



Pacific Northwest
NATIONAL LABORATORY

Integrated Capture and Conversion of CO₂ into Materials (IC³M): Expanding IC³M for C₁ and C₂ Production

FWP-80562

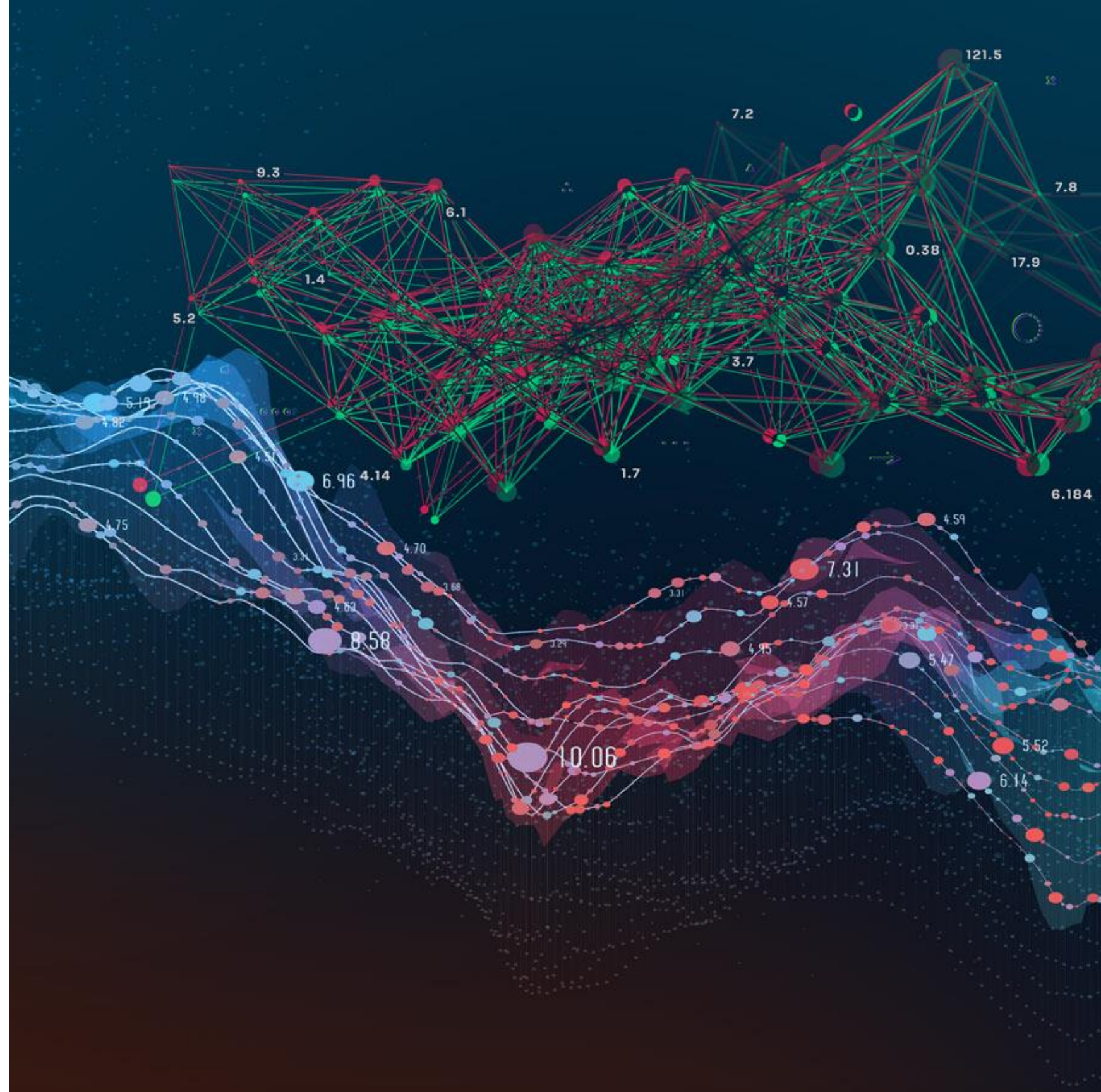
Jothi Kothandaraman
PNNL

2024 FECM/NETL Carbon Management
Research Project Review Meeting



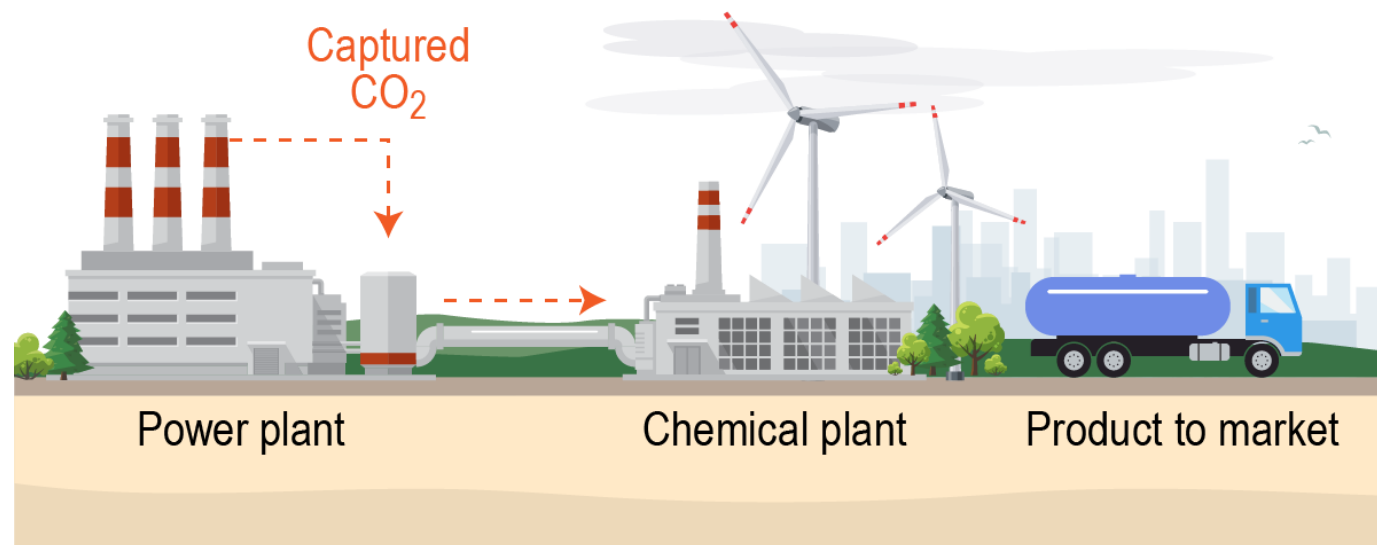
PNNL is operated by Battelle for the U.S. Department of Energy

August 5-9, 2024



Technology Description

Integrated CO₂ Capture and Conversion to Methanol (IC³M) Process Technology.



- **Objective:** Design and demonstrate effectiveness for an IC³M prototype for continuous flow, combined capture/catalytic conversion of CO₂ into methanol
- **Motivation:** Potential for reductions to capital and operating costs by at least 20% relative to the separate CO₂ capture and gas-phase CO₂ hydrogenation

Expected Outcomes: Development of a new catalytic process that can be subsequently installed and demonstrated at an industrial CO₂ source (e.g., for power generation or anaerobic digestion)

TEA confirms the potential for market viability against conventional methanol synthesis



IC³M Team!



Robert A. Dagle

PM



David J. Heldebrant

PI



Jothi Kothandaraman

PI



NETL/DOE PM: [Dylan Leary](#)



Johnny Saavedra Lopez

Materials and Catalysis



Mike Hubbard

Catalysts Testing



Jaelynn King

Characterization



Ben Moskowitz

Characterization



Dushyant Barpaga

Capture solvent



Jared Kroll

Capture solvent



Eric Walter

Operando studies

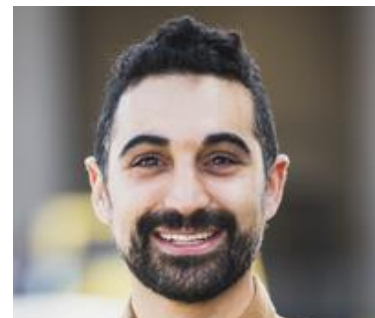


Yuan Jiang

TEA/LCA



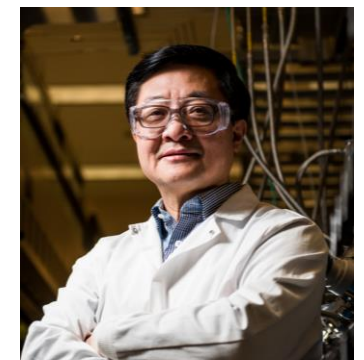
Flavio da Cruz



Ethan Simonoff



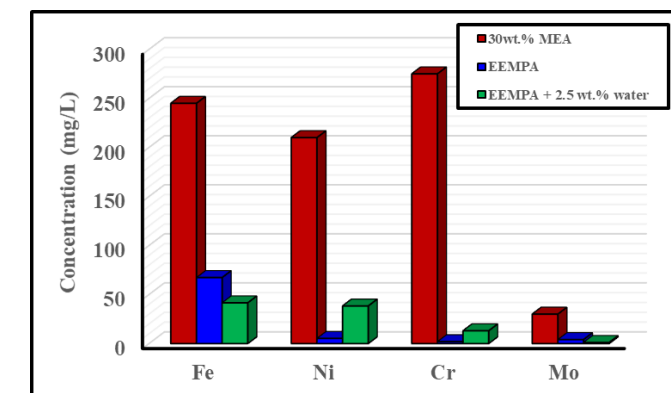
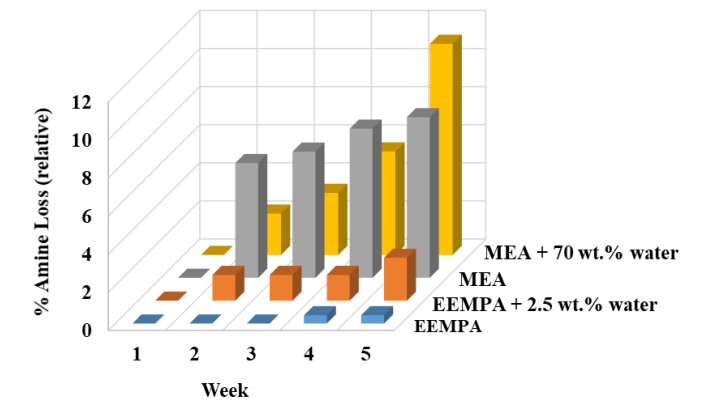
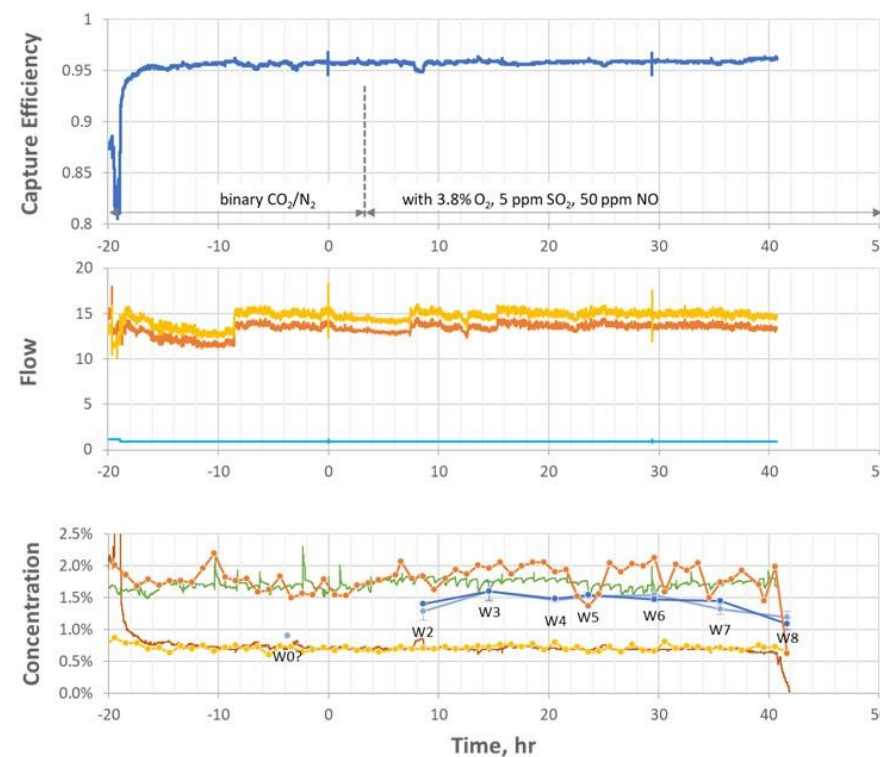
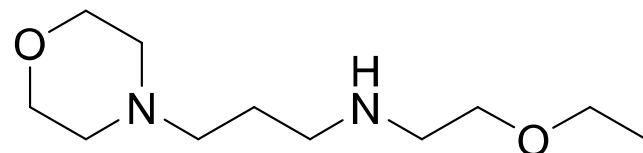
Siari Sosa



Yong Wang

Using a Post-Combustion Solvent: EEMPA

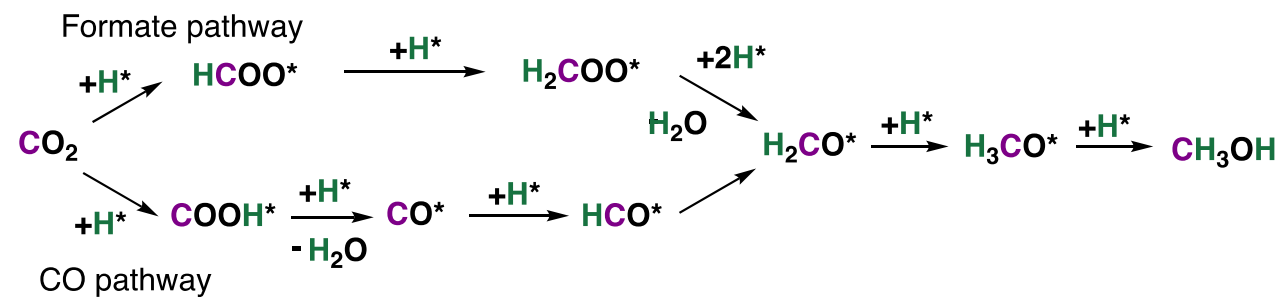
EEMPA has the lowest energy solvent (2.0 GJ/tonne CO₂)¹ and lowest projected total cost of capture \$39/tonne² CO₂ of any capture technology.



