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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
Hydrogen Selective Membranes in IGCC Plants

Challenges under WGS conditions of IGCC plants
• high temperature and pressure
• presence of impurities ($H_2S$)

Bracht et al., Energy Convers. Mgmt 38, S159-164 (1997)
IGCC efficiency
• without CO$_2$ capture: 46.7%
• with conventional CO$_2$ removal: 40.5%

With WGS-MR and CO$_2$ recovery: 42.8% (LHV) based on
• 35 atm feed, 20 atm permeate (15 atm pressure drop)
• 330°C in the feed
• hydrogen/carbon dioxide selectivity = 15
• hydrogen permeability = 0.2 mol/(m$^2$.s.bar)

Membrane Area Needed: 2,200 m$^2$ (400MW)

Bracht et al., Energy Convers. Mgmt 38, S159-164 (1997)
Motivation: Hierarchical Manufacturing of Zeolite Films

Crystal Structure (nm)

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

Shaped Crystal (10-100nm)

Oriented Monolayer of Crystals (meso-macro)

Intergrown Film

AlChE Journal, 42(11), 3020-3029 (1996)
Chemistry of Materials 10, 2497-2504 (1998)
Science 325 (5940), 590-594 (2009)
Layer by Layer Deposition (JACS 132(2), 448-449 (2010))

5 layers of MCM-22/surfactant-templated-mesoporous-silica on porous alumina

![Diagram of layers with symbols for H₂ and CO₂]
Comparison of Ideal Selectivity

The ideal selectivity (H₂/CO₂ and H₂/N₂) increased monotonically with temperature and improved with the number of deposition cycles.
MCM-22/Silica Membranes for Hydrogen Separations

*Open symbols: selectivity through $\alpha$-Al$_2$O$_3$ discs


Experimental Demonstration of Selective Flake Composite Concept
Advantages by Reduction in Flake Thickness

Increase selectivity without decreasing throughput

Increase throughput without decreasing selectivity

H₂ N₂
Membrane Preparation Procedure

Purified nanosheets in toluene were filtered through porous alumina supports and then secondary growth was conducted.
- Exfoliated ITQ-1 on Alumina Disk
- After Secondary Growth of ITQ-1
Performance of ITQ-1 Membrane

Varoon et al., *Science* 334(6052), 72–75 (2011)
Steam Stability Studies

Four layered zeolites (MCM-22, ITQ-1, NU-6(2), RUB-24) with 6-MR perpendicular to the layers were investigated.
Hydrothermal Stability Setup
Hydrothermal Stability of MCM-22 and ITQ-1

- Temperatures: 350°C, 600°C
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21-day intervals for 84 days

Both MCM-22 and ITQ-1 showed poor steam stability at 600°C. MCM-22 outperformed its all silica counterpart (ITQ-1) at 350°C. This behavior was related to the lower concentrations of structural defects in MCM-22.
Hydrothermal Treatment Conditions for RUB-24 and NU-6(2)

- Temperature: 350°C
- Pressure: 10 bar (35% steam in nitrogen)
- Duration: 6 months

Nu-6(2) was structurally stable after 6 months of steaming. RUB-24 lost its crystallinity after 6 months of steaming.
Summary of Stability Analysis & Future Work

• Achievement
  • long-term steam stability of zeolites MCM-22, ITQ-1, NU-6(2), and RUB-24 were investigated
  • NU-6(2) preserved its crystallinity after 6 months of steaming (35% H$_2$O, 65% N$_2$) at 350°C

• Future Work
  • study of membrane performances at high temperatures
  • hydrothermal stability study of membranes
Systems Modeling: Objectives and Approach

• **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% CO₂ capture \(^{(1),(2)}\)
  • satisfy stream constraints for CO₂ capture and gas turbine fuel (H₂ rich) \(^{(3)}\)
  • quantify process efficiency and power generation
• **Perform preliminary techno-economic analysis of integrated IGCC-MR process**
• **Received input from DOE/NETL personnel (John Marano and Jared Ciferno)**

