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solutions that transform

U.S. DEPARTMENT OF ENERGY

DE-FE0031909

Dehydration Membrane Reactor for Production of Valuable Chemicals from CO_2 and H_2

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2024 FECM/NETL Carbon Management Research Project Review Meeting

August 5 – 9, 2024

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CCUS is one of GTI strategic focus areas

- **Carbon capture**
  - **FE0031946**: 20 TPD facilitated transport membrane (FTM) for power plant application
  - **FE0032466**: 3 TPD ROTA-CAP for steel plant application
  - **FE0032463**: 3 TPD FTM for cement plant (sub to OSU)
  - **FE0031598**: Bench-scale GO-based membrane
  - **FE0032215**: Nano-confined ionic liquid membrane
  - **FE0031730**: Size-sieving adsorbent (sub to UB)
- **Carbon conversion**
  - **FE0031909:** Membrane reactors for conversion of CO_2 to fuels/chemicals
  - **FE0032246:** Converting CO_2 to carbon-negative alternative cement (sub to WashU)
- **Carbon dioxide removal (CDR)**
  - **FE0031969**: Trapped small amines in capsules (sub to UB)
- **Carbon transport and storage**
  - **FE0032239**: CarbonSAFE Phase II

Project Overview

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- **Performance period**: 1/1/21 – 3/31/25
- **Total funding**: $1,269,664 (DOE: $1.0MM, cost share: $269,664)
- **Objectives**: Develop membrane reactor for production of liquefied petroleum gas (LPG) valuable chemicals from CO_2 and H_2
- **Goal:** CO_2 conversion >50%, LPG yield >45%
- **Team**:

Member	Roles
GTI ENERGY solutions that transform	• Project management and planning • Parametric and deactivation tests • Techno-economic and life-cycle analyses
UB	• Membrane and membrane reactor development
Missouri S&T; Washington University in St. Louis	• Catalyst development

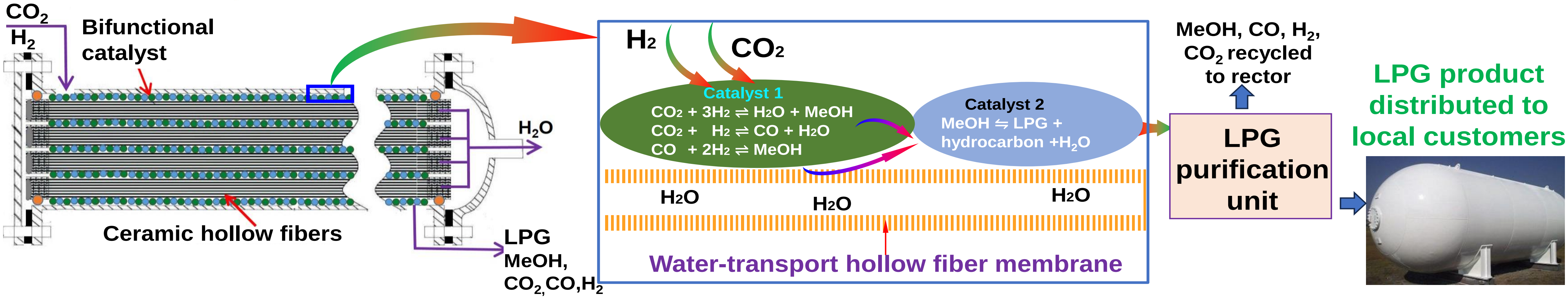
The rising need for LPG

- Global LPG production ~330 million tonnes in 2022
- The Europe LPG market was roughly 42 million tonnes in 2021, and is expected to grow to 59 million tonnes by 2027
- Nearly 2% of the U.S. energy needs are supplied LPG
- LPG is an economically efficient, cooking energy solution already used by over 2.5 billion people worldwide

LPG: liquefied petroleum gas

Technology description

10-35 bar and 220-330°C



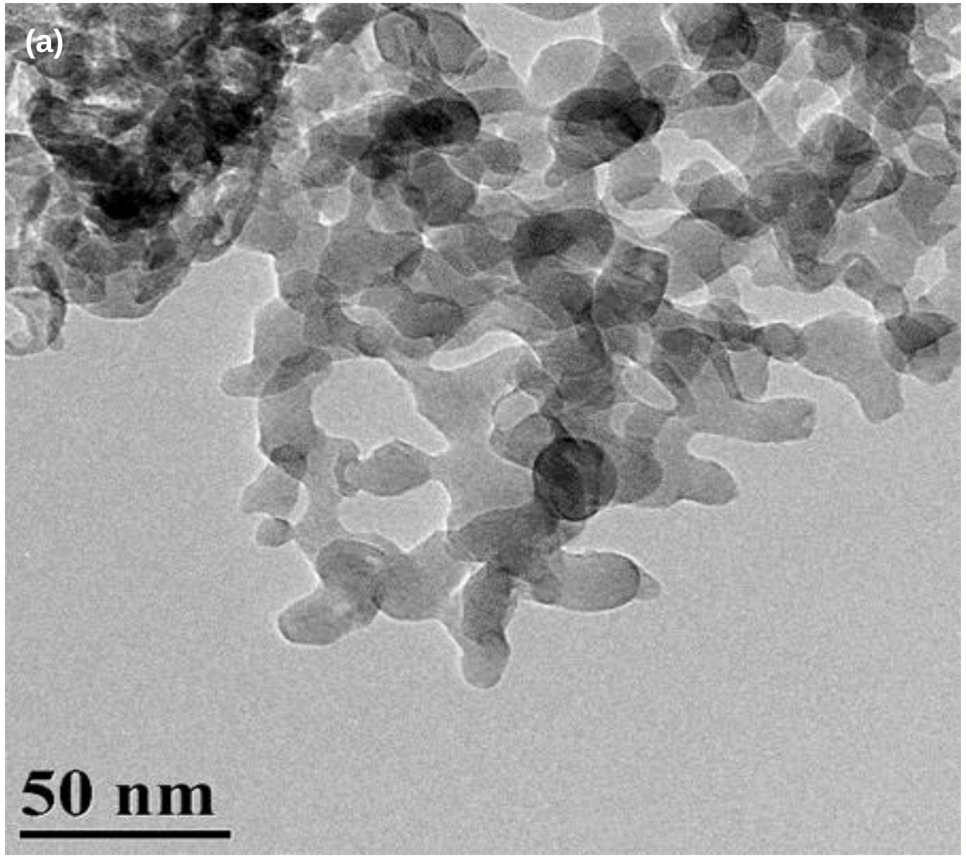
- One-step process with bifunctional catalyst intensifies a process that would otherwise require multiple steps:
  - Methanol synthesis: $CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$ Catalyst 1: $CuO/ZnO/Al_2O_3$ based
  - LPG synthesis: $MeOH \leftrightharpoons LPG + hydrocarbon + H_2O$ Catalyst 2: Zeolite β based
- Na^+-gated membrane (***Science***, vol. 367, pp. 667, 2020) removes water *in situ*, shifting the equilibrium towards product formation

