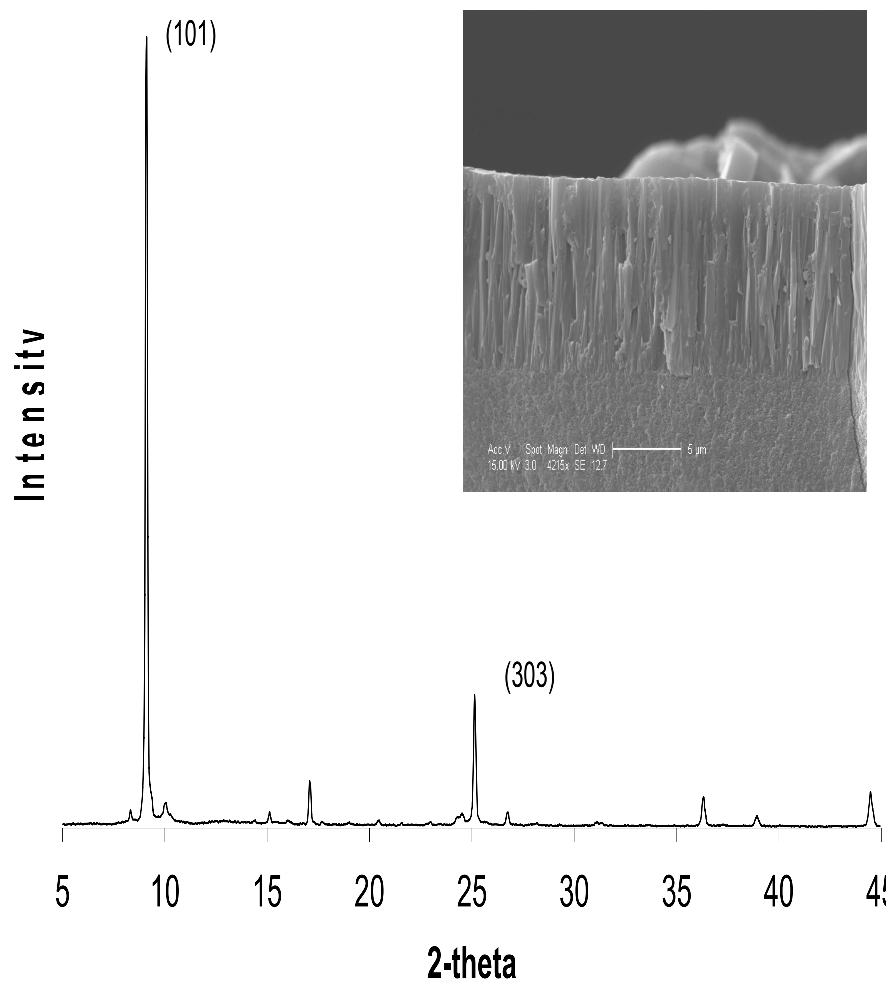


Technical Progress

- **Micro-structural Variations of Silicate Membranes**



C-oriented structure



hoh structure

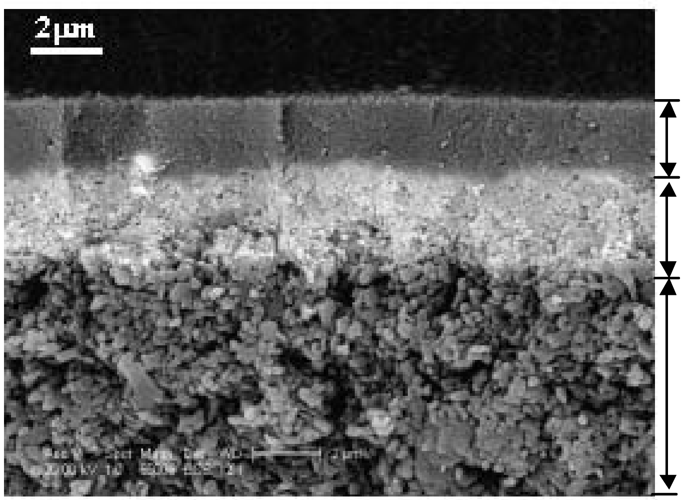
Technical Progress

- **Preparation of silicalite membranes by template-free synthesis**

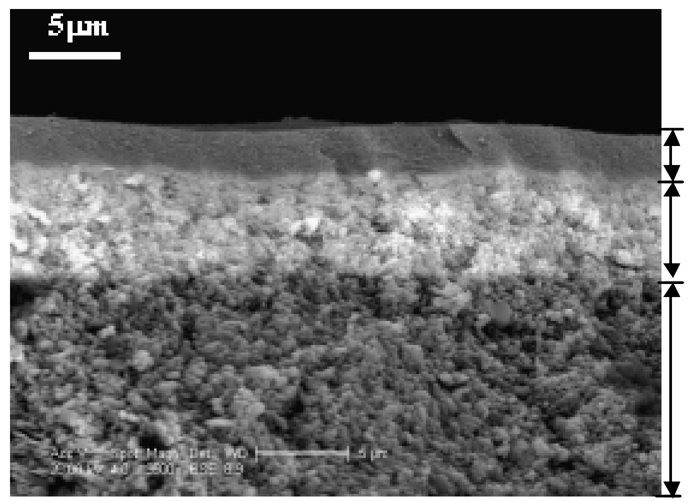
Defect-free continuous zeolite film could be formed on ZrO_2 intermediate layer .

Reproducibility of preparation of silicalite membranes was confirmed.

Membrane thickness could be controlled by dip coating times with stable suspension.



