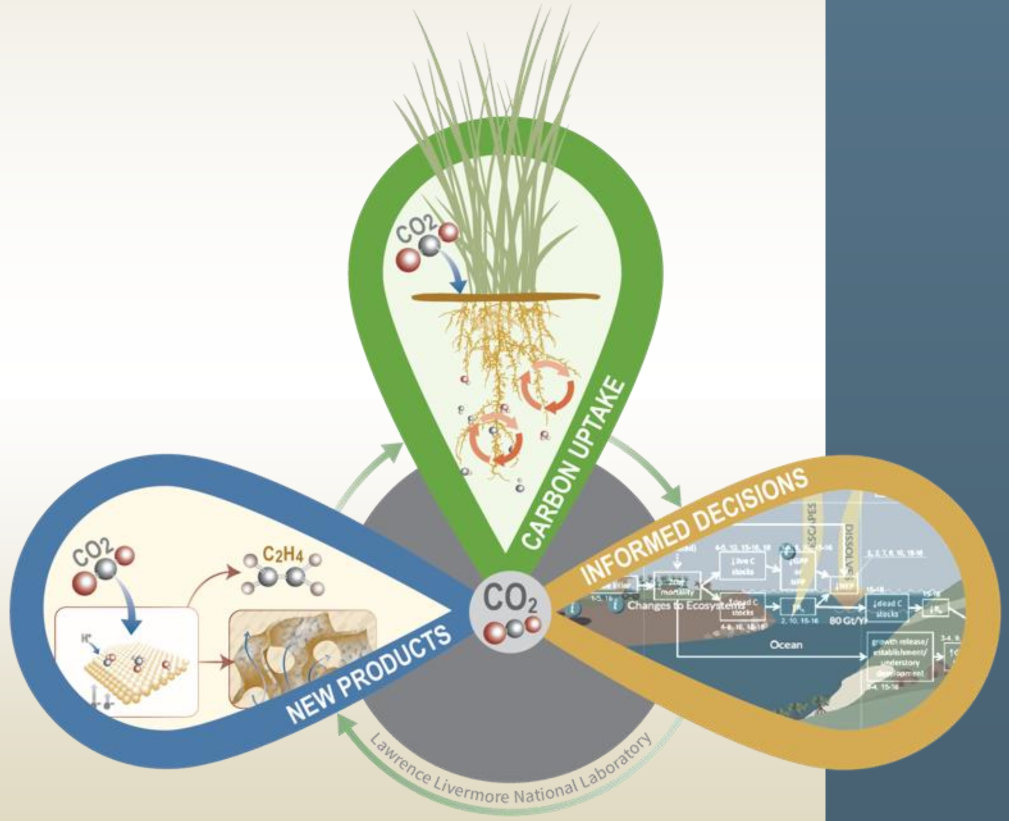
THE LLNL CARBON INITIATIVE

Anticipating the threat and preparing DOE for the next major phase of climate mitigation technology



Direct Air Reactive Capture and Conversion for Utility-Scale Energy Storage

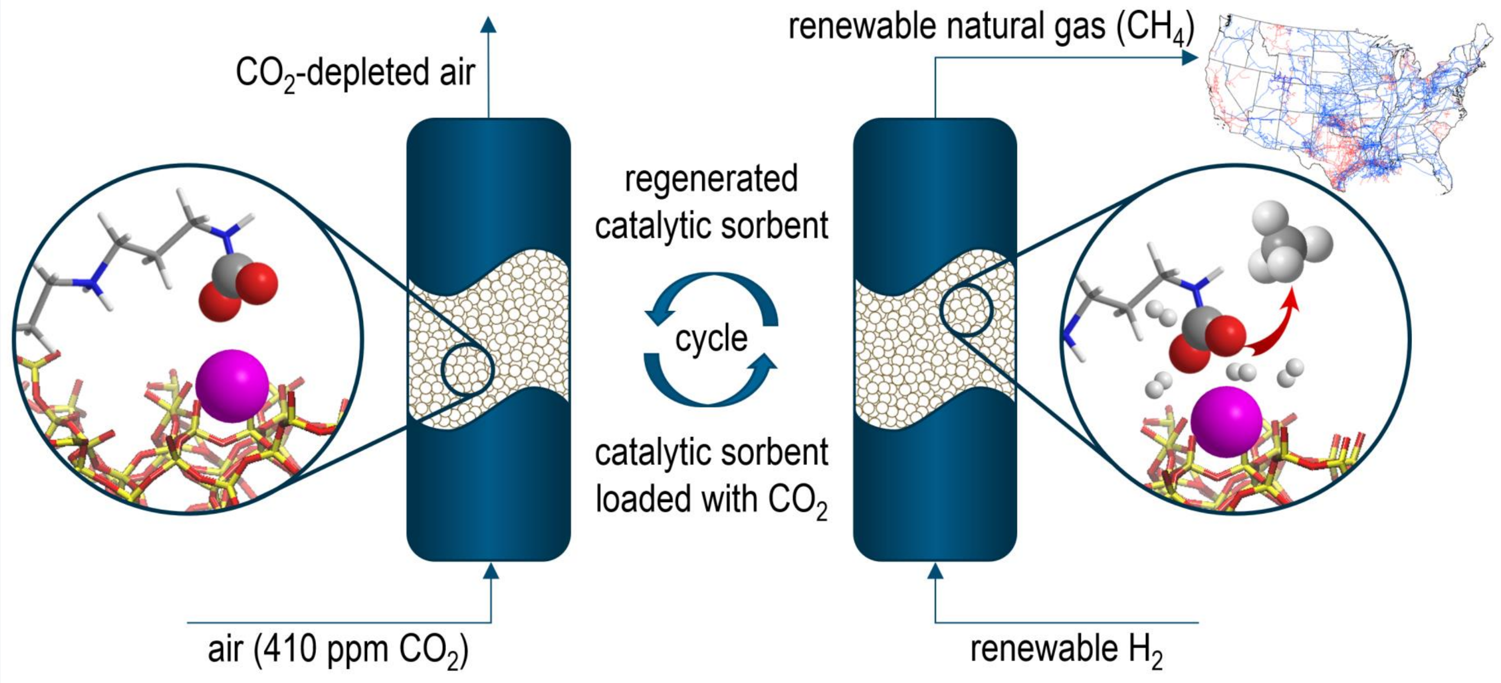
FWP-FEW0277

Simon Pang
Lawrence Livermore National Laboratory

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 16, 2022

Lawrence Livermore National Laboratory

Direct Air Reactive Capture and Conversion for Utility-Scale Energy Storage



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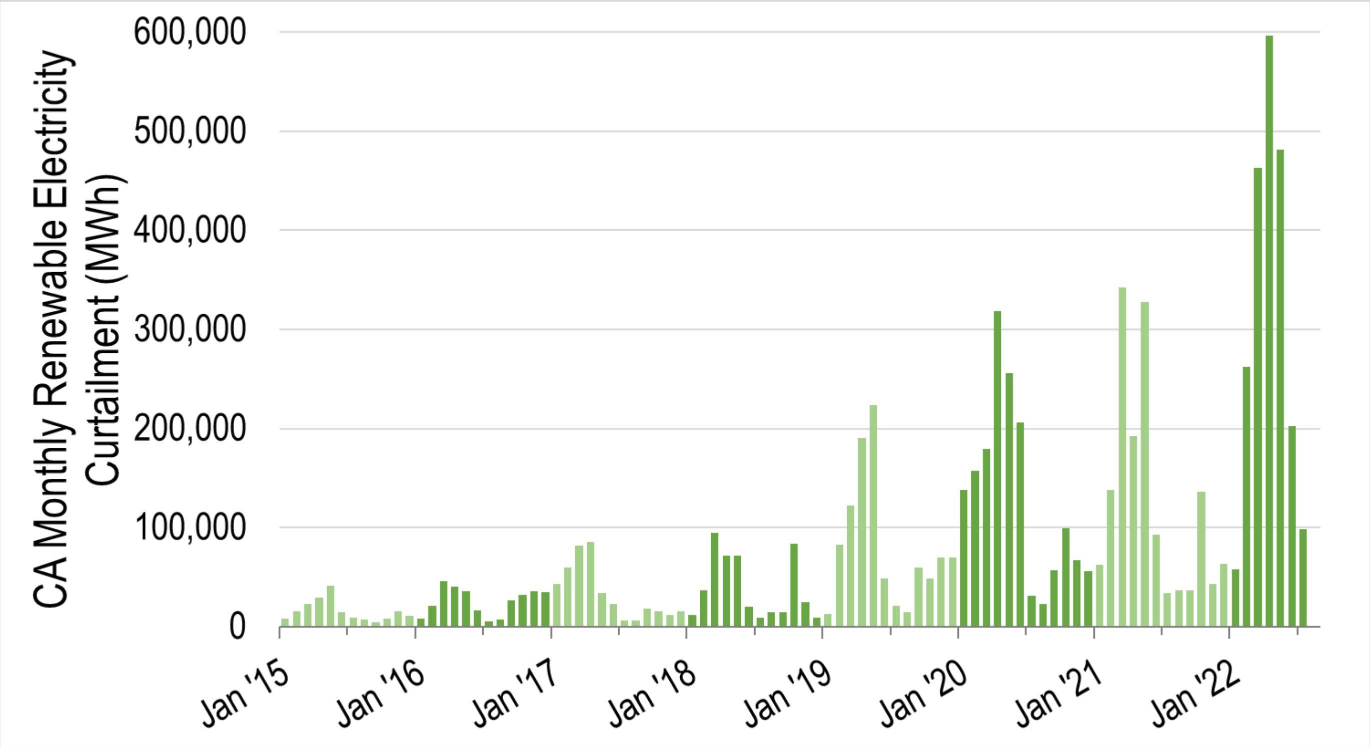
NREL NATIONAL RENEWABLE ENERGY LABORATORY

Reactive Capture & Conversion R&D
FEW0277: $3,000k over FY22–FY24
10/1/2021 – 09/30/2024
Project Manager: Issac "Andy" Aurelio

