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

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Project PDP11

# Overview

## Timeline

- Project start date:
  **July 1, 2005**
- Project end date:
  **June 30, 2009**
- Percent complete: **0%**

## 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 FY04: **0**
- Funding for FY05: **$702,608**

## Partners

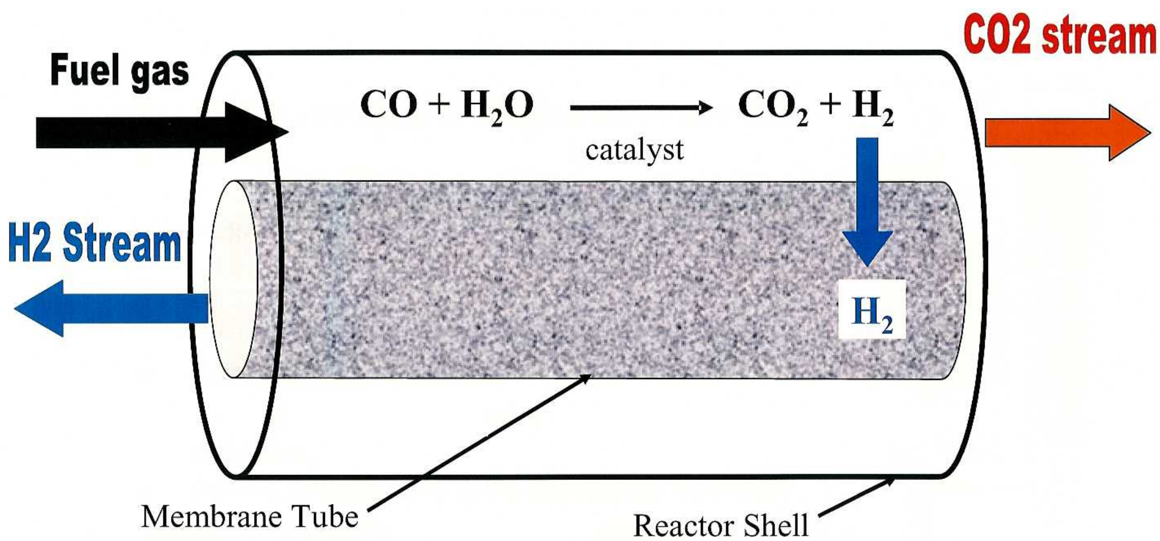
- University of Cincinnati
- Arizona State University
- Ohio State University
- New Mexico Tech

# 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 400$^oC$)
- Two product streams: pure $H_2$ and pure $CO_2$

## Membrane Requirments:

- Operated in 350-450$^oC$
- Chemically stable in $H_2S$, thermally stable at ~400$^oC$
- Hydrogen permance > $5x10^{-7}$ mol/$m^2$.s.Pa
- Hydrogen selective > 50

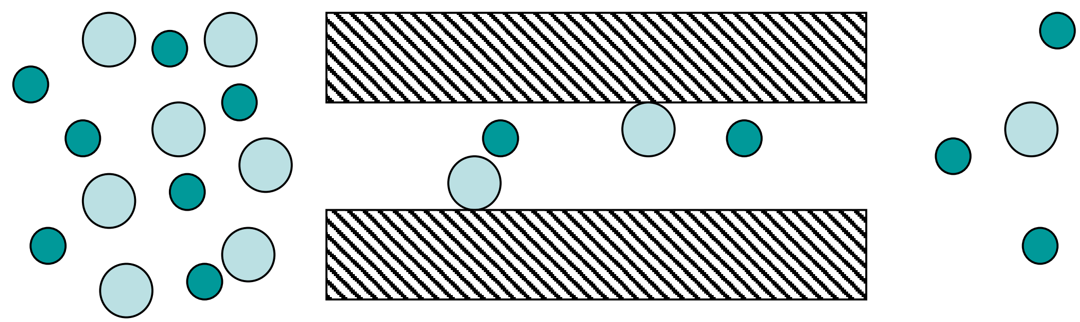
# Comparison of Major Properties of Inorganic Membranes for WGS Membrane Reactor Application (350-550°C)

