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

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Project PD6

Overview

Timeline

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

Barriers

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

Budget

- Total project funding
  - DOE **$1,999,727**
  - Contractor: **$501,310**
- Funding received in FY06: **$300,000**
- Funding for FY07: **$702,165**

  Funding for FY07 delayed

Partners

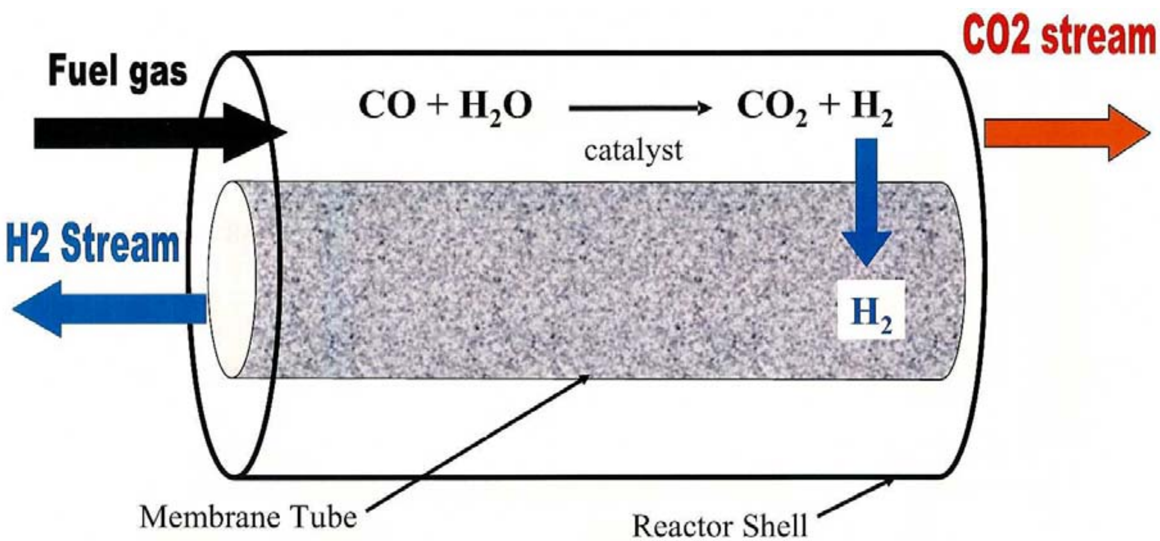
- University of Cincinnati
- Arizona State University
- Ohio State University

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*

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

Membrane Requirements:

- Operated in 350-450ºC
- Chemically stable in H_2S, thermally stable at ~400ºC
- Hydrogen permeance > 5×10^{-7} mol/m^2.s.Pa
- Hydrogen selectivity > 50

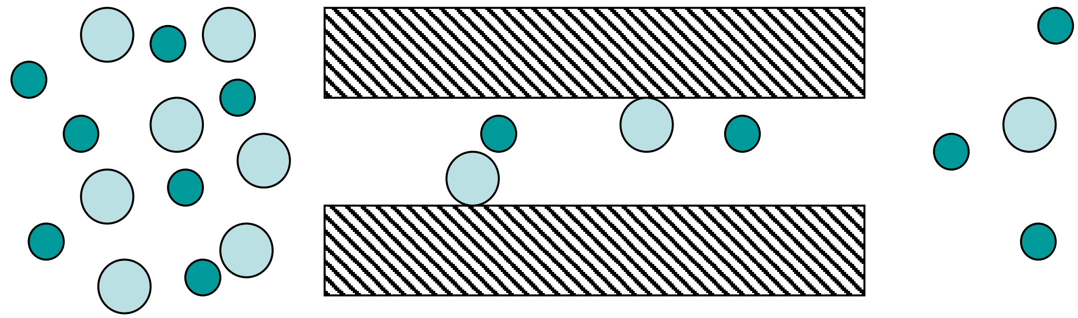
Comparison of Major Properties of Inorganic Membranes for WGS Membrane Reactor Application (350-550°C)

Membrane	Sol-gel silica	Pd-alloy	H^+-conducting ceramic	Silicalite membrane
Hydrogen permeability	High	High	Low	***High***
H_2/CO_2 selectivity	Intermediate	High	High	***Intermediate***
Chemical thermal stability	Poor	Poor	Good	***Excellent***

Transport Mechanism for Good Quality Silicalite Membrane

High temperature

⇔diffusion



$$\mathbf{J = [Diffusivity]_{average}[Solubility]}$$

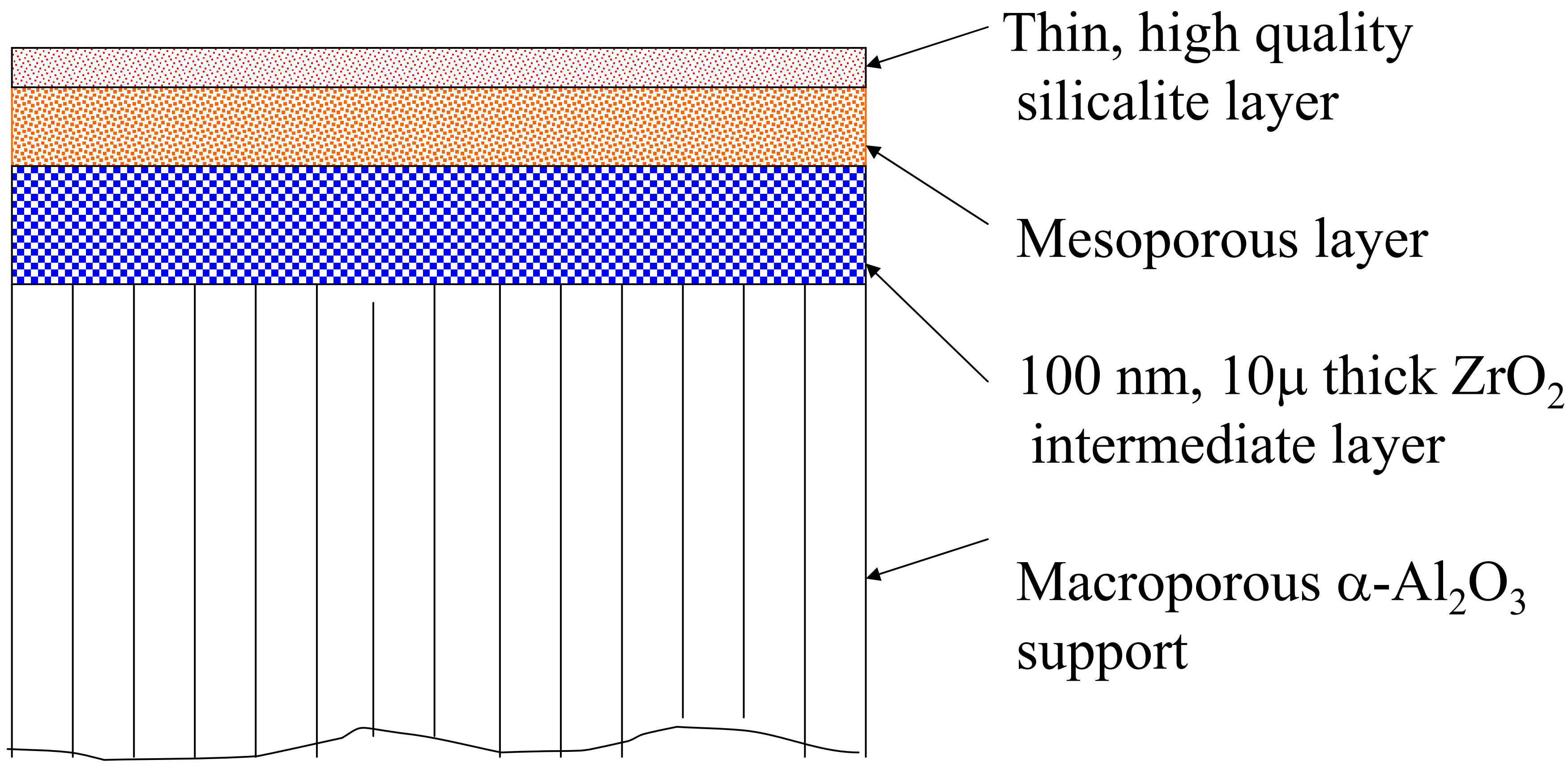
1

Diffusivity in intercrystalline pores – non-selective for hydrogen

Zeolitic pore diffusivity – selective for hydrogen ($H_2/CO_2 > 100$)

$$\mathbf{J = [Diffusivity]_{zeolitic}[1]}$$

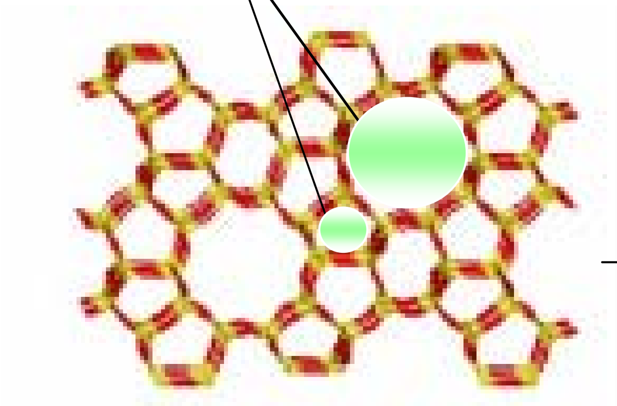
New Structure of Silicalite Composite Membrane with Improved Chemical/Thermal Stability and Permselectivity



