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

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Project
PDP11

This presentation does not contain any proprietary or confidential information

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

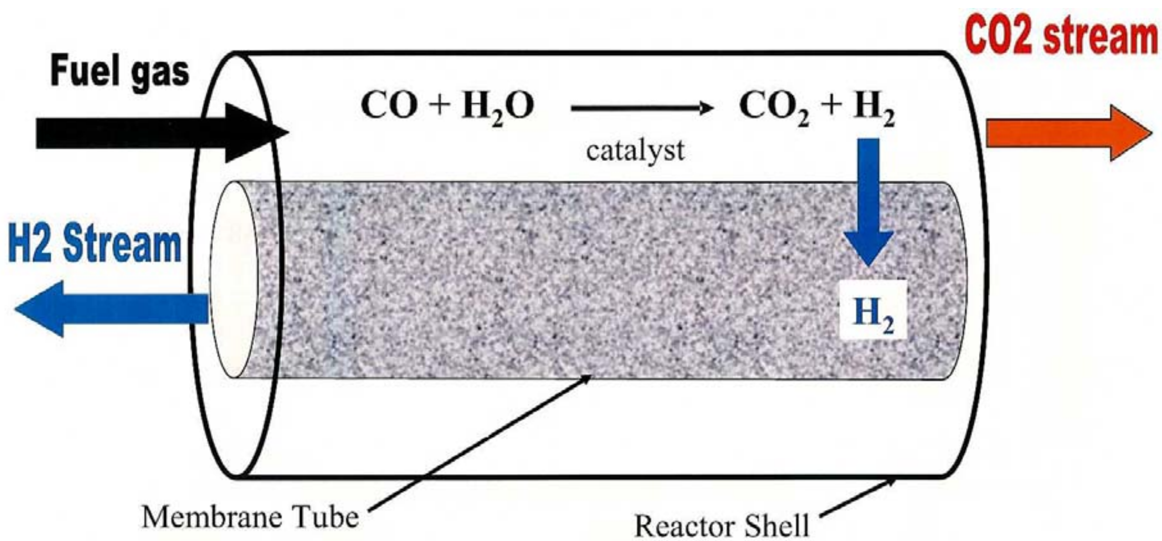
- University of Cincinnati
- Arizona State University
- Ohio State University
- New Mexico Tech

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°C)
- Two product streams: pure H_2 and pure CO_2

Membrane Requirments:

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

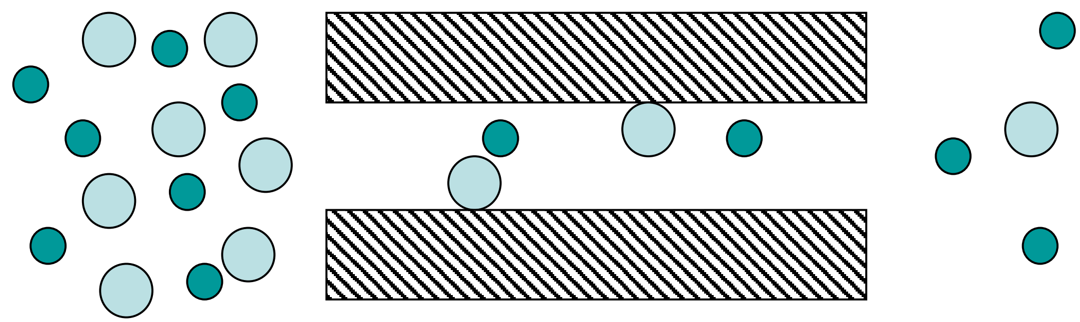
Comparison of Major Properties of Inorganic Membranes for WGS Membrane Reactor Application (350-550°C)

