# Modular System for Direct Conversion of Methane into Methanol via Photocatalysis

DE-FE-0031867


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U.S. Department of Energy

National Energy Technology Laboratory

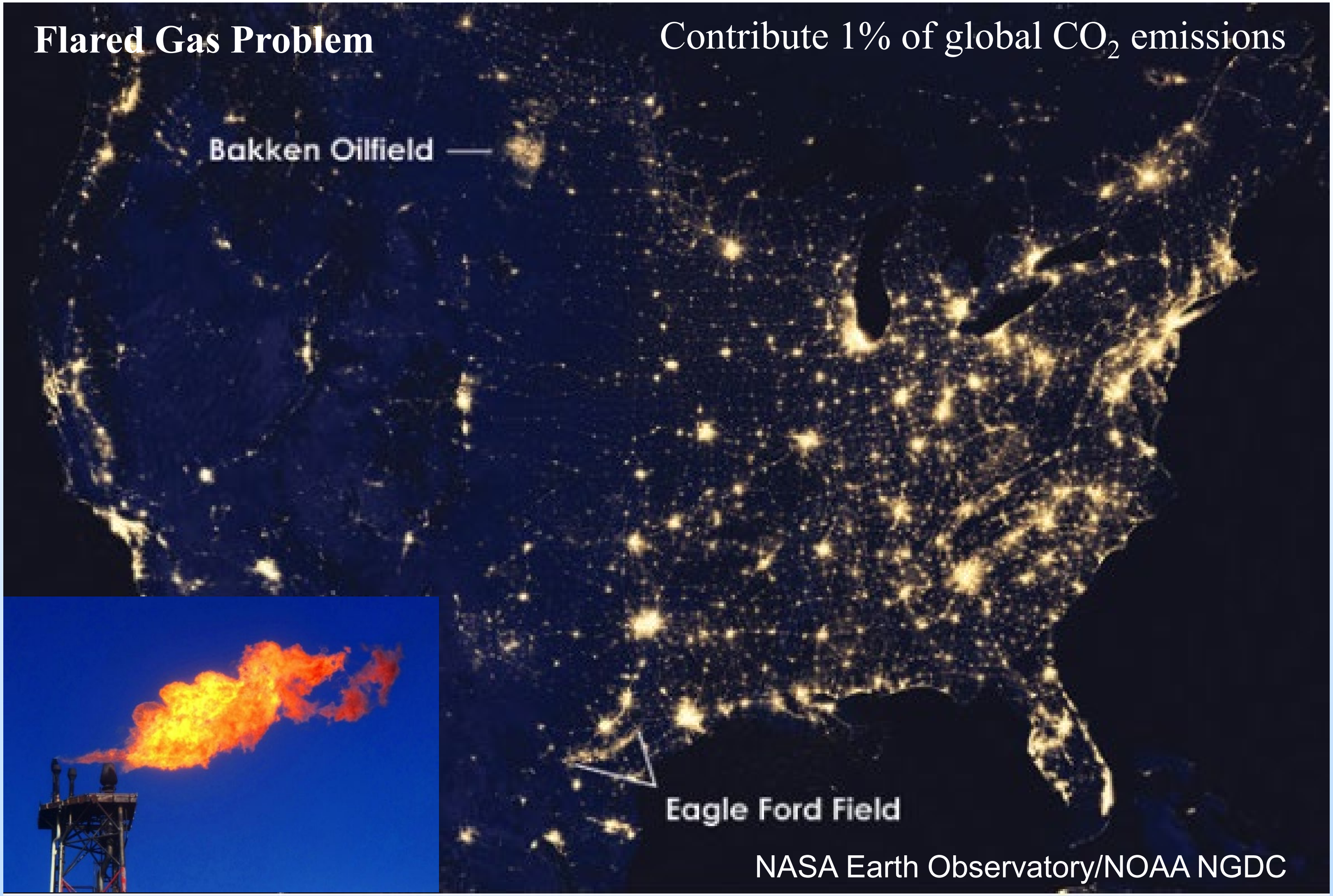
Resource Sustainability Project Review Meeting

October 25 - 27, 2022

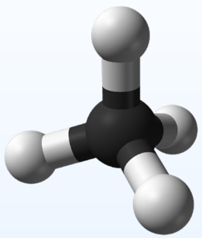
# Project Overview

| | | |
|---|---|---|
| **Title** | **A Modular System for Direct Conversion of Methane into Methanol via Photocatalysis** | |
| Award No. | DE-FE0031867 | |
| Period of Performance | 10/01/2020 – 09/30/2023 | |
| Project Funding | DOE: $1,300,000 | Cost-Share: $325,000 |
| Overall Project Goal | Develop a liquid phase photocatalytic process for direct conversion of methane in flare gas into methanol | |
| Project Participants | Stanford University, Susteon Inc., Casale SA | |
| DOE/NETL Project Manager | Bruce Brown | |
| Principal Investigator | Dr. Arun Majumdar | |

# Technology Background: Methane Flaring

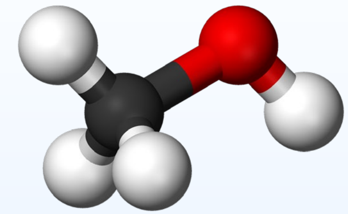


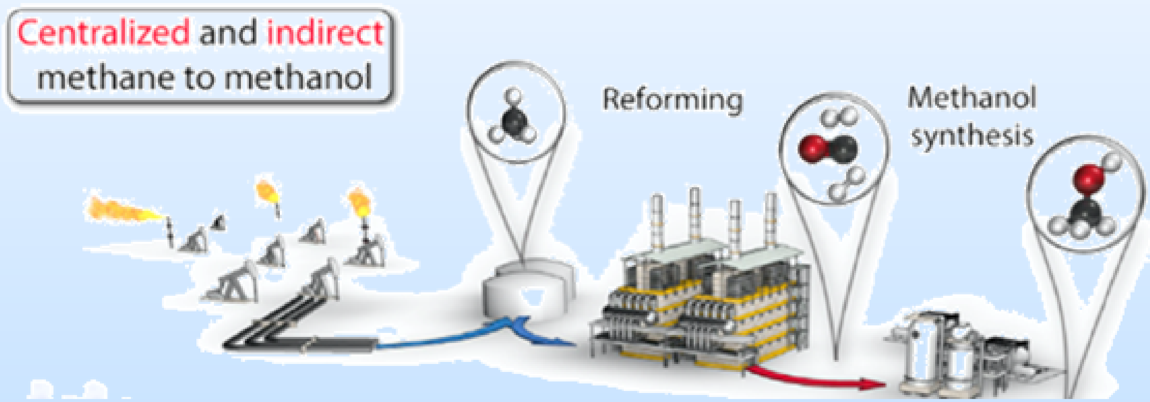
# Current Industrial Methanol Production from $CH_4$



