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

Jerry Y.S. Lin, Henk Verweij, Peter Smirniotis and Junhang Dong

University of Cincinnati
Arizona State University
The Ohio State University

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Project ID: PD073

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Overview

Timeline

• Project start date: July 1, 2005
• Project end date: April 30, 2012
• Percent complete: 90%

Barriers

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

Budget

• Total project funding
  – DOE $1,999,727
  – Contractor: $501,310
• Funding for FY10: $50,000
• Funding for FY11: $388,009

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:

- Operate at 350-550°C
- Chemically stable in H₂S, thermally stable at ~400°C
- Hydrogen permeance ~ 5x10⁻⁷ mol/m².s.Pa
- Hydrogen selectivity ~ 50
- Two product streams: H₂ (>94% purity) and CO₂ (>97 purity)
Approach – Chemical Stable Microporous MFI (Silicalite) and DDR-type Zeolite Membranes

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

DDR: 8-T-Ring, Windows of 3.6-4.4 Å in size

(studied as a reference)

Intersecting channels
cages separated by narrow windows

Approach – Counter-diffusion CVD of Silica for Improving Membrane Quality

- CVD reaction temp: 550°C,
- Bubbling temp: room temp.

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

methyldiethoxysilane (MDES)

TMOS 0.89nm
TEOS 0.95nm
MDES 0.4 × 0.9nm

On stream CVD
Previous Technical Accomplishments  
(Milestones Achieved)

- Obtain disk-shaped MFI zeolite membranes on the desired intermediate layers with $H_2/CO_2$ separation factor over 25 and $H_2$ permeance larger than $1 \times 10^{-7}$ mol/m$^2$.s.Pa.

- Tubular membrane supports with desired intermediate barrier layers for stability improvement were developed.

- Obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst but with improved chemical stability in SO$_2$ and H$_2$S containing WGS reaction stream at temperatures higher than 500°C.

- 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 $H_2/CO_2$ perm-selectivity over 10 and $H_2$ permeance larger than $4 \times 10^{-7}$ mol/m$^2$.s.Pa.

- Obtain CVD modified tubular silicalite membranes with $H_2/CO_2$ separation factor over 120 and $H_2$ permeance larger than $2.0 \times 10^{-7}$ mol/m$^2$.s.Pa.
Technical Accomplishment – Gas Permeation/Separation and CVD Modification Study

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>H₂</th>
<th>CO₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetic Diameter, ( d_m ) (nm)</strong></td>
<td>0.26</td>
<td>0.289</td>
<td>0.33</td>
<td>0.376</td>
</tr>
<tr>
<td><strong>L-J Length, ( \sigma_m ) (nm)</strong></td>
<td>0.255</td>
<td>0.283</td>
<td>0.394</td>
<td>0.369</td>
</tr>
<tr>
<td><strong>Molecular Weight, ( M_w ) (g/mol)</strong></td>
<td>4</td>
<td>2</td>
<td>44</td>
<td>28</td>
</tr>
</tbody>
</table>

1. Gas cylinder
2. Mass flow controller
3. Two-way valve
4. Mixing valve
5. Three-way valve
6. Silane saturator
7. Box furnace
8. Permeation cell
9. Cold trap
10. Pressure gauge
11. Bubble flow meter
12. Gas chromatograph
13. Computer
Technical Accomplishment – Limited Separation Ability of Defect-Free Microporous Zeolite Membranes

\[
F_i = \left( \frac{\phi \alpha}{L z} \right) \left( \frac{8}{\pi R M_w T} \right)^{1/2} \exp\left( -\frac{E_{d,i}}{RT} \right) \\
\alpha_{H2/CO2} = \left( \frac{M_{wCO2}}{M_{wH2}} \right)^{1/2} \exp\left( \frac{E_{d(CO2)} - E_{d(H2)}}{RT} \right)
\]

The maximum H\textsubscript{2}/CO\textsubscript{2} selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.
H₂/CO₂ 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$_2$/CO$_2$ Perm-Selectivity**

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

H$_2$/CO$_2$ perm-selectivity of 140 and H$_2$ permeance about 4x10$^{-7}$ mol/s.m$^2$.Pa at 450$^\circ$C was obtained for the CVD modified membranes.
CVD modified tubular zeolite membrane exhibits molecular sieving properties.
Effect of WHSV on CO-conversion and hydrogen recovery for a fixed $R_{H2O/CO}$ of 3.5: (---) Equilibrium conversion ($\chi_{CO,e}$); (□) Conversion in membrane reactor ($\chi_{CO}$); (△) Conversion in traditional reactor ($\chi_{CO}$); (×) $H_2$ recovery.
Technical Accomplishment – Stability Testing of Sulfur Resistant, High Temperature WGS Catalyst

Long term time on stream stability experiments over Fe/Ce catalyst for 30 days in the presence of 400 ppm of sulfur.

Methane yield formation during long term time on stream stability experiments over Fe/Ce catalyst for 30 days in the presence of 400 ppm of sulfur.