Schematic Illustration of Template Removal from Zeolite Channel by Calcination

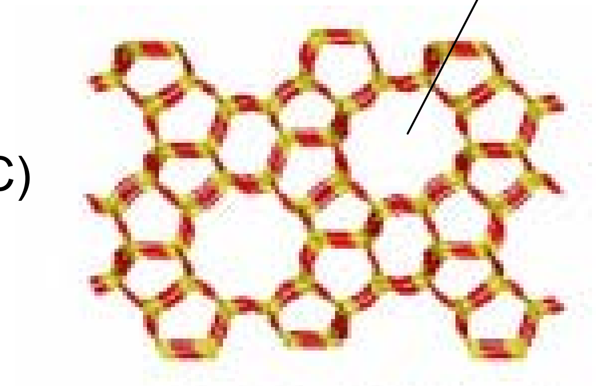
Template: (TPA)OH

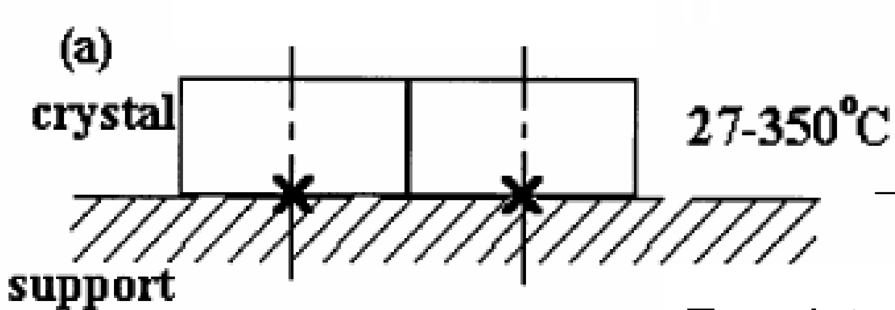
Volume shrinks after calcination



Template removed

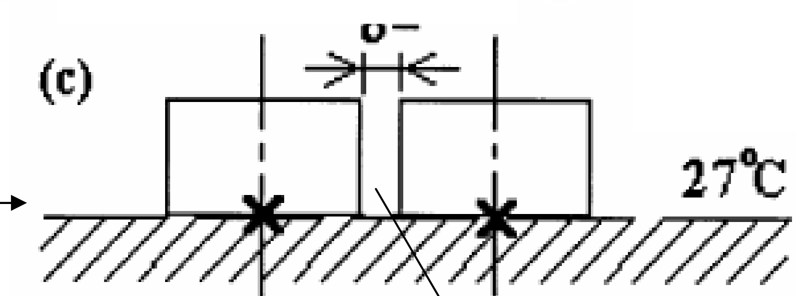
by calcination (500°C)





27-350°C

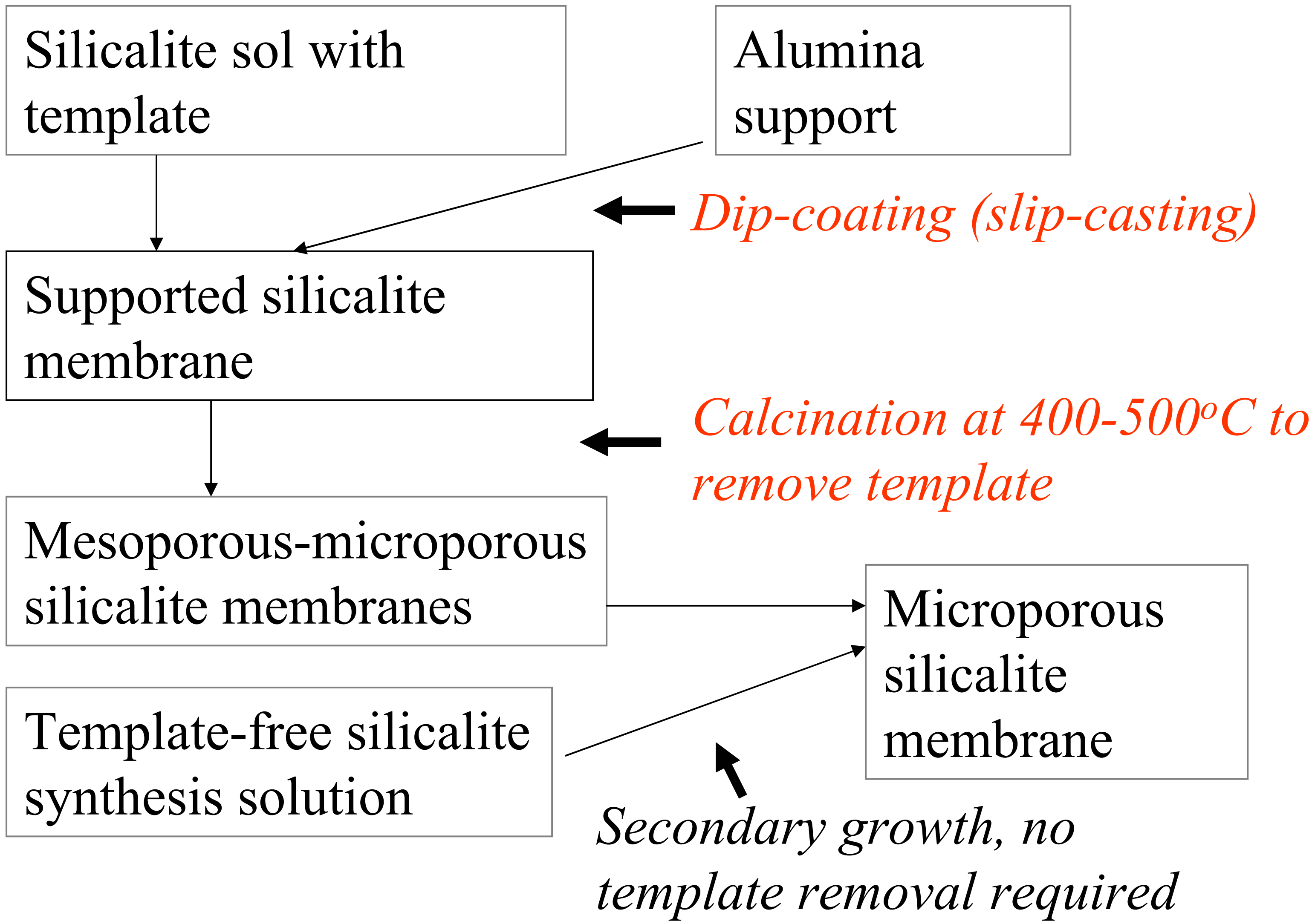
Template removed (~500°C) and cooling down



Intercrystalline gap

Intercrystalline gaps tend to form in the membranes due to the difference in thermal expansion between zeolite layer and support and/or by changes in lattice parameters of zeolite crystals.

Template-free Synthesis of Silicalite Membranes

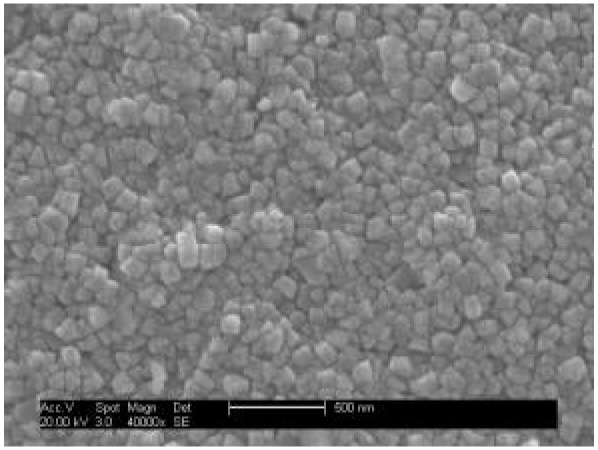


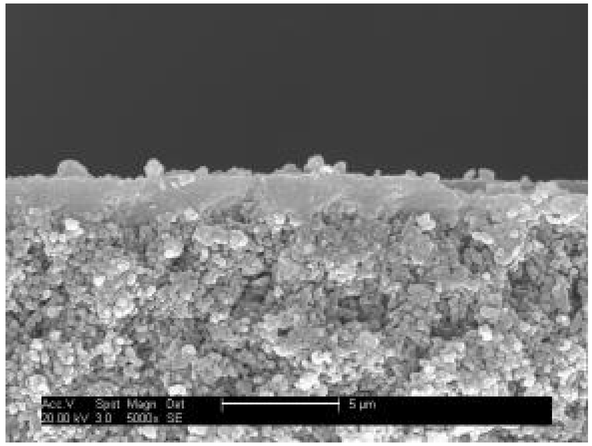
Plan and Approach

- **Task A- Synthesis and modification of silicalite membranes (70% complete)**
- **Task B-** Separation and stability study (Phase II)
- **Task C Fabrication of tubular support and membrane module (60% complete)**
- **Task D-** Hydrothermal synthesis and CVD modification of tubular silicalite membranes and gas (Phase II)
- **Task E- Microwave synthesis of silicalite membranes (50%)**
- **Task F- Water-gas-shift reaction catalyst and reaction kinetics (40%)**
- **Task G-** Membrane reactor modeling and experiments (Phase II)

Technical Accomplishments

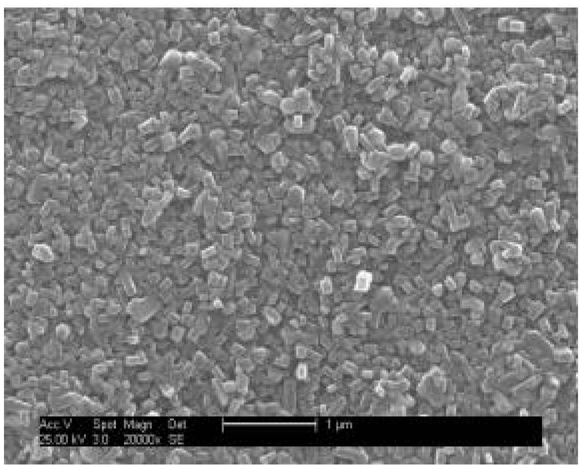
- **Template-free secondary growth synthesis by conventional (upper) and microwave (bottom) heating methods**

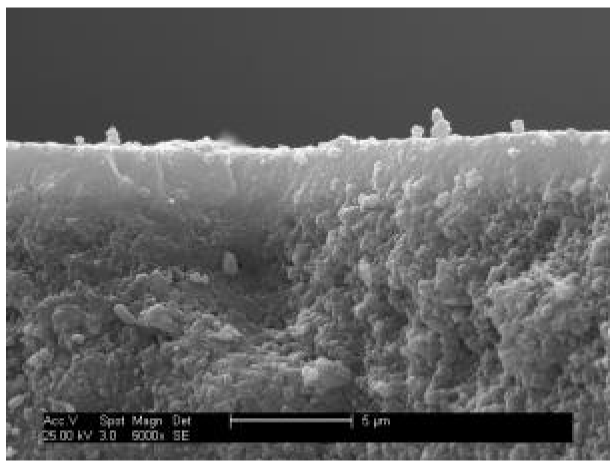




MFI membrane obtained from precursor without aluminum contents.
(Density was poor)