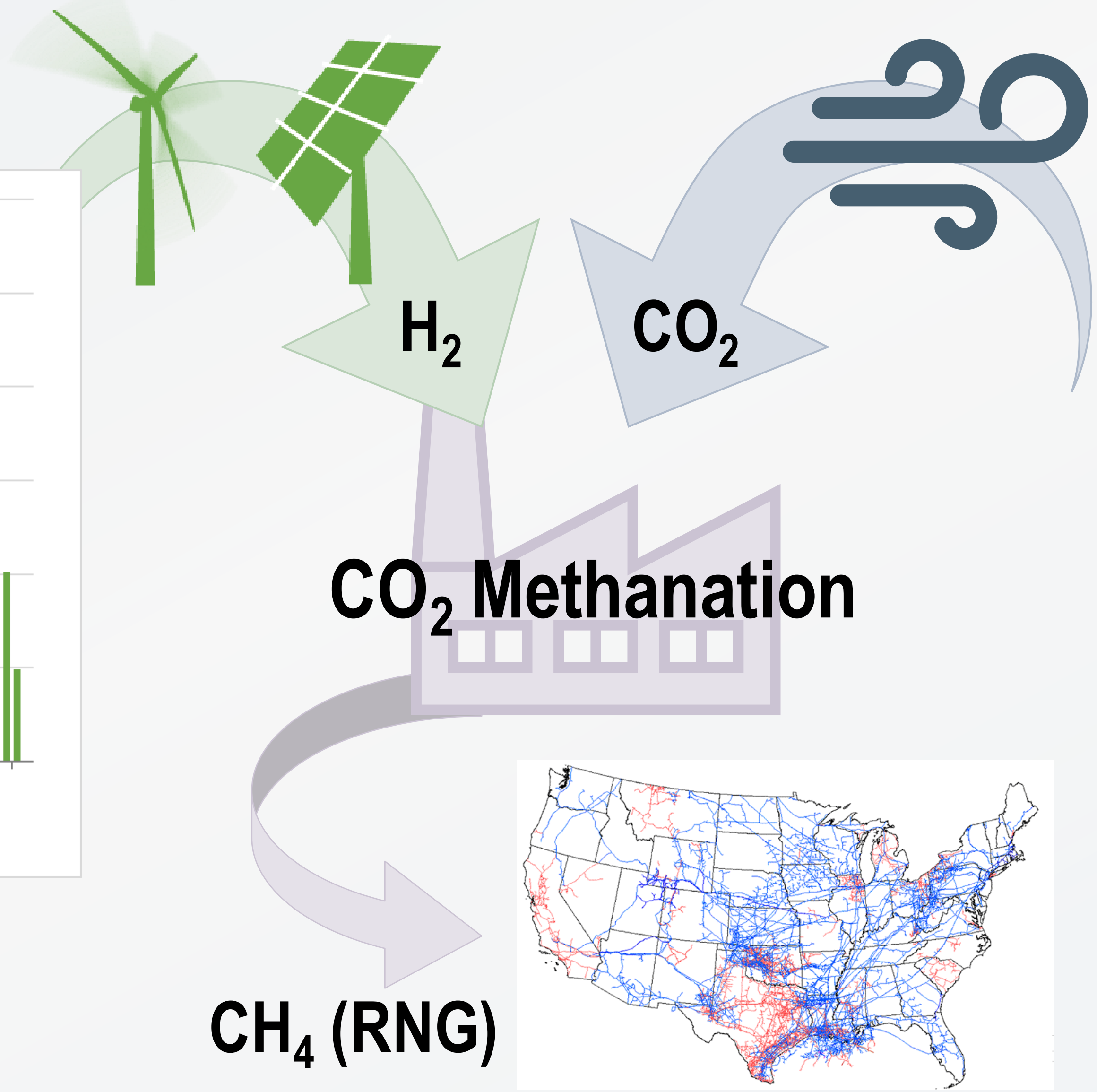
Goal: develop dual-functional material and process for capturing CO_2 from the air and converting it to RNG

Four parallel tracks in direct air capture materials synthesis/characterization, catalysts for CO_2 conversion, mechanistic investigations via *ab initio* simulations, and process modeling and systems analysis

Methanation of CO_2 from the air can provide a distributable source of long-duration energy storage using a (nearly) carbon-neutral fuel

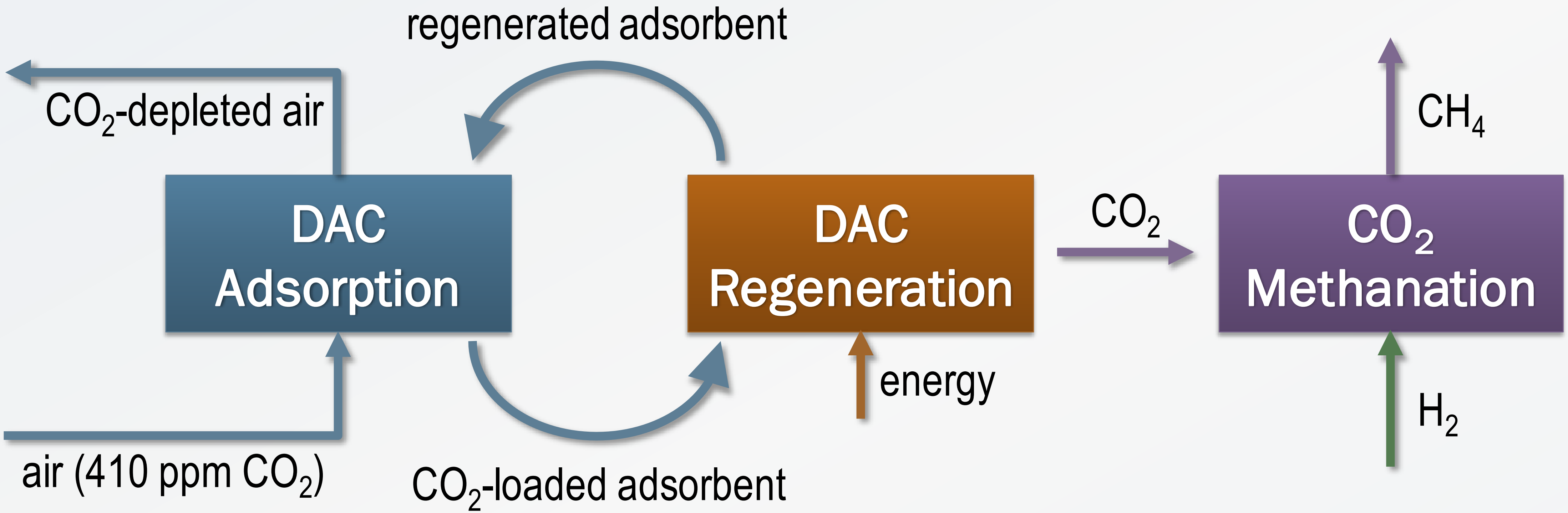


Renewable electricity curtailed over the last year could have powered over 150,000 homes in CA



Our goal is to develop a material and process to directly convert captured CO_2 into methane without explicitly requiring desorption

Separate Direct Air Capture and CO_2 Methanation



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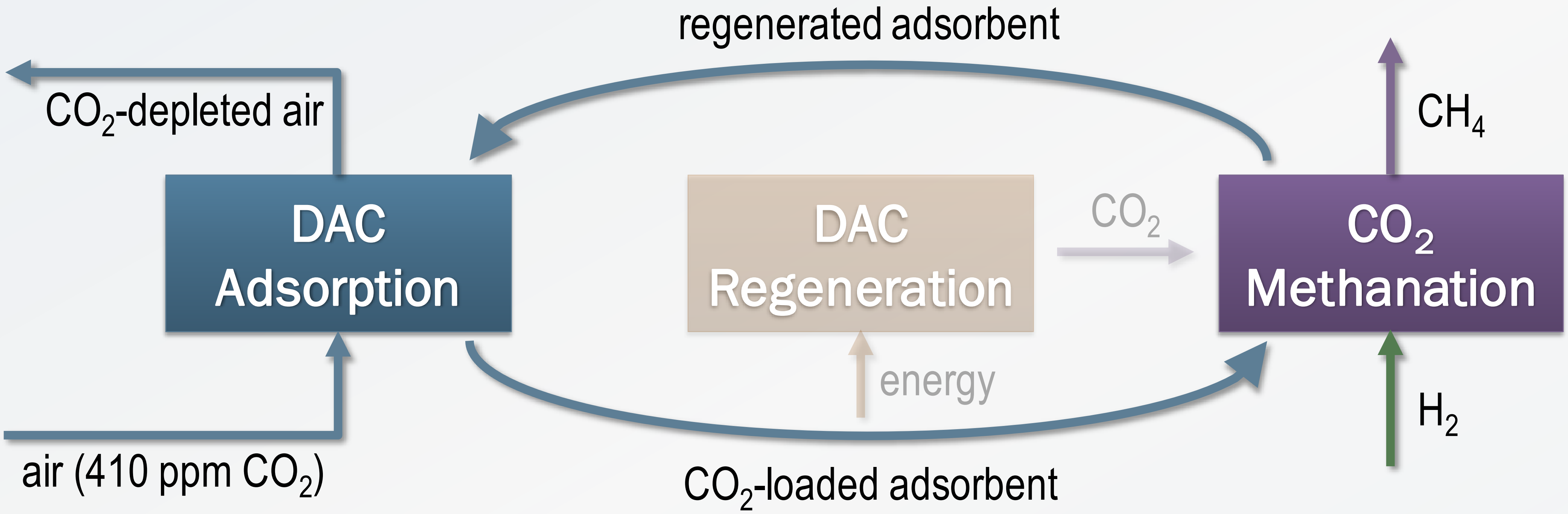
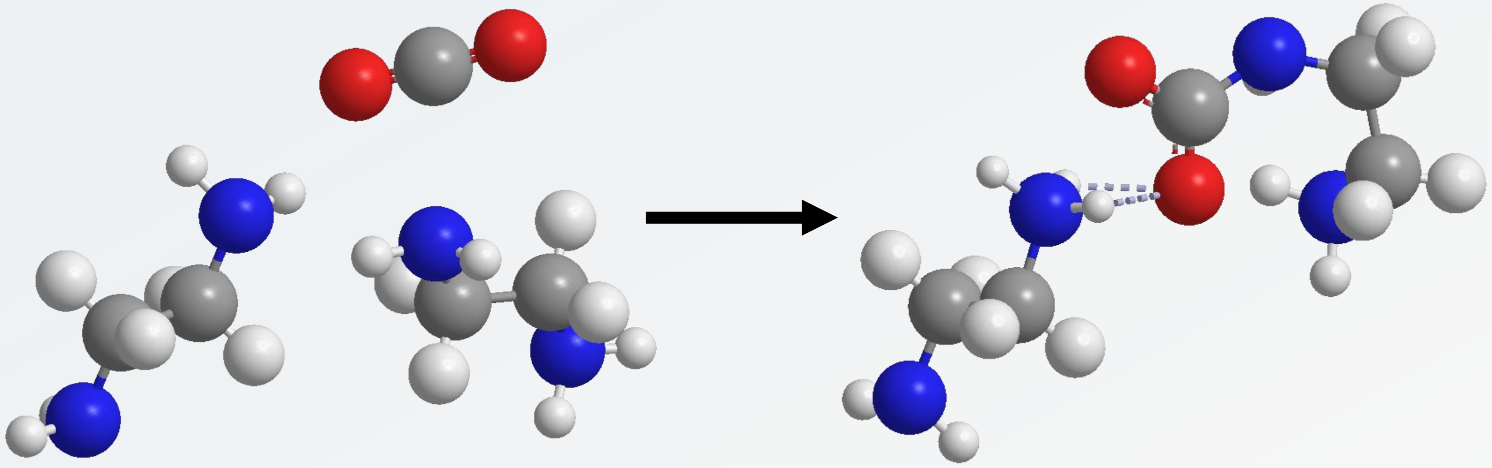
Direct Air Reactive Capture and Methanation

