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

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Overview

Timeline
• Project start date: July 1, 2005
• Project end date: August 30, 2010
• Percent complete: 60%

Budget
• Total project funding
  – DOE $1,999,727
  – Contractor: $501,310
• Funding received in FY08: $459,553
• Funding for FY9: $0

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

Partners
• University of Cincinnati
• Arizona State University
• Ohio State University
Relevance - Project 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
Approach - Zeolite Membrane Reactor for Water-Gas Shift Reaction

Zeolite Membrane Requirements:

- Operated in 350-550°C
- Chemically stable in H₂S, thermally stable at ~400°C
- Hydrogen permeance ~ $5 \times 10^{-7}$ mol/m².s.Pa
- Hydrogen selectivity ~ 50

- Water-gas-shift reaction at one temperature (about 400°C)
- Two product streams: H₂ (>94% purity) and CO₂ (>97 purity)
Approach- Chemical Stable Microporous MFI (Silicalite) and DDR-type Zeolite Membranes

Intersecting channels

MFI (Silicalite): 10-T-Ring intersecting channels of 5.1-5.6 Å in size

Cages separated by narrow windows

8-T-Ring, Windows of 3.6-4.4Å in size (studied as a reference)

Approach Counter-diffusion CVD of Silica for Improving Membrane Quality

- CVD reaction temp: 500°C,
- Bubbling temp: room temp.

Hydrothermal stability test shows this is less likely the result of CVD
Approach – CVD Narrowing Zeolite Pores to Further Improve Selectivity

methyldiethoxysilane (MDES)

<table>
<thead>
<tr>
<th></th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMOS</td>
<td>0.89nm</td>
</tr>
<tr>
<td>TEOS</td>
<td>0.95nm</td>
</tr>
<tr>
<td>MDES</td>
<td>0.4 × 0.9nm</td>
</tr>
</tbody>
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On stream CVD
Previous Technical Accomplishments
(Milestones Achieved)

- Obtain disk-shaped silicalite membranes on the desired intermediate layers with $\text{H}_2/\text{CO}_2$ perm-selectivity over 10 and $\text{H}_2$ permeance larger than $1 \times 10^{-7}$ mol/m$^2$.s.Pa

- Develop methods to fabricate tubular membrane support with desired intermediate layers

- Obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst but with much improved chemical stability $\text{SO}_2$ and $\text{H}_2\text{S}$ containing WGS reaction stream

- Develop a membrane module and sealing system for tubular membrane reactor that can be operated in the WGS conditions for at least 1 month

- Develop micro-wave synthesis method to prepare tubular silicalite membranes with $\text{H}_2/\text{CO}_2$ perm-selectivity over 10 and $\text{H}_2$ permeance larger than $1 \times 10^{-7}$ mol/m$^2$.s.Pa

- Obtain disk and tubular silicalite membranes with $\text{H}_2/\text{CO}_2$ perm-selectivity over 50 and $\text{H}_2$ permeance larger than $2 \times 10^{-7}$ mol/m$^2$.s.Pa
Technical Accomplishment: Synthesis of High Quality MFI-type Zeolite Membranes

- Synthesized by template-free secondary growth method to minimize intercrystalline gaps
- Post-CVD modification with TEOS to repair the defects
- Zeolite membranes can be prepared by microwave method
- Zeolite membranes can be grown on YSZ intermediate layer to improve chemical stability

P-xylene pervaporation flux ~ 1 kg/m².hr; p- to o-xylene (pervaporation) selectivity larger than 20
Technical Accomplishment - Gas Permeation/Separation Study

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>H₂</th>
<th>CO₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter, ( d_m ) (nm)</td>
<td>0.26</td>
<td>0.289</td>
<td>0.33</td>
<td>0.376</td>
</tr>
<tr>
<td>L-J Length, ( \sigma_m ) (nm)</td>
<td>0.255</td>
<td>0.283</td>
<td>0.394</td>
<td>0.369</td>
</tr>
<tr>
<td>Molecular Weight, ( M_w ) (g/mol)</td>
<td>4</td>
<td>2</td>
<td>44</td>
<td>28</td>
</tr>
</tbody>
</table>
Technical Accomplishment – Limited Separation Ability of Defect-Free Microporous Zeolite Membranes

\[ F_i = \left( \frac{\phi \alpha}{L_z} \right) \left[ \frac{8}{\pi R M_{W,i} T} \right]^{1/2} \exp\left(-\frac{E_{d,i}}{RT}\right) \]

\[ \alpha_{H_2/CO_2} = \left( \frac{M_{W_{CO_2}}}{M_{W_{H_2}}} \right)^{1/2} \exp\left(\frac{E_{d(CO_2)} - E_{d(H_2)}}{RT}\right) \]

The maximum H$_2$/CO$_2$ selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.
H$_2$/CO$_2$ selectivity of MFI type zeolite membrane can be effectively improved by CVD of MDES via controlled catalytic cracking deposition (CCD) in selective sites in zeolite pores.
Technical Accomplishment: Zeolite Membrane with High H$_2$ Selectivity Selectivity