Time required:
180°C for **20 hours**



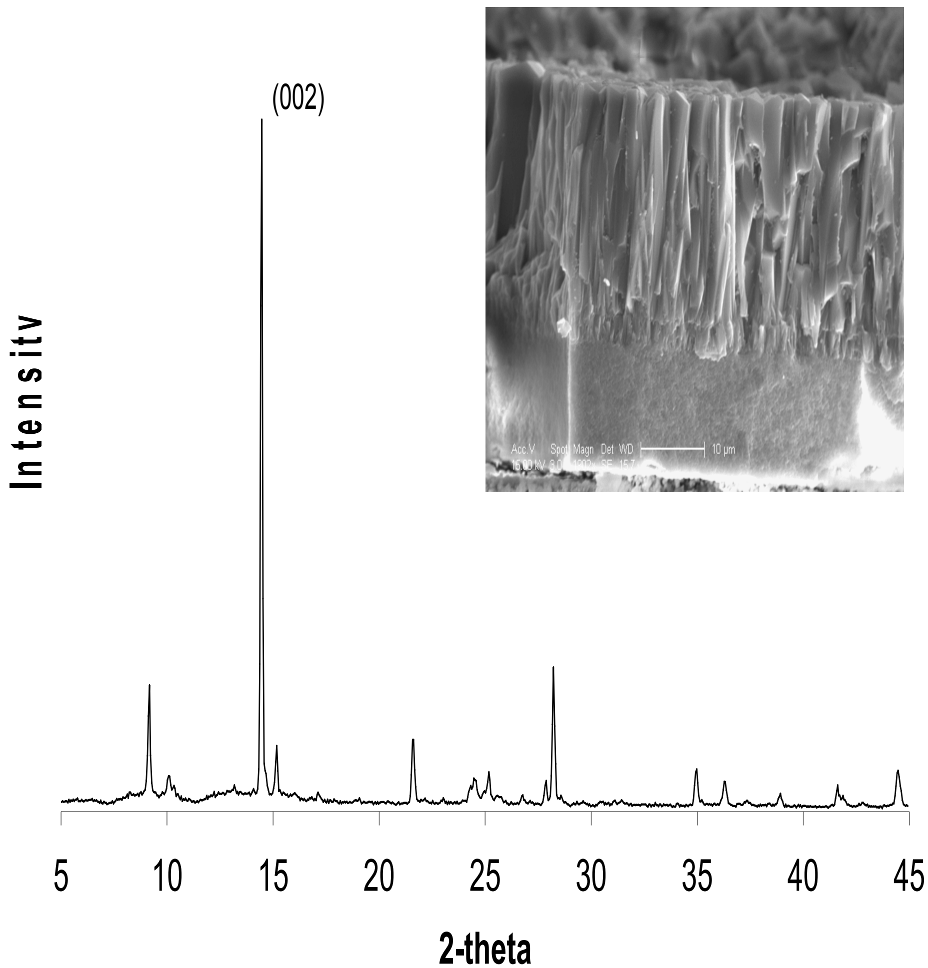


Dense MFI membrane obtained from precursor without aluminum contents.

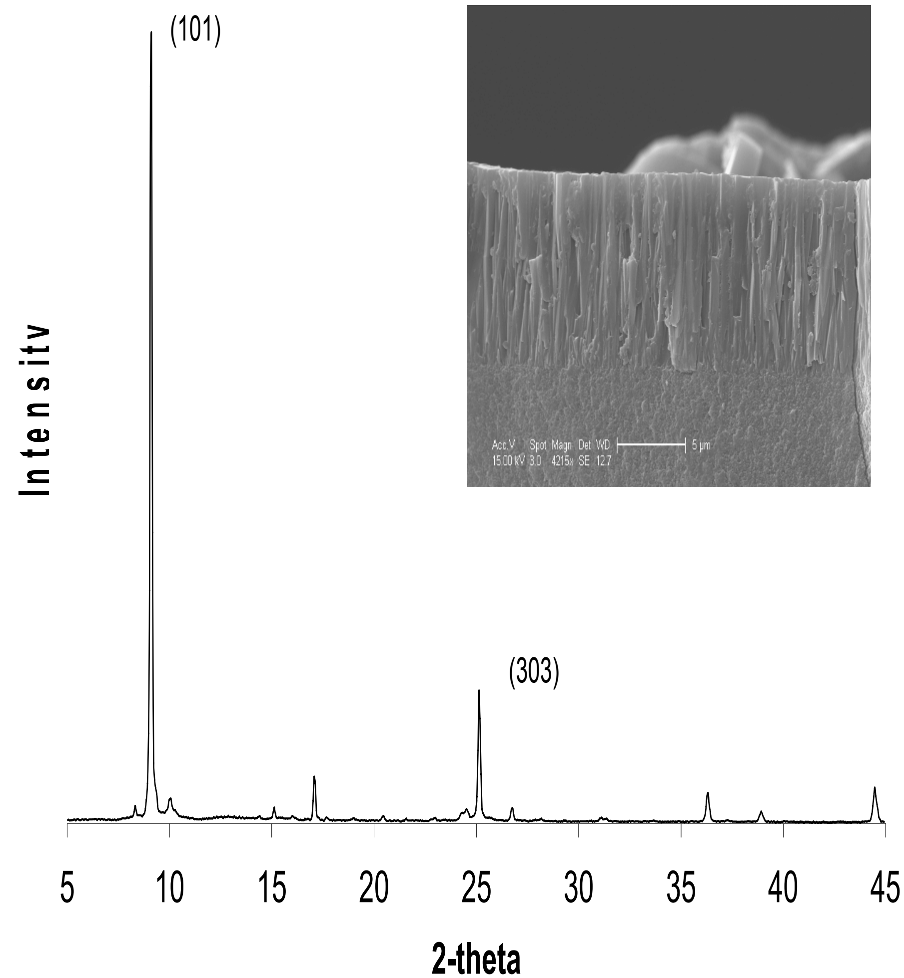
Time required:
180°C for **4 hours**

Technical Progress

- <u>Micro-structural Variations</u>



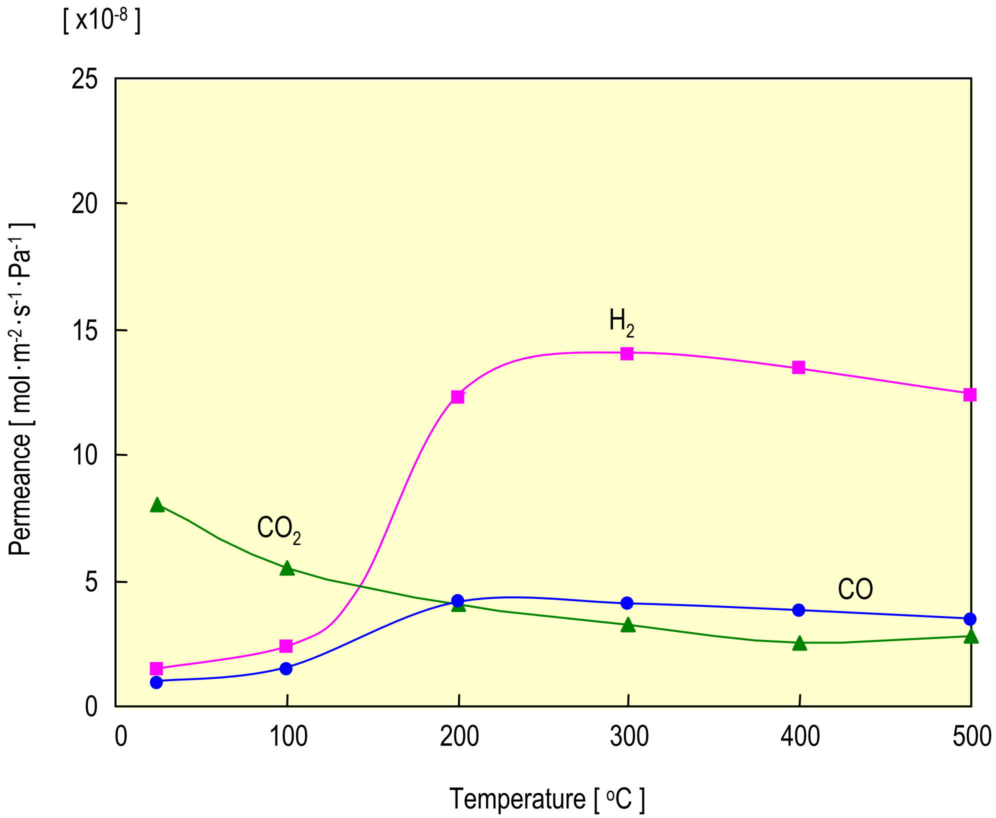
<u>C-oriented structure</u>



<u>hoh structure</u>

Technical Progress

- **Multi-component gas separation test**



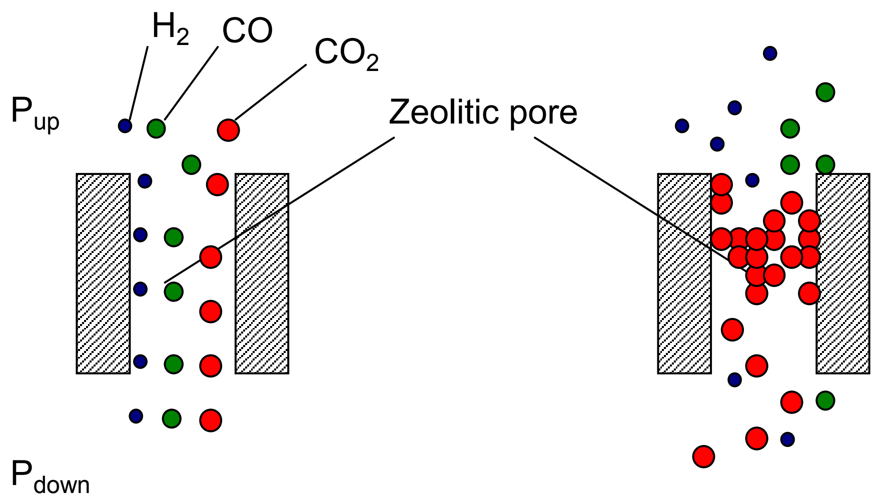
Temperature dependency of gas permeances for MFI-type zeolite membrane

Experimental condition

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

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.