(a)

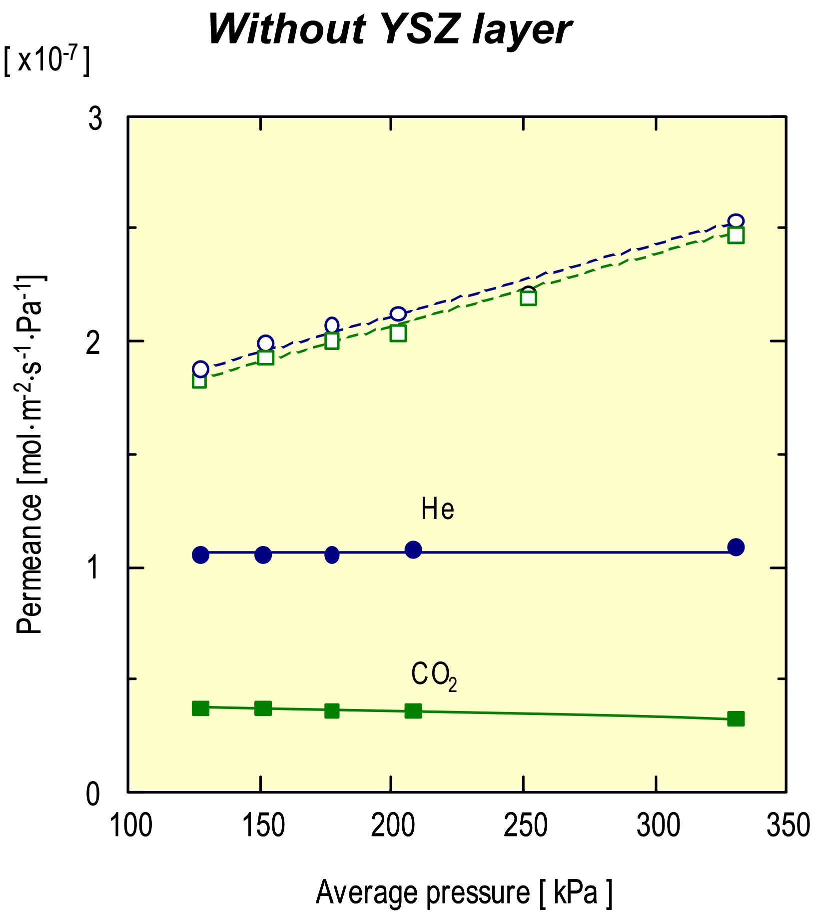


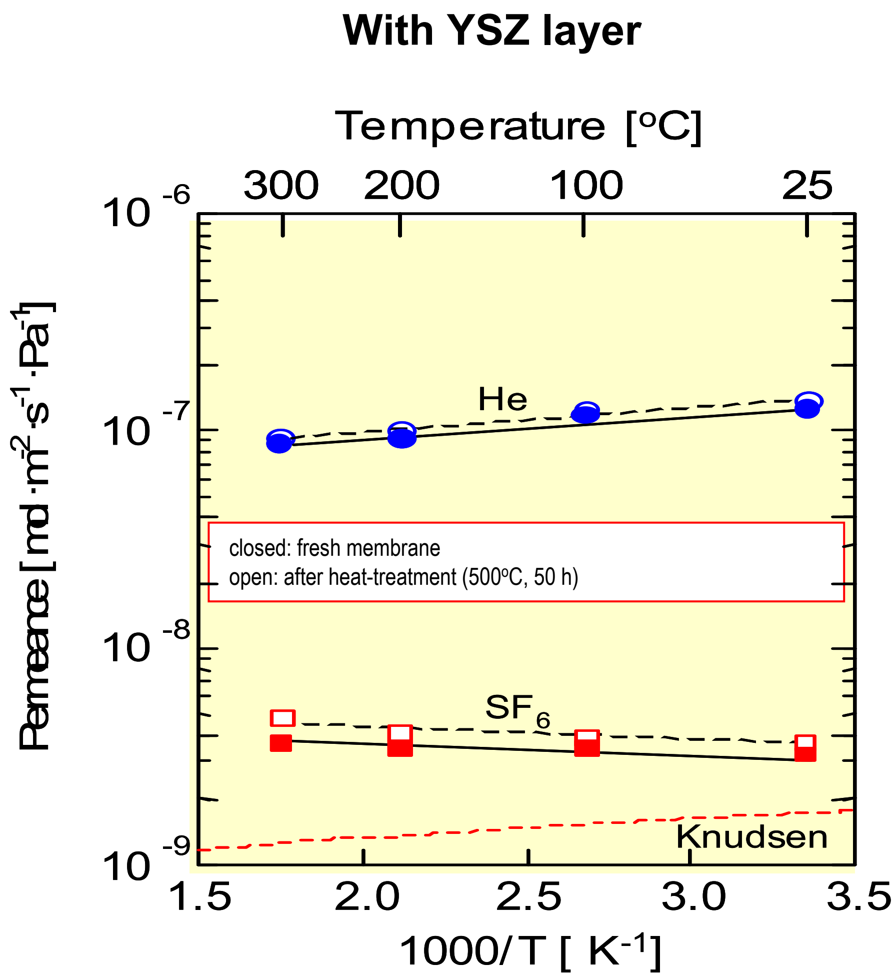
(b)

SEM image of the cross section of silicalite membranes after secondary growth (180^{o}C, 4h); (a) once dip-coating (YSZ), (b) twice dip-coating (YSZ)