Catalyst development

- Methanol synthesis ($CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$)
  - Zirconium (Zr) modified $CuO/ZnO/Al_2O_3$ (CZZA)
- LPG synthesis: MeOH ⇋ LPG + hydrocarbon + H_2O
  - Previously, we had used Pd-zeolite β catalyst
  - Currently, we are developing Pd-free acid treated zeolite β

CZZA nano-particles (~15 nm)

TEM image



TEM: Transmission Electron Microscopy

Bench-mark LPG synthesis with packed bed reactor: LPG yield of 11% when using bifunctional catalyst

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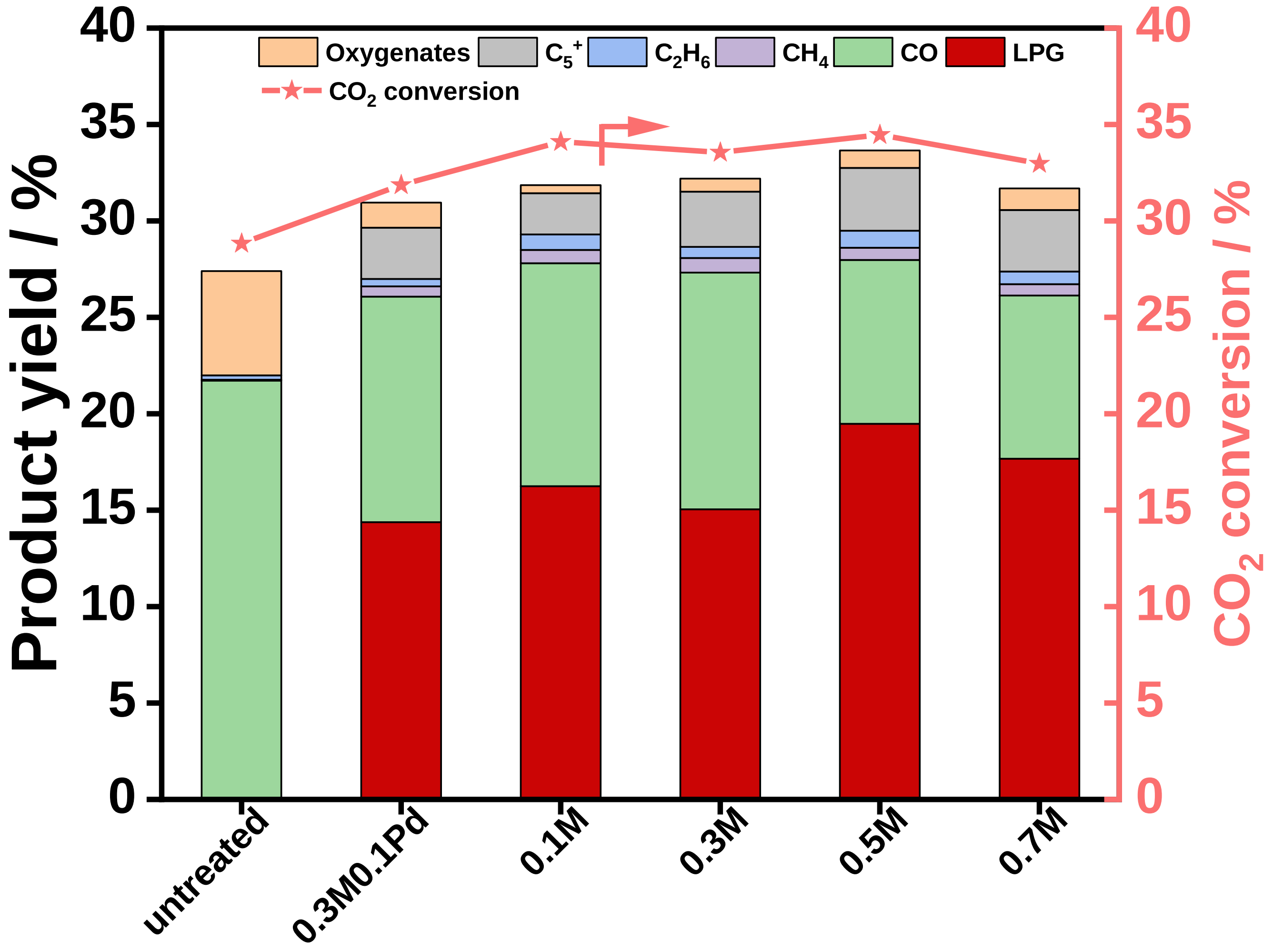
- **Reaction temperature**: 300°C
- **Pressure**: 20 bara
- **Bifunctional catalyst**: 0.5 g CZZA and 1 g Pd-β zeolite
- **Reaction products**: CO, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, C_5+, CH_3OH, DME
- **Results**:

CO_2 conversion	31%
Hydrocarbons selectivity	46%
LPG selectivity	35%
LPG yield	11%

LPG: liquefied petroleum gas; CZZA: Zirconium (Zr) modified $CuO/ZnO/Al_2O_3$; DME: dimethyl ether

Acid treated β-zeolite catalysts, even without Pd, showed high LPG yield

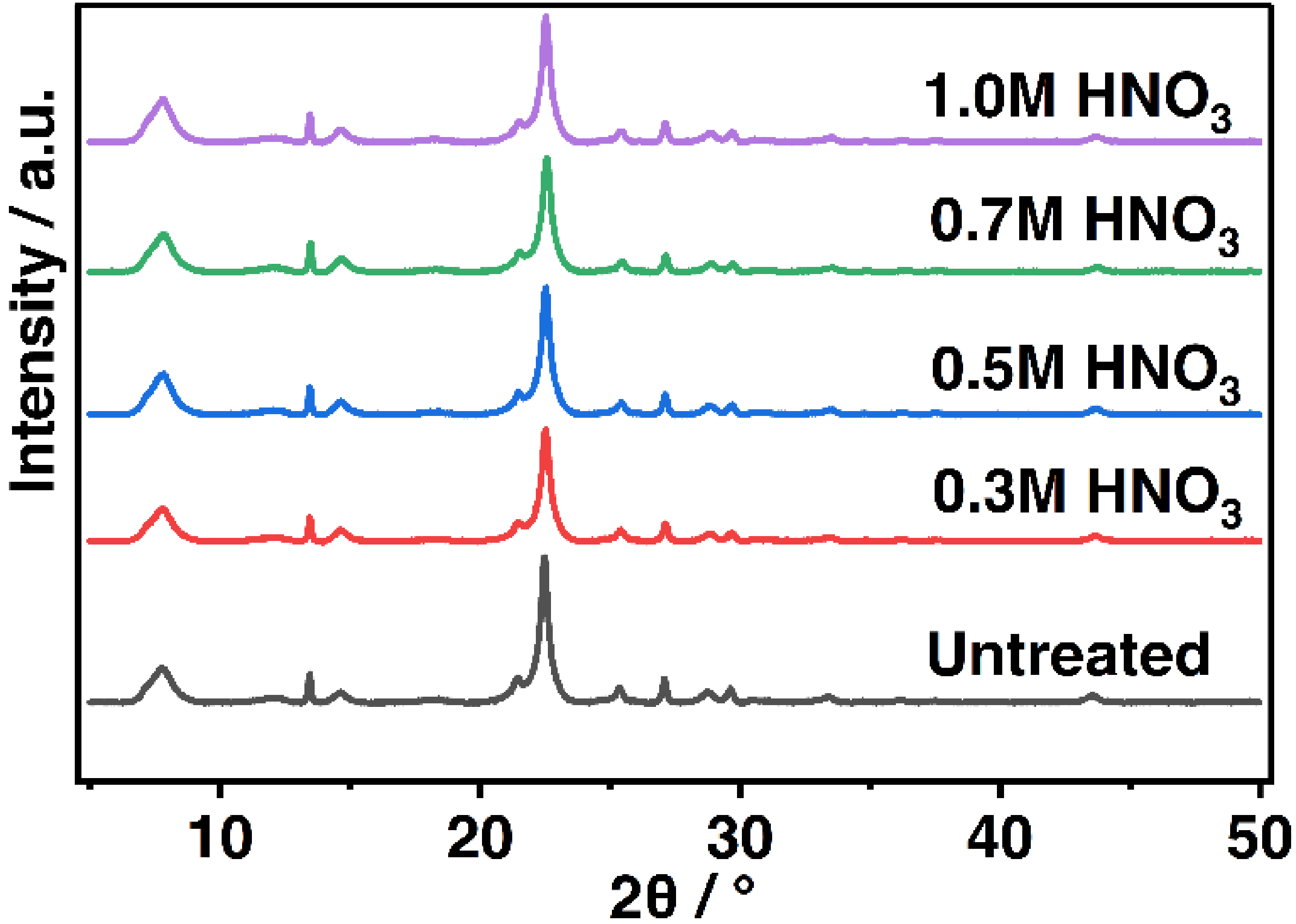
- T = 300ºC
- Pressure = 20 bara
- CZZA : β-zeolite = 0.5g : 1g
- GHSV = 1,200 mL·g^{-1}·h^{-1}