(a) high temperature
No adsorption effect

(b) low temperature
Adsorption effect (block the permeation)

Schematic image of CO_2 adsorption on zeolitic pores

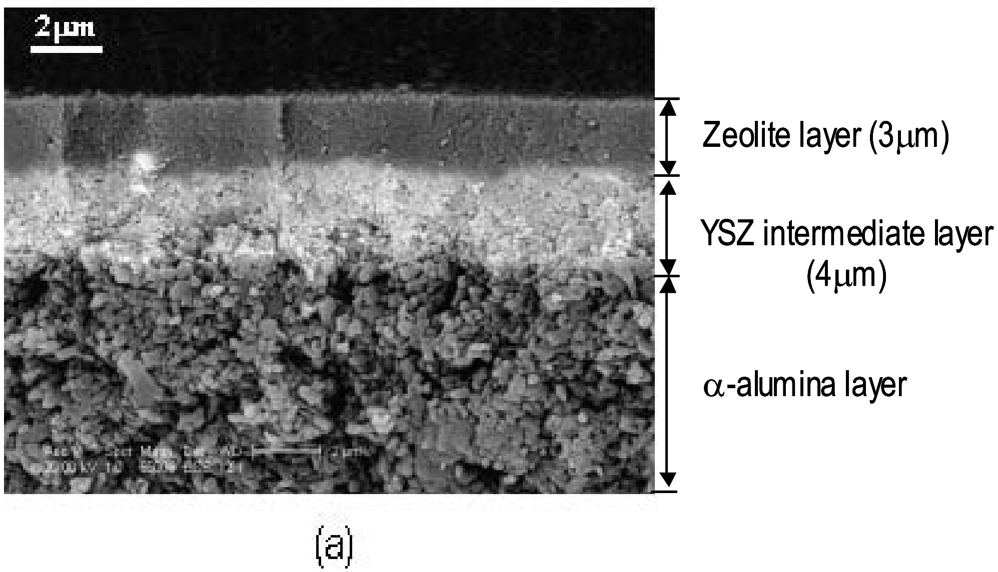
Technical Progress

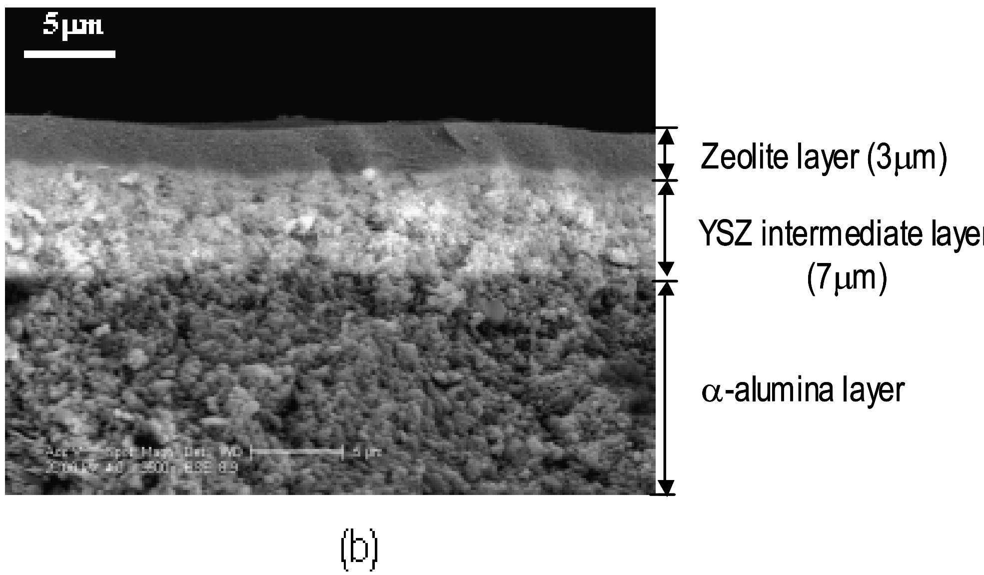
- **Preparation of silicalite membranes by template-free synthesis**

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.

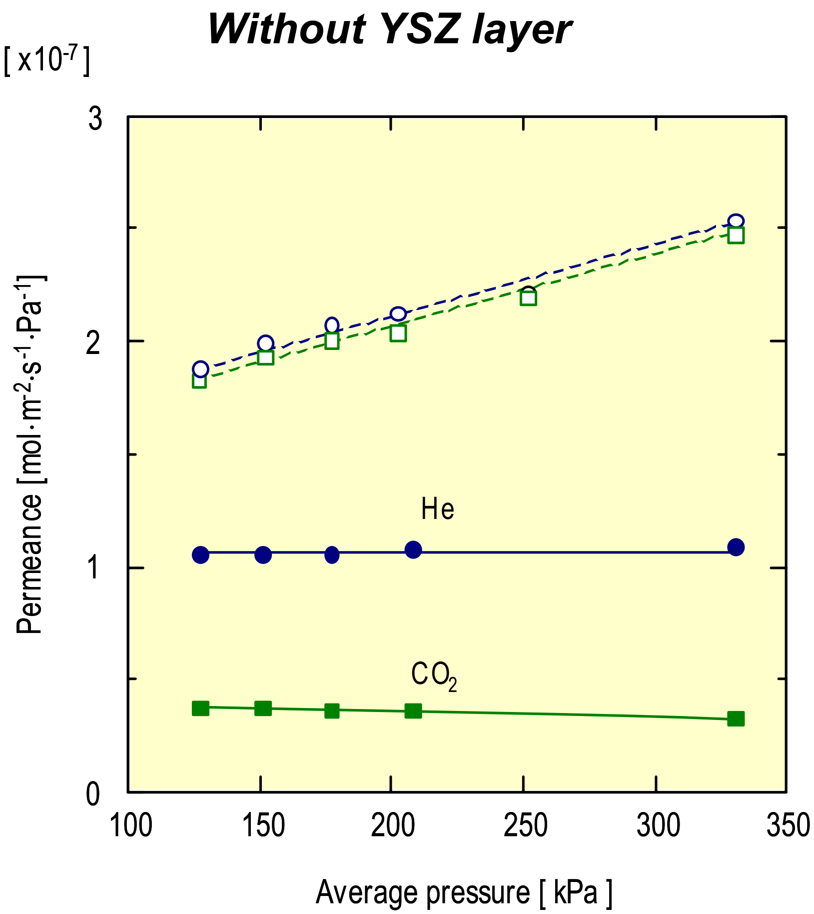


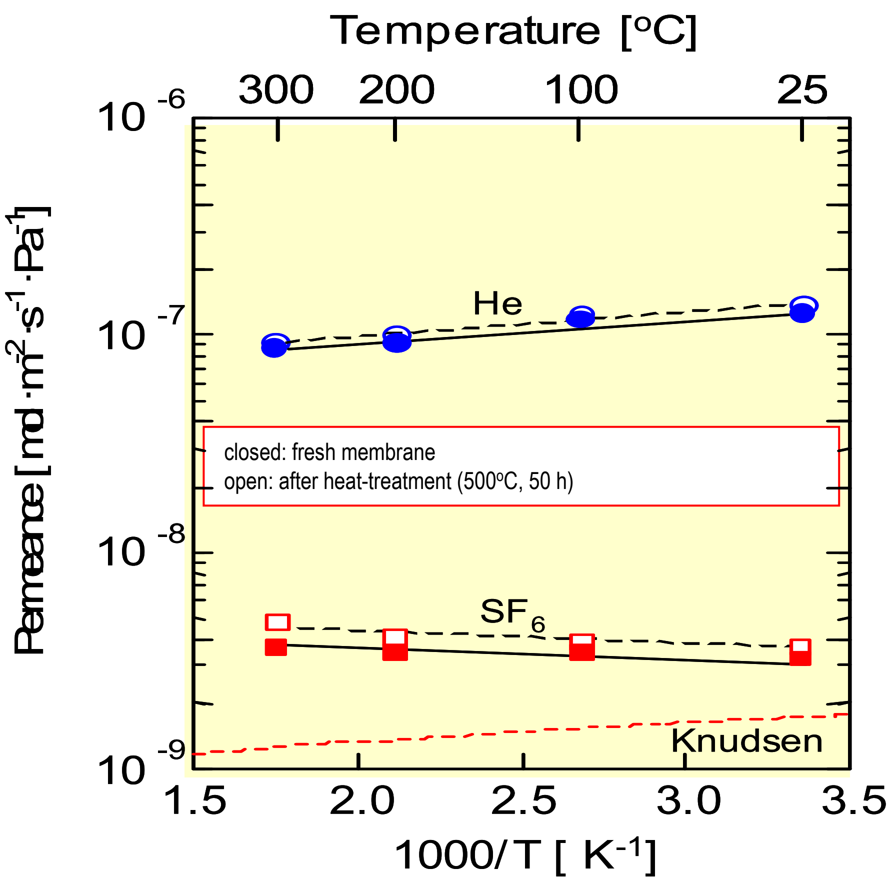


SEM image of the cross section of silicalite membranes after secondary growth (180^{o}C, 4h); (a) 1 time dip coating (YSZ), (b) 2 time dip coating (YSZ)