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



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

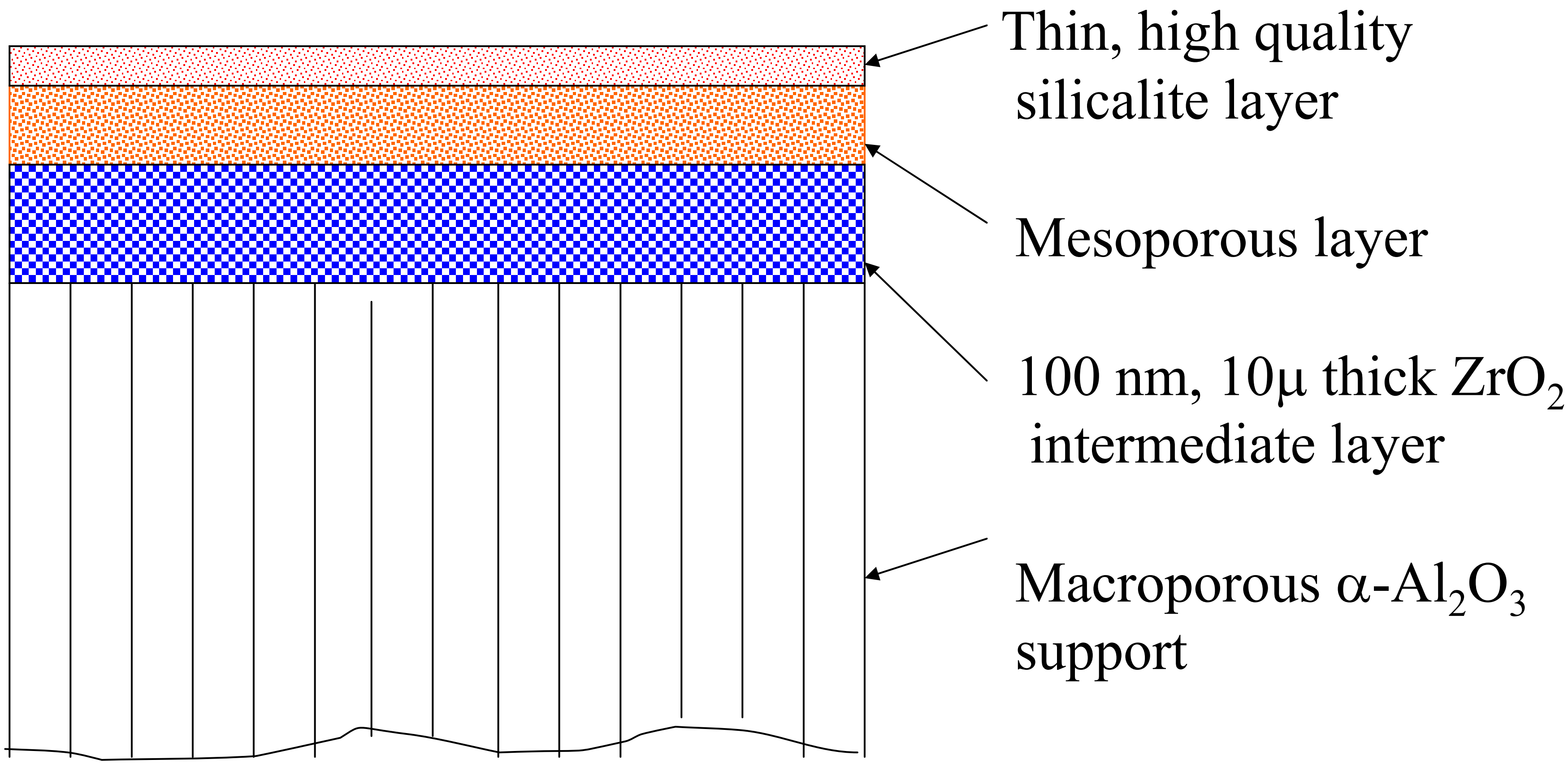
1

Diffusivity in intercrystalline pores – non-selective for hydroge

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

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

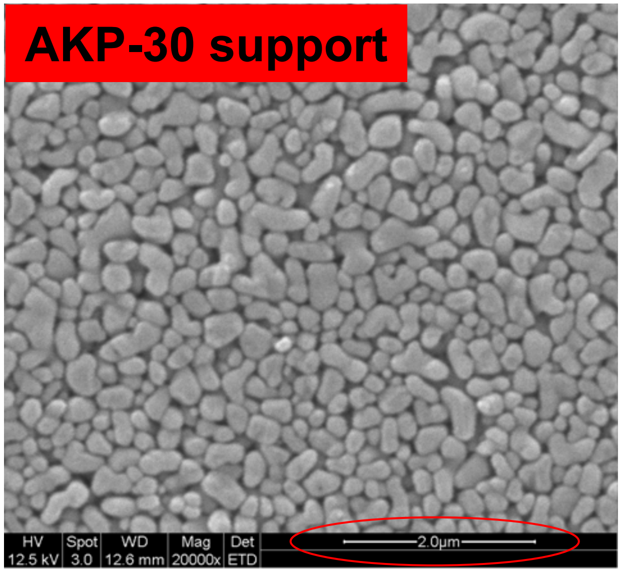
New Structure of Silicalite Composite Membrane with Improved Chemical/Thermal Stability and Permselectivity