(1) Marano, Report to DOE/NETL (2010)
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**

Composition (1):
- CO = 30.63%
- H₂O = 36.76%
- CO₂ = 8.41%
- H₂ = 23.57%

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

IGCC Plant Modeling Assumptions

- **Simplified systems-level model of entire process (ASU, gasifier, turbines, and heat exchangers) in MATLAB**

- **Assumptions:** few basic components, lumped compartments in gasifier/turbines, static heat exchanger models

- **Developed model validated using published simulation data**

Integration of MR into IGCC Plant (MATLAB)

- Scale up MR model at steady state
- Integration directly downstream of gasifier \(^{(1),(2)}\)
- Effect on heat exchangers/turbines
- Perform preliminary technical assessment of IGCC-MR integrated plant

\(^{(1)}\) Marano and Ciferno, Energy Procedia 1, 361-368 (2009)
\(^{(2)}\) Bracht et al., Energy Convers. Mgmt 36, S159-164 (1997)
Integration of MR into IGCC Plant (MATLAB): Simulation Results

- **Process simulation conditions** $(1),(2),(3)$
  - $P_t = 53.29$ atm, $P_s = 25.86$ atm
  - $T_t = 380^\circ \text{C}$, $T_s = 380^\circ \text{C}$
  - $S_{H_2/\text{all}} = 1000$, $Q_{H_2} = 0.2 \text{ mol/(s.m}^2\text{.atm)}$
  - $A_m = 6800$ m$^2$

- **Performance variables** $(2)$
  - **carbon capture** $C_{\text{CO}_2} = \frac{\text{carbon captured}}{\text{carbon in feed}} = 98.94\%$
  - **process efficiency** $\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} = 40.83\%$
  - **power generation** $W = 716.78$ MW

$(2)$ Haslbeck et al., *Baseline Report to DOE/NETL* (2010)
IGCC-MR Simulation Results: Changing Membrane Characteristics

<table>
<thead>
<tr>
<th>IGCC Performance Variable</th>
<th>Value ((S_{H2/all} = 1000, Q_{H2} = 0.2))</th>
<th>Value ((S_{H2/all} = 1000, Q_{H2} = 0.1))</th>
<th>Value ((S_{H2/all} = 100, Q_{H2} = 0.2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{\text{CO}_2}) = \frac{\text{carbon captured}}{\text{carbon in feed}} [%])</td>
<td>98.94</td>
<td>99.55</td>
<td>89.79</td>
</tr>
<tr>
<td>(\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} [%])</td>
<td>40.83</td>
<td>34.14*</td>
<td>41.15</td>
</tr>
<tr>
<td>(W = \text{power generated} [\text{MW}])</td>
<td>716.78</td>
<td>599.31</td>
<td>722.27</td>
</tr>
</tbody>
</table>

\(^*\) \(P_{H2,P} \leq 44\%\)
Integration of MR into IGCC Flowsheet (Aspen)

**GE IGCC with CO₂ Capture**

- **MR integration into Aspen flowsheet (Ongoing)**
  - use available baseline IGCC model (MITEI) (1)
  - MR model implemented (co-current) in Aspen Custom Modeler
  - similar results to MATLAB model obtained

- **Perform simulation & techno-economic analysis**
  - feasibility of replacing current technology (CO shift followed by physical absorption) for CO₂ capture
  - achieve DOE target goals (CO₂ capture, COE)

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Modeling Conclusions & Future Work

**Conclusions**
- MR model integrated into IGCC process model in MATLAB
- preliminary technical assessment of IGCC-MR plant performed
- MR model (co-current) implemented in Aspen

**Future Work**
- develop relationships between membrane parameters and cost
- carry out IGCC-MR design optimization (MATLAB)
- develop counter-current MR model (Aspen)
- adjust MR model to incorporate into Aspen IGCC baseline model