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

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Project
PDP8

Overview

Timeline

- Project start date: **July 1, 2005**
- Project end date: **June 30, 2009**
- Percent complete: **15%**

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 FY05: **$100,000**
- Funding for FY06: **$300,000**
- FY06 funding reduced: **Fund received for FY06 is 48% of the budgeted**

Partners

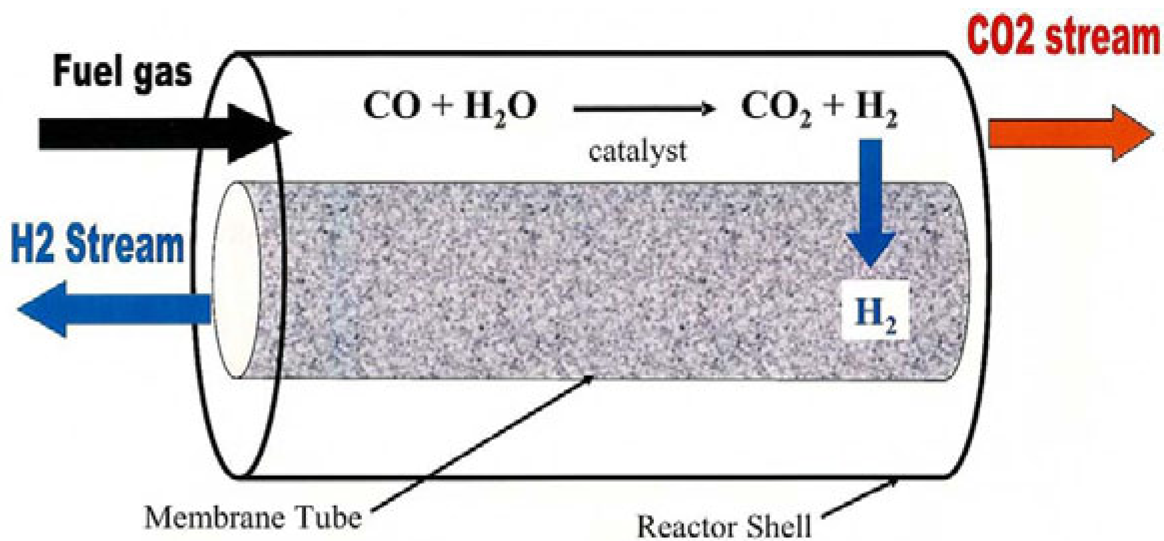
- University of Cincinnati
- Arizona State University
- Ohio State University
- New Mexico Tech

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 Requirements:

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

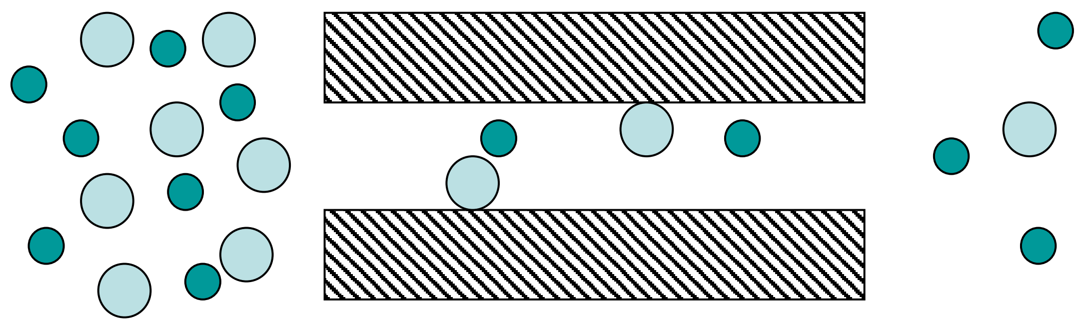
Comparison of Major Properties of Inorganic Membranes for WGS Membrane Reactor Application (350-550°C)

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



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

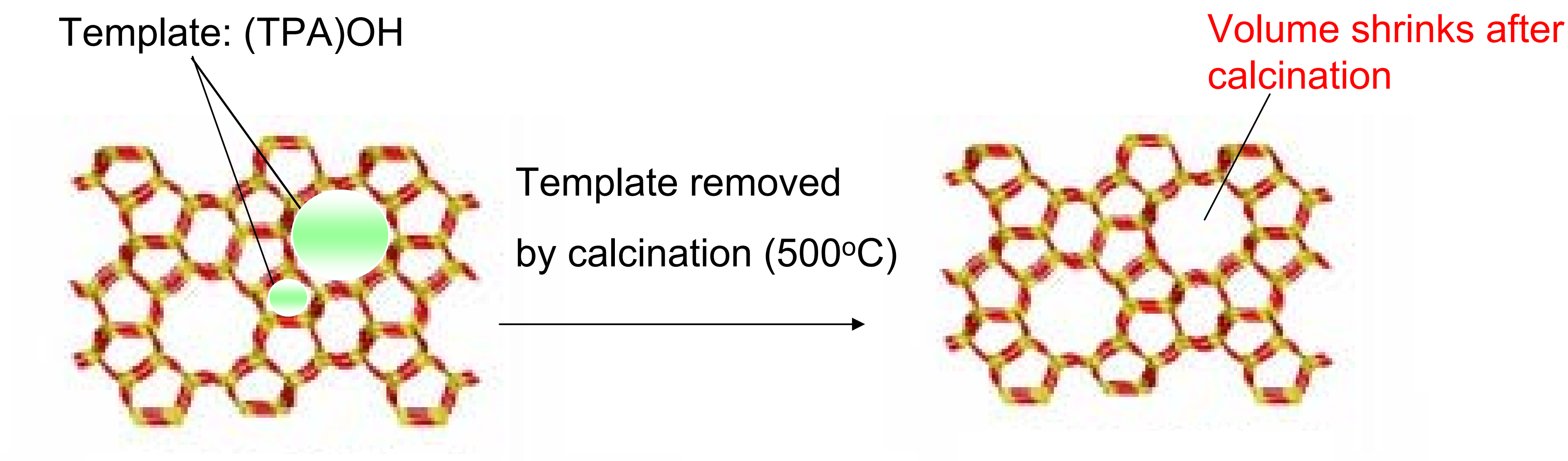
1

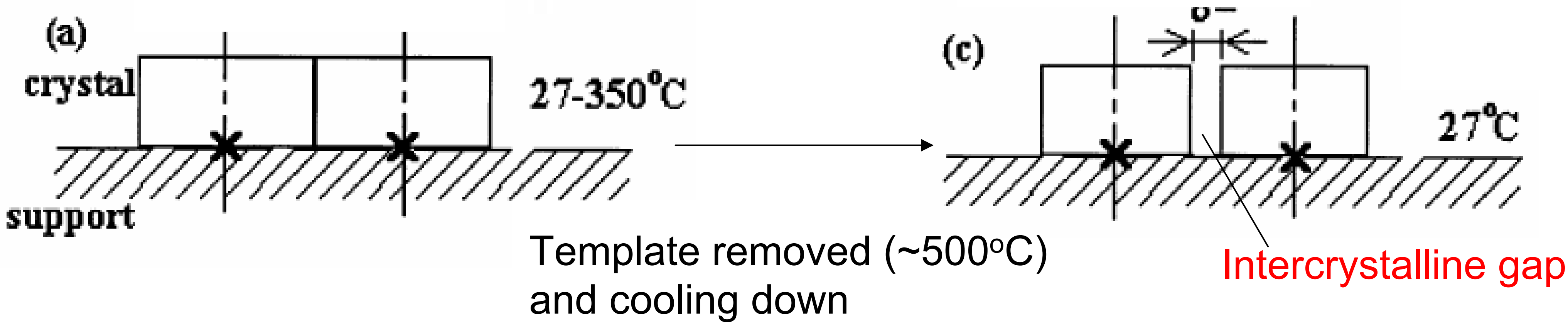
Diffusivity in intercrystalline pores – non-selective for hydrogen

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

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

Schematic Illustration of Template Removal from Zeolite Channel by Calcination

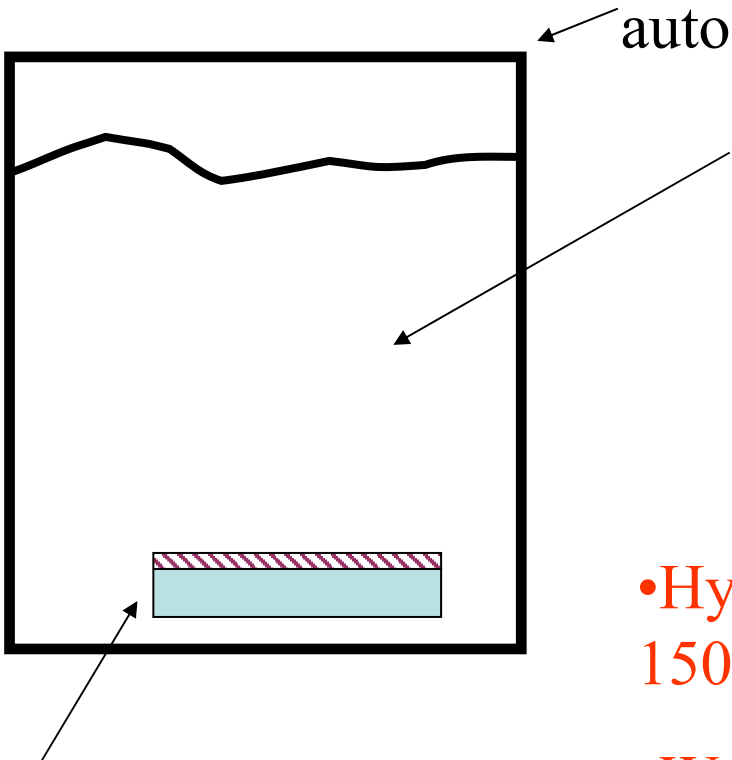




Intercrystalline gaps tend to form in the membranes due to the difference in thermal expansion between zeolite layer and support and/or by changes in lattice parameters of zeolite crystals.

Template-Free Synthesis of Silicalite Membranes

autoclave



Typical synthesis solution:

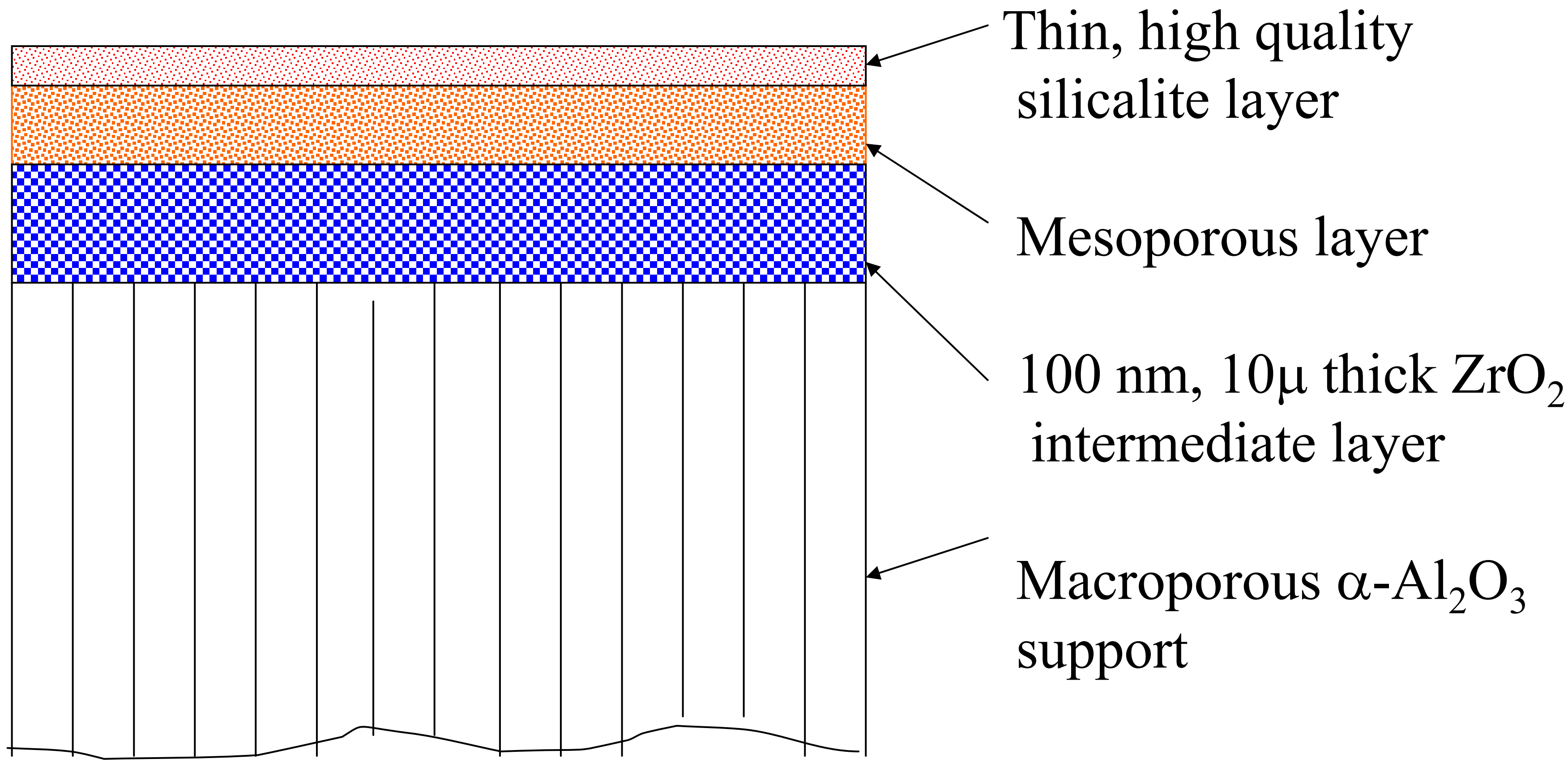
0.16 g NaOH-1g SiO_2-10.5 gH_2O

No template, aged a few hrs, ultrasonically dispersed

Mesoporous silicalite membrane

- Hydrothermally treated at 150-200°C for 2-10 hr
- Washed, dried at 40°C
- No calcination

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



Plan & Approaches (Year 1)

- **Task A-1:**
  Synthesis of disk-shaped supports with intermediate zirconia and silicalite layers
  (60% completed)
- **Task A-2:**
  Synthesis of good quality silicalite membranes with hydrothermal template-free method
  (50% completed.)
- **Task A-3:**
  Optimization of hydrothermal synthesis condition for silicalite membranes
  (50% completed)
- **Task A-4:**
  Set up the pervaporation and multi component gas permeation and separation unit for silicalite membrane characterization
  (65% completed)
- **Task A-5:**
  Installation of H_2 cylinder cabinet and transport system in the lab
  (85% completed.)
- **Task A-6:**
  Characterization and study of hydrogen separation properties of disk-shaped zeolite membranes
  (10%)

Plan & Approaches (Year 1)

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

(60% 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

(20% 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.