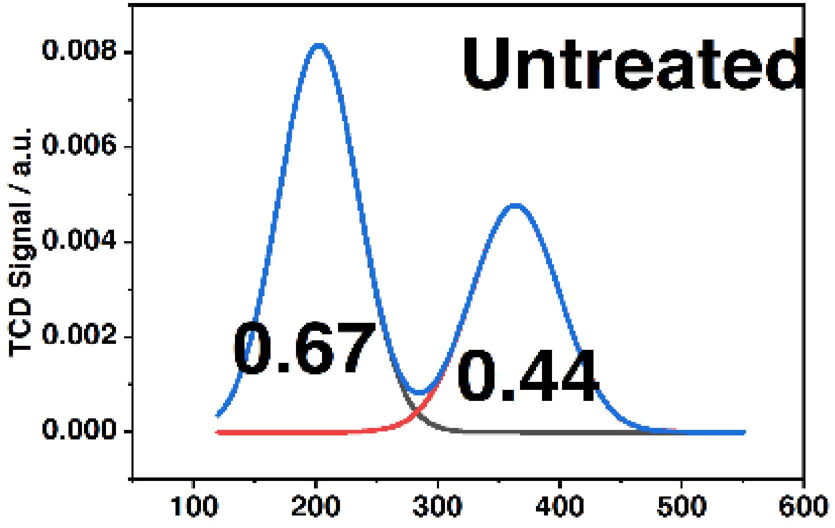
- "0.3M0.1Pd": β-zeolite catalyst with 0.1 wt.% Pd treated by 0.3 M HNO_3 solution during Pd loading
- "0.1M": β-zeolite catalyst treated by 0.1 M HNO_3 solution

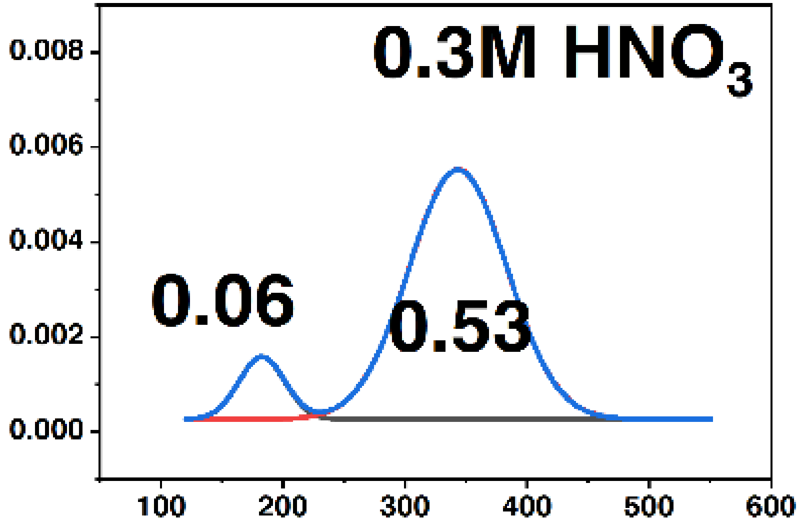
- The 0.5M nitric acid treated catalyst without Pd showed the highest LPG yield

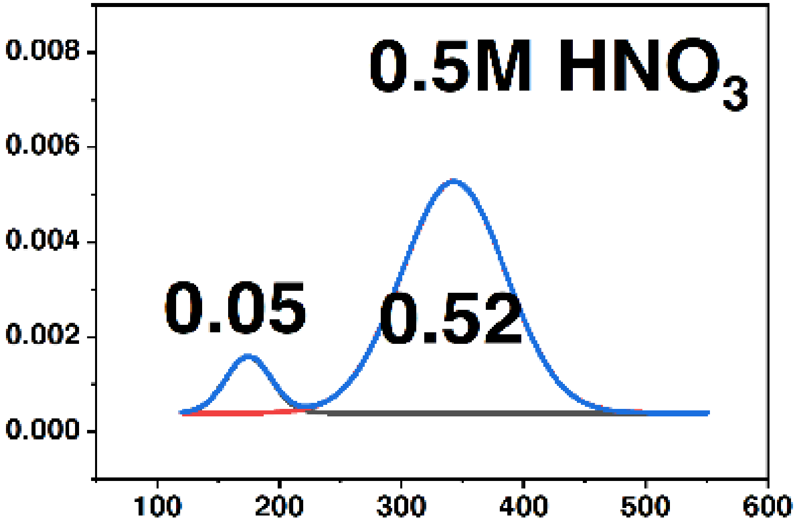
XRD shows no structure changes after acid treatments

