Dehydration Membrane Reactor for Direct Production of Dimethyl Carbonate (DMC) from CO$_2$ and H$_2$

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Project overview

- **Performance period**: Jan. 1, 2021 – Dec. 31, 2022
- **Total funding**: $1,269,664 (DOE: $1.0 MM, Cost share: $269,664)
- **Objectives**: Develop a unique catalytic membrane reactor for producing a valuable liquid product, dimethyl carbonate (DMC) from captured CO₂ and H₂
  - DMC is used predominately in polycarbonate production. Its market is projected to grow from $895 million in 2019 to $1,207 million by 2024, at a CAGR of 6.2% from 2019 to 2024
- **Goal**: Achieve CO₂ conversion >50%, DMC selectivity >60%, and production rate of 600 g_{DMC}/kg_{cat}/h

**Team:**

<table>
<thead>
<tr>
<th>Member</th>
<th>Roles</th>
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</thead>
</table>
| gti    | • Lead on project management and planning  
        | • Lead on membrane reactor parametric and deactivation tests  
        | • Lead on detailed techno-economic and life-cycle analyses |
| UB     | • Lead on membrane and module development  
        | • Lead on catalytic membrane reactor design, testing, and optimization  
        | • Supporting techno-economic and life-cycle analyses |
| S&T    | • Lead on catalyst development  
        | • Supporting techno-economic and life-cycle analyses |
One-step process intensifies a process that would otherwise require multiple reaction steps:

- Methanol production: \( \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \) \( \Delta H^0 = -49 \text{ kJ/mol} \) Catalyst 1: CuO/ZnO/Al\(_2\)O\(_3\) based
- DMC synthesis: \( 2\text{CH}_3\text{OH} + \text{CO}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O} \) \( \Delta H^0 = -17.3 \text{ kJ/mol} \) Catalyst 2: CeO\(_2\) based
- Combined reaction: \( 3\text{CO}_2 + 6\text{H}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + 3\text{H}_2\text{O} \)

Consumes three moles of CO\(_2\) for every mole of DMC formed

Recently developed Na\(^+\)-gated membrane (Science, vol. 367, pp. 667, 2020) removes water \textit{in situ}, shifting the equilibrium towards product formation, while decreasing kinetic inhibition from water adsorption onto the catalyst surface.
Palladium-CuO/ZnO/Al$_2$O$_3$ (Pd-CZA) catalyst developed for methanol synthesis

**TEM image:** uniform nanoscale particles (ca. 15 nm)

**EDX mapping:** elements of Cu, Pd, O, Al, Zn homogeneously dispersed

TEM: Transmission Electron Microscopy; EDX: Energy-dispersive X-ray Spectroscopy
0.9Pd/CZA shows the highest CO\textsubscript{2} conversion and methanol yield during methanol synthesis using packed bed reactor

Reaction conditions: T = 140-240°C, P = 2.8 MPa, H\textsubscript{2}/CO\textsubscript{2} molar ratio at 3:1, GHSV = 2,880 mL/(g\textsubscript{cat}·h)

GHSV: Gas Hourly Space Velocity
CeO$_2$-based catalyst developed for DMC synthesis

TEM image: nanorods catalyst

TEM: Transmission Electron Microscopy; XRD: X-ray Diffraction
Breakthrough development of Na\textsuperscript{+}-gated, nanochannel membrane for dehydration

Na\textsuperscript{+}-gated water-conducting nanochannels for boosting CO\textsubscript{2} conversion to liquid fuels

Huazheng Li, Chenglong Qiu, Shoujie Ren, Qiaobei Dong, Shenxiang Zhang, Fanglei Zhou, Xinhua Liang, Jianguo Wang, Shiguang Li and Miao Yu

Na\textsuperscript{+} neutralizes the negatively charged NaA framework and position inside zeolite nanocavities, allowing fast transport of small H\textsubscript{2}O molecules, whereas blocking the permeation of larger molecules, such as H\textsubscript{2}, CO\textsubscript{2}, CO, and methanol.
SEM, EDX and XRD analyses indicate uniform membrane layer with intergrown crystals and LTA structure