Technical Progress

- **Thermal stability Improvement of Silicalite Membranes**

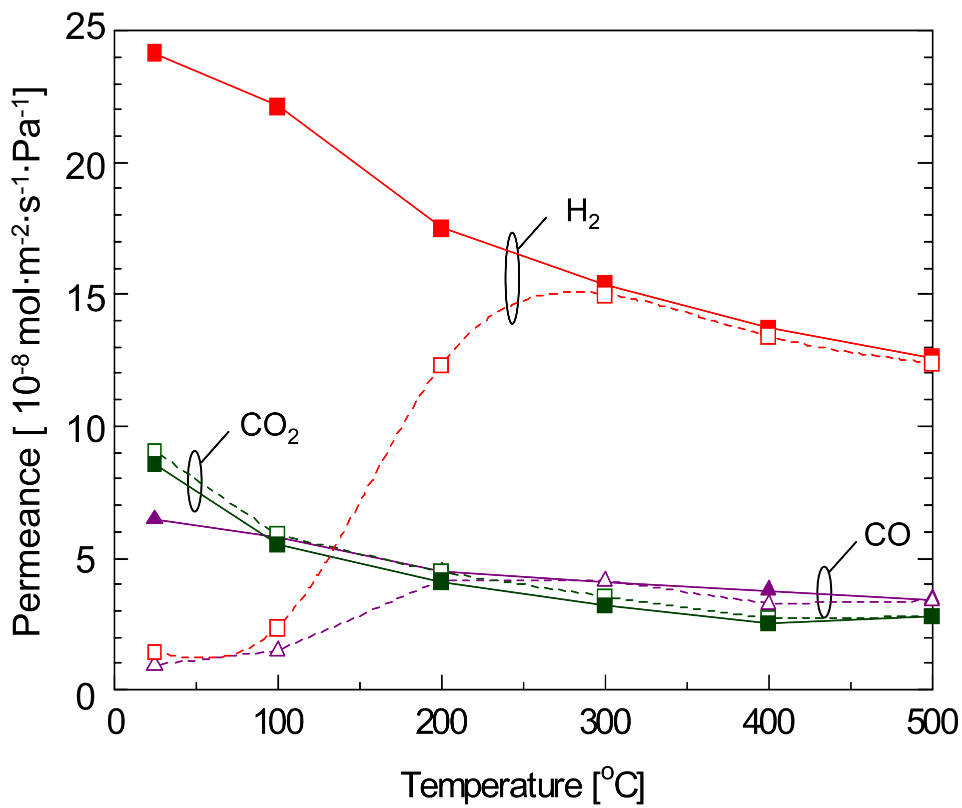




(closed symbols on solid line: permeances for fresh membrane, open symbols on broken line: those for after heat treatment in air at 500°C for 100 hrs)

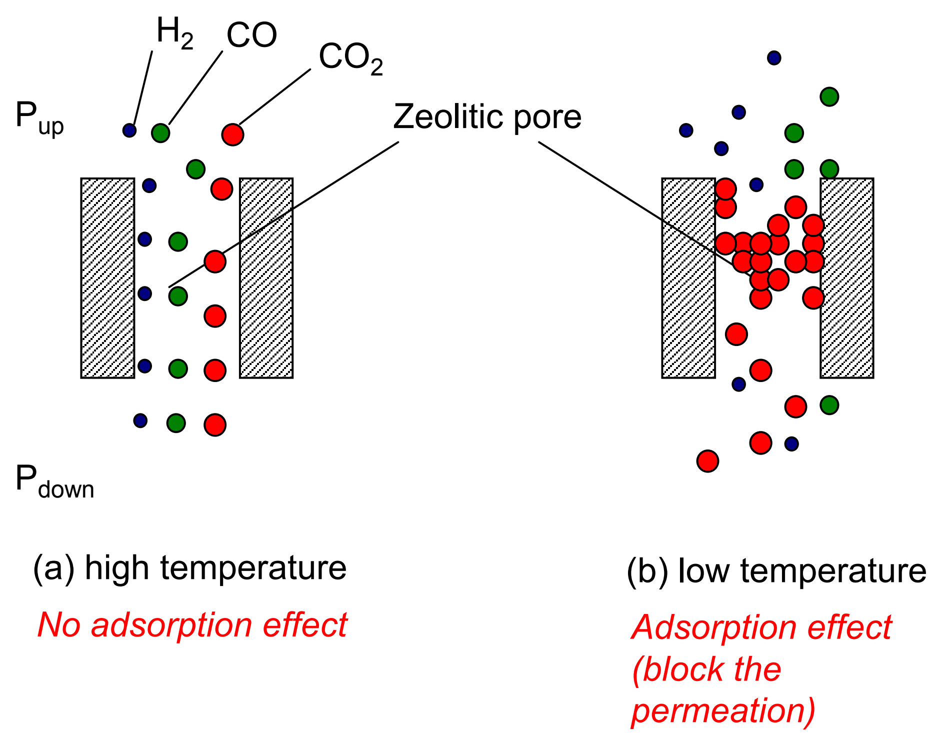
Technical Progress

- **Multi-component gas separation test on Silicalite Membrane**



At low temperature, this membrane shows CO_2 permeable characteristic.

H_2 permeance increases drastically with increasing the temperature, showing the H_2 permeable membrane at high temperatures.



Schematic image of CO_2 adsorption on zeolitic pores

Experimental condition

Feed gas composition (H_2:CO:CO_2=1:1:1)
P_{up}: 0.3 MPa
P_{down}: 0.1 MPa

Technical Progress

- **Diffusion-Controlled Permeation through Microporous Zeolite Membrane**

diffusion length (~ d_p for Knudsen)

activation energy for diffusion

$$F = [\frac{\phi}{L}\frac{\alpha}{z}][\frac{8}{\pi R M_W T}]^{1/2} \exp(\frac{-E_d}{RT})$$

Diffusion coordination Number (4 for MFI-type zeolite)

Molecular weight

$$E_d = f[\lambda, \gamma] = f(d_m, d_p)$$

$$\lambda = \frac{d_m}{d_p}$$

Molecule diameter

Pore diameter

$$\gamma = \frac{\sigma_m}{d_m}$$

L-J Length (spherical diameter)