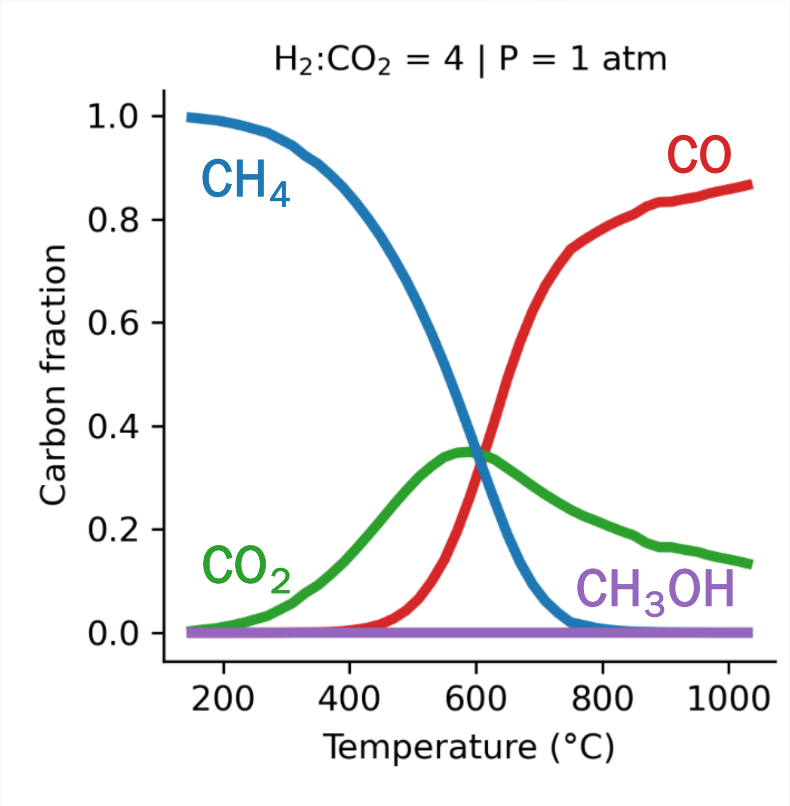


Amines have high CO_2 selectivity, capture kinetics, and capacity, and may serve as a CO_2 transfer agent for low temperature methanation



CO_2 bound as a **carbamate**

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

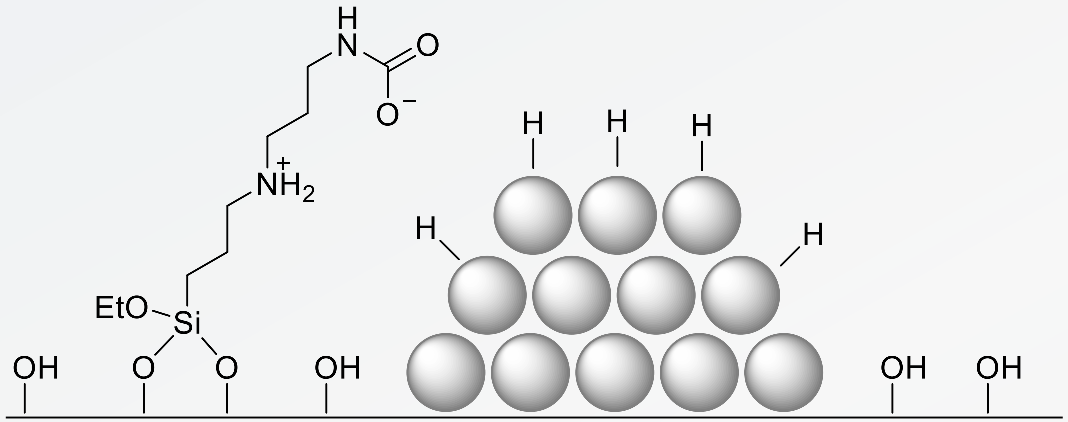


Technical Challenges/Risks:

- Thermal/oxidative stability of amines under reactive swing
- Process temperature difference between DAC and methanation

Hybrid organic-inorganic adsorbent-catalyst materials will allow capture of CO_2 from the air and conversion into methane

By binding and reacting CO_2 as a carbamate or carbamic acid, we hypothesize…



Bound CO_2 reactive species

Hypothesis 1: …methanation will occur via a lower energy barrier pathway than for gas-phase CO_2 due to activation by the amine ligand, allowing use of lower reaction temperature

Hypothesis 2: …mechanism of bound-CO_2 hydrogenation avoids formation of C and coking/deactivation of catalyst, reducing the need for catalyst regeneration

Project Methodology

Direct air capture

- Tether oligoamines on commercial oxides
- Evaluate adsorption performance (gravimetric and flow/breakthrough)

Measured DAC capacity and kinetics for hybrid materials
Q3, Q8

Catalytic methanation

- Deposit highly dispersed metal catalysts
- Evaluate CO_2 conversion performance (continuous and cyclic)

Achieved high CO_2 conversion and CH_4 selectivity
Q4, Q9

Downselected materials and achieved stable performance with extended cyclic operation
Q6, Q11

Atomistic mechanism

- Simulate interaction between amine, CO_2, and metal catalyst surface
- Simulate interaction with oxide surface

Developed mechanism of amine-assisted CO_2 methanation
Q5

Evaluated effect of water/humidity
Q12

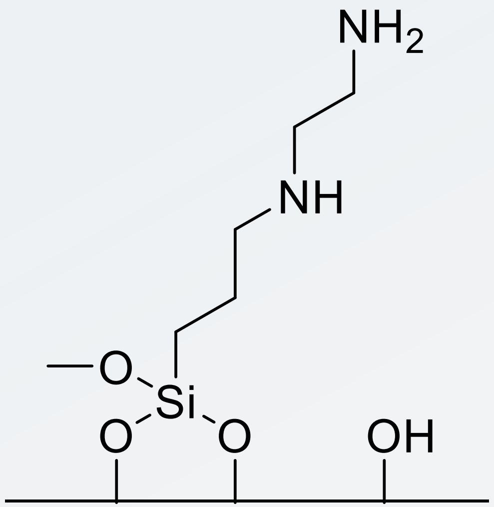
Reactive capture analysis

- Develop M&EB, TEA, LCA for baseline scenarios
- Develop reactive capture process model for comparison

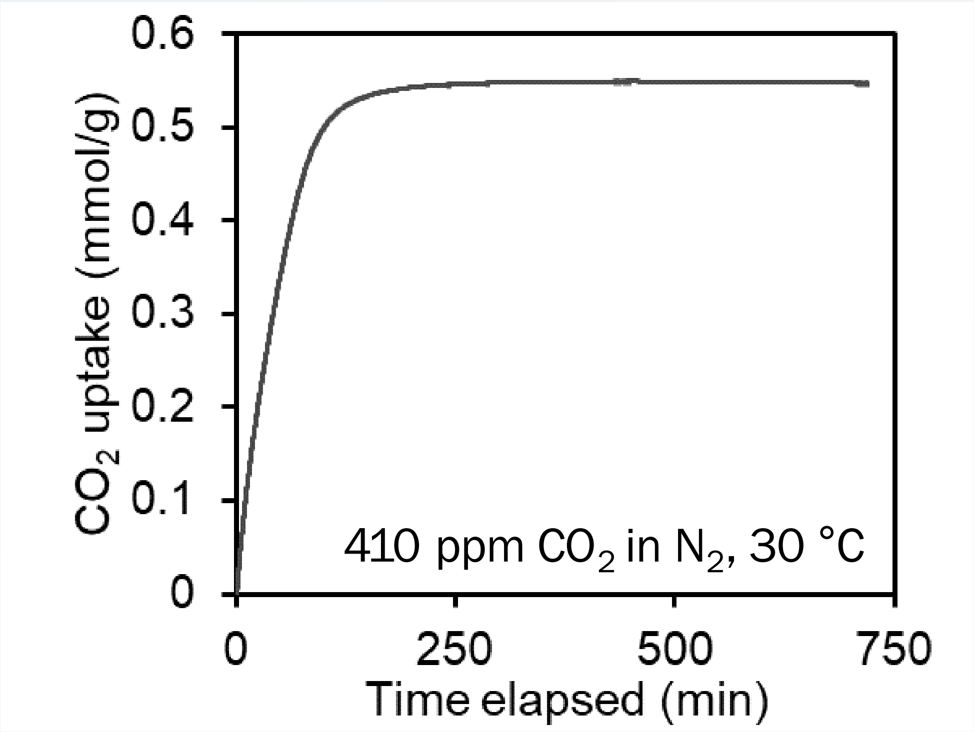
Demonstrated improvement for reactive capture compared to baseline
Q6, Q12

End-of-project success criteria: demonstrate 15% relative improvement in RNG Minimum Fuel Selling Price and Carbon Intensity using a reactive capture process compared to baseline scenario(s)