Technical Progress

- **Thermal stability Improvement**

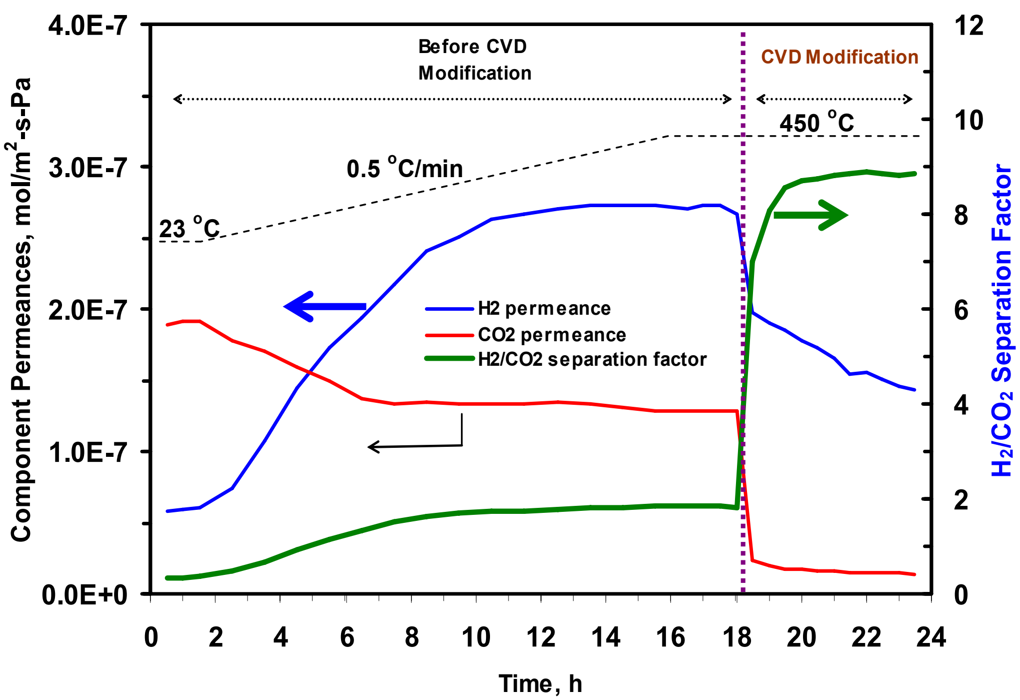




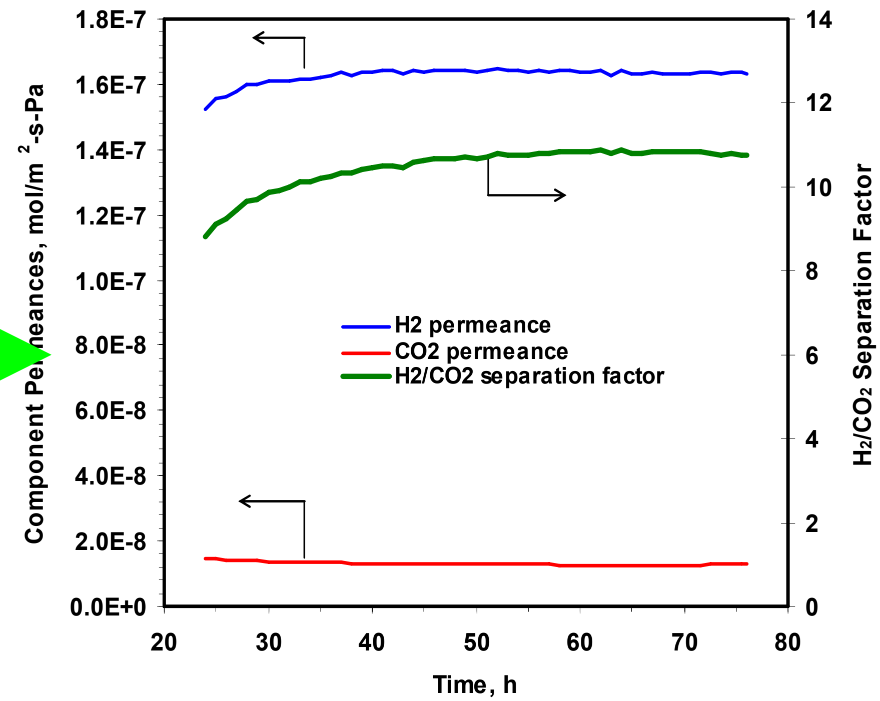
(closed symbols on solid line: permeances for fresh membrane, open symbols on broken line: those for after heat treatment in air at 500°C for 100 hrs)

Technical Progress

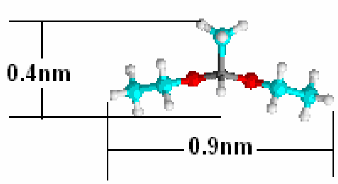
- **Zeolite membrane modification by catalytic thermal cracking of methyldiethoxysilane (MDES) during CO_2/H_2 separation at 450°C**

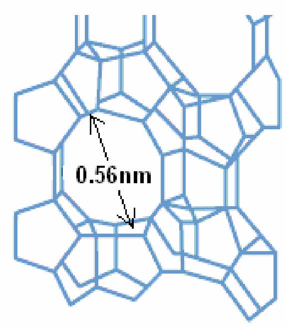


Results of H2/CO2 separation
During on-stream membrane modification



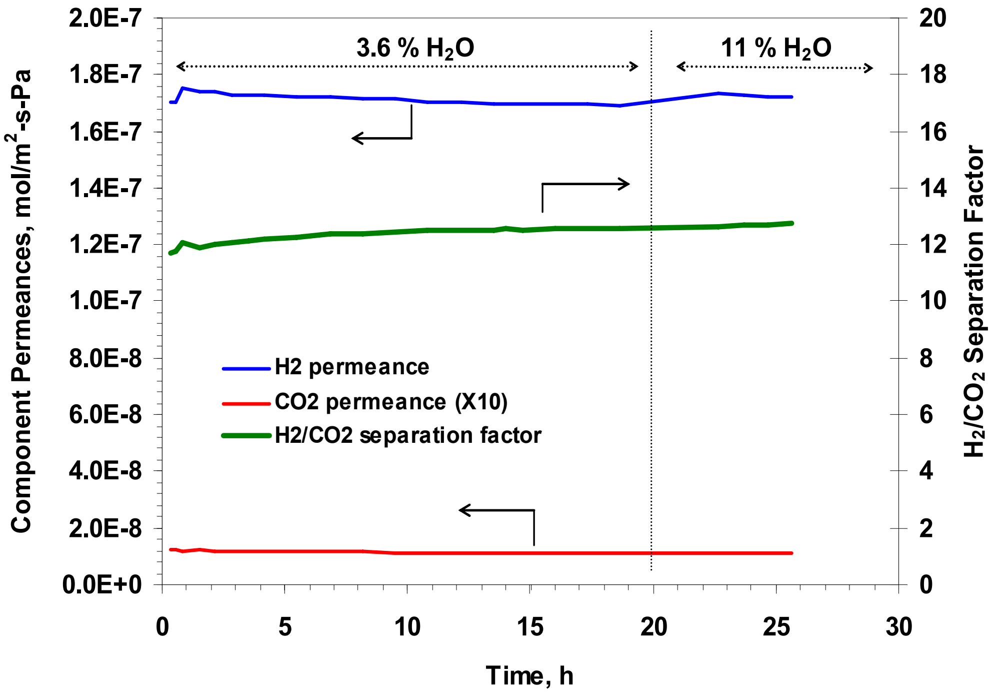
After stop the MDES feed, H2/CO2 permeation continued until stabilized



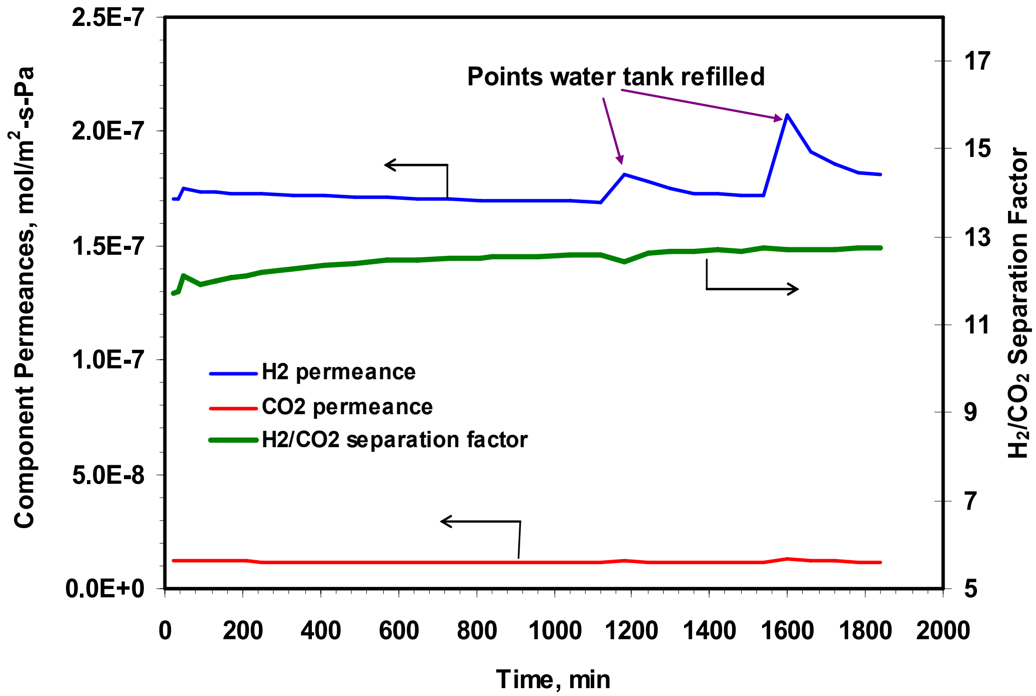


Technical Progress

- <u>H_2/CO_2 separation in presence of water were tested on modified membrane for limited periods at 450°C</u>



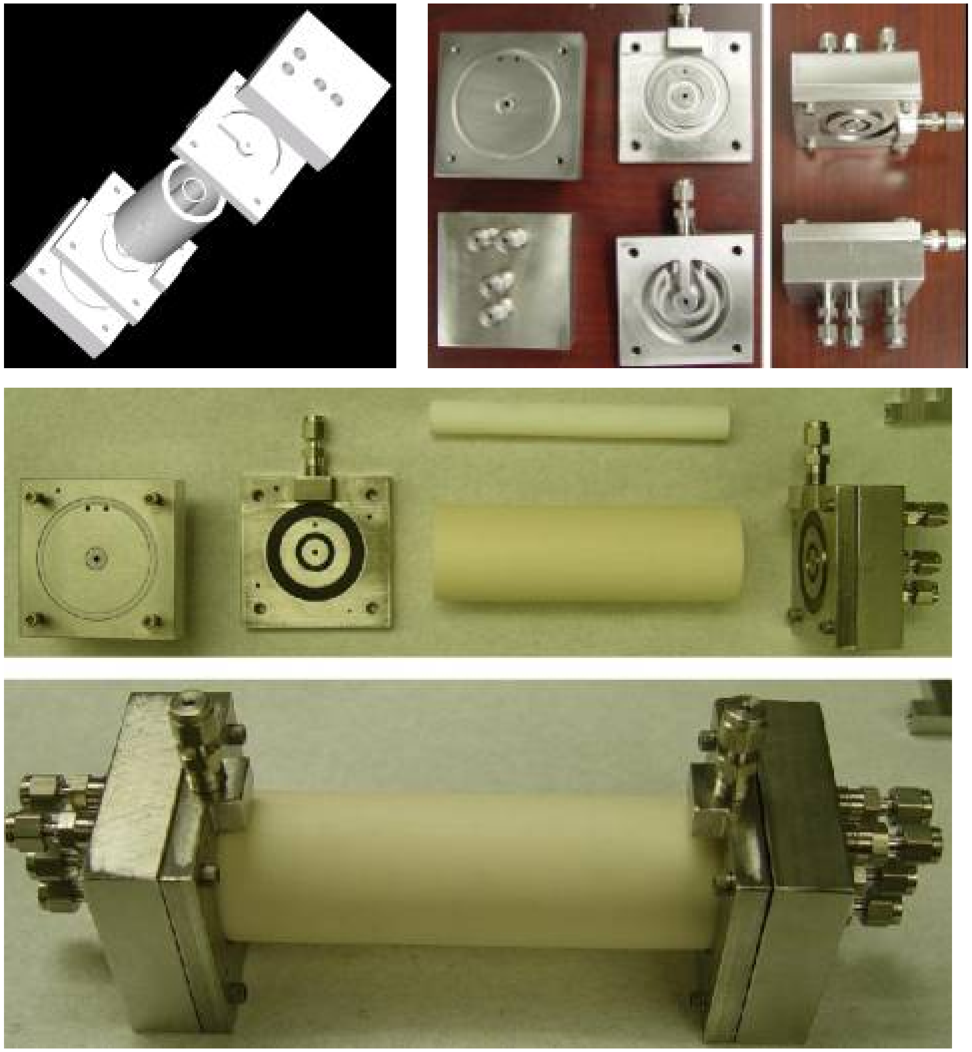
50/50 H_2/CO_2
Stream content: 3.6% and 11%



