DOE Contract DE-FE0031909

Dehydration Membrane Reactor for Direct Production of Dimethyl Carbonate (DMC) from CO_2 and H_2

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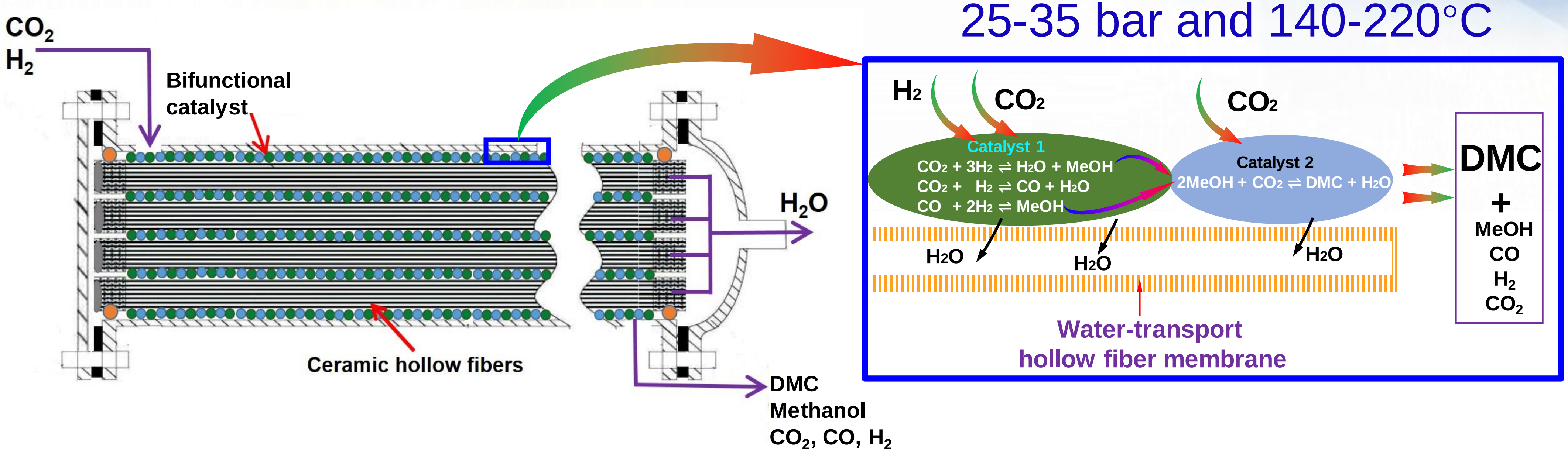
U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings, August 31, 2021

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 CO_2 and H_2
  - 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 CO_2 conversion >50%, DMC selectivity >60%, and production rate of 600 $g_{DMC}/kg_{cat}/h$
- **Team**:

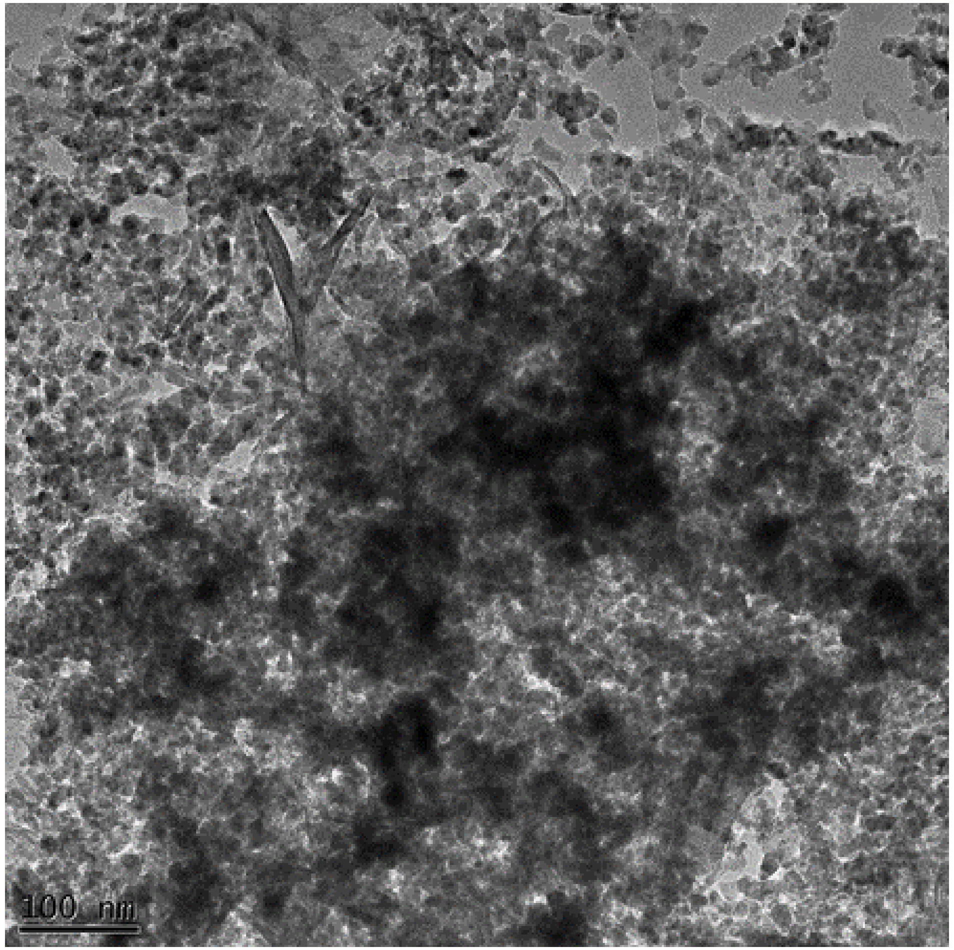
Member	Roles
gti	• Lead on project management and planning • Lead on membrane reactor parametric and deactivation tests • Lead on detailed techno-economic and life-cycle analyses
UB	• Lead on membrane and module development • Lead on catalytic membrane reactor design, testing, and optimization • Supporting techno-economic and life-cycle analyses
Missouri S&T	• Lead on catalyst development • Supporting techno-economic and life-cycle analyses