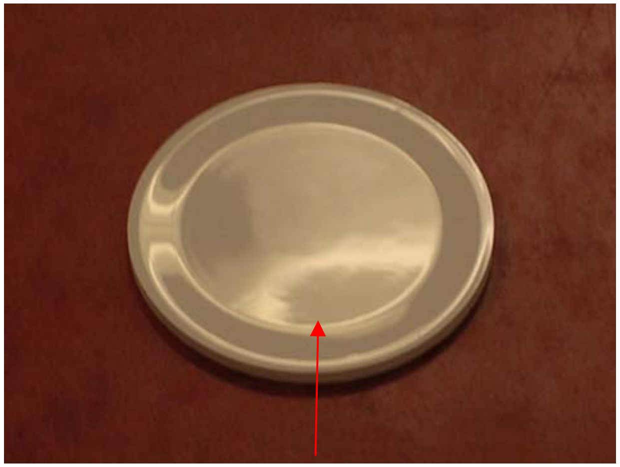


Porous Membrane Supports

- Colloidal stable aqueous solutions
  - Dispersed sub-micron α-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

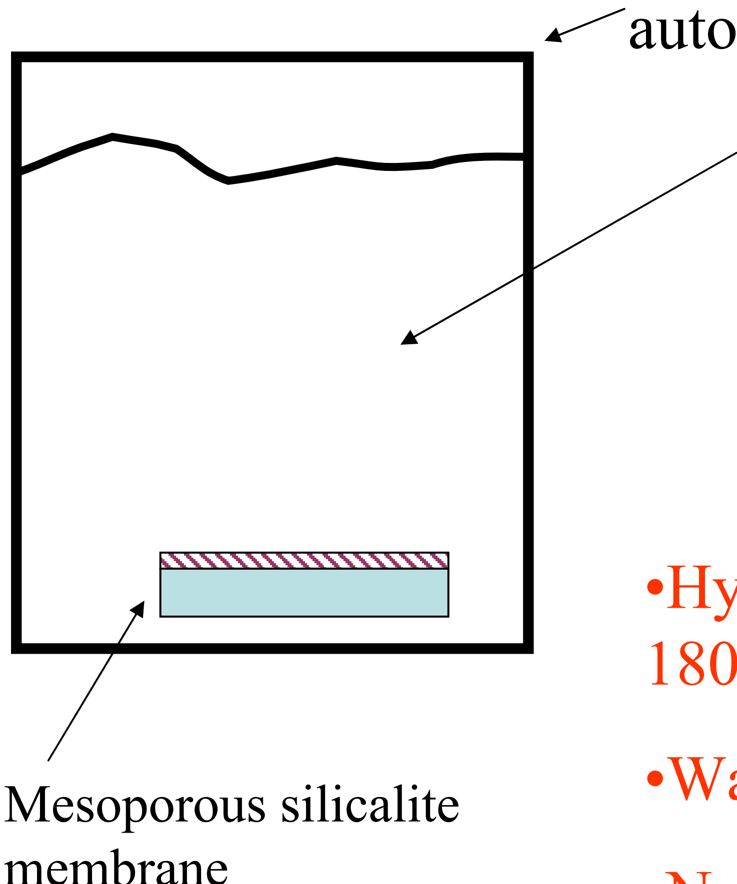
Ordered random closed packed structure





Homogeneous as-prepared surface

Template-Free Synthesis of Silicalite Membranes



Synthesis solution:

0.16 g NaOH-1g SiO_2-10.5 gH_2O

No template, aged 1.5 hr, ultrasonically dispersed

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

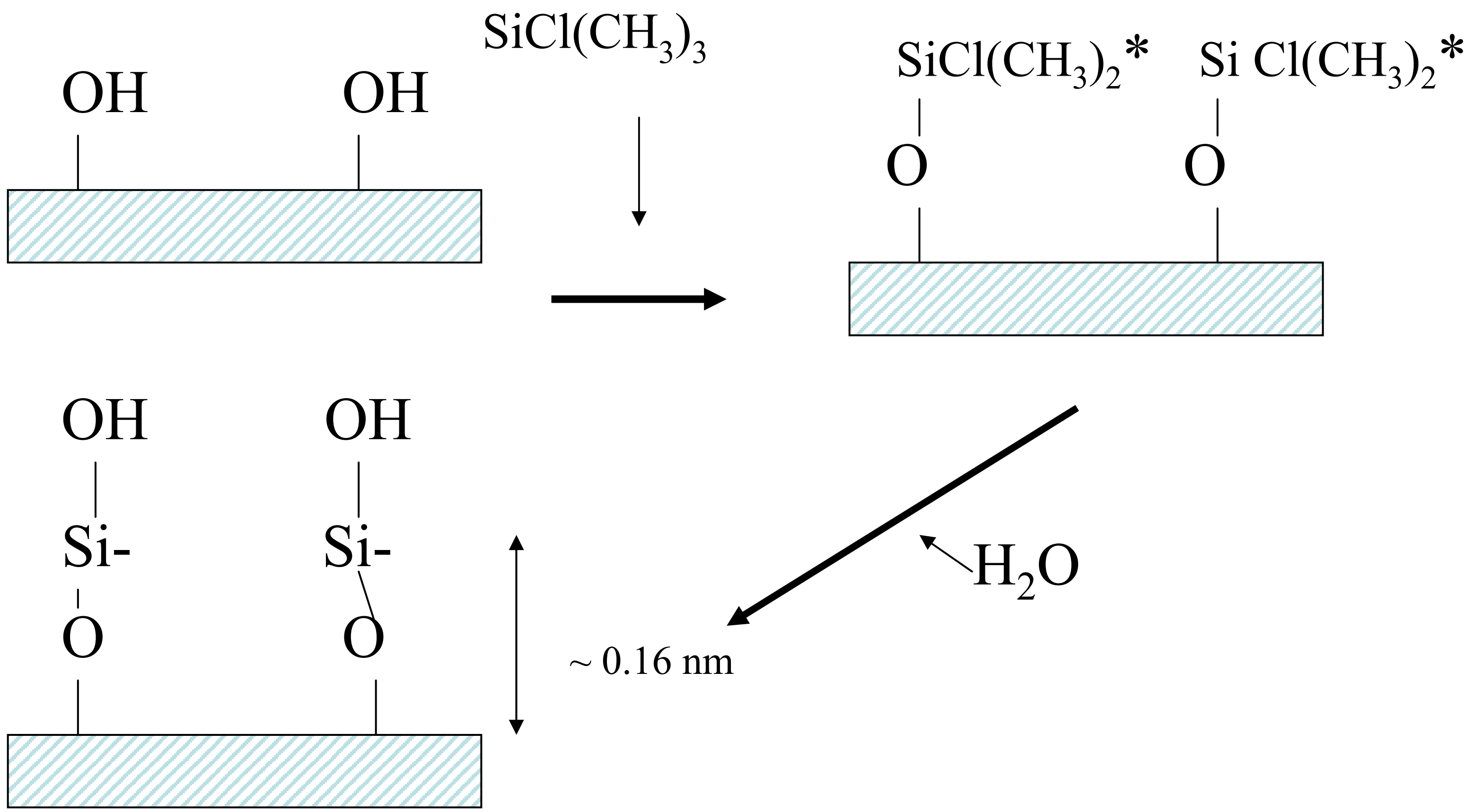
Microwave Assisted Synthesis of Silicalite Membranes

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

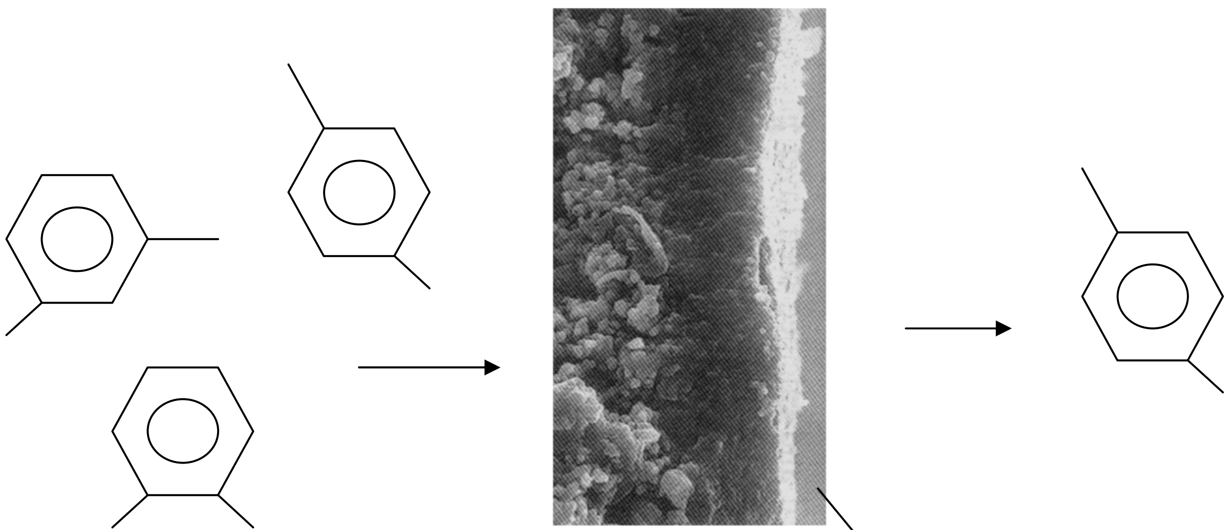
- To optimize microwave synthesis of silicalite nanocrystal seed suspensions.
- To coat defect-free mesoporous silicalite seed layers on zirconia/ alumina substrates
- To convert the seed layers to defect-free silicalite membranes in template-free solutions by microwave heating.