(50% completed)

Plan & Approaches (Year 1)

- **Task E-1:**
  Synthesis of silicalite colloidal suspensions (particle size <100nm) – using microwave heating to enhance synthesis efficiency.
  (60% completed.)

- **Task E-2:**
  Coating silicalite nanoparticle seed layers on porous substrates – quality control by optimizing suspension and coating conditions.
  (60% completed.)

- **Task E-3:**
  Secondary growth of the silicalite seed layer into inter-grown membrane by microwave heating.
  (30% completed.)

- **Task E-4:**
  Synthesis of tubular silicalite membranes by in-situ crystallization for testing membrane modification and separation.
  (70% completed.)

Plan & Approaches (Year 1)

- **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.
  (40% 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…)
  (15% completed.)

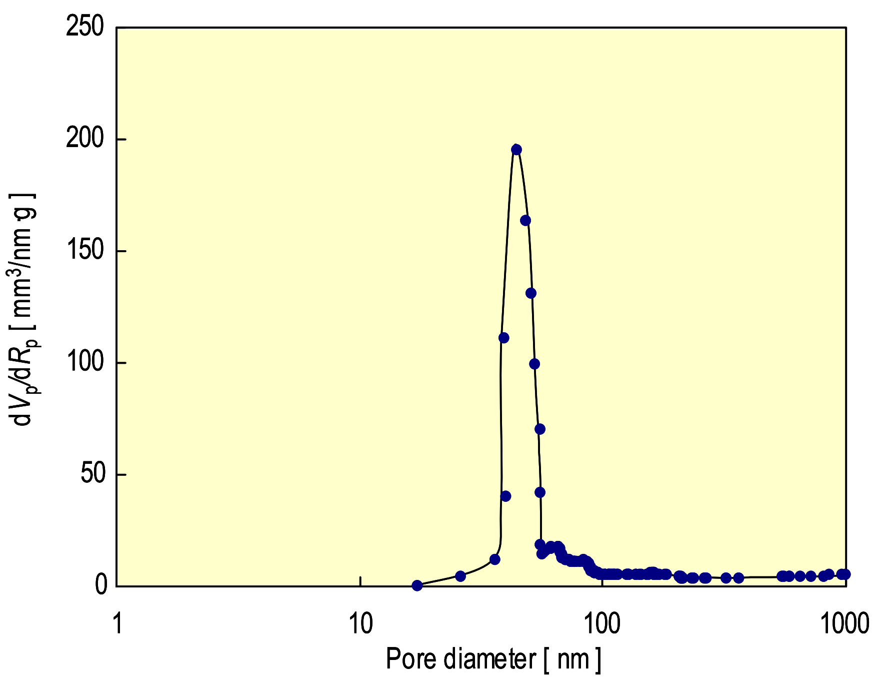
- **Task F-3:**
  Perform selected sets of catalytic experiments for WGS with synthetic feeds simulating the membrane recator operations namely
  (1) CO_2-rich
  (2) H_2O-rich environments
  (30% completed)

- **Task F-4:**
  Characterize the synthesized WGS catalysts with state-of-the art techniques; Perform chemical stability studies
  (15% completed.)

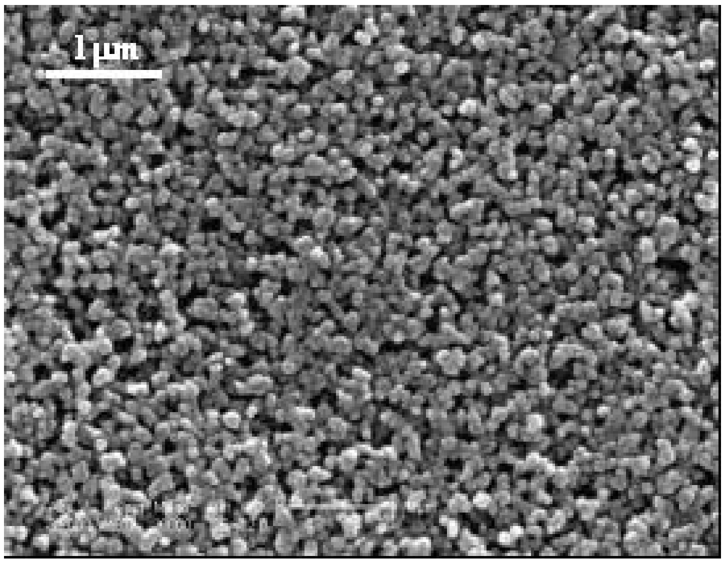
Technical Progress (ASU)

- **Preparation of Yttria stabilized zirconia (YSZ) intermediate layer on alumina support**

  Average pore size< 100nm, porosity: 44%
  Defect-free supported YSZ membranes fired could be prepared with stable YSZ suspension.



Pore size distribution of unsupported YSZ membrane fired at 750°C for 3h



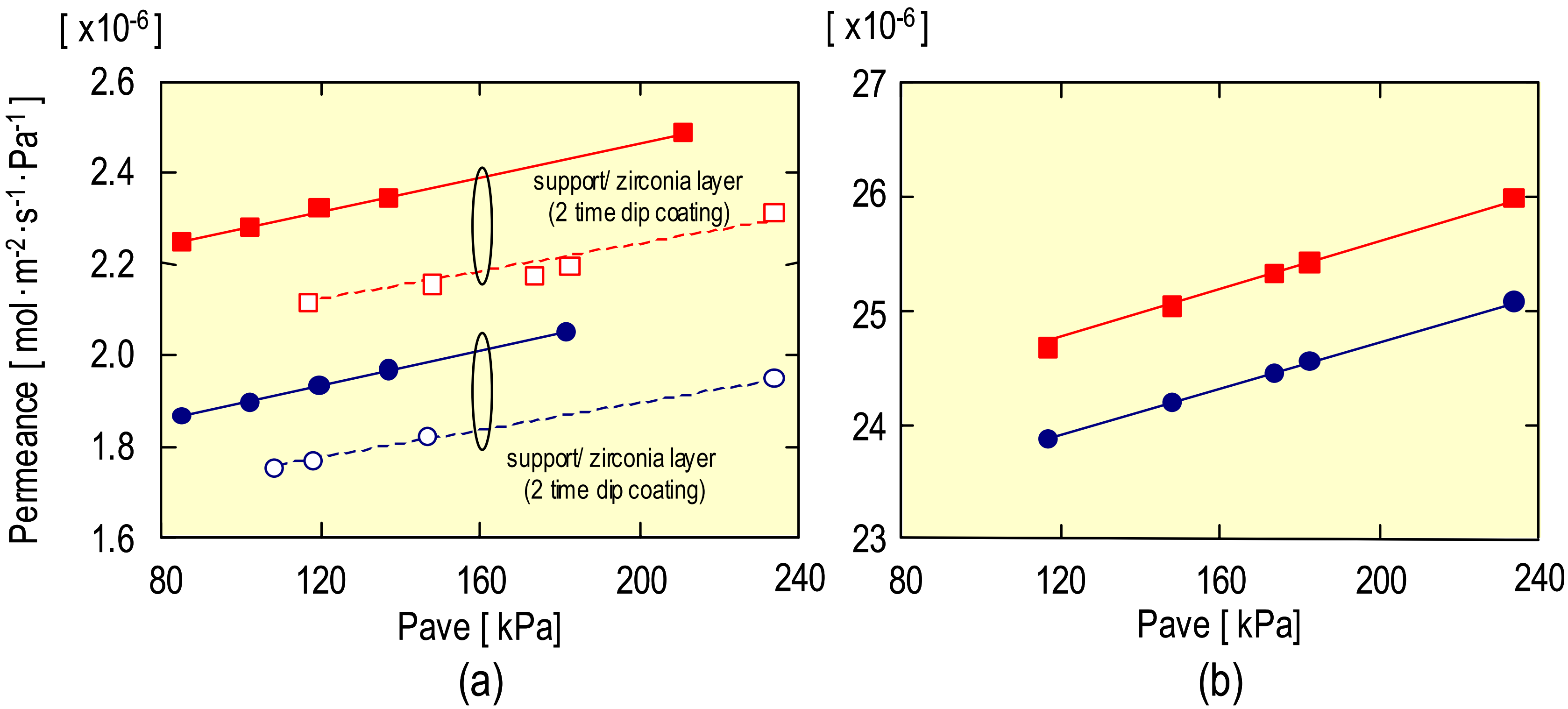
SEM image of the top surface of supported YSZ membrane fired at 750°C

Technical Progress (ASU)

- <u>**Helium permeation test for supported YSZ membranes**</u>

The permeance of He for YSZ layer was calculated by using resistance-in-series model.

The calculated pore diameter (~110nm) for YSZ supported membrane was in good agreement with that measured from mercury porosimetry.



Average pressure dependency of He permeance at room temperature;
(a) α-alumina support and supported YSZ membrane, (b) calculated YSZ layer

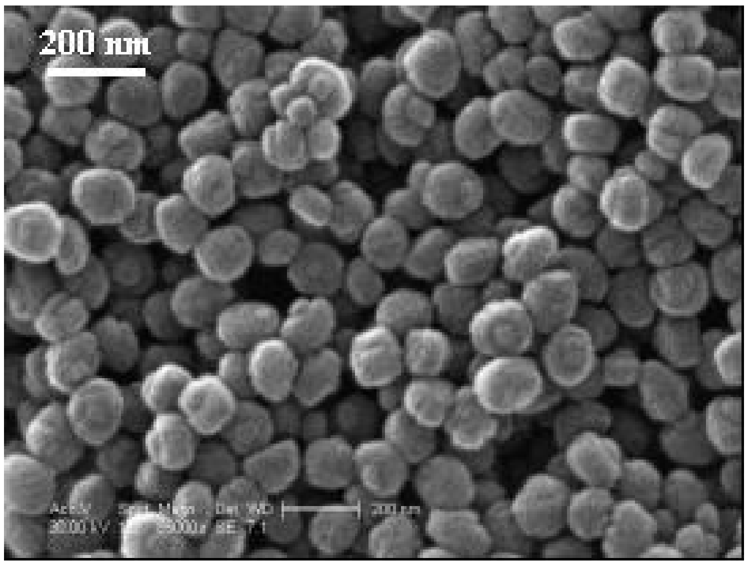
Technical Progress (ASU)