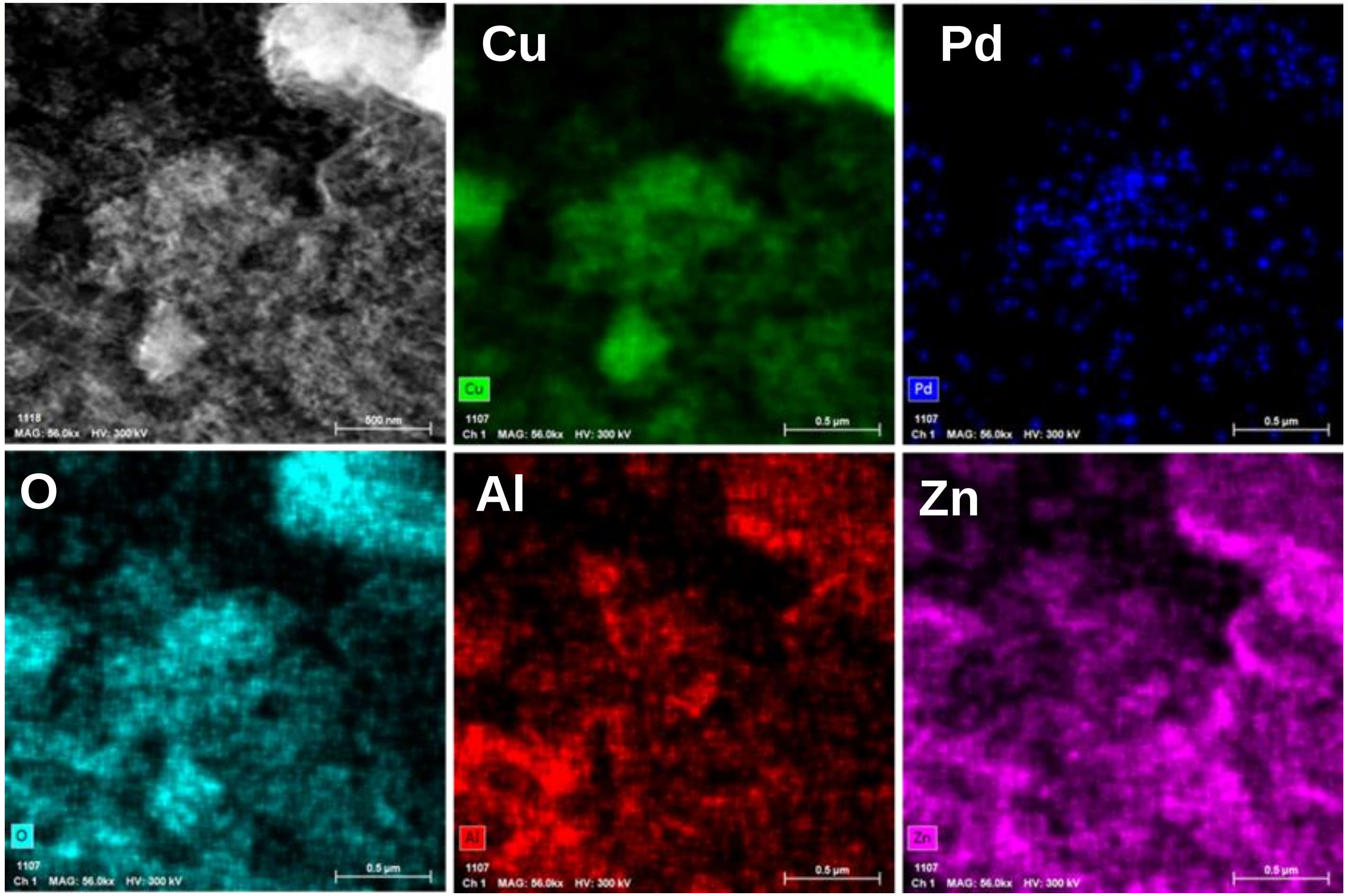
Technology description



- One-step process intensifies a process that would otherwise require multiple reaction steps:
  - Methanol production: $CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$ $\Delta H^0 = -49$ kJ/mol Catalyst 1: $CuO/ZnO/Al_2O_3$ based
  - DMC synthesis: $2CH_3OH + CO_2 \leftrightharpoons (CH_3O)_2CO + H_2O$ $\Delta H^0 = -17.3$ kJ/mol Catalyst 2: CeO_2 based
  - Combined reaction: $3CO_2 + 6H_2 \leftrightharpoons (CH_3O)_2CO + 3H_2O$
- 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 *in situ*, shifting the equilibrium towards product formation, while decreasing kinetic inhibition from water adsorption onto the catalyst surface

Palladium-CuO/ZnO/Al_2O_3 (Pd-CZA) catalyst developed for methanol synthesis





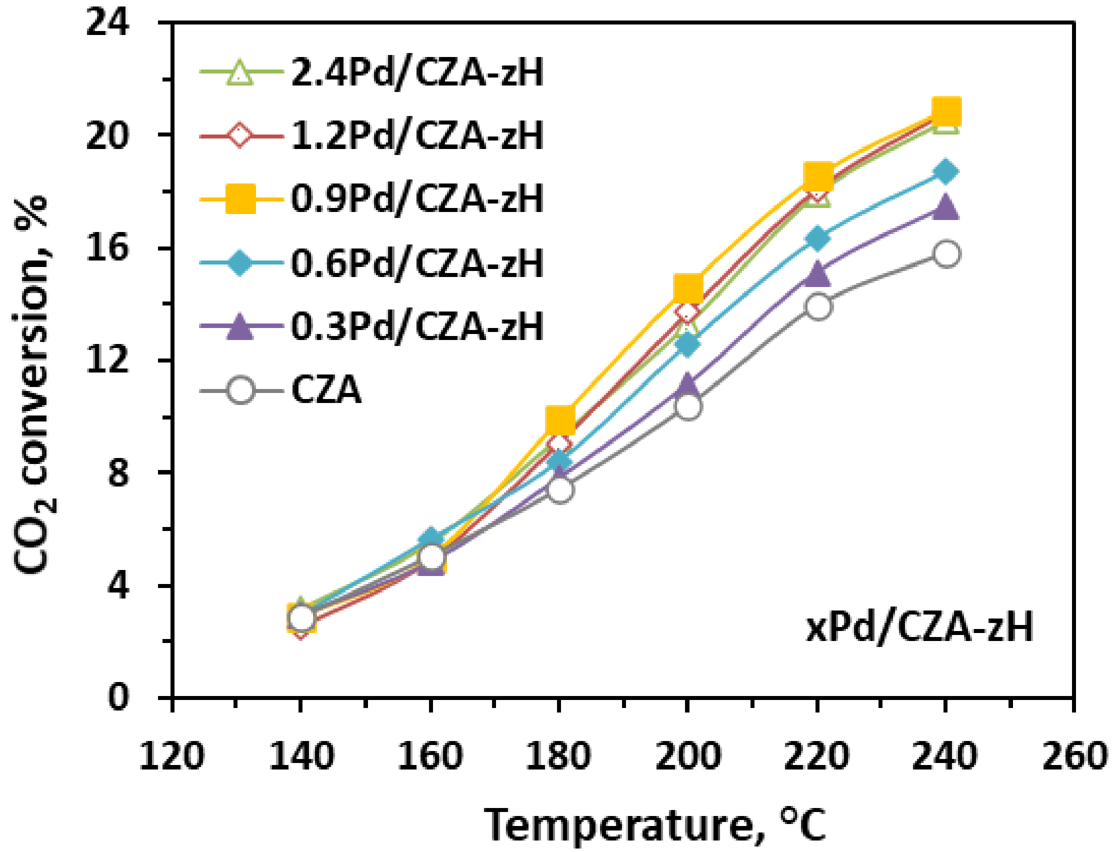
TEM image: uniform nanoscale particles (ca. 15 nm)

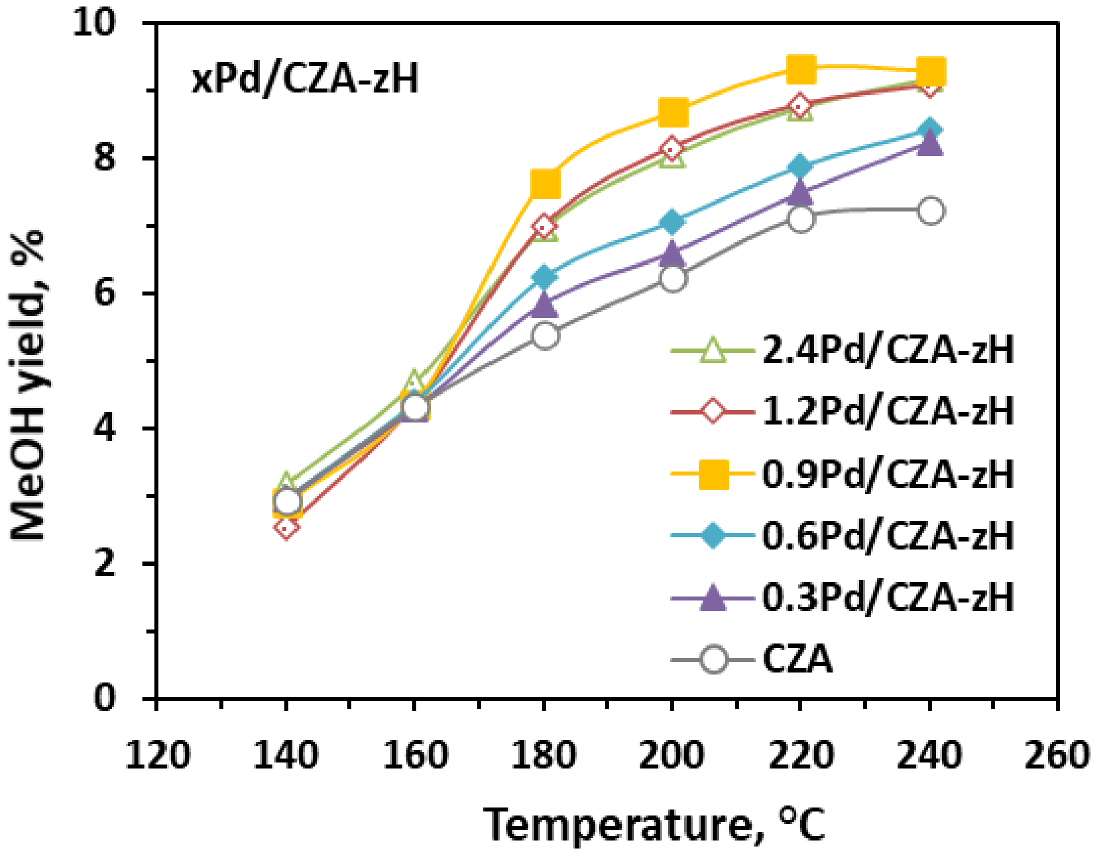
EDX mapping: elements of Cu, Pd, O, Al, Zn homogeneously dispersed

