

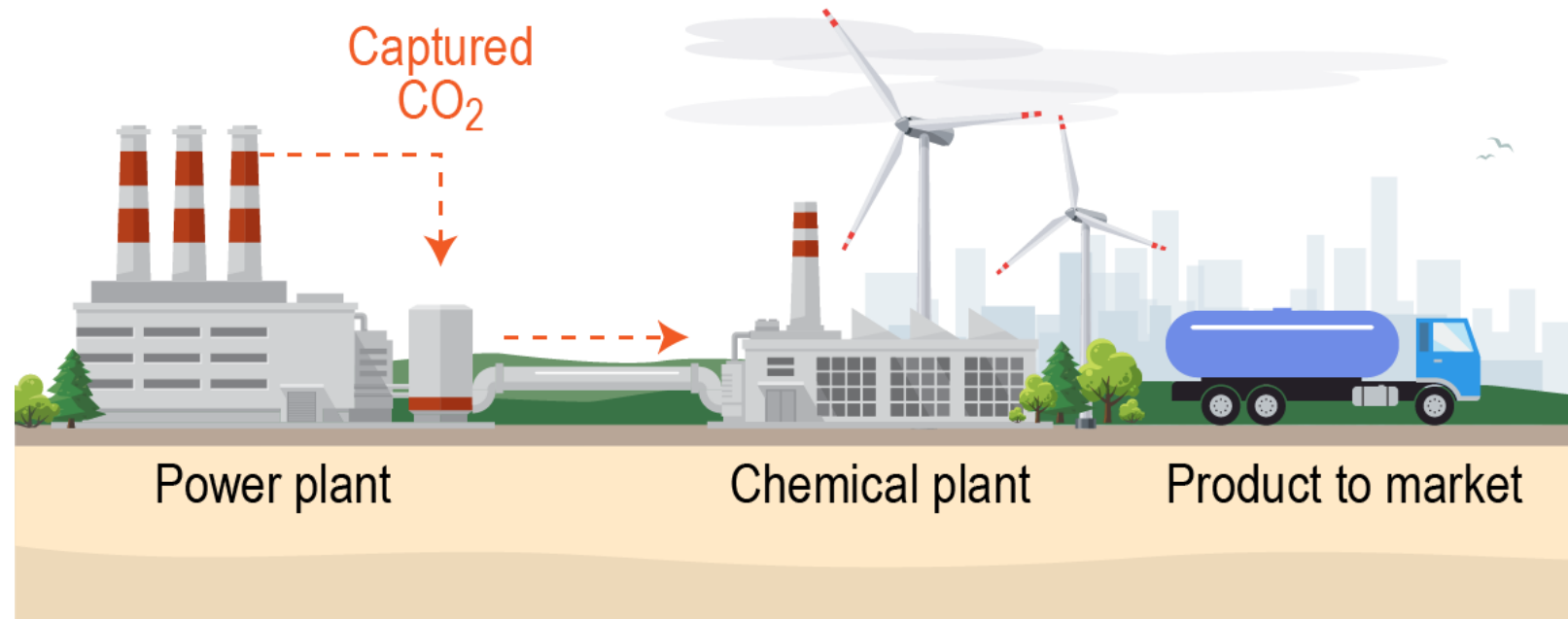
Exploring the Chemical Synergies Between Capture and Conversion of CO₂

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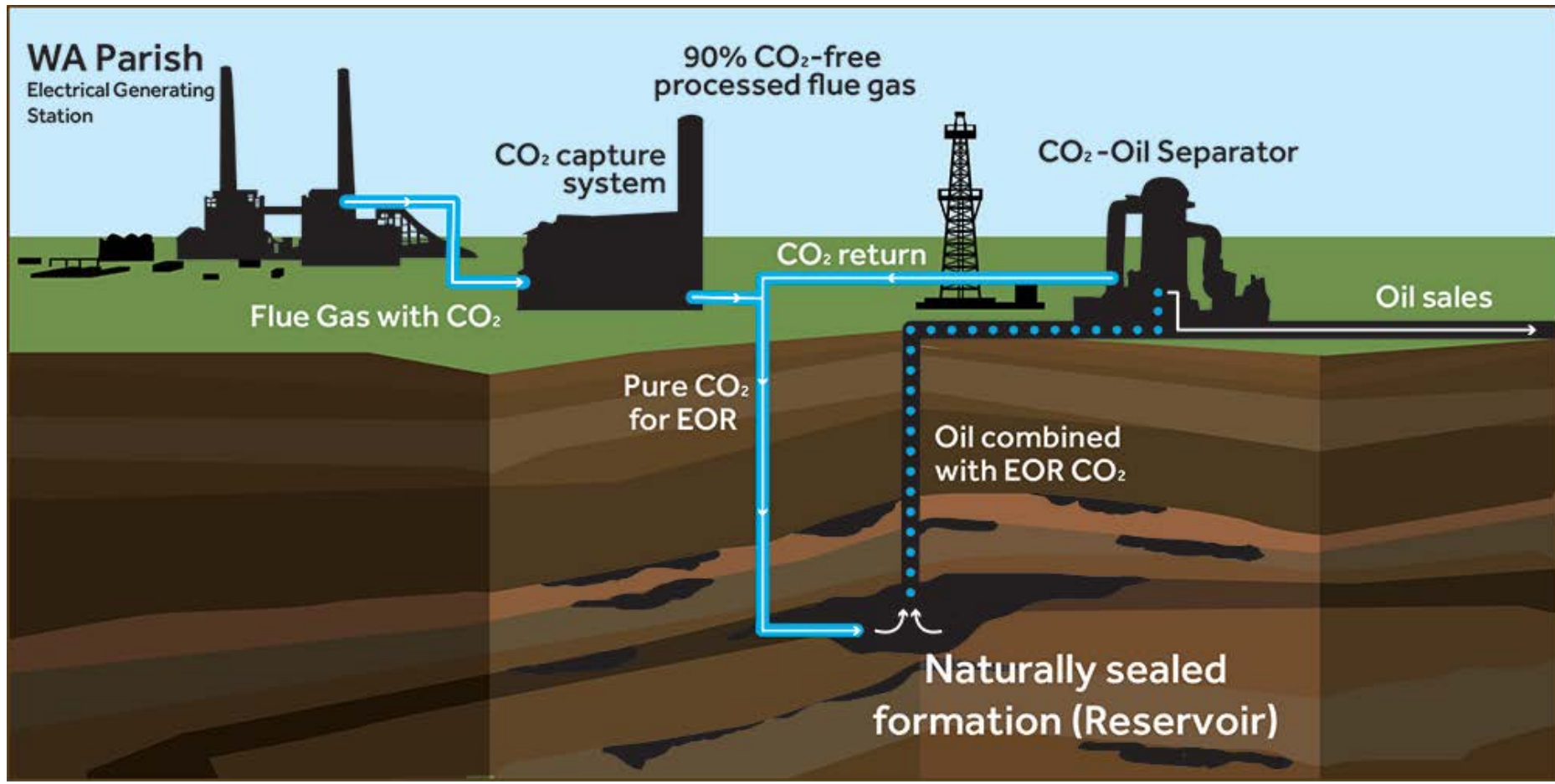
Outline

- ▶ CO₂ capture chemistry
- ▶ Thermocatalytic CO₂ conversion chemistry
- ▶ Historical integration
- ▶ Designing and TEA of integrated processes
- ▶ Opportunities
- ▶ Barriers and research needs



