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U.S. DEPARTMENT OF ENERGY

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
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Carbon Management Project Review Meeting
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Project overview

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- **<u>Background</u>**: Membrane reactor DME production successfully developed through an ARPA-E project (DE-AR0000806)
- **<u>Current project objective</u>**: Develop membrane reactor for production of dimethyl carbonate (DMC) from CO_2 and H_2
  - DMC's market projected to grow from $895 million in 2019 to $1,207 million by 2024, at a CAGR of 6.2% from 2019 to 2024
- **<u>Performance period</u>**: 1/1/21 – 9/30/23
- **<u>Total funding</u>**: $1,269,664 (DOE: $1.0 MM, cost share: $269,664)
- **<u>Goal</u>**: CO_2 conversion >50%, DMC selectivity >60%
- **<u>Team</u>**:

Member	Roles
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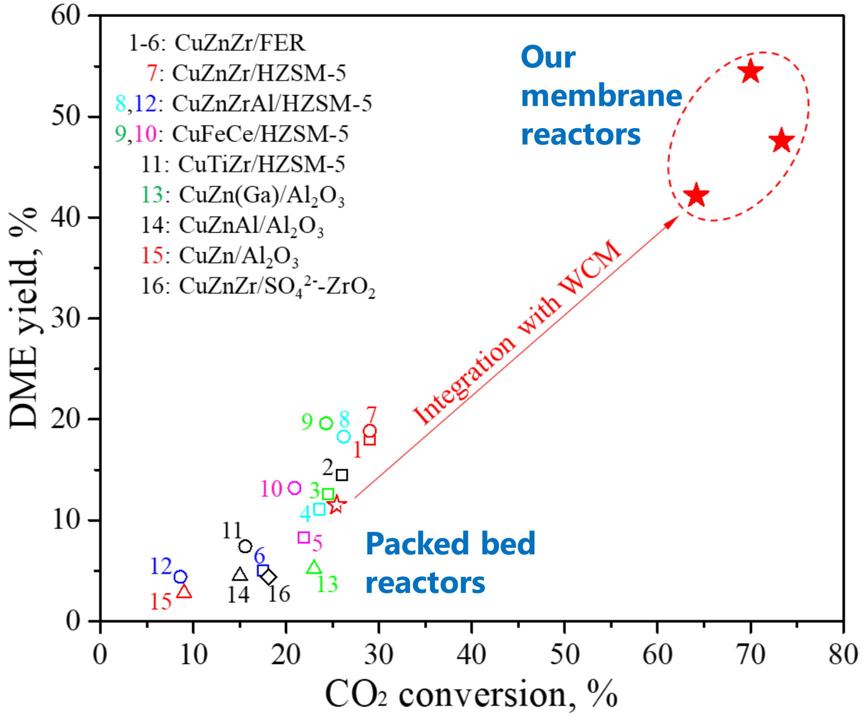
UB	• Membrane and membrane reactor development
MISSOURI S&T	• Catalyst development



- $2CO_2 + 6H_2 \leftrightharpoons CH_3OCH_3 + 3H_2O$
- CO_2 conversion and DME yield significantly greater than packed bed reactors reported in the literature

DME: dimethyl ether; DMC: dimethyl carbonate

Technology description

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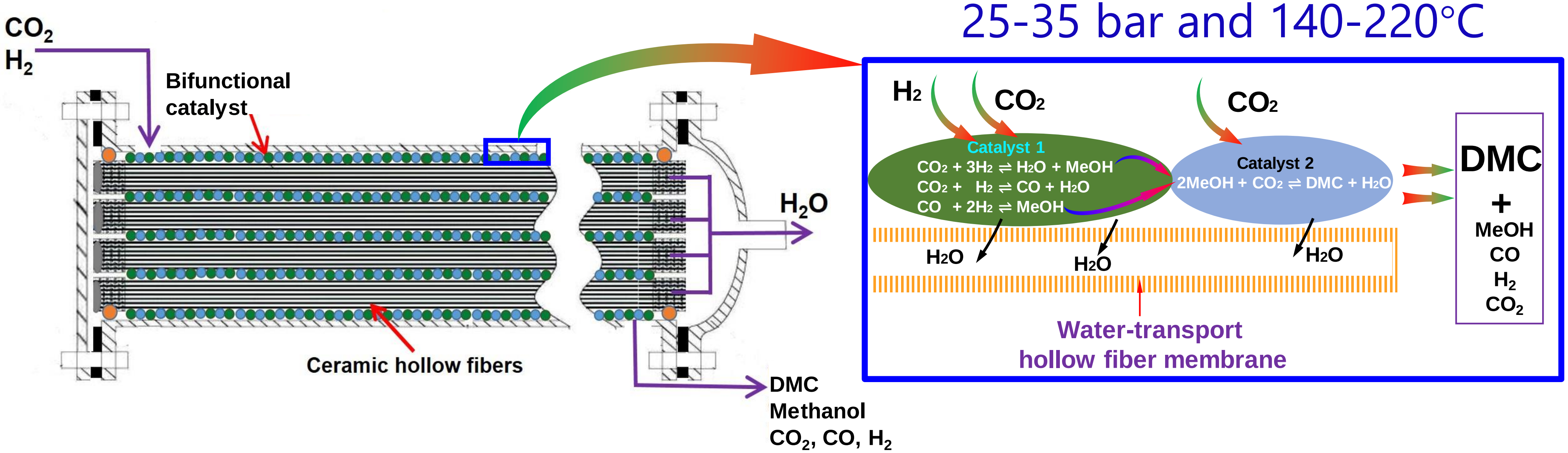
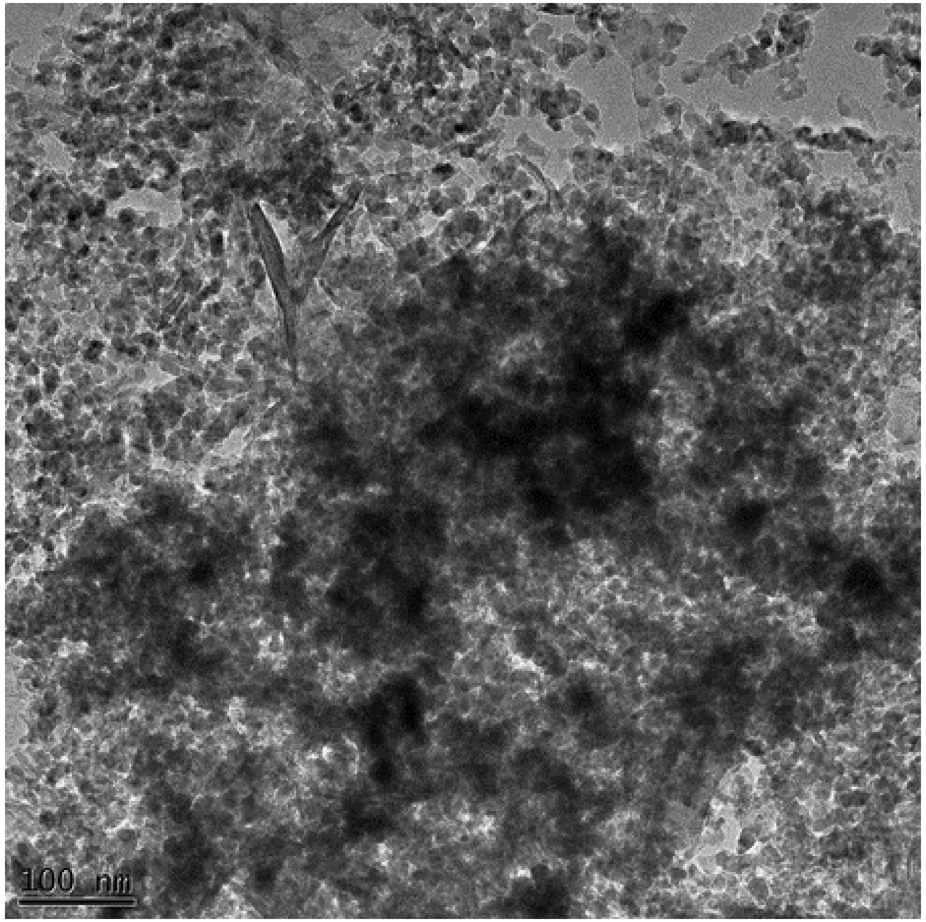