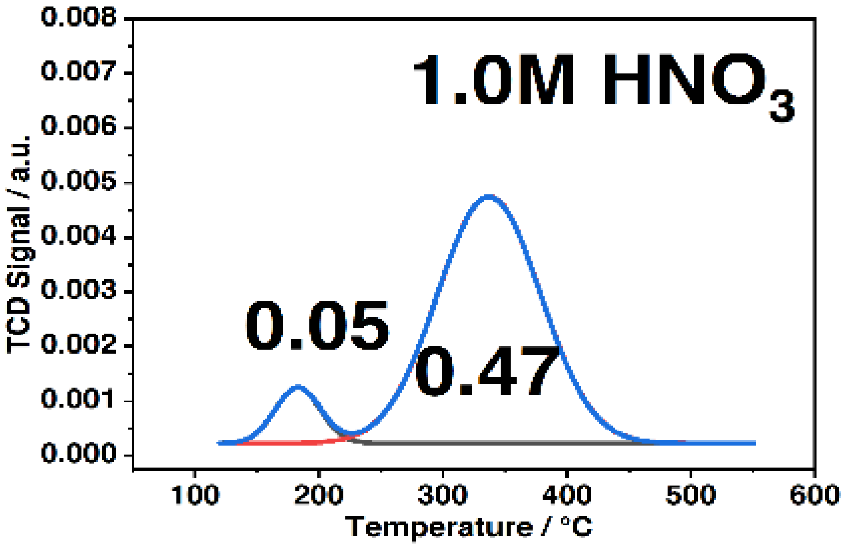


Characterization of β-zeolite catalyst after treatments – NH_3 temperature-programed desorption









- NH_3 temperature-programed desorption indicate acid treatment increased the ratio of strong acid sites (i.e., Brønsted acid) to weak acid sites in β-zeolite, which might be critical to the LPG synthesis

Membrane and Membrane Reactor Development

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

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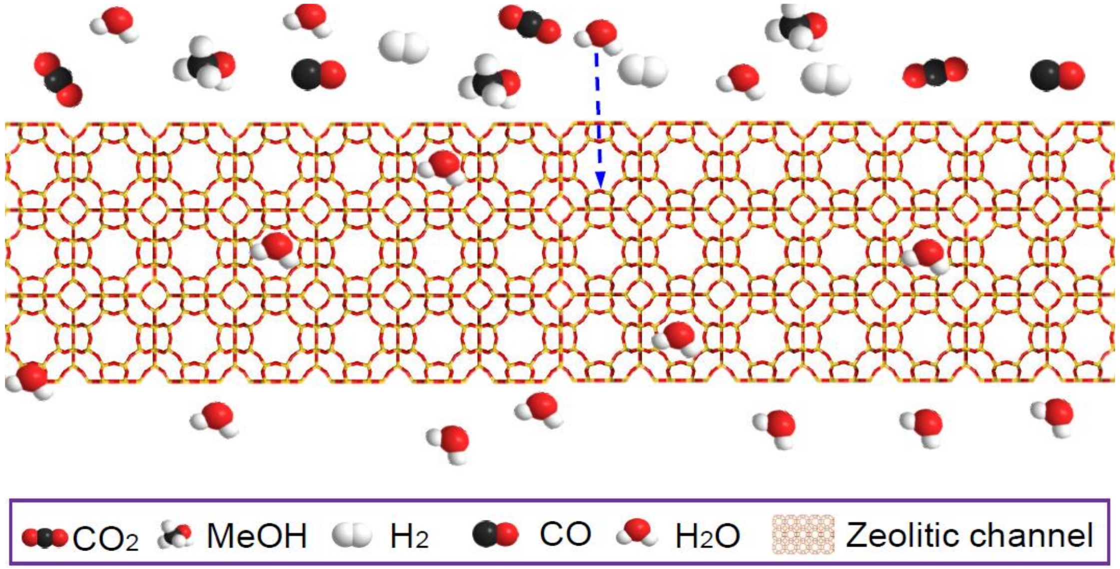
Science

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
- Methanol: 0.36 nm
- CO_2: 0.33 nm

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

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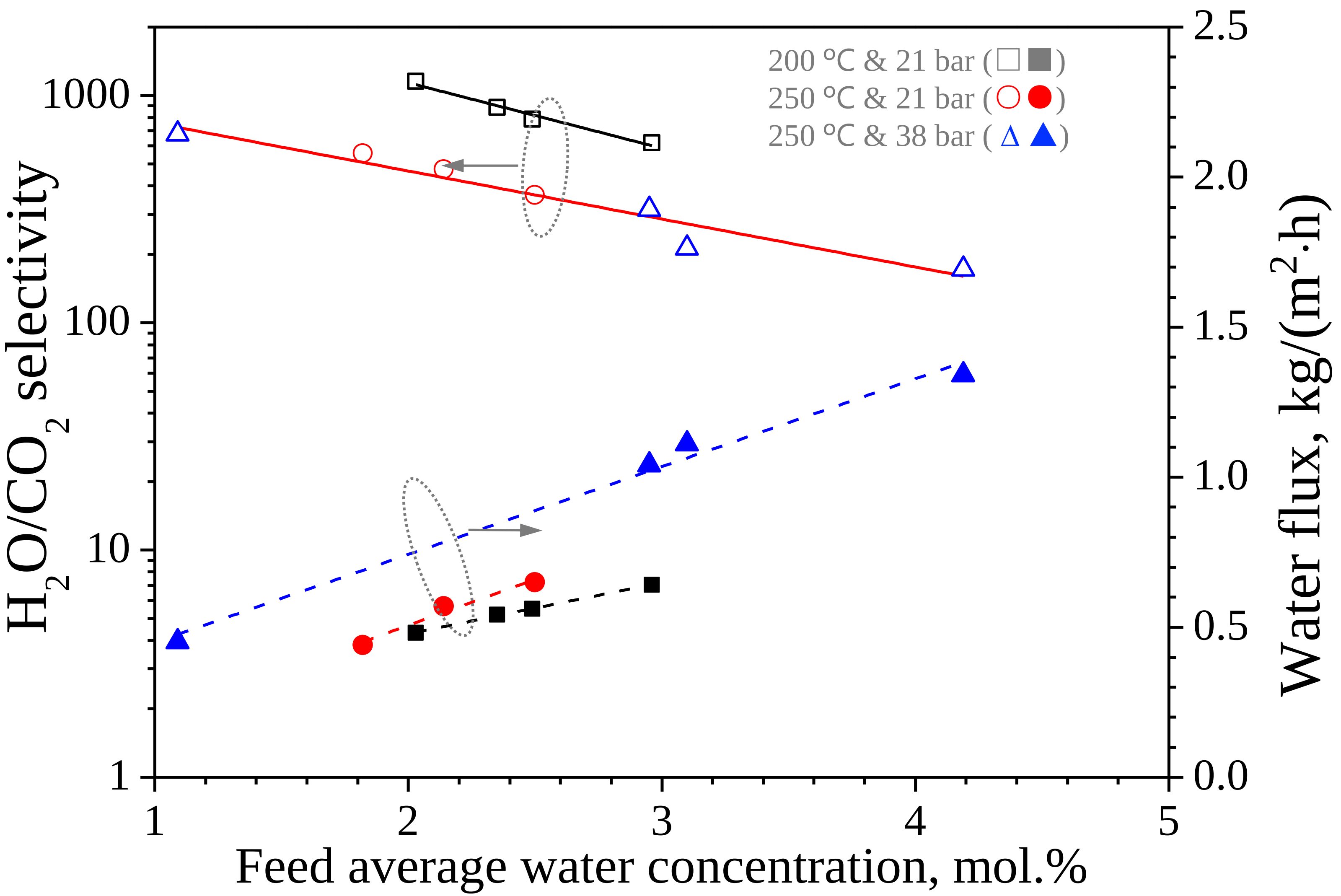