TEM: Transmission Electron Microscopy; EDX: Energy-dispersive X-ray Spectroscopy

0.9Pd/CZA shows the highest CO_2 conversion and methanol yield during methanol synthesis using packed bed reactor

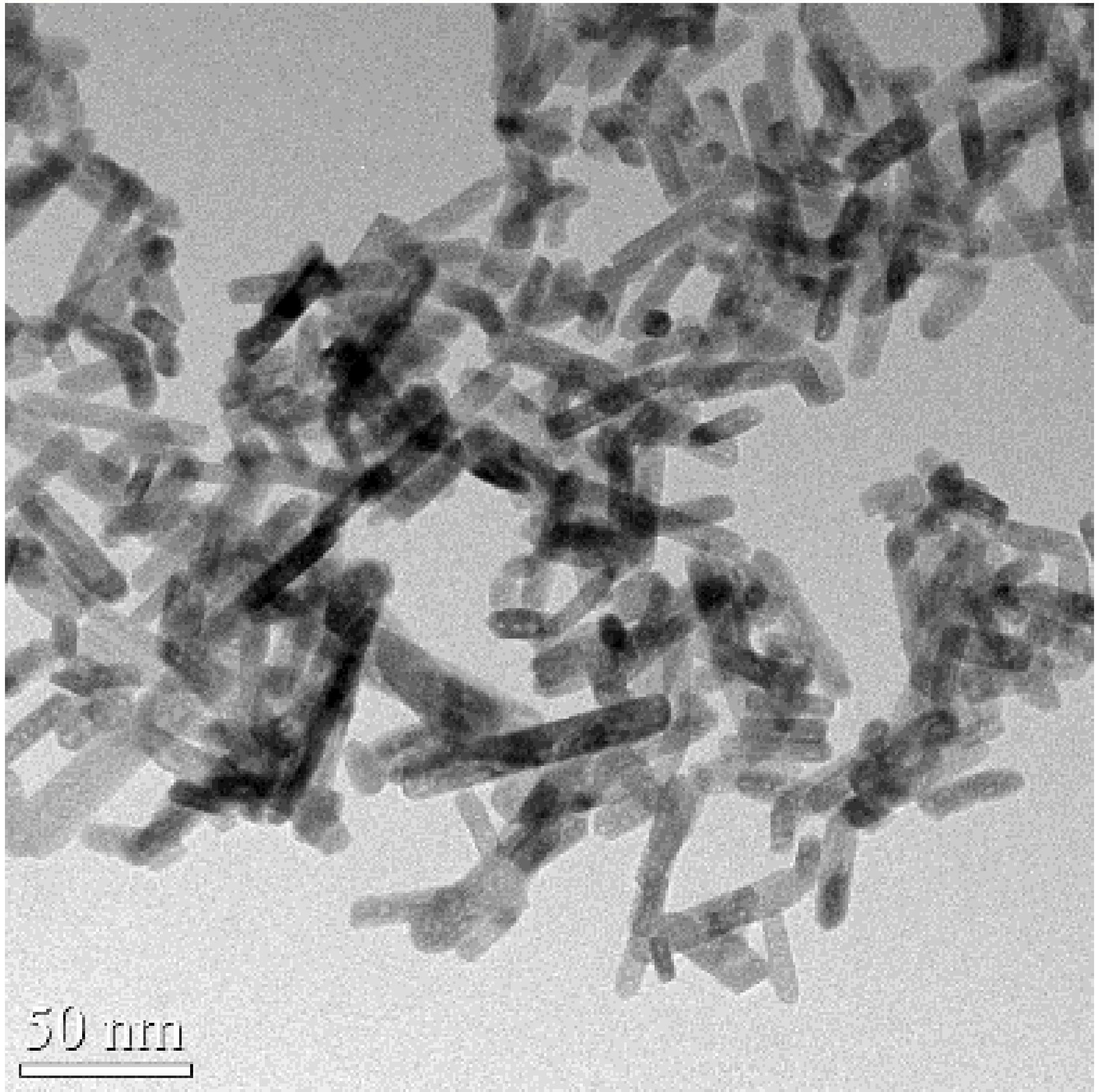
Reaction conditions: T = 140-240°C, P = 2.8 MPa, H_2/CO_2 molar ratio at 3:1, GHSV = 2,880 mL/(g_{cat}·h)





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

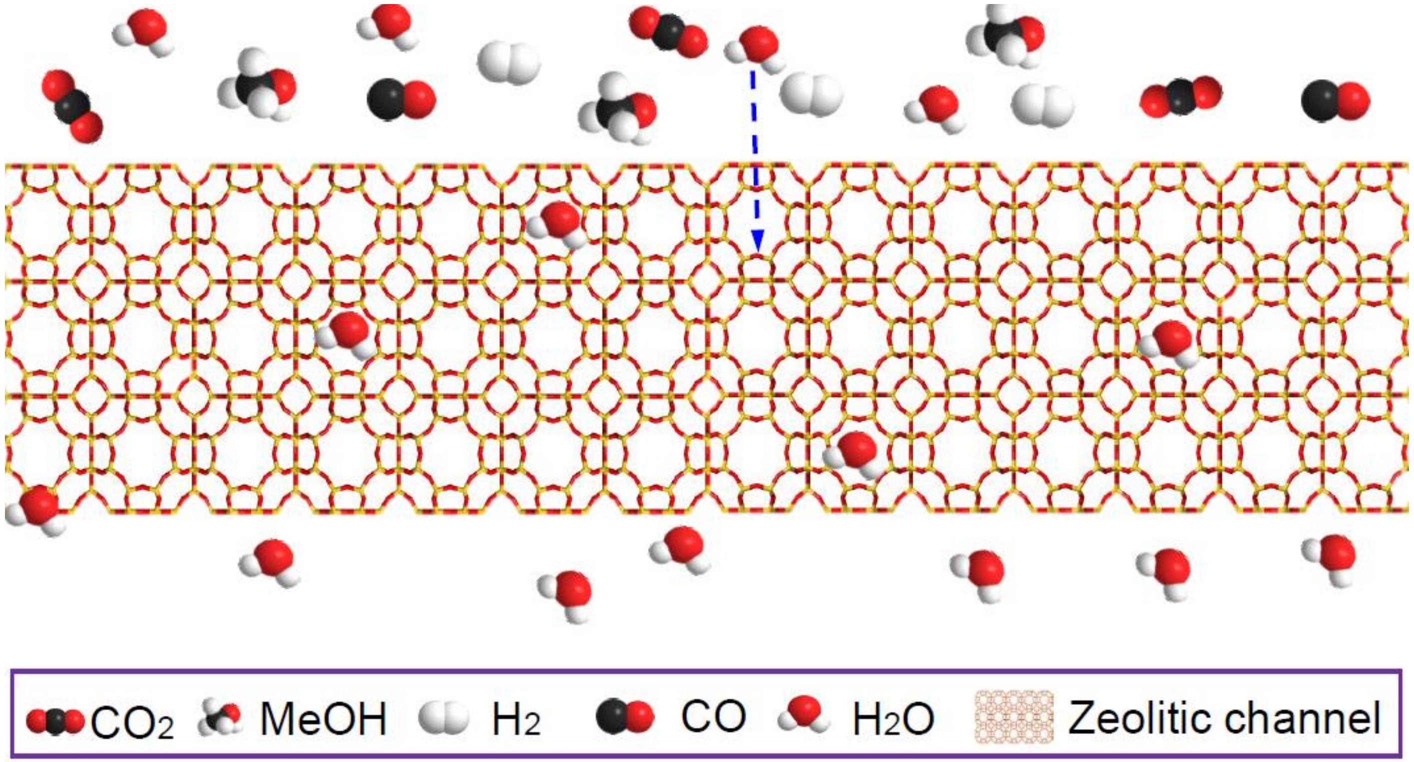
Breakthrough development of Na^+-gated, nanochannel membrane for dehydration