| 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



1

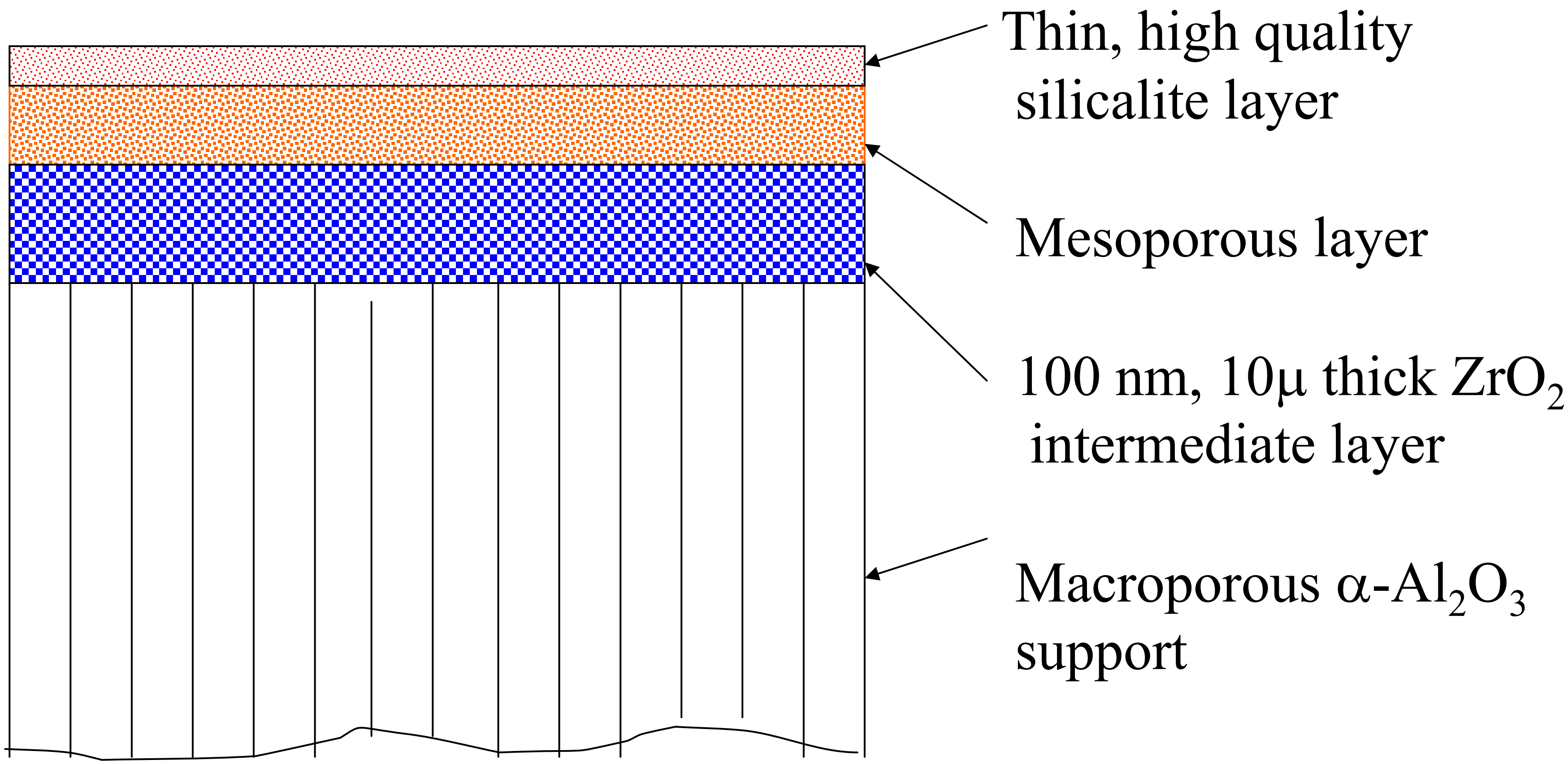
$$J = [\text{Diffusivity}]_{average}[\text{Solubility}]$$

Diffusivity in intercrystalline pores – non-selective for hydroge

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

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

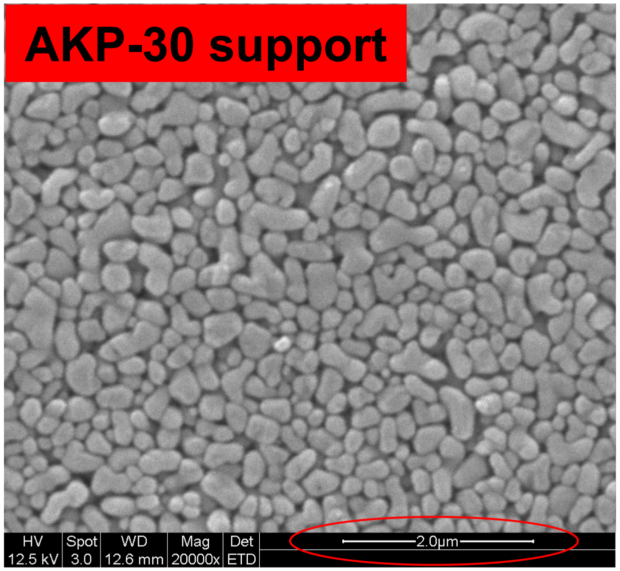
# New Structure of Silicalite Composite Membrane with Improved Chemical/Thermal Stability and Permselectivity

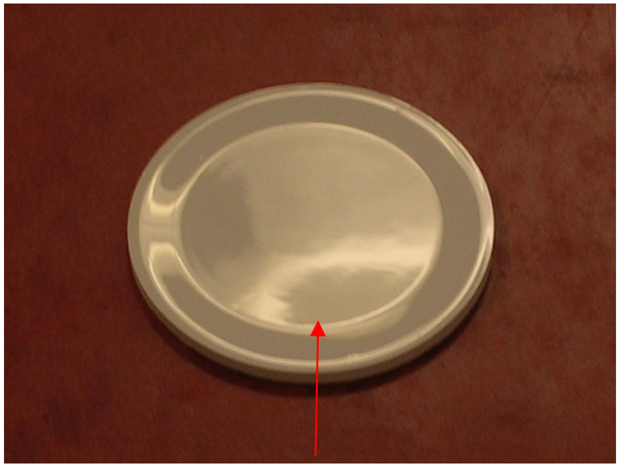


# Porous Membrane Supports

- Colloidal stable aqueous solutions
  - Dispersed sub-micron $\alpha$-$Al_2O_3$ particles
- Stabilization
  - Surface charge
    - Dilute aqueous $HNO_3$
  - Electrosteric hinderance
    - Darvan C
    - Aluminon/Tyron
- Disk shaped supports by 'slipcasting' in polymer molds