- **Preparation of silicalite suspension by hydrothermal synthesis**

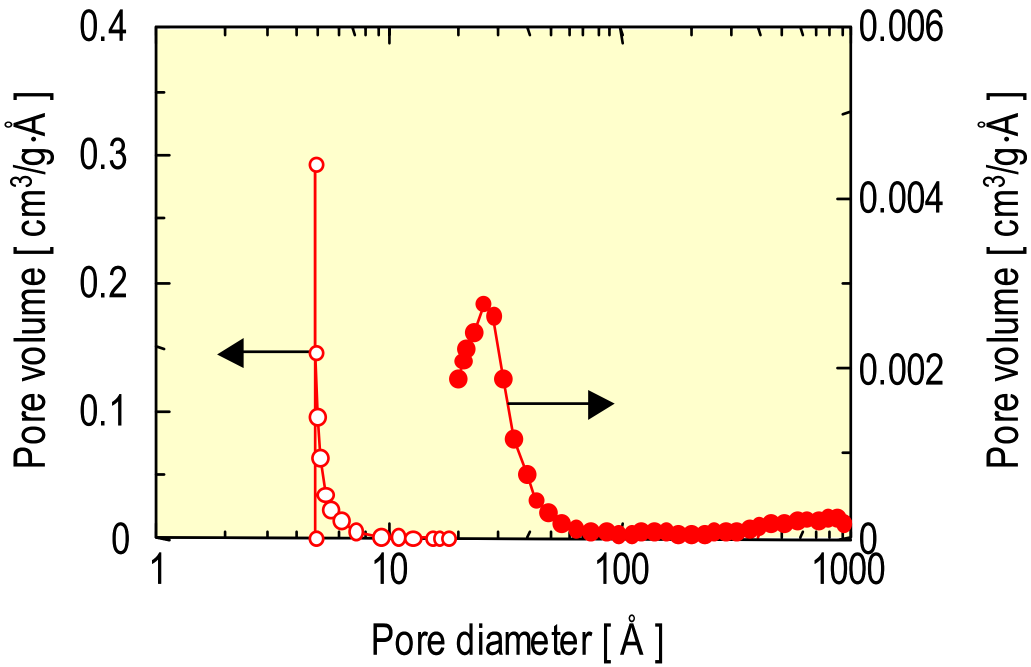
Silicalite seed particle size: ~100nm (hydrothermal synthesis condition: 120^{o}C, 12h)

Pore diameter of micropores by N_2 adsorption porosimeter (H-K method): 5.5 Å (intracrystalline pores of silicalite)

Pore diameter of mesopores by N2 adsorption porosimeter (BJH model): 30-40 Å (grain boundaries created between zeolite crystallites)



SEM image of the surface of silicalite seed layer on α-alumina substrate



Pore size distribution of silicalite powder by N_2-adsorption

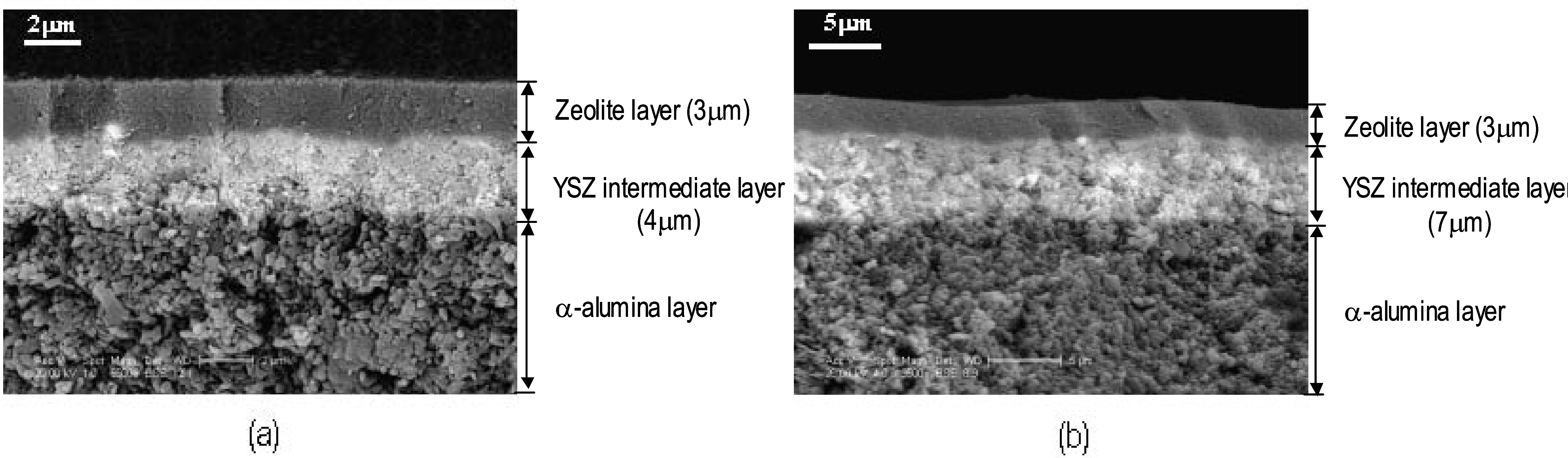
Technical Progress (ASU)

- <u>**Preparation of silicalite membranes by template-free synthesis**</u>

  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°C, 4h); (a) 1 time dip coating (YSZ), (b) 2 time dip coating (YSZ)

Technical Progress (ASU)

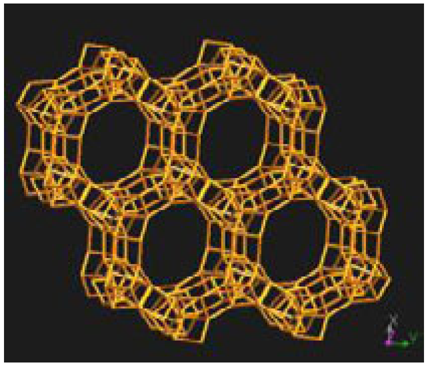
- **Membrane quality examined by xylene pervaporation separation (at 25°C)**

Molecule size

p-xylene 0.58 nm

o-xylene 0.68 nm

Silicalite pore size: 0.6 nm



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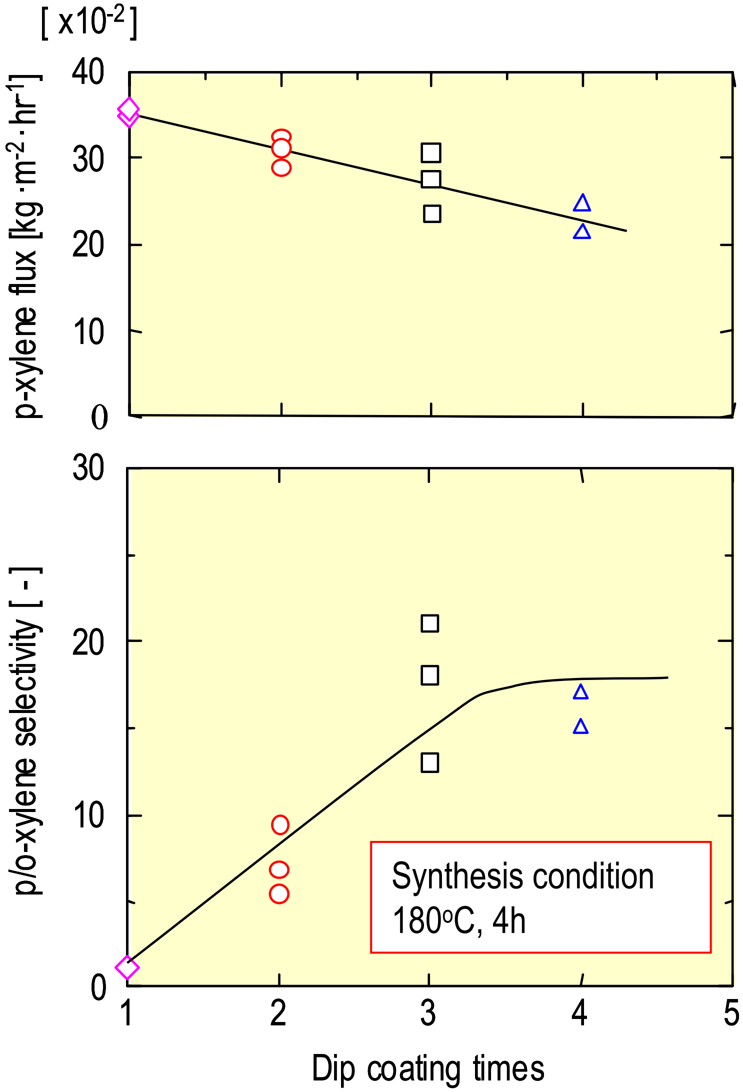
Molecular sieving effect by MFI structure

Optimization of dip coating times

Membrane quality can be substantially improved on supports with a good quality seed-layer .



Effect of dip coating times with silicalite suspension on p-xylene separation performance for silicalite membranes without zirconia intermediate layer

Technical Progress (ASU)

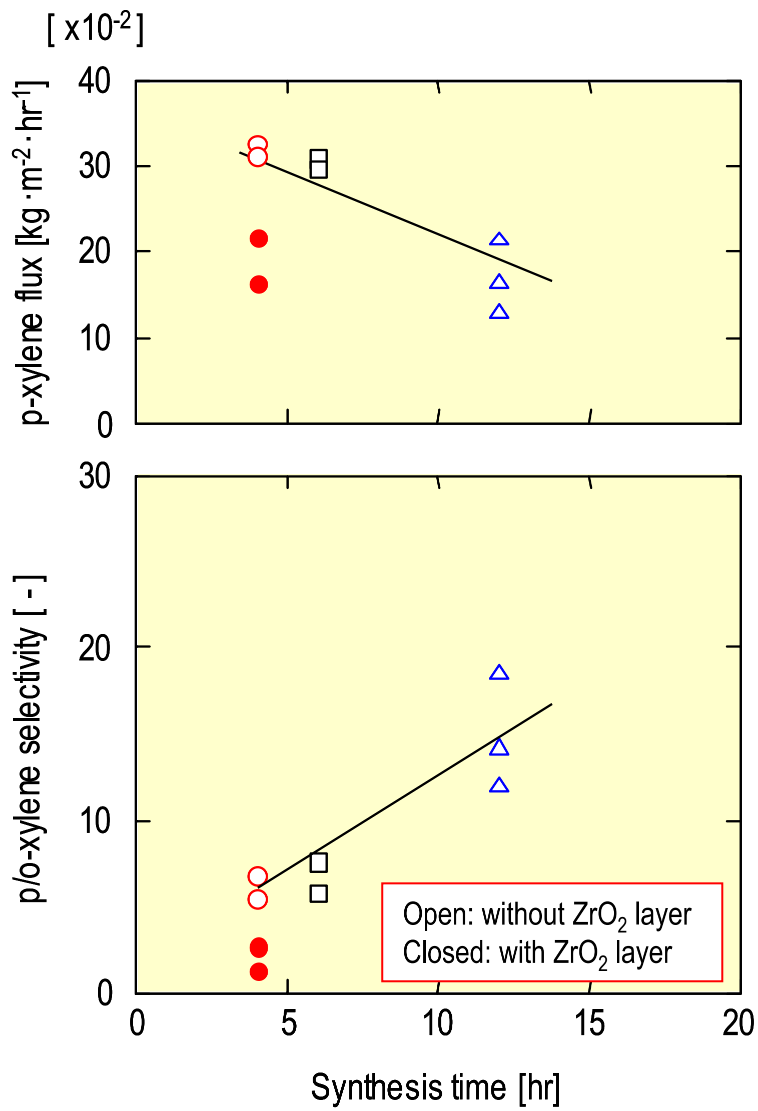
- Membrane quality examined by xylene pervaporation separation (at 25^oC)

Optimization of synthesis time

The p/o-xylene selectivity increases with synthesis time, while p-xylene flux decreases with synthesis time.

The p-xylene separation performance for silicalite membranes with ZrO_2 intermediate layer is less than those for the membranes without ZrO_2 intermediate layer.

The optimum calcinations program for silicalite seed layer with ZrO_2 intermediate layer is being examined.



Synthesis time dependency of p-xylene separation performance for silicalite membranes (2 time dip coating with silicalite suspension)

Technical Progress (ASU)

- <u>Preparation for hydrogen separation experiments</u>

Installation of H_2 cylinder cabinet required by the safety plan
Set up the multi component gas permeation and separation unit for silicalite membrane characterization

H_2 cylinder cabinet

Multi component gas permeation unit

Technical Progress (OSU)

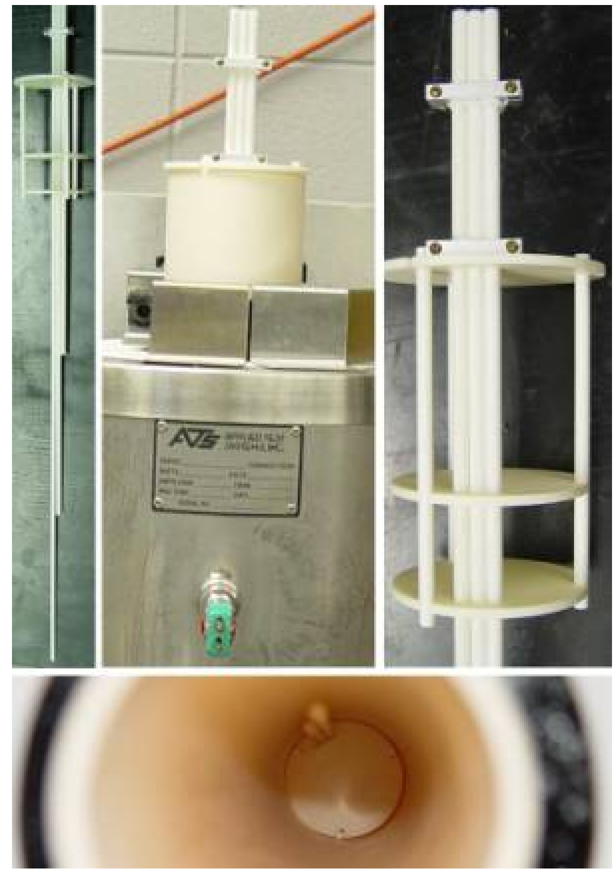
• Centrifugal support casting

• *Custom Delron® bowls*
• *Two tubular specifications*
    • *L tubes (∅: 25mm; L: 0.6m)*
    • *S tubes (∅: 10mm; L: 10cm)*