**Two-step process with a syngas intermediate**

**High temperatures and pressure required**





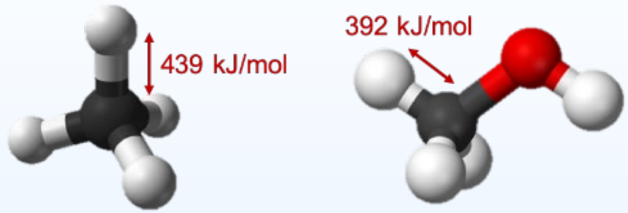

$$CH_4 \xrightarrow[\text{1,023-1,173K, 30 bar}]{+H_2O} H_2 + CO \xrightarrow[\text{623K, 60 bar}]{Cu/Zn/Al_2O_3} CH_3OH$$

$$CH_4 \xrightarrow{\text{Direct Method}} CH_3OH$$



C. G. Morales-Guio et.al., *Joule*, **2019**, *3*, 2589–2593

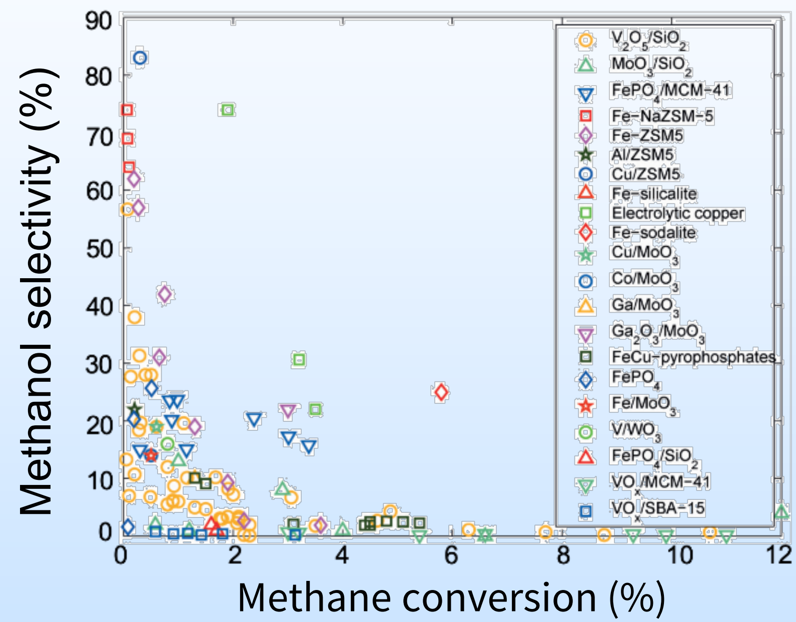
# Fundamental Challenges in Direct Methane to Methanol (M2M)




**Methane** **Methanol**

- Intrinsic inertness of the C-H bond in $CH_4$
- Ease of overoxidation of $CH_3OH$ to $CO_2$

**Selectivity-Conversion Trade-off**




**Catalyst Design Requirement**

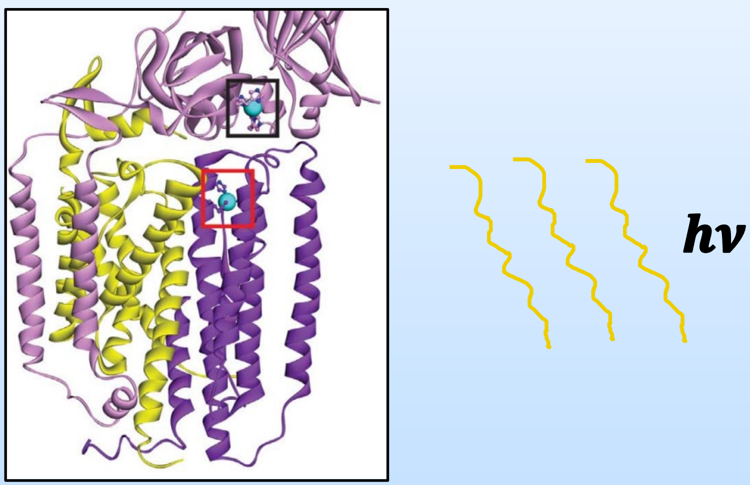
Simultaneously activate methane AND mitigate methanol over-oxidation

X. Bao, *et.al., Chem,* **2019**, 5, 2296–2325

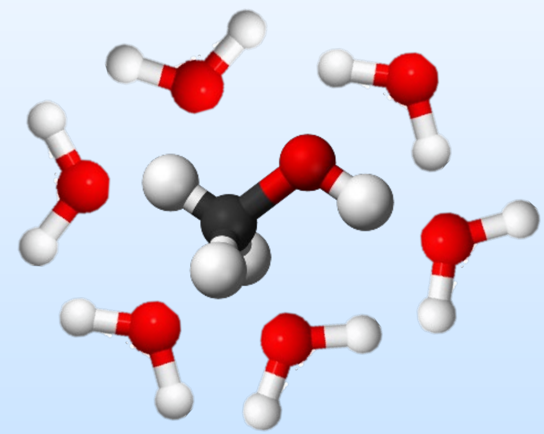
J. A. van Bokhoven, *et al., Angew. Chem. Int. Ed.* **2017**, *56*, 16464 – 16483

