DE-FE0001322 Hydrogen Selective Exfoliated Zeolite Membranes

Proposal in response to Funding Opportunity NO. DE-PS26-08NT00699-01

Pre-combustion carbon capture technologies for coal-based gasification plants

Topic Area 1 – High-Temperature, High-Pressure Membranes

Total Project Funding: $993,772, DOE/Non-DOE Share: 793,775 / 199,997

Period of Performance: 10/1/2009 to 9/30/2014
Objective

To develop a technically and economically viable membrane for H₂ separation from typical water-gas-shift (WGS) mixture feeds at high temperatures.

Outline

• Preparation of hydrogen selective membranes using zeolite nanosheets.

• Steam stability of layered zeolites (MCM-22, ITQ-1, RUB-24, Nu-6(2)).

• Modeling and optimization of IGCC plant with membrane reactor.
Layered zeolites with 6-MR pores

MCM-22 (Si/Al=40)

ITQ-1 (Si/Al=∞)

H₂  CO₂

{ layer 1 }

{ layer 2 }
Hierarchical manufacturing of zeolite membranes

Layered zeolite (thickness ~50 nm)

Nanosheets with high aspect ratio (thickness 2.5 nm)

Exfoliation

Oriented monolayer of crystals

Coating

Secondary growth

Membrane

For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. 2007, 46, 7560–7573
Membrane preparation

Exfoliation with polystyrene → Swelling with CTAB

\[ \text{H}_3\text{C}(\text{H}_2\text{C})_{15}-\text{N}^+-\text{CH}_3 \]

Extrude

20 nm

4 nm

Dissolution of the nanocomposite in toluene, purification and filtration

1 μm

4 nm

Swelled MWW

MWW

Nanosheets

Varoon K., et al Science 334 (2011) 72–75,
Membrane preparation

- Exfoliation with polystyrene

- Dissolution of the nanocomposite in toluene, purification and filtration

- Gel-based secondary growth (misorientation)

Performance of an ITQ-1 Membrane

c-oriented MWW membranes

- Preserve the orientation of the MWW layers along the $ab$ plane.
- Fabrication of $b$-oriented MFI membranes have shown a superior performance in the separation of xylenes.

Secondary growth methods for MWW

- Pre-crystallization of the gel and secondary growth
- Gel-free growth: with HMI as the SDA
- Gel-free growth: MWW/MFI mixed matrix membrane

Analogy: $b$-oriented MFI membranes

Pham et. al Angewandte Chemie 2013, 125,33, 8855.
Secondary growth of MWW nanosheets – Pre-crystallization of the gel

Precrystallization of the gel
150° C/18h. SG 150° C/24h

Precrystallization of the gel
150° C/40h. SG 150° C/24h

• Misoriented growth on the surface of the MWW nanosheets.

• Longer pre-crystallization times of the gel prior to secondary growth might lead to c-oriented growth of MWW flakes.
MEMBRANE 3:
2nd growth condition: Gel aged at 150° C/40 h and secondary growth at 150° C/24 h

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Permeance (mol/m².Pa.s)</th>
<th>Selectivity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>Bare Al support</td>
<td>22</td>
<td>2.53E-06</td>
<td>3.08E-06</td>
</tr>
<tr>
<td>Membrane #90</td>
<td>80</td>
<td>1.37E-08</td>
<td>1.34E-08</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>1.58E-08</td>
<td>1.19E-08</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>2.60E-08</td>
<td>1.56E-08</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.26E-08</td>
<td>1.27E-08</td>
</tr>
</tbody>
</table>

![Graph showing permeance vs temperature for Membrane Al#90](image-url)
MWW / MFI (30 / 70 ratio) mixed membranes.
SG conditions: Impregnation with 0.025M TpaOH. Hydrothermal at 170° C/ (9h - 36h)

Hydrothermal at 170° C/9h. Hydrothermal at 170° C/18h.
p-xylene/o-xylene SF = 4.2  p-xylene/o-xylene SF = 4.7

Hydrothermal at 170° C/27h.
p-xylene/o-xylene SF = 1.7

However, these membranes gave poor separation of H₂, He, CO₂ or N₂.
MWW membranes

- With membranes made by the pre-crystallization method, a He permeance of 2.60E-08 and a He/N$_2$ separation of 10 was obtained.

- MWW/MFI membranes did not give high separation factors for gases.

- Under gel-free conditions with HMI, hydrothermal treatment resulted in formation of amorphous silica or destruction of MWW nanosheets.
Steaming conditions for ITQ-1 and MCM-22

- Temperature: 350°C
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21 days intervals for 84 days.
Stability of ITQ-1 and SiCl$_4$-treated ITQ-1

Treating ITQ-1 with SiCl$_4$ to heal structural defects

Flow of nitrogen saturated with SiCl$_4$ vapor at room temperature

450°C for 40 min

bed of zeolite
quartz wool
fritted quartz disk

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TEM images of ITQ-1 before and after 84 days of steaming
TEM images of ITQ-1 before and after 84 days of steaming

ITQ-1

Steamed ITQ-1
TEM images of **healed ITQ-1** before and after 84 days of steaming

- In ITQ-1, there is a major loss in crystallinity after steaming.
- SiCl₄ treatment improved the resistance of the ITQ-1 to water vapor attack.
- Holes are seen in the flakes of healed ITQ-1. However, regions around the cavities are crystalline.
XRD of MCM-22 steam treated at 350°C

- MCM-22 keeps its crystallinity.
- No change in crystal morphology was seen in the SEM pictures.
TEM images of MCM-22 before and after 84 days of steaming
TEM images of MCM-22 before and after 84 days of steaming
Summary of membranes and stability analysis