Science

Na^+-gated water-conducting nanochannels for boosting CO_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

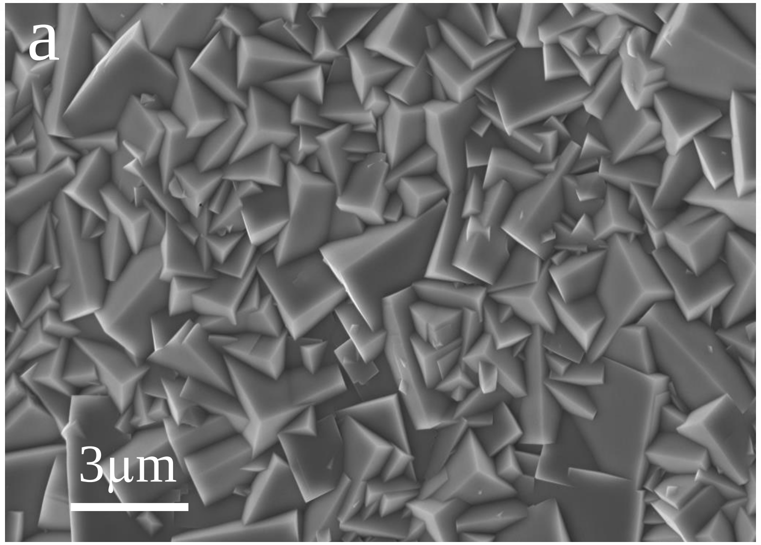
Science **367** (6478), 667-671.
DOI: 10.1126/science.aaz6053

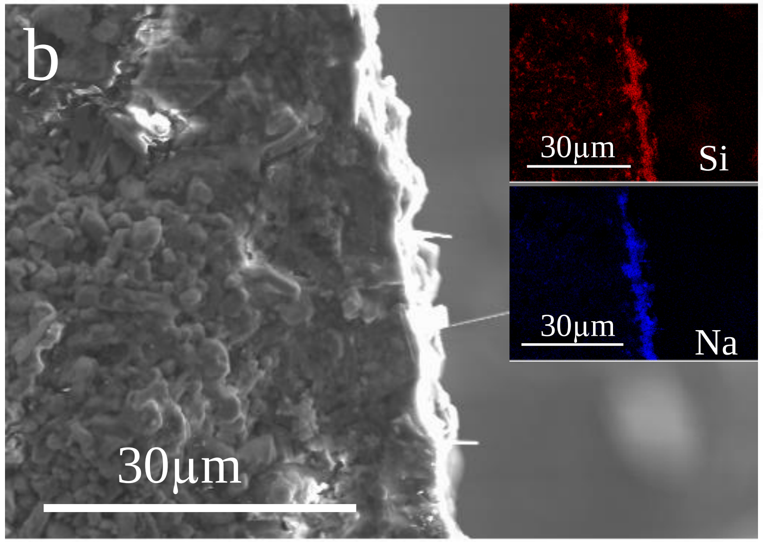


Na^+ neutralizes the negatively charged NaA framework and position inside zeolite nanocavities, allowing fast transport of small H_2O molecules, whereas blocking the permeation of larger molecules, such as H_2, CO_2, CO, and methanol

SEM, EDX and XRD analyses indicate uniform membrane layer with intergrown crystals and LTA structure

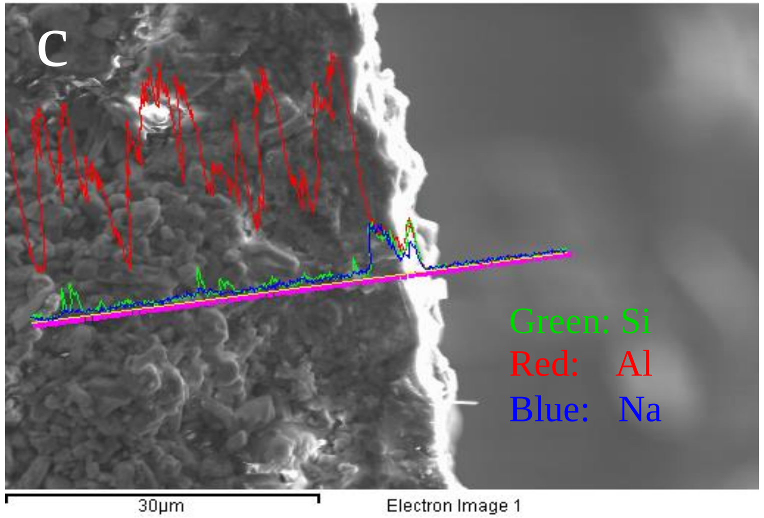
Surface SEM: Intergrown crystals for the membrane layer