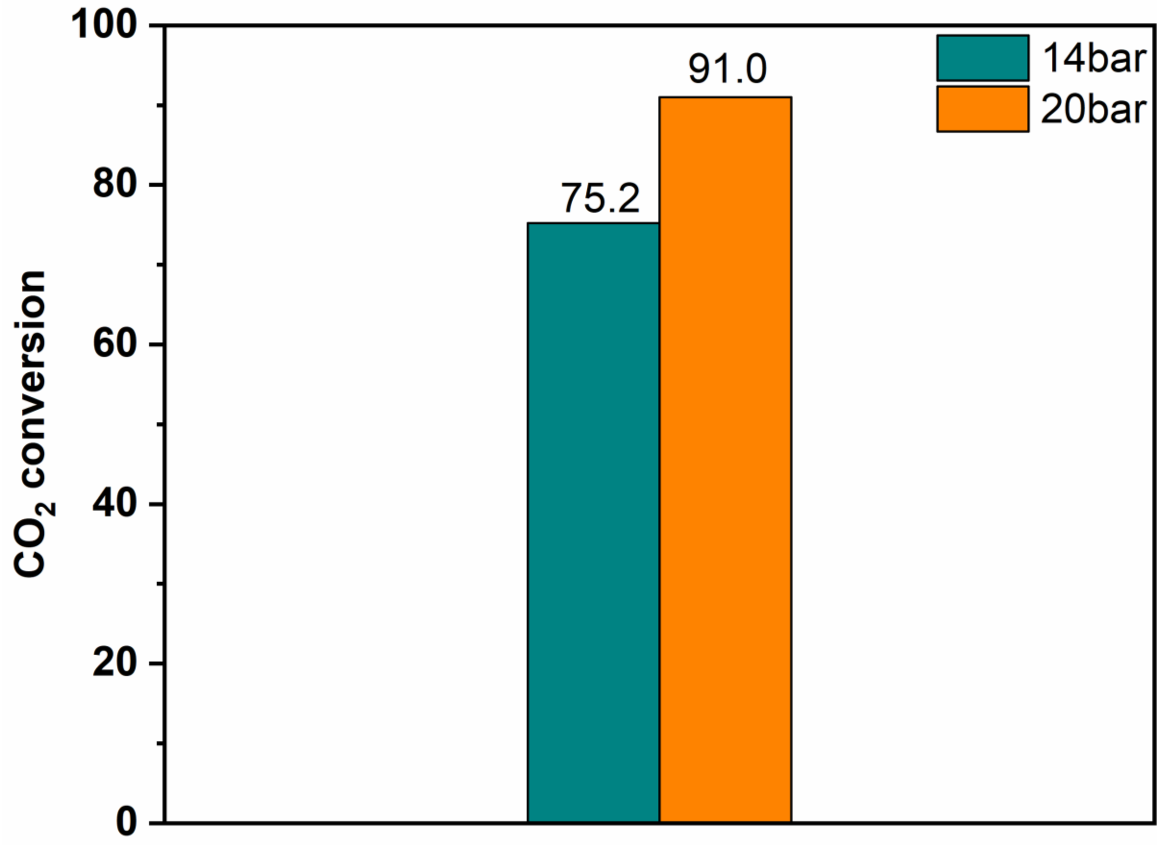
- **Other selectivities**
  - H_2O/H_2 >190
  - H_2O/CO >170
  - H_2O/MeOH >80

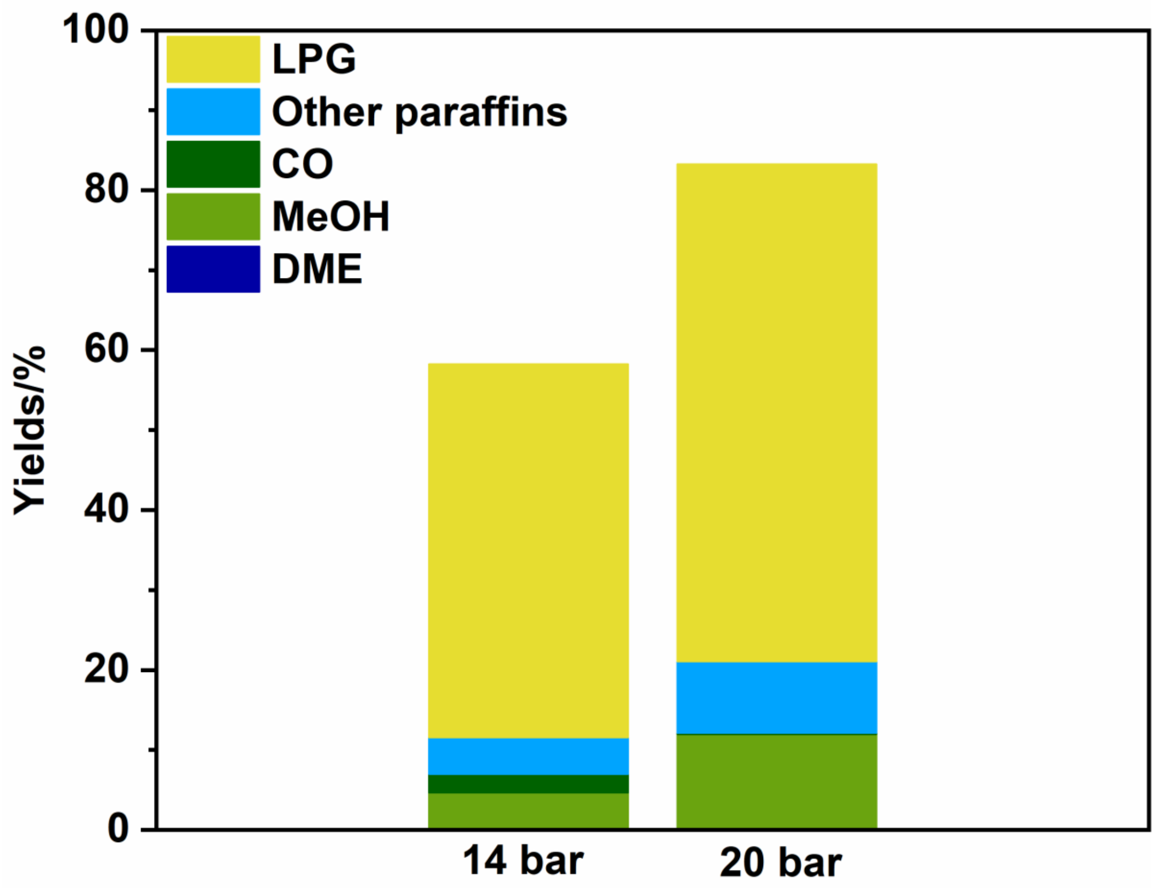
Kinetic diameters:

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

Membrane reactor LPG synthesis: CO_2 conversion as high as 91%, LPG yield as high as 62%

300°C, CZZA/β-zeolite (0.5M nitric acid treated) catalyst, H_2/CO_2 ratio = 5:1, W/F = 23.7 g(cat)/(mol/h)





W/F = weight of catalyst / flow rate of the feed stream; LPG: liquefied petroleum gas; DME: dimethyl ether