**Surface SEM:**
Intergrown crystals for the membrane layer

**Cross sectional SEM:** membrane thickness of 3-4 µm

**EDX:** membrane contains Si, Al, and Na

**XRD:** zeolite LTA structure for the membrane

Membrane shows high flux and selectivity for dehydration with a feed of \( \text{H}_2\text{O}/\text{CO}_2/\text{CO}/\text{H}_2/\text{methanol} \)

- **Other selectivities**
  - \( \text{H}_2\text{O}/\text{H}_2 > 190 \)
  - \( \text{H}_2\text{O}/\text{CO} > 170 \)
  - \( \text{H}_2\text{O}/\text{MeOH} > 80 \)
  - \( \text{H}_2\text{O}/\text{DMC}: \text{not tested yet, but expected to be} >200 \)

Kinetic diameters:
- DMC: 0.63 nm
- Methanol: 0.36 nm
- \( \text{CO}_2 \): 0.33 nm
- \( \text{H}_2 \): 0.289 nm
Methanol synthesis and DMC synthesis in membrane reactor

- Membrane reactor methanol synthesis from CO\textsubscript{2} and H\textsubscript{2} using a CZA-based catalyst
  - Compared to a traditional packed bed reactor (TR) without membrane, both CO\textsubscript{2} conversion and methanol yield increased 3 times

- Membrane reactor DMC synthesis from methanol and CO\textsubscript{2} using a CeO\textsubscript{2}-based catalyst
  - CO\textsubscript{2} conversion of 21.8\% and DMC productivity as high as 1.16 g/h/g\textsubscript{cat}. In contrast, no CO\textsubscript{2} conversion was observed in packed bed reactor indicating the great advantage of using Na\textsuperscript{+}-gated membrane for dehydration
Technical challenge – the presence of 1st reaction catalyst (CZZA) may cause consumption of DMC by hydrogenation

- **Mitigation strategy**: coating the external surface of CZZA catalyst (pore size: 0.4-0.6 nm) to prevent DMC hydrogenation by the CO₂ hydrogenation catalyst (CZZA) while still allowing free access of CO₂ and H₂ to the catalyst surface.

- **Liquid-phase interfacial reaction to form microporous coatings on porous materials**

- **Coating pore size adjustment by controlling synthesis conditions**

Kinetic diameters:
- DMC: 0.63 nm
- Methanol: 0.36 nm
- CO₂: 0.33 nm
- H₂: 0.289 nm
Roadmap of the current project

**Task 1** Project management and planning (*throughout the project*)

**Catalyst Development**
- **Task 2** – Preparation, characterization, and optimization of catalysts
- **Task 4** – Coated catalyst development and catalytic performance evaluation
- **Task 6** – Optimization of bifunctional catalyst

**Membrane Reactor Testing**
- **Task 3** – Baseline membrane reactor testing and optimization
- **Task 5** – Bifunctional membrane reactor testing and optimization
- **Task 7** – Membrane reactor parametric and deactivation tests
- **Task 8** – Detailed techno-economic and life-cycle analyses

Year 1 (12 months)