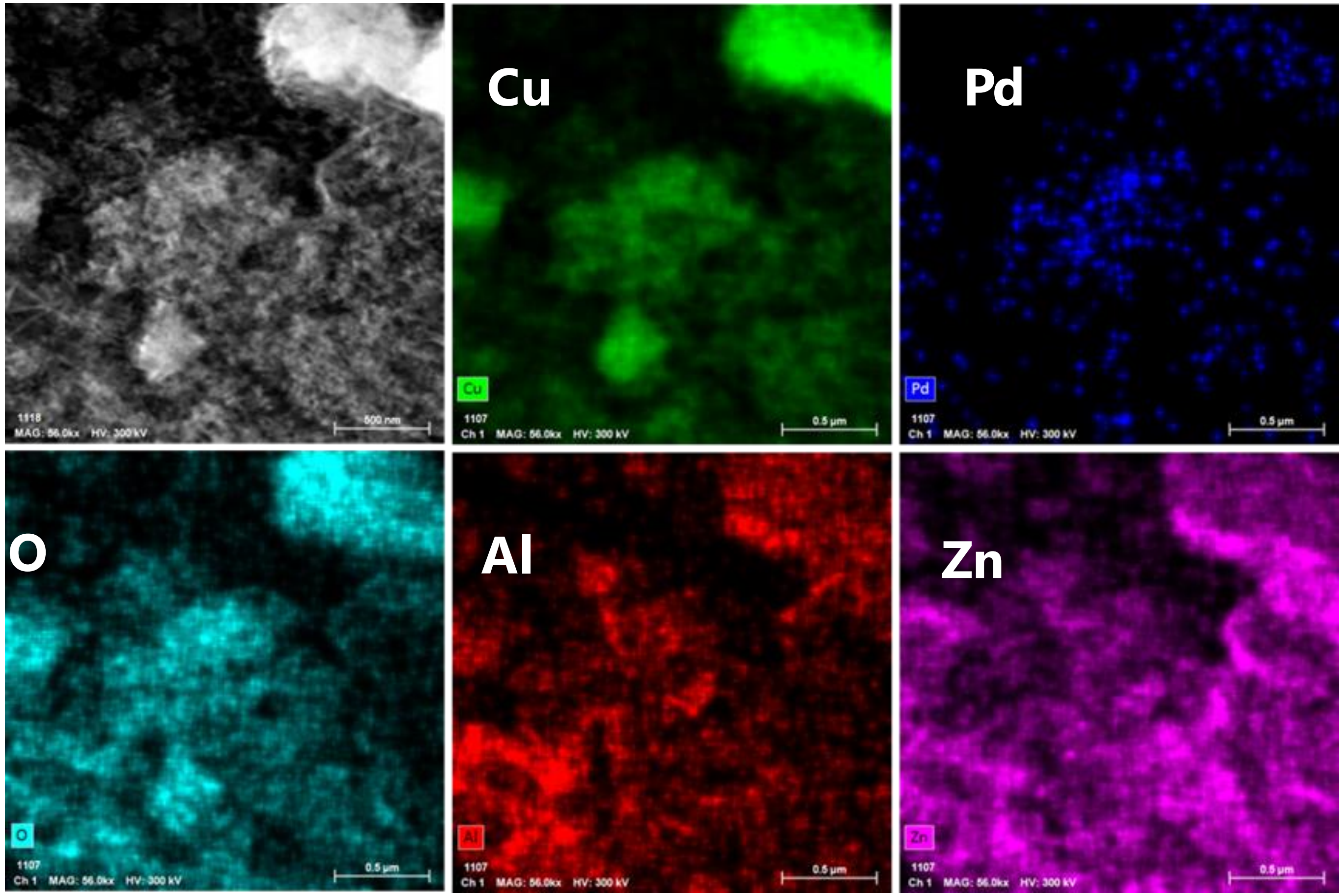
- One-step process intensifies a process that would otherwise require multiple steps:
  - Methanol synthesis: $CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$ $\Delta H^0 = -49$ kJ/mol Catalyst 1: $CuO/ZnO/Al_2O_3$ based
  - DMC synthesis: $2CH_3OH + CO_2 \leftrightharpoons (CH_3O)_2CO + H_2O$ $\Delta H^0 = -17.3$ kJ/mol Catalyst 2: CeO_2 based
  - Combined reaction: $3CO_2 + 6H_2 \leftrightharpoons (CH_3O)_2CO + 3H_2O$
- Na^+-gated membrane (***Science***, vol. 367, pp. 667, 2020) removes water *in situ*, shifting the equilibrium towards product formation

Catalyst Development

Palladium-CuO/ZnO/Al_2O_3 (CZA) developed for the first reaction – methanol synthesis



TEM image: uniform nanoscale particles (~15 nm)



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

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

0.9 wt.% Pd/CZA shows the best methanol synthesis performance in a packed bed reactor