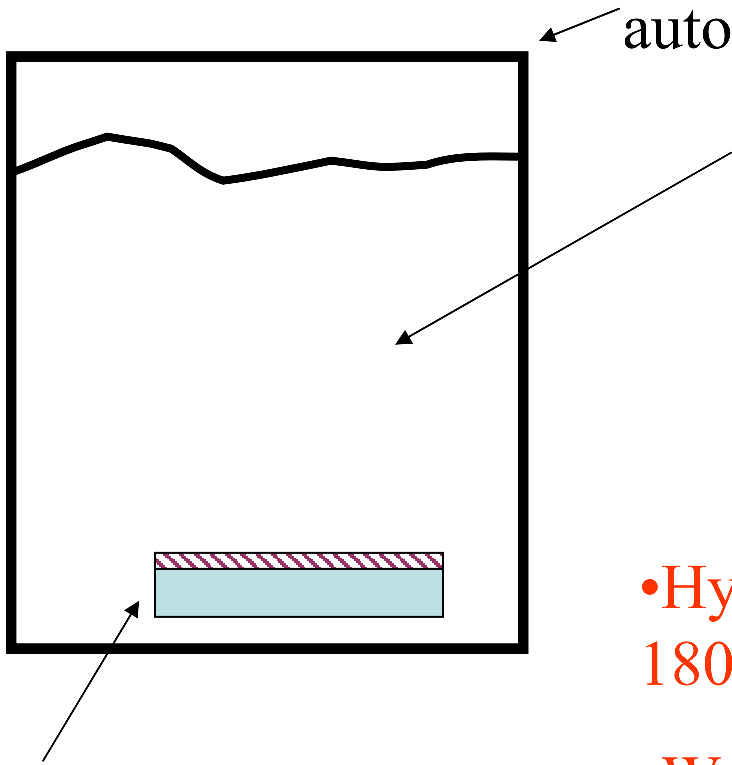
Ordered random closed packed structure



Homogeneous as-prepared surface

# Template-Free Synthesis of Silicalite Membranes



autoclave

Synthesis solution:

0.16 g NaOH-1g $SiO_2$-10.5 g$H_2O$

No template, aged 1.5 hr, ultrasonically dispersed

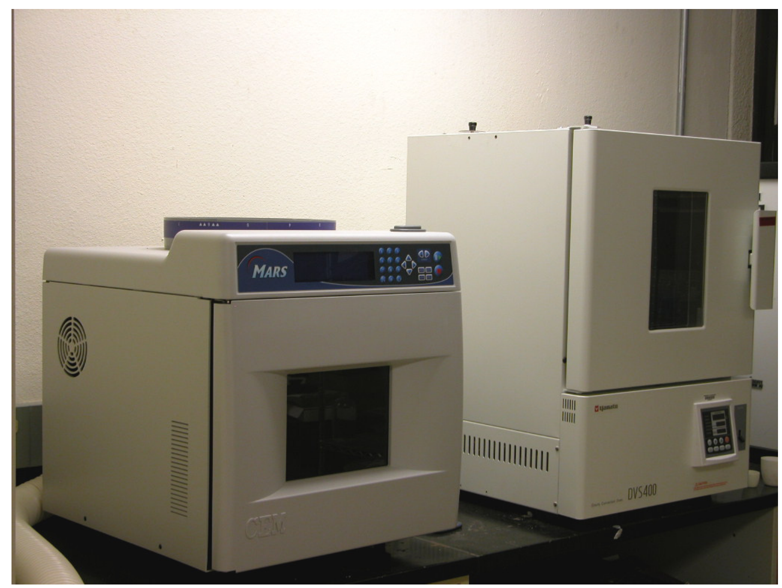
Mesoporous silicalite membrane

- Hydrothermally treated at 180°C for 4 hr
- Washed, dried at 40°C
- No calcination