# Motivation for *Photocatalytic* Direct M2M

**Room temperature** photoactivation of methane like methane monooxygenase




**Liquid-phase:** water can help protect methanol

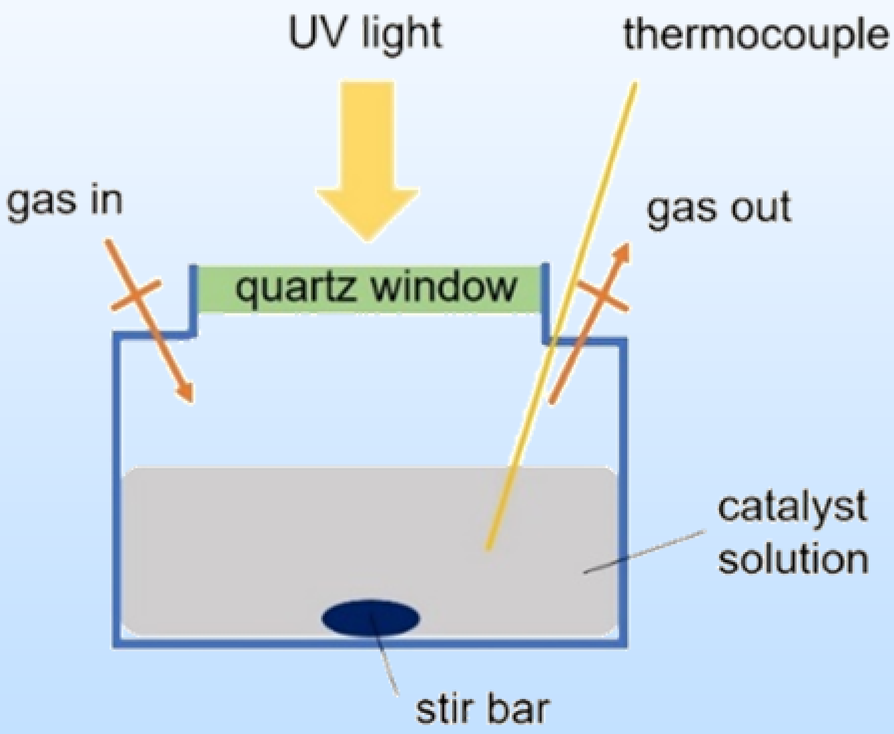


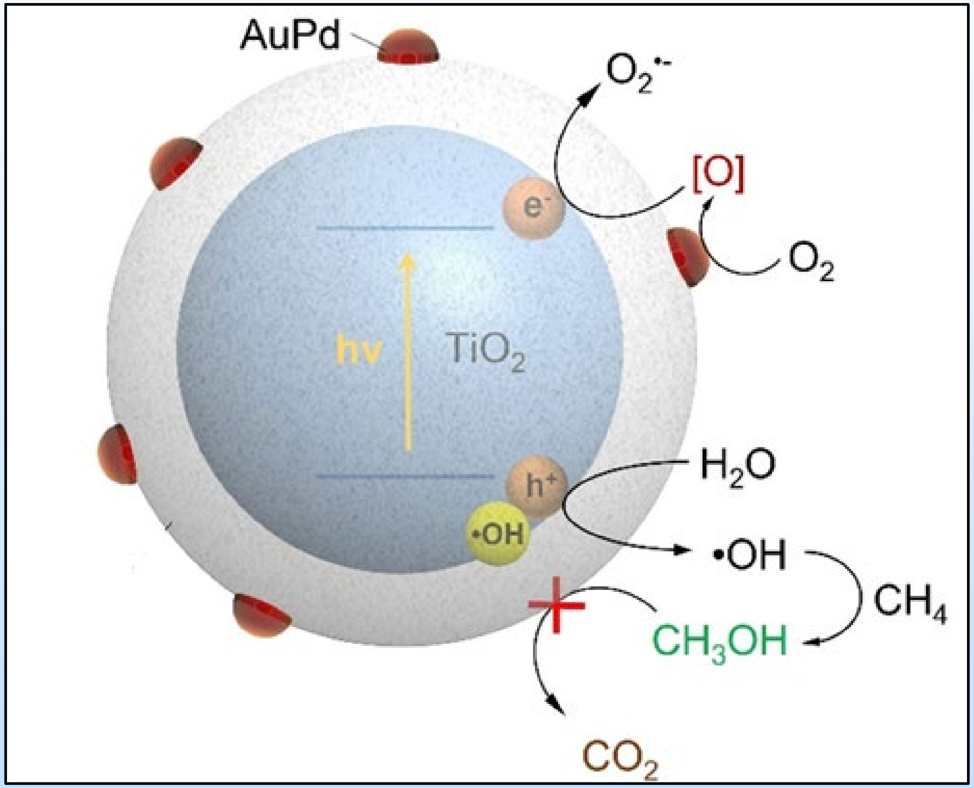
"Solvation Cage"

# Project Schedule

| Task/Subtask | Key Milestone | Planned Completion Date |
|---|---|---|
| Task 1 | Kickoff meeting and submission of revised project management plan (PMP), technology maturation plan and techno-economic analysis | 04/01/2020 |
| Task 2 | Successful demonstration of the ability to incorporate the co-catalyst clusters and molecular complexes with the semiconductor catalyst while controlling co-catalyst loading and proximity to semiconductor sites. | 01/31/2021 |
| Task 3 | Successful optimization of semiconductor material and synthesis conditions for maximizing hydroxyl radical production. | 01/31/2021 |
| Task 4 | Successful optimization of a bifunction photocatalyst with a capable of converting methane into methanol with high selectivity and yield. | 09/30/2021 |
| GO/NO-GO Decision | Test results show approaching 7-10% methane conversion with 80-90% methanol selectivity under commercially reasonable operating conditions. | 09/30/2021 |
| Task 5 | Complete one final iteration for optimizing bifunctional catalyst for methane to methanol conversion and potential for future catalyst scaleup and large-scale production. | 03/31/2022 |
| Task 6 | Obtain key operating catalyst performance data under realistic conditions with simulated natural gas for commercial application. | 06/30/2022 |
| Task 7 | Identification of effective reactor configuration to optimize methane transfer onto the catalyst surface across the aqueous media. | 09/30/2022 |
| Task 8 | Demonstrate production of photocatalytic methane to methanol conversion using $H_2O$ as reagent for hydroxyl radical production | 09/30/2022 |
| Task 9 | Demonstration of activation of methane or $CO_2$ in a mixture with other gases | 07/30/2023 |
| Task 10 | Pilot plant design for modular operation | 09/30/2023 |