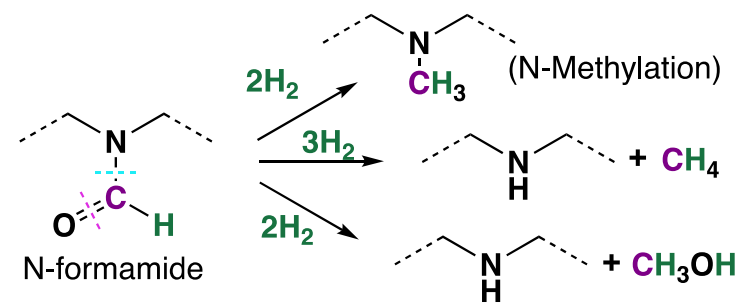
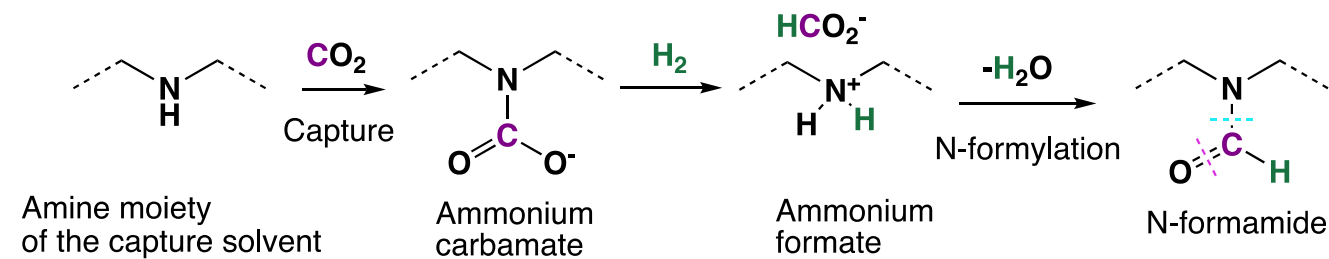
- ▶ 19% cheaper and efficient than Shell's CANSOLV
- ▶ 90% lower corrosion and degradation than 5M MEA
- ▶ 0.5 MW coal fired plant demonstration (2,000 gallons) late this month at the National Carbon Capture Center
- ▶ Conversion pathways utilizing dehydration reaction(s) facilitated in the presence of organic versus aqueous solvents

Condensed Phase CO₂ Hydrogenation

(A) Gas-phase methanol synthesis

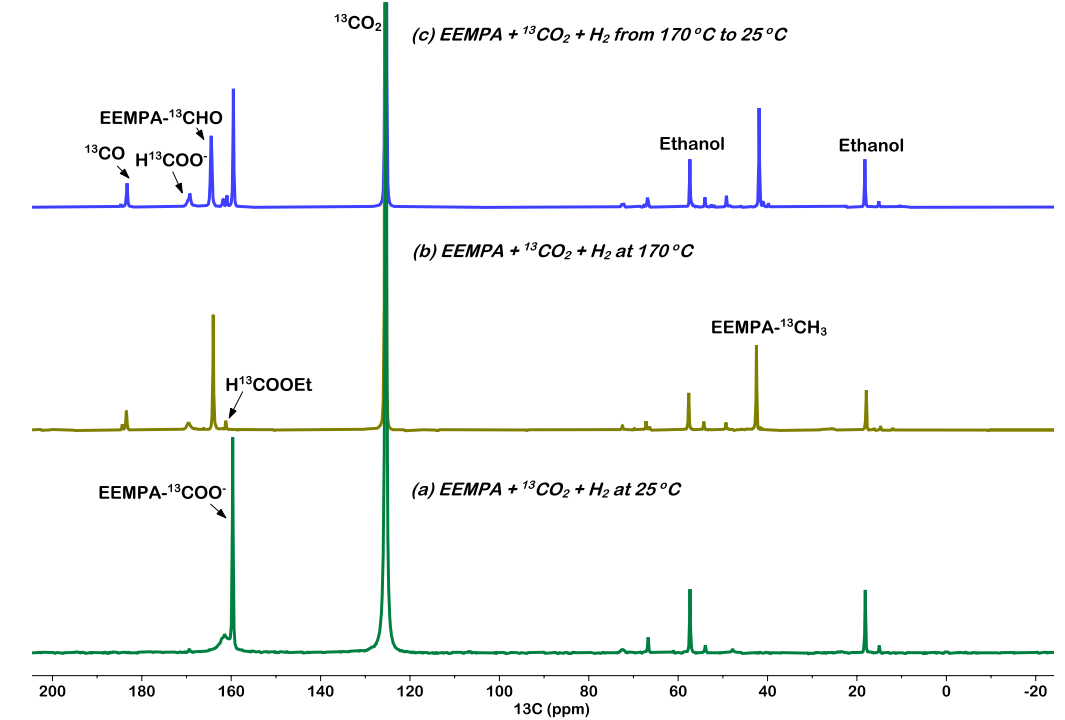


(B) Condensed-phase methanol synthesis

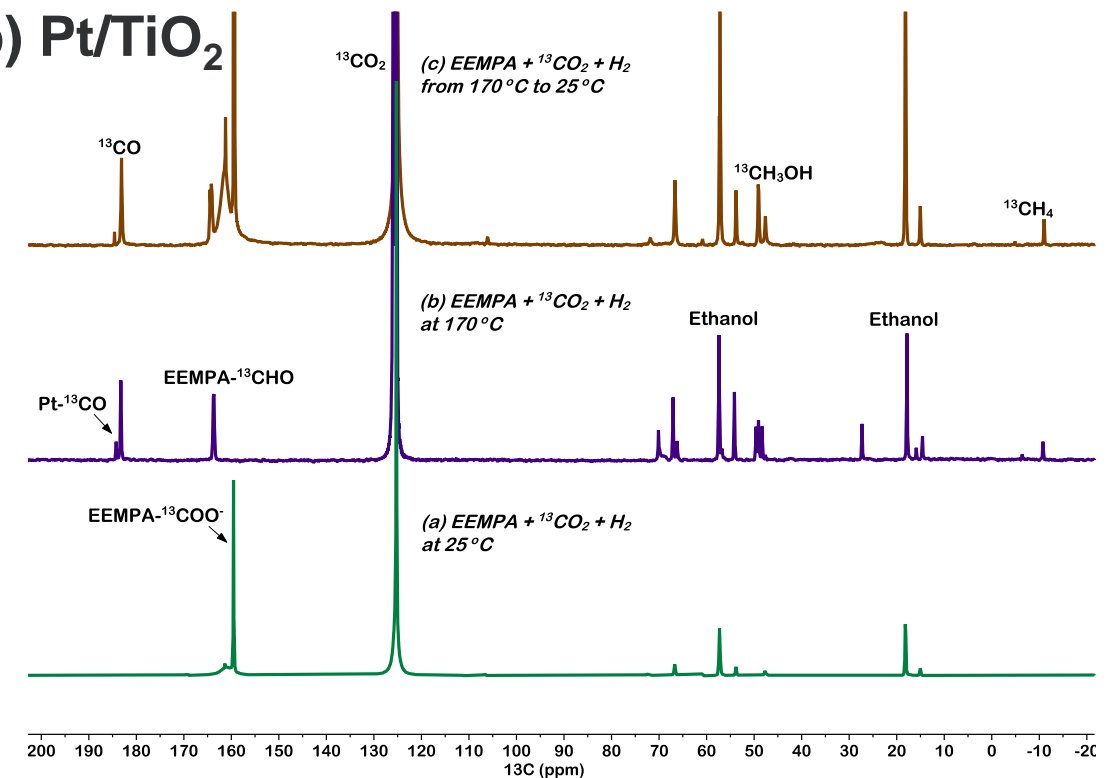


--- C-N cleavage
- - - C-O cleavage

(a) Cu/ZnO/Al₂O₃

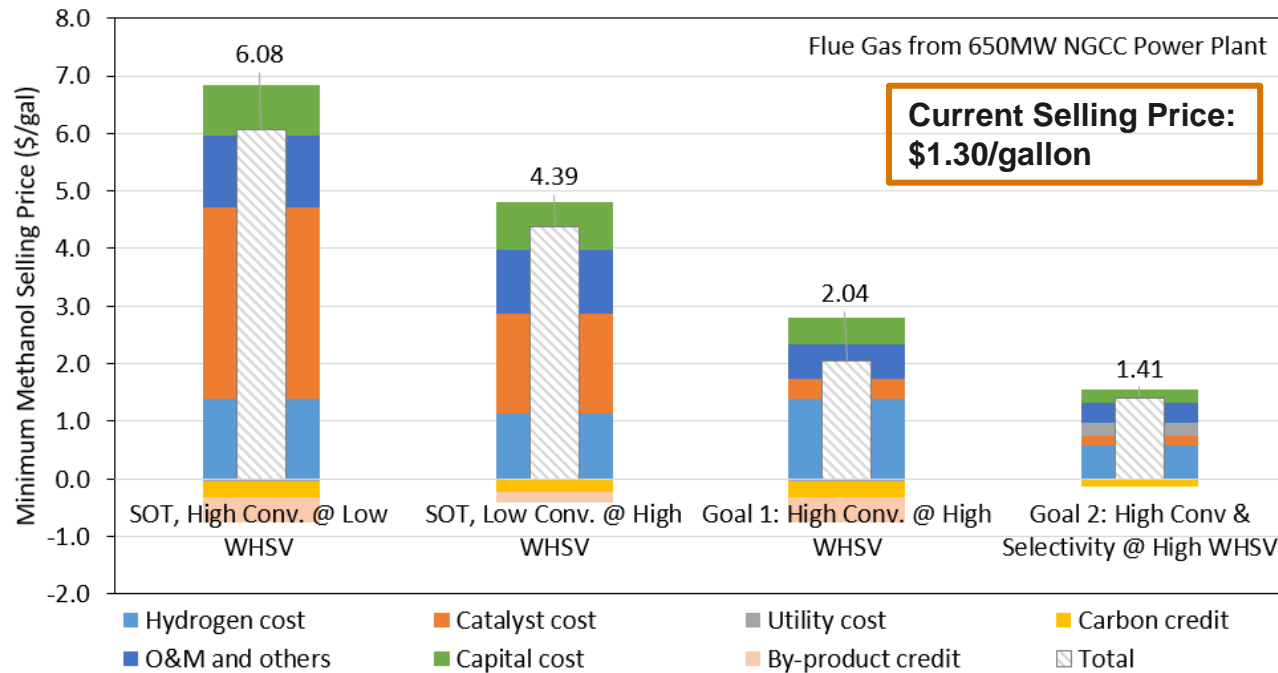


(b) Pt/TiO₂



In situ ¹³C MAS-NMR in an ethanol co-solvent

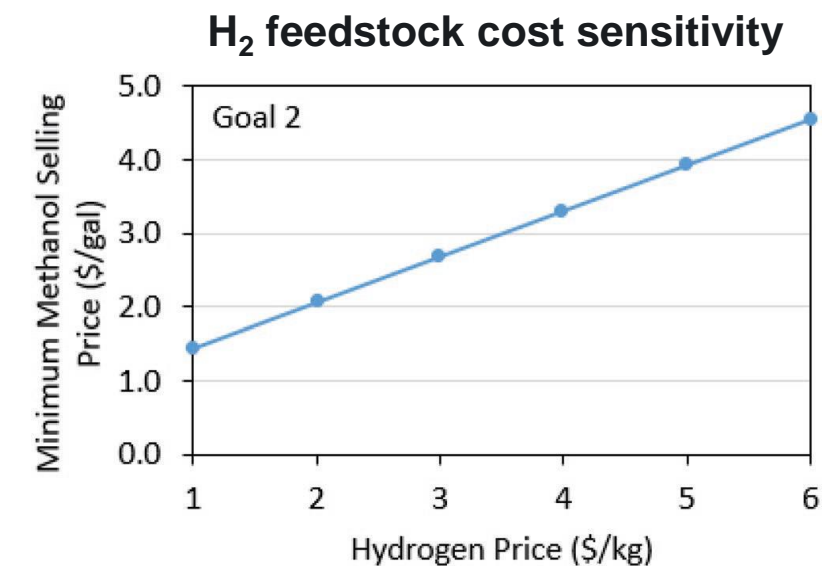
Techno-Economic Assessment (TEA) – 2022 SOT