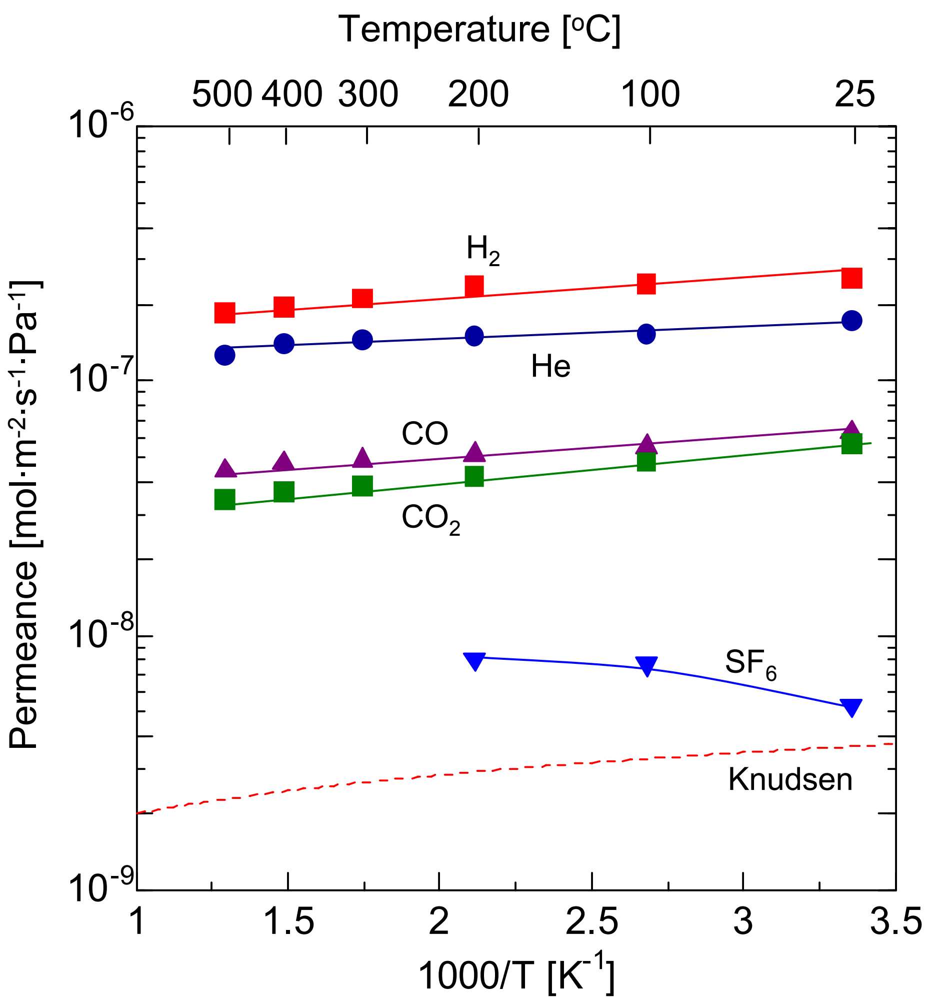
Kinetic diameter (circular diameter)

* K. Kanezashi et al., AIChE J. (2008)