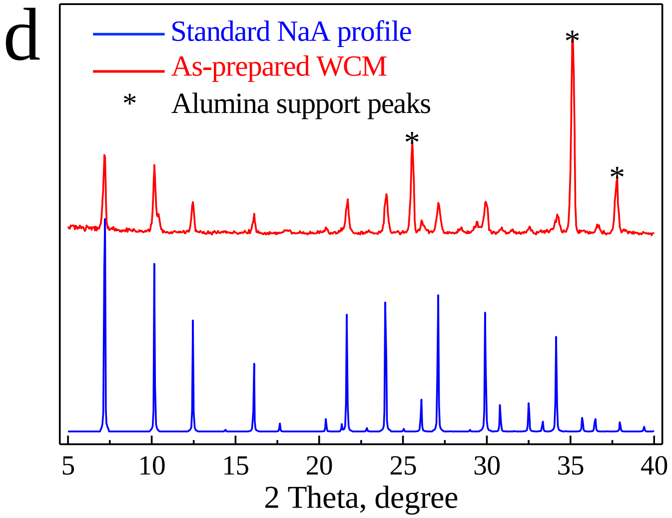




Cross sectional SEM: membrane thickness of 3-4 μm

EDX: membrane contains Si, Al, and Na

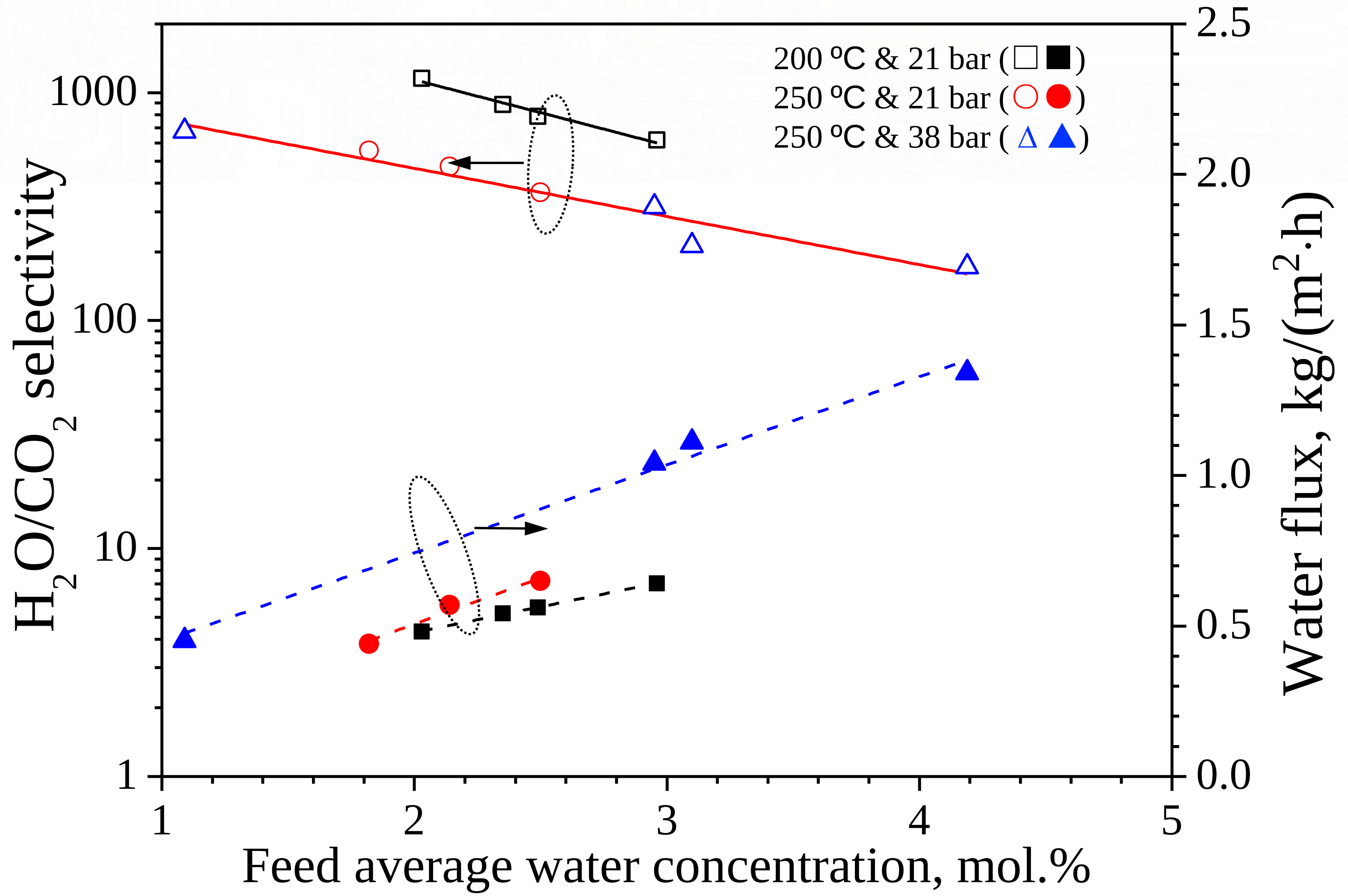




XRD: zeolite LTA structure for the membrane

SEM: Scanning Electron Microscopy; EDX: Energy-dispersive X-ray Spectroscopy; XRD: X-ray Diffraction

Membrane shows high flux and selectivity for dehydration with a feed of $H_2O/CO_2/CO/H_2$/methanol

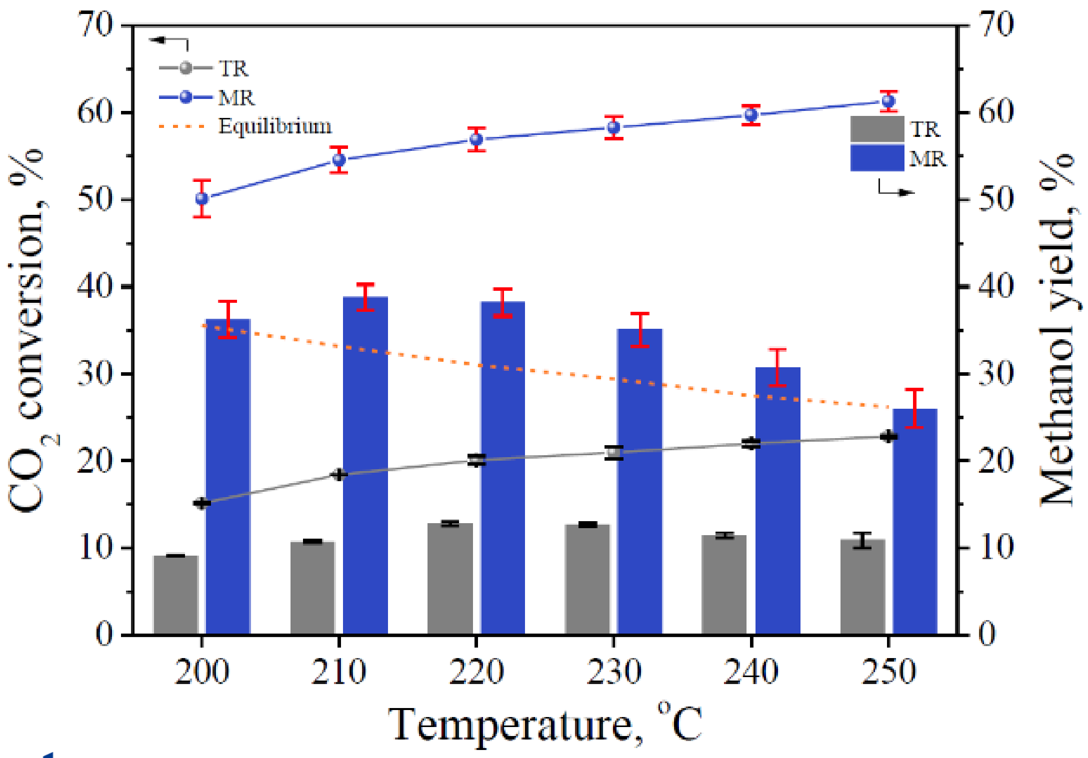


- **Other selectivities**
  - $H_2O/H_2 > 190$
  - $H_2O/CO > 170$
  - $H_2O/MeOH > 80$
  - H_2O/DMC: not tested yet, but expected to be >200

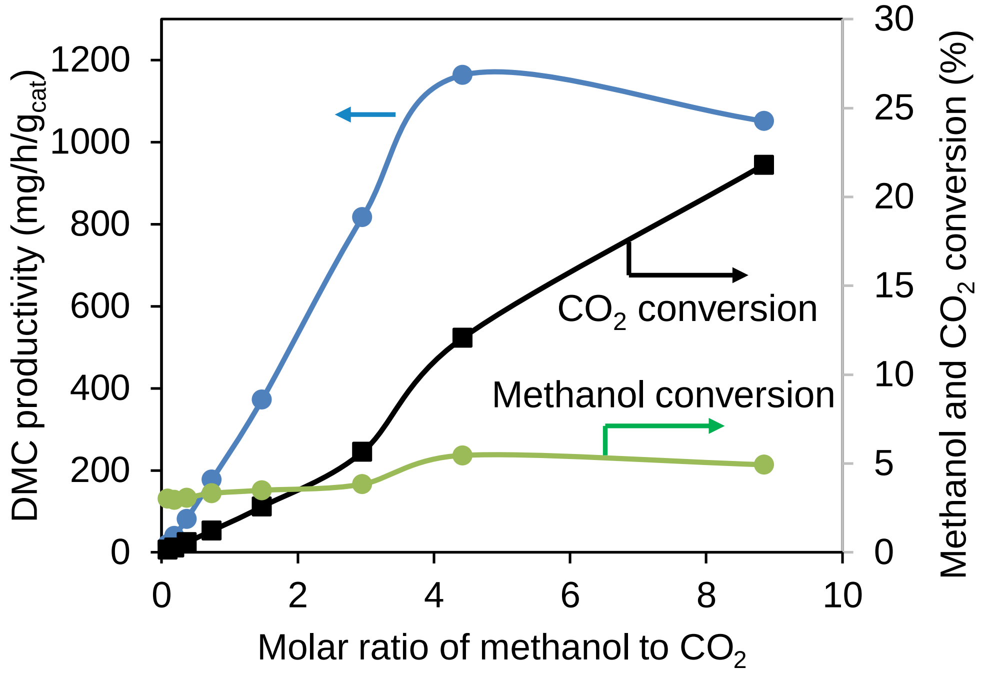
Kinetic diameters:
- DMC: 0.63 nm
- Methanol: 0.36 nm
- CO_2: 0.33 nm
- H_2: 0.289 nm