Compared with the optimistic case (High Conv. w/o Alcohol in 2021, the 2022 SOT shows:

- Increase in hydrogen consumption due to the production of by-products (i.e. CH₄)
- Increase in capital cost because of the additional cost associated with product separation
 - Extractive distillation to break azeotrope between methanol-ethanol-water,
 - PSA to separate CH₄ from H₂

| | SOT @ Low WHSV | SOT @ High WHSV | Goal 1 High Conversion | Goal 2 High Conversion and Selectivity |
|--|----------------|-----------------|------------------------|--|
| WHSV (gCO ₂ /gCat/hr) | 0.015 | 0.075 | 0.15 | 0.15 |
| Single-pass CO ₂ conversion (%) | 85.7 | 26.9 | 85.7 | 85.7 |
| Methanol selectivity (C %) | 51.5 | 63.6 | 51.5 | 100 |
| Methane selectivity (C %) | 27.1 | 26.4 | 27.1 | 0 |
| Source | Experiment | Experiment | R&D Target | R&D Target |



IC³M Outputs

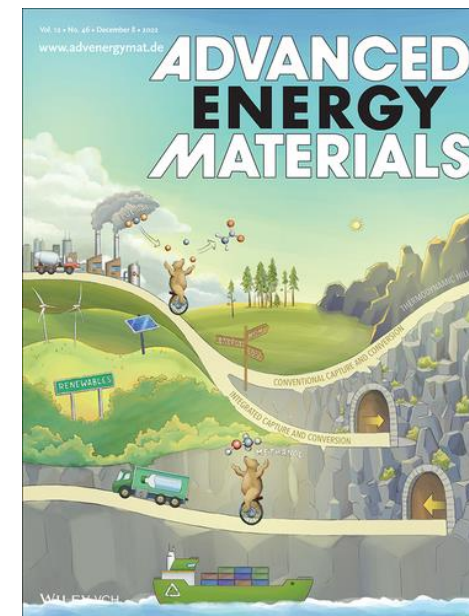
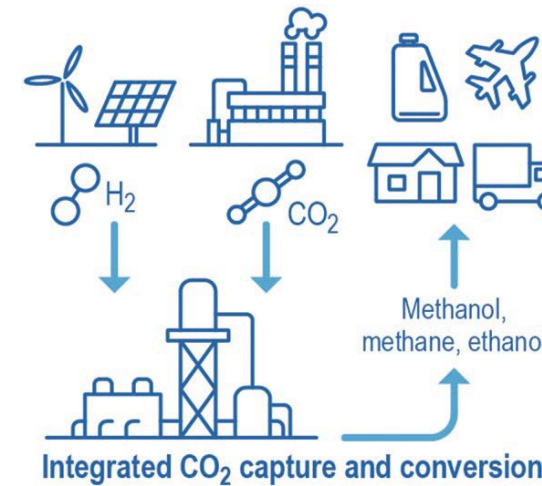
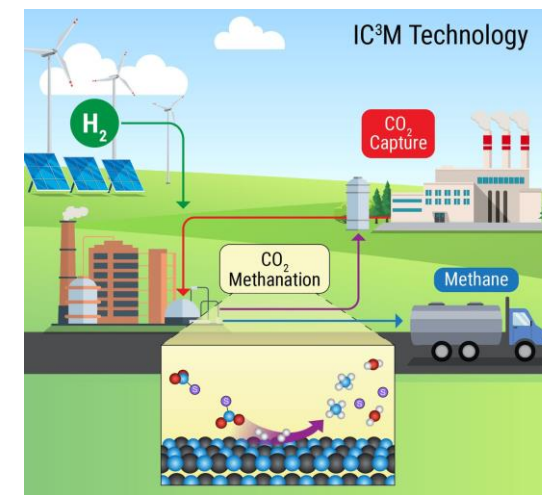
- Papers

- 2 published
- 1 drafted

- Patents

- U.S. patent 10,961,173
- U.S. patent 1,492,302

- In discussions with companies about potential licensing and co-development activities



*Integrated Capture and Conversion of CO₂ to **Methane** Using a Water-lean, Post-Combustion CO₂ Capture Solvent*

ChemSusChem **2021**,14,4812– 4819

*Integrated Capture and Conversion of CO₂ to **Methanol** in a Post-Combustion Capture Solvent: Heterogeneous Catalysts for Selective C-N Bond Cleavage*

Adv. Energy Mater., **2022**, 2202369

Cover art published in Advanced Energy Materials Journal (Volume 12, Issue 46)

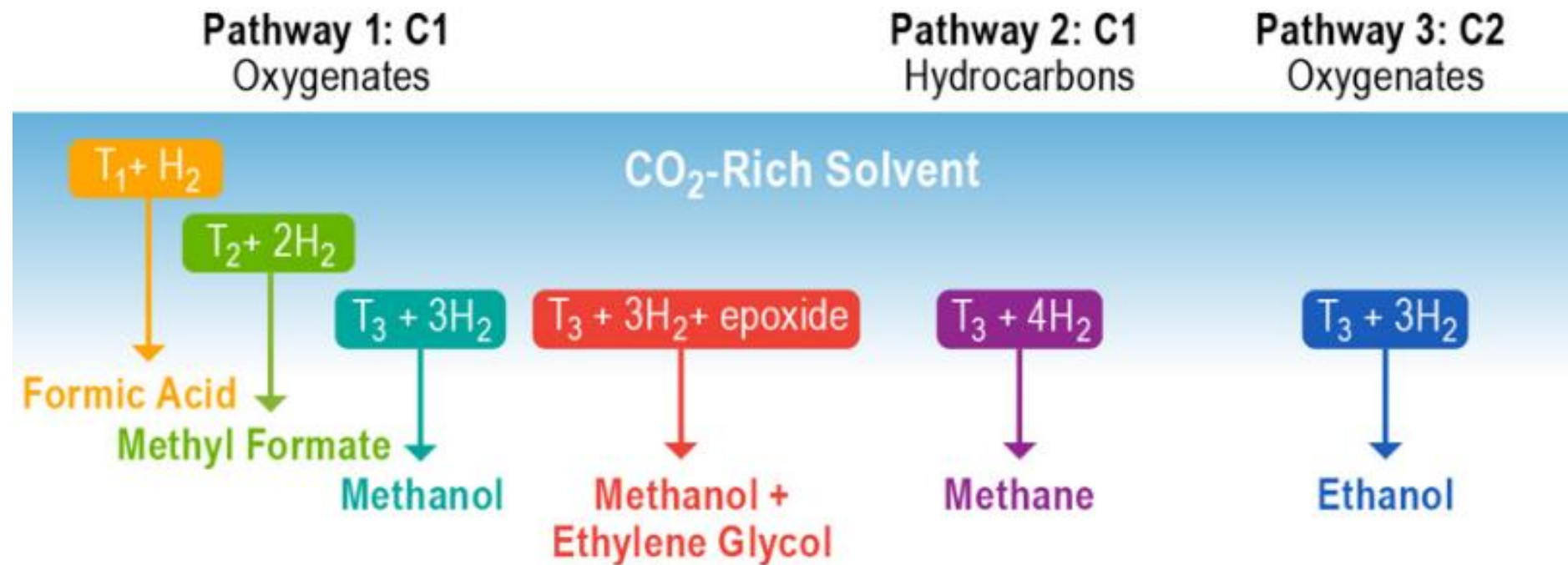
New Project – FWP-80562

DOE Funding: \$2640K

SoCalGas Cost Share: \$660K (funds-in)

Start: Jan 1, 2023

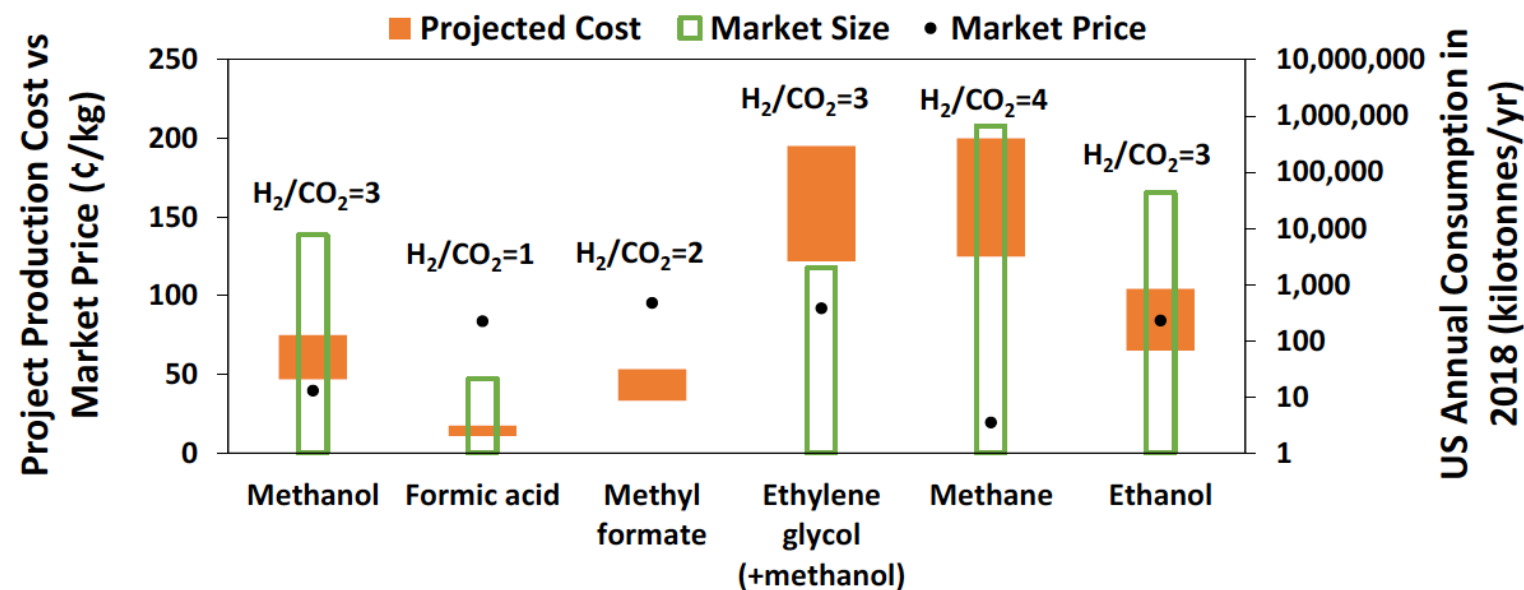
End: Dec 31, 2025



Goal: continue the catalytic process development for methanol and methane, develop new routes to additional products, and develop new commercial partnering opportunities

Preliminary Economic Projections

Estimated Production Cost, and Market Size and Cost, for Different Products Derived from CO₂



Preliminary economic projections for the production of methanol, formic acid, methyl formate, ethylene glycol, methane, and ethanol using IC3M technology. Projected production cost assumes H₂ price = \$2/kg where H₂ cost contributes to 50-80% of total production cost. Required H₂:CO₂ feedstock ratios (based on stoichiometry) are also shown.