Custom tubes complemented by commercial tubes

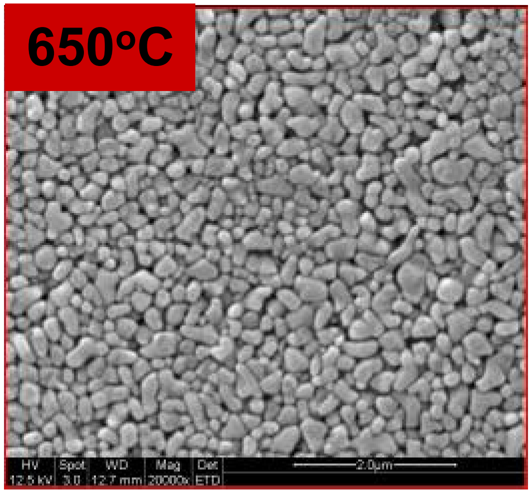
• Multi-zone Furnace

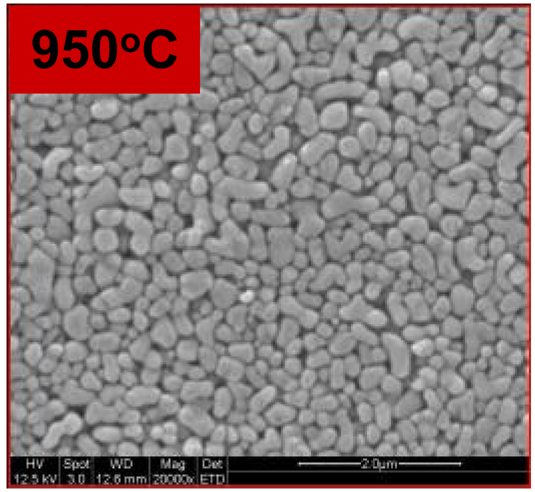
• *Controlled tubular support firing*
• *Three zone furnace*
• *Three element & sample TCs*

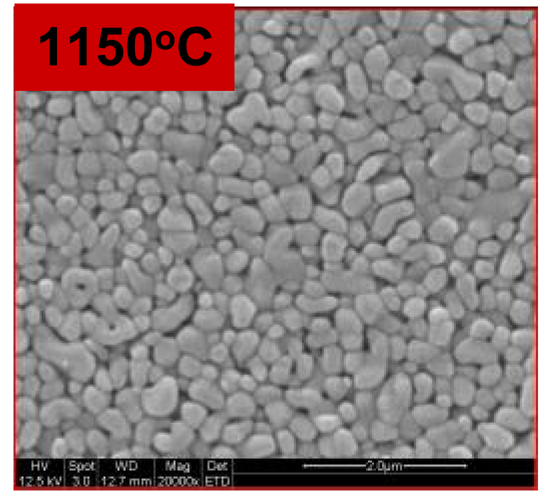


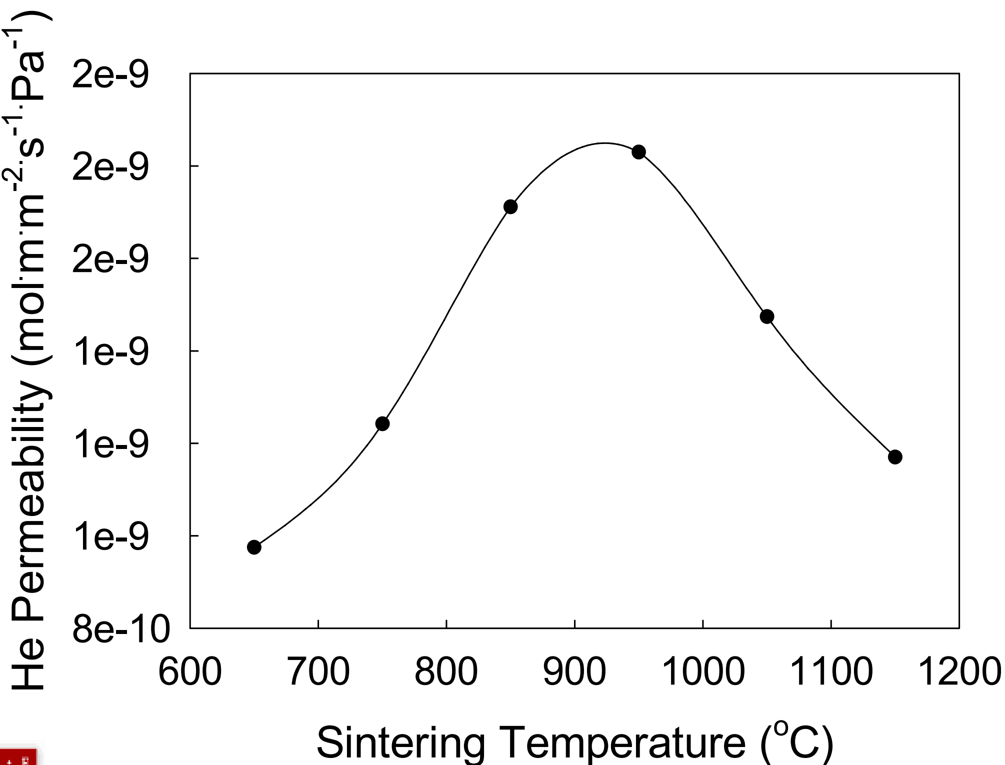
Technical Progress (OSU)

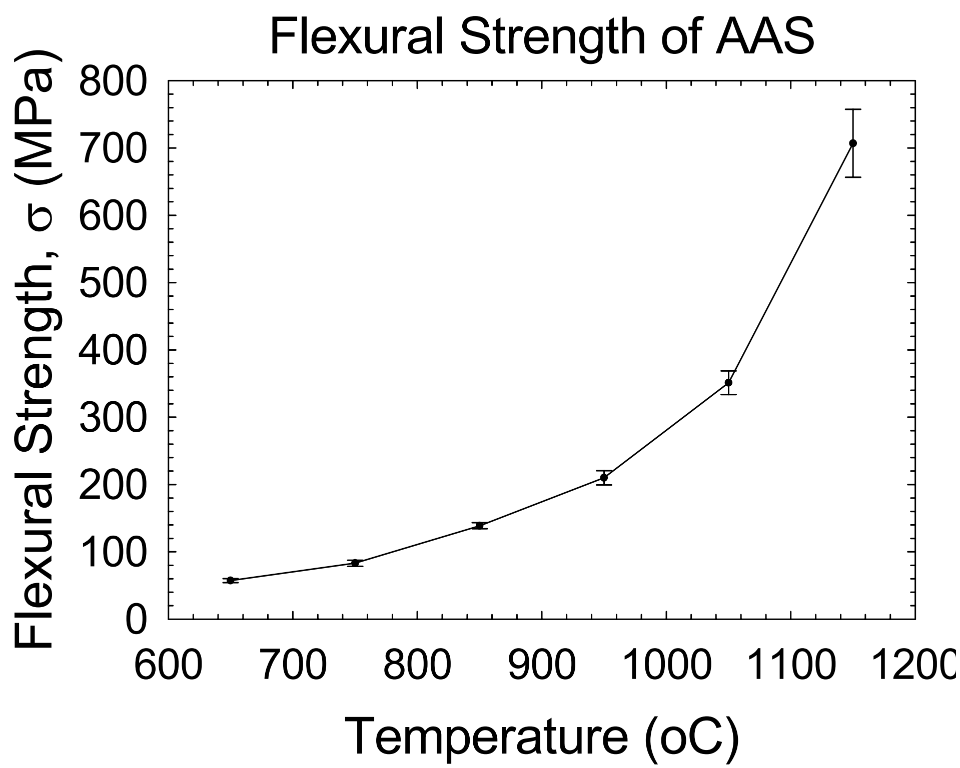
- **α-Al_2O_3 support (AKP30, HNO_3)**





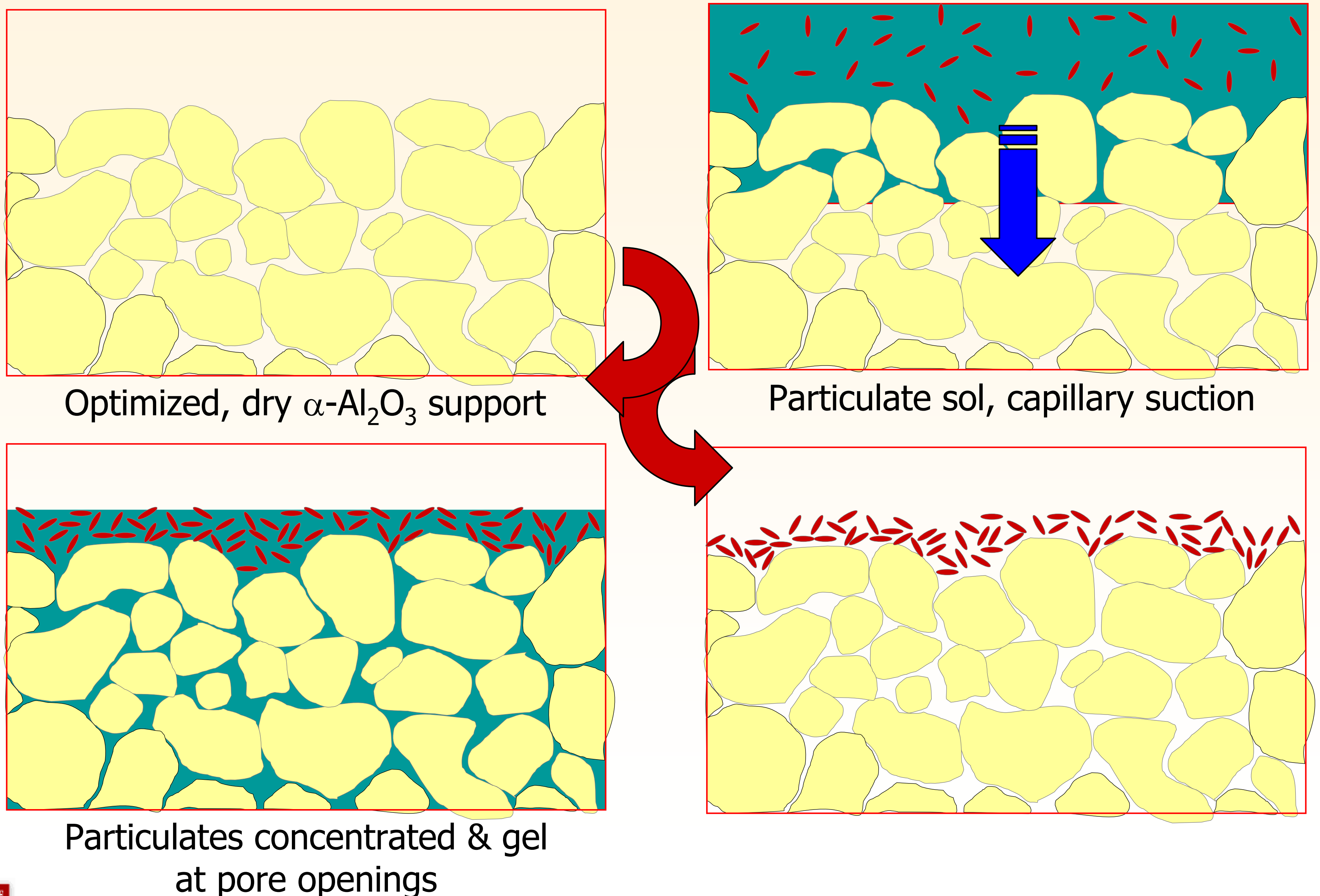






Technical Progress (OSU)

- **Slip casting: Intermediate layer**



Technical Progress (OSU)

- **Slip casting of commercial tubes**

- *Generic slip casting apparatus*

- *Initial results for intermediate layers appear promising*

- *Acquisition of controlled velocity mechanical lift elevator*

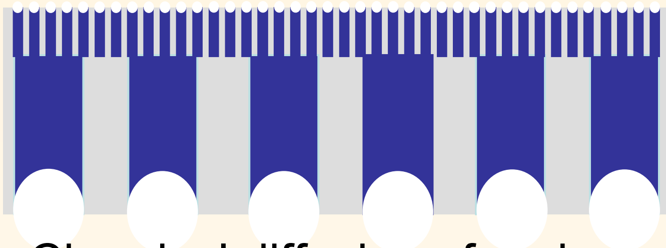
- *Flow coating of large commercial tubes*

- *Flow coating of custom porous tubes*

Technical Progress (OSU)

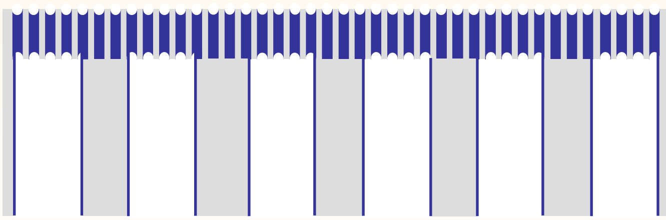
- **Permeation Porometry**

(a)