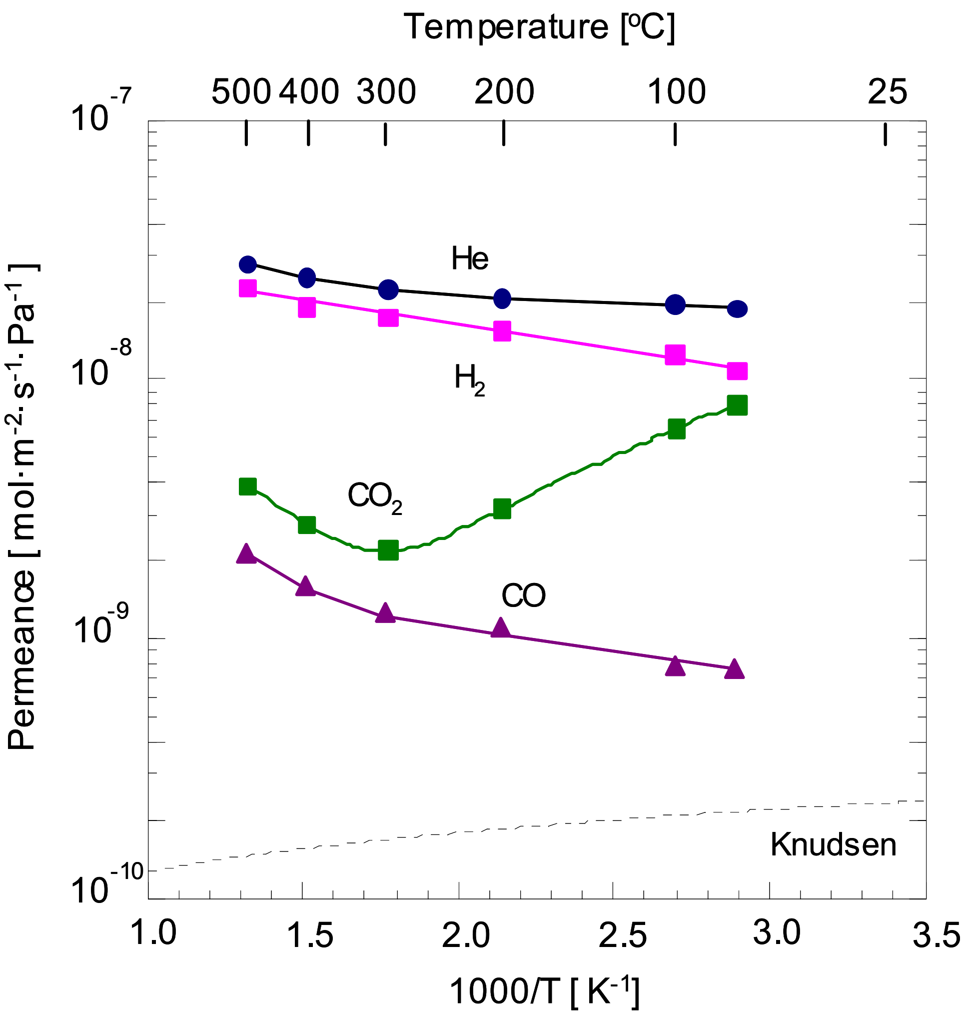
Technical Progress

- **Single Gas Permeation Silicalite and DDR Zeolite Membranes**

SIlicalite



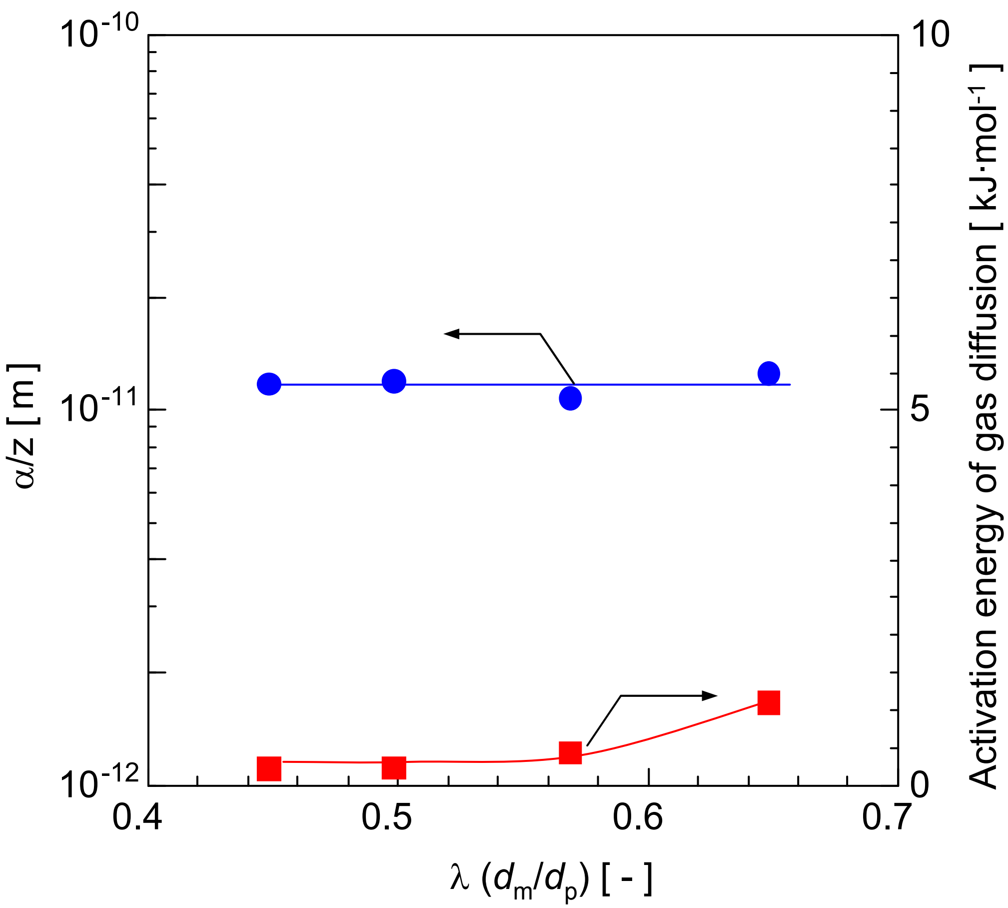
DDR



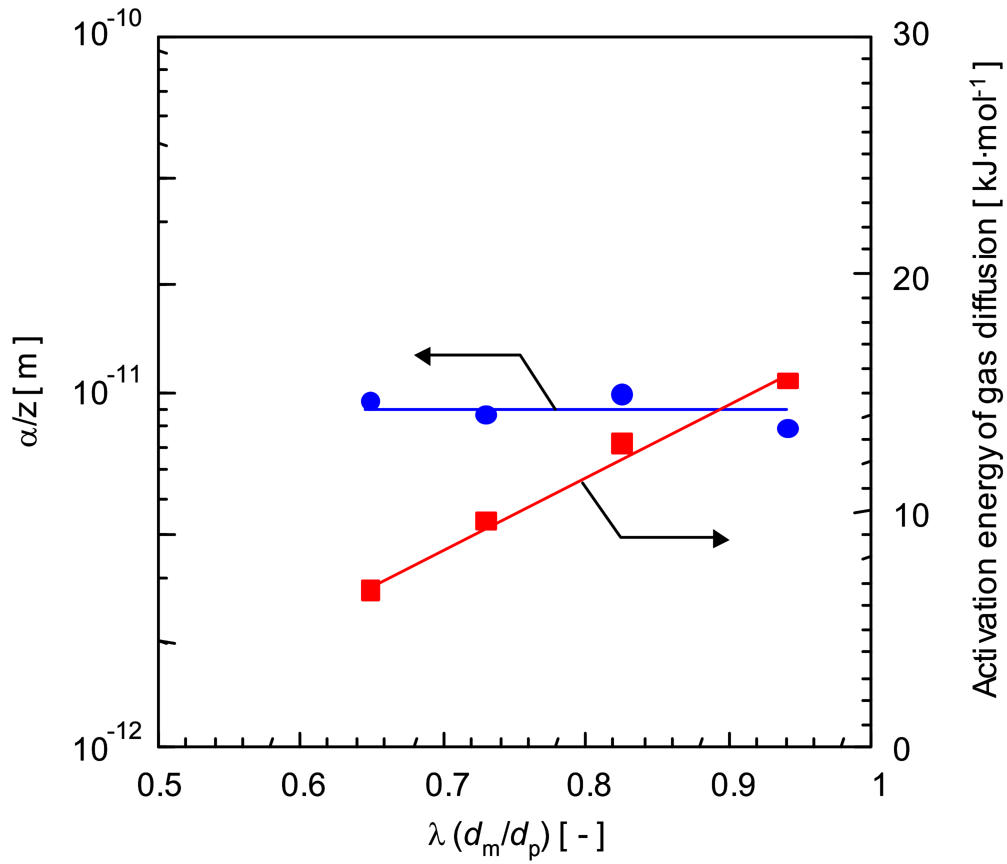
Technical Progress