Amines grafted on a variety of oxide surfaces can capture CO_2

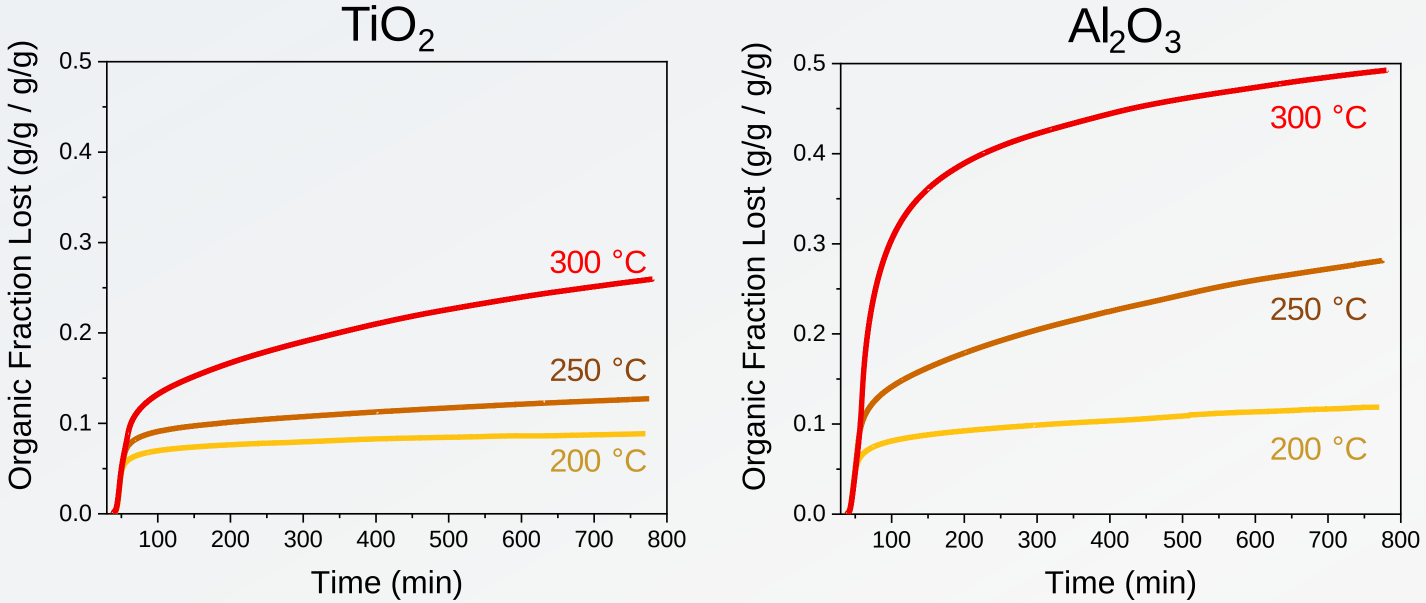


Grafted diamine



Oxide	CO_2 DAC capacity ($mmol/g_{sorbent}$)
SiO_2 – SBA-15 powder	0.55
SiO_2 – commercial pellet	0.50
Al_2O_3 – commercial powder	0.54
TiO_2 – commercial powder	0.42
TiO_2 – commercial pellet	0.18

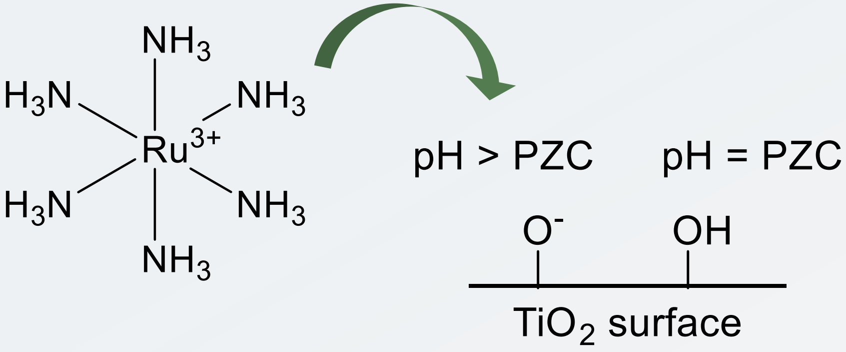
Grafted amines show oxide surface-dependent thermal stability at temperatures relevant to CO_2 methanation

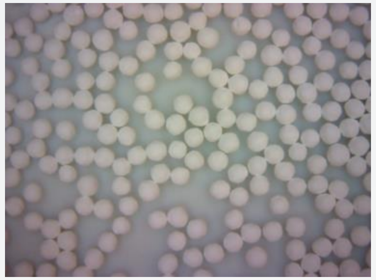


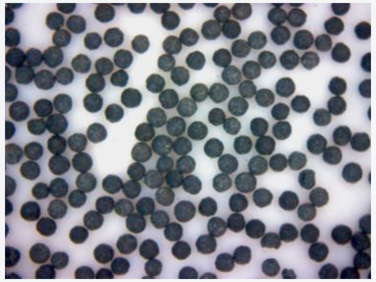
Oxide	As synthesized	CO_2 DAC capacity ($mmol/g_{sorbent}$) 200 °C, 12 hr	250 °C, 12 hr	300 °C, 12 hr
SiO_2	0.50	0.57	0.55	0.35
Al_2O_3	0.54	0.63	0.29	0.05
TiO_2	0.18	0.23	0.28	0.22

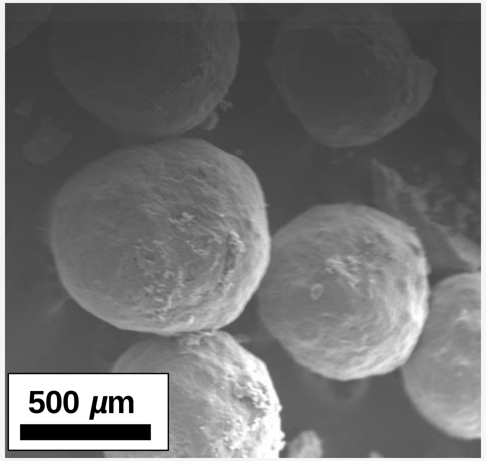
We have synthesized several materials with DAC capacity > 0.25 mmol CO_2 / g material (Milestone #1) that retain DAC capacity after an extended thermal treatment at methanation-relevant temperatures

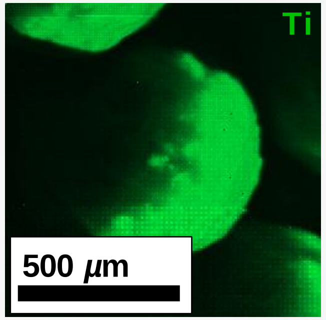
Strong-electrostatic adsorption produces catalytic materials with high metal dispersion and active metal at relevant reaction temperatures