Methanol synthesis and DMC synthesis in membrane reactor

- **Membrane reactor methanol synthesis from CO_2 and H_2 using a CZA-based catalyst**
  - Compared to a traditional packed bed reactor (TR) without membrane, both CO_2 conversion and methanol yield increased 3 times

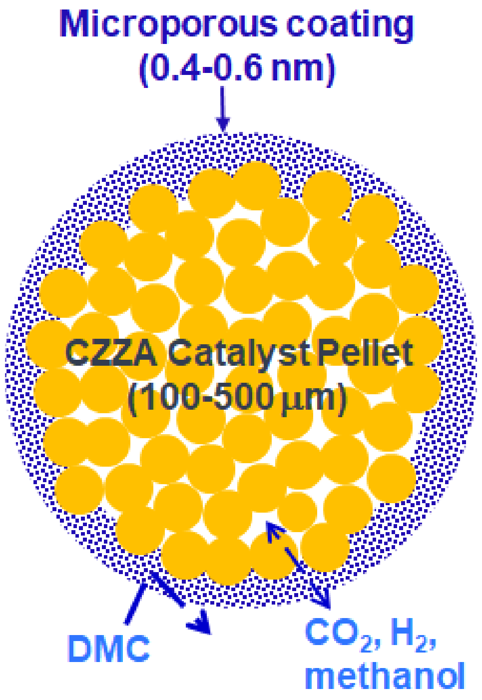


- **Membrane reactor DMC synthesis from methanol and CO_2 using a CeO_2-based catalyst**
  - CO_2 conversion of 21.8% and DMC productivity as high as 1.16 g/h/g_{cat}. In contrast, no CO_2 conversion was observed in packed bed reactor indicating the great advantage of using Na^+-gated membrane for dehydration



Technical challenge – the presence of 1st reaction catalyst (CZZA) may cause consumption of DMC by hydrogenation

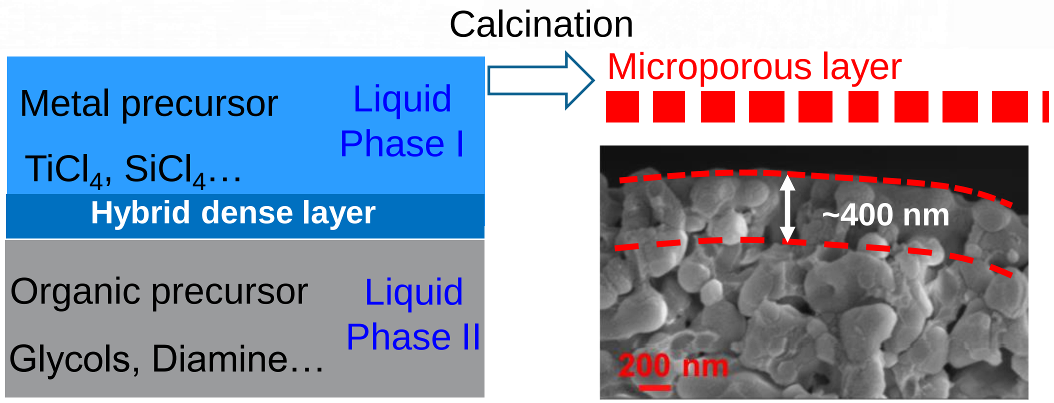
- **Mitigation strategy**: coating the external surface of CZZA catalyst (pore size: 0.4-0.6 nm) to prevent DMC hydrogenation by the CO_2 hydrogenation catalyst (CZZA) while still allowing free access of CO_2 and H_2 to the catalyst surface



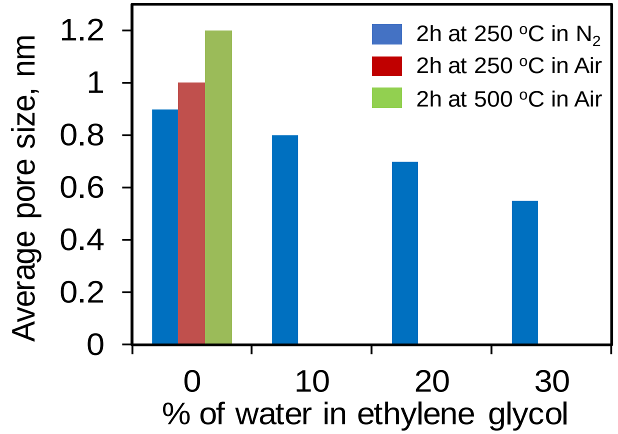
Kinetic diameters:

- DMC: 0.63 nm
- Methanol: 0.36 nm
- CO_2: 0.33 nm
- H_2: 0.289 nm

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



- Coating pore size adjustment by controlling synthesis conditions



Roadmap of the current project

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

Catalyst Development

Membrane Reactor Testing

Year 1 (12 months)

Task 2 – Preparation, characterization, and optimization of catalysts

Task 3 – Baseline membrane reactor testing and optimization

We are here

Task 4 – Coated catalyst development and catalytic performance evaluation

Year 2 (12 months)