- Except for methane, the estimated production costs for all the products are relatively close to market prices (+50% / -83%)
- Methanol, ethylene glycol, and ethanol are preferred product options due to their relatively large market sizes and favorable economic projections
- Formic acid is a promising option due to its relatively low hydrogen requirement and favorable cost projection
- While estimated cost is less favorable for methane, relative to market price, there are additional regulatory incentives driving demand for synthetic natural gas production
- Further, improvements to methanol synthesis catalyst (increased activity and/or selectivity) will further reduce methanol costs (per next slide)

Success Criteria

- Demonstrate **>50% CO₂ conversion** (single pass) with **>80% methanol selectivity** at a **WHSV > 0.05 gCO₂/g_{cat}/hr** in a post-capture solvent/catalyst processing system operating under continuous flow
- Establish feasibility for producing and separating at least **two other C1 or C2 products** with at least > 10% conversion, using post-combustion capture solvent

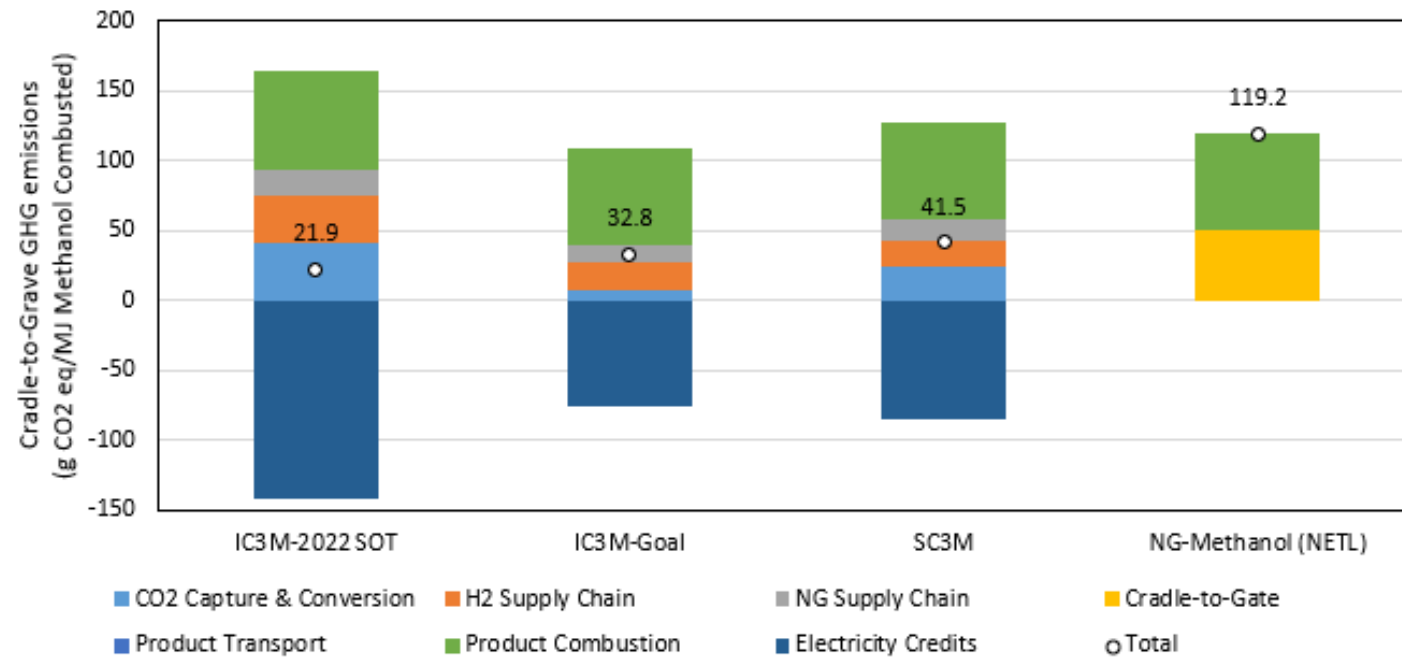
Current Project Updates

- LCA for the IC³M process for GHG reduction (**Q1 FY24 Milestone**)
- 3rd simultaneous CO₂ capture and conversion demo with improved results
- Methanol synthesis (PNNL-led)
 - With Pt/MoO₃ catalyst (offering enhanced EEMPA durability and methanol productivity):
 - ✓ Performed 100-hour time-on-stream experiment (**Q2 FY24 Milestone**)
 - With Pt/ZrO₂ catalyst (offering enhanced methanol selectivity ~100%):
 - ✓ Performed 100-hour time-on-stream experiment (**Q2 FY24 Milestone**)
 - Demonstrated separability of methanol, ethanol and water from EEMPA via distillation (**Q2 FY24 Milestone**)
 - Characterized at least 5 new catalyst formulations and correlated properties of acid and metal sites on methanol productivity (**Q3 FY24 Milestone**)
- Methane production demonstrated with Ni-based catalysts, previously shown with Ru catalyst
- Ethanol (WSU-led)
 - Pivoting to recent report for multifunctional catalyst for CO₂-to-ethanol (*gas phase*)
CO₂/H₂ → methanol/CO → acetic acid → ethanol (single bed)

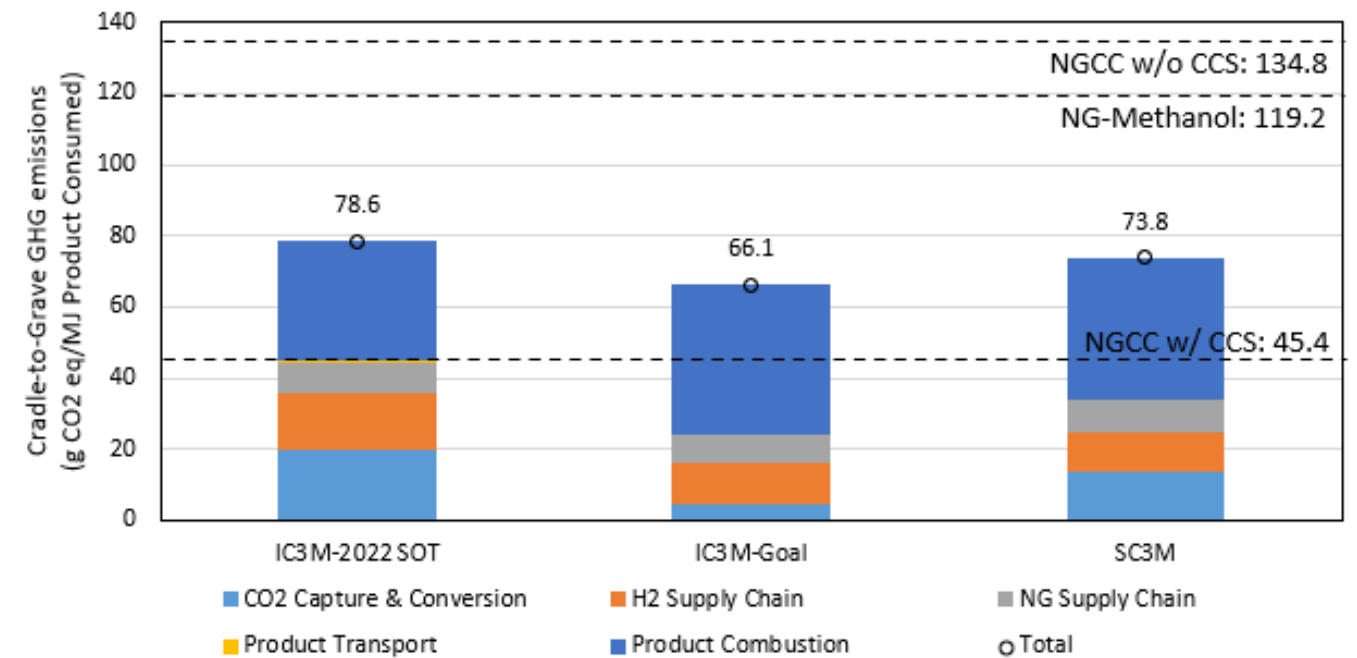


Life Cycle GHG Emission Impact Assessment

❖ System expansion



❖ Energy allocation



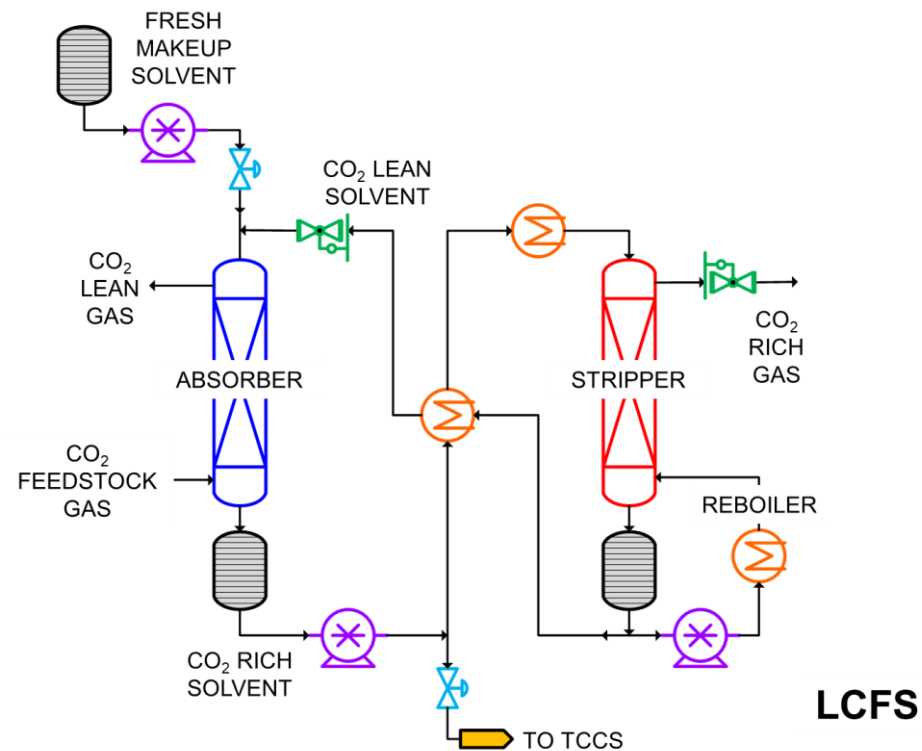
- Regardless which method is selected, the proposed IC³M technology can achieve significant GHG emission reduction comparing with the industrial benchmark
- A GHG emissions reduction up to 81.6% is achieved via the 2022 SOT of IC³M
- The life cycle GHG emissions reduction of the proposed technology can be further improved via continuous improvement in the catalyst performance (i.e., higher methanol selectivity)

Demonstration of Continuous CO₂ Capture and Catalytic Conversion to Methanol

Integrated capture and conversion bench scale processing designed and fabricated

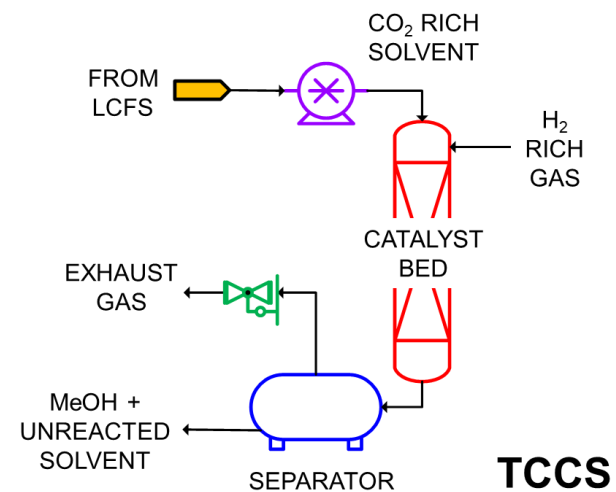
CO₂ Capture

Laboratory Continuous Flow System (LCFS)



Captured CO₂ Conversion

Thermochemical Catalytic Conversion System (TCCS)