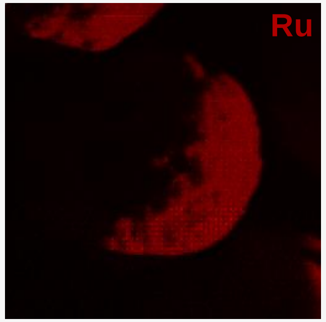




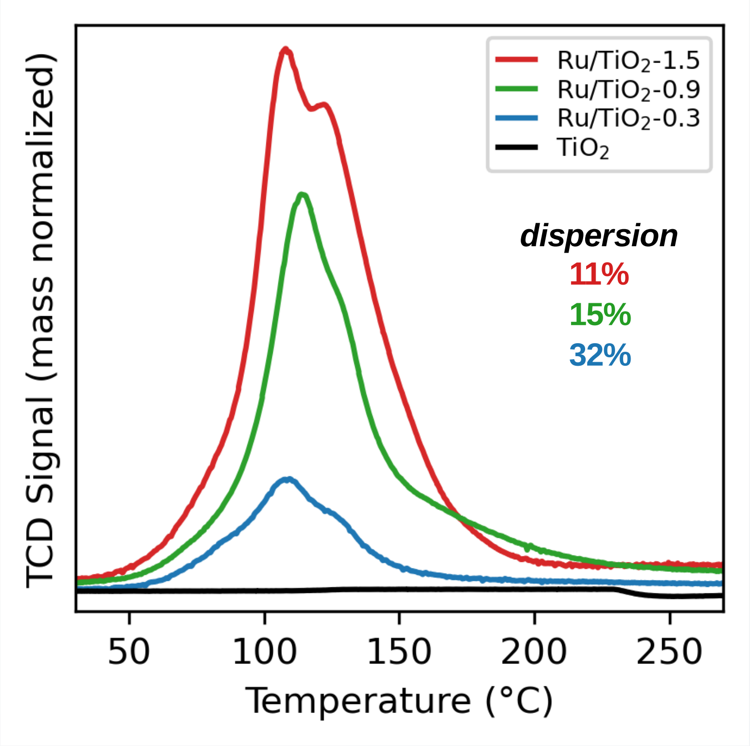




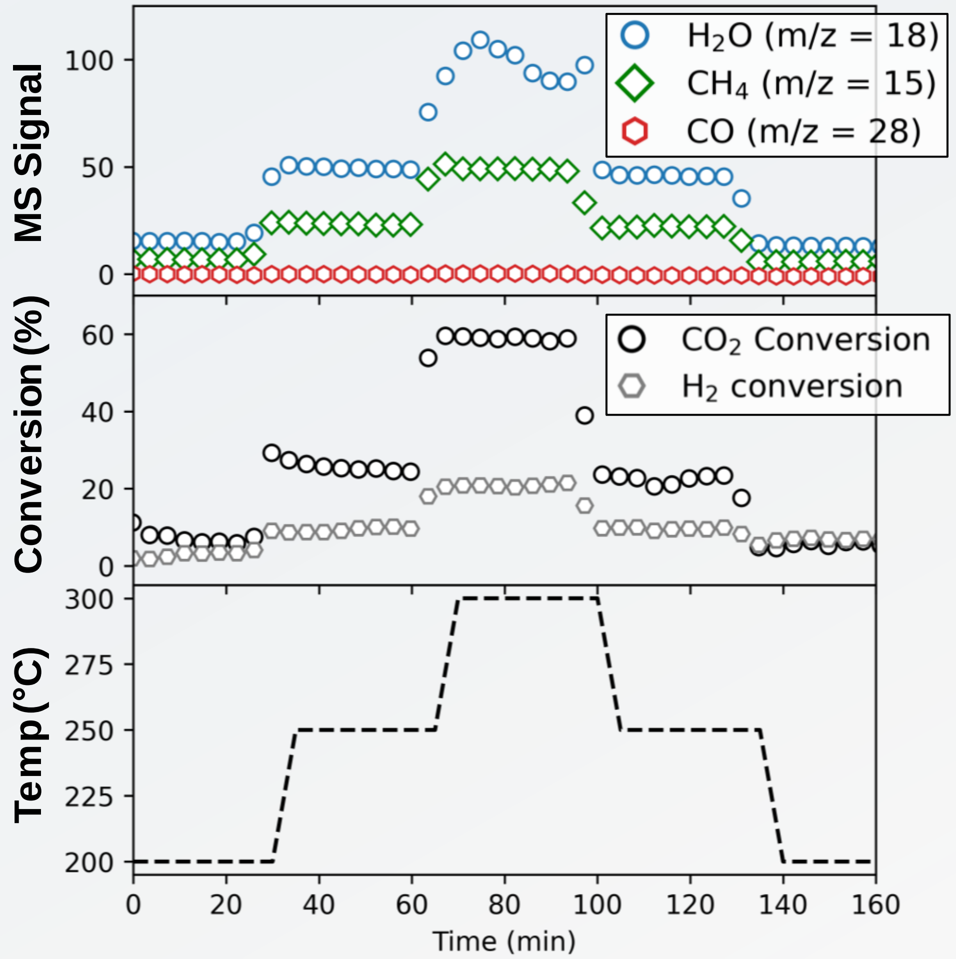




Temperature-Programmed Reduction

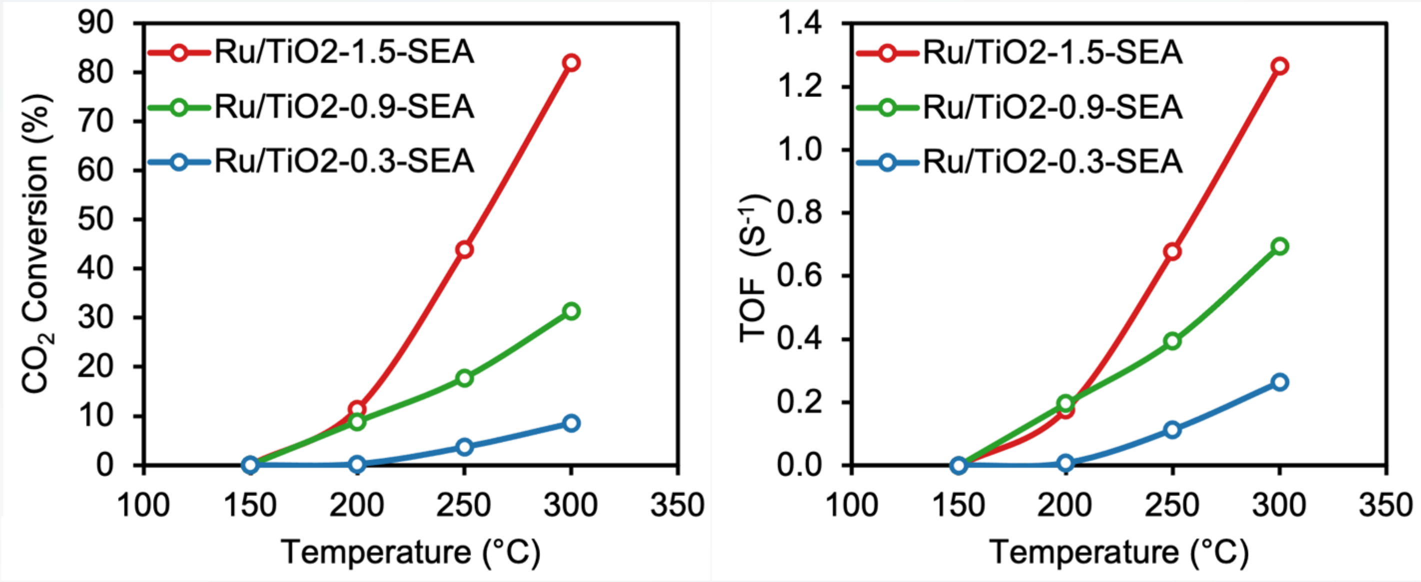


We have developed materials capable of CO_2 methanation within the stability window of our grafted amines



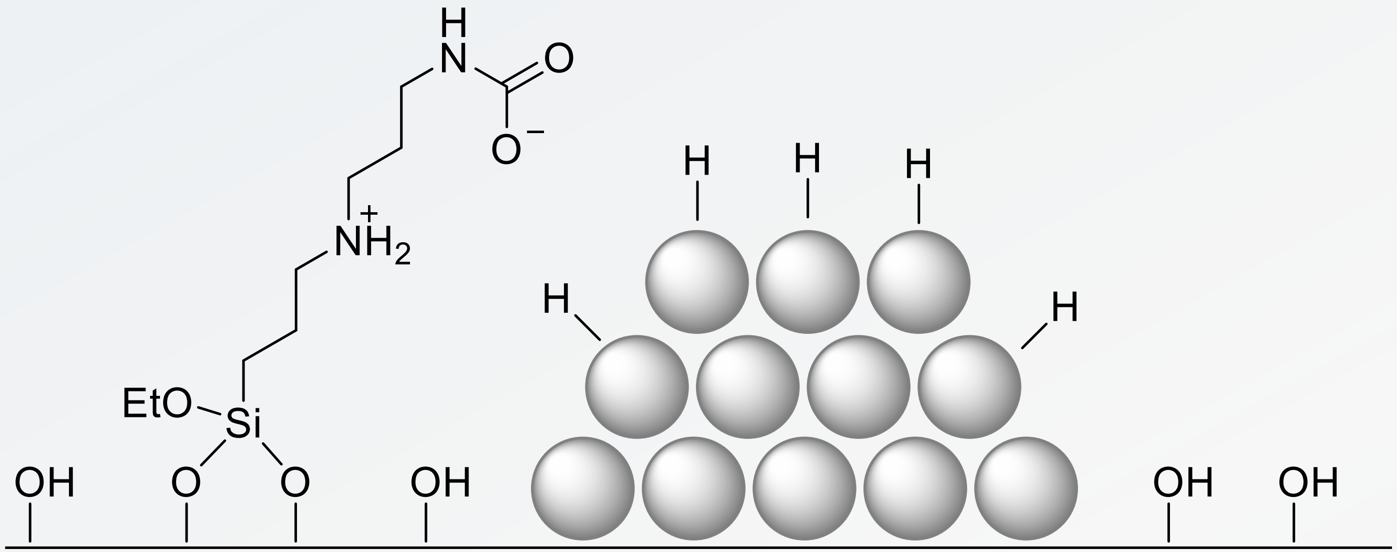
$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

Reaction conditions:
50 mg catalyst, 2 sccm CO_2, 16 sccm H_2, 82 sccm N_2



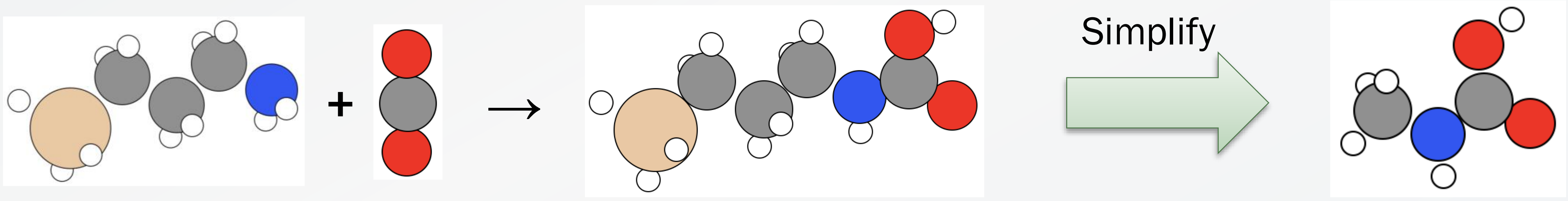
Ru/TiO$_2$ catalyst materials prepared with high dispersion can achieve > 25% single-pass conversion (Milestone #2) at temperatures within the stability window of grafted amines

We have the individual components – how might their interactions affect the reaction mechanism?



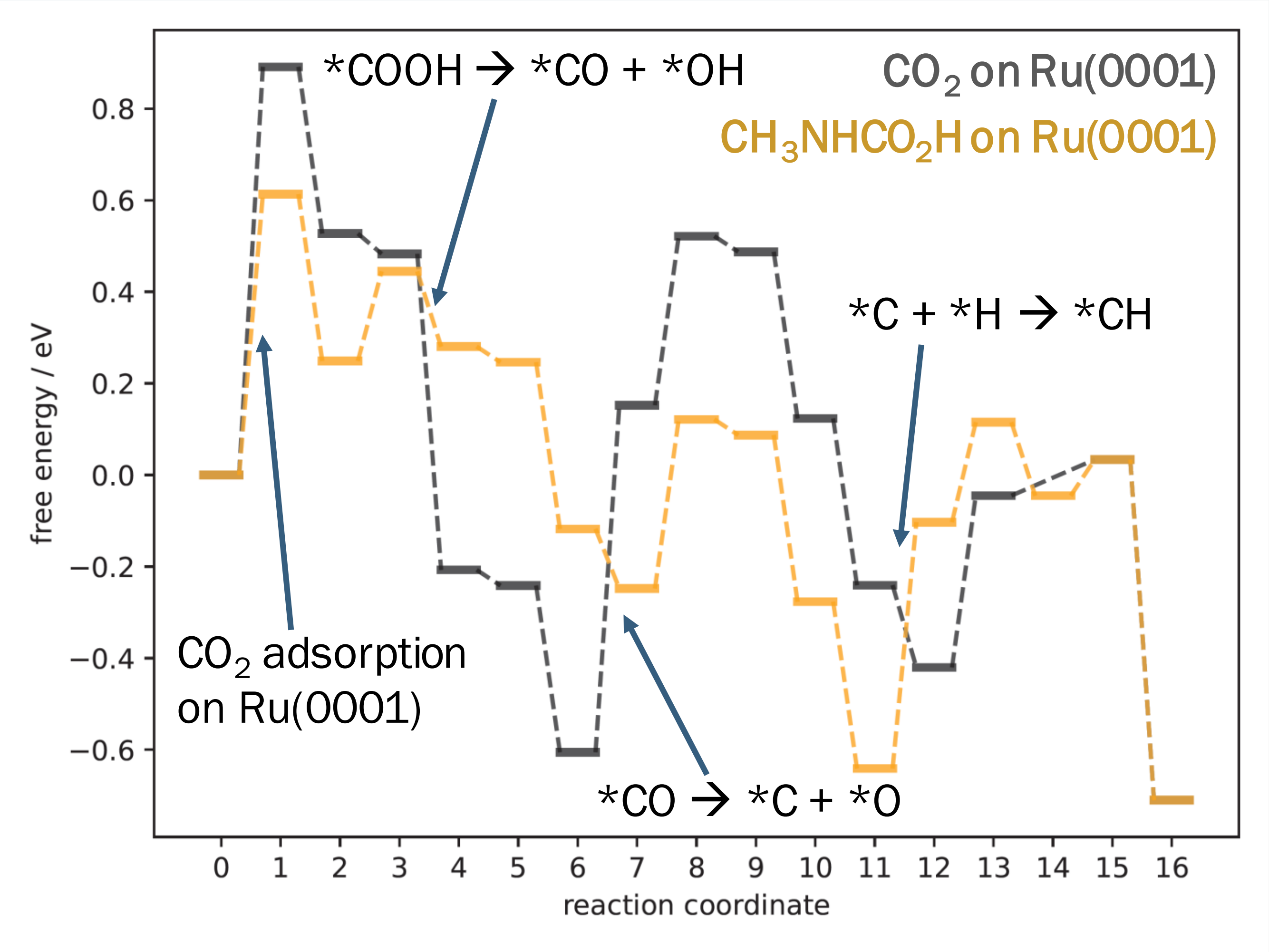
Bound CO_2 reactive species

Carbamic acid model for amine-bound CO_2:

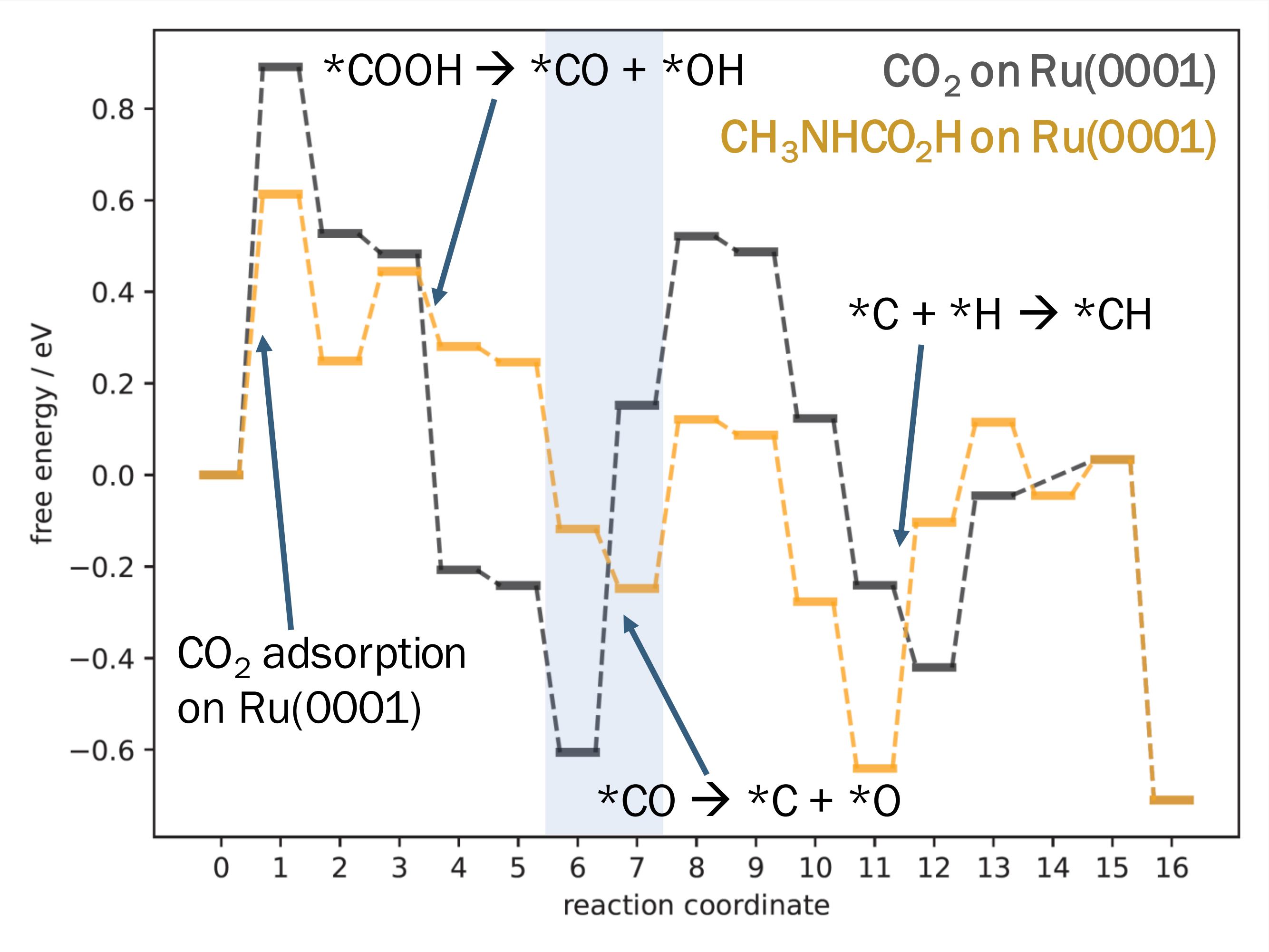


methylcarbamic acid

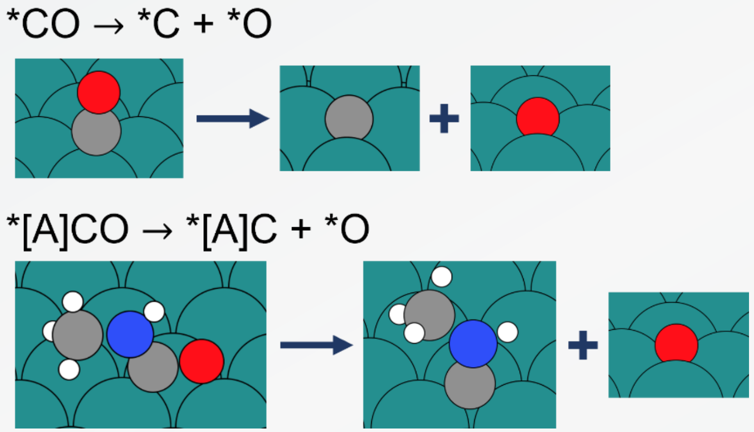
Amine ligand stabilizes undercoordinated species such as surface C



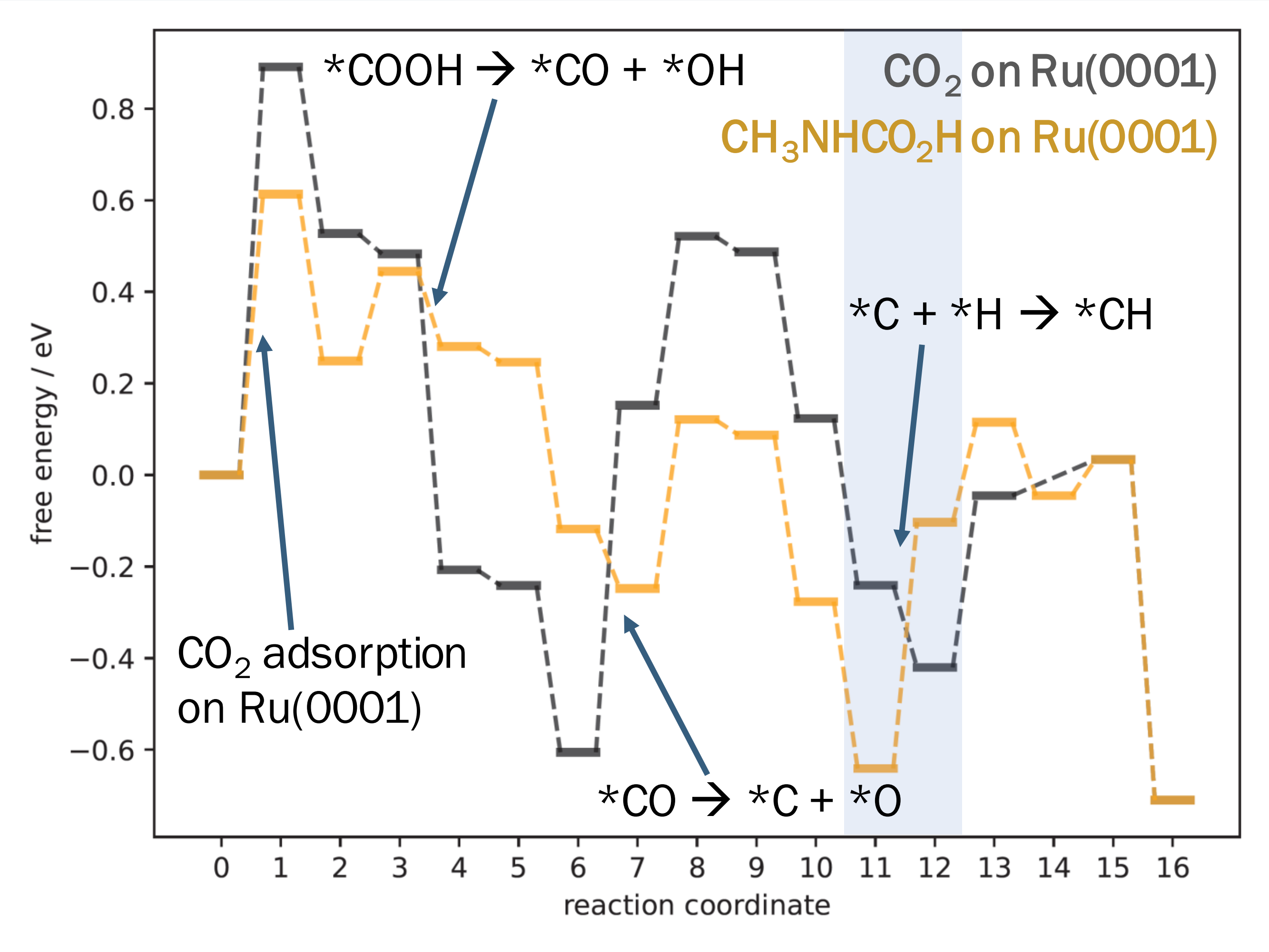
Amine ligand stabilizes undercoordinated species such as surface C



Reaction 6 → 7



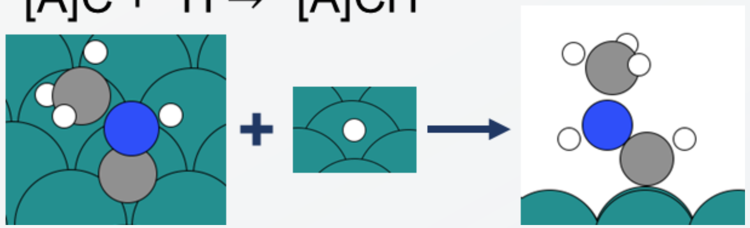
Amine ligand stabilizes undercoordinated species such as surface C