# Microwave Assisted Synthesis of Silicalite Membranes

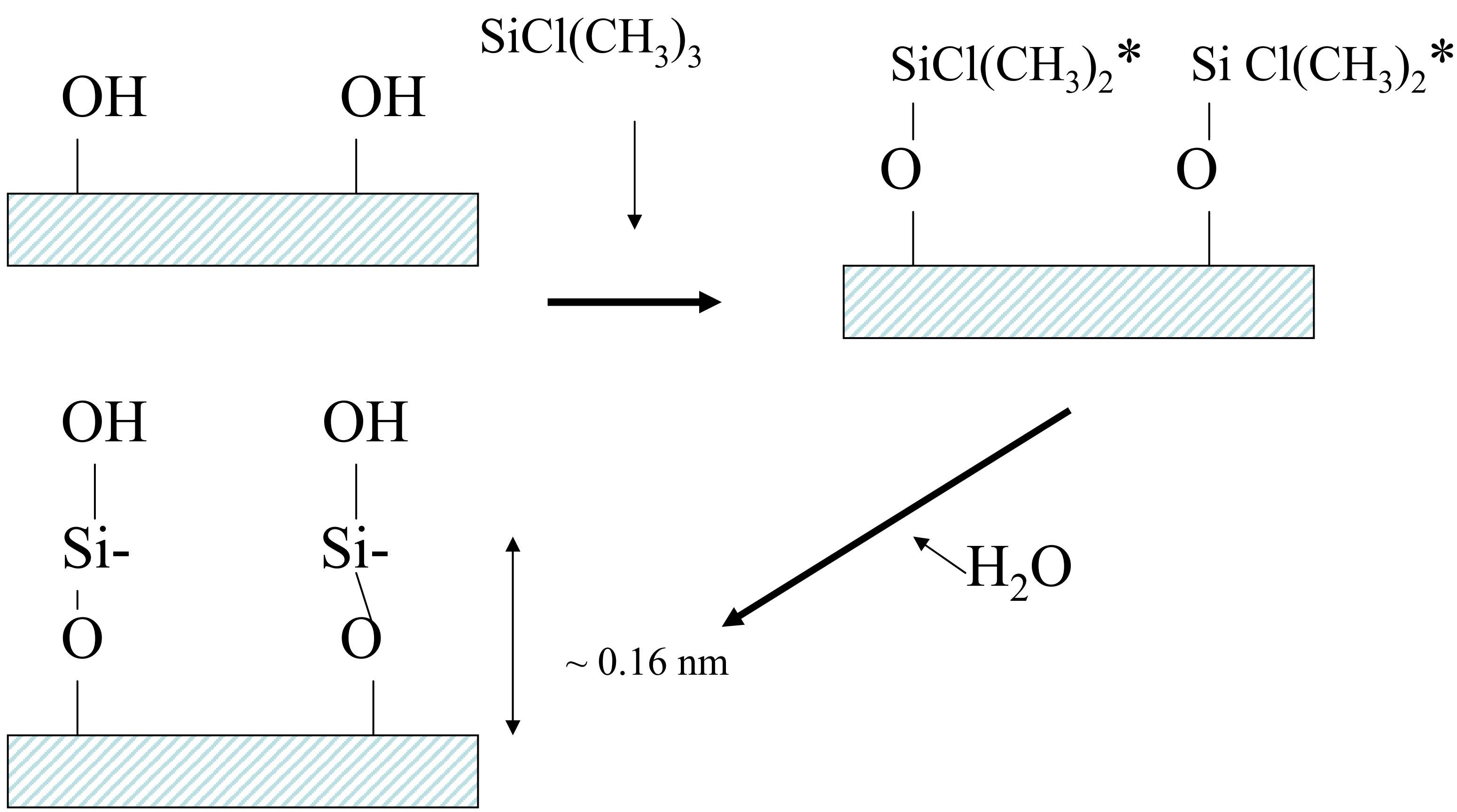
**To improve efficiency and cost-effectiveness of fabricating high quality silicalite membranes;**

- To optimize microwave synthesis of silicalite nanocrystal seed suspensions.
- To coat defect-free mesoporous silicalite seed layers on zirconia/ alumina substrates
- To convert the seed layers to defect-free silicalite membranes in template-free solutions by microwave heating.