CVD Modification of Silicalite Membranes

To reduce membrane defects and improve membrane permselectivity



Characterization of Zeolite Membrane by Xylene Pervaporation Separation



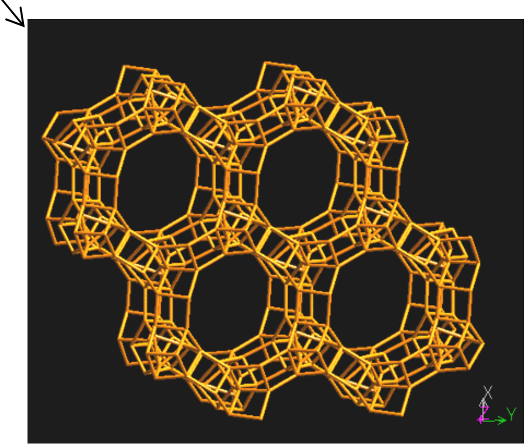
Molecule size:

p-xylene 0.58 nm

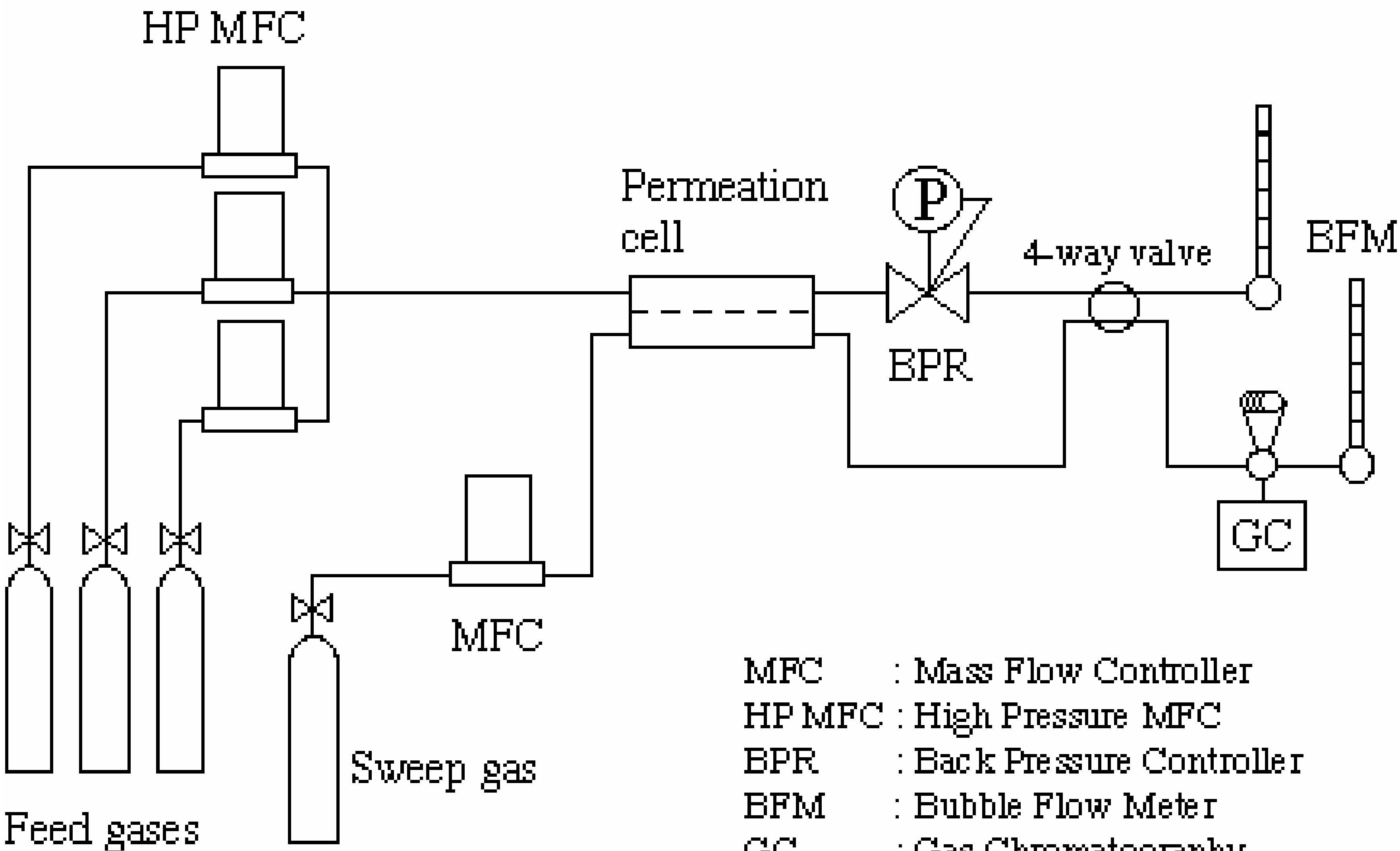