CO₂ Capture and Utilization Today

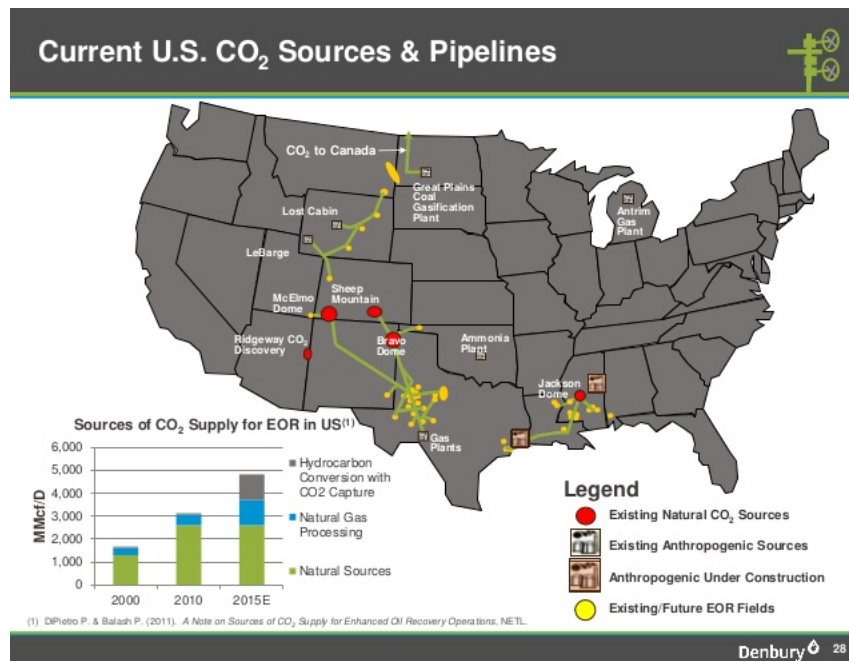
Point-source CO₂ capture and utilization deliver concentrated CO₂ streams for EOR.



The Case for Integrating CO₂ Capture with Conversion

The energy cost of collecting, concentrating and purifying CO₂ is not free.

- ▶ Global CO₂ demand (80Mtpa) is met via extraction from geological reservoirs (e.g. Bravo Dome), while anthropogenic sources exceed 18,000Mtpa.¹



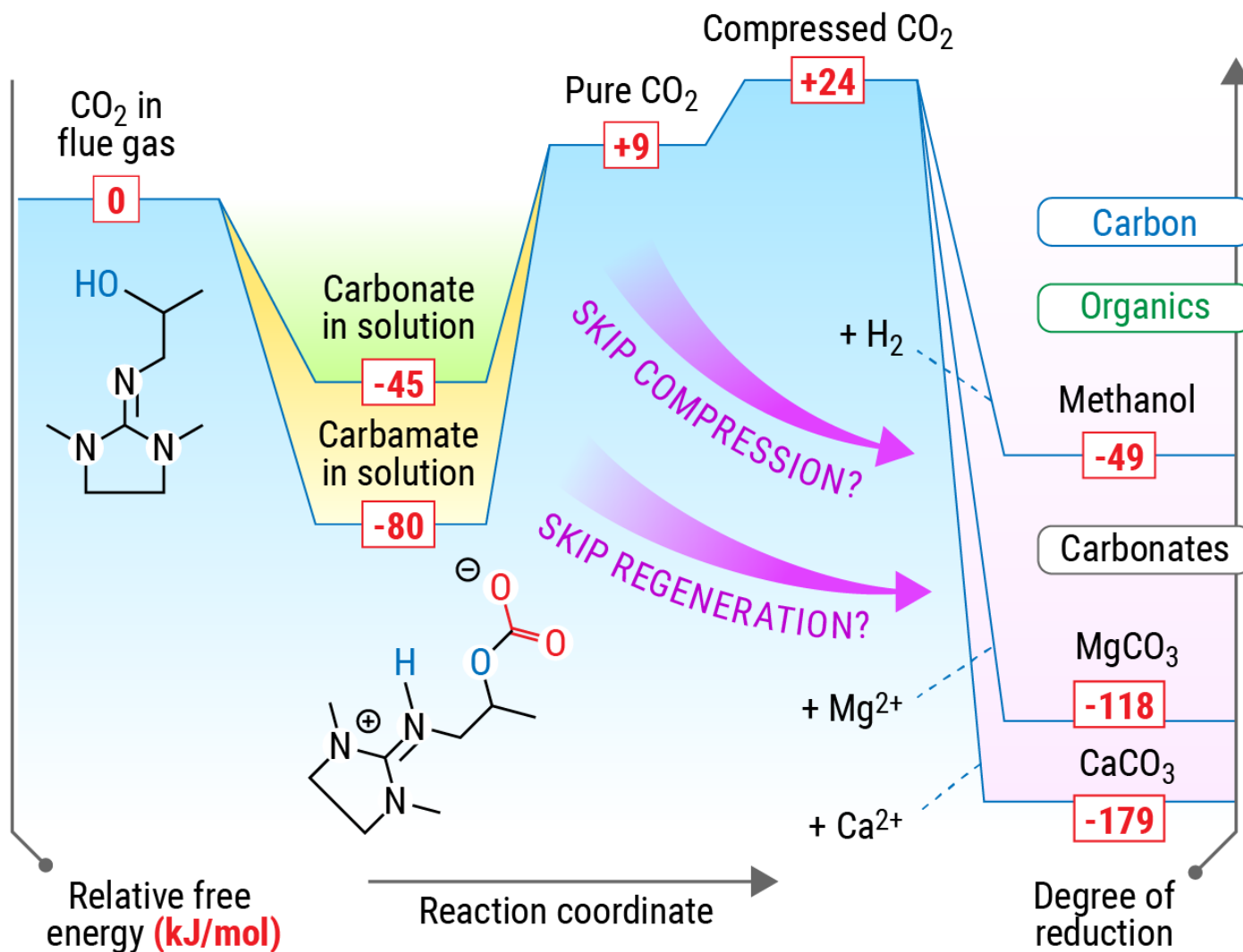
When natural supplies are exhausted, CO₂ must be captured before use.

- Natural CO₂: \$20/tonne²
- Direct air capture: \$1,000-100/tonne^{2,3}
- Flue gas: \$100/tonne²
 - Capture: **-85 kJ/mol**
 - Compression: **-12 kJ/mol**
 - Transport: **Variable**

1) "Accelerating the uptake of CCS: industrial use of captured carbon dioxide." Global CCS Institute, 2015

2) Herzog et al. PNAS, 2011, 108, 20428–20433. 3) Joule, 2018, 2, (8), P1573-1594, 4) Image from NETL.gov

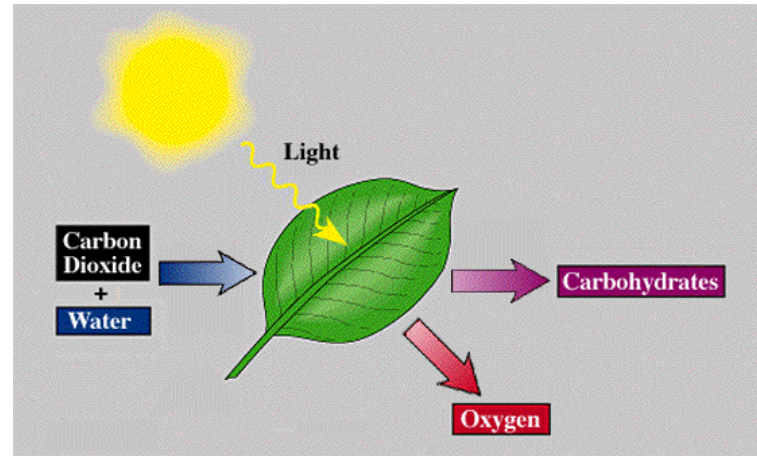
The Case for Integrating CO₂ Capture With Conversion



Performing catalysis on CO₂ captured in solution avoids the process energies with capture and compression.