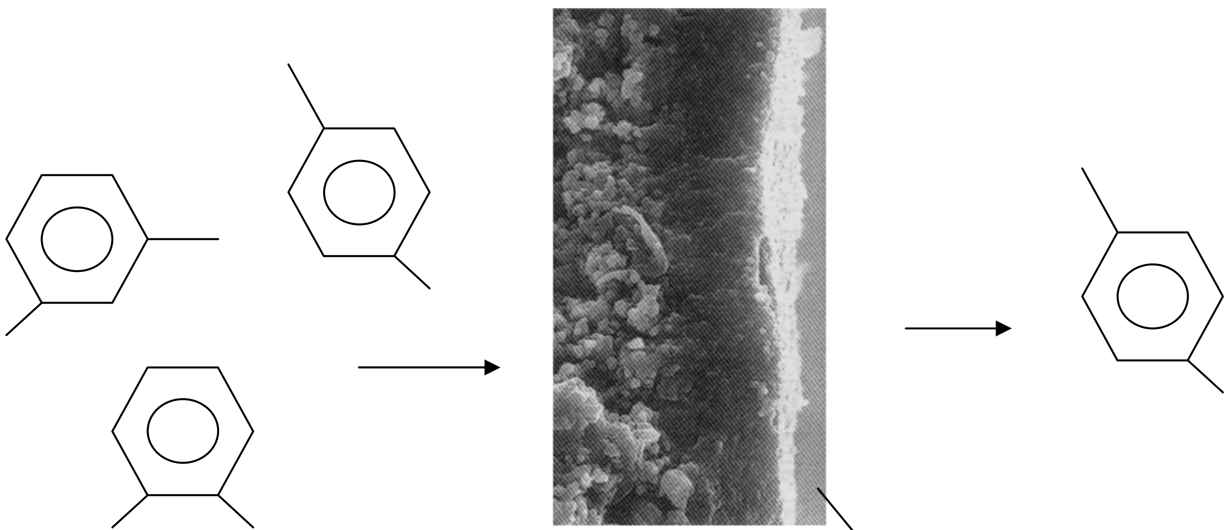


# CVD Modification of Silicalite Membranes

**To reduce membrane defects and improve membrane permselectivity**



# Characterization of Zeolite Membrane by Xylene Pervaporation Separation



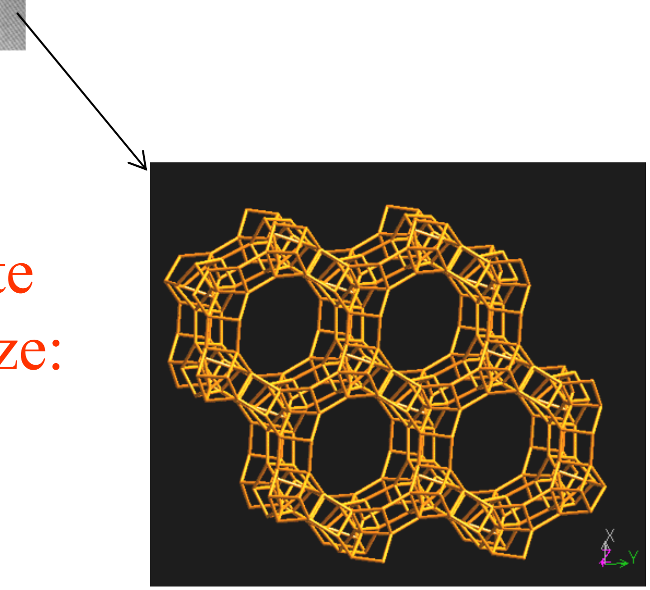
Molecule size:

p-xylene 0.58 nm

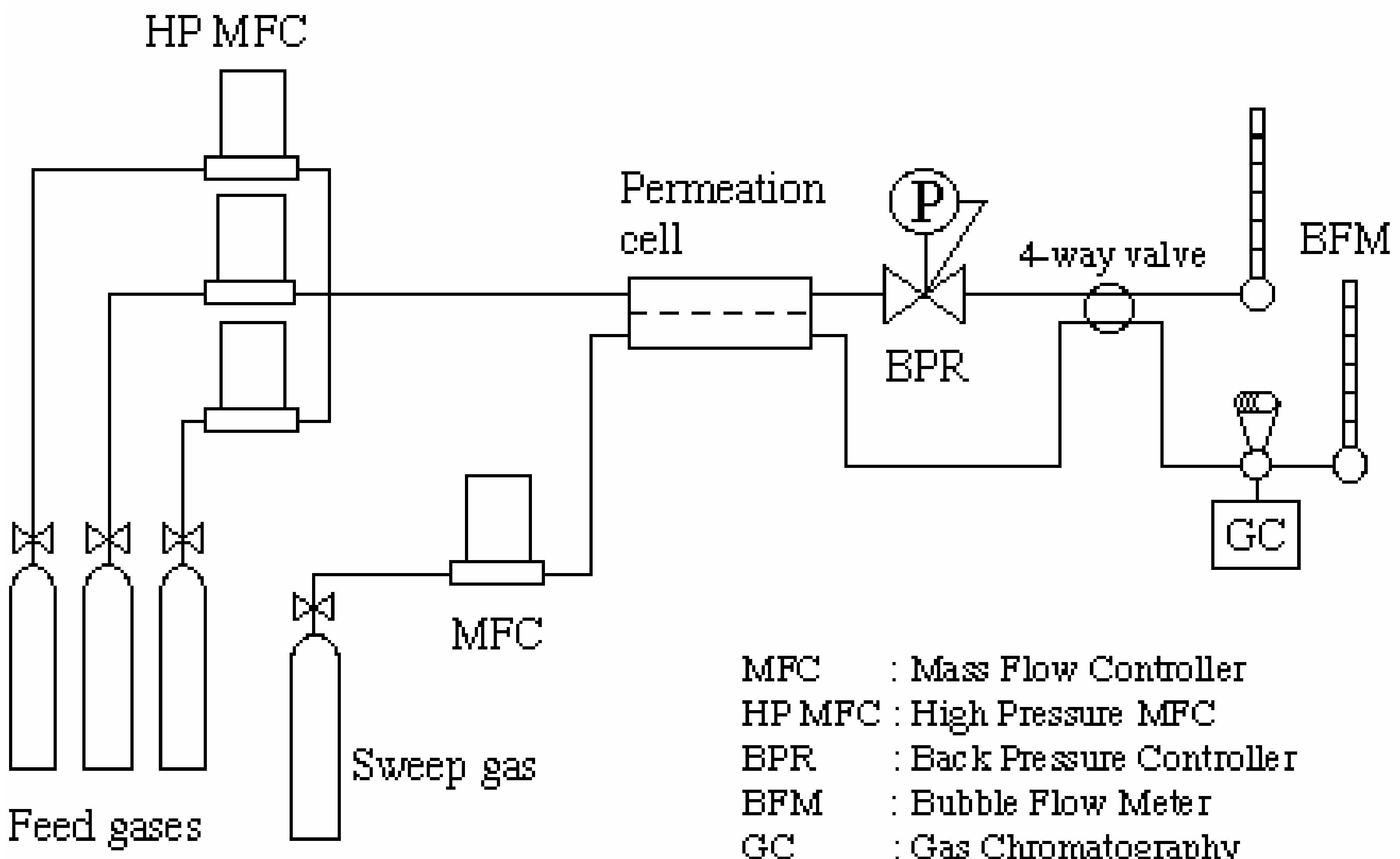
o-xylene 0.68 nm

m-xylene 0.68 nm

silicalite pore size: 0.6 nm

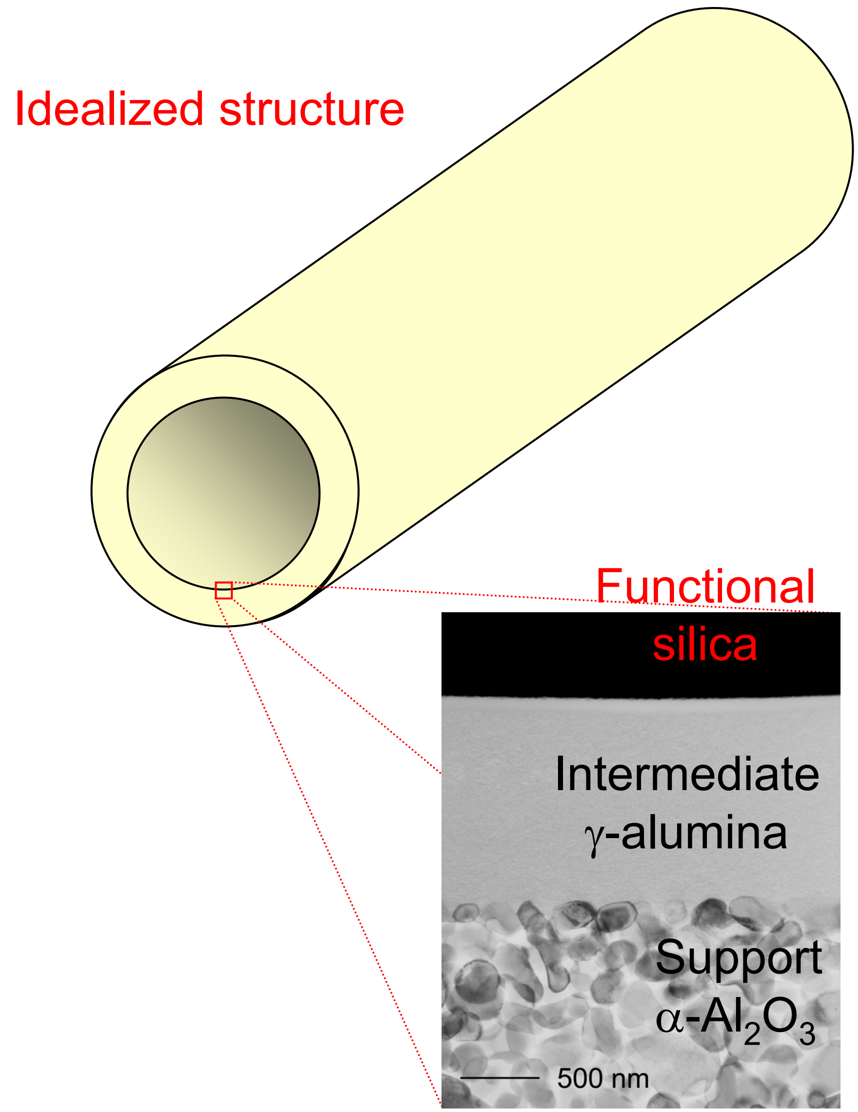


# Experimental Setup for Multi-component Gas Permeation



# Tubular Membrane Supports

- Commercial microfiltration tubes (CMT)
  - Immediately available
- Colloidally cast tubes (CCT)
  - Developing
  - Tube dimensions
    - 1 cm I.D. & 10 cm length
- Advantages of CCT
  - Roundness
  - Surface quality
  - Strength
  - Graded structures