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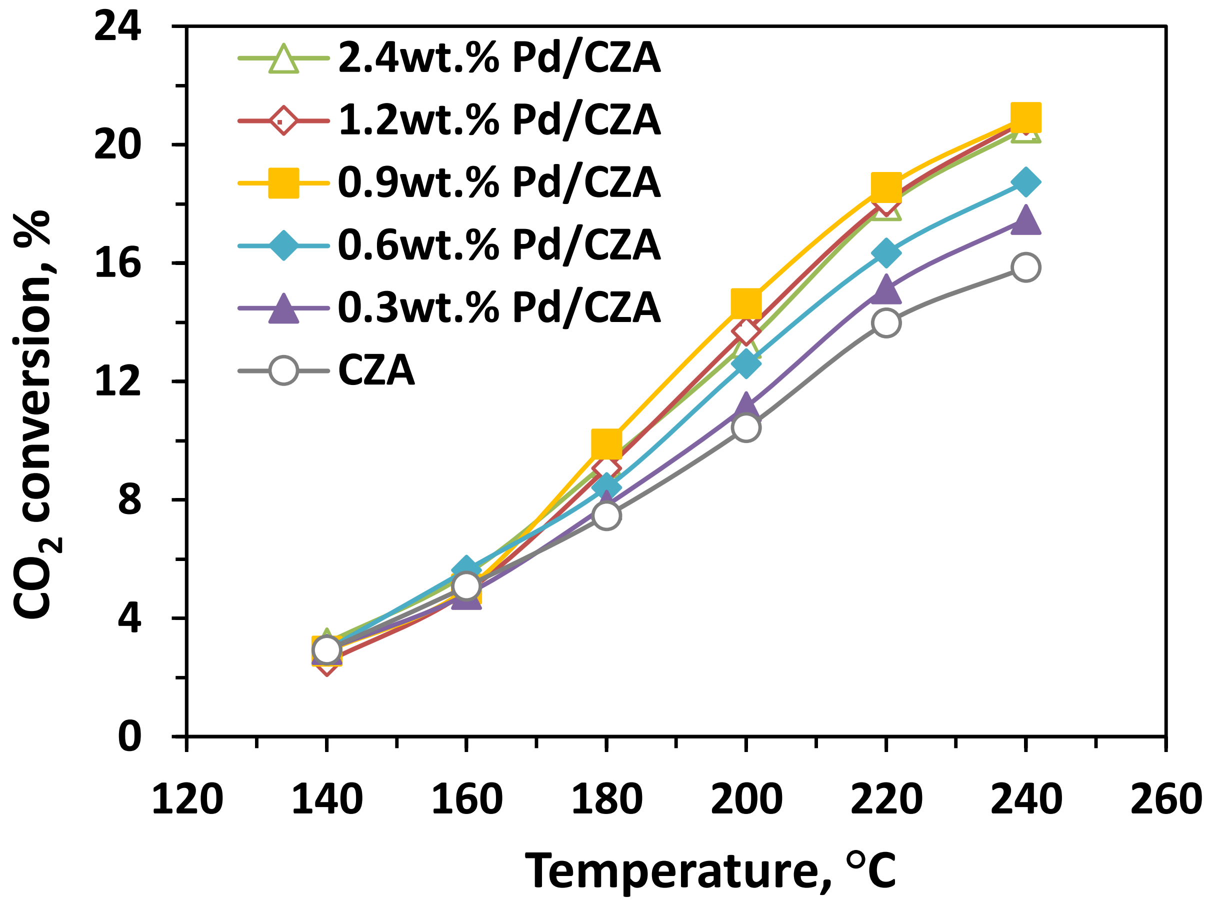
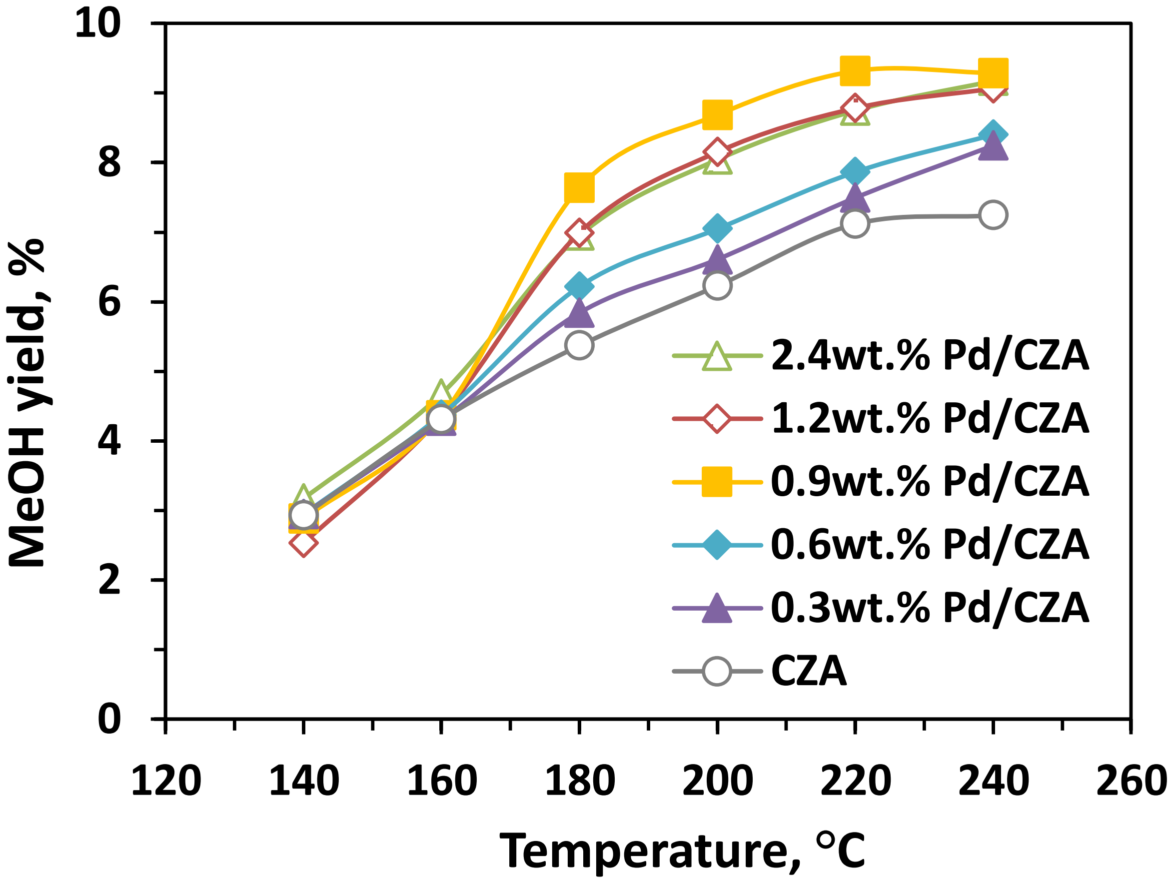
Reaction conditions: T = 140-240°C, P = 2.8 MPa, H_2/CO_2 molar ratio = 3:1, GHSV = 2,880 mL/(g_{cat}·h)





GHSV: Gas Hourly Space Velocity; CZA: $CuO/ZnO/Al_2O_3$

CeO_2-based catalyst developed for the second reaction – methanol dehydration

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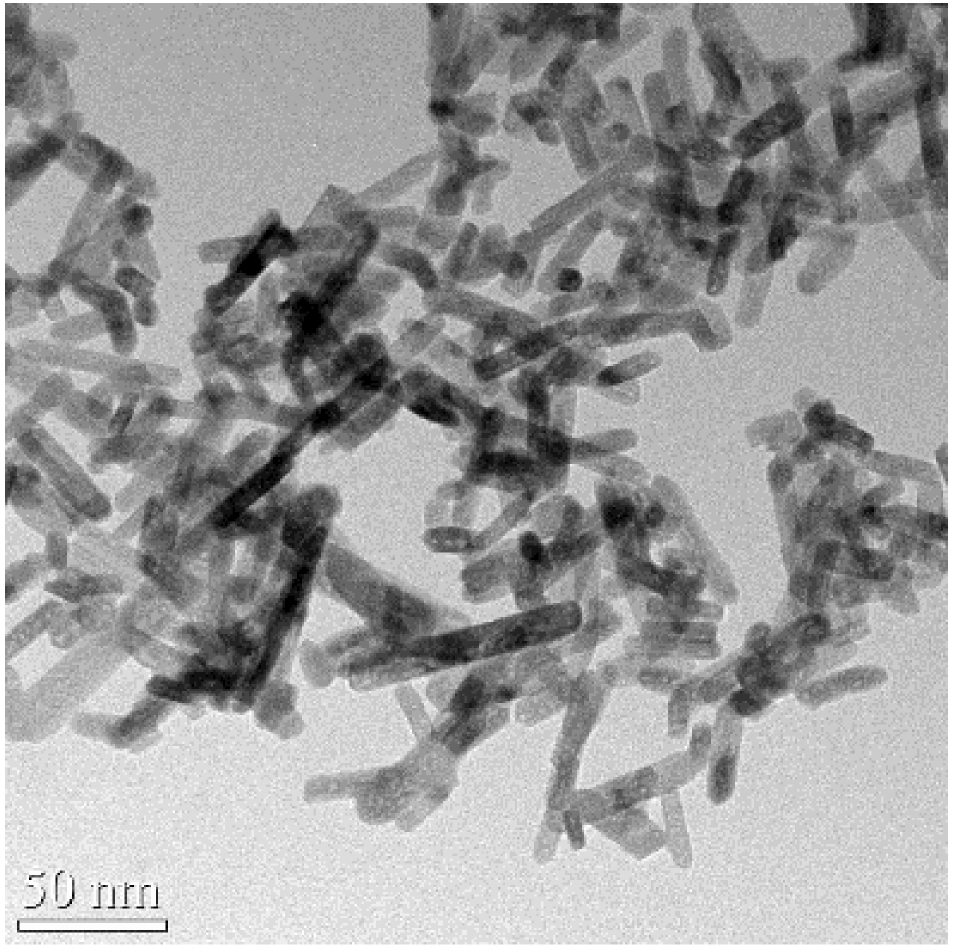