o-xylene 0.68 nm

m-xylene 0.68 nm

silicalite pore size: 0.6 nm



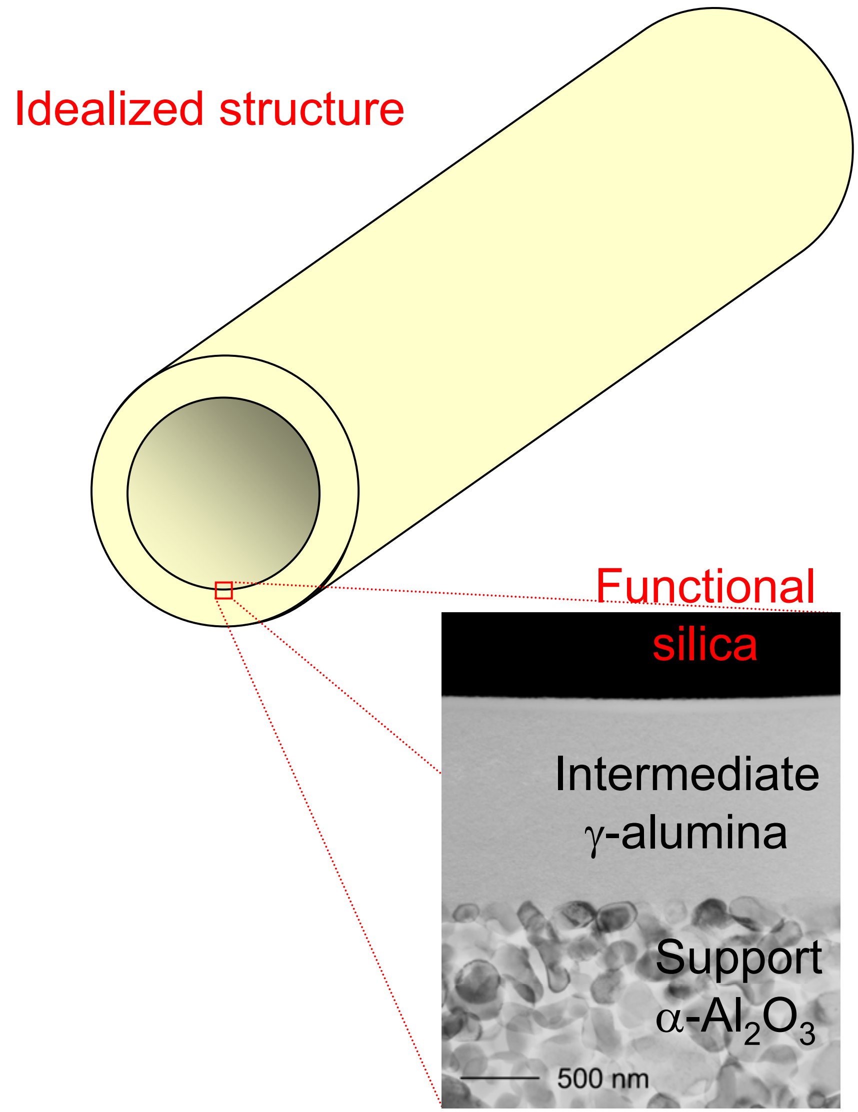
Experimental Setup for Multi-component Gas Permeation



MFC : Mass Flow Controller
HP MFC : High Pressure MFC
BPR : Back Pressure Controller
BFM : Bubble Flow Meter
GC : Gas Chromatography