# Progress and Current Status of Project

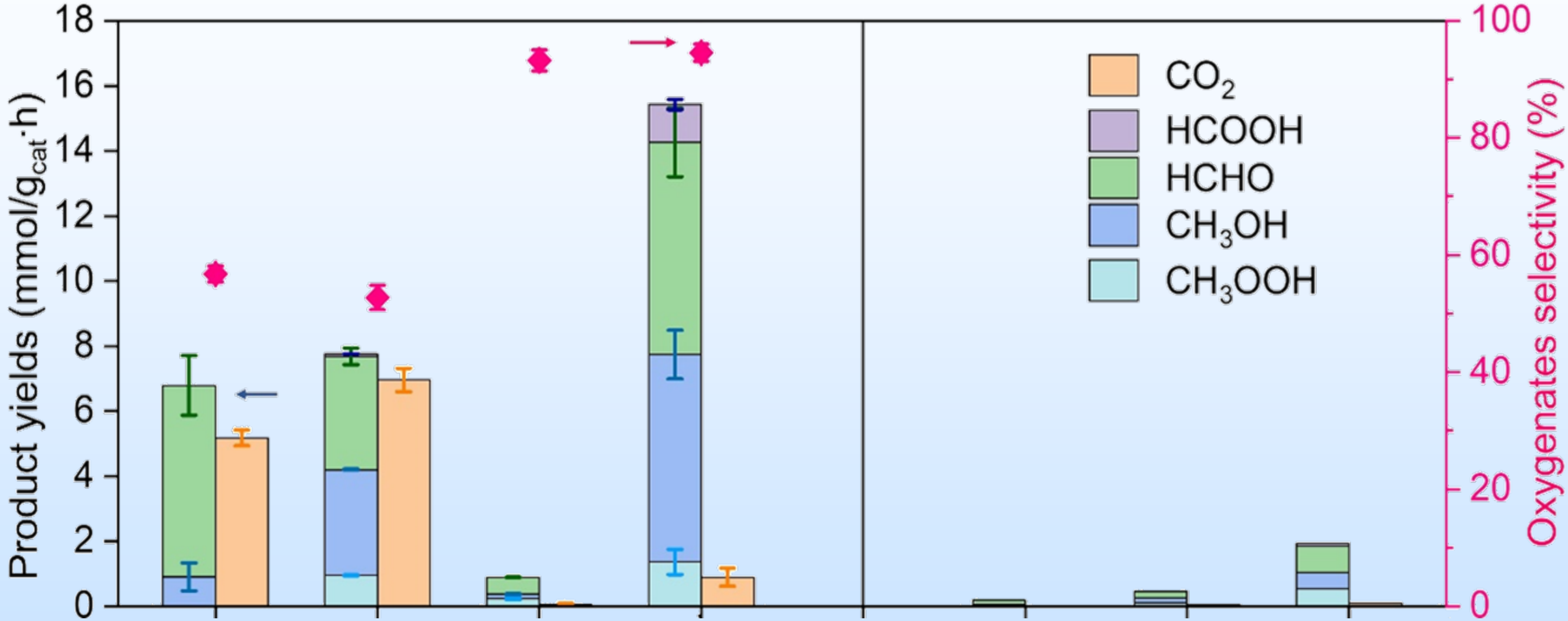



$TiO_2$-based designed photocatalyst

# Progress and Current Status of Project

**Methane Conversion Ratio (0.4 %) + Liquid Product Selectivity (94.5%)**



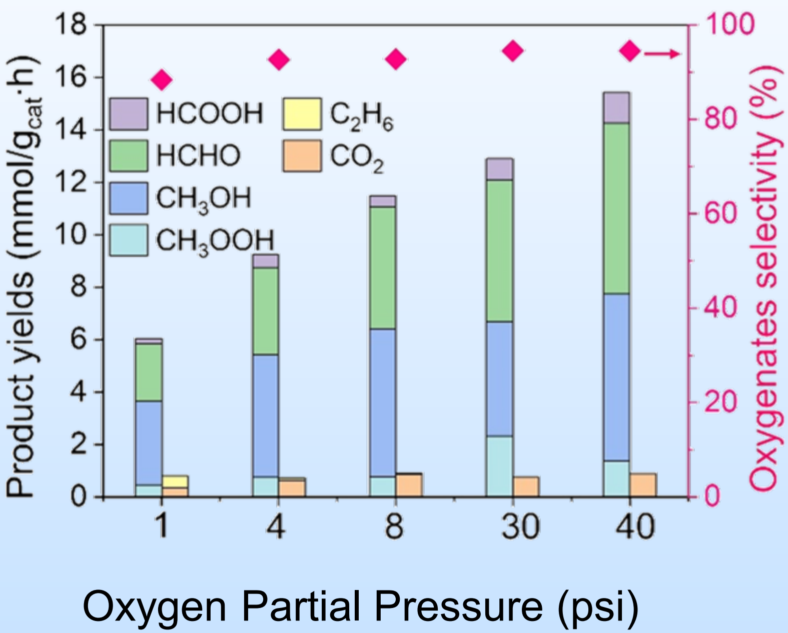

TiO$_2$ TiO$_2$/AuPd **TiO$_2$/Oxide/AuPd** Controlled Samples

**<u>Liquid product selectivity:</u>**

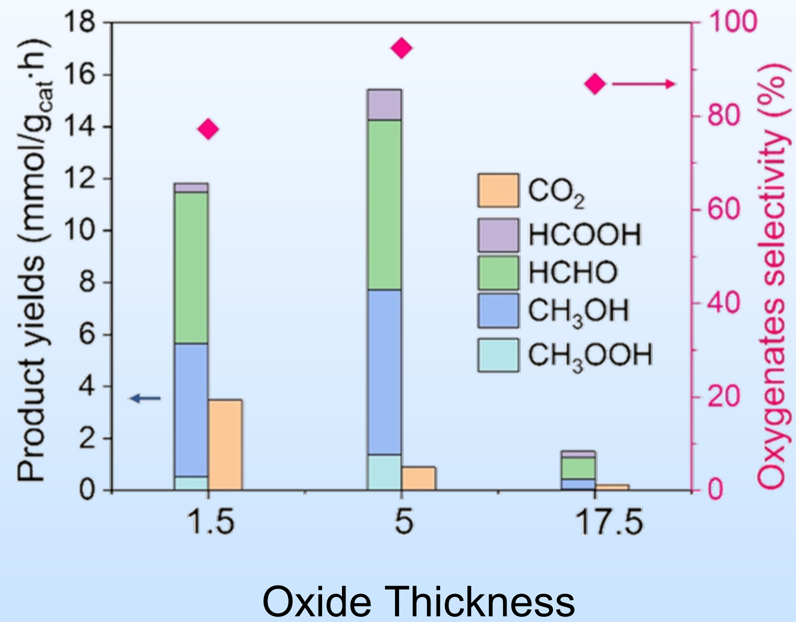
w/o oxide: 53%; w/ oxide: 94.5%

# Progress and Current Status of Project

**Reaction optimization**
(gas partial pressures)




**Catalyst optimization**
(oxide layer thickness)

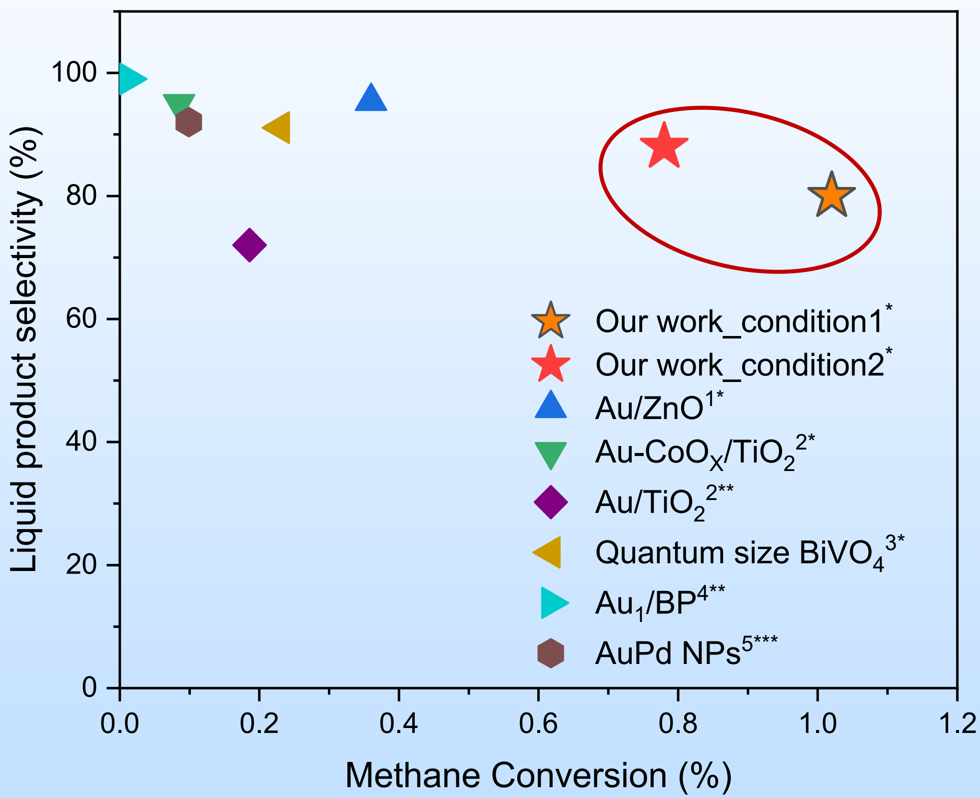