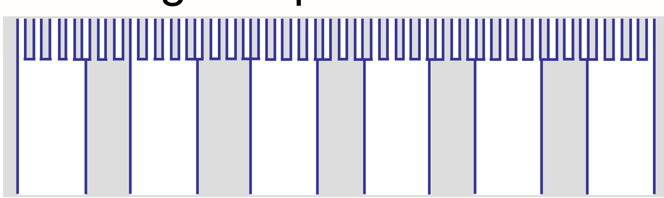
Chemical diffusion of probe through saturated structure ➔
- Membrane and/or support saturated (a) & (b)

(b)

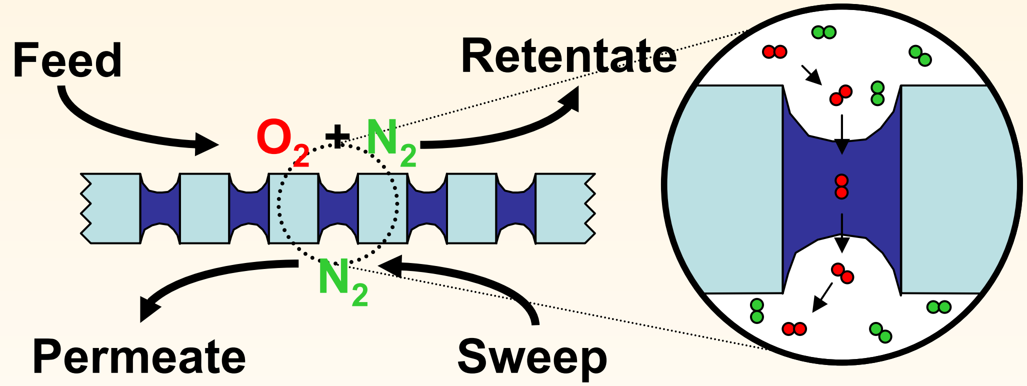


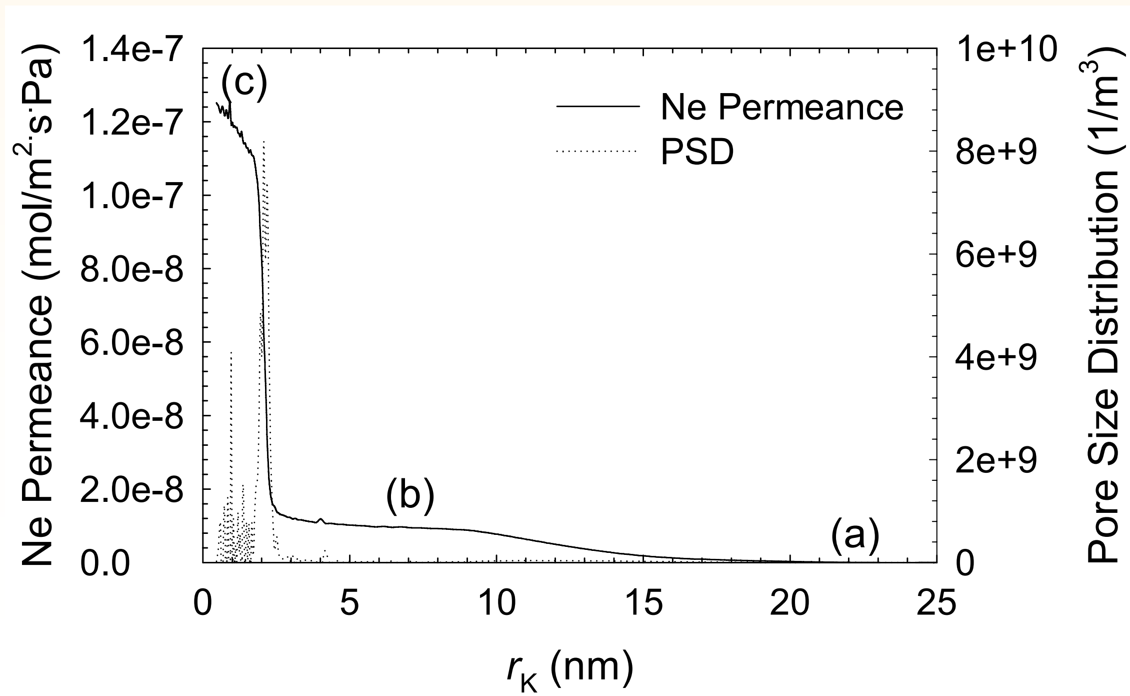
Knudsen diffusion of probe through emptied structure

(c)



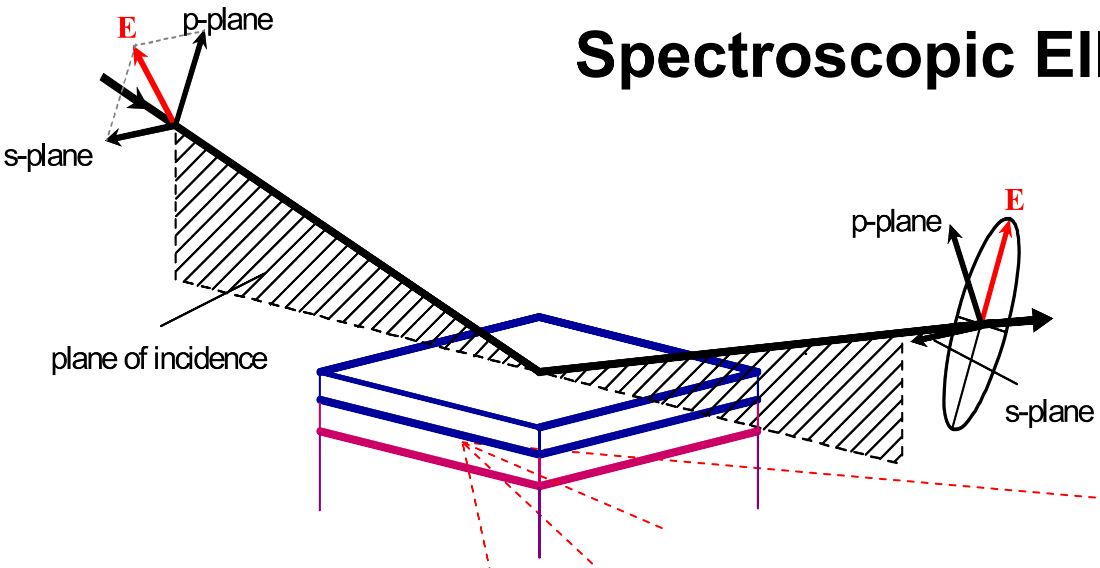
Determination of the Active pore size distribution



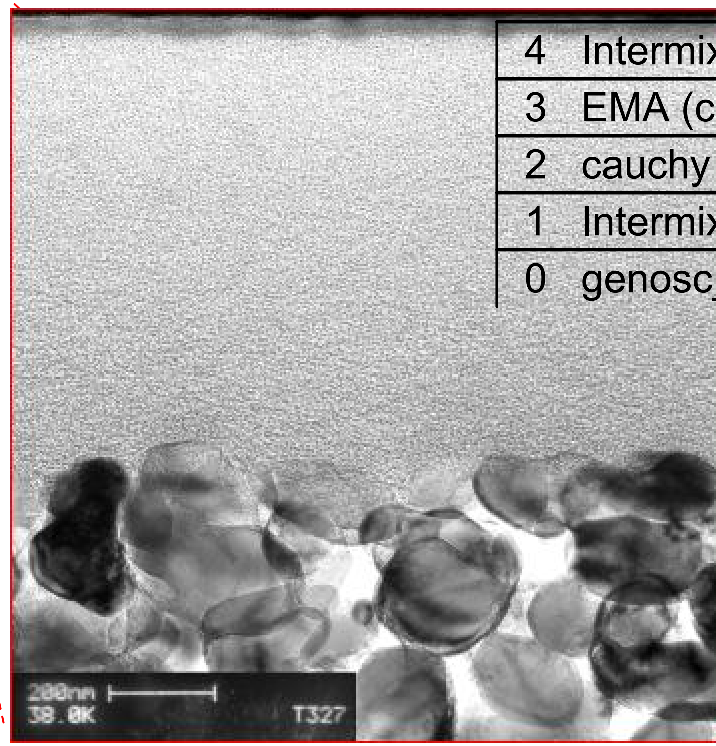


Technical Progress (OSU)

Spectroscopic Ellipsometry



- **Membrane Structure**
  - *AKP30 HNO_3 stabilized α-Al_2O_3*
  - *Generalized oscillator model*
  - *Single layer γ-alumina membrane*
  - *Cauchy dispersion*
  - *Bruggeman effective media approximation*



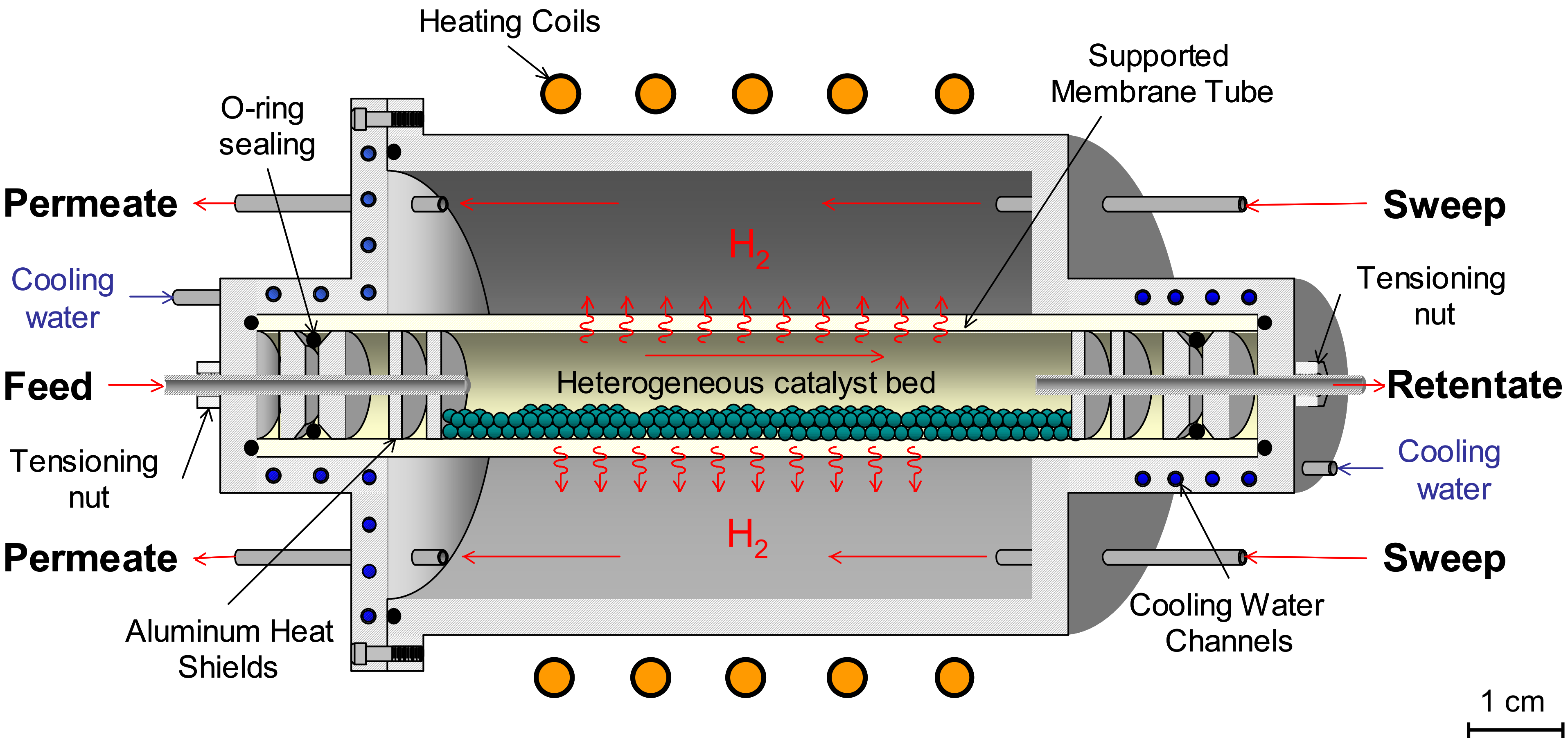
4	Intermix	7.744 nm
3	EMA (cauchy)/35.6% void	743.430 nm
2	cauchy	0.000 nm
1	Intermix	48.915 nm
0	genosc_al2o3	1 mm

- **SE Attributes**
  - *Refractive index*
  - *Extinction coefficient*
  - *Layer thickness*
  - *Porosity*
  - *Roughness, etc.*

Technical Progress (OSU)

• Membrane Reactor Approach

- *Reactor shell α-Al_2O_3*
- *Stainless steel end-caps*
- *Cooling water unnecessary*
- *O-ring seals viable*
- *Heating cable wrap*
- *Multiple tensioning nuts*