Task 5 – Bifunctional membrane reactor testing and optimization

Task 6 – Optimization of bifunctional catalyst

Task 7 – Membrane reactor parametric and deactivation tests

Task 8 – Detailed techno-economic and life-cycle analyses

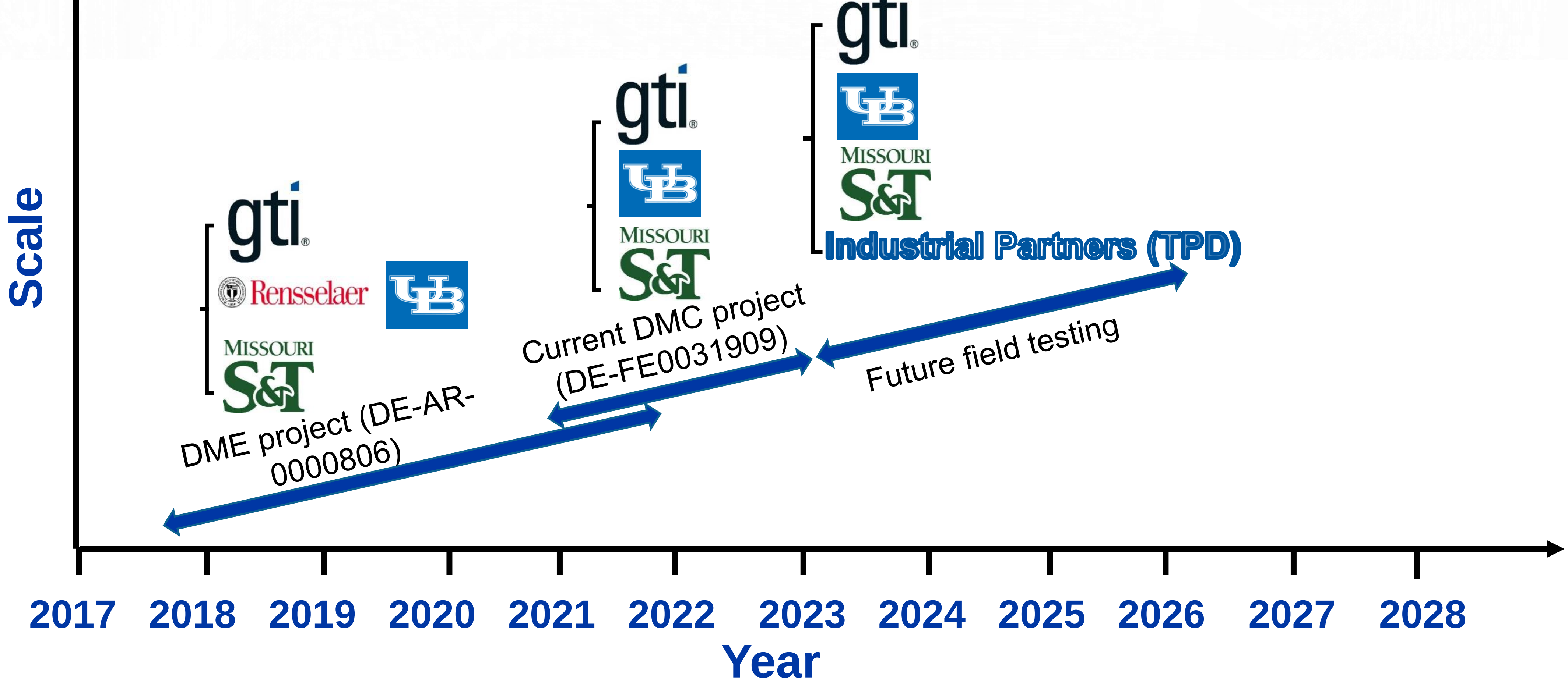
Milestones and success criteria

#	Task/ Subtask	Milestone Title/Description	Planned Completion Date	Actual Completion Date
M1.1	1	Submit updated Project Management Plan to DOE	2/28/21	2/18/21
M1.2	1	Complete Kickoff Meeting	3/31/21	3/19/21
M1.3	1	Submit technology maturation plan to DOE	3/31/21	3/23/21
M2.1	2	Ship >20 g of catalysts w/ BET surface area >100 m^2/g to RPI from MS&T	6/30/21	
M3.1	3	Achieve CO_2 conversion >20%, DMC selectivity >20%, DMC production rate >200 $g_{DMC}/kg_{cat}/h$ at 140-220ºC and 25-35 bar	6/30/21	
M4.1	4.1	Complete development of coated CZZA-based catalyst with coating layer thickness <0.5 mm and pore size between 0.4 and 0.6 nm	12/30/21	
M4.2	4.2	Achieve CO_2 conversion >15% and methanol yield >10% in methanol synthesis at 140-220ºC and 25-35 bar for the coated CZZA-based catalyst using a fixed bed reactor	12/30/21	
M5.1	5	Achieve CO_2 conversion >40%, DMC selectivity >50%, DMC production rate >500 $g_{DMC}/kg_{cat}/h$ at 140-220ºC and 25-35 bar	9/30/22	
M6.1	6	Achieve CO_2 conversion >20% and methanol yield >12% in methanol synthesis at 140-220ºC and 25-35 bar for the coated CZZA-based catalyst using a fixed bed reactor	9/30/22	
M7.1	7	Complete 100-500 hours continuous testing; achieve steady-state CO_2 conversion >50%, DMC selectivity >60%, and DMC production rate >600 $g_{DMC}/kg_{cat}/h$ at 140-220ºC and 25-35 bar	12/30/22	
M8.1	8	Issue Final TEA report with a Technology Gap Analysis	12/30/22	
M8.2	8	Issue Final LCA report	12/30/22	
M1.4	1	Submit Final Technical Report	3/30/23	

Technology development path

DME: $2CO_2 + 6H_2 \leftrightharpoons CH_3OCH_3 + 3H_2O$

DMC: $3CO_2 + 6H_2 \leftrightharpoons (CH_3O)_2CO + 3H_2O$



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 *in situ*, shifting equilibrium towards product formation
- **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
- **Next step** is to develop coated catalyst and test bifunctional membrane reactor

Acknowledgements

- Financial and technical support

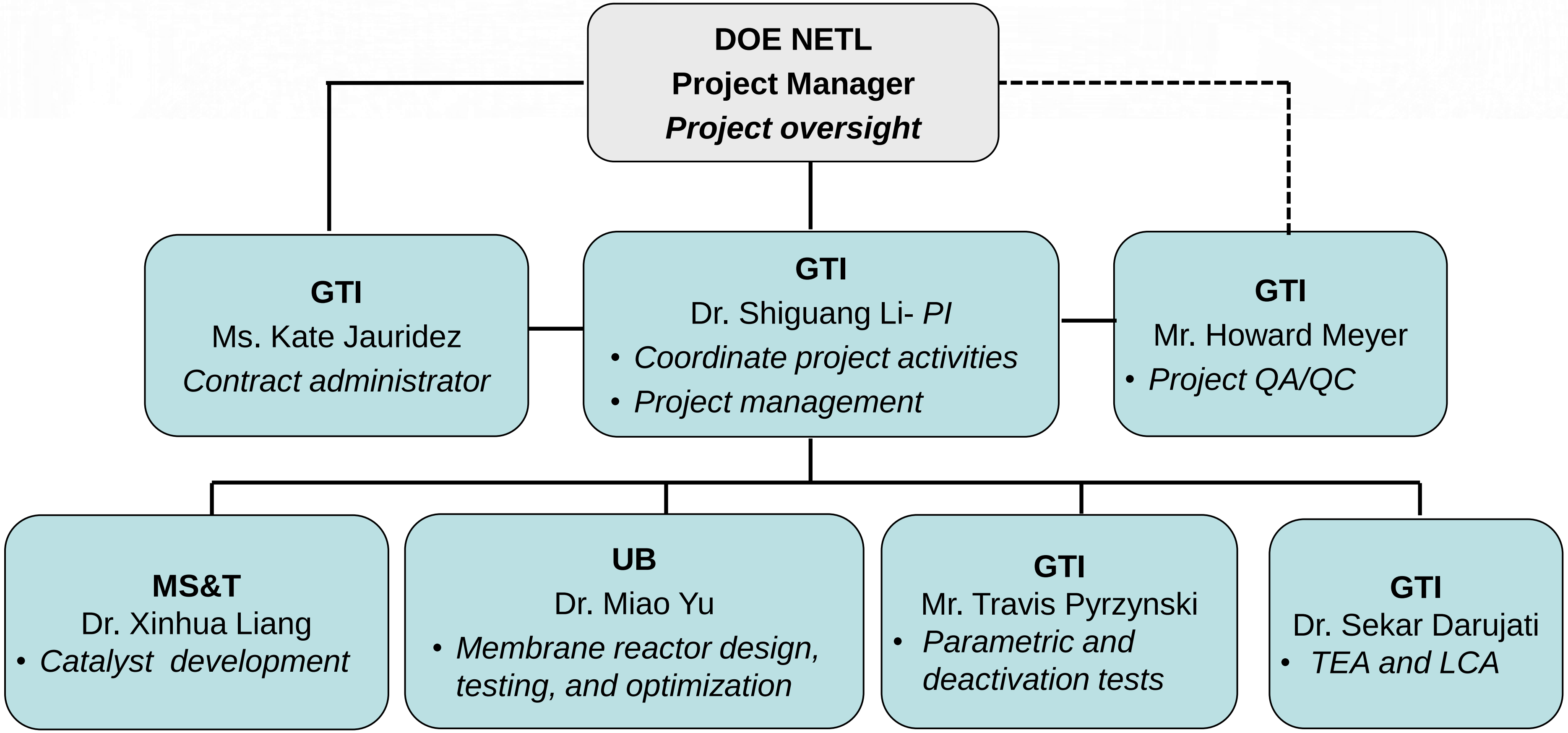
U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