Comparison of the CCD-modified zeolite membrane with literature membrane performance for H$_2$/CO$_2$ separation

H$_2$/CO$_2$ selectivity of 140 and H$_2$ permeance about 4x10$^{-7}$ mol/s.m$^2$.Pa at 450$^\circ$C
Technical Accomplishment: Gas Permeance at different Temperatures

Modified zeolite membrane exhibits molecular sieving properties
Technical Accomplishment – High Quality Tubular Supports Developed

• Application of intermediate layers onto tubular supports by flow coating
  – AKP30 coating:
    8 wt% AKP30 coating (w/ 0.1 wt% Darvan 821A, 1.2 wt% PVP) onto AA3 α-Al₂O₃ (provided by MetaMateria Partners) and Pall α-Al₂O₃ (Øp=0.8 μm) supports
  – γ-Al₂O₃ deposition:
    γ-Al₂O₃ deposition onto AKP30-AA3 supports with Böhmiet sol [AlO(OH)] mixed with PVA (3:2 by vol.)
Technical Accomplishment – High Quality Tubular Supports Developed (Cont’d)

AKP30-AA3 (surface)

γ-Al₂O₃-AKP30-AA3 (surface)

~600 nm γ-Al₂O₃
Technical Accomplishment – Sulfur Resistant WGS Catalyst Developed (Cont’d)

Effect of Time on stream on various modified ferrite catalysts in presence of $\text{H}_2\text{S}$

Sulfur Tolerant WGS Activity:
$\text{Fe}_{3-(x+y)}\text{Cr}_x\text{Cu}_y\text{O}_4 > \text{Commercial} > \text{Fe}_{3-x}\text{Ce}_x\text{O}_4 > \text{Fe}_{3-x}\text{Cr}_x\text{O}_4$
Technical Accomplishment - Preliminary Test of WGS on Zeolite Membrane Reactor

CO conversion under $H_2O/CO$ ratio of 1 and space velocity of 3500 h\(^{-1}\) in a disk-shaped silicalite membrane reactor with UC WGC catalyst – Membrane reactor gives higher CO yield.

Tubluar WGS reactor also set up and tested; Zeolite membrane exhibit good hydrothermal stability under WGS reaction conditions for about 1 wk.
Collaboration

• Within DoE H₂ Program
  – Arizona State University (membrane synthesis and WGS reaction)
  – University of Cincinnati (membrane modification and catalyst development)
  – Ohio State University (membrane support and module development)

• Outside of DoE H₂ Program
  – NGK Co. (Japan) (synthesis of DDR membranes)
  – Sintef Research (Norway) (CO₂ permselective membrane)
  – University of Victoria (Australia) (zeolite membrane synthesis)
  – Ecotality Inc. (US) (hydrogen storage technology)

Propose Future Work for FY09 and FY10

1. Fabrication of high quality membrane supports for growing silicalite membranes (OSU)
   a) Disk and tubular alumina supports
   b) Disk and tubular support with zirconia intermediate layer

2. Synthesis of high quality silicalite membranes by secondary growth and CVD modification (UC, ASU)
   a) $\text{H}_2/\text{CO}_2$ selectivity > 100, $H_2$ permeance > $5 \times 10^{-7}$ mol/ms.s.Pa
   b) Silicalite membranes on zirconia support with improved chemical stability

3. Separation and stability study of silicalite membranes (ASU, UC)
   a) Measuring single and mixture gas permeability and selectivity in larger temperature (200-500°C) and pressure (1-10 atm) range.
   b) Studying stability of the membranes in WGS gas stream conditions (with steam) for up to 1 month.
Propose Future Work for FY09 and FY10

4. Stability and kinetic study of new WGS catalyst (UC)
   a) Long term stability study in sulfur containing gas (about 1 month)
   b) Kinetic study of WGS reaction on the catalyst (UC)

5. WGS reaction on silicalite membrane reactor (ASU, UC)
   a) Modeling WGS reaction in zeolite membrane reactor with known permeation and kinetic data
   b) Improving membrane reactor system including setup (operable up to 20 atm and 550°C) and membrane module
   c) Experimental study on WGS reaction in silicalite membrane reactor
   d) Optimization of the performance of WGS reaction in the silicalite membrane reactor
   e) Studying stability of the membrane reactor for WGS reaction under optimum conditions.

6. Cost analysis of zeolite membrane reactor for WGS
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 and separation properties of high quality, stable zeolite membranes, and develop the zeolite membrane reactor for water-gas-shift reaction and hydrogen separation

• **Technical Accomplishment and Progress:**
  Improved understanding of synthesis and gas transport mechanism in zeolite membranes, developed and studied methods and techniques to prepare zeolite membranes with high $H_2$ permance ($>10^{-7}$ mol/m$^2$.s.Pa) and selectivity ($>100$) suitable for WGS membrane reactor application, and catalysts with improved properties for WGS reaction

• **Proposed Future Research:**
  Prepare high performance zeolite membranes and catalyst and study WGS reaction in zeolite membrane reactors.