- **Activation Energy for Diffusion for Silicalite and DDR Zeolites**

SIlicalite



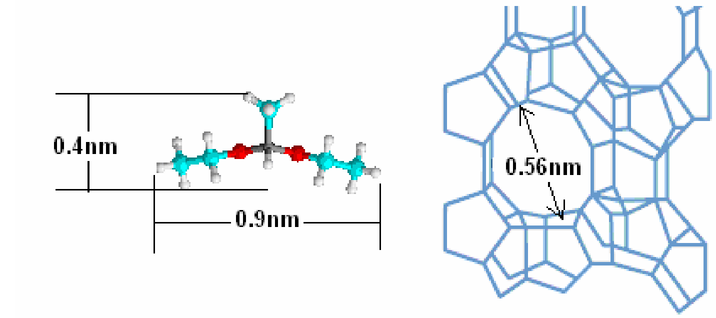
DDR



Technical Progress

- **CVD Modification to Improve Selectivity**

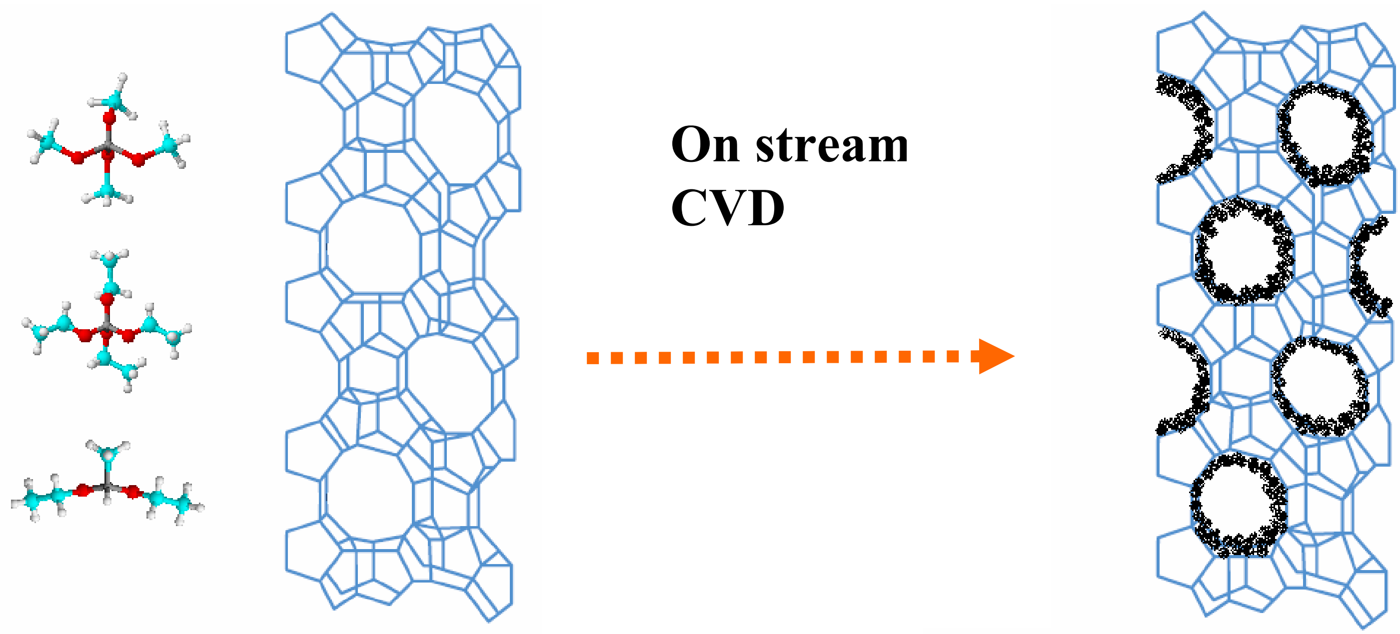
methyldiethoxysilane
(MDES)