Membrane reactor showed significantly faster startup than other reactors after dormancy

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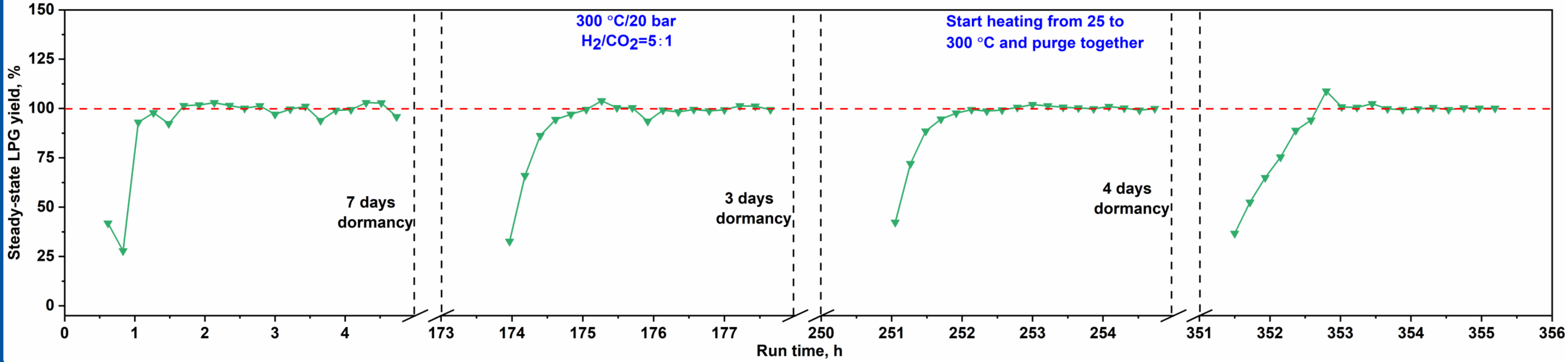
- **Our membrane reactor**



- **Comparison to other reactors reported in the literature**

Studies	Reactor type	Catalysts	Temp. (˚C)	Pressure (bar)	CO_2 conversion	LPG yield	Time to reach steady state (h)
Wang et al., *Nature Comm.* 4 (2023) p 2627	Fixed bed	InZrOx-β zeolite	315	30	20.4%	7.1%	25
Wang et al., *Nature Catalysis*, 5 (2022) p 1038	Fixed bed	GaZrOx/SSZ-13	300	30	9.1%	8.4%	80
Zhao et al., *Appl. Catal., B* (2024) p123936	Fixed bed	$MoS_{x/}$HSSZ-39	300	40	13.0%	12%	40
Li et al., *Fuel Proc. Tech.* 136 (2015) p50	Fixed bed	CZZA/Pd-β zeolite	260	20	29.4%	4.8%	10
Ullah et al. *Int. J. Hyd. Energy*, 48 (2023) p21735	Plasma	Ni/CeO_2	300	1	86%	6.7%(C_{2+})	3.5
Wang et al. *Green Chemistry*, 23 (2021) p1642	Plasma	Co/Al_2O_3	400	1	74%	8.8	2
This study	**Membrane**	**CZZA/Pd-β zeolite**	**300**	**20**	**90.2%**	**61%**	**<1**

Literature comparison: superior performance to packed bed reactors for LPG synthesis

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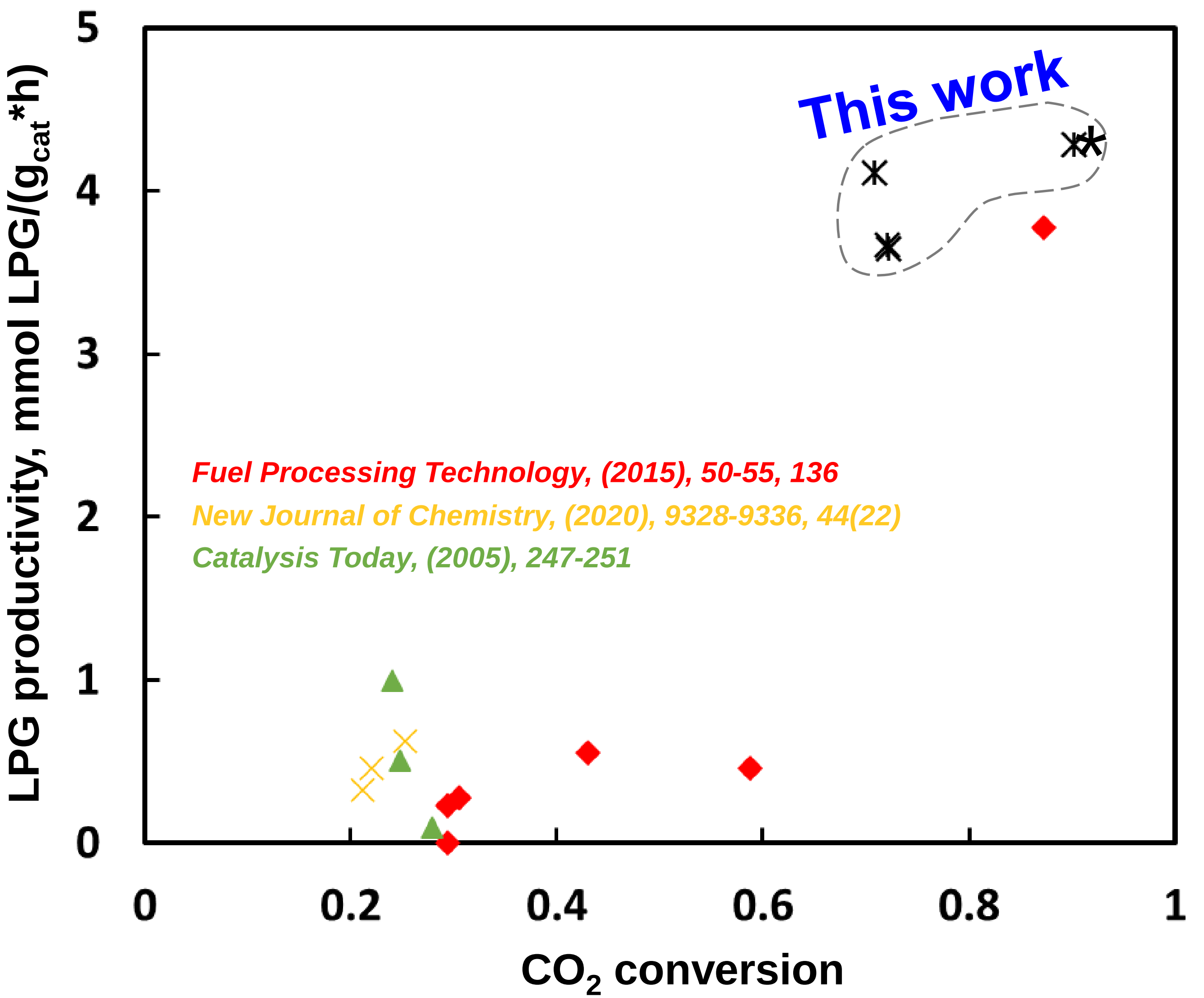