50/50 H_2/CO_2
Stream content: 30%

Technical Accomplishments

- **Membrane reactor assembly**



- Cooled sealing
- Adaptive housing

Technical Progress

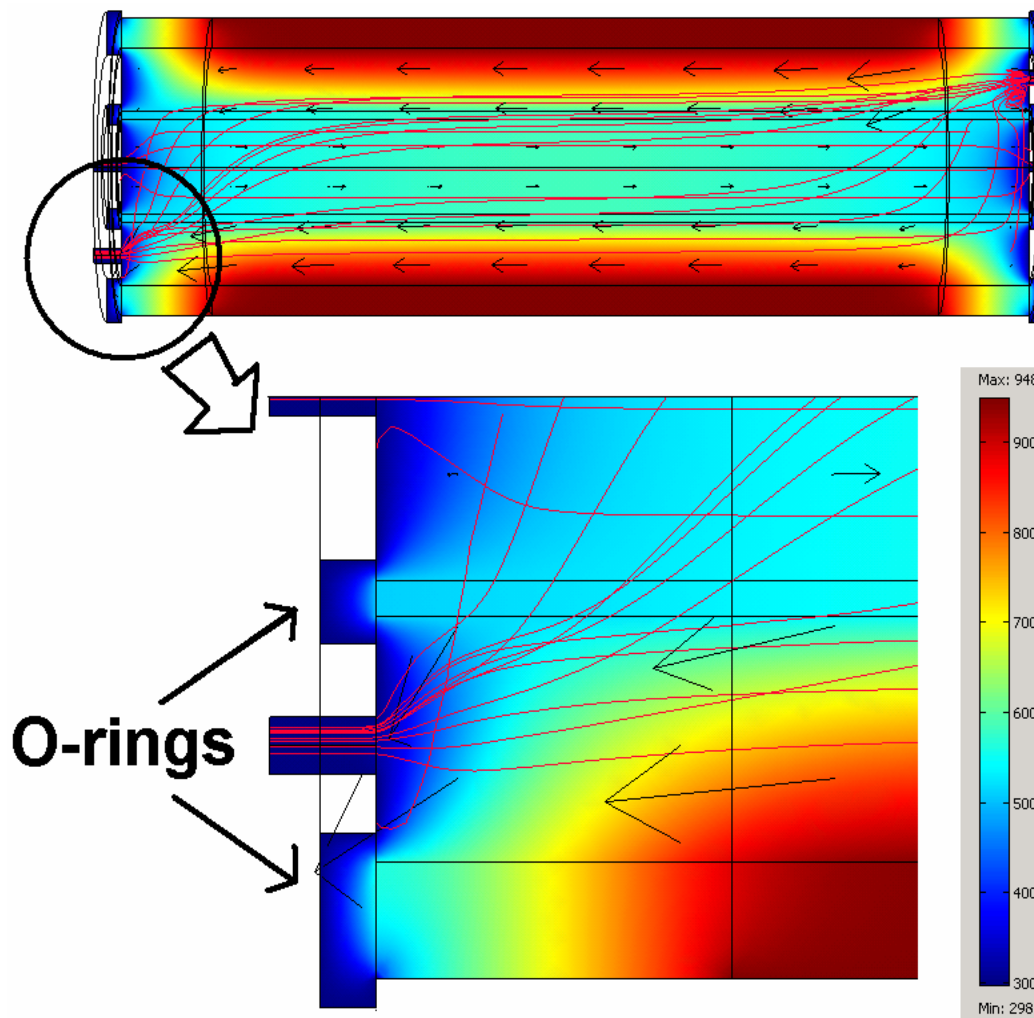
- <u>**Small reactor thermal design**</u>

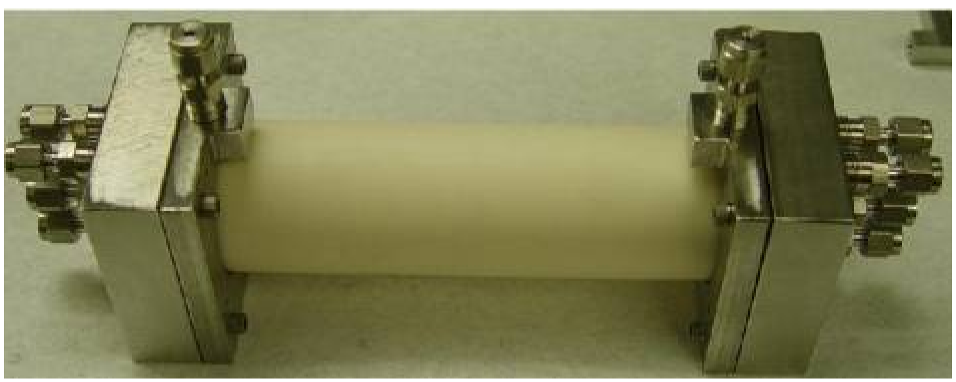
3D finite element heat+flow

- *O-ring seals may survive*
- ***T**-distribution inadequate*
- *Requires internal heater*

Hard, steam-resistant seals:

- *PTFE (**230°C**), FEP (**200°C**)*

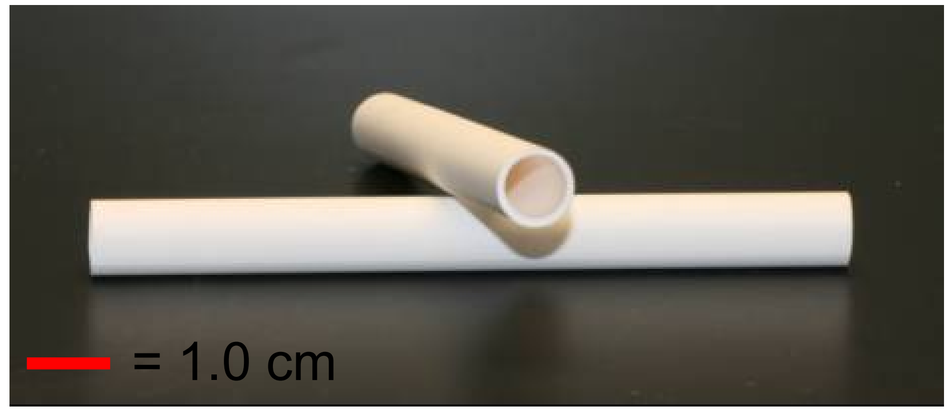


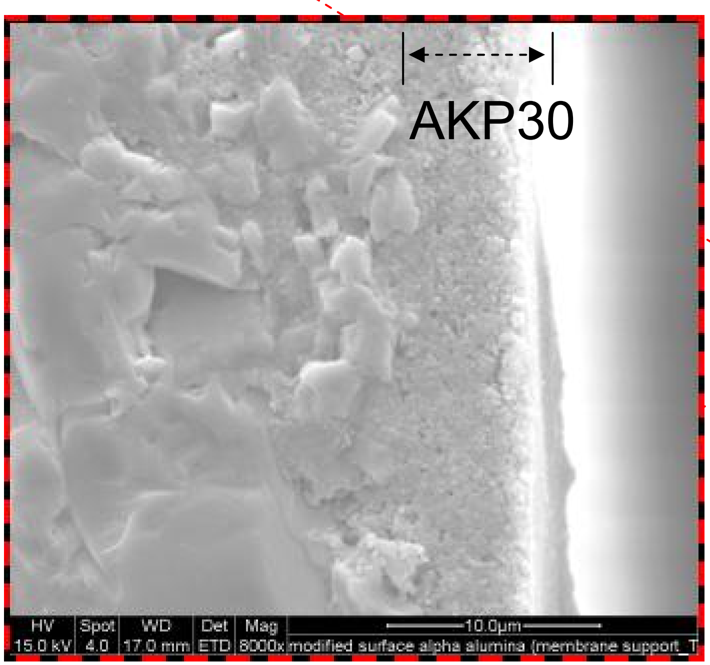


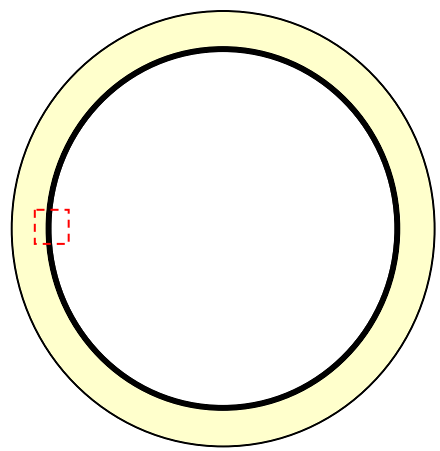
Technical Progress

- **Commercial tubular carriers**

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







To be characterized:
- Permeability
- Porosity
- Pore size
- Surface quality

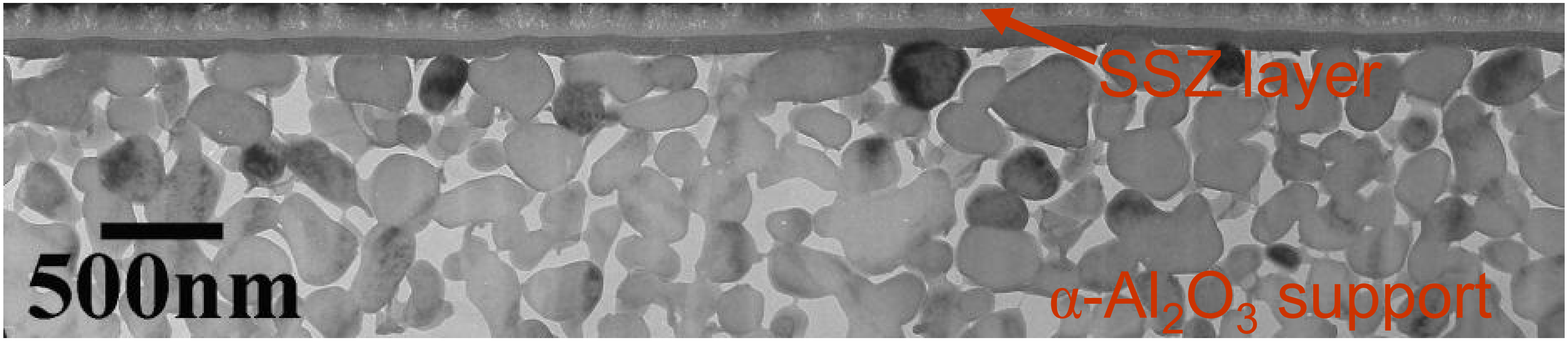
Technical Progress

- **Zirconia (SSZ) intermediate layer**

SSZ **$Ø_p$ = 4 nm, *X* = 50 nm** on porous α-Al_2O_3

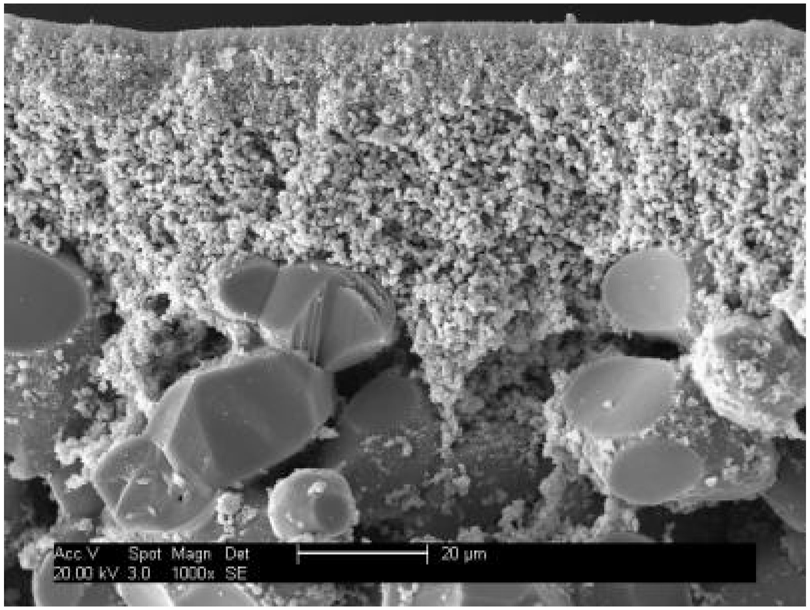
- With industrial partner:
  - sono-chemical synthesis 3 nm SSZ particles
- Polymer-assisted film coating

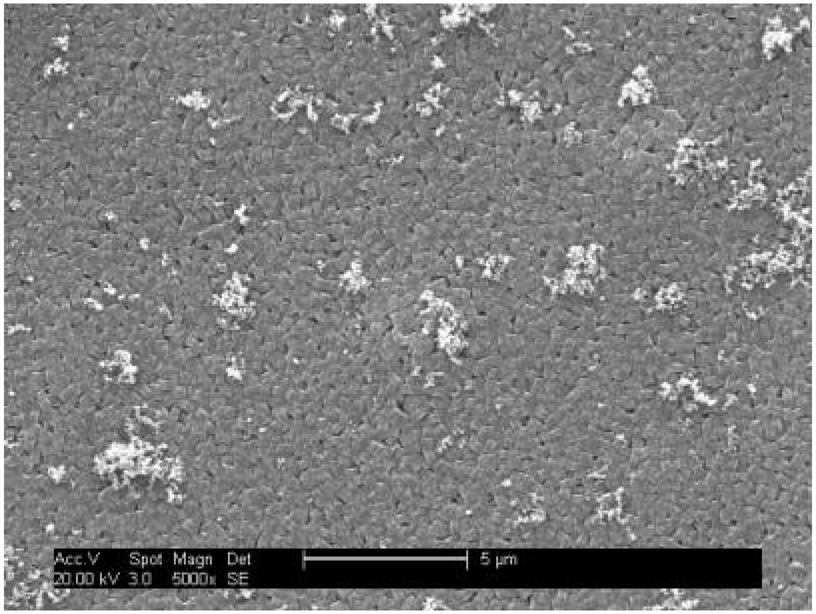
Focused Ion Beam/TEM cross section:



Technical Progress

- **Synthesis of tubular MFI membrane**





MFI membranes also synthesized on practical tubular supports (Pall Co.) by conventional heating and microwave heating from templated or template-free precursors in rotated synthesis vessels.

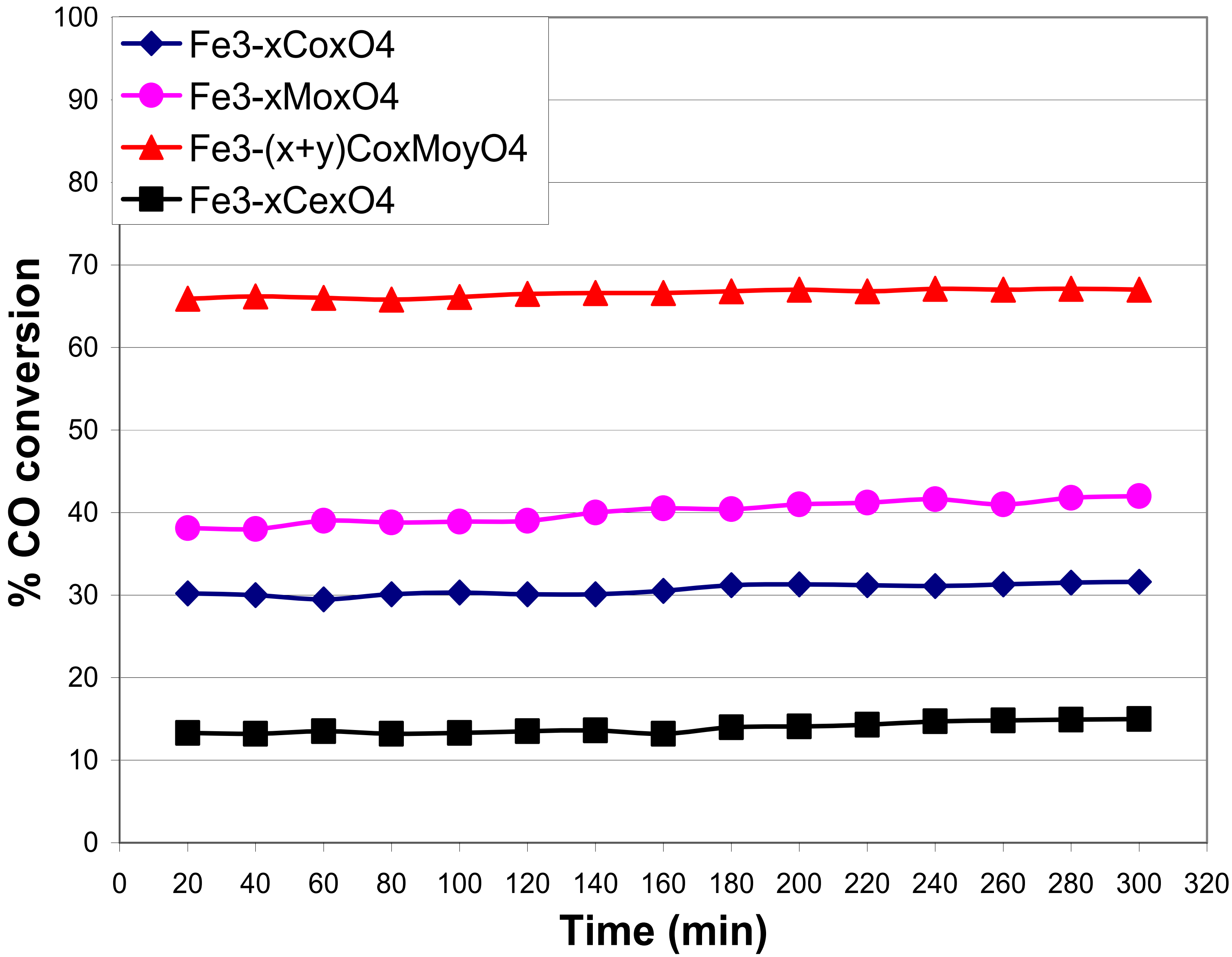
Technical Progress

- <u>Synthesis of improved catalysts and catalyt activity</u>

  - ✓ ***Test performed in H_2 lean conditions to mimic membrane reactor (MR) conditions.***
  - ✓ ***Catalysts tested in exceedingly H_2O-rich environments to mimic MR conditions.***
  - ✓ ***The WGS reaction was performed at very higher temperature (350–550^{o}C).***
  - ✓ ***Exceedingly higher space velocities than industrial were employed.***
  - ✓ ***WGS activity (% CO conversion) of 94-97 % was observed in single pass.***
  - ✓ ***Parameters pertaining to pretreatment conditions were optimized.***
  - ✓ ***Maximum activity observed at 550^{o}C, which also happens to be most favorable for the silicalite membranes operations.***
  - ✓ ***Fe/Ce-based inverse spinel catalyst are found to be very promising, their activity results are encouraging for possible commercialization.***