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



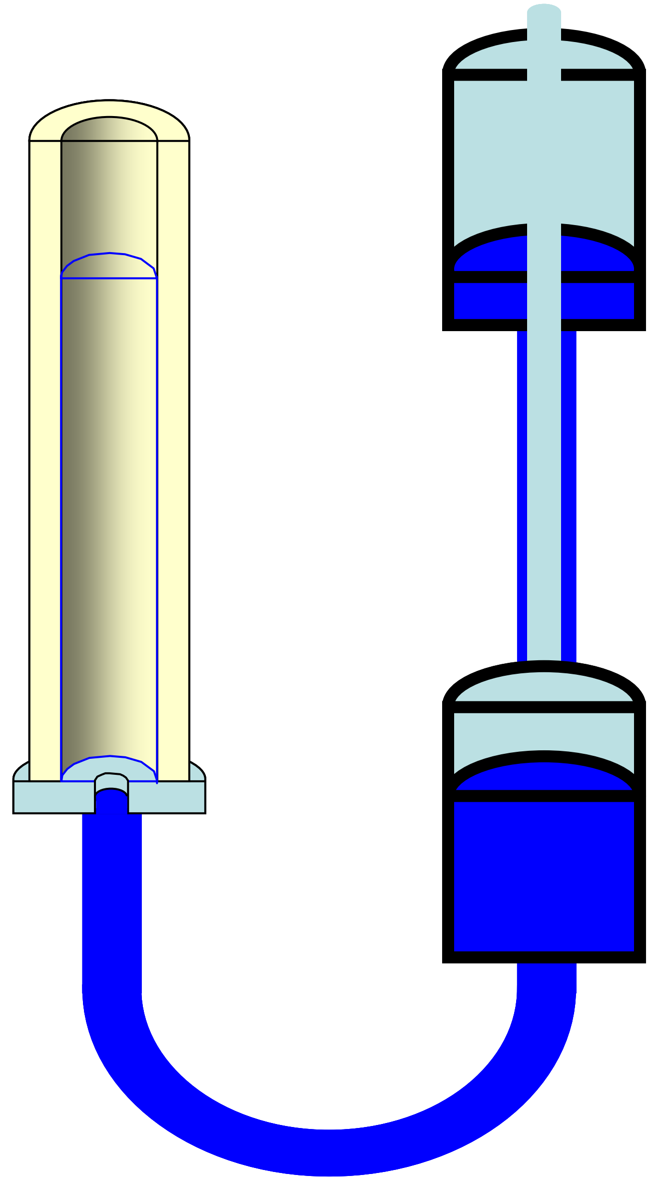
Flat disk membrane microstructure

Porous Support Tubes by Centrifugal Casting

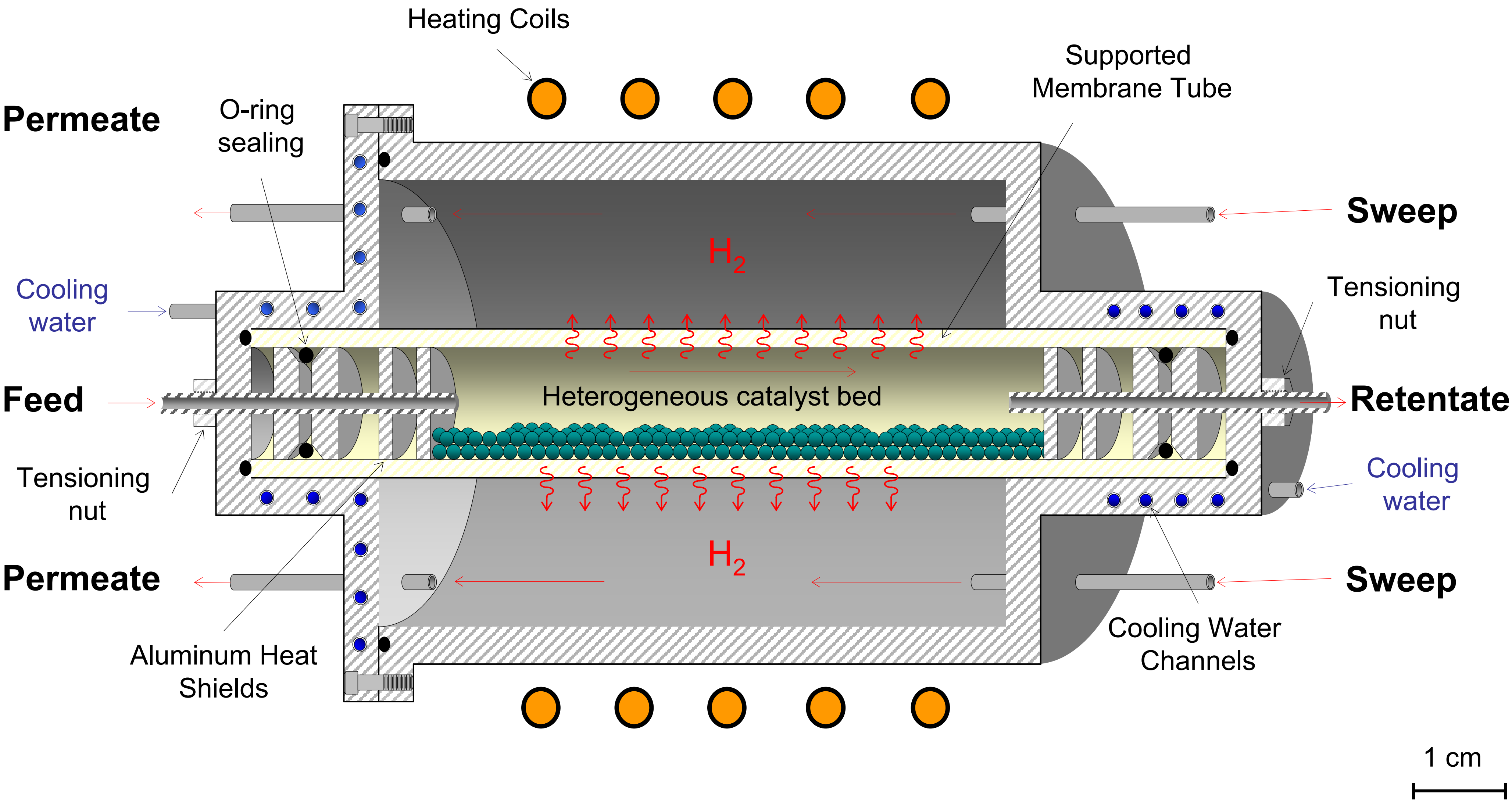
- Newly acquired **high speed centrifuge**
  - CEPA, Model: Z 41
  - Maximum cylinder ∅
    - 7.6 cm
  - Maximum Rotation Speed
    - 20,000 RPM
- Charge with stable dispersions