Stability testing of sulfur resistant catalyst was conducted in a traditional fixed bed reactor.
Technical Accomplishment – CCD Modification of Disk MFI Zeolite Membrane with YSZ Barrier Layer
Technical Accomplishment – Water Gas Shift Reaction in a Modified Disk Membrane Reactor at Different Pressures

CO conversion for a fixed WHSV=7,500h⁻¹ and various temperature of (a) 400°C, (b) 450°C, (c) 500°C and (d) 550°C: (---) equilibrium CO conversion; (△) CO conversion under feed pressure 1.5 atm in tube MR of previous work; (□) CO conversion in disk MR; (○) CO conversion in TR.
Technical Accomplishment – Water Gas Shift Reaction in a Modified Membrane Disk Membrane at Different Conditions

Effect of WHSV on CO conversion for a fixed $R_{H2O/CO}$ of 3.5:

(- - -) equilibrium conversion;

(□) conversion in disc MR at $P_{feed}$=6atm;

(△) conversion in tube MR at $P_{feed}$=1.5atm;

(o) conversion in TR at $P_{feed}$=1.5atm.

Effect of N₂ sweeping flow rate on CO-conversion for a fixed WHSV=7,500 h⁻¹ and 500°C:

(- - -) equilibrium conversion;

(×) conversion in disc MR at $P_{feed}$=2atm;

(△) conversion in disc MR at $P_{feed}$=4atm;

(□) conversion in disc MR at $P_{feed}$=6atm.
### Long-Term Test for Alumina-Supported Modified MFI-Zeolite Membranes

<table>
<thead>
<tr>
<th>Description</th>
<th>Operation T &amp; P ranges</th>
<th>Time on stream (days)</th>
<th>Accumulative time on stream (days)</th>
<th>( \text{H}_2/\text{CO}_2 ) perm-selectivity</th>
<th>( \text{H}_2 ) permeance ( \text{mol/s.m}^2.\text{Pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>400 – 550°C 1 atm</td>
<td>NA</td>
<td>0</td>
<td>15</td>
<td>1.3 ( 10^{-7} )</td>
</tr>
<tr>
<td>After dry gas separation</td>
<td>400 – 550°C 1 atm</td>
<td>20</td>
<td>20</td>
<td>16</td>
<td>1.4 ( 10^{-7} )</td>
</tr>
<tr>
<td>After WGS</td>
<td>400 – 550°C 2 - 6 atm</td>
<td>110</td>
<td>130</td>
<td>12</td>
<td>0.9 ( 10^{-7} )</td>
</tr>
<tr>
<td>After WGS with H(_2)S</td>
<td>400 – 550°C 2 atm</td>
<td>50</td>
<td>180</td>
<td>11</td>
<td>0.8 ( 10^{-7} )</td>
</tr>
<tr>
<td>After WGS &amp; Gas Sep.</td>
<td>400 – 550°C 2 atm</td>
<td>20</td>
<td>200</td>
<td>10</td>
<td>0.7 ( 10^{-7} )</td>
</tr>
</tbody>
</table>
Synthesized by a 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 are grown on YSZ intermediate layer to improve chemical stability
Technical Accomplishment – Stability
Testing of MFI Zeolite Membrane with YSZ Barrier Layer under WGS Conditions

At 500 °C, $\text{H}_2\text{O}/\text{CO}=3$, WHSV=60,000 h$^{-1}$
CO conversion at equilibrium state is 91.76%
Technical Accomplishment – High Quality Tubular Supports with YSZ Barrier Layer for Stability Improvement

(a) SEM cross section of an YSZ-coated AA3 $\alpha$-Al$_2$O$_3$ support, (b) SEM surface image of an YSZ-coated AA3 $\alpha$-Al$_2$O$_3$ support.

MFI zeolite membrane will be synthesized on the tubular supports with YSZ barrier layer and subsequently modified for $\text{H}_2/\text{CO}_2$ separation factor improvement.
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 FY11

1. Synthesis of high quality tubular silicalite membranes by secondary growth and CVD modification (UC, ASU)
   a) $H_2/CO_2$ selectivity > 50, $H_2$ permeance > $3 \times 10^{-7}$ mol/m².s.Pa
   b) Silicalite membranes on zirconia support with improved chemical stability

2. 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.

3. WGS reaction on silicalite membrane reactor (ASU, UC)
   a) Improving membrane reactor system including setup (operatable up to 20 atm and 550 °C) and membrane module
   b) Optimization of the performance of WGS reaction in the silicalite membrane reactor
   c) Studying stability of the membrane reactor for WGS reaction under optimum conditions.

4. 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 $\text{H}_2$ permeance ($>2 \times 10^{-7}$ mol/m$^2$.s.Pa) and selectivity ($>120$) suitable for WGS membrane reactor application, and catalysts with improved properties for WGS reaction; improved WGS conversion and stable operation with zeolite membrane reactor demonstrated.

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