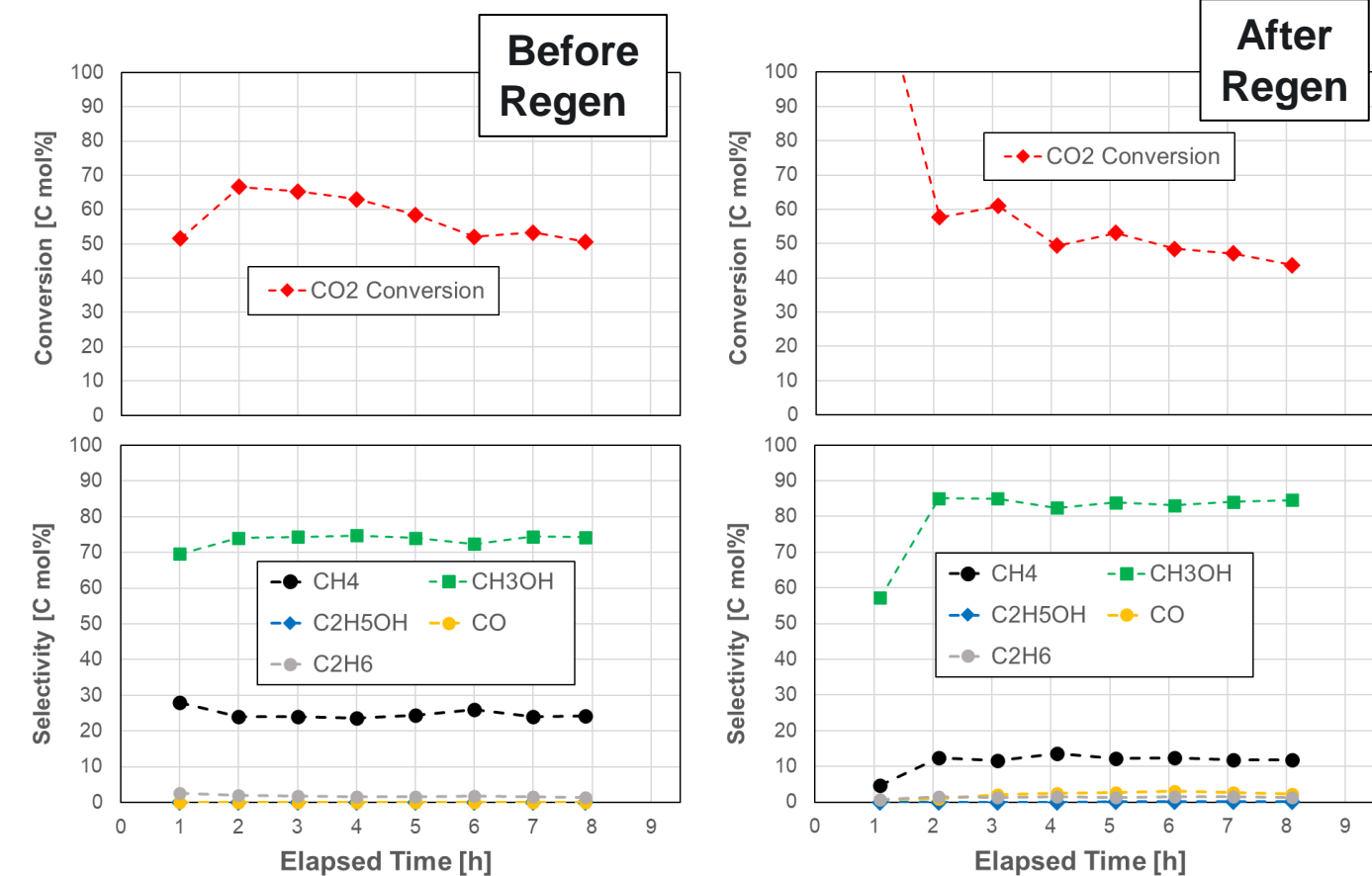
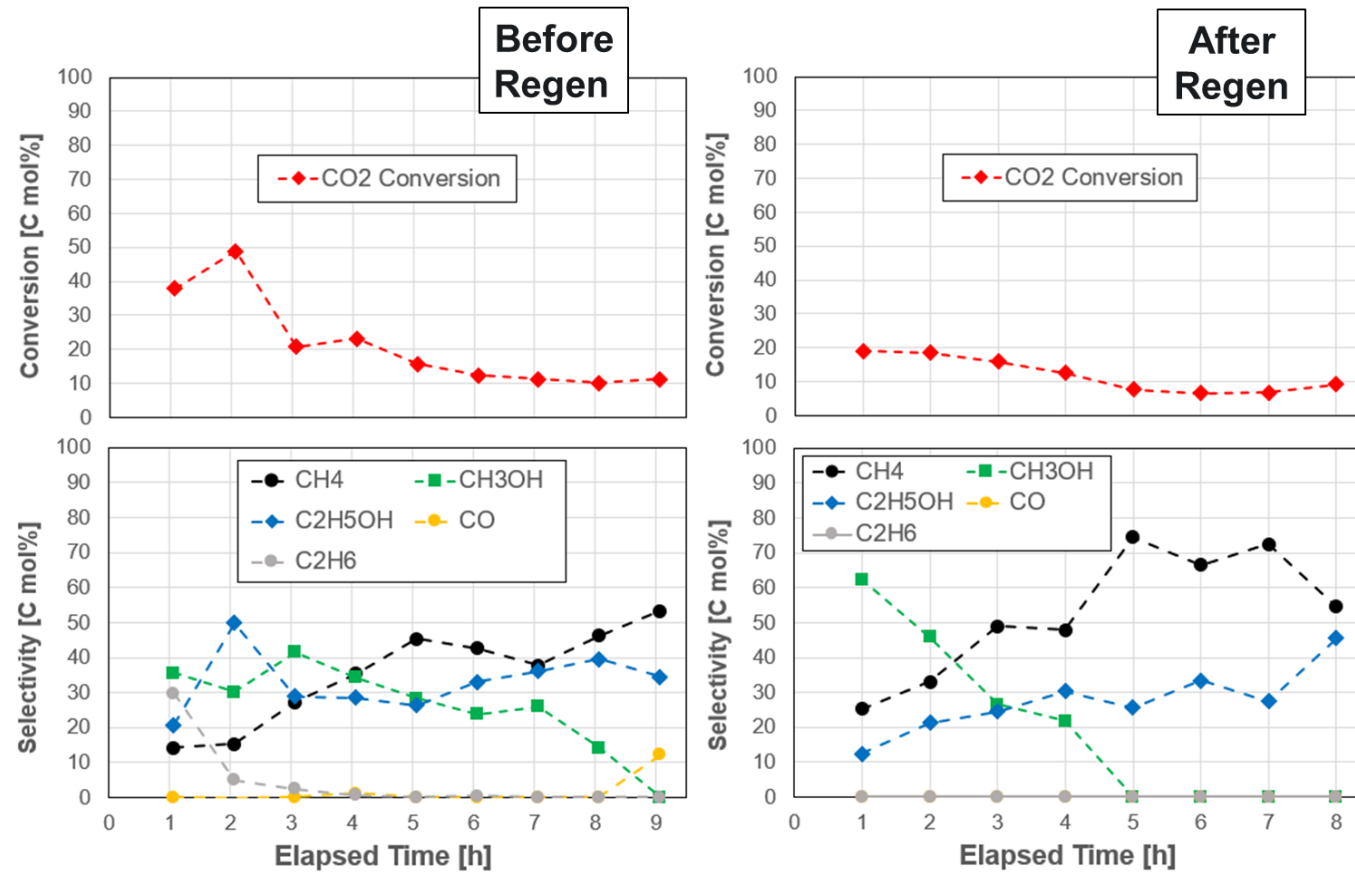
Combined Capture and Conversion Recently Demonstrated with Improved Results

Demo 2 – 2022

LCFS: 15/85 CO₂/N₂ with a dewpoint 15.6 °C
 TCSS: 190°C, 865 psig, 0.053 g_{CO2}/g_{cat}/hr

Demo 3 – 2023

LCFS: 15/85 CO₂/N₂ *no water vapor*
 TCSS: 190°C, 865 psig, 0.053 g_{CO2}/g_{cat}/hr



- Demo 3 performed with **water excluded** from the simulated flue gas. Significantly improved stability achieved with Demo 3
- Comparative spent catalyst characterizations suggest that the presence of **water in the feedstock is enriching the formation of carbonates and blocking the active sites of the catalysts**
- It is likely that the excess carbonate concentration on the catalyst surface is getting converted to CO, which can bind with the Pt strongly and deactivate the catalyst

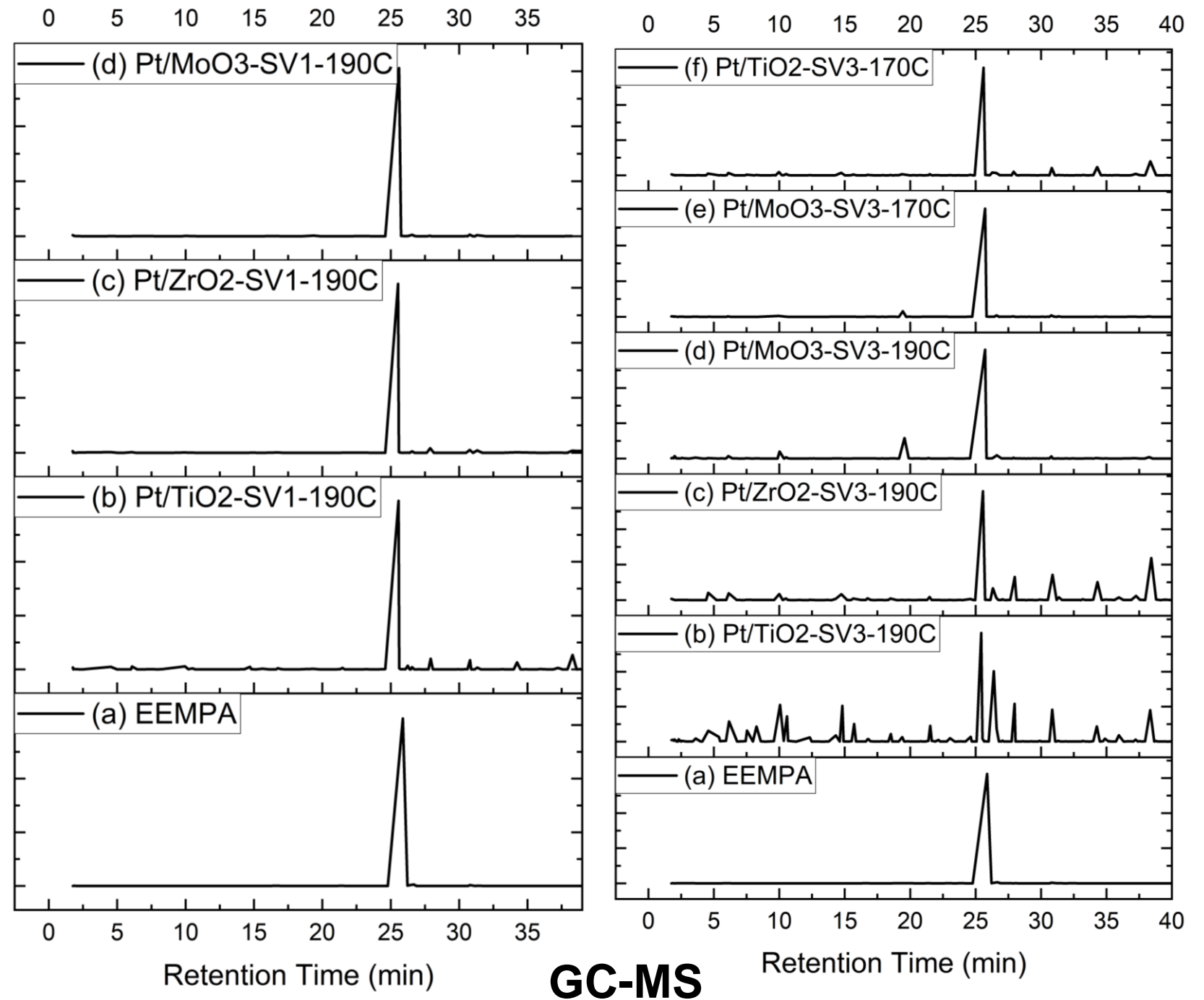
New Catalyst Formulations for CO₂ Hydrogenation to Methanol – Continuous flow

| Run | T (C) | SV gCO ₂ /gCat/h | Conv. (%) | MeOH Sel. (%) | CH ₄ Sel.(%) | CO Sel. (%) |
|---|-------|-----------------------------|-----------|---------------|-------------------------|-------------|
| 5wt% Pt/TiO ₂ (1g), 5wt%CO ₂ EEMPA feed | | | | | | |
| IC3M22 | 190 | 0.15 | 29.4 | 51.2 | 31.4 | 17.4 |
| IC3M22 | 190 | 0.015 | 77.2 | 55.1 | 44.9 | 0.0 |
| IC3M12 | 170 | 0.015 | 33.4 | 88.8 | 11.2 | 0.0 |
| 5wt% Pt/ZrO ₂ (1g), 5wt%CO ₂ EEMPA feed | | | | | | |
| IC3M14 | 190 | 0.15 | 10.8 | 25.8 | 0.0 | 74.2 |
| IC3M14 | 190 | 0.015 | 33.3 | 100.0 | 0.0 | 0.0 |
| 5wt% Pt/MoO ₃ (1g), 5wt%CO ₂ EEMPA feed | | | | | | |
| IC3M17 | 190 | 0.15 | 32.1 | 59.4 | 24.3 | 16.3 |
| IC3M19 | 190 | 0.06 | 57.1 | 64.6 | 33.0 | 2.4 |
| IC3M17 | 190 | 0.015 | 77.6 | 59.1 | 40.9 | 0.0 |
| IC3M16 | 170 | 0.15 | 16.5 | 58.2 | 23.1 | 18.7 |
| IC3M16 | 170 | 0.015 | 86.6 | 52.6 | 47.4 | 0.0 |
| IC3M18-1 | 150 | 0.015 | 47.6 | 76.8 | 23.2 | 0.0 |