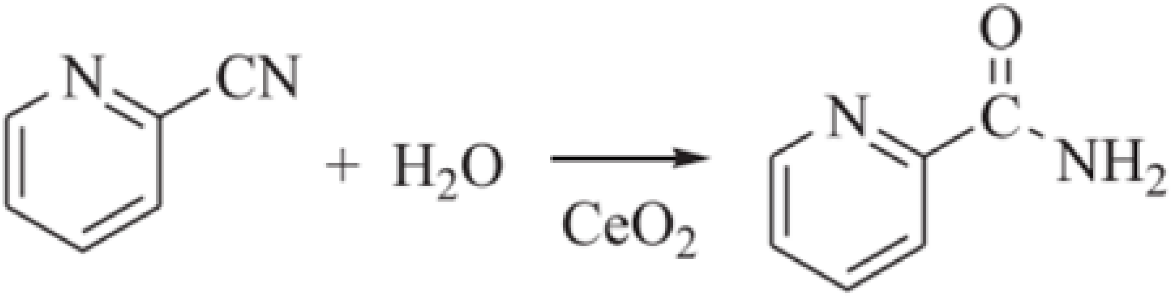
TEM image: nanorods catalyst

- **Liquid phase reaction at 140°C for DMC synthesis**:
  - DMC selectivity: 100%
  - Methanol conversion: 0.48%
  - DMC yield: 8.1 mmol DMC/$g_{catalyst}$

TEM: Transmission Electron Microscopy

Removal of H_2O using a dehydration agent boosts methanol dehydration

- Dehydration agent 2-cyanopyridine (2-CP) reacts with H_2O to form 2-picolinamide



- DMC synthesis at 140°C:

Methanol (g)	2-CP (g)	CeO_2 (g)	Pressure (MPa)	Methanol conversion (%)	DMC yield ($mmol_{DMC}/g_{cat}$)
12	0	0.1	3	0.48	8.1
6.4	1.04	0.1	3	5.5	28
6.4	10.4	0.3	3	73	240
6.4	10.4	0.3	5	87	290

Membrane and Membrane Reactor Development

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

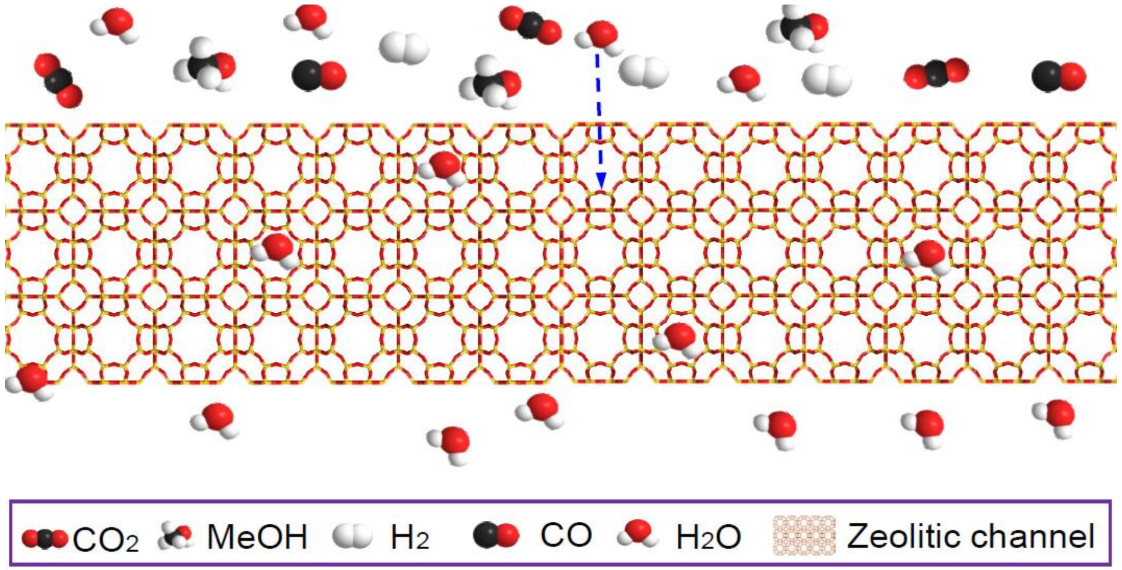
Science

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



Kinetic diameters:

- H_2O: 0.265 nm
- H_2: 0.289 nm
- CO_2: 0.33 nm
- Methanol: 0.36 nm
- DMC: 0.63 nm

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

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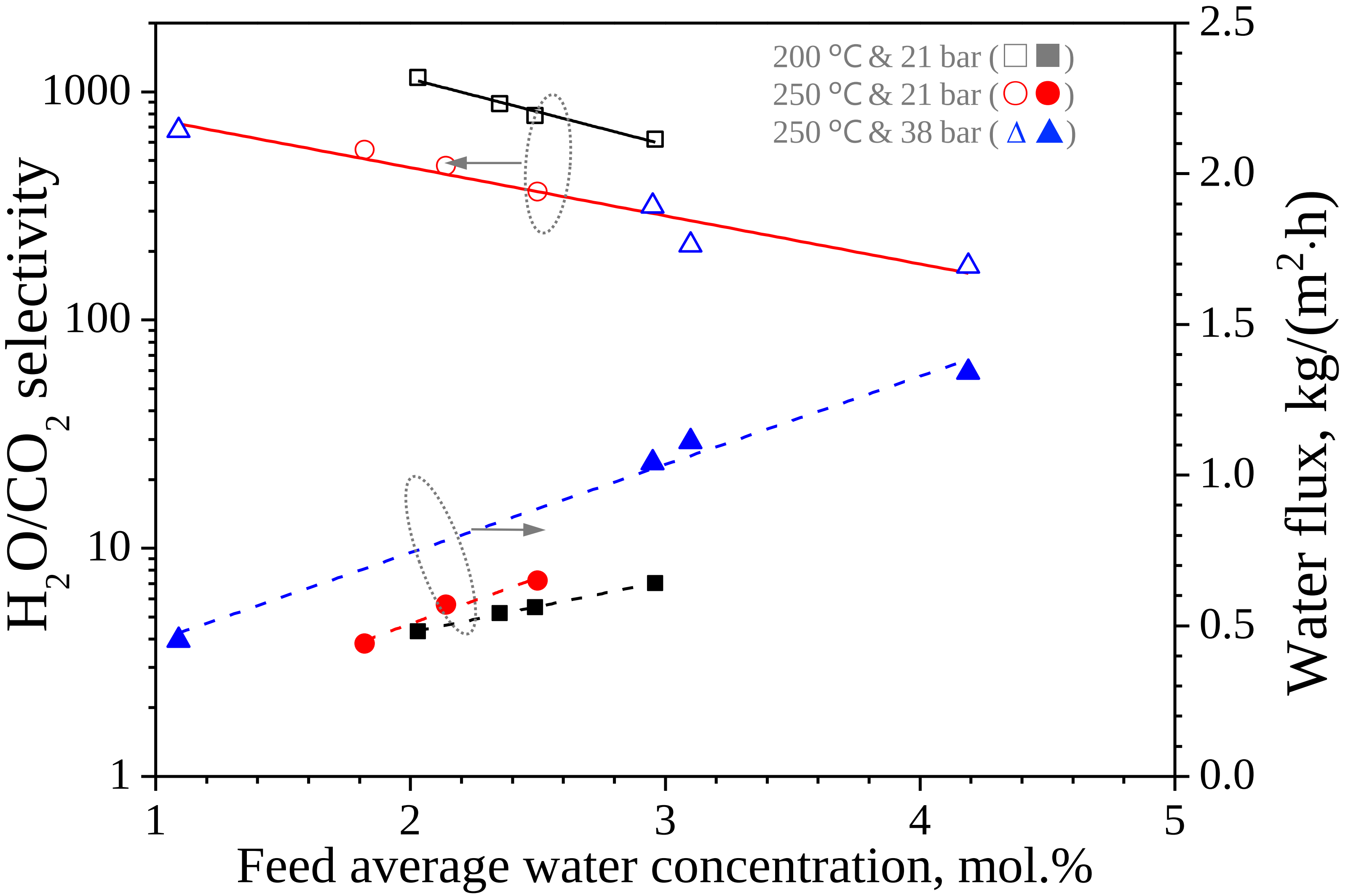