Year 2 (12 months)
## Milestones and success criteria

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<tr>
<th>#</th>
<th>Task/ Subtask</th>
<th>Milestone Title/Description</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
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<tbody>
<tr>
<td>M1.1</td>
<td>1</td>
<td>Submit updated Project Management Plan to DOE</td>
<td>2/28/21</td>
<td>2/18/21</td>
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<tr>
<td>M1.2</td>
<td>1</td>
<td>Complete Kickoff Meeting</td>
<td>3/31/21</td>
<td>3/19/21</td>
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<tr>
<td>M1.3</td>
<td>1</td>
<td>Submit technology maturation plan to DOE</td>
<td>3/31/21</td>
<td>3/23/21</td>
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<tr>
<td>M2.1</td>
<td>2</td>
<td>Ship &gt;20 g of catalysts w/ BET surface area &gt;100 m²/g to RPI from MS&amp;T</td>
<td>6/30/21</td>
<td></td>
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<tr>
<td>M3.1</td>
<td>3</td>
<td>Achieve CO₂ conversion &gt;20%, DMC selectivity &gt;20%, DMC production rate &gt;200 g₃DMC/kgₙcat/h at 140-220°C and 25-35 bar</td>
<td>6/30/21</td>
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<tr>
<td>M4.1</td>
<td>4.1</td>
<td>Complete development of coated CZZA-based catalyst with coating layer thickness &lt;0.5 mm and pore size between 0.4 and 0.6 nm</td>
<td>12/30/21</td>
<td></td>
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<tr>
<td>M4.2</td>
<td>4.2</td>
<td>Achieve CO₂ conversion &gt;15% and methanol yield &gt;10% in methanol synthesis at 140-220°C and 25-35 bar for the coated CZZA-based catalyst using a fixed bed reactor</td>
<td>12/30/21</td>
<td></td>
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<td>M5.1</td>
<td>5</td>
<td>Achieve CO₂ conversion &gt;40%, DMC selectivity &gt;50%, DMC production rate &gt;500 g₃DMC/kgₙcat/h at 140-220°C and 25-35 bar</td>
<td>9/30/22</td>
<td></td>
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<tr>
<td>M6.1</td>
<td>6</td>
<td>Achieve CO₂ conversion &gt;20% and methanol yield &gt;12% in methanol synthesis at 140-220°C and 25-35 bar for the coated CZZA-based catalyst using a fixed bed reactor</td>
<td>9/30/22</td>
<td></td>
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<tr>
<td>M7.1</td>
<td>7</td>
<td>Complete 100-500 hours continuous testing; achieve steady-state CO₂ conversion &gt;50%, DMC selectivity &gt;60%, and DMC production rate &gt;600 g₃DMC/kgₙcat/h at 140-220°C and 25-35 bar</td>
<td>12/30/22</td>
<td></td>
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<tr>
<td>M8.1</td>
<td>8</td>
<td>Issue Final TEA report with a Technology Gap Analysis</td>
<td>12/30/22</td>
<td></td>
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<tr>
<td>M8.2</td>
<td>8</td>
<td>Issue Final LCA report</td>
<td>12/30/22</td>
<td></td>
</tr>
<tr>
<td>M1.4</td>
<td>1</td>
<td>Submit Final Technical Report</td>
<td>3/30/23</td>
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Technology development path

DME: \(2\text{CO}_2 + 6\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O}\)
DMC: \(3\text{CO}_2 + 6\text{H}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + 3\text{H}_2\text{O}\)
Summary

▪ We are developing a catalytic membrane reactor technology for production of DMC, which consumes three moles of CO$_2$ for every mole of DMC formed
  ▪ Bifunctional catalyst designed to combine two reactions, methanol formation and dehydration, enabling higher overall CO$_2$ conversion
  ▪ Na$^+$-gated nanochannel membrane designed to remove water \textit{in situ}, shifting equilibrium towards product formation

▪ \textbf{Progress to date:}
  ▪ Catalysts and membranes prepared
  ▪ Methanol synthesis and DMC synthesis were separately studied in membrane reactor, which showed much higher CO$_2$ conversion and product yield than traditional packed bed reactors

▪ \textbf{Next step} is to develop coated catalyst and test bifunctional membrane reactor
Acknowledgements

- Financial and technical support

![U.S. Department of Energy][1]  [NETL][2]  DE-FE0031909

- DOE NETL: Andrea McNemar and Andrew O'Palko
Appendix – Organization chart

DOE NETL
Project Manager
*Project oversight*

**GTI**
Ms. Kate Jauridez
*Contract administrator*

**GTI**
Dr. Shiguang Li - *PI*
- Coordinate project activities
- Project management

**GTI**
Mr. Howard Meyer
*Project QA/QC*

**MS&T**
Dr. Xinhua Liang
*Catalyst development*

**UB**
Dr. Miao Yu
*Membrane reactor design, testing, and optimization*

**GTI**
Mr. Travis Pyrzynski
*Parametric and deactivation tests*

**GTI**
Dr. Sekar Darujati
*TEA and LCA*
Appendix – Gantt chart
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