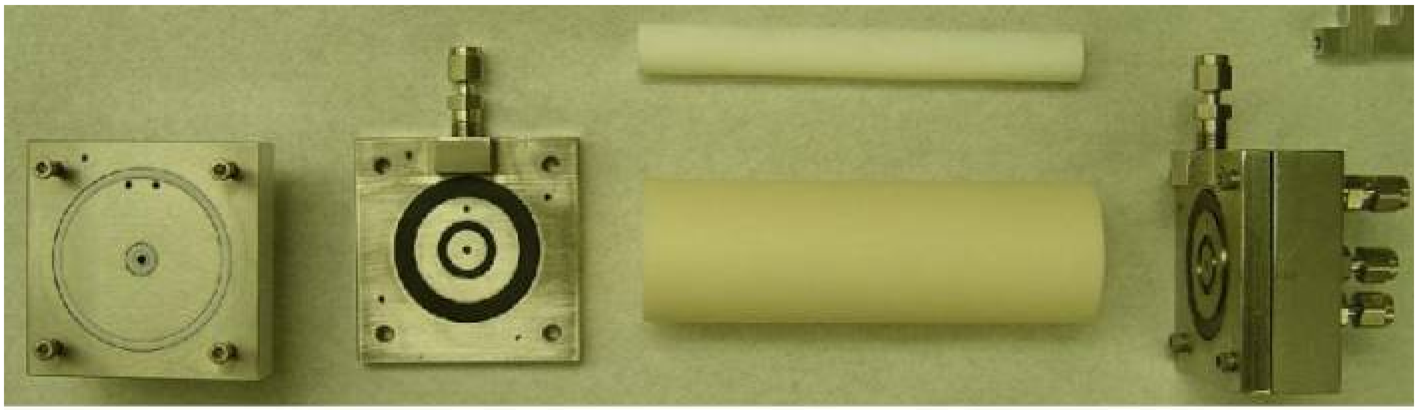
Technical Progress (OSU)

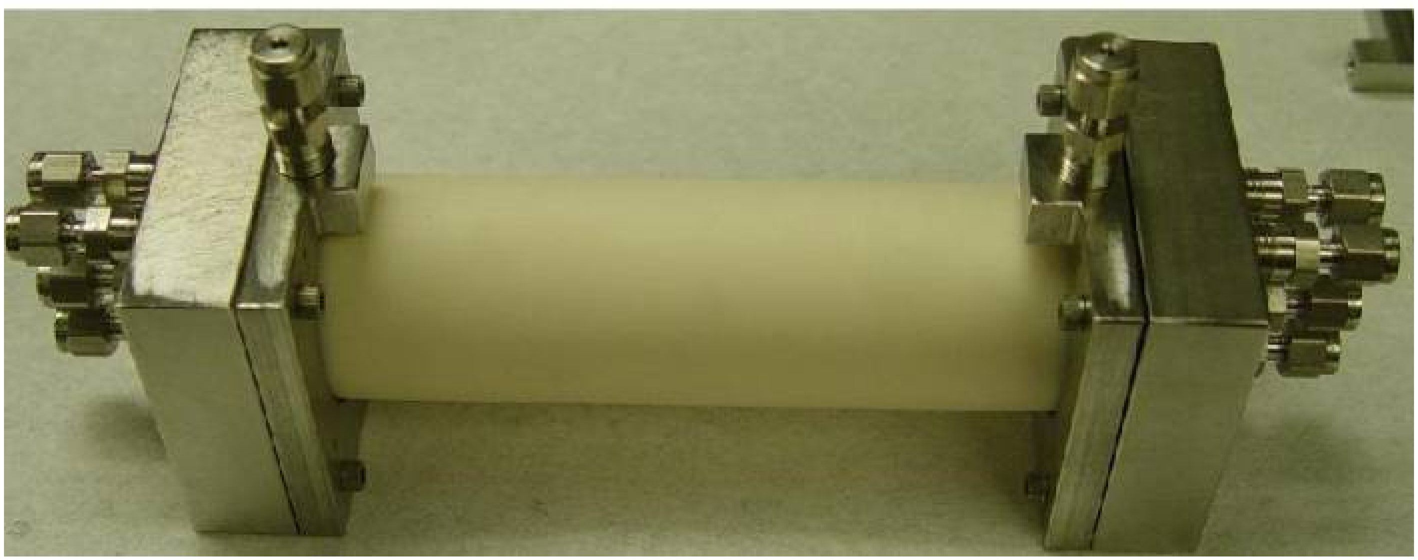
- **Large Membrane Reactor**
  - *Incorporates large tube*
  - *Max operating temp $650^{o}C$*
  - *Simple construction*
  - *Cylindrical design*
  - *Commercial ceramic tube*
  - *Stainless steel end-caps*

Technical Progress (OSU)

• Small Membrane Reactor

- *Colloidally cast tubes*
- *Small membrane test tubes*
- *Commercially available tubes*
- *Compact design*
- *Stainless steel end-caps*
- *Elastomer seals*

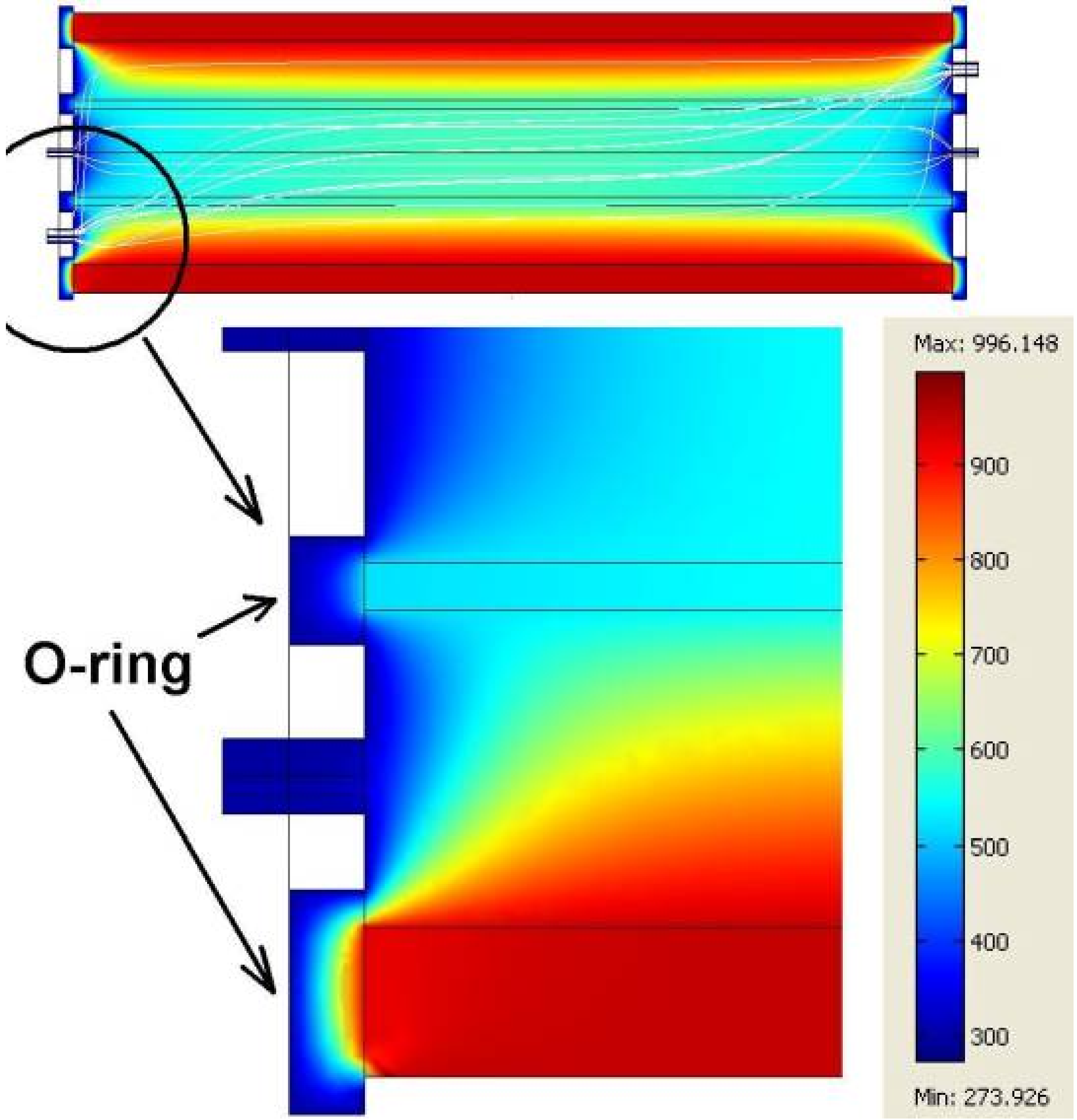




Technical Progress (OSU)

- <u>**Comsol Thermal Modeling**</u>

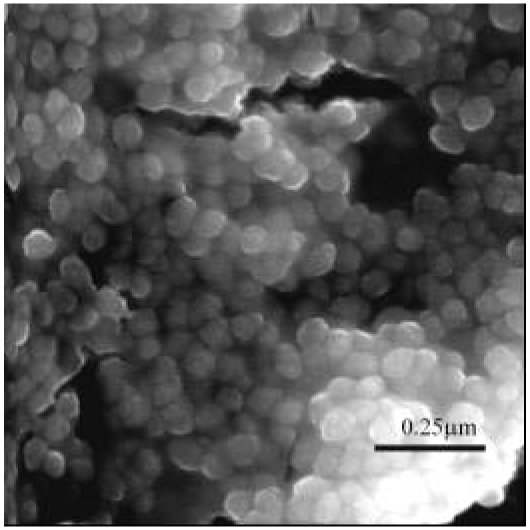
- *Initial thermal modeling*
- *Uniform hot-zone*
    - *1000^{o}C heating generates ~550^{o}C at Reactor center line*
- *Full length heating coils*
    - *Expected thermal damage to elastomer seal*
    - *Reduce heating coil length*
- *Expected asymmetry due to gas flow in model is not present!*



Technical Progress (NMT)

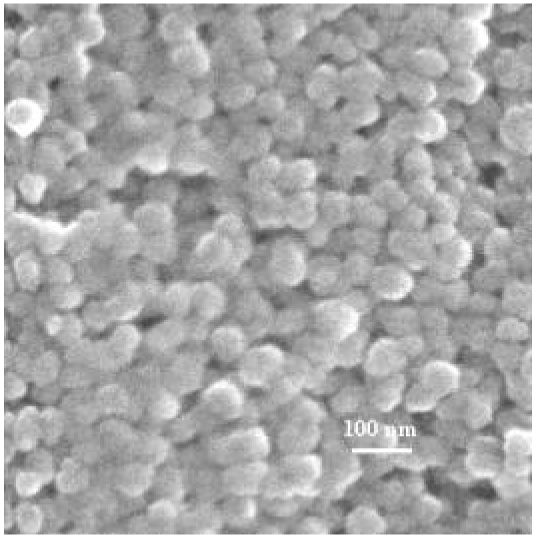
- **Microwave synthesis of silicalite nano particles**

  Silicalite nanoparticle synthesis efficiency can be dramatically enhanced by microwave heating, i.e. shorter time and less energy consumption.



Microwave heating 50°C 6 h + 120°C 1 h

Conventional heating at 65°C for 360 hours



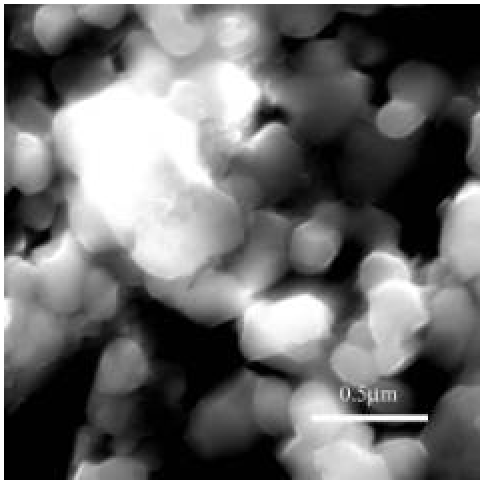
  - *Silicalite nanoparticle synthesis*

Synthesis Methods	Synthesis conditions	Particle size
Conventional heating, one step	*360 hours at 65 ℃*	*55~65 nm*
Microwave heating, one step	*12 hours at 90 ℃*	*70~80 nm*
Microwave heating, two steps	*6 h at 50℃ + 1 h at 120℃*	*50~60 nm*

Technical Progress (NMT)

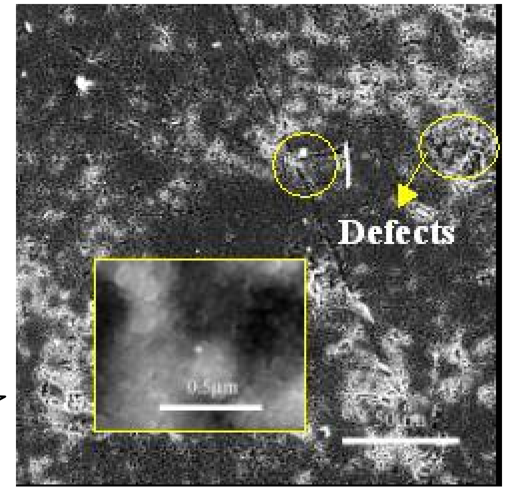
- <u>Coating silicalite nanoparticle seed layer</u>