- **Other selectivities**
  - H_2O/H_2 >190
  - H_2O/CO >170
  - H_2O/MeOH >80
  - H_2O/DMC: not tested yet, but expected to be >200

Kinetic diameters:

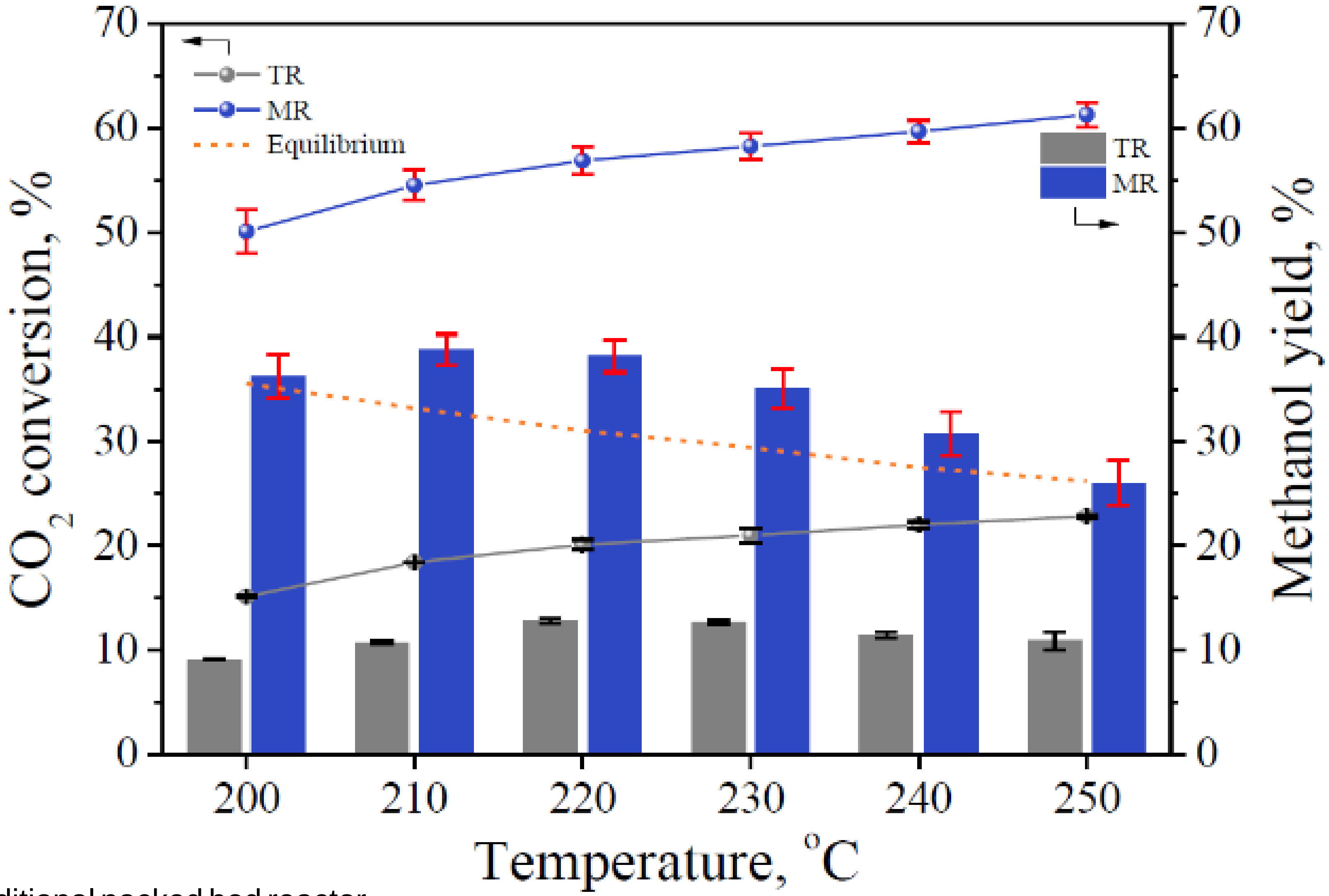
- DMC: 0.63 nm
- Methanol: 0.36 nm
- CO_2: 0.33 nm
- H_2: 0.289 nm
- H_2O: 0.265 nm

Membrane also showed good dehydration capability at even lower water concentrations

- Tested with CO_2/H_2O mixtures

Temperature (°C)	Feed water		Retentate water		Water permeance ($mol/m^2/s/Pa$)
	Partial pressure (psi)	Concentration (vol%)	Partial pressure (psi)	Concentration (vol%)	
120	1.76	0.35	1.35	0.27	6.8×10^{-7}
150			0.95	0.19	8.1×10^{-7}
180	0.94	0.19	0.49	0.10	7.9×10^{-7}