- Highest LPG productivity and CO_2 conversion of any work found in literature (CO_2 conversion to LPG)
- Only other competitive performance used a highly impractical configuration of **two** packed bed reactors with intercooling and reheating in between
  - 1st packed bed reactor: 260°C
  - Cooling to 0°C
  - Reheating from 0°C to 330°C
  - 2nd packed bed reactor: 330°C

Milestone status

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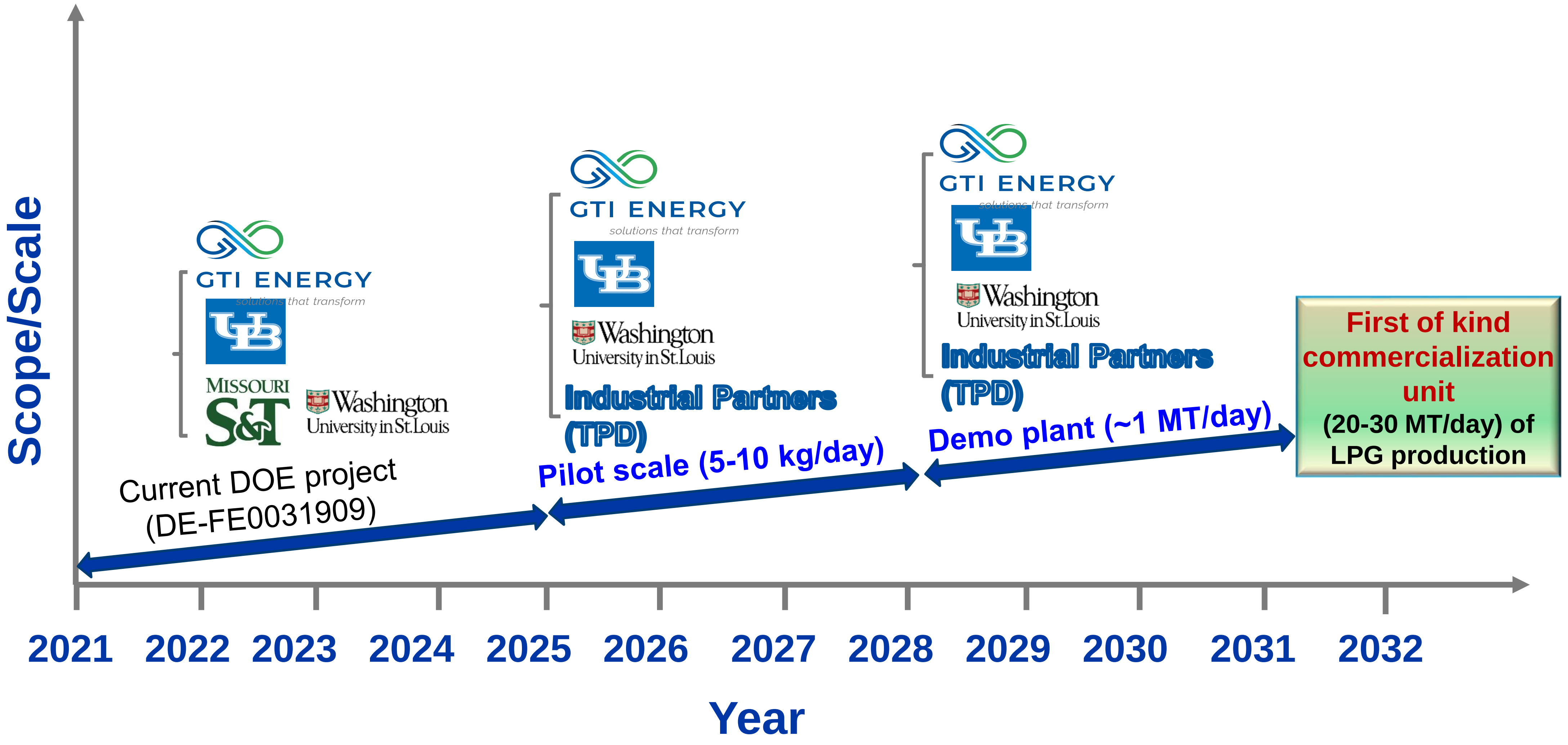
#	Task/ Subtask	Milestone Title/Description	Planned Completion Date	Revised Completion Date	Actual Completion Date
M1.1	1	Submit updated Project Management Plan to DOE	2/28/21	2/28/21	2/18/21
M1.2	1	Complete Kickoff Meeting	3/31/21	3/30/21	3/18/21
M1.3	1	Submit technology maturation plan to DOE	3/31/21	3/30/21	3/23/21
M2.1	2	Ship >20 g of catalysts with BET surface area >100 m^2/g to UB from MS&T	6/30/21	6/30/21	3/31/22
M3.1	3	Achieve CO_2 conversion >30%, hydrocarbon yield >25% at 200-350ºC and 10-35 bar	6/30/21	3/31/23	3/31/23
M4.1	4.1	Complete development of CZZA-based catalyst with surface area > 100 m^2/g, and palladium (Pd) loading ≥ 0.1 wt.% for the Pd-β zeolite catalyst	12/30/21	9/30/23	6/5/23
M4.2	4.2	Achieve CO_2 conversion >40%, hydrocarbon yield >15%, and LPG yield >7% at 220-350ºC and 10-35 bar in a fixed bed reactor; achieve CO_2 conversion >80%, hydrocarbon yield >60%, and LPG yield >35% at 220-330ºC and 10-35 bar in a membrane reactor	12/30/21	9/30/23	6/6/23
M5.1	5	Achieve CO_2 conversion >85%, hydrocarbon yield >75%, and LPG yield >45% at 220-330ºC and 10-35 bar	9/30/22	6/30/24	10/31/23
M6.1	6	Achieve CO_2 conversion >90%, hydrocarbon yield >80%, and LPG yield >45% at 220-330ºC and 10-35 bar using optimized catalyst and tested in membrane reactor	9/30/22	12/31/24	6/30/24
M7.1	7	Complete 100-500 hours continuous testing; achieve steady-state CO_2 conversion >85%, LPG yield >45% at 220-330ºC and 10-35 bar	12/30/22	3/31/25	
M8.1	8	Issue Final TEA report with a Technology Gap Analysis	12/30/22	3/31/25	
M8.2	8	Issue Final LCA report	12/30/22	3/31/25	
M1.4	1	Submit Final Technical Report	3/30/23	6/30/25	

Membrane reactor technology development path



Summary

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- GTI and partners are developing a membrane reactor for production of valuable chemicals
    - Na^+-gated membrane removes water *in situ*, shifting equilibrium towards product formation
    - Bifunctional catalyst allows for higher conversion of CO2 and higher yield of the product
- One-step membrane reactor LPG synthesis using bifunctional catalyst: CO_2 conversion as high as 91% and LPG yield as high as 62%
- Significantly faster startup (relative to other reactors) and good dynamic stability
- Superior performance to packed bed reactors

Acknowledgements

- Financial and technical support

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

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Appendix – Organization chart

