Design of Transition-Metal/Zeolite Catalysts for Direct Conversion of Coal-derived CO_2 to Aromatics

DOE Award #: DE-FE0031719

Georgia Tech Research Corporation
Georgia Institute of Technology

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U.S. Department of Energy
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Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021

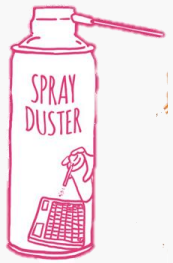
Funding

Federal funds	Non-Federal Cost Share
Budget Period 1 – 1/1/19 – 6/30/2020	
Baseline: $400,000 Actual Incurred Costs: $338,972 Variance: $61,028	Baseline: $117,560 Actual Incurred Costs: $154,418 Variance: $-36,858 (Excess cost-share)
Budget Period 1+2 – 1/1/19 – 12/31/2021	
Baseline: $800,000 Current Incurred Costs: $596,160 **(6/30/2021)** Variance: TBD	Baseline: $235,119 Actual Incurred Costs: $154,418 **(6/30/2021)** Variance: $76,958

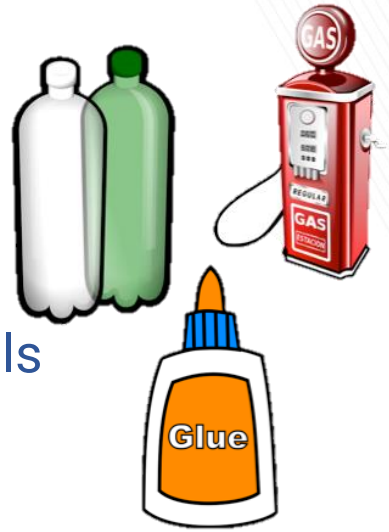
NETL Program Manager
Naomi O'Neil

Background