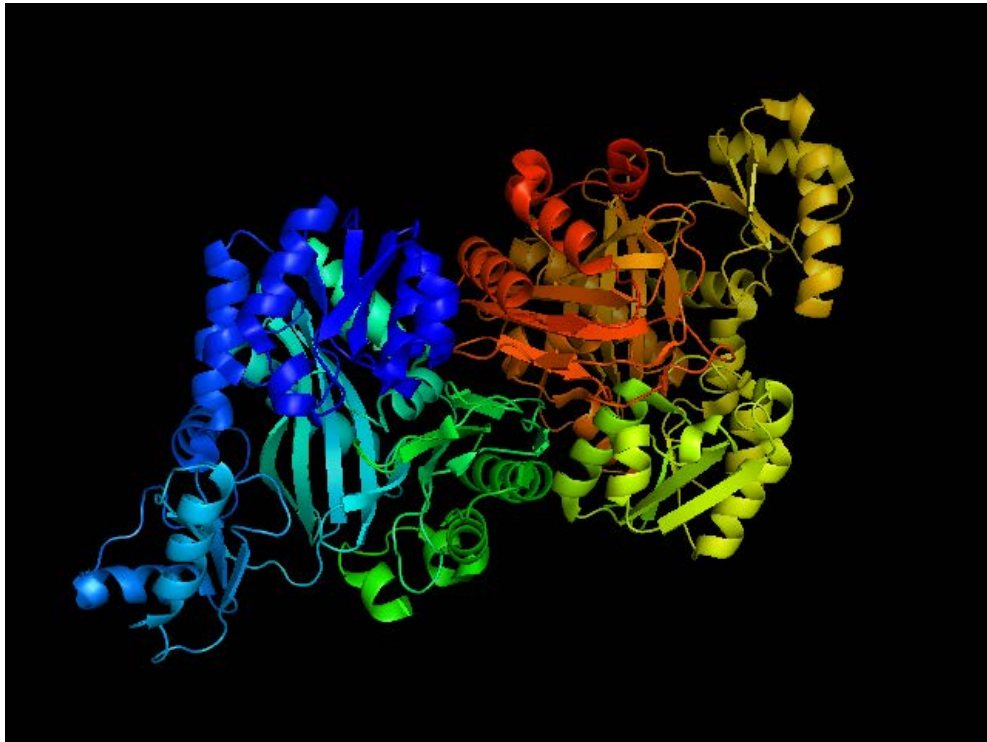
How Nature Does Reactive Capture and Conversion

Photosynthesis has perfected reactive capture and conversion over millennia.

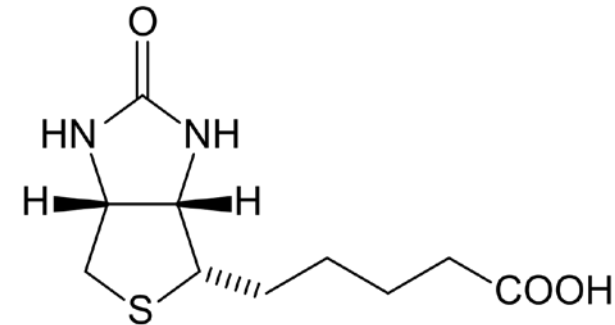


Nature Has Long-Perfected CO₂ Capture and Conversion

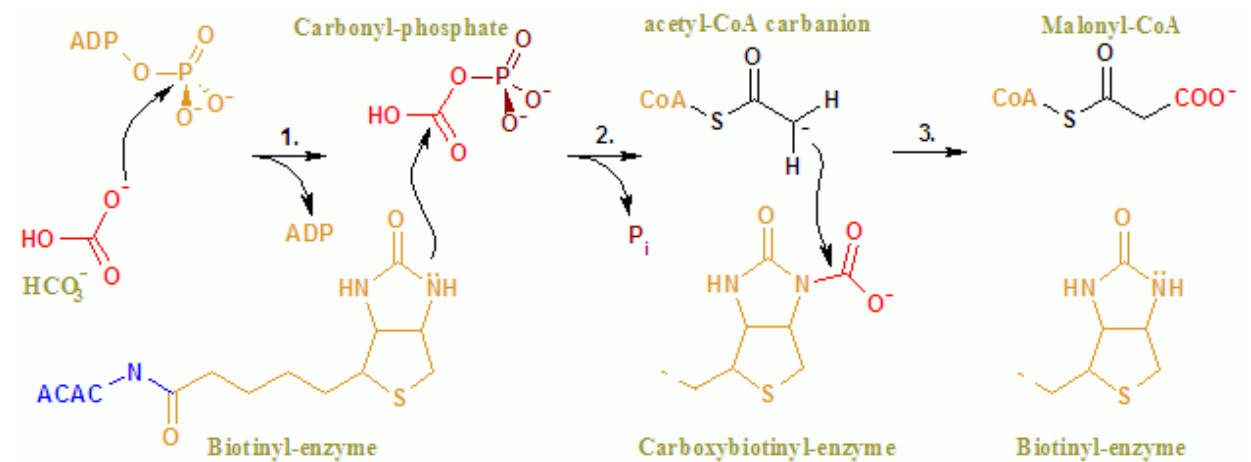
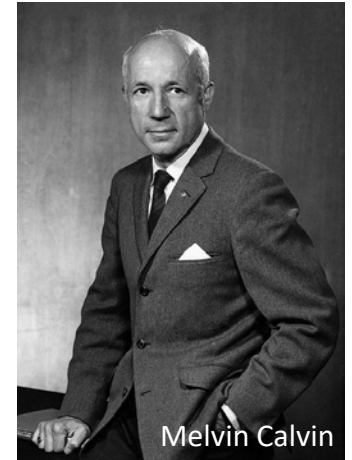
Biotin transfers anionic carboxylates in solution to grow fatty acids via the Calvin cycle.