**Increased oxygen partial pressure promotes the methane oxidation and selectivity**

**Identified an optimal thickness for oxide composite**

# Progress and Current Status of Project

**Comparison with Other Catalysts in Literature Reports**

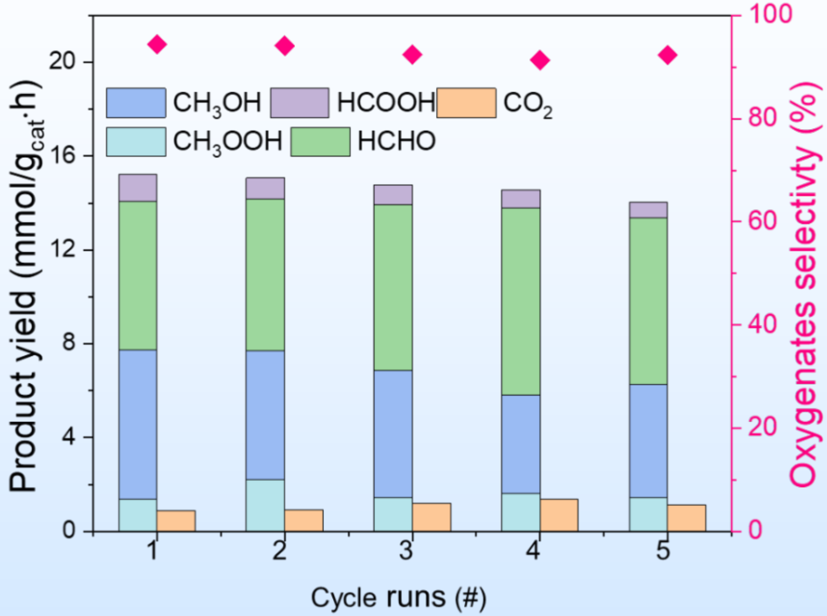



Highest combination of **methane conversion** and **liquid product selectivity** reported thus far in the literature

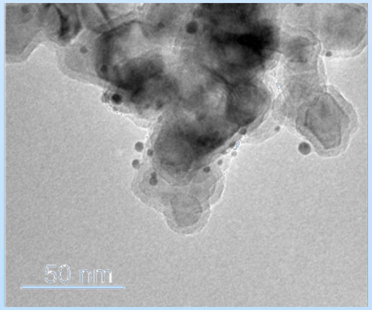
[1] *JACS*, **2019**, 141, 20507−20515 [2] *ACS Catal*. **2020**, 10, 14318−14326 [3] *Nat. Sustain.* **2021,** 4, 509–515; [4] *Nat. Commun.* **2021,** 12, 1218 [5] *Science*, **2017**, 358, 223–227

* Reaction time 3h ** Reaction time 2h *** Reaction time 1h

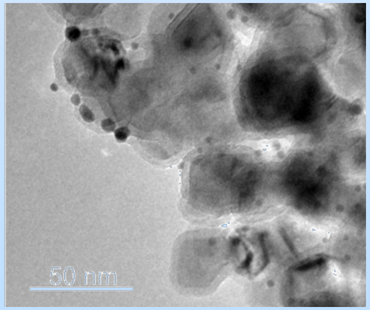
# Progress and Current Status of Project