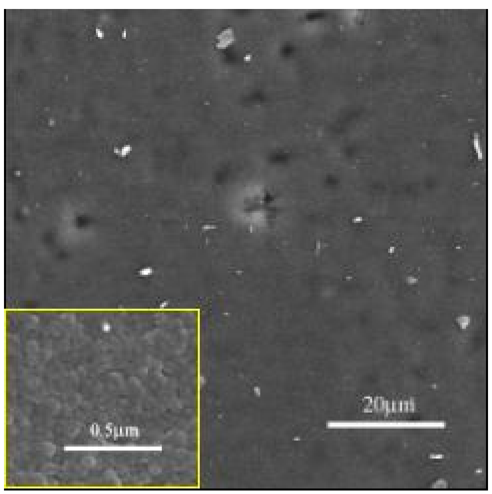
  Solid content; pH; dipping time; repeating …



One-time coating: PS ~60 nm; pH ~7
Result: *Poor coverage)*

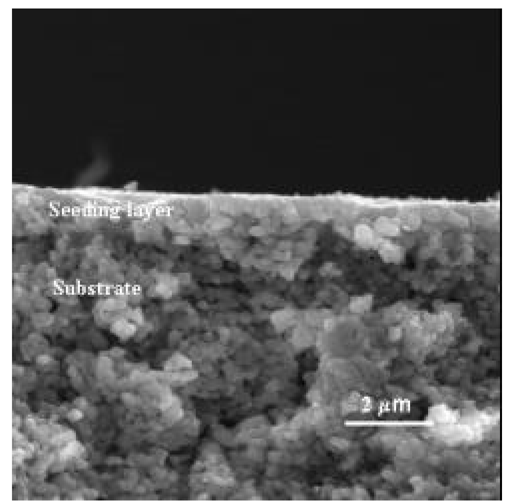
One-time coating: PS ~60 nm; pH 3~4
Result: *Large defects*





Two-time coating: PS ~60 nm; pH 3~4
Result: *Good*

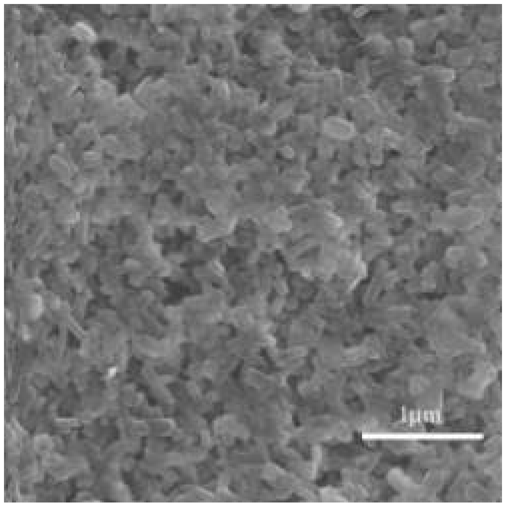
Cross-section of the supported seed layer



Technical Progress (NMT)

- **Secondary growth to inter-grown membranes**

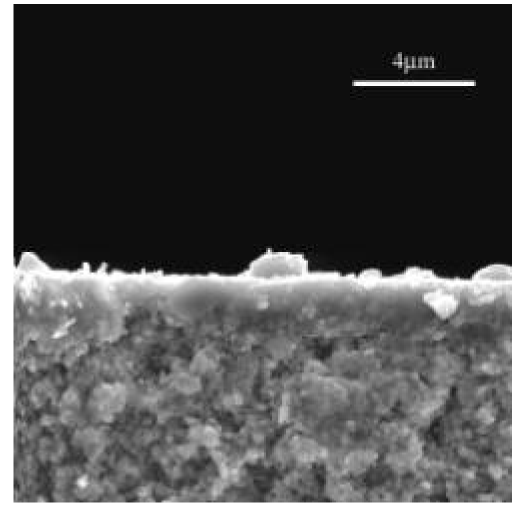
  Using template-free and Al-free precursor

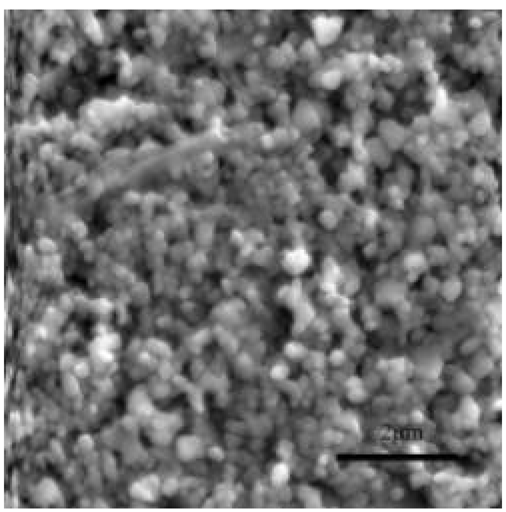


Secondary growth by conventional heating at 180°C

Surface

Cross-section

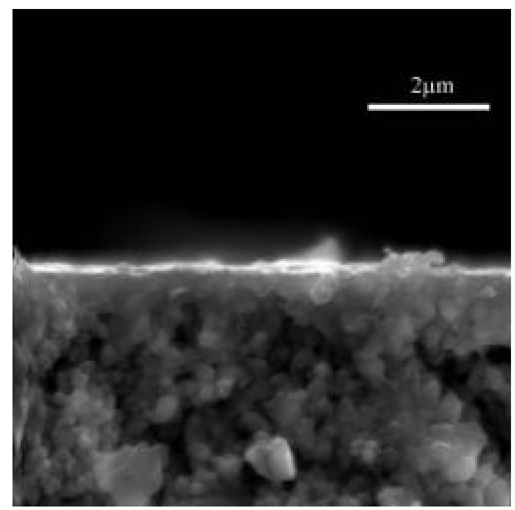




Secondary growth by microwave heating at 180°C

Surface

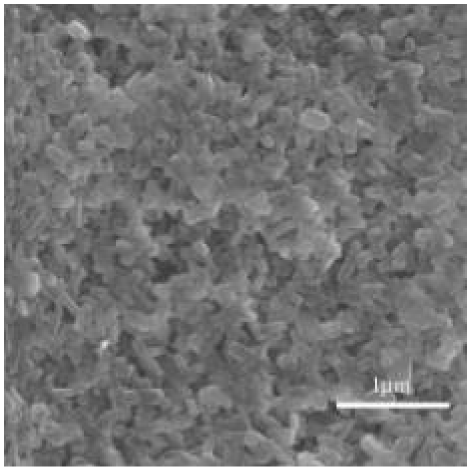
Cross-section

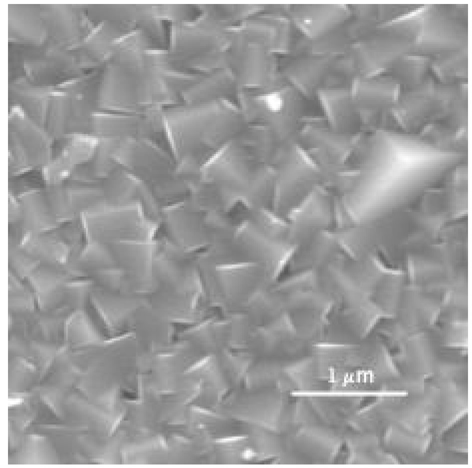


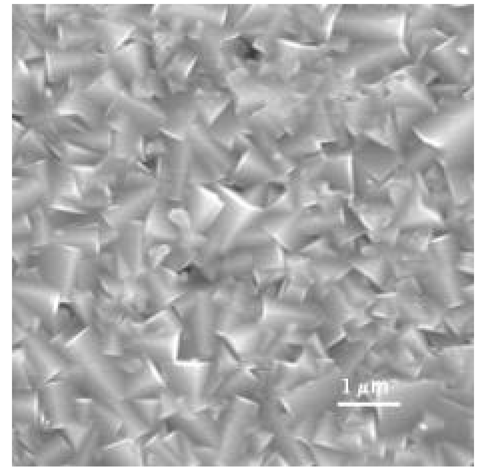
Technical Progress (NMT)

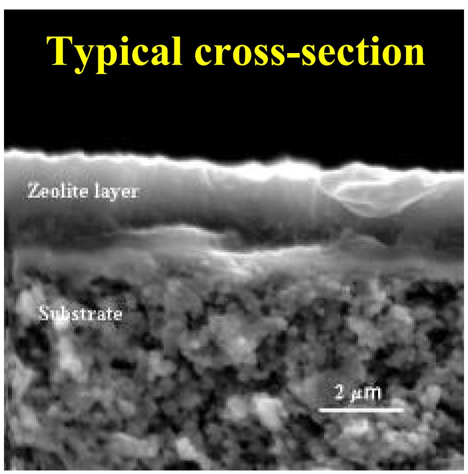
- <u>**Secondary growth to inter-grown membranes**</u>

  *Template-free precursor*s with and without Al sources







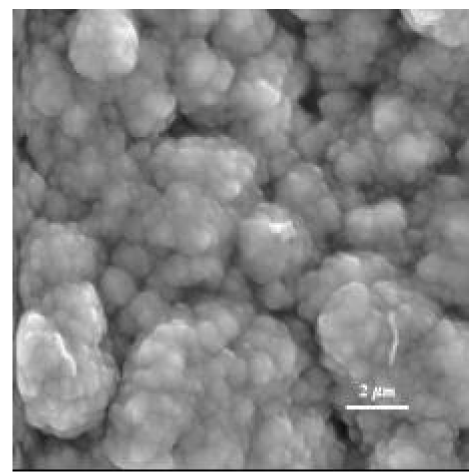


Si/Al: ∞

Si/Al: 65

Si/Al: 50

Si/Al: 40

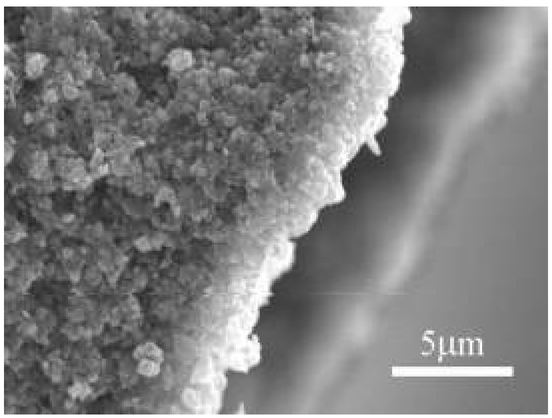


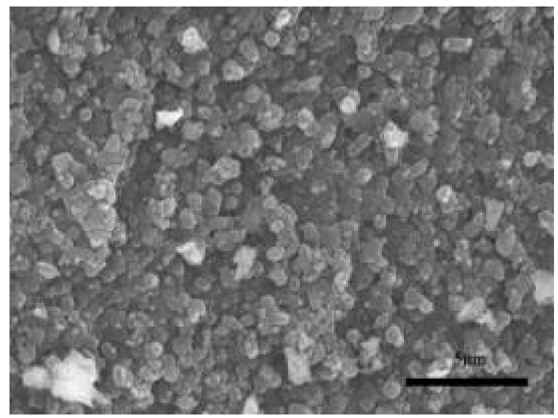
Conventional heating

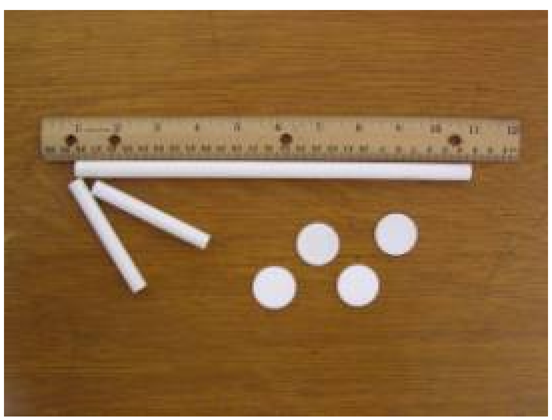
Technical Progress (NMT)

- **Synthesis of tubular silicalite membrane by in situ crystallization**
  (Tube: α-Al_2O_3 top layer PS ~0.2 μm; Pall Co.)

- **Separation tests**
  p-/o- xylene vapor (50:50 mixture) separation factor >30 at 250^{o}C and ~ 1kPa
  CO_2/H_2 Separation factor of 11.3 at 23^{o}C.







Technical Progress (UC)

- **Catalyst Preparation**

  Synthesized ferrite based inverse spinelsincorporated with various transition/non-transition

  Ammonia assisted co-precipitation route explored for high yield preparation of various modified ferrite catalysts using ultrahigh dilute metal nitrate precursor solutions.

  UCFe-1 to UCFe-7 were obtained by the above method. Successfully functionalized the catalyst surface to attract CO (weak base), repel CO_2 (weak acid) and retain water molecules.

  A series of similar catalyst obtained byultrasonic treatment were designated as UCFe-1us to UCFe-7us.