Biotin carboxylase subunit of *E. coli*
acetyl-CoA carboxylase



Biotin co-factor

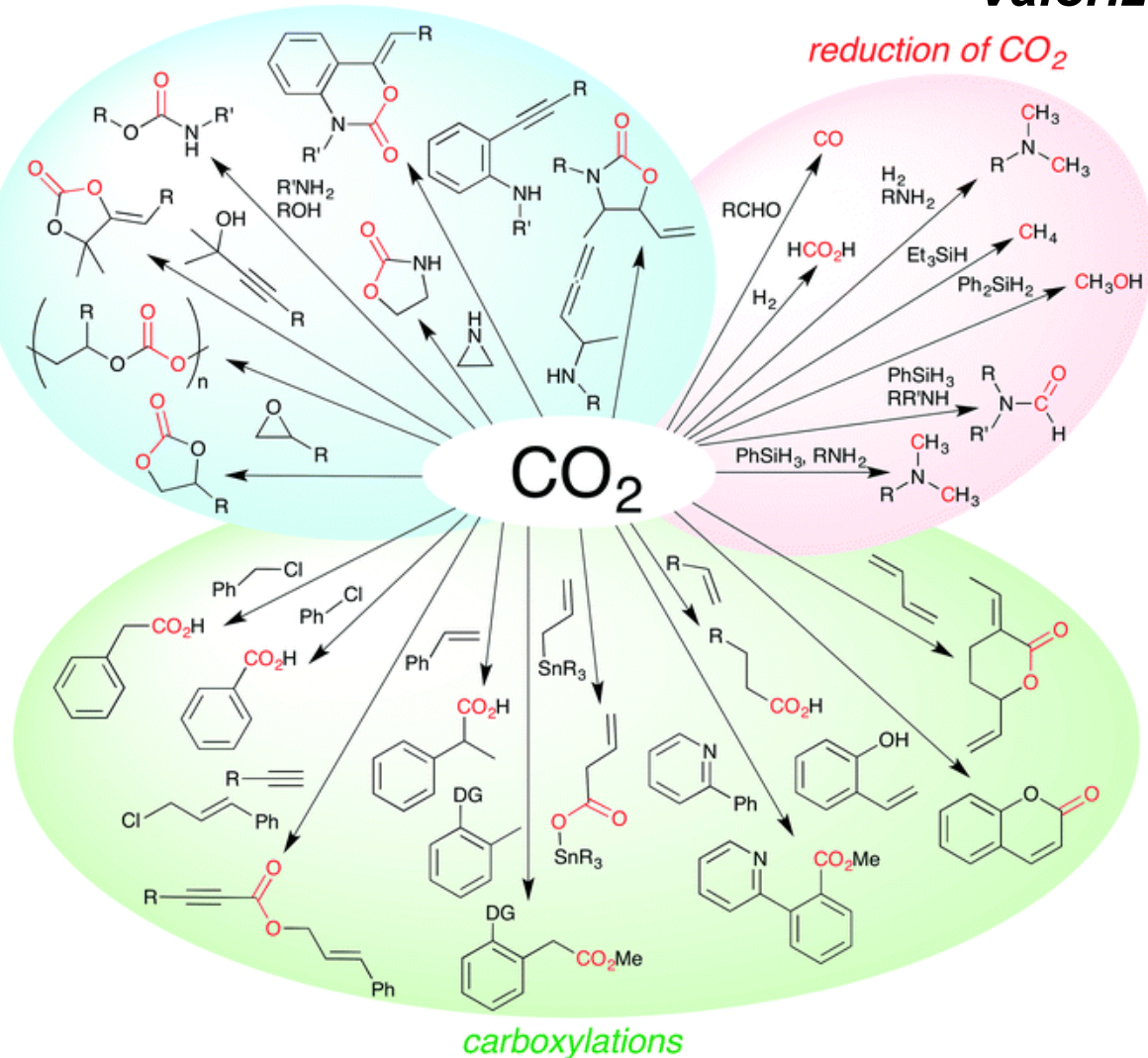


Products That Can Be Made From CO₂

carbonates and carbamates

Valorizing CO₂ introduces market drivers to implement CCS.

reduction of CO₂



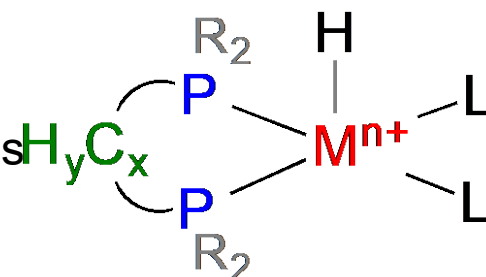
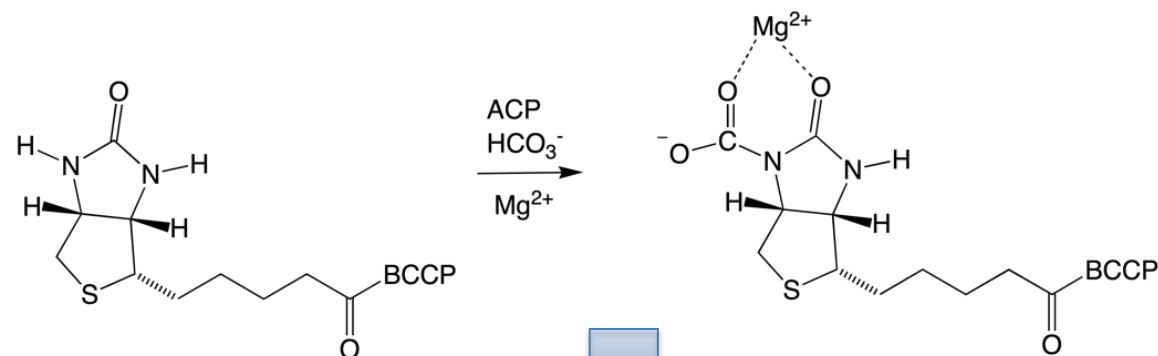
- Numerous products can be made from CO₂, but reactive pathways are limited.
- All chemical reactions of CO₂ proceed via nucleophilic attack on the central carbon or electrophilic coordination to the oxygens.
- Historical efforts changed catalyst, reagent, T & P, here, we are changing the CO₂

Reaction Advantages of Converting Captured CO₂

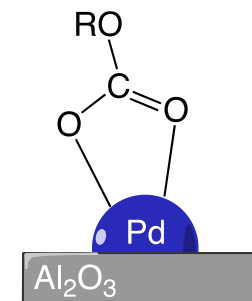
Condensed-phase reactions provide energy and cost benefits and new reactive landscapes.

- ▶ Same solvent used for both steps
 - ▶ Catalytic with respect to solvent
- ▶ Multiple products available by changing reagent feed
- ▶ Catalysis at atmospheric (CO₂) pressures
 - CO₂ concentration >5 wt% in solution at 1 atm
 - Potentially faster liquid phase kinetics
- ▶ Potentially lower free-energy pathways
 - Rehybridization complete, similar intermediates
 - High dielectric provides stabilization for polar transition states
- ▶ Heterogeneous or homogeneous pathways viable
 - Direct coordination to catalysts

Like Biotin, catalysts can operate on captured CO₂



Inner-sphere chelation
of “captured” CO₂ (L)



Chelation of “captured”
CO₂ to metal surfaces

Thermodynamics of Conversion (Hydrogenation)

**Hydrogenation of CO₂ with H₂ is Exothermic but Endergonic.
Thermal Regeneration of CO₂ capture is endothermic.**

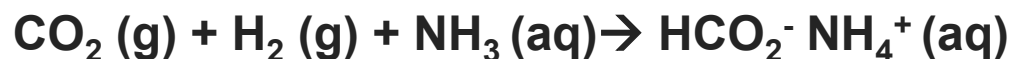


■ $\text{DG}^\circ = 32.9 \text{ kJ mol}^{-1}$

■ $\text{DH}^\circ = -31.2 \text{ kJ mol}^{-1}$

■ $\text{DS}^\circ = -215 \text{ J K mol}^{-1}$

Base Makes the Reaction Exergonic

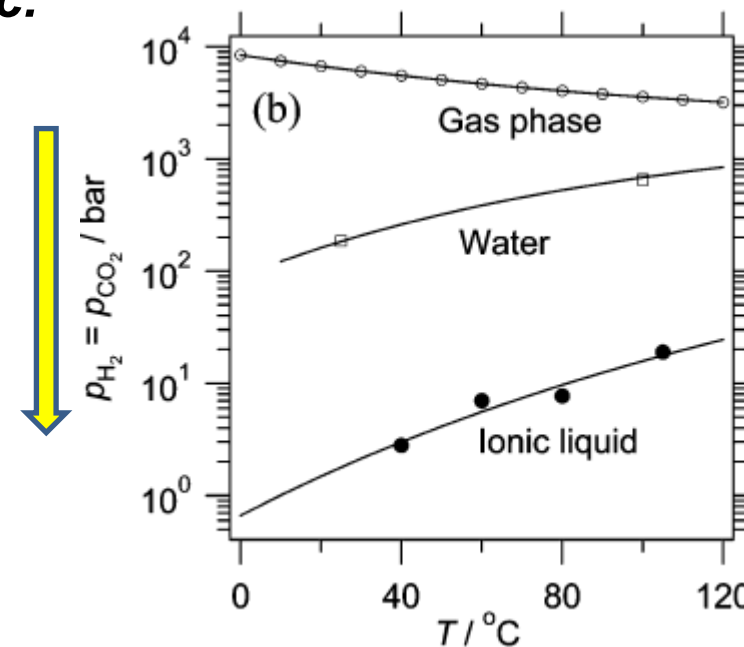


■ $\text{DG}^\circ = -9.5 \text{ kJ mol}^{-1}$

■ $\text{DH}^\circ = -84.3 \text{ kJ mol}^{-1}$

■ $\text{DS}^\circ = -250 \text{ J K mol}^{-1}$

Hydrogenation of captured CO₂ is downhill energetically.



Pressures Necessary To Reach
H₂ + CO₂ = HCOOH Equilibria*

Water-lean capture
solvents *are* ILs!

The First Synergies of Capture and Conversion

Noyori & Jessop noted enhancement in yield and rate when alcohols and amines are added.