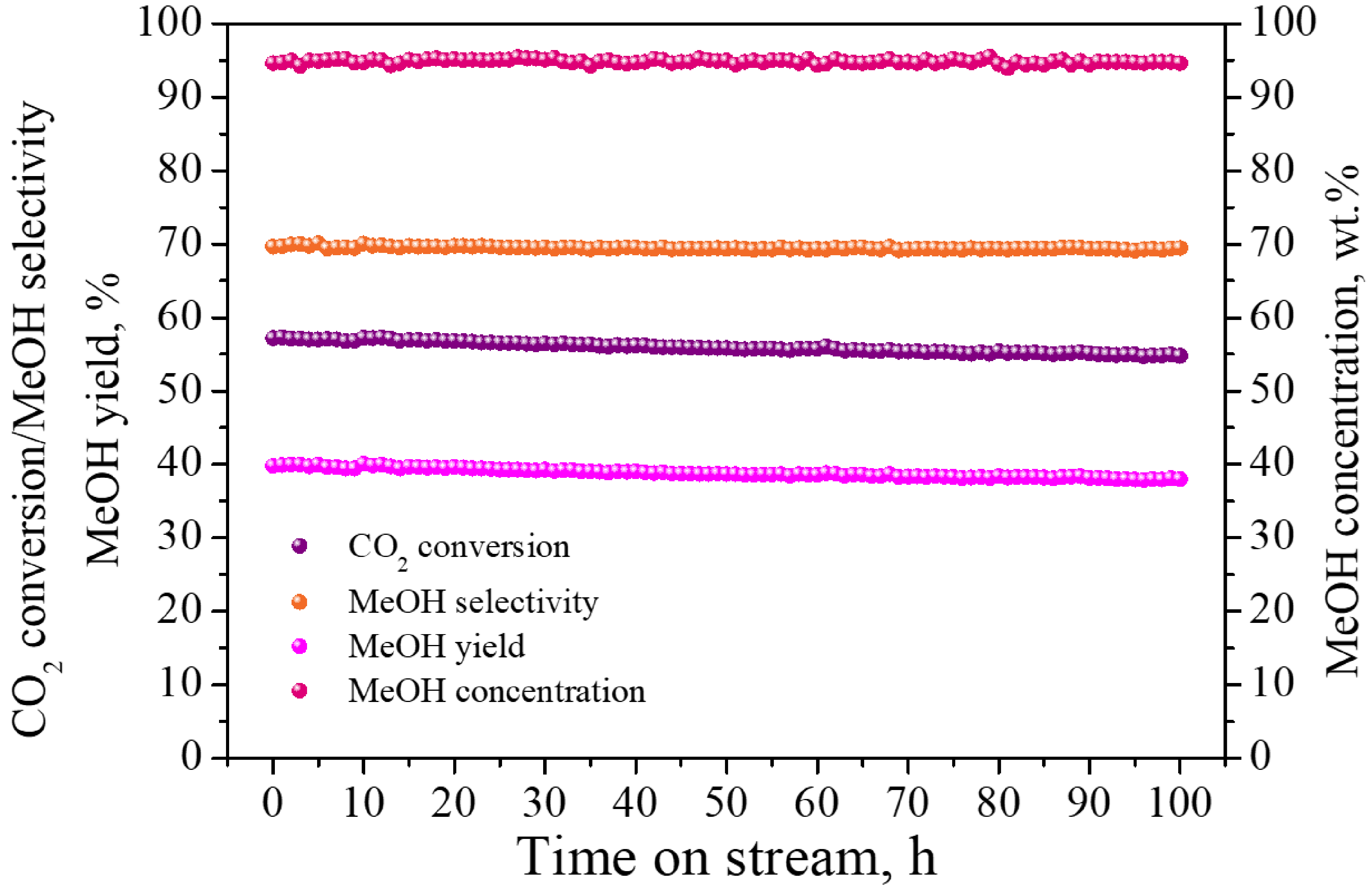
Membrane reactor methanol synthesis (first reaction): superior performance to packed bed



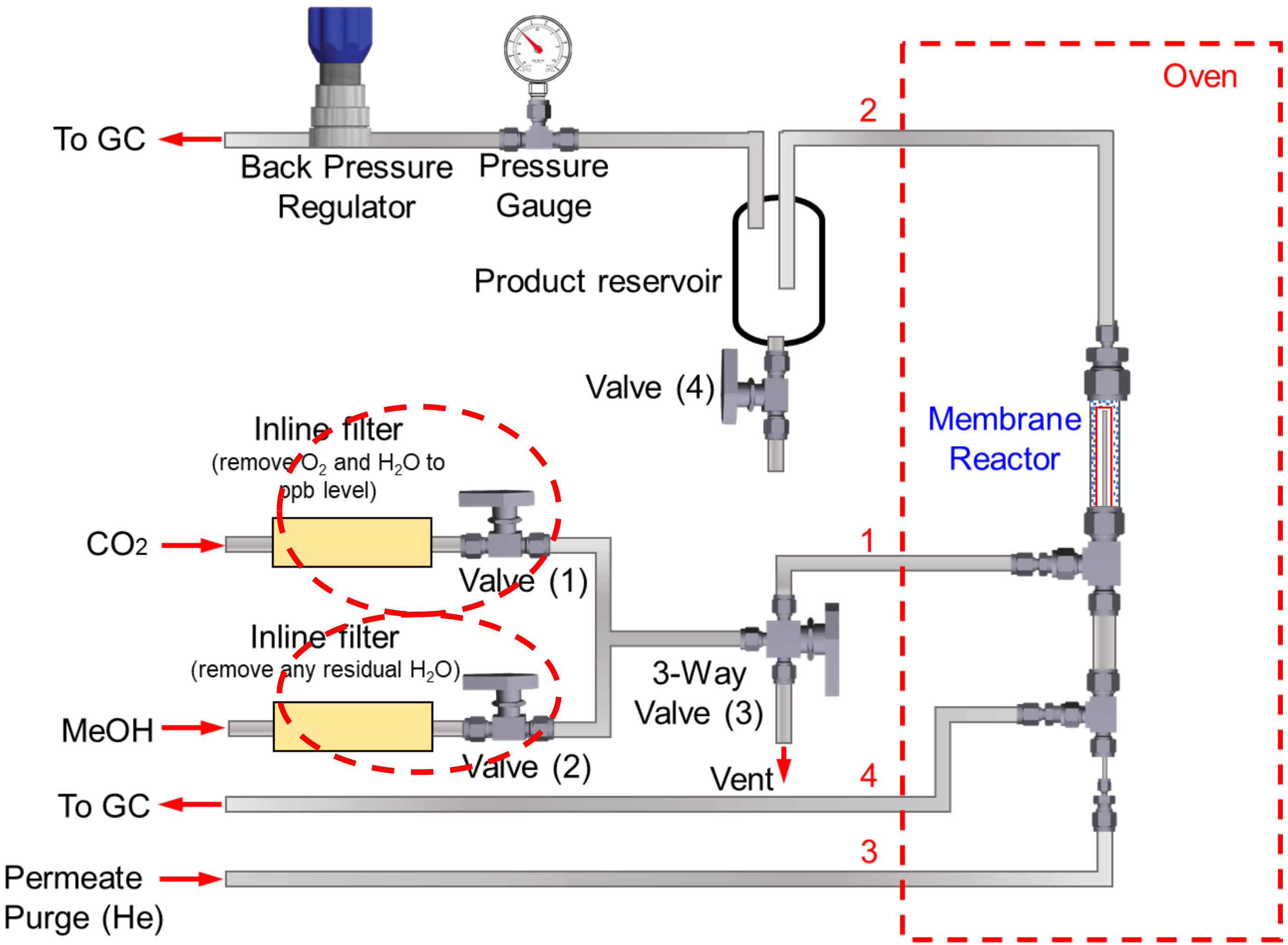
TR: traditional packed bed reactor
MR: membrane reactor

- **Compared to a traditional packed bed reactor without membrane, both CO_2 conversion and methanol yield increased 3 times in membrane reactor**

Methanol synthesis (first reaction): good stability during 100-h testing



Technical challenge – low methanol conversion for the second reaction



- **Testing conditions:**
  - Catalyst: CeO_2
  - Pressure: 500 psig
  - Temperature: 150-180 °C
- **Testing results:**