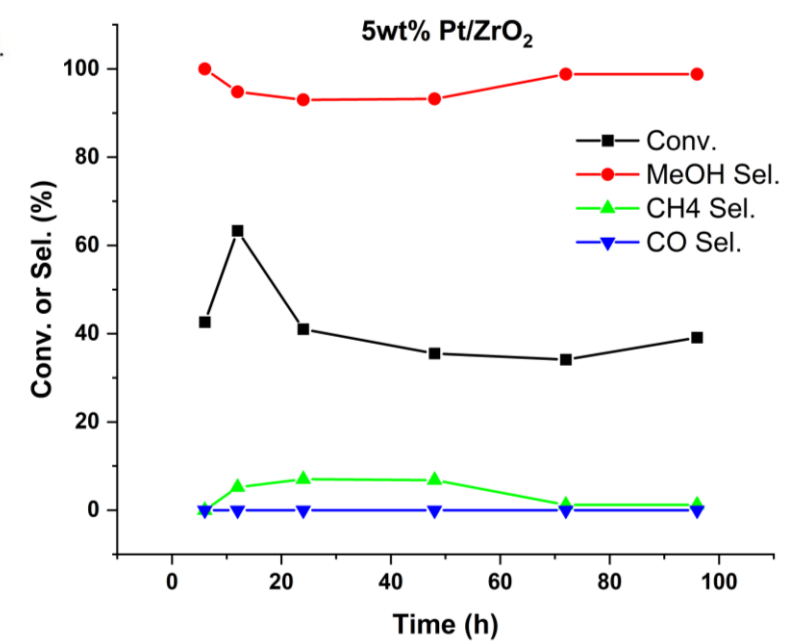
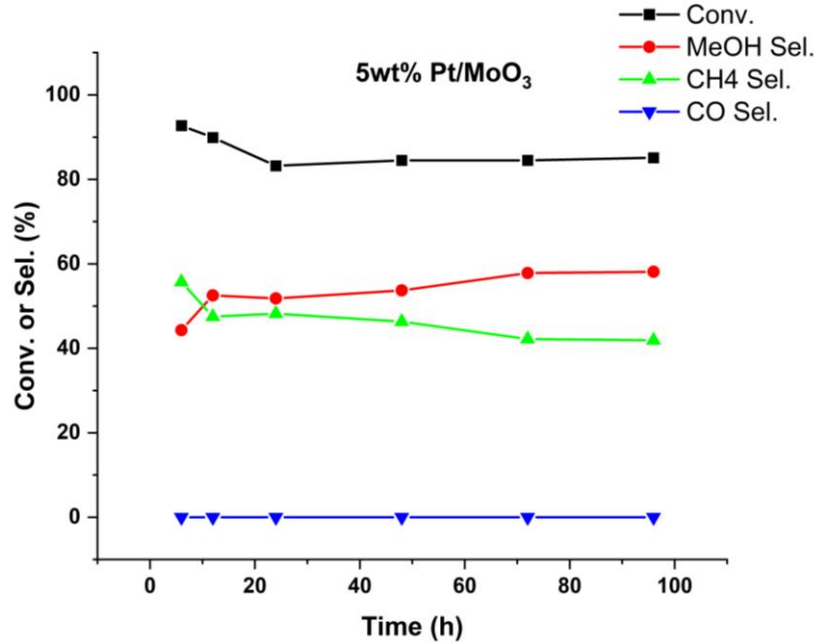
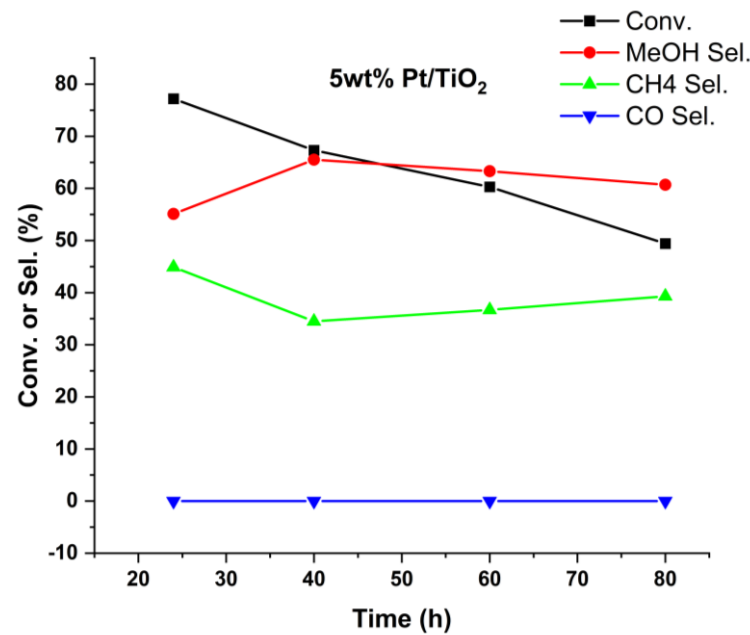
- 5wt% Pt/MoO₃ exhibits improved methanol productivity and minimal decomposition of the EEMPA solvent
- Demonstrated separability of methanol, ethanol and water from EEMPA via distillation

Pt/ZrO₂ and Pt/MoO₃ Enhanced the Stability of the EEMPA Solvent Compared to Pt/TiO₂

- The order of the solvent's durability in the presence of different catalysts is as follows: Pt/MoO₃ > Pt/ZrO₂ > Pt/TiO₂
- The degradation of EEMPA was observed to depend on both space velocity and reaction temperature
 - At 190°C, the **EEMPA degradation products were reduced at SV1 compared to SV3**, where the contact time between the catalyst and solvent is greater
 - At 170°C, the EEMPA degradation products were significantly lower



Pt/MoO₃ and Pt/ZrO₂ Demonstrate Stable Catalytic Performance for 100h TOS



Reaction conditions: pressure: 860 psi, temperature: 190°C, space velocity 0.015g CO₂/g catalyst/h (1g of catalyst).

- Pt/TiO₂ demonstrates clear deactivation over the course of the experiment. Despite maintaining stable methanol selectivity (approximately 60%), the conversion decreased from 77% to 49% over a span of ~80 hours
- In contrast, Pt/MoO₃ and Pt/ZrO₂ exhibit remarkable stability:
 - Pt/MoO₃ consistently achieves approximately 80% conversion
 - Pt/ZrO₂ maintains a stable conversion rate around 40%
 - Very importantly, **Pt/ZrO₂ exhibits almost complete selectivity towards methanol**
- In all these experiments, the low space velocity enables good CO₂ conversion

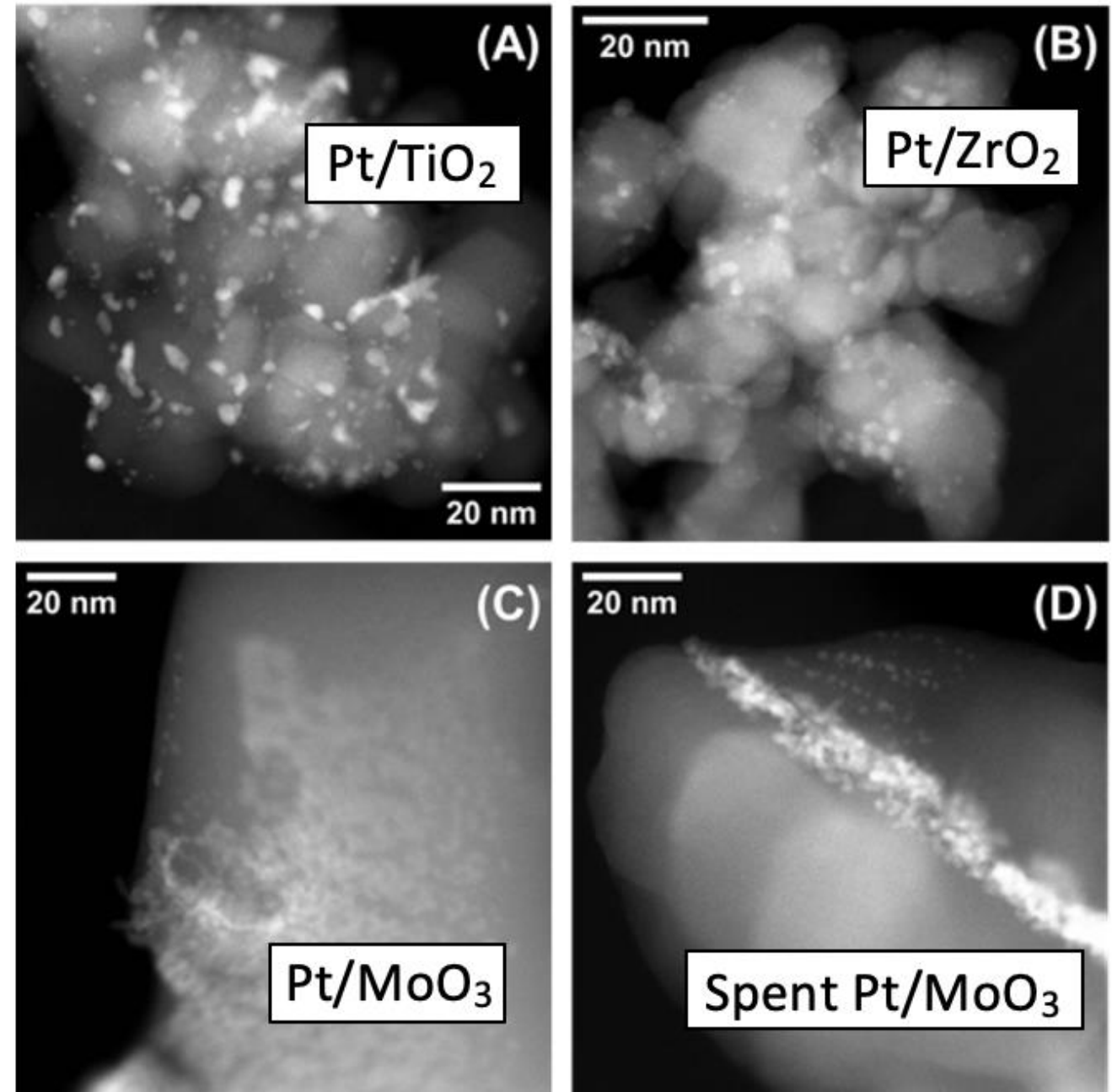


TEM Observations: Pt Aggregation into Thin Film-like Coating on MoO₃

- BET: Pt/ZrO₂ (92.01 m²/g) exhibited a higher surface area compared to Pt/TiO₂ (57.14 m²/g). MoO₃ samples, in contrast, display a very low surface area of ~3 m²/g
- Supported Pt/TiO₂ and Pt/ZrO₂ exhibited well-defined Pt nanoparticles
- The mean Pt particle size and distribution is about 2 nm for the three supports
- The main difference occurs for MoO₃, where most of the Pt exists as a thin film-like coating. MoO₃ also shows aggregation of Pt nanoparticles populating the ridges of its crystals

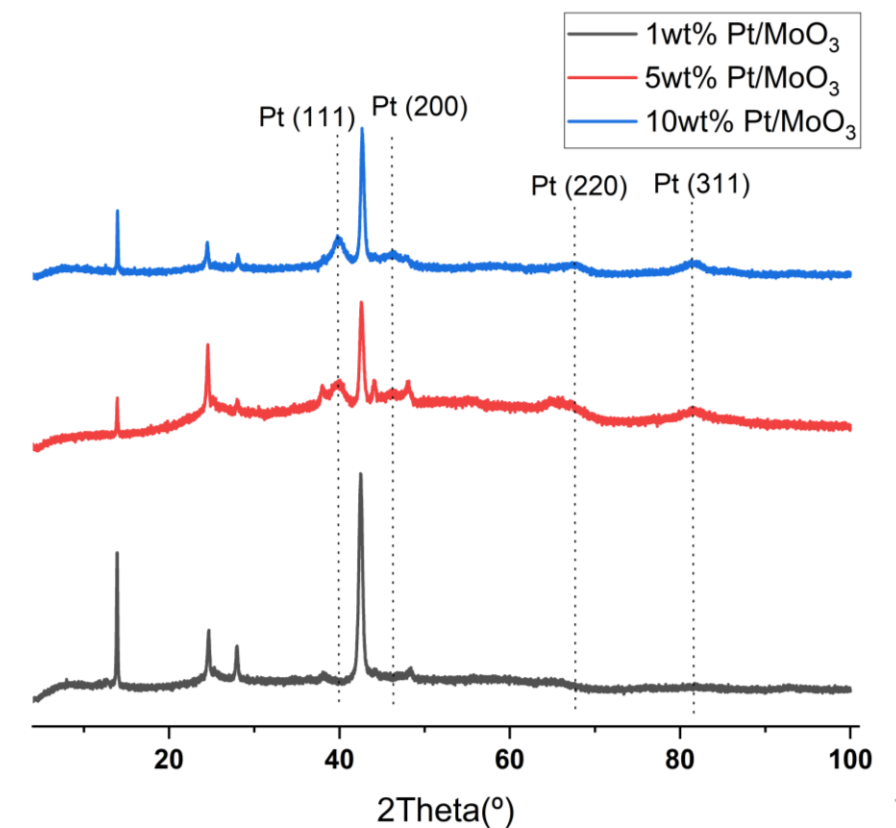
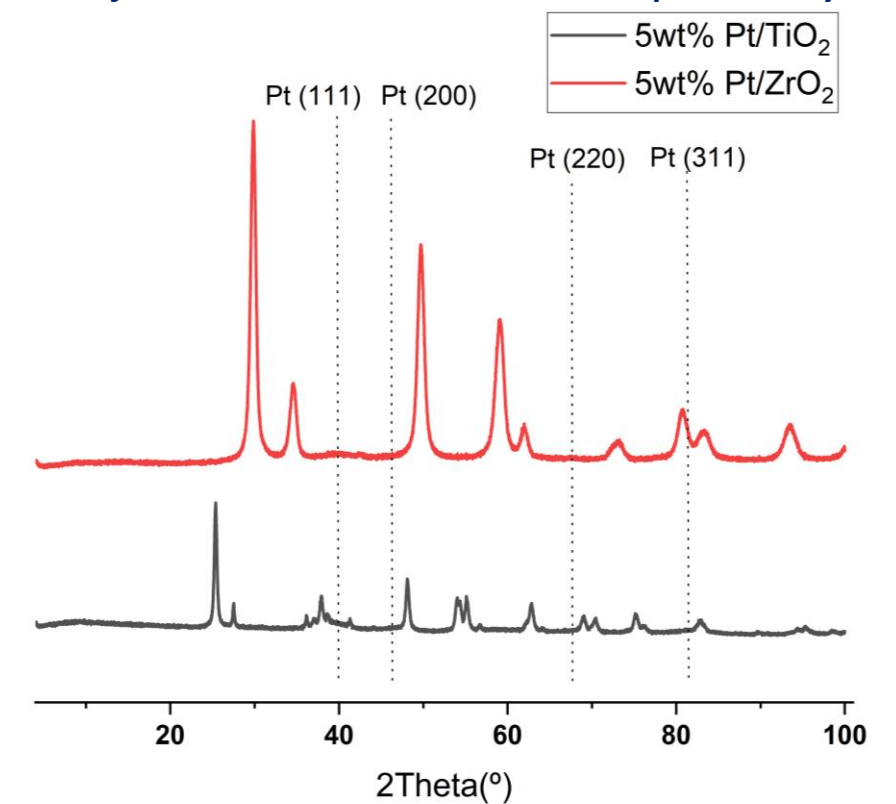
| Catalyst | n | D _{mean} (nm) |
|------------------------------|------|------------------------|
| 5% Pt/MoO ₃ | 28 | 2.4 ± 0.8 |
| Spent 5% Pt/MoO ₃ | 45 | 2 ± 1 |
| 5% Pt/TiO ₂ | 1020 | 2 ± 1 |
| 5% Pt/ZrO ₂ | 1017 | 2.0 ± 0.7 |