- MWW membranes were tested for gas separation.
- Depending on the secondary growth method applied, misoriention of the MWW channels or destruction of MWW nanosheets were observed.
- Hence, these membranes did not show optimum performance in gas separation.
- Systematic studies on the long-term steam stability of zeolites: MCM-22, ITQ-1, NU-6(2), and RUB-24 were completed.
- MWW may not be a suitable candidate for membrane reactor applications as structural defects developed due to water vapor attack.
- Healing of defects in the ITQ-1 crystal enhanced its steam stability.
Systems Modeling: Objectives and Approach

- Work done by Dr. Fernando Lima (now at WVU) and Prof. Prodromos Daoutidis (UMN)
- Develop a WGS membrane reactor (MR) model
- Integrate MR model into IGCC system model
- Analyze effect of reactor design and membrane characteristics on integrated plant performance
  - achieve DOE R&D target goal of 90% CO$_2$ capture $^{(1),(2)}$
  - satisfy stream constraints for CO$_2$ capture and gas turbine fuel (H$_2$ rich)$^{(3)}$
  - quantify process efficiency and power generation
- Perform optimization studies and techno-economic analysis for integrated plant
- Received input from DOE/NETL personnel (John Marano and Jared Ciferno)

$^{(1)}$ Marano, Report to DOE/NETL (2010)
$^{(2)}$ Marano and Ciferno, Energy Procedia 1, 361-368 (2009)
MR Modeling Assumptions and Simulation Set Up

- **Assumptions**
  - 1-dimensional shell and tube reactor
  - catalyst packed in tube side
  - thin membrane layer placed on surface of tube wall
  - sweep gas flows in shell side
  - plug-flow operation
  - constant temperature and pressure
  - steady-state operation
  - ideal gas law

- **Flow configurations**
  - co-current
  - counter-current

- **Simulation conditions**
  - catalyst type and reaction rate
  - reactor dimensions (lab)
  - consistent with IGCC specifications

- **Model used to perform simulation and optimization studies**

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Integration of MR into IGCC Plant (MATLAB)

- Scale up MR model at steady state
- MR integration downstream of gasifier \(^{(1),(2)}\)
- Effect on turbines/heat exchangers
- Steam integration for MR utilization

Simulation studies performed

- Novel optimization problem formulation
  - minimize cost of membrane as function of surface area
  - determine optimal operating point that satisfies all constraints

IGCC-MR Optimization Results: Different Membrane Characteristics

<table>
<thead>
<tr>
<th>IGCC Performance Variable</th>
<th>Nominal ((S_{H2/all} = 1000, Q_{H2} = 0.2 ))</th>
<th>Nominal Optimal</th>
<th>Case I ((S_{H2/all} = 100, Q_{H2} = 0.2))</th>
<th>Case II ((S_{H2/all} = 1000, Q_{H2} = 0.1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_m = \text{membrane area} \ [m^2])</td>
<td>6800</td>
<td>4989</td>
<td>4739</td>
<td>7271</td>
</tr>
<tr>
<td>(C_{CO2} = \frac{\text{carbon captured}}{\text{carbon in feed}} \ [%])</td>
<td>98.54</td>
<td>99.02</td>
<td>91.13</td>
<td>99.28</td>
</tr>
<tr>
<td>(\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} \ [%])</td>
<td>47.96</td>
<td>47.55</td>
<td>47.63</td>
<td>46.96</td>
</tr>
<tr>
<td>(W = \text{power generated} \ [MW])</td>
<td>614.07</td>
<td>617.60</td>
<td>618.41</td>
<td>615.00</td>
</tr>
</tbody>
</table>

\(Q_{H2} = \text{mol/(s.m}^2\text{.atm)}\)
IGCC Differential Cost Analysis

- Cost comparison between IGCC with and without MR
- Same amount of coal and power generation (≈ 615 MW)
- Cost differences
  - larger ASU (IGCC) \(^{(1)}\): ≈ $290 million/30 years
  - steam and gas turbines differences (IGCC) \(^{(1)}\): ≈ $40 million/30 years; ≈ $117 million/30 years (with oxy-combustion corrections);
  - extra heat exchangers (IGCC-MR) \(^{(2)}\): $3.78 million/30 years
  - added MR with \(A_m \approx 5000 \text{ m}^2\) (IGCC-MR nominal): ≈ $5-50 million/lifetime

(2) Turton et al., *Analysis, Synthesis and Design of Chemical Processes* (2012)
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- Calculate MR cost to break even in a 30 year period
- Results based on present value of annuity calculation – nominal case

<table>
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<tr>
<th>Lifetime [year]</th>
<th>Cost [$/m²]</th>
<th>Cost Corrected [$/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5,840</td>
<td>7,210</td>
</tr>
<tr>
<td>2</td>
<td>11,680</td>
<td>14,420</td>
</tr>
<tr>
<td>3</td>
<td>17,520</td>
<td>21,630</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Haslbeck et al., *Baseline Report to DOE/NETL* (2010)
\(^{(2)}\) Turton et al., *Analysis, Synthesis and Design of Chemical Processes* (2012)
Modeling Conclusions

- Conclusions
  - MR model integrated into IGCC process model in MATLAB
  - Simulation and optimization studies for IGCC-MR plant performed
    - simulation results indicated successful nominal case
    - novel constrained optimization problem formulated and solved
  - Techno-economic assessment of IGCC-MR process completed (MATLAB)
  - MR cost analysis showed break even costs within feasible range (estimated to be $1000-10000/m²).
Acknowledgements

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