Technical Progress

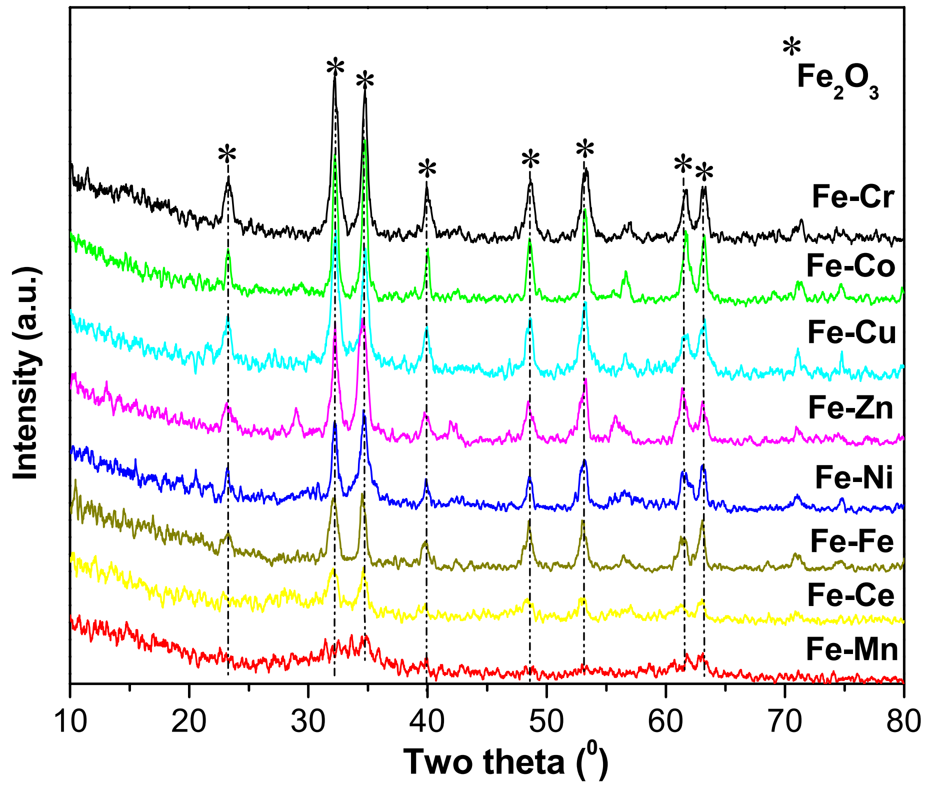
- **High temperature WGS reaction with 100 ppm SO_2 in feed stream**



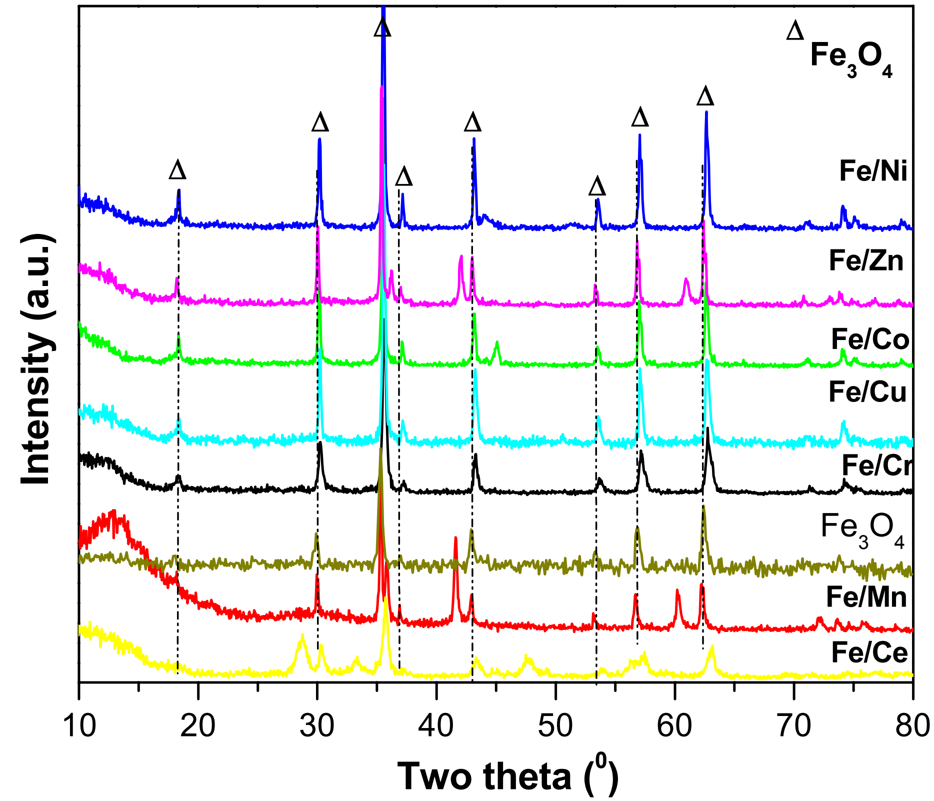
Technical Progress

- X-ray Diffraction Patterns of Various Ferrites

Fresh Catalysts



Spent Catalysts



→ Fe_2O_3 type phase

→ No other diffractions observed

→ Fe/Mn exhibits paracrystallinity

→ Fe_3O_4 type phase

→ No other diffraction observed

→ No XRD peaks due to Fe_xC, Fe or carbonaceous matter

Upon pre-activation Hematite (Fe_2O_3) → Magnetite (Fe_3O_4) [WGS Active]

Future Work for FY07 and FY08

- *Optimize synthesis of disk shaped supports with desired intermediate layers and silicalite membranes*
- *Synthesize and characterize (hydrogen separation test) high quality zeolite membranes*
- *Modify and characterize disk-shaped silicalite membranes by CVD*
- *Test separation and hydrothermal stability of silicalite membranes under syngas conditions*
- *Synthesize tubular silicalite membranes by hydrothermal method*

Future Work for FY07 and FY08

- *Testing AKP30 modified tubes (MetaMateria)*
  Colloidal casting AA3 phosphate/AKP tubes

- *Deposition intermediate layer/membrane by Flow-coating and thermal processing*

- *Fabricate fully operational membrane module-*
  Leak testing with dense ceramic tubes, optimization control dynamics, optimization temperature distribution

Future Work for FY07 and FY08

- *Test of MFI membrane synthesized by microwave heating*
- *Optimize membrane synthesis by microwave oven*
- *Microwave synthesis (secondary growth) of tubular MFI membranes*
- *Optimize membrane modification by on-stream catalytic CVD*
- *Separation test for mixtures containing H_2 ,CO_2 , CO, H_2O and trace H_2S*
- *Provide membrane to teams for WGS membrane reactor tests*

Future Work for FY07 and FY08

- ***Test the performance of sulfur-tolerant hybrid WGS catalysts developed by simulating SO_2 & H_2S in the feed stream***
- ***Develop "ultra high sulfur-tolerant catalysts" for WGS membrane reactor***
- ***Chemical stability studies and catalyst deactivation phenomena and plausible regeneration with the help of Operando techniques***
- ***State-of-the-art characterization on the best catalysts***

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 membrane reactor for water-gas-shift reaction and hydrogen separation

- **Technical Accomplishment and Progress**:

  Developed and studied methods and techniques to prepare support with adequate intermediate laye, zeolite membranes with molecular sieving properties, tubular support and modules, and catalysts with improved properties for WGS reaction

- **Proposed Future Research**:

  Prepare and characterize high quality zeolite membrane for hydrogen separation and catalysts for WGS reaction

Plan & Approaches (Year 2)

- **Task A-1:**
  Synthesis of disk-shaped supports with intermediate zirconia and silicalite layers
  (70% completed)
- **Task A-2:**
  Synthesis of good quality silicalite membranes with hydrothermal template-free method
  (60% completed.)
- **Task A-3:**
  Optimization of hydrothermal synthesis condition for silicalite membranes
  (60% completed)
- **Task A-4:**
  Set up the pervaporation and multi component gas permeation and separation unit for silicalite membrane characterization
  (100% completed)
- **Task A-5:**
  Installation of H_2 cylinder cabinet and transport system in the lab
  (100% completed.)
- **Task A-6:**
  Characterization and study of hydrogen separation properties of disk-shaped zeolite membranes
  (75%)

Plan & Approaches (Year 2)

Task C-1:

- Commercial tube supplier
- Centrifugal casting set-up
- Custom centrifugal casting bowls
- Modify slurry chemistry & rheology
- Three zone furnace set-up
- Preparation of tubular supports

(70% completed)

Task C-2:

- Flow coating apparatus set-up
- Controlled filling/empting velocity
- Slip casting of tubular supports
- Calcination of intermediate layers
- Preparation & calcination of top layers
- Characterization of layer properties

(70% completed)

Task C-3:

- Set-up of large membrane reactor
- Set-up of small membrane reactor
- Thermal modeling membrane reactors
- Characterization of membrane reactors
- Optimization of reactors, supports, etc.
- Leak/flow testing membrane module

(70% completed)

Plan & Approaches (Year 2)

- **Task E-1A:**

  Optimize the synthesis condition for silicalite colloidal suspensions (particle size <100nm).
  (100% completed.)

- **Task E-1B:**

  Coating silicalite nanoparticle seed layers on porous substrates – optimization of coating conditions
  (100% completed.)

- **Task E-1C:**

  MFI membrane synthesis by secondary growth from template-free precursors using microwave heating.
  (70% completed.)

- **Task E-1D:**

  On-stream modification of MFI membrane to enhance high temperature hydrogen separation.
  (40% completed.)

Plan & Approaches (Year 2)

- **Task F-1:**
  Dope spinel structures of Fe_3O_4/Cr_2O_3 of (HTS catalysts) with specific atoms
  (1) increase water activation,
  (2) attract CO, and
  (3) repel CO_2 from the surface.
  (50% completed)

- **Task F-2:**
  Tailor design the catalysts described above in order to allow operation under atmospheres containing poisons (i.e. SO_2, H_2S…)
  (40% completed)

- **Task F-3:**
  Perform selected sets of catalytic experiments for WGS with synthetic feeds simulating the membrane reactor operations namely
  (1) CO_2-rich
  (2) H_2O-rich environments
  (30% completed)

- **Task F-4:**
  Characterize the synthesized WGS catalysts with state-of-the art techniques; Perform chemical stability studies
  (60% completed)

- **Task F-5:**
  Evaluate critically the success of all the above tasks undertaken. Use the feed-back obtained to develop a fundamental understanding of the structure-performance relationships.
  (10% completed)

- **Task F-6:**
  Perform full optimization of the WGS catalysts in conjunction to the membrane-WGS reactor
  (10% completed)