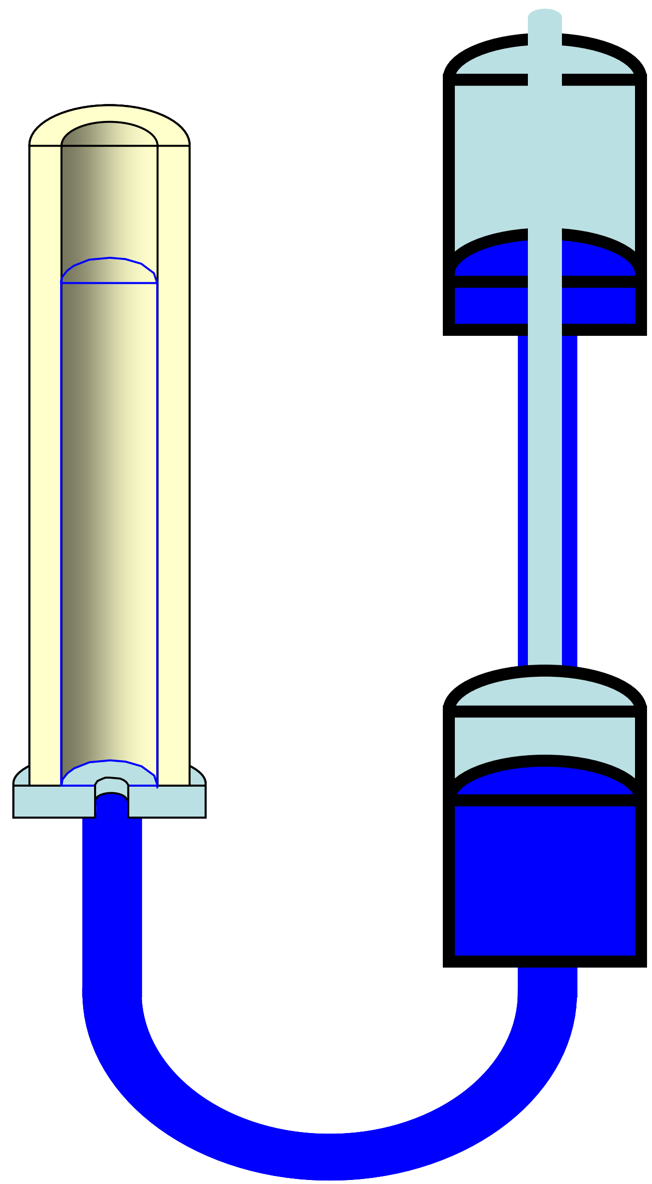

Flat disk membrane microstructure

# Porous Support Tubes by Centrifugal Casting

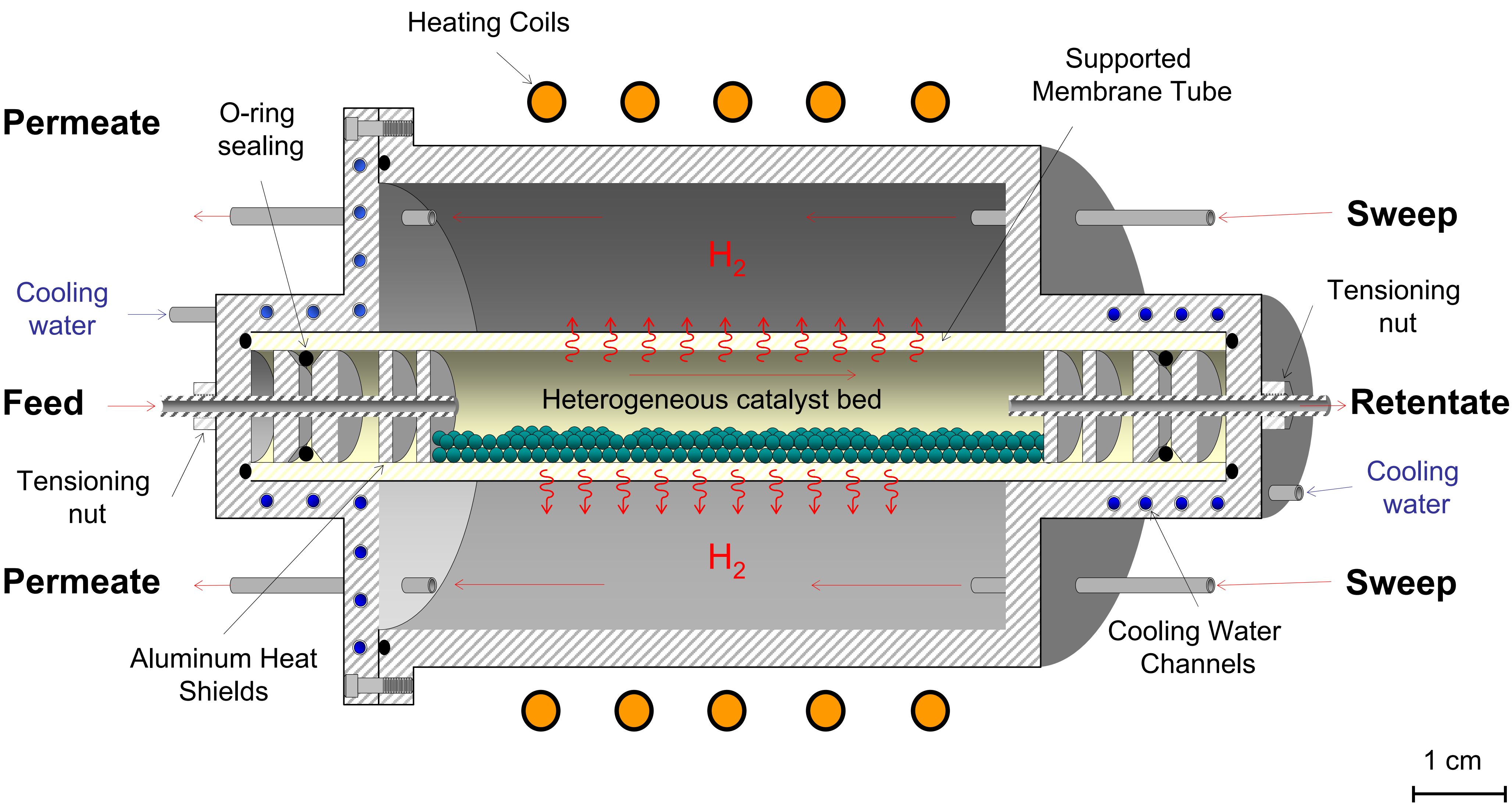
- Newly acquired **high speed centrifuge**
  - CEPA, Model: Z 41
  - Maximum cylinder ∅
    - 7.6 cm
  - Maximum Rotation Speed
    - 20,000 RPM
- Charge with stable dispersions

# Intermediate Layer Flow Coating

- Intermediate layer formed by 'slipcasting'
  - Driving force capillary action
  - Particles deposit forming dense packed layer
- Tube gravity filled
  - Filling process may also be pressure controlled