n is the number of particles measured, D_{mean} is the mean particle diameter

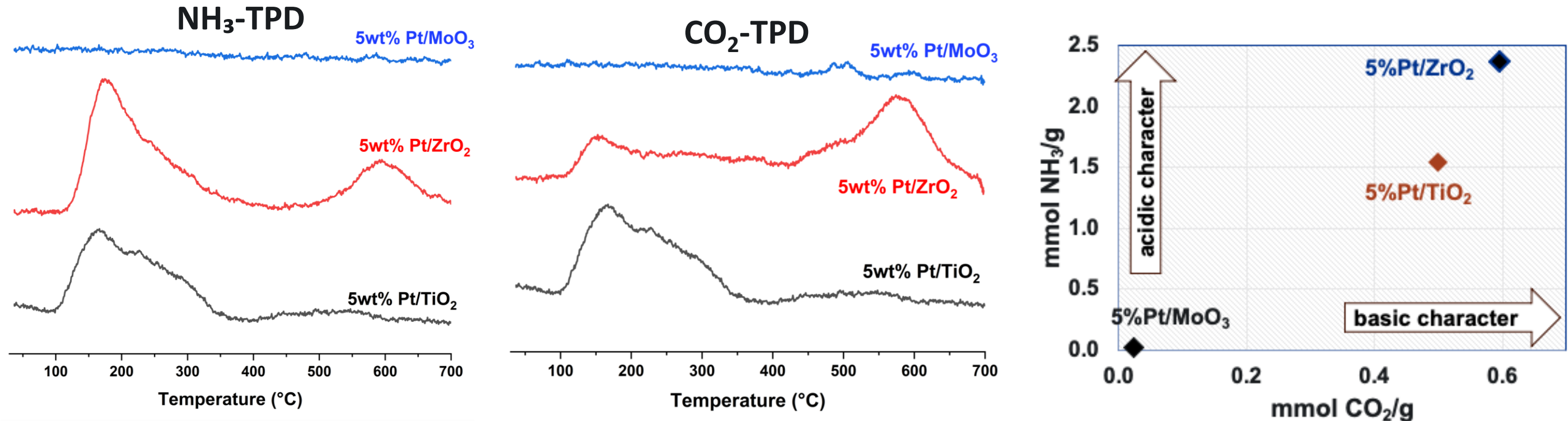


Significant Alterations in Crystal Structure of MoO_3 Following Pt Introduction

- XRD patterns for 5%Pt/ TiO_2 and 5%Pt/ ZrO_2 show characteristic peaks for the anatase and tetragonal phases of TiO_2 and ZrO_2 , respectively
 - High dispersion prevents observation of features related to Pt crystallites
- In contrast, 5%Pt/ MoO_3 displayed significant changes in crystalline structure after Pt incorporation, potentially creating oxygen vacancies compensated by alloyed Pt atoms in the lattice
 - The prominent features observed for 5%Pt/ MoO_3 correspond to a PtMo alloy. Additionally, Pt particles are evident as broad small peaks



Absence of Detectable Acidic or Basic Sites in the Pt/MoO₃ Catalyst



- Pt/TiO₂ possesses both acidic and basic sites. Similarly, the Pt/ZrO₂ catalyst also exhibits both types of sites; however, it includes some stronger acidic and basic sites compared to Pt/TiO₂
- Notably, the Pt/MoO₃ catalyst lacks any detectable acidic or basic sites. These findings imply that the acidic and basic properties provided by the TiO₂ and ZrO₂ supports are likely responsible for the degradation of the EEMPA capture solvent

Pt Dispersion and Hydrogen Spillover

- The H₂ chemisorption results indicate that at 190 °C, the extent of hydrogen spillover follows the order Pt/MoO₃ >> Pt/ZrO₂ > Pt/TiO₂
- These varying degrees of hydrogen spillover can alter the adsorption and activation of intermediates, potentially explaining the higher selectivity to methanol observed with the Pt/ZrO₂
- High H₂ spillover observed in Pt/MoO₃ catalysts can promote H₂ activation and subsequent conversion of HCOO* intermediate to *OCH₃

| Catalyst | $N_{H^*,40^\circ C}$ ($\mu\text{mol/g}$) | $N_{H^*,190^\circ C}$ ($\mu\text{mol/g}$) | D (%) | $\theta_{H^*/Pt,190^\circ C}$ |
|-------------------------|---|--|-------|-------------------------------|
| 5% Pt/TiO ₂ | 106.3 (4) | 58.9 (9) | 42 | 0.554 (9) |
| 5% Pt/ZrO ₂ | 129 (2) | 226 (3) | 50 | 1.75 (3) |
| 1% Pt/MoO ₃ | 1.51 (9) | 1140 (6) | 3.0 | 753 (43) |
| 5% Pt/MoO ₃ | 4.4 (2) | 750 (10) | 1.7 | 170 (31) |
| 10% Pt/MoO ₃ | 4 (1) | 1014 (9) | 0.8 | 263 (67) |

*standard error=100.1 ± 0.5 = 100.1 (5) and 300 +/- 50 = 300 (50)

Metal dispersion (D) was calculated assuming a dispersion of 1 mol H* (mol Pt)⁻¹:

$$Dispersion (D) = \frac{N_{H^*,40^\circ C}}{N_{Pt}} \cdot 100\%$$

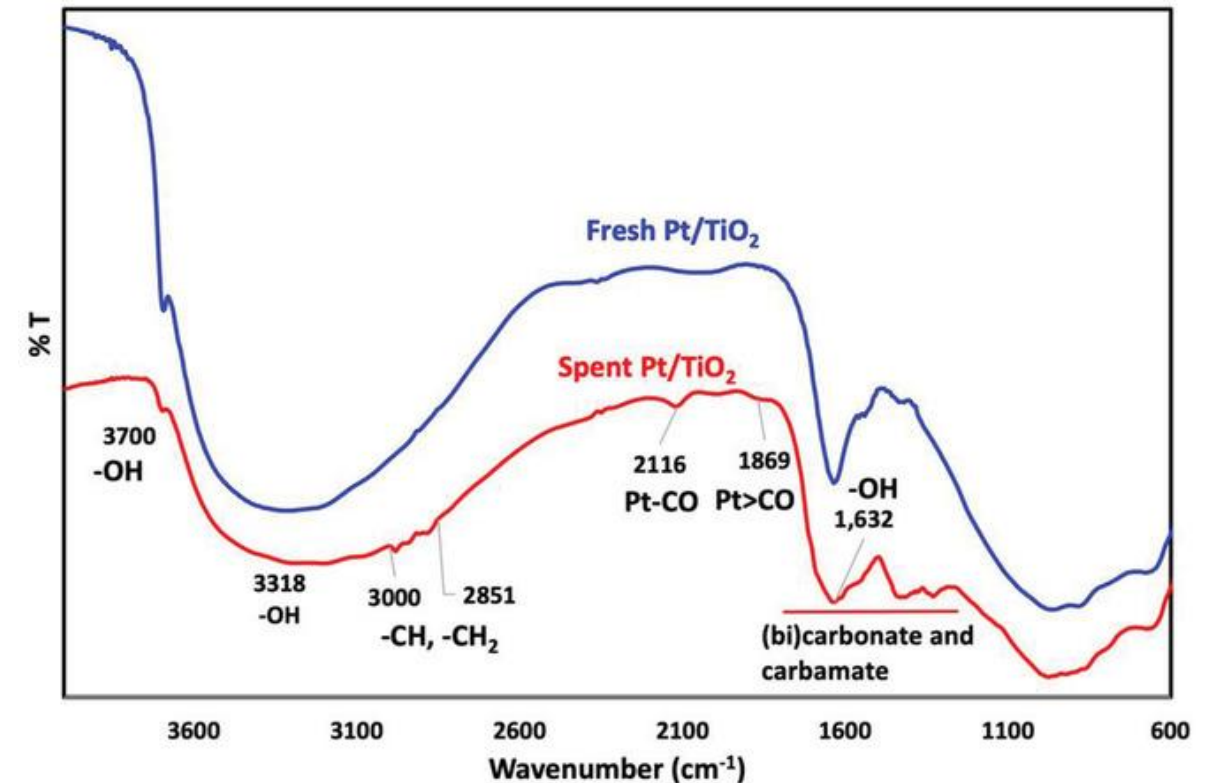
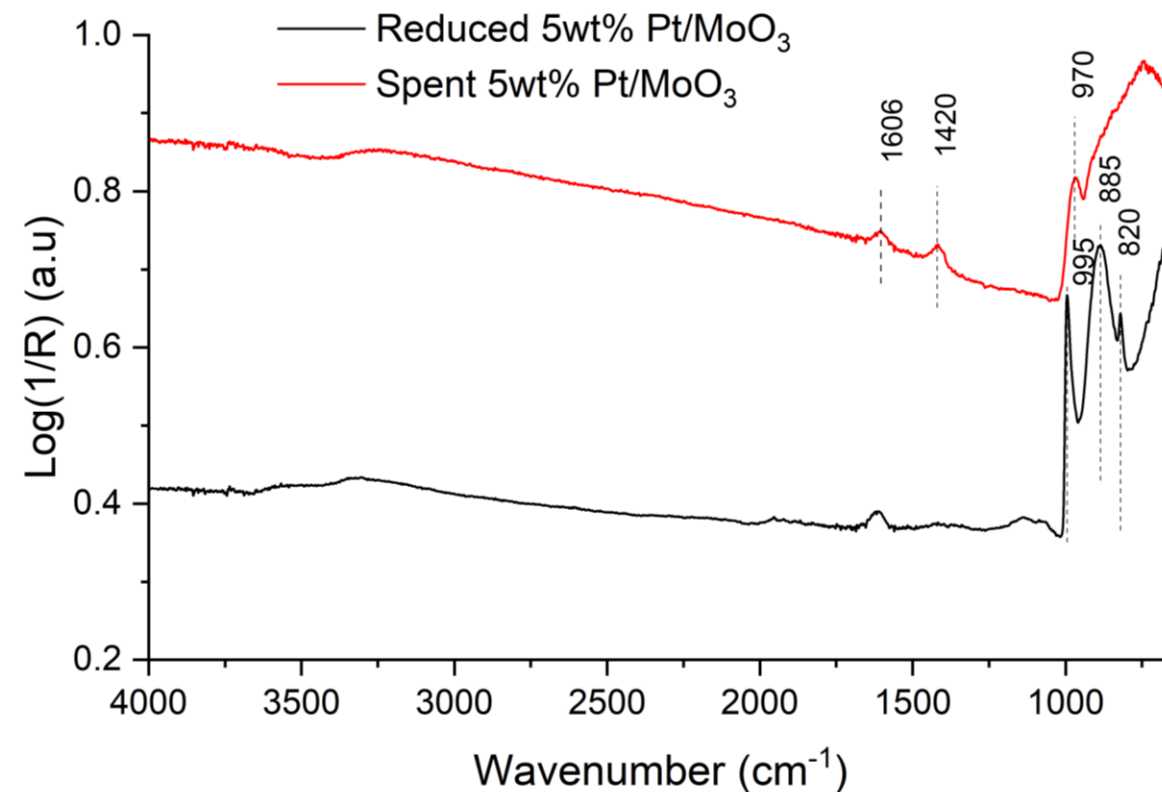
N_{H^*} is the molar quantity of chemisorbed H* from the strong isotherm at 190 °C or 40 °C.