Temp. (ºC)	Methanol/CO_2 molar ratio	Methanol conversion (%)
150	2.2	0.66
180	2.2	0.86
180	4.4	0.54

- **Future plan:**
  - Optimize operating conditions to improve performance

State-point data

	Units	Measured/Current Performance	Projected/Target Performance
Synthesis Pathway Steps			
Step 1 (based on CO_2)	mol^{-1}	$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$	
Step 2	mol^{-1}	$2CH_3OH + CO_2 \leftrightharpoons (CH_3O)_2CO + H_2O$	
Source of external intermediate 1		H_2 from reforming of natural gas or electrolysis	
Source of external intermediate 2		No external intermediate	
Reaction Thermodynamics			
Reaction		Total: $3CO_2 + 6H_2 \leftrightharpoons (CH_3O)_2CO + 3H_2O$	
ΔH^o_{rxn}	KJ/mol	Total: -116.1 (Step 1: -49.4, and Step 2: -17.3)	
ΔG^o_{rxn}	KJ/mol	Total: 31.5 (Step 1: 4.0, and Step 2: 23.5)	
Conditions		(range)	(range)
CO_2 Source		Captured CO_2 from coal-, natural gas-fired or industrial flue gases	
Catalyst		Step1: CZA-based catalyst,; Step2: CeO_2 catalyst	
Pressure	Bar	Step 1: 28; Step 2: 4-16	25-35
CO_2 Partial Pressure	Bar	Step1: 7; Step 2: 1.3-5.3	1.5-7
Temperature	℃	Step 1: 160-260; Step 2: 100-160	140-220
Performance		(range)	(minimum)
Nominal Residence Time	Sec	Step 1: 2,240; Step 2: 1,180	~4,480
Selectivity to Desired Product	%	Step 1: 50-65; Step 2: 60-90	60.4
Product Composition		(range)	(optimal)
Desired Product-DMC	mol%	~0.1	18.0
Desirable Co-Products-MeOH	mol%	~32.3	10
Desirable Co-Products-CO	mol%	~17.5	0
Unwanted By-Products-H_2O	mol%	~50.1	70.0
Unwanted By-Product-DME	mol%	0	2.0
Grand Total	**mol%**	--	100%

Membrane reactor technology development path

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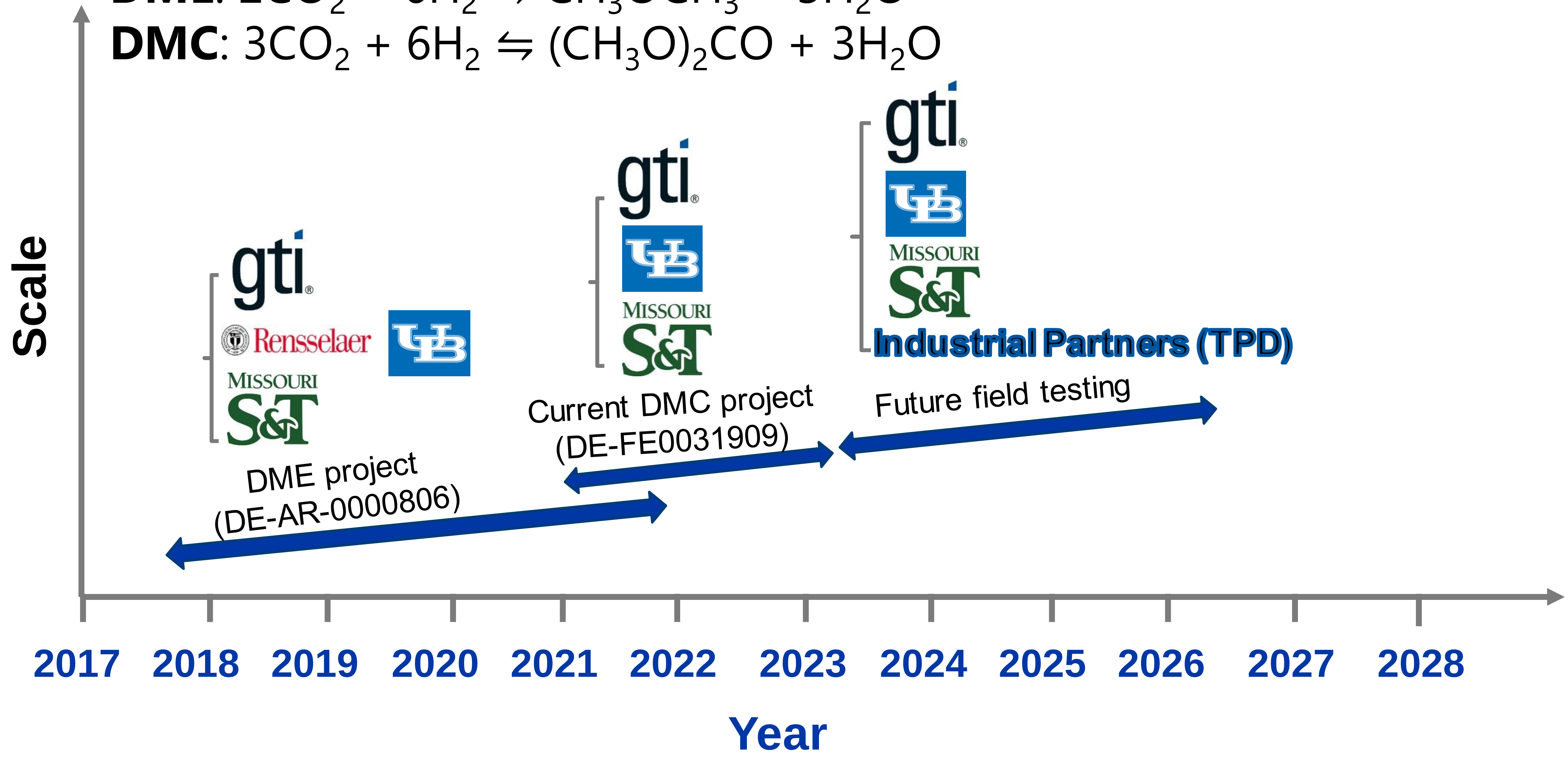
DME: $2CO_2 + 6H_2 \leftrightharpoons CH_3OCH_3 + 3H_2O$

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



Summary

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- We are developing a membrane reactor for production of DMC.
  - Na^+-gated membrane removes water *in situ*, shifting equilibrium towards product formation.
- First reaction (methanol synthesis): membrane reactor CO_2 conversion and methanol yield are 3 times greater than packed bed reactor.
- Second reaction (methanol dehydration): methanol conversion is low; approaches to resolve this technical challenge are ongoing.