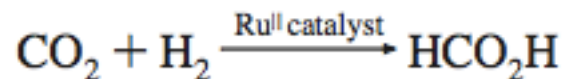
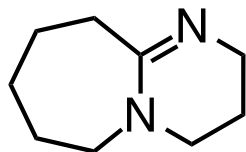


Table 4. The Yield of Formic Acid after 1 or 10 h in the Presence of Various Additives or Cocatalysts^a

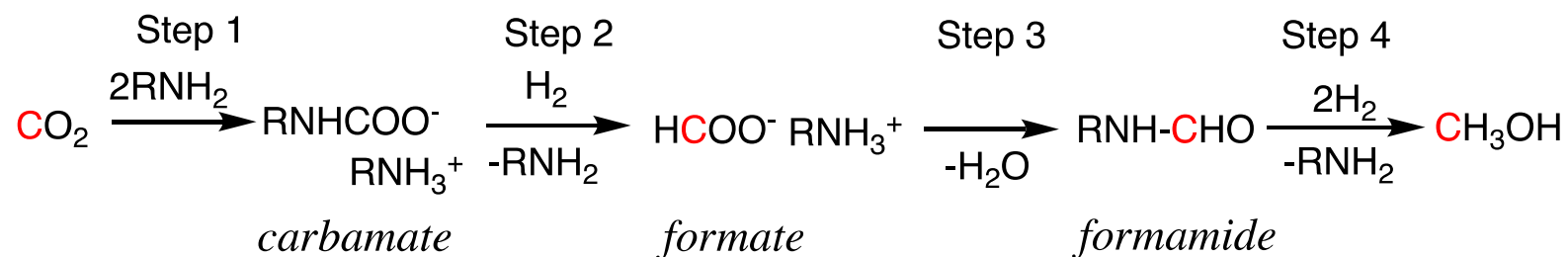
| Additive | Yield of Formic Acid (%) | |
|----------------------------------|--------------------------|------------|
| | after 1 h | after 10 h |
| triethylamine | 0.03 | 0.04 |
| THF | 0.02 | 0.02 |
| C ₆ H ₆ | 0.09 | 0.13 |
| MeCN | 0.06 | 0.28 |
| H ₂ O | 0.09 | 0.54 |
| MeOH | 0.05 | 0.76 |
| DBU | 0.92 | 1.42 |
| MeOH | 1.36 | 1.60 |
| C ₆ F ₅ OH | | |



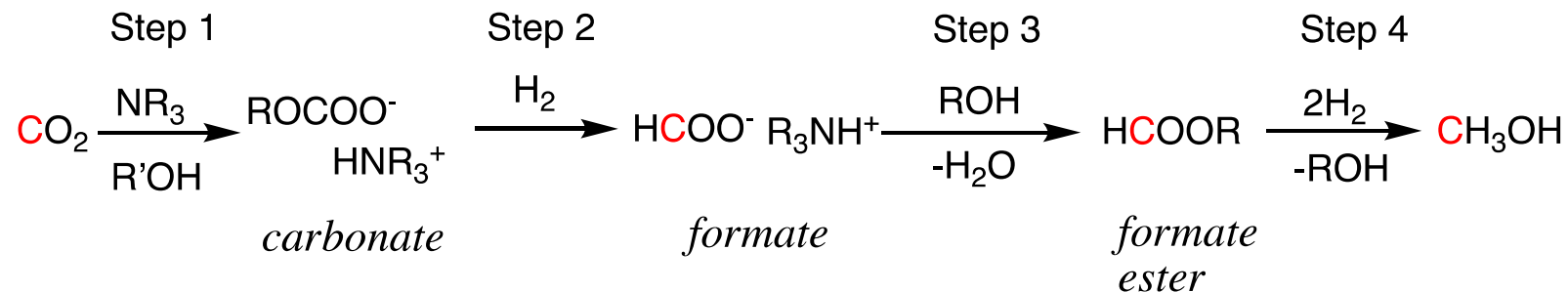
Condensed-Phase Methanol Synthesis Exploits Similar Chemical Reactivity

The same chemicals that capture CO₂ also promote conversion.

Pathway (a)



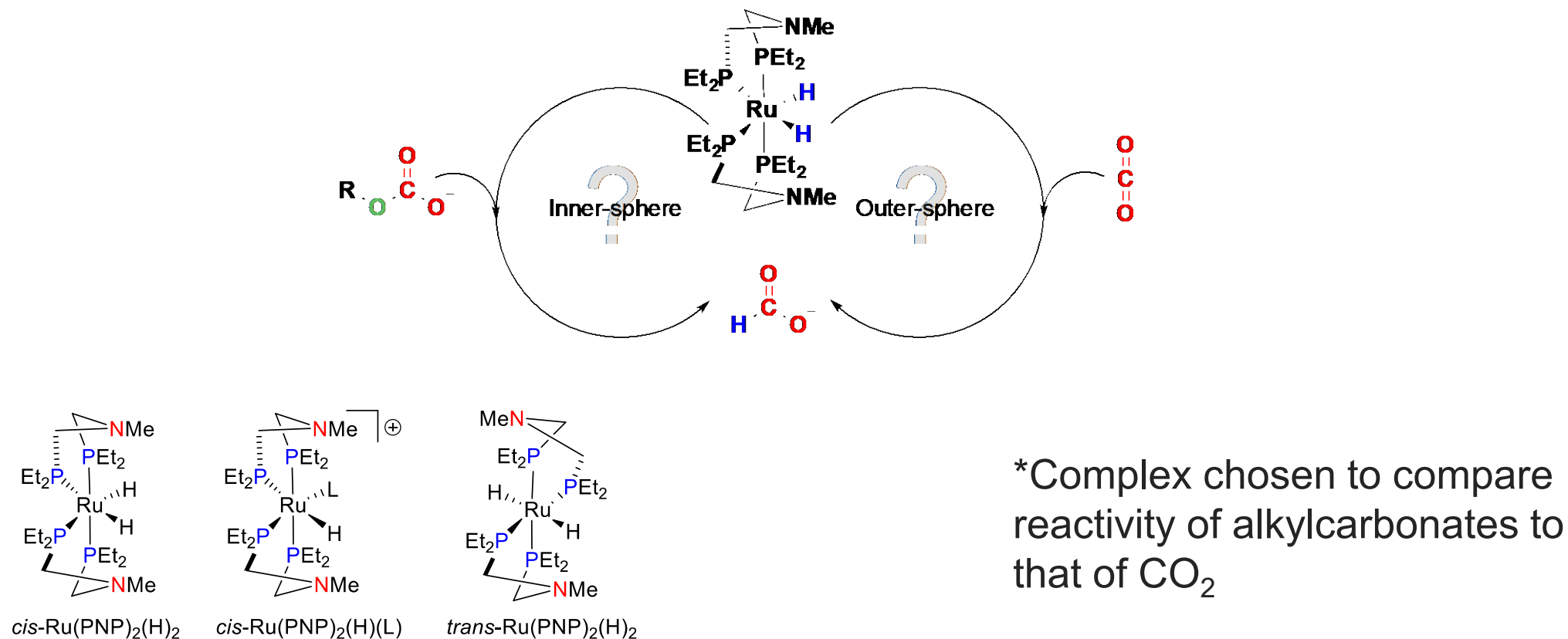
Pathway (b)



Addition of amine or alcohol additives to homogeneous catalysis promotes the formation of methanol via formate ester and formamide intermediates.