TMOS
0.89nm

TEOS
0.95nm

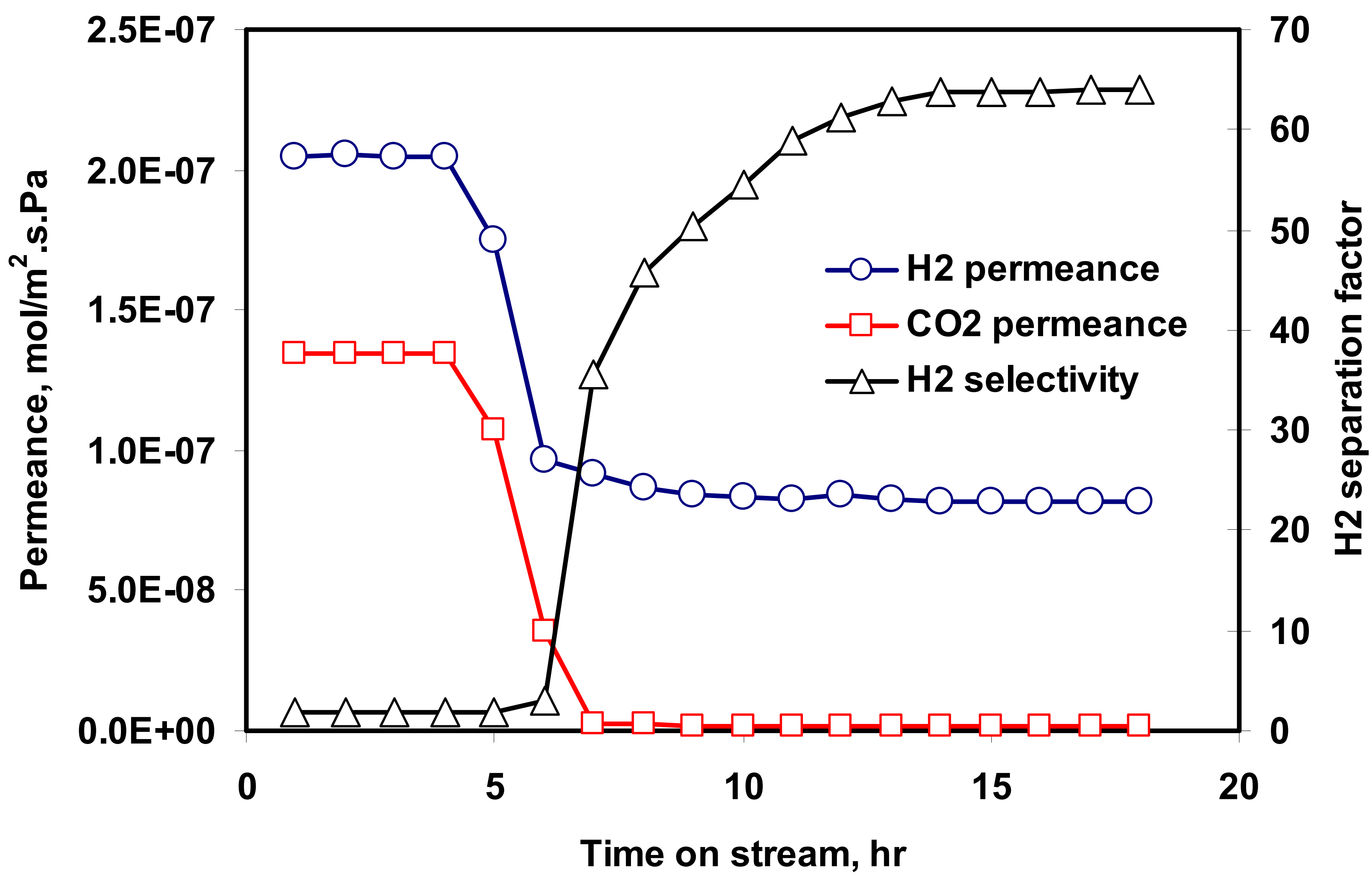
MDES
0.4 × 0.9nm



Technical Progress

- **CVD Modification on Tubular MFI Type Zeolite Membrane**

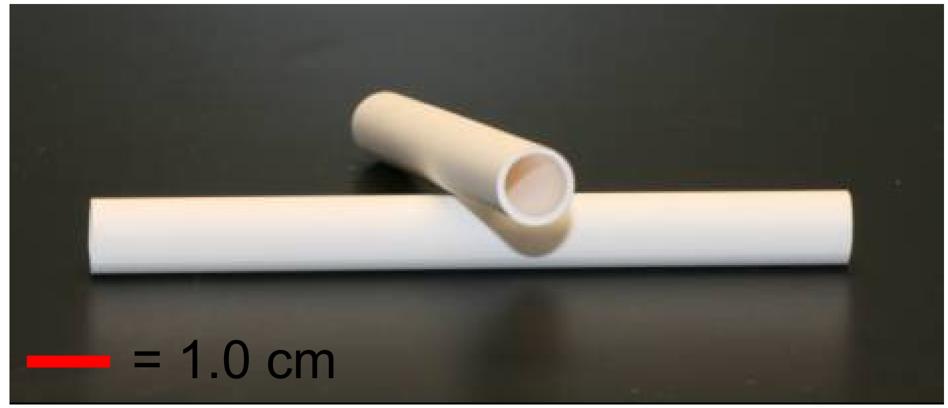
On Stream CVD Modification with MDES in H_2/CO_2 stream at 450°C.

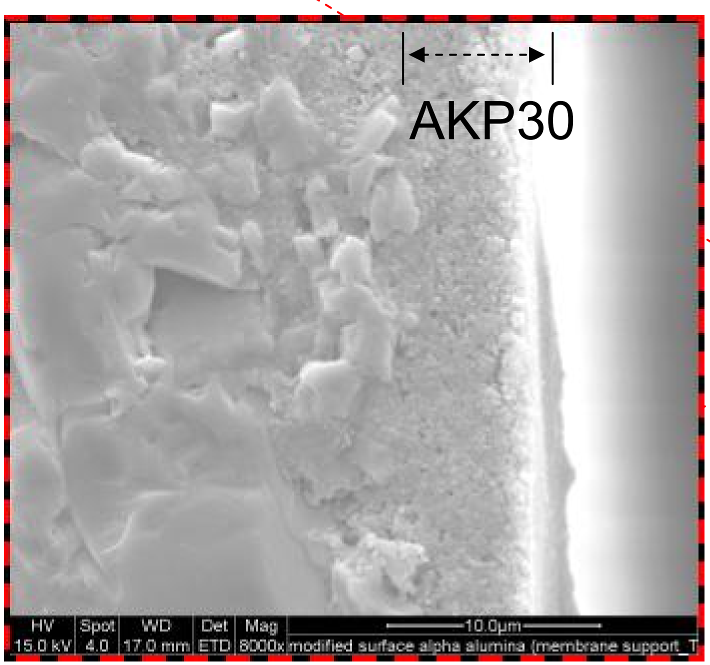


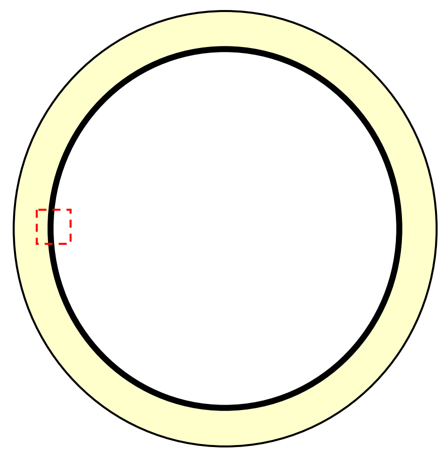
Technical Progress

- **Synthesis of Improved Tubular Supports**

- Gel-cast tubes (α-Al_2O_3)
- Commercially available (industrial partner)
- AKP30 support on inner surface