N_{Pt} is the total molar quantity of Pt loaded on the catalyst.

Coverage of H* on Pt sites at 190 °C ($\theta_{H^*/Pt,190^\circ C}$) = $\frac{N_{H^*,190^\circ C}}{N_{H^*,40^\circ C}}$

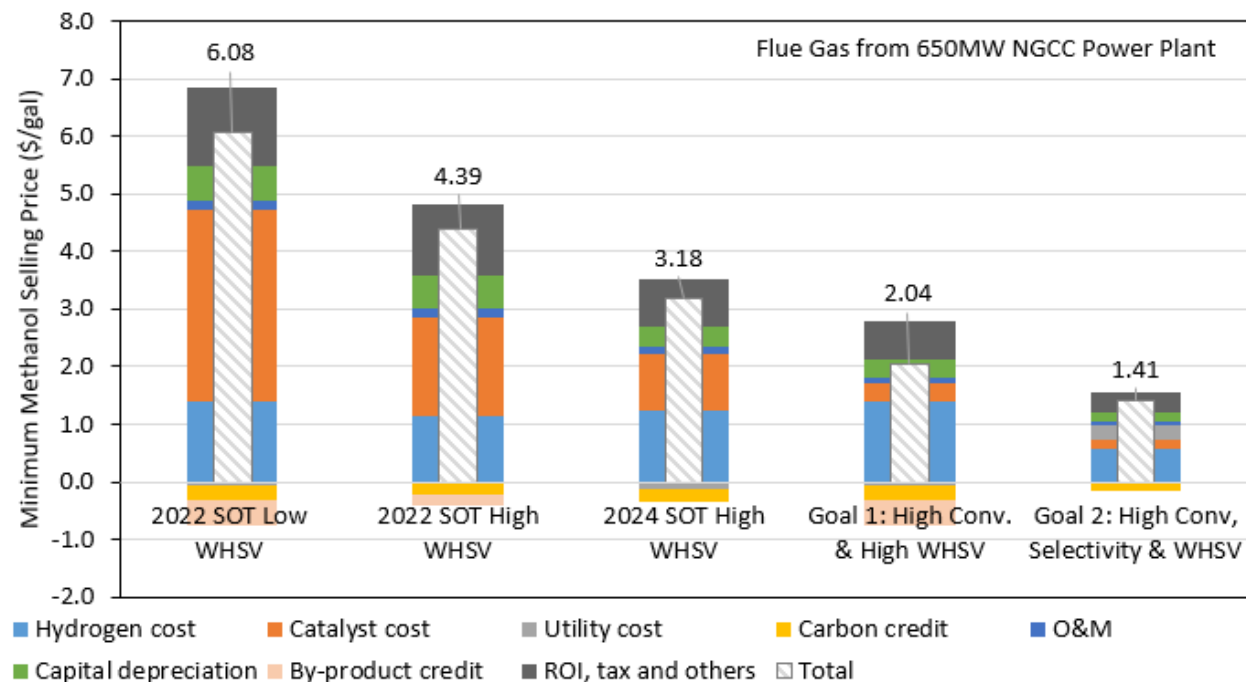
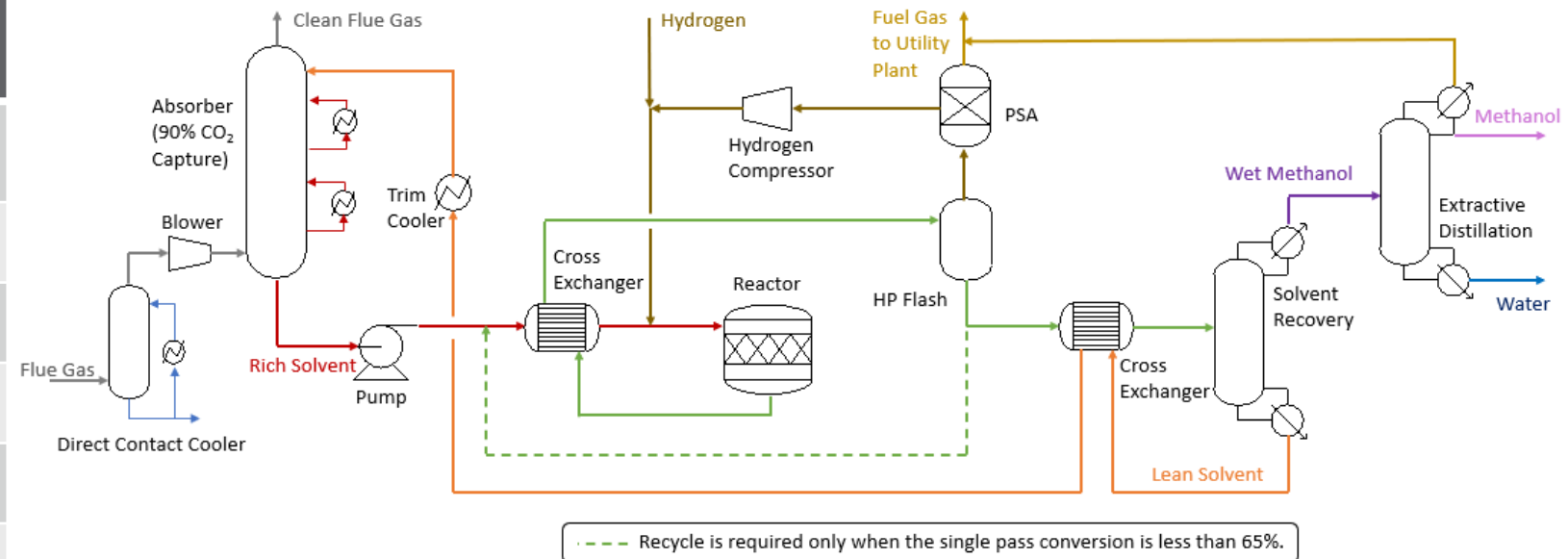
Minimal Surface-Bound “Carbon” Species on Pt/MoO₃, Contributing to its Stable Catalytic Performance

- No distinct CO absorption bands are visible in DRIFTS for Pt/MoO₃. Absorption bands corresponding to bicarbonate/carbonate are visible in both fresh and spent Pt/MoO₃ catalyst
- Spent Pt/TiO₂ catalyst showed distinct CO bands and a significant amount of bicarbonates, possibly causing catalyst deactivation



2024 SOT Case Demonstrates Significant Reduction in Methanol Selling Price

| | 2022 SOT Low WHSV | 2022 SOT High WHSV | 2024 SOT High WHSV | Goal 1 | Goal 2 |
|--|-------------------|--------------------|--------------------|--------|--------|
| WHSV (gCO ₂ /gCat/hr) | 0.015 | 0.075 | 0.06 | 0.15 | 0.15 |
| Single-pass CO ₂ conversion (%) | 85.7 | 26.9 | 57.1 | 85.7 | 85.7 |
| CH ₃ OH selectivity (C%) | 51.5 | 63.6 | 64.6 | 51.5 | 100 |
| CH ₄ and light gases selectivity (C%) | 36.3 | 26.4 | 35.4 | 36.3 | |
| C ₂₊ alcohols selectivity (C%) | 12.2 | 4.8 | 0 | 12.2 | |
| Source | Exp. | Exp. | Exp. | Target | Target |



- The 2024 SOT MSP of methanol is about 29% lower than the best 2022 SOT cases due to savings in catalyst and capital depreciation
- The 2024 SOT estimates a methanol MSP of \$3.18/gal (\$1070/metric ton), **33% lower than renewable methanol** (\$1600/metric ton) from captured CO₂ at \$50/metric ton
- Results indicate a clear path from 2022 SOT to our performance and cost goals through continuous catalyst and reactor development
- Assumptions for key cost drivers: H₂=\$1/kg; solvent loss=<0.01%; catalyst lifetime=3 years

Reduction in methanol selling price enabled by performance improvements

WSU Attempts to Reproduce CO₂ Hydrogenation to Ethanol from Literature

- Literature reports ethanol selectivity of over 90%, using batch and continuous flow reactors with various catalysts
- However, we observed a maximum ethanol selectivity of only 6%, significantly lower than the reported 99.7%
 - **CO** is consistently observed as a major product with at least 70% selectivity, contrary to reports of negligible CO in some studies
 - **CH₄** is also commonly detected as a product, while some publications report it as undetectable

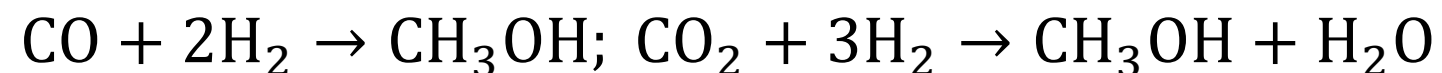
| Heterogenous Catalyst | Literature Reports | | | WSU Results | | |
|---|--------------------|---------------------------|------------------------|------------------|---------------------------|------------------------|
| | Ethanol Sel. (%) | CO ₂ Conv. (%) | TOF (h ⁻¹) | Ethanol Sel. (%) | CO ₂ Conv. (%) | TOF (h ⁻¹) |
| Ir₁-In₂O₃ | 99.7 | - | 481 | 1.1 | 0.02 | 18.41 |
| CoAlO_x-600 | 92.1 | - | - | 5.9 | 0.19 | 0.01 |
| Pd₂Cu-NPs/P25 | 92 | - | 359 | 2.5 | 0.24 | 20.03 |
| Pd₂/CeO₂ | 99.2 | 9.2 | 211.7 | 2.9 | 1.05 | 27.88 |
| Rh/CeTiO_x | 99.1 | 6.3 | 493.1 | 3.9 | 0.57 | 15.74 |

Synthesis procedure and experimental reaction conditions were same as the literature reports.

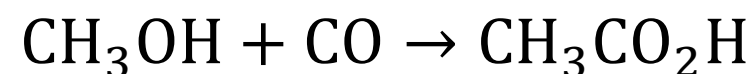
WSU: Triple Tandem Catalysis Approach to Enhance Ethanol Selectivity

Triple tandem approach involves the following steps:

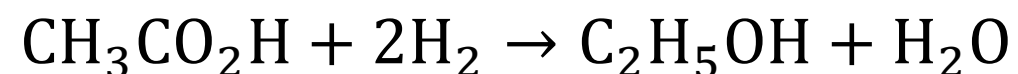
Step 1 CuZnAl catalyst for CO (CO₂) hydrogenation to methanol:



Step 2 Iridium/MOR (or Re/SiO₂) catalyst for methanol carbonylation to acetic acid:



Step 3 Cu nanoparticles for acetic acid hydrogenation to ethanol:



- Optimized catalysts and conditions identified for each individual step.
- Current focus on integrating all the optimized steps effectively

Conclusion and Future Work of IC³M

- Catalytically reacting CO₂ in capture medium can bypass CO₂ release and compression energy
- Methanol synthesis
 - Pt/MoO₃ and Pt/ZrO₂ demonstrate **stable catalytic performance** over 100 hours on stream
 - Notably, Pt/ZrO₂ exhibits **~100% selectivity** towards methanol
 - The Pt/MoO₃ catalyst shows minimal surface-bound carbon species compared to the Pt/TiO₂ catalyst, contributing to its stable catalytic performance
- Increase yield and selectivity for CH₃OH (success criteria #1)
 - Continue investigating new catalyst formulations to enhance methanol productivity and EEMPA solvent stability, aiming to meet the TEA goal case
- Expand reactivity to >C₂ products (success criteria #2)
 - Develop catalysts for ethanol synthesis (WSU)
 - Show proof-of-concept for the co-production of methanol and glycols using heterogenous catalyst



Thank you!



U.S. DEPARTMENT OF ENERGY

Fossil Energy and Carbon Management



NETL/DOE PM: Dylan Leary



Johnny Saavedra Lopez

Materials and Catalysis



Mike Hubbard

Catalysts Testing



Jaelyne King

Characterization



Ben Moskowitz

Characterization



Dushyant Barpaga

Capture solvent



Jared Kroll

Capture solvent



Eric Walter

Operando studies



Yuan Jiang

TEA/LCA



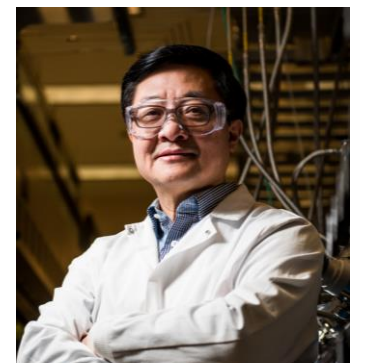
Flavio da Cruz



Ethan Simonoff



Siari Sosa



Yong Wang