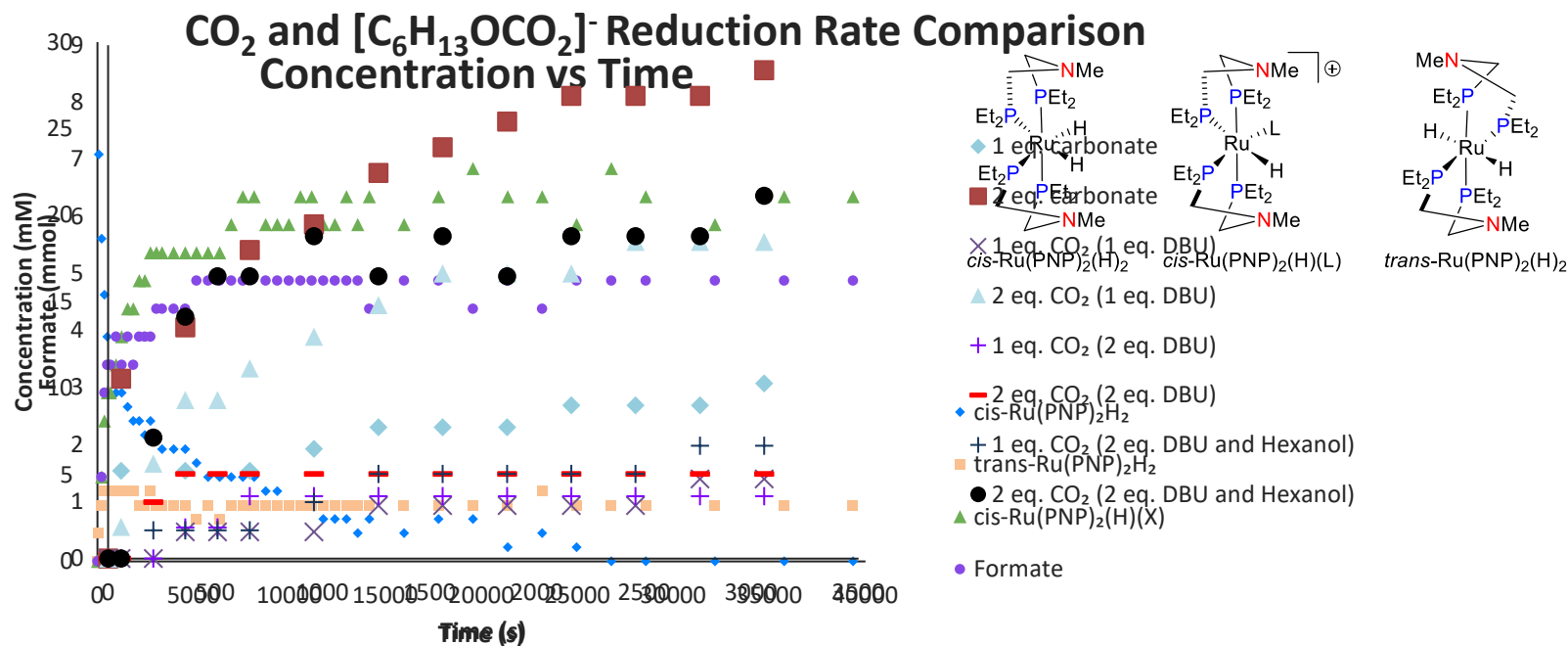
Probing Captured CO₂ Reactivity

Reduction of CO₂ Could be Catalytic With Respect to Capture Solvent, but alkylcarbonate or carbamate reactivity had not yet been verified.



Captured CO₂ and CO₂ Differ in Reactivity

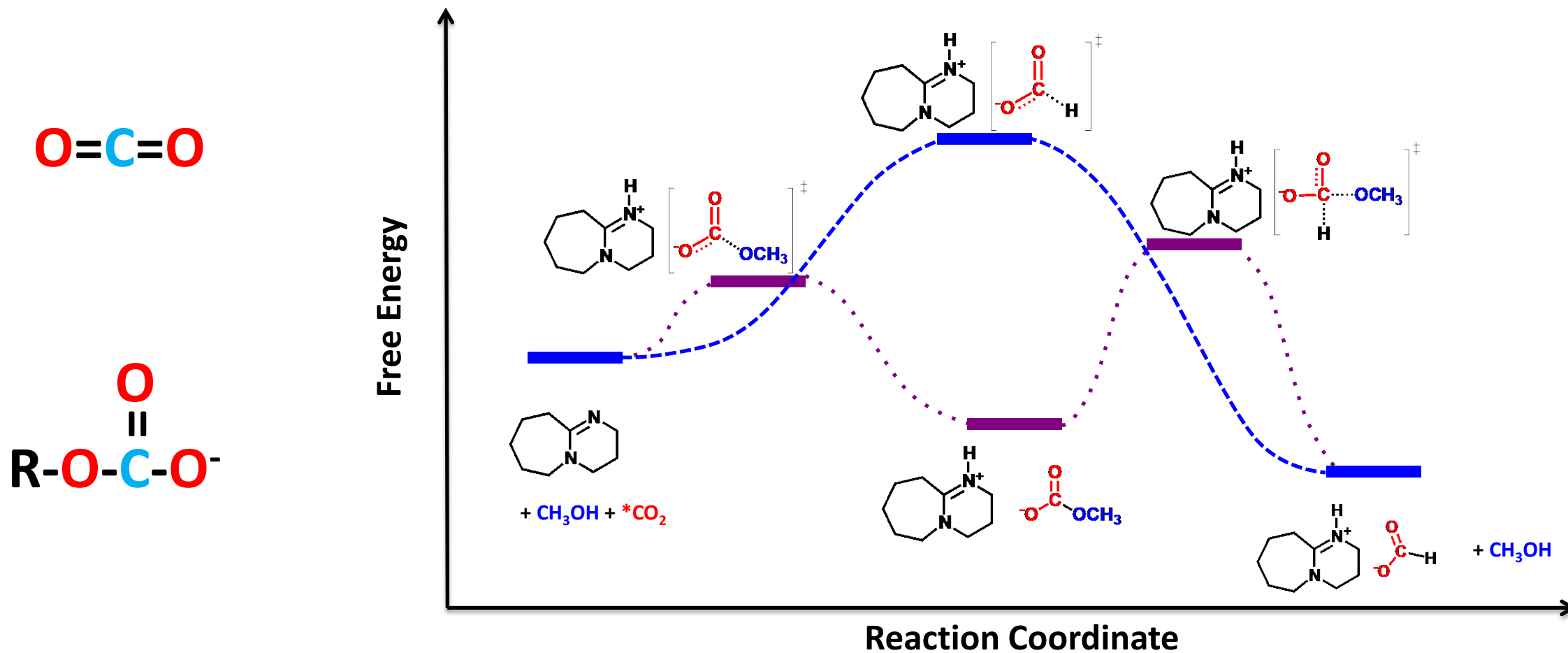
Alkylcarbonates appear to be reduced by Ru(PNP)₂H₂ via an inner-sphere reduction while CO₂ goes through an outer-sphere.



- ▶ Only *cis*-Ru(PNP)₂(H)₂ was consumed in the reduction of hexylcarbonate
- ▶ Free CO₂ consumes *cis*-Ru(PNP)₂(H)(L) and *trans*-Ru(PNP)₂(H)₂
- ▶ Rates of hydrogenation are faster, suggesting lower E_{act}