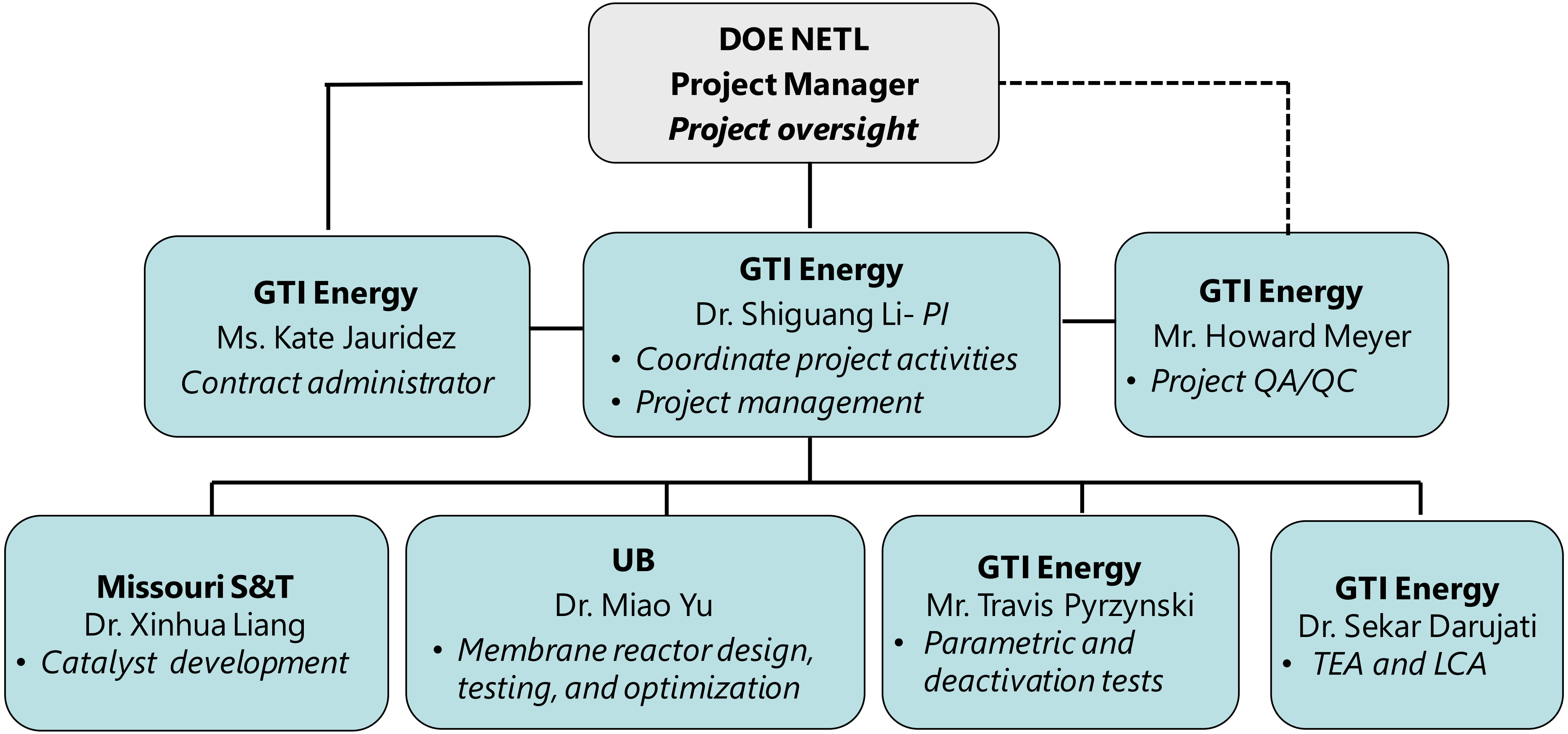
Acknowledgements

- Financial and technical support

DE-FE0031909

- DOE NETL: Andy Aurelio, Andrea McNemar and Andrew O'Palko

Appendix – Organization chart



Appendix – Gantt chart

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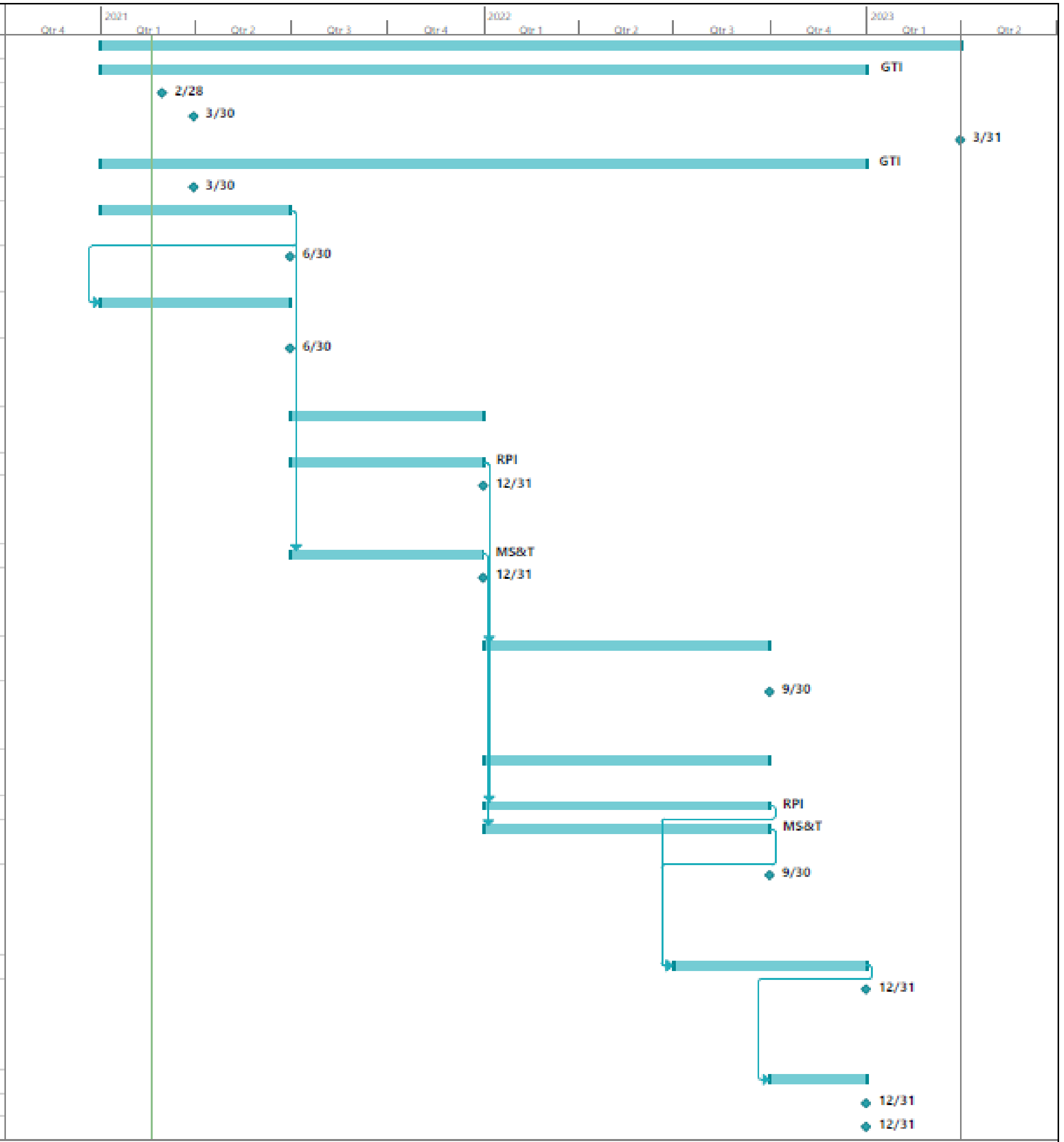
ID	Task No	SubT No	MS	Task Name	Start	Finish
1	1.0			Project Management and Planning	Fri 1/1/21	Fri 3/31/23
2		1.01		Project Management Plan	Fri 1/1/21	Sat 12/31/22
3			M1.1	Submit updated Project Management Plan to DOE	Sun 2/28/21	Sun 2/28/21
4			M1.2	Complete Kickoff Meeting	Tue 3/30/21	Tue 3/30/21
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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