Reaction 11 → 12

*C + *H → *CH

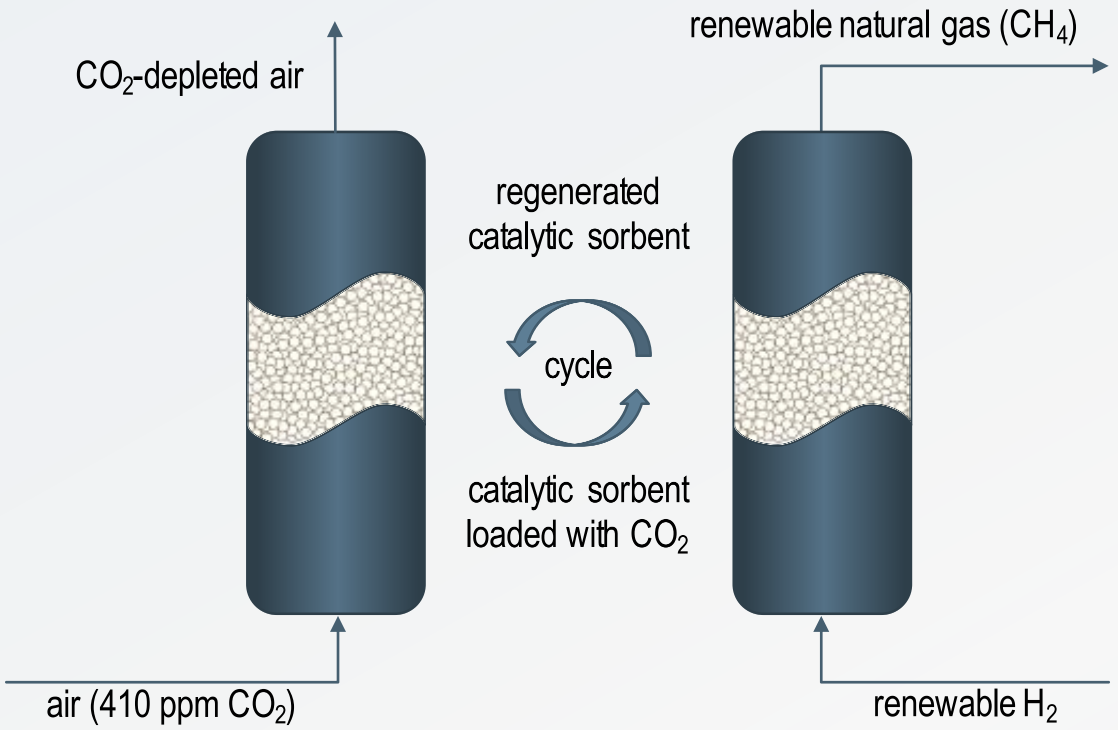
*[A]C + *H → *[A]CH



The mechanism for reaction of amine-bound CO_2 is likely to have different rate-limiting steps compared to the traditional CO_2 methanation pathway

Stepping back to the bigger picture: how else can low-carbon natural gas be made and how do we compare?

Cyclic adsorption-methanation process



Baseline scenarios for comparison:

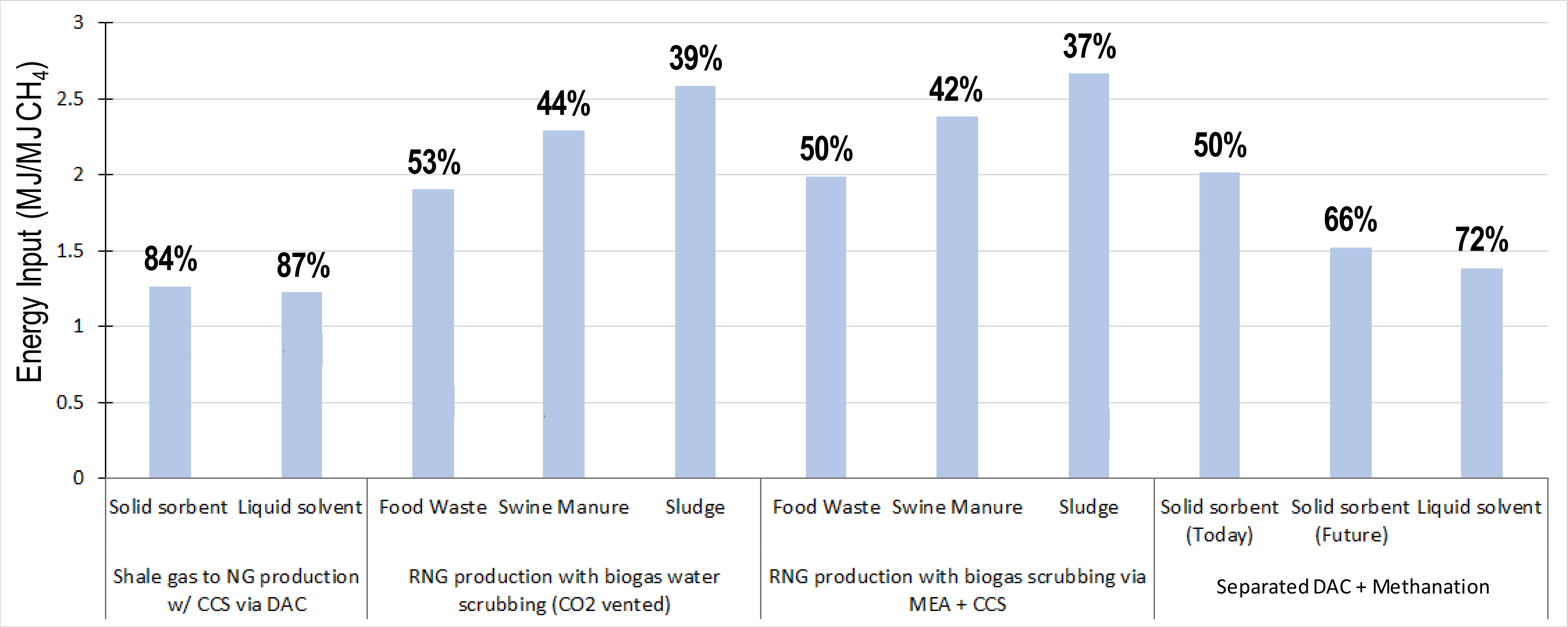
(1) business-as-usual shale gas production + DAC to achieve carbon neutrality

(2) conventional RNG production (e.g. biogas water scrubbing)

(3) RNG production with CCS (e.g. biogas with amine capture)

(4) separate DAC + CO_2 methanation processes

As a long-term energy storage technology, RNG has many possible options with different energy efficiencies of production



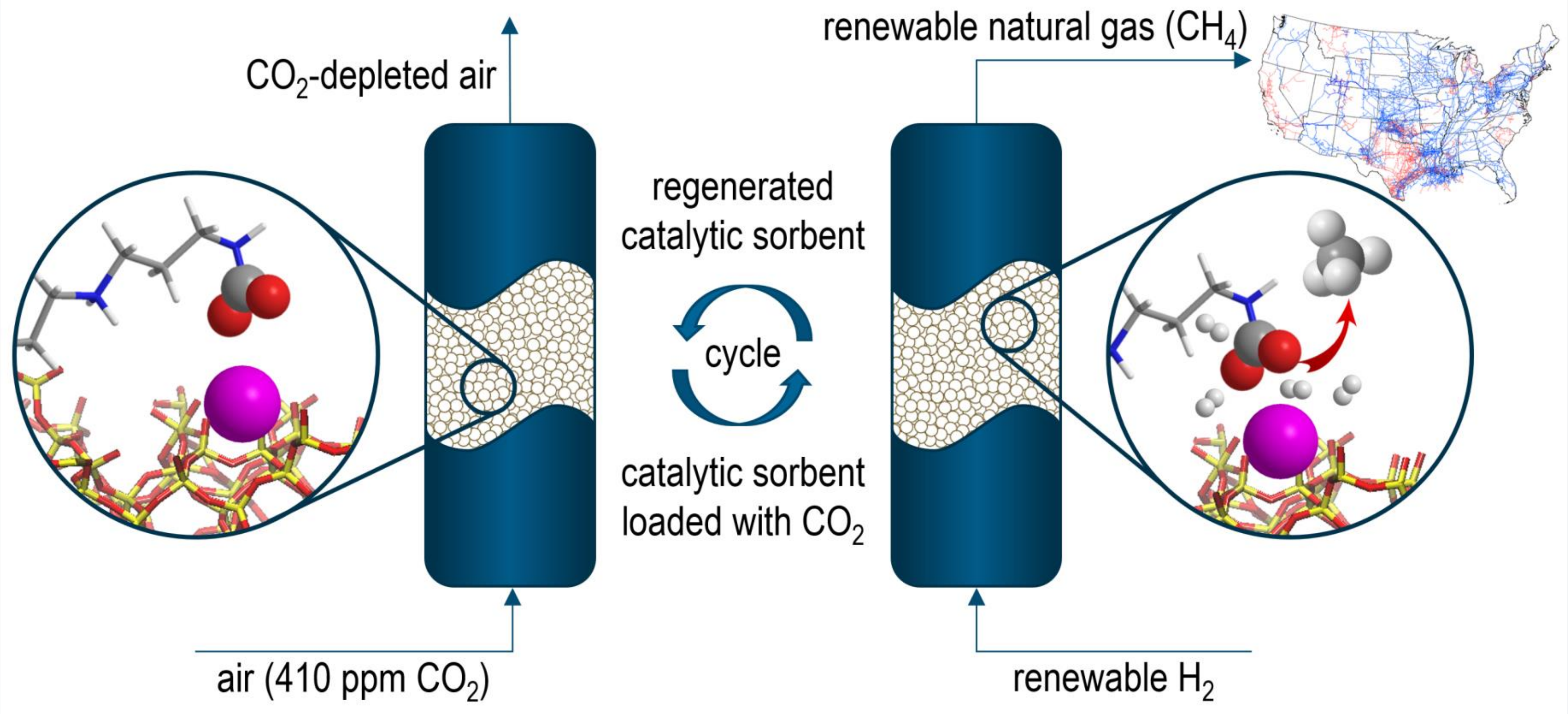
Our direct air reactive capture and methanation process may be a competitive alternative to other forms of RNG production for efficient long-duration energy storage

Coming up next...