**Before Reaction**




**After Reaction**

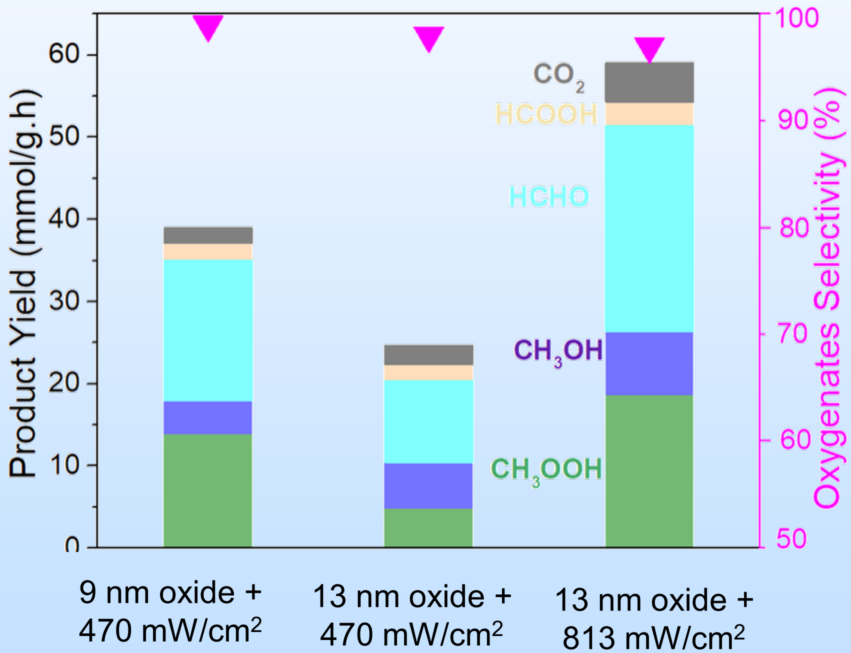


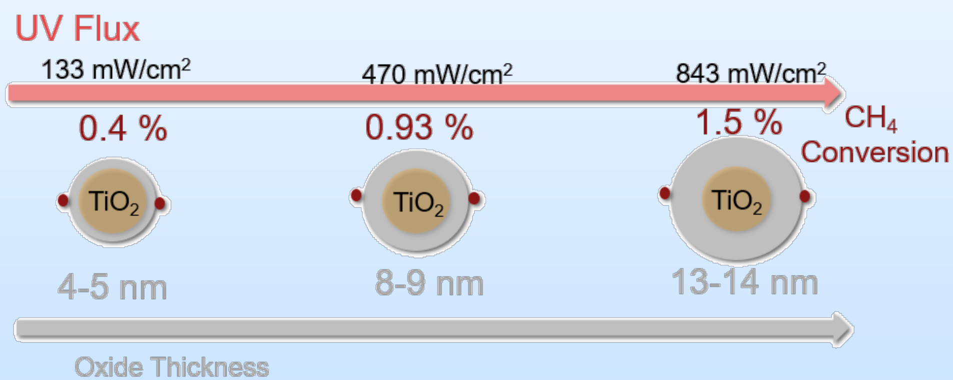

**Stable catalyst and reproducible product yield**

**No observed changes in catalyst after 5 runs**

# Progress and Current Status of Project

## Increasing methane conversion by increasing UV flux and oxide layer thickness

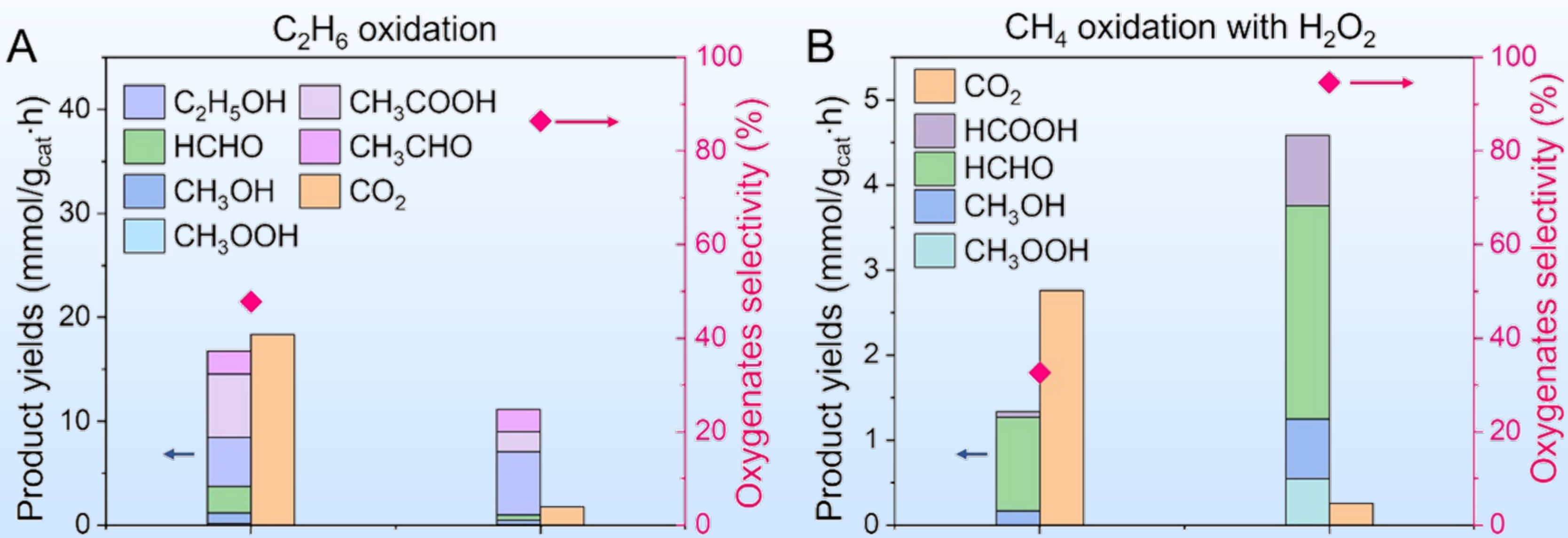



1 h reaction

# Progress and Current Status of Project

## Extension to other alkane oxidation and $H_2O_2$ systems




TiO$_2$/AuPd    TiO$_2$/Oxide/AuPd

Co-catalyst-free System

**<u>Liquid product selectivity:</u>**

w/o oxide layer: 48%

w/ oxide layer: 85%

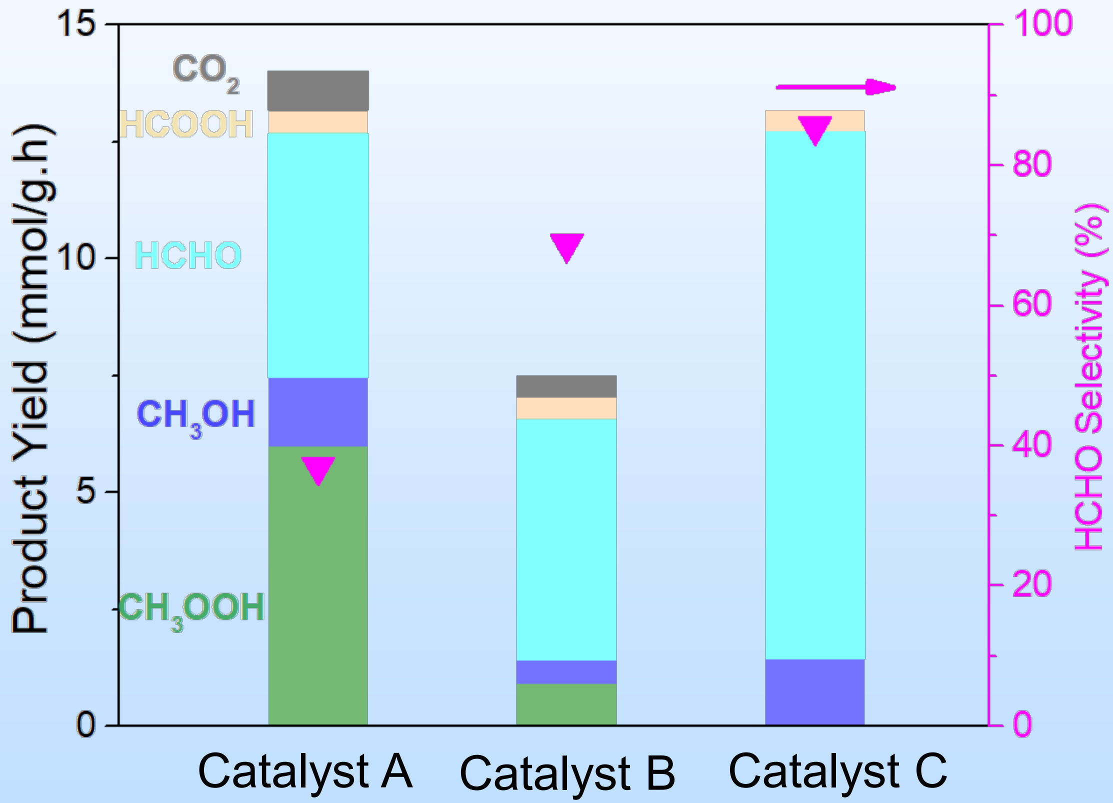
**<u>Liquid product selectivity:</u>**

w/o oxide: 30%

w/ oxide: 95%

# Progress and Current Status of Project

## Selective Methane Oxidation to Formaldehyde (HCHO)



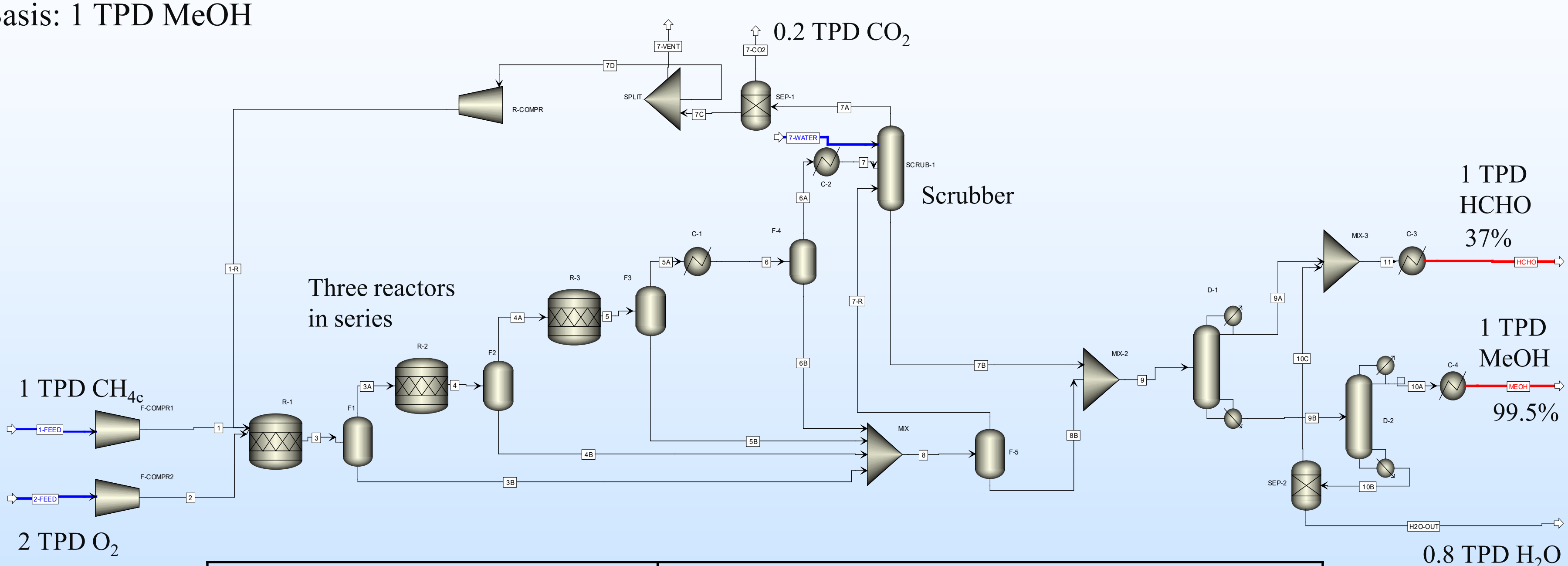

In industry, **20%** of produced methanol is used to synthesize HCHO

We developed a **highly selective** (84%) pathway to convert CH4 to HCHO

# Progress and Current Status of Project

## Initial Process Model (in AspenPlus™)

Basis: 1 TPD MeOH




| # of Reactors in Series | Three |