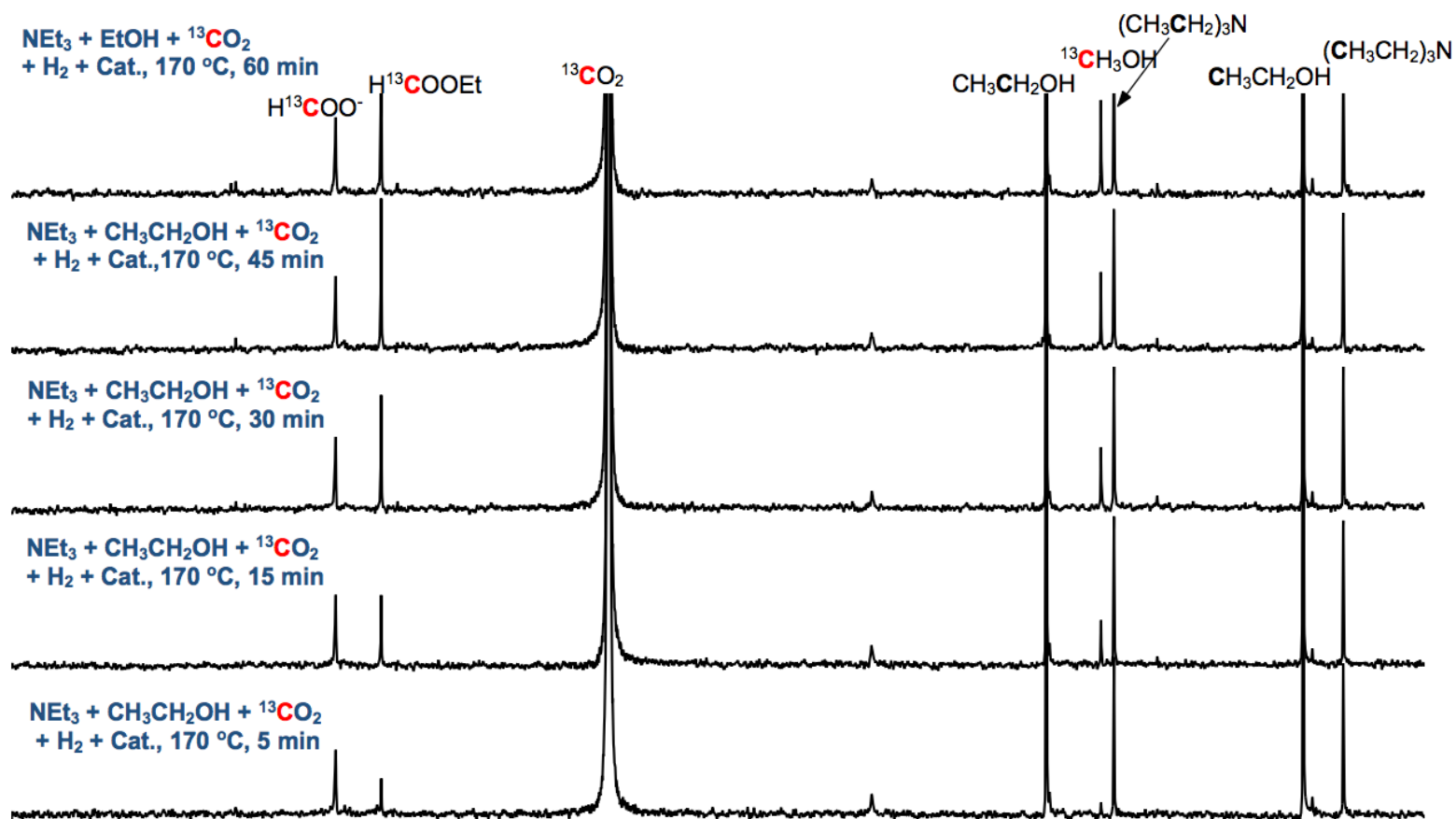
Captured CO₂ and CO₂ Differ in Reactivity

Alkylcarbonates may offer different free-energy landscapes offering potentially faster kinetics.



In-Situ ^{13}C MAS NMR Enables an Unprecedented View of Speciation and Kinetics of Catalytic Reactions

Operando catalysis supports proposed mechanism of hydrogenation.



*Results led to TCF project with SoCalGas

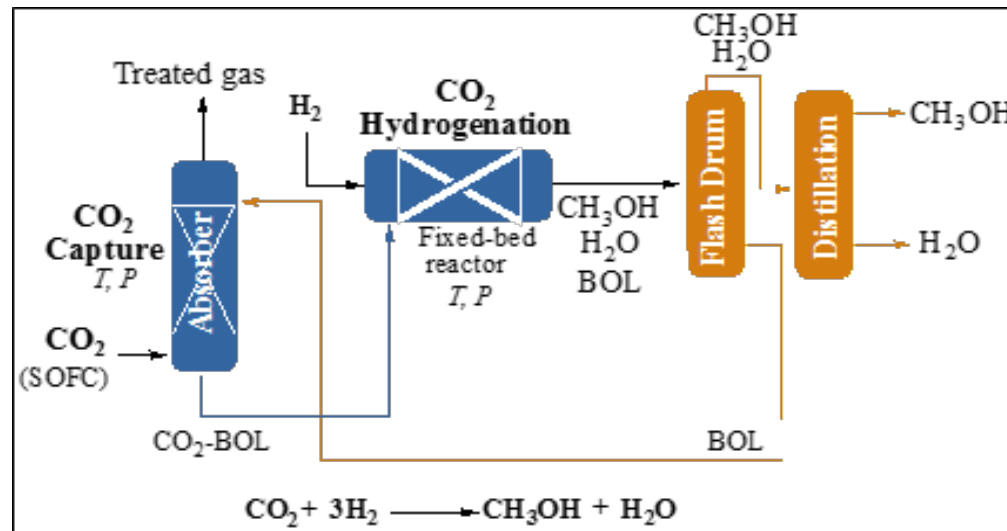
$\text{Cu/ZnO/Al}_2\text{O}_3$, EtOH, TEA, 120 °C, 30 bar CO_2

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Integrated Capture and Conversion of CO₂ to Methanol (ICCCM). TCF-19-17862

► Process configuration for the ICCCM technology

- Excess H₂ is then separated in a low-T flash drum and recycled back to reactor
- Liquid phase product from the H₂ recovery drum contains methanol, CO₂-lean CO₂BOL solvent, and water
- The non-volatile solvent is recovered in flash drums at lower pressure and recycled back to the absorber
- Methanol and water is pumped to a distillation column designed to produce methanol 99.6% purity

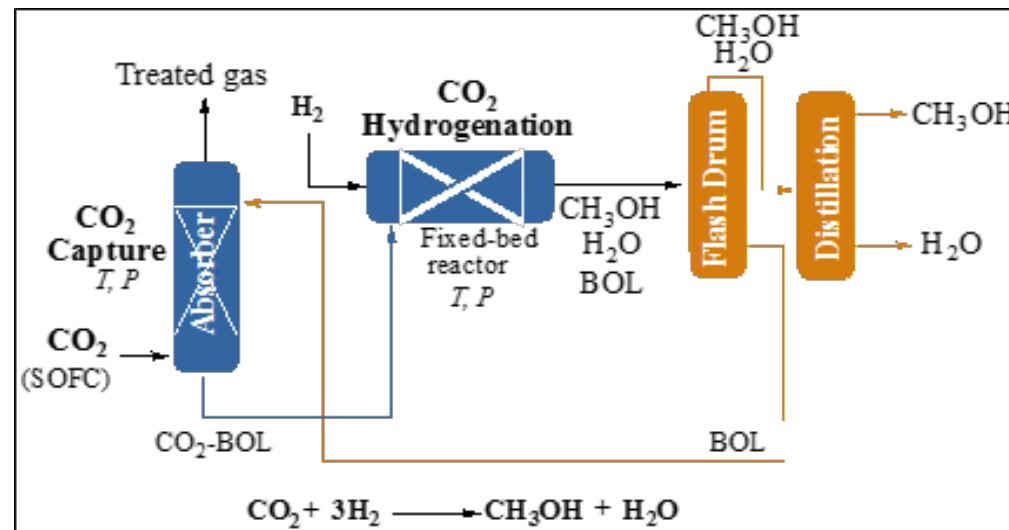


Advantages of Technologies With Capture and Conversion

Integration provides cost and energy benefits.

► **Energy saving features of the ICCCM process:**

- Combined units of operation and solvent
- Hydrogenation of CO₂ to methanol is exothermic partially offsetting endothermic CO₂ release
- Heat recovered from the reactor can be used to generate low-pressure steam which can be used in other parts of the process, and as a utility
- Condensed product bypasses mechanical compression of CO₂



Techno-economic Assessment (TEA) for Integrated Processes Like ICCCM

Integration enables competitive market pricing with 45Q and renewable fuel standards.