Test adsorption and reaction on hybrid amine + metal adsorbent-catalyst materials

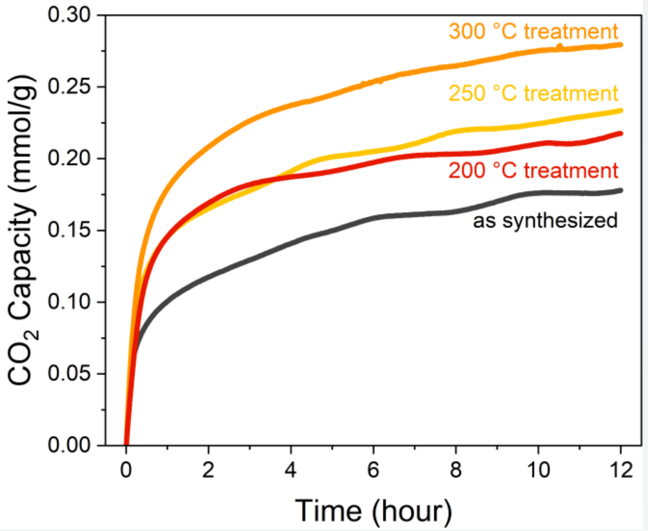
Evaluate activation barriers for amine-assisted reactions in methanation mechanism

Develop models for cyclic reactive capture process

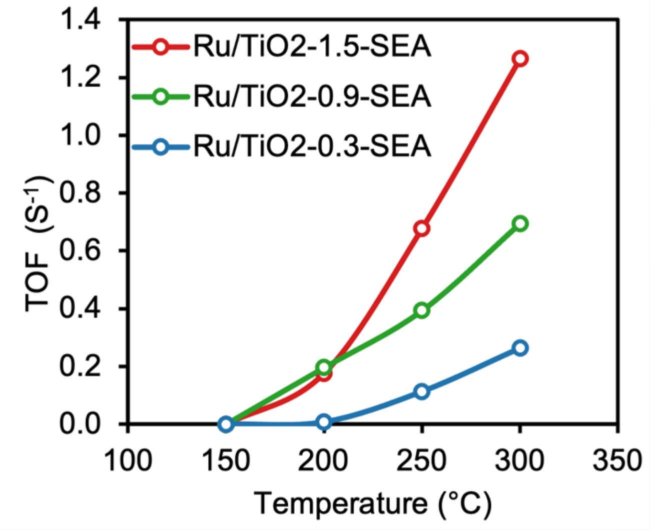


CO_2 reactive capture and methanation shows potential promise as a technology for long-duration energy storage

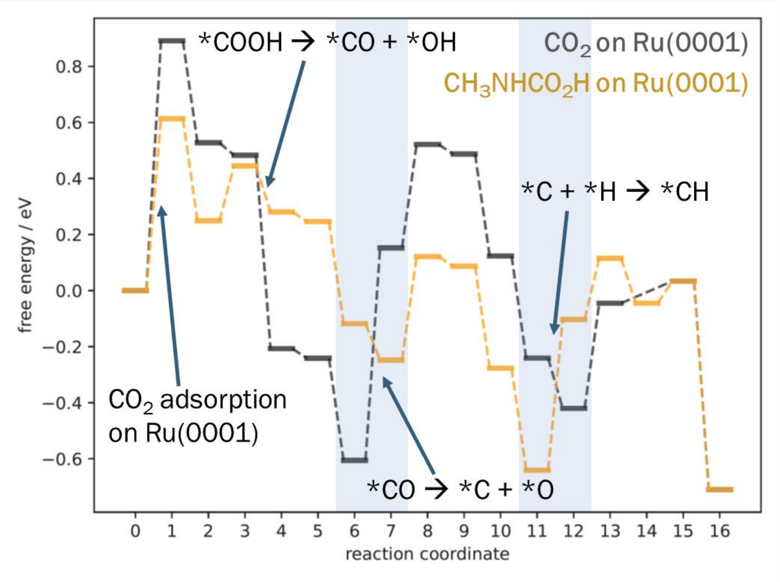
DAC adsorbents with CO_2 capacity retention after thermal treatment



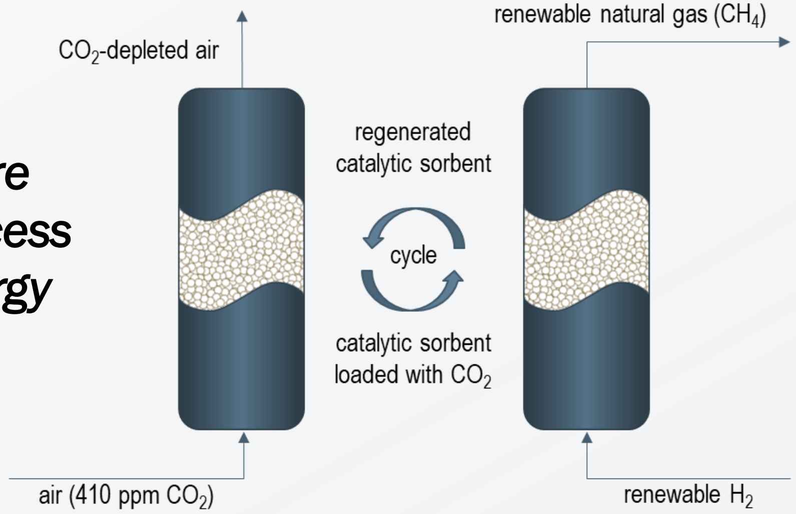
Methanation catalysts with high activity at desired temperature range



Revealed mechanistic differences for amine-bound CO_2



Reactive capture material and process for efficient energy storage



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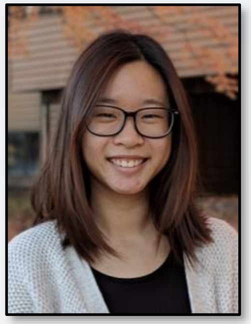
Sneha Akhade



Alvina Aui

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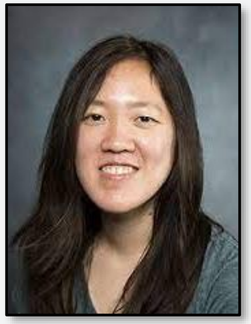

Melinda Jue

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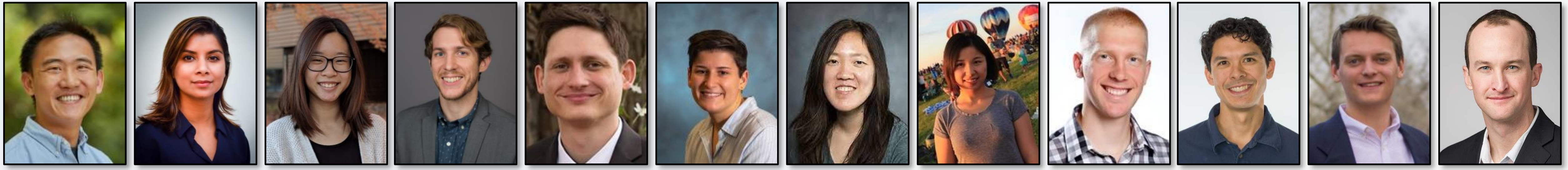
Michael Griffin

U.S. DEPARTMENT OF ENERGY | Fossil Energy and Carbon Management

Project Manager: Issac "Andy" Aurelio
Reactive Capture & Conversion R&D
FWP FEW0277

Appendix

Project Team



Simon Pang | Sneha Akhade | Alvina Aui | Nathan Ellebracht | Brandon Foley | Hannah Goldstein | Melinda Jue | Wenqin Li | Tom Ludwig | Matthew Yung | James Crawford | Michael Griffin

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Project Management
Simon Pang (PI)

Project Management
Matthew Yung

* capability lead

Synthesis & Characterization
Nathan Ellebracht*
Melinda Jue
Brandon Foley

Tasks: 1, 2, 7

Advanced Simulation
Sneha Akhade*
Tom Ludwig

Tasks: 4, 9

Systems Analysis
Wenqin Li*
Hannah Goldstein
Alvina Aui

Tasks: 5, 6, 10

Catalytic Evaluation
Matthew Yung*
Michael Griffin
James Crawford

Tasks: 3, 8

Tasks, Milestones, and Deliverables	Budget Period:	BP 1						BP 2					
	Project Year:	Oct '21 – Sep '22				Oct '22 – Sep '23				Oct '23 – Sep '24			
	Project Quarter:	1	2	3	4	5	6	7	8	9	10	11	12
Task 0: Project management and planning		■	■	■	■	■	■	■	■	■	■	■	■
Task 1: Synthesize hybrid adsorbent-catalyst materials		■	■	■	■	■	■						
Task 2: Evaluate adsorption performance with dilute CO_2		■	■	■	■	■	■						
Milestone 1: Measured DAC adsorption capacity >0.25 mol CO_2/kg				✓									
Task 3: Characterize catalysts and perform methanation with dilute CO_2		■	■	■	■	■	■						
Milestone 2: Achieved >25% CO_2 single-pass conversion from dilute CO_2					■								
Task 4: Simulate interaction between captured CO_2 and single-atom catalyst site		■	■	■	■	■	■	■	■				
Milestone 3: Established energetics for conversion of captured CO_2 into CH_4						■							
Task 5: Develop preliminary technoeconomic assessment		■	■	■	■	■	■						
Deliverable 1: Report detailing preliminary technoeconomic assessment							■						
Task 6: Develop preliminary life cycle assessment		■	■	■	■	■	■						
Deliverable 2: Report detailing preliminary life cycle assessment							■						
Milestone 4: Downselected material composition							■						
Success Criteria BP1: Demonstrate 10% improvement in RNG MFSP and carbon intensity compared to baseline							■						
Task 7: Synthesize second-generation materials								■	■	■	■	■	■
Milestone 5: Measured DAC adsorption capacity >0.40 mol CO_2/kg									■				
Task 8: Develop cyclic air capture-methanation process and test performance								■	■	■	■	■	■
Milestone 6: Converted >50% of captured CO_2 into CH_4										■			
Milestone 7: Retained >75% performance after extended cyclic operation												■	
Task 9: Simulate adsorption and conversion processes with humidity										■	■	■	■
Task 10: Refine technoeconomic and life cycle analyses								■	■	■	■	■	■
Deliverable 3: Report documenting refined TEA and LCA for DAC-RCC process													■
Success Criteria BP2: Demonstrate 15% improvement in RNG MFSP and/or carbon intensity compared to baseline													■