|---|---|
| Reactions Considered | $CH_4 + 0.5O_2 \rightarrow CH_3OH$ (0.92% yield from $CH_4$)<br>$CH_4 + O_2 \rightarrow CH_2O + H_2O$ (0.92% yield)<br>$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (0.16% yield)<br>$H_2 + 0.5O_2 \rightarrow H_2O$ (100% $H_2$ to $H_2O$) |
| Reactor Operating Conditions | 30°C, 10 bar |
| Feed Flows | Methane: 1 TPD and Oxygen: 2 TPD |
| Product Flows | Methanol: 1 TPD; Formaldehyde: 1 TPD;<br>$CO_2$: 0.2 TPD; $H_2O$: 0.8 TPD |

# Progress and Current Status of Project

## Initial Techno-Economic Analysis

Purchased Equipment Cost (PEC) + Installation Cost = Bare Erected Cost (BEC)

From scaling factors, quotes, and AspenPlus™ simulation
- Photo-catalytic reactor
- Compressors
- Methanol/Formaldehyde purification

Includes the cost of piping and other auxiliary equipment involved in installation

**2.47x PEC**

+ Engineering, Procurement and Construction Fees (EPC) — **15% of BEC**
+ Process contingency (PC1) — **X% of PEC** (**X = 0 (mature); = 25 (fairly developed); = 50 (novel)**)
+ Project contingency (PC2) — **15% of (BEC + EPC + PC1)**
+ Owners' Cost — **20% of (BEC + EPC + PC1 + PC2)**
+ Land Cost — **0.5 acre @ $36,000 per acre**