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

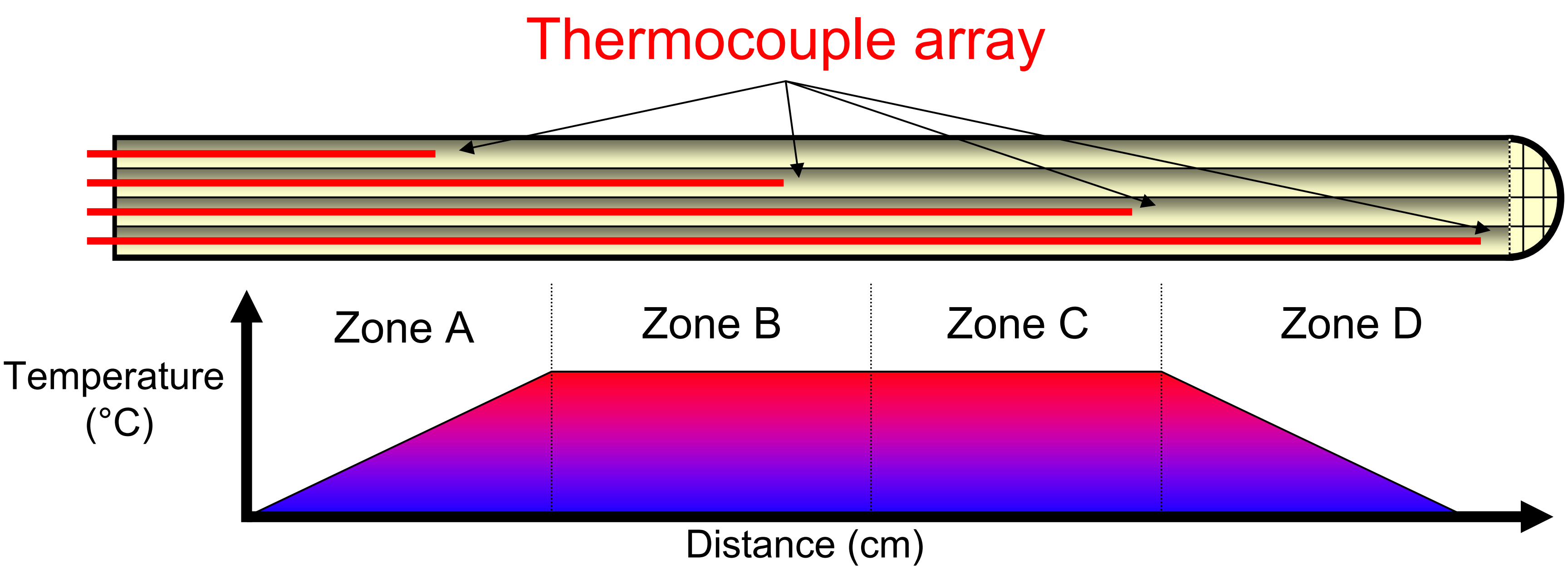


Zeolite Membrane Reactor Module



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

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

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