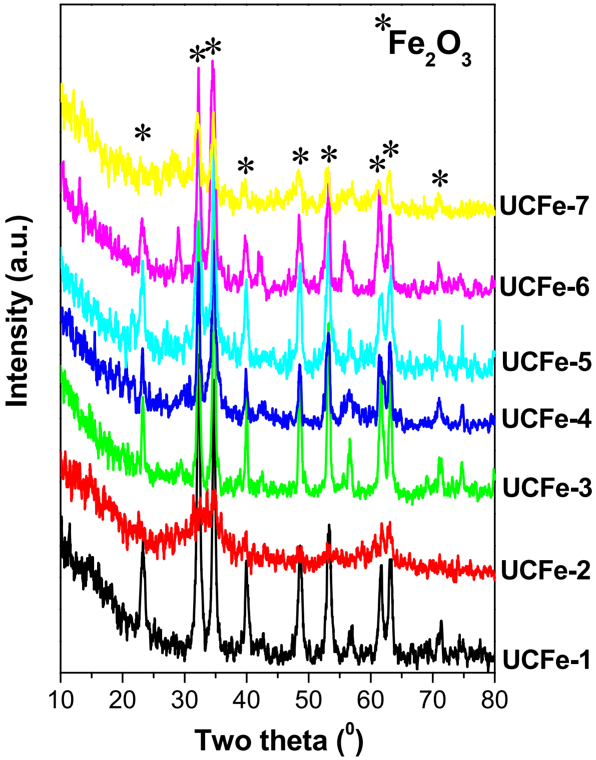
  A new family of sulfur tolerant (ST) catalysts developed (UCST-1 to UCST-5) using similar synthetic methodology (as above).

BET Surface area, XRD phase, and Crystallite size

Catalyst	BET SA (m^2g^{-1})	XRD phase┴	Cryst. size (nm)	XRD phase*
UCFe-1	81.7	Fe_2O_3 type	12.5	Fe_3O_4 type
UCFe-2	175.9	Fe_2O_3 type	10.1	Fe_3O_4 type
UCFe-3	34.0	Fe_2O_3 type	16.3	Fe_3O_4 type
UCFe-4	80.1	Fe_2O_3 type	11.8	Fe_3O_4 type
UCFe-5	75.3	Fe_2O_3 type	10.1	Fe_3O_4 type
UCFe-6	46.1	Fe_2O_3 type	10.7	Fe_3O_4 type
UCFe-7	95.9	Fe_2O_3 type	7.1	Fe_3O_4 type
UCFe-1us	50.5	Fe_2O_3 type	15.3	Fe_3O_4 type
UCFe-2us	130.5	Fe_2O_3 type	7.8	Fe_3O_4 type
UCFe-3us	60.7	Fe_2O_3 type	15.1	Fe_3O_4 type
UCFe-4us	51.4	Fe_2O_3 type	13.1	Fe_3O_4 type
UCFe-5us	43.6	Fe_2O_3 type	12.9	Fe_3O_4 type
UCFe-6us	30.3	Fe_2O_3 type	10.4	Fe_3O_4 type
UCFe-7us	97.9	Fe_2O_3 type	6.6	Fe_3O_4 type

┴(PDF-ICDD: 33-0664) ex situ; *(PDF-ICDD: 26-1136) in situ

Technical Progress (UC)



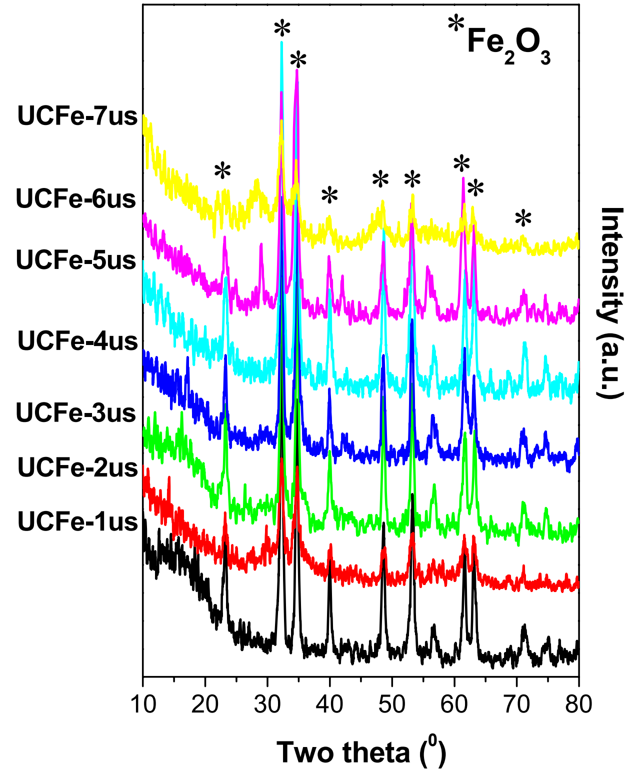
- <u>**Catalyst Characterization**</u>

Fe_2O_3 type phases, prerequisite for the active Fe_3O_4 inverse spinel phase.

Fe_3O_4 phase observed in the spent catalysts.

Preliminary Raman characterization gave insight into the existence of Fe_3O_4 phase

Appropriate stoichiometry exists between 3+ and 2+ species in order maintain the redox couple needed for the progress of WGS reaction.



Laser Raman Spectrometer

Rigaku D-2000 Powder X-ray diffractometer

Technical Progress (UC)

- **Catalytic Activity**

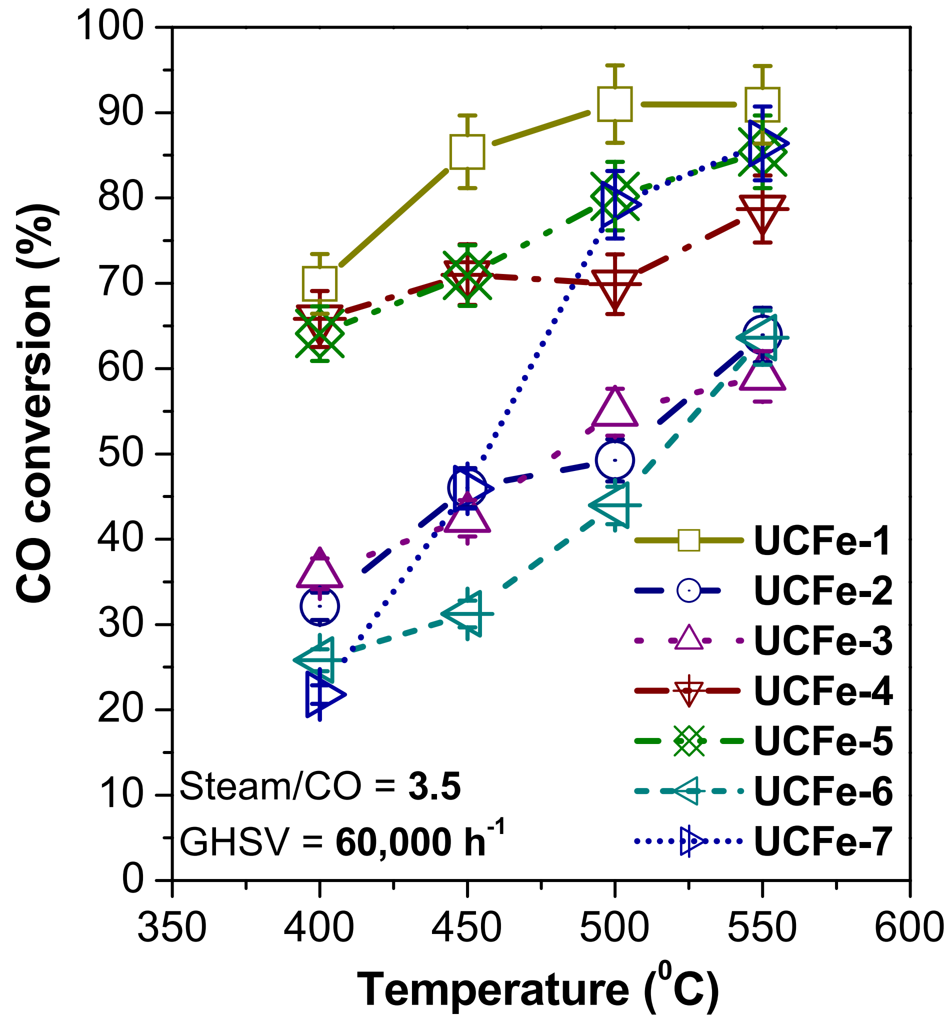
Test performed in H_2 lean conditions to mimic membrane reactor (MR) conditions.

Catalysts tested in exceedingly H_2O-rich environments to mimic MR conditions.

The WGS reaction was performed at very higher temperature (500– 550 ℃).

Exceedingly higher space velocities than industrial were employed.

WGS activity (% CO conversion) of 94-97 % was observed in single pass.



WGS reaction activity over modified Ferrite catalysts

Technical Progress (UC)

- **Catalytic Activity**

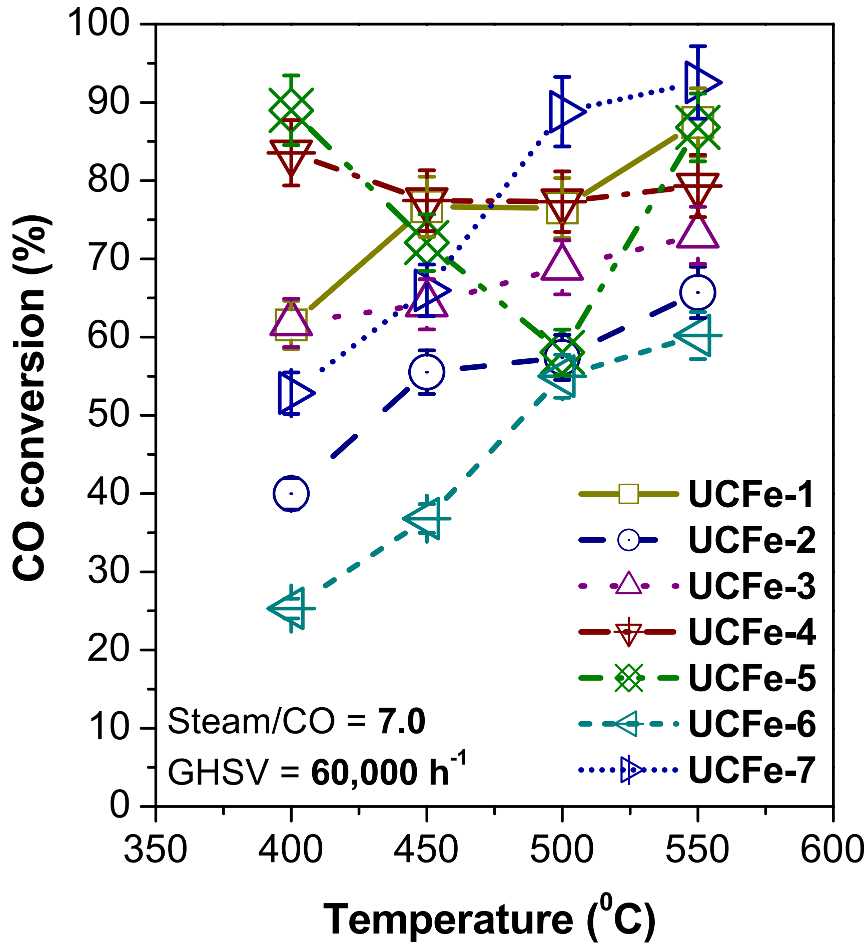
Parameters pertaining to pretreatment conditions were optimized.

WGS activity tested as function of operating temperature between 400 to 550°C.

Maximum activity observed at 550°C, which also happens to be most favorable for the silicalite membranes operations.

UCFe-7 (primarily Fe_2O_3/CeO_2) catalysts is found to be very promising, its activity results are encouraging for possible commercialization.

The ultrasonic treated catalysts were found to be less active for WGS reaction than their untreated counterparts.



WGS reaction activity over Ferrite-based catalysts

Future Work for FY06 and FY07

- ***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 FY06 and FY07

- ***Synthesize tubular silicalite membranes by hydrothermal method***
- ***Identify optimum conditions for microwave synthesis of colloidal silicalite suspension and template-free synthesis of disk-shaped silicalite membranes by microwave method***
- ***Establish the micro-wave system for tubular membrane synthesis***
- ***Optimize the secondary growth synthesis step; and perform preliminary synthesis of tubular silicalite membranes by microwave method***

Future Work for FY06 and FY07

- *Optimize methods for coating intermediate layer on tubes*
- *Complete development of support tubes by colloidal casting*
- *Coat Intermediate layer deposition on the support tube*
- *Develop and design intermediate layer/tube Leak/flow testing membrane module*

Future Work for FY06 and FY07

- ***Optimize the composition of Fe_3O_4/Cr_2O_3 based catalysts (HTS catalysts) with specific atoms***
- ***Perform UHT-WGS reaction in CO_2-rich environment***
- ***Test the performance of sulfur-tolerant hybrid WGS catalysts developed by simulating SO_2 & H_2S in the feed stream***
- ***Study catalyst deactivation phenomena and plausible regeneration with the help of Operando techniques***

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 layer, zeolite membranes with molecular sieving properties, tubular support and modules, and catalysts with improved properties.

- **Proposed Future Research**:

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