DE-FE0031909

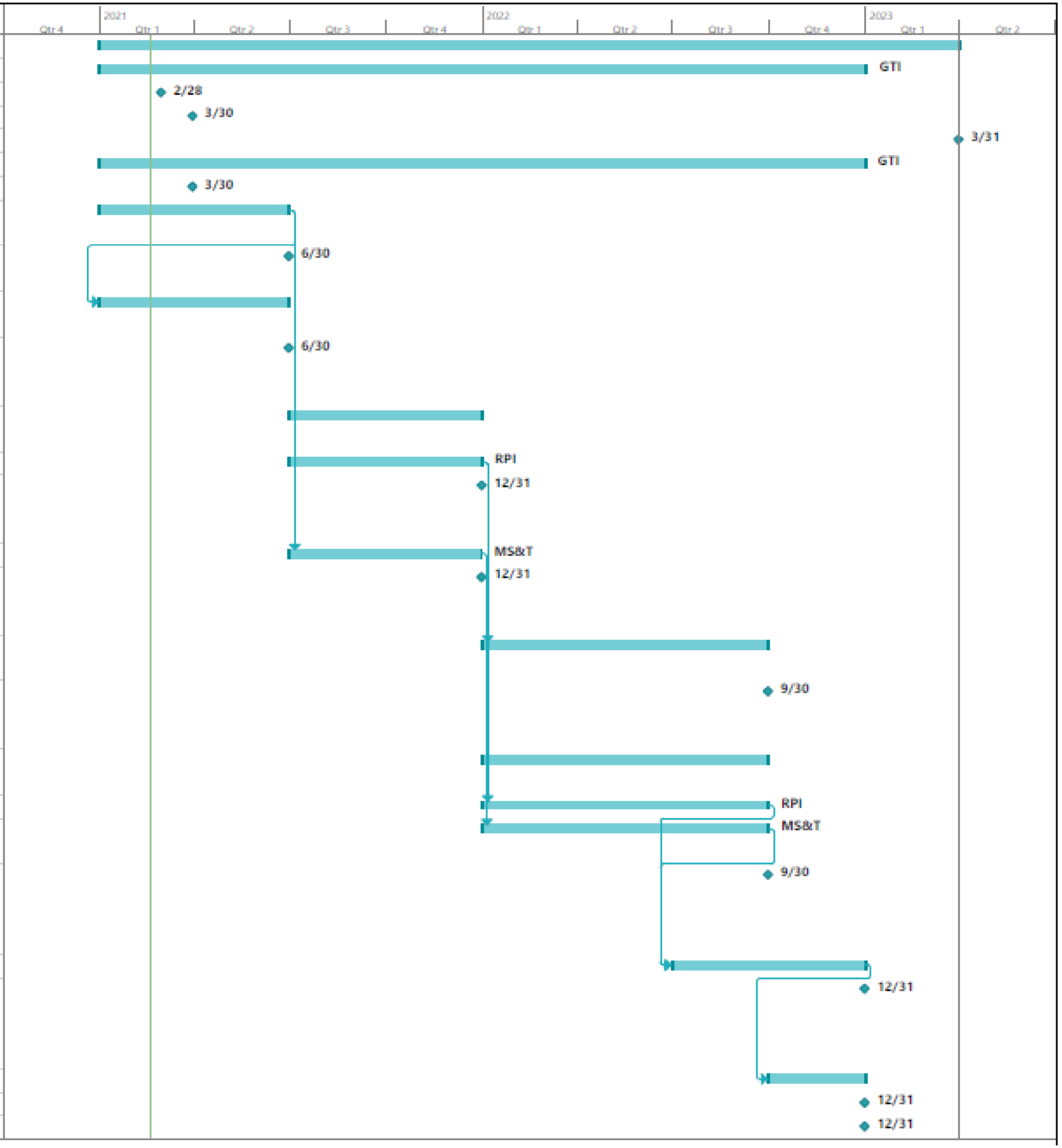
- DOE NETL: Andrea McNemar and Andrew O'Palko

Appendix – Organization chart



Appendix – Gantt chart

ID	Task No	SubT No	MS	Task Name	Start	Finish
1	1.0			Project Management and Planning	Fri 1/1/21	Fri 3/31/23
2		1.01		Project Management Plan	Fri 1/1/21	Sat 12/31/22
3			M1.1	Submit updated Project Management Plan to DOE	Sun 2/28/21	Sun 2/28/21
4			M1.2	Complete Kickoff Meeting	Tue 3/30/21	Tue 3/30/21
5			M1.4	Submit Final Technical Report	Fri 3/31/23	Fri 3/31/23
6		1.02		Technology Maturation Plan	Fri 1/1/21	Sat 12/31/22
7			M1.3	Submit technology maturation plan to DOE	Tue 3/30/21	Tue 3/30/21
8	2.0			Preparation, characterization, and optimization of catalyst	Fri 1/1/21	Wed 6/30/21
9			M2.1	Ship > 20 g of catalyst with BET surface area > 100 m2/g shipped	Wed 6/30/21	Wed 6/30/21
10	3.0			Sequential membrane reactor testing and optimization	Fri 1/1/21	Wed 6/30/21
11			M3.1	Achieve CO2 conversion >20%, DMC selectivity >20%, DMC production rate >200 g_DMC/kg_cat/h at 140-220C and 25-35 bar	Wed 6/30/21	Wed 6/30/21
12	4.0			Coated catalyst development and catalytic performance evaluation	Thu 7/1/21	Fri 12/31/21
13		4.01		Coated catalyst development	Thu 7/1/21	Fri 12/31/21
14			M4.1	Complete development of coated CZZA-based catalyst with coating layer thickness <0.5 um and pore size between 0.4 and 0.6 nm	Fri 12/31/21	Fri 12/31/21
15		4.02		Catalytic performance evaluation of the coated catalyst	Thu 7/1/21	Thu 12/30/21
16			M4.2	Achieve CO2 conversion >15% and methanol yield >10% in methanol synthesis at 140-220C and 25-35 bar for the coated CZZA-based catalyst using a fixed bed reactor	Fri 12/31/21	Fri 12/31/21
17	5.0			Bifunctional membrane reactor testing and optimization	Sat 1/1/22	Fri 9/30/22
18			M5.1	Achieve CO2 conversion >40%, DMC selectivity >50%, DMC production rate >500 g_DMC/kg_cat/h at 140-220C and 25-35 bar	Fri 9/30/22	Fri 9/30/22
19	6.0			Optimization of bifunctional catalyst for membrane reactor testing	Sat 1/1/22	Fri 9/30/22
20		6.01		Optimization of the coated catalyst	Sat 1/1/22	Fri 9/30/22
21		6.02		Catalytic performance evaluation of optimized coated catalyst	Sat 1/1/22	Fri 9/30/22
22			M6.1	Achieve CO2 conversion >20% and methanol yield >12% in methanol synthesis at 140-220C and 25-35 bar for the optimized coated CZZA-based catalyst using a fixed bed reactor	Fri 9/30/22	Fri 9/30/22
23	7.0			Membrane reactor parametric and deactivation tests	Fri 7/1/22	Sat 12/31/22
24			M7.1	Complete 100-500 hours continuous testing; achieve steady-state CO2 conversion >50%, DMC selectivity >60%, and DMC production rate >600 g_DMC/kg_cat/h at 140-220C and 25-35 bar	Sat 12/31/22	Sat 12/31/22
25	8.0			Detailed techno-economic and life-cycle analysis	Sat 10/1/22	Sat 12/31/22
26			M8.1	Issue Final TEA report with a Technology Gap Analysis	Sat 12/31/22	Sat 12/31/22
27			M8.2	Issue Final LCA report	Sat 12/31/22	Sat 12/31/22



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