= **Total Overnight Cost (TOC)**

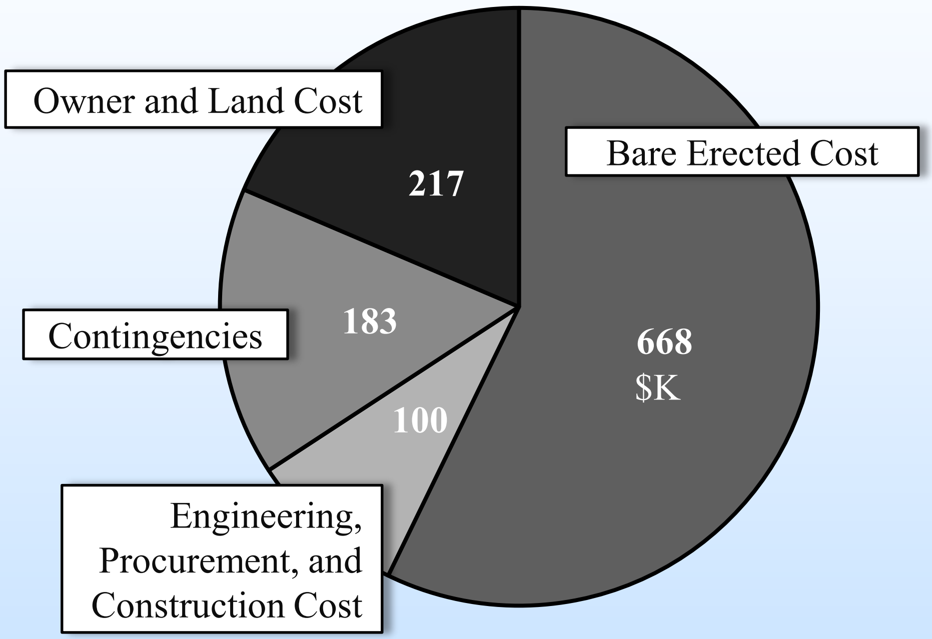
### Assumptions

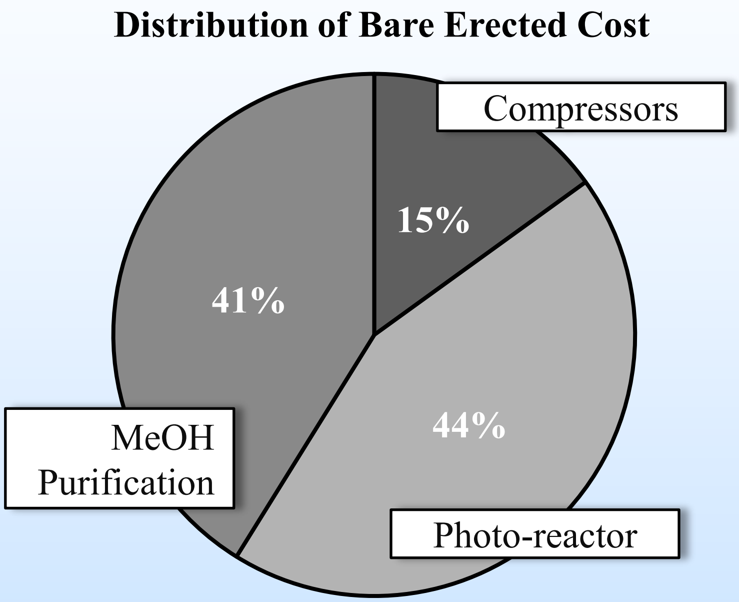
- Methanol production: 1 TPD
- Formaldehyde production: 1 TPD

- Compressor capital: $750/hp
- Required power: 40 kWe
- Methanol purification capital: $120,000

# Progress and Current Status of Project

## Initial Techno-Economic Analysis




| Cost Contribution | Unit Cost ($/t MeOH) | Contribution |
|---|---|---|
| **Capital** | 455 | 43% |
| **Feedstocks/Consumables** | 269 | 26% |
| **Power & Utilities** | 199 | 19% |
| **O&M** | 128 | 12% |
| **Formaldehyde credit** | -400 | |
| **Adjusted Total** | **650** | |

Current market price:
**$500-700/t MeOH**

# Plans for future testing/development/ commercialization

- Increasing methane conversion and methanol selectivity (>5% and ≥ 90 % resp.)
- Developing preliminary basic engineering design package for a pilot test unit
- Leveraging photoactivated radicals for GHG-reducing chemical transformations

# Take-Away Message

- Successfully developed a modular photocatalytic system that has achieved both high methane conversion (>1%) and high liquid product selectivity (>90 %)
- Conducted the initial process design for the photocatalytic methane conversion

# Appendix

# Organization Chart

**Integrating Catalyst Development, Separation, Scale-up and Reactor Design**

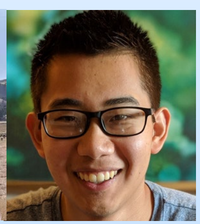
**Arun Majumdar**

**Principal Investigator**

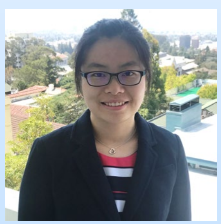
**Raghubir Gupta**

**CO-PI (Susteon President)**

**Gang Wan (Postdoc)**



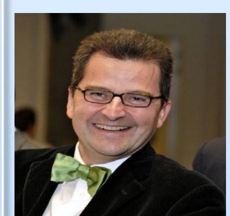
**Eddie Sun (Grad Student)**



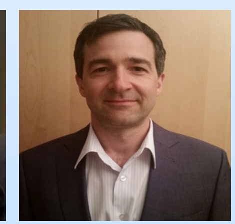
**Chenlu Xie (Former Postdoc)**

**Jian Zheng (Susteon)**

**Vasudev Haribal (Susteon)**



**Ermanno Filippi (Casale)**



**Michal Bialkowski (Casale)**

**Pierdomenico Biasi (Casale)**

# Gantt Chart

| Project Timeline | Assigned Resources | Budget Period 1 10/1/2020-09/30/2021 | Budget Period 2 10/1/2021-09/30/2023 |
|---|---|---|---|
| | | 1 2 3 4 5 6 7 8 9 10 11 12 | 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 |
| **Task 1. Project Management and Planning** | **Stanford** | | |
| Subtask 1.1 Project Management Plan | | | |
| Subtask 1.2 Technology Maturation Plan | | | |
| Subtask 1.3 Techno-Economic Analysis | | | |
| **Task 2: Catalyst Synthesis** | **Stanford** | | |
| Subtask 2.1: Semiconductor catalyst synthesis | | | |
| Subtask 2.2: Co-catalyst synthesis | | | |
| Subtask 2.3: Integration of semiconductor and co-catalyst into bifunctional catalysts | | | |
| Milestone 2: Successful demonstration of the ability to incorporate the co-catalyst clusters and molecular complexes with the semiconductor catalyst while controlling co-catalyst loading and proximity to semiconductor sites. | | ✣ | |
| **Task 3. Multiplex Fluorescence Array High-Throughput Screening** | **Stanford** | | |
| Milestone 3: Successful optimization of semiconductor material and synthesis conditions for maximizing hydroxyl radical production. | | ✣ | |
| **Task 4: Bifunctional Catalyst Testing** | | | |
| Milestone 4: Successful optimization of a bifunction photocatalyst with a capable of converting methane into methanol with high selectivity and yield. | | ✣ | |
| **Go/No-Go Decision Milestone: Test results show approaching 7-10% methane conversion with 80-90% methanol selectivity under commercially reasonable operating conditions.** | **09/30/2021** | ★ | |
| **Task 5: Study of Structure-Property Relationships** | **Stanford** | | |
| Milestone 5: Complete one final iteration for optimizing bifunctional catalyst for methane to methanol conversion and potential for future catalyst scaleup and large-scale production. | | | ✣ |
| **Task 6: Experimental Identification of Optimal Operating Window** | **Stanford** | | |
| Milestone 6: Obtain key operating catalyst performance data under realistic conditions with simulated natural gas for commercial application. | | | ✣ |
| **Task 7: Evaluation of Reactor Design** | **Stanford & Susteon** | | |
| Milestone 7: Identification of effective reactor configuration to optimize methane transfer onto the catalyst surface across the aqueous media. | | | ✣ |
| **Task 8: Evaluation of Water as Hydroxyl Radical Source** | **Stanford** | | |
| Milestone 8: Demonstrate production of photocatalytic methane to methanol conversion using H2O as reagent for hydroxyl radical production. | | | ✣ |
| **Task 9: Activation of CH4 or CO2 in a mixture of other gases** | **Stanford** | | |
| Milestone 9: Demonstration of activation of methane or carbon dioxide in a mixture with other gases | | | ✣ |
| **Task 10: Pilot plant design for modular operation** | **Susteon** | | |
| Milestone 10: Design pilot plant for the modular operation | | | ✣ |