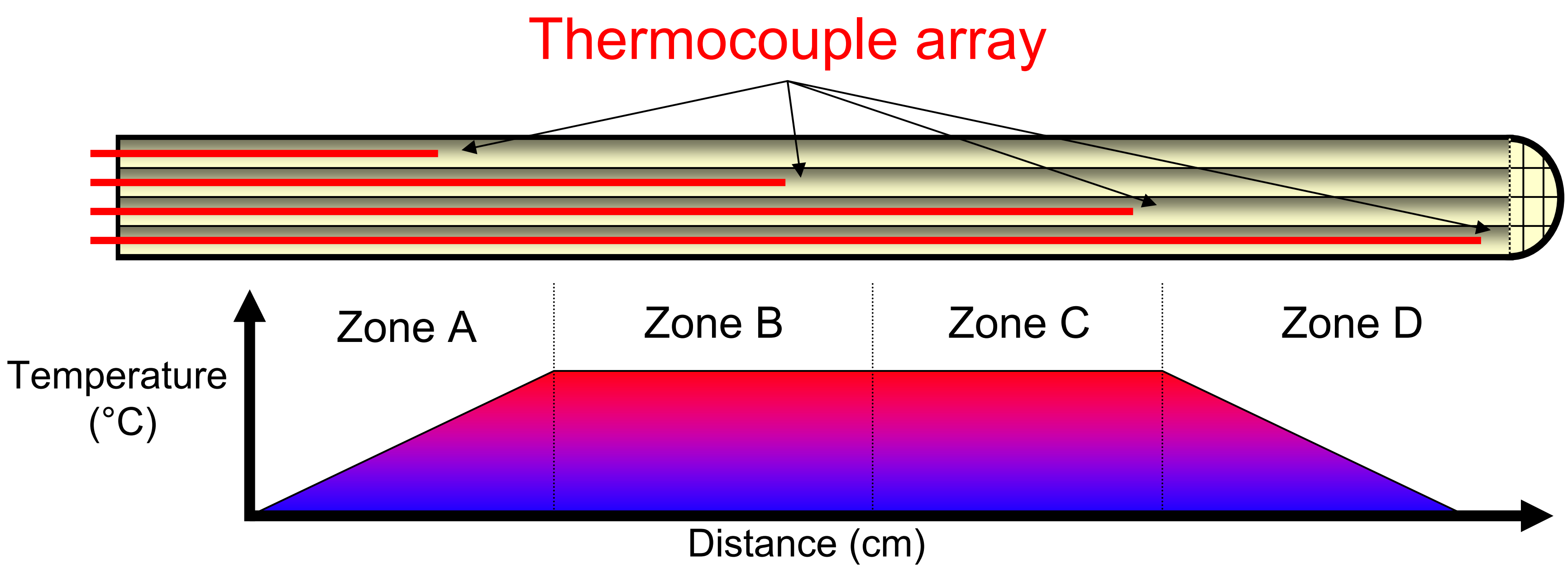


# Zeolite Membrane Reactor Module



# Temperature Monitoring in Membrane Reactor

- Thermocouple arrays
- Multi capillary $Al_2O_3$ tube
- Temperature control
  - Process-adaptive PID cascade control
- Optimized multi-zone control



# Catalysts for WGS Membrane Reactor

$CO + H_2O <=> CO_2 + H_2$   $\Delta H = -41.1$ KJ/mol

*Current Limitations*

- The low temperature shift catalysts are very sensitive to even traces of poisons
- Possible reaction hindrance due to excessive amount of $CO_2$ in the membrane reactor
- Increase the activation of water

Süd Chemie LT shift catalysts (C18-7)

# How to Improve Catalyst

- Synthesize Fe-Cr spinel hight temperature shift catalysts with composition around 55 wt% Fe and 6wt%Cr.
- Conduct a systematic study to select optimal combinations of dopants
- Functionalize the surface to become more acidic. In this manner,
  - the surface will attract CO (weak base),
  - the surface will repel $CO_2$ (weak acid).
- Make the surface hydrophilic so that it attracts and retains water molecules.

# Research Tasks

- **Task A** Synthesis and modification of silicalite membranes
  - A-1 Synthesis of disk-shape supports with intermediate zirconia and silicalite layers
  - A-2 Synthesis of good quality silicalite membranes with hydrothermal template-free method
  - A-3 CVD modification of silicalite membranes
  - A-4 Characterization of silicalite membranes
- **Task B** Separation and stability study
  - B-1 Set up high temperature and high pressure separation and membrane reactor system
  - B-2 Permeation and separation characterization of silicalite membranes
  - B-3 Chemical and thermal stability study of silicalite membranes

# Research Tasks

- **Task C** Fabrication of tubular support and membrane module
  - C-1 Fabrication of tubular alumina support with optimized structure
  - C-2 Fabrication of tubular alumina support with zirconia and silicalite intermediate layer
  - C-3 Designing, fabricating and testing of membrane module for tubular silicalite membranes
- **Task D** Hydrothermal synthesis and CVD modification of tubular silicalite membranes and gas separation study
  - D-1 Hydrothermal template-free synthesis of tubular silicalite membranes
  - D-2 CVD modification of tubular silicalite membrane
  - D-3 Permeation and separation study (including modeling) on tubular silicalite membranes

# Research Task

- Task E Microwave synthesis of silicalite membranes
    - E-1 Identification of optimum conditions for microwave synthesis of silicalite suspension and template-free synthesis of silicalite membranes
    - E-2 Establishment of microwave system for tubular membrane synthesis
    - E-3 Microwave template-free synthesis of tubular silicalite membranes
    - E-4 CVD modification of the tubular silicalite membranes prepared by the microwave method

# Research Tasks

- Task F Water-gas-shift reaction catalyst and reaction kinetics
  - F-1 Catalyst improvement for water-gas-shift reaction
  - F-2 Chemical stability study
  - F-3 Kinetic study of WGS reaction under hydrogen-lean conditions for WGS catalysts
- Task G Membrane reactor modeling and experiments
  - G-1 Performance study of WGS reaction on silicalite membrane reactor
  - G-2 Stability study of WGS silicalite membrane reactor
  - G-3 Modeling WGS silicalite membrane reactor