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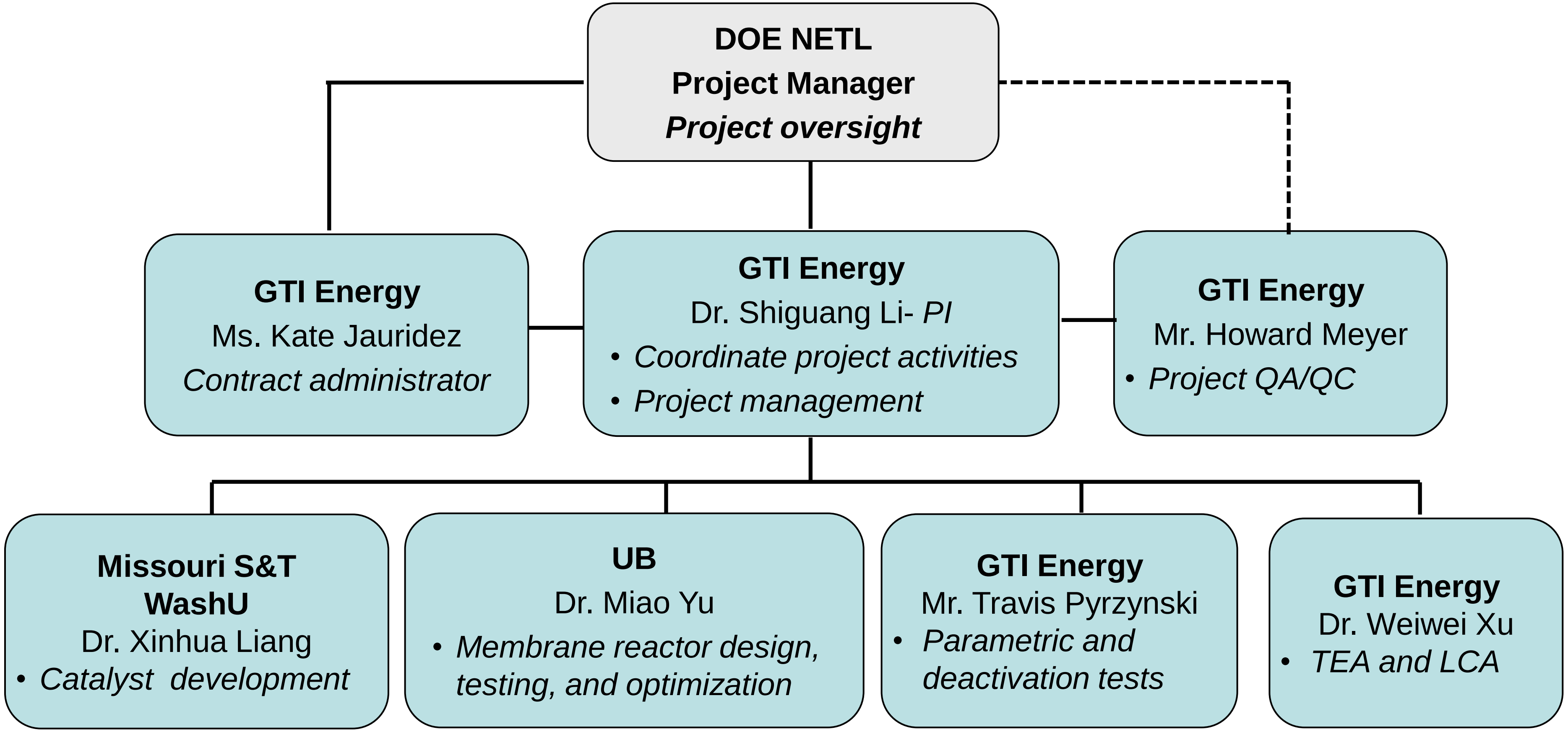

Appendix – Gantt chart

ID	Task NO	SubT NO	MS	Task Name	Start	Finish
1	1.0			Project Management and Planning	Fri 1/1/21	Mon 3/31/25
2		1.01		Project Management Plan	Fri 1/1/21	Mon 3/31/25
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			M1.3	Submit technology maturation plan to DOE	Tue 3/30/21	Tue 3/30/21
6			M1.4	Submit Final Technical Report	Mon 6/30/25	Mon 6/30/25
7		1.02		Technology Maturation Plan	Fri 1/1/21	Mon 3/31/25
8	2.0			Preparation, characterization, and optimization of catalysts	Fri 1/1/21	Fri 3/31/23
9			M2.1	Ship >20 g of catalysts with BET surface area >100 m2/g to UB from MS&T	Wed 6/30/21	Wed 6/30/21
10	3.0			Sequential membrane reactor testing and optimization	Fri 1/1/21	Fri 3/31/23
11			M3.1	Achieve CO2 conversion >30%, hydrocarbon yield >25% at 200-350ºC and 10-35 bar	Fri 3/31/23	Fri 3/31/23
12	4.0			Catalyst optimization and catalytic performance evaluation	Sat 4/1/23	Sat 9/30/23
13		4.01		Catalyst optimization	Sat 4/1/23	Sat 9/30/23
14			M4.1	Complete development of CZZA-based catalyst with surface area > 100 m2/g, and palladium (Pd) loading ≥ 0.1 wt.% for the Pd-B zeolite catalyst	Sat 9/30/23	Sat 9/30/23
15		4.02		Catalytic performance evaluation of the optimized catalyst	Sat 4/1/23	Sat 9/30/23
16			M4.2	Achieve CO2 conversion >40%, hydrocarbon yield >15%, and LPG yield >7% at 220-350ºC and 10-35 bar in a fixed bed reactor; achieve CO2 conversion >80%, hydrocarbon yield >60%, and LPG yield >35% at 220-330ºC and 10-35 bar	Sat 9/30/23	Sat 9/30/23
17	5.0			Bifunctional membrane reactor testing and optimization	Sun 10/1/23	Sun 6/30/24
18			M5.1	Achieve CO2 conversion >85%, hydrocarbon yield >75%, and LPG yield >45% at 220-330ºC and 10-35 bar	Sun 6/30/24	Sun 6/30/24
19	6.0			Optimization of bifunctional catalyst for membrane reactor testing	Mon 7/1/24	Mon 3/31/25
20		6.01		Optimization of the catalyst	Mon 7/1/24	Mon 3/31/25
21		6.02		Catalytic performance evaluation of the optimized catalyst	Mon 7/1/24	Mon 3/31/25
22			M6.1	Achieve CO2 conversion >90%, hydrocarbon yield >80%, and LPG yield >45% at 220-330ºC and 10-35 bar using optimized catalyst and tested in membrane reactor	Tue 12/31/24	Tue 12/31/24
23	7.0			Membrane reactor parametric and deactivation tests	Tue 10/1/24	Mon 3/31/25
24			M7.1	Complete 100-500 hours continuous testing; achieve steady-state CO2 conversion >85%, LPG yield >45% at 220-330ºC and 10-35 bar	Mon 3/31/25	Mon 3/31/25
25	8.0			Detailed techno-economic and life-cycle analyses	Sun 12/1/24	Mon 3/31/25
26			M8.1	Issue Final TEA report with a Technology Gap Analysis	Mon 3/31/25	Mon 3/31/25
27			M8.2	Issue Final LCA report	Mon 3/31/25	Mon 3/31/25