- ▶ **Preliminary TEA performed on two different flue gas sources:** a 50 MW SOFC power plant and a 550 MW NGCC plant, and baselined against a **conventional natural gas-to-methanol plant.**
- ▶ **H₂ price set at \$2/kg**

- 1) Methanol from natural gas by the ICI copper-based catalytic process (PEP Yearbook, 2014).
- 2) Key modeling assumptions: 90% capture of CO₂ from flue gas, 5.3 mol/mol H₂/CO₂ target at reactor inlet, 120 °C reactor temperature, 25 bar reactor pressure, equilibrium reactor performance and methanol selectivity of 100%, reactor space velocity of 0.9 kg/h MeOH/ liter of catalyst, flue gas compositions reported by ⁸ and ⁹ used for the respective SOFC and NGCC cases.
- 3) Carnot efficiency is used to convert thermal energy to electricity.
- 4) Defined as heating value of methanol over total energy fed into the system (H₂, steam and electricity). Carnot cycle efficiency is used to convert electricity to thermal energy.
- 5) Current industrial price of methanol. H₂ price and 45Q carbon credit are set to \$2/kg (DOE, 2015) and \$35/tonne CO₂ ¹⁰.
- 6) Based on Aspen Process Economic Analyzer.
- 7) Assuming 15% ROI.

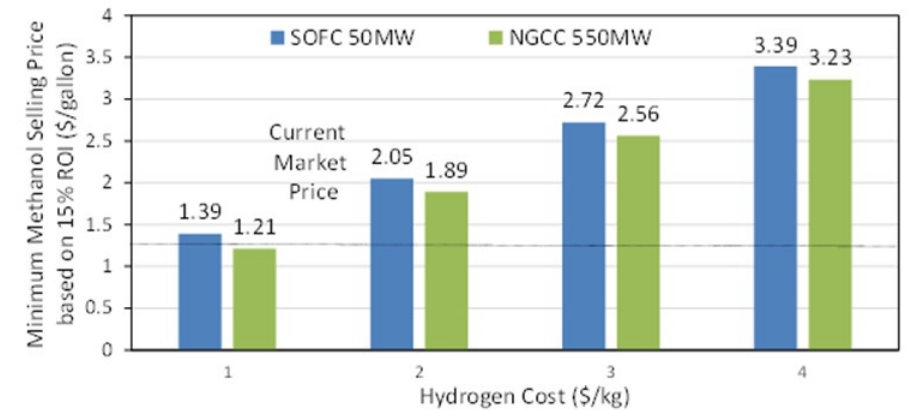
| | Reference Technology | Proposed Technology ⁽²⁾ | |
|---|--|------------------------------------|-----------------------------|
| | Conventional Natural Gas based Syngas ⁽¹⁾ | NGCC-Based Flue Gas (550 MW) | SOFC-Based Flue Gas (50 MW) |
| Capacity (millions of gallons MeOH /yr) | 329 | 329 | 23 |
| Energy into system (% , HHV) | | | |
| Natural gas | 99.6 | | |
| Hydrogen | | 77.4 | 83.2 |
| Steam | 0.0 | 13.2 | 15.0 |
| Electricity | 0.4 | 9.4 | 1.8 |
| CO ₂ concentration at inlet (mol %) | NA | 4.0 | 29.0 |
| CO ₂ conversion in reactor (%) | NA | 70 | 70 |
| H ₂ consumption (mol H ₂ /mol MeOH) | NA | 3.1 | 3.1 |
| Equivalent work of capture/ conversion (kJ _c /mol CO ₂) ⁽³⁾ | NA | 43.9 | 35.4 |
| Overall energy efficiency (% , HHV) ⁽⁴⁾ | 65.4 | 58.3 | 66.4 |
| Production costs (\$/gallon MeOH) | | | |
| Raw Materials ⁽⁵⁾ | 0.53 | 1.27 | 1.27 |
| Carbon Credits ⁽⁵⁾ | 0.00 | 0.15 | 0.15 |
| Utilities | 0.02 | 0.20 | 0.16 |
| Total Fixed Capital (\$/gal MeOH) ⁽⁶⁾ | 0.32 | 0.22 | 0.28 |
| Minimum MeOH Selling Price (\$/gal)⁽⁷⁾ | 1.29⁽⁵⁾ | 1.89 | 2.05 |

Commercial Viability for Integrated Processes Like ICCCM

Reagent (H_2) costs drive economics and market competitiveness.

- ▶ Given \sim \\$1/kg H_2 both ICCCM processes compete with current methanol market prices
- ▶ Q45 carbon credit (\\$35/tonne CO_2) was considered in the economics but additional carbon taxes could facilitate economic viability

H_2 cost sensitivity analysis



- ▶ **Hydrogen co-feed** is expensive. However, in the ICCCM system hydrogen serves an indirect energy source to drive the carbon capture process, versus steam or electricity.
- ▶ **Modular distributed-scale processing platforms**, which in turn could enable distributed applications, such as the separation and conversion of CO_2 from **landfill**, **waste-water treatment**, and **manure off-gas**.
- ▶ **Stranded hydrogen sources** are also more likely to be co-sourced when considering distributed processing, which could enable lower cost/ renewable hydrogen supplies in many applications.

Opportunities and Critical Challenges in Merging CO₂ capture and CO₂ utilization.

“Reports that say that something hasn't happened are always interesting to me, because as we know, there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know.” *

▶ Known Knowns

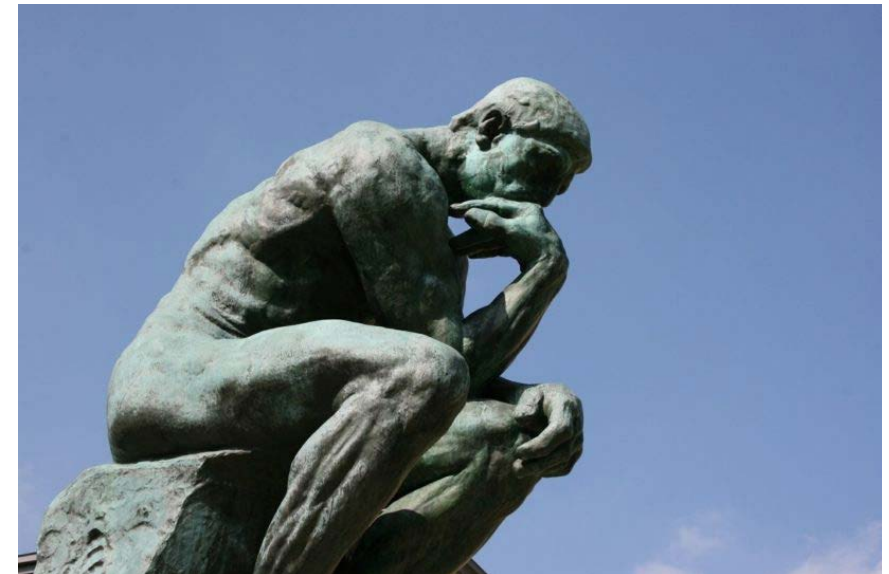
- Catalytic with respect to capture solvent
- New reactive landscapes
- Adaptable to post-source, direct air, blue carbon sources
- Modular process with multiple product streams (change co-feed)

▶ Known Unknowns

- Chemical tolerance (oxidative then reductive environment)
- Catalyst lifetime/tolerance of O₂ etc...
- Logistics of delivering reagents and transporting products
- Market size and emission reduction potential
- Lifecycle of CO₂ produced products

▶ Unknown Unknowns

- ?



Barriers and Research Needs for Capture and Conversion

“Basic research is what I'm doing when I don't know what I am doing.” *

- ▶ US Department of Energy Leadership
- ▶ National Laboratory, academia Industry partnerships
- ▶ Process intensification
- ▶ Market drivers and incentives
- ▶ Environmental Permitting
- ▶ Capital Investment and Risk Abatement
- ▶ NIMBY, NUMBY, BANANA, CAVE



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Low Carbon
Fuel Standard

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Solvent-Based Capture
FWP's 72396, 70924



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Catalysis of Captured CO₂
BES Early Career FWP 67038

Integrated ICCCM
TCF-19-17862



Exploring the Chemical Synergies Between Capture and Conversion of CO₂

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