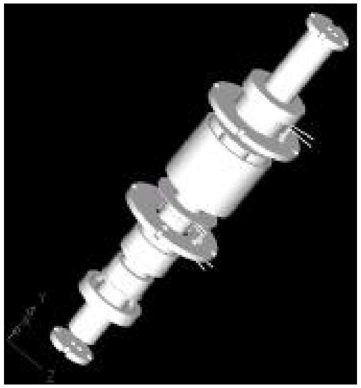


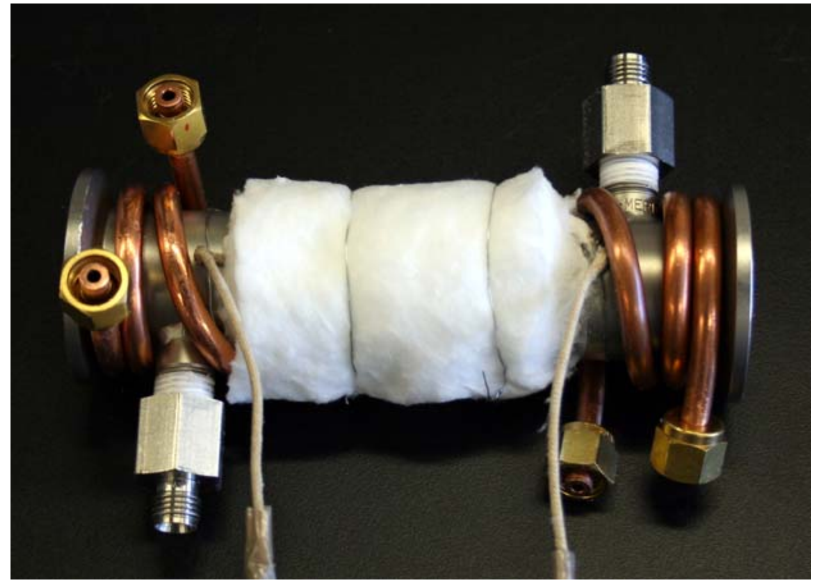


Characterized for:
- Permeability
- Porosity
- Pore size
- Surface quality

Technical Accomplishments

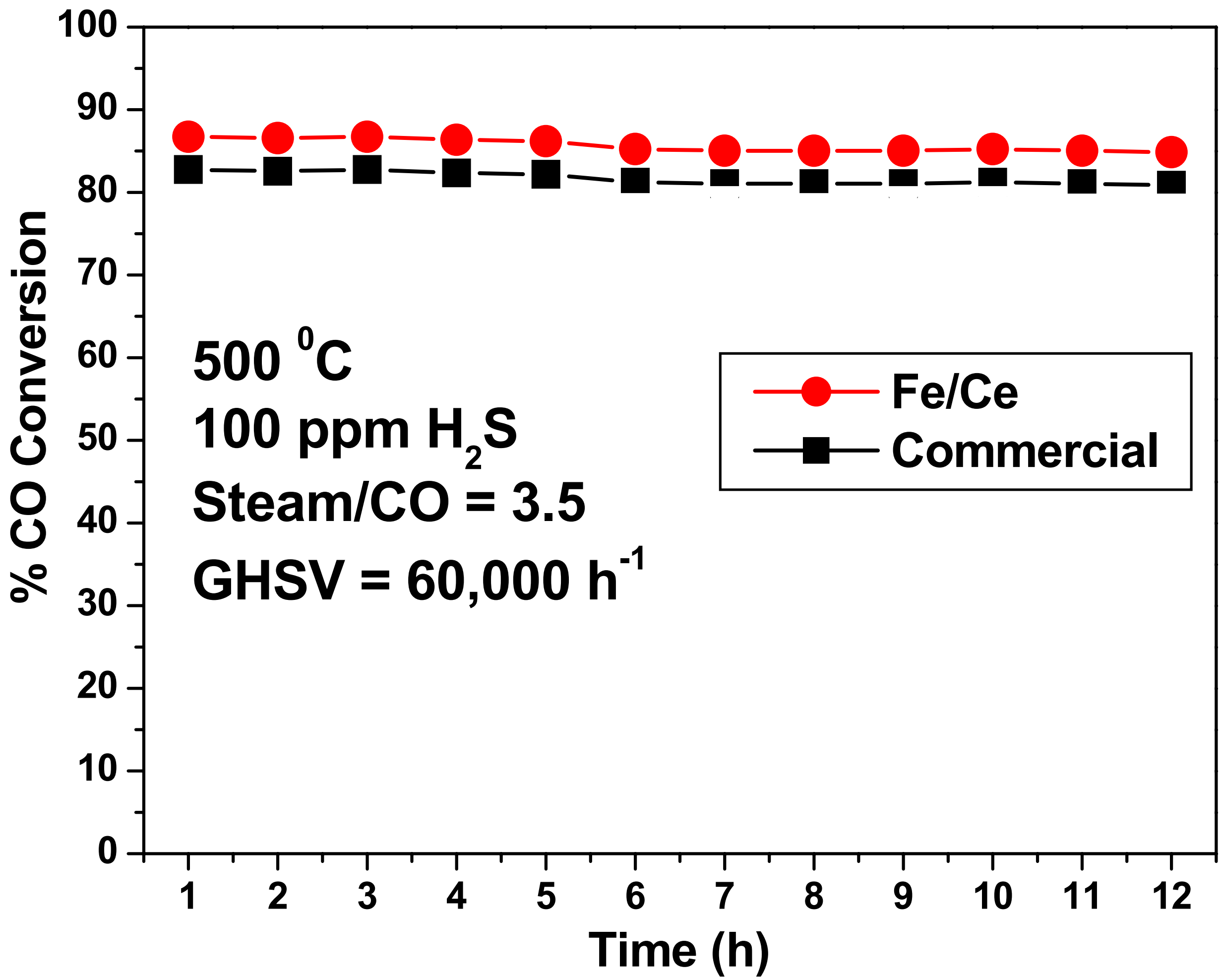
- **Membrane Reactor Module Developments**





Technical Progress

- **Sulfur Tolerant HT-WGS Catalysts**



Sulfur Tolerant WGS Activity:

$Fe_{3-(x+y)}Cr_xCu_yO_4$ > Commercial > $Fe_{3-x}Ce_xO_4$ > $Fe_{3-x}Cr_xO_4$

Future Work for FY08 and FY09

- Task A- Synthesis and modification of silicalite membranes (90% complete)
- **Task B- Separation and stability study (Phase II)**
- Task C Fabrication of tubular support and membrane module (80% complete)
- **Task D- Hydrothermal synthesis and CVD modification of tubular silicalite membranes (Phase II)**
- Task E- Microwave synthesis of silicalite membranes (70%)
- Task F- Water-gas-shift reaction catalyst and reaction kinetics (50%)
- **Task G- Membrane reactor modeling and experiments (Phase II)**

Summary

- **Relevance:**

  Help to develop processes for cost-effective production of hydrogen from natural gas and renewable liquids

- **Approach**:

  Study fundamental issues related to synthesis of high quality, stable zeolite membranes and performance of the membrane reactor for water-gas-shift reaction and hydrogen separation

- **Technical Accomplishment and Progress**:

  Developed and studied methods and techniques to prepare disk and tubular supports with adequate intermediate layer, zeolite membranes with high H2 permenace and selectivity suitable for WGS membrane reactor application, and catalysts with improved properties for WGS reaction

- **Proposed Future Research**:

  Prepare high performance zeolite membranes and WGS catalysts and study WGS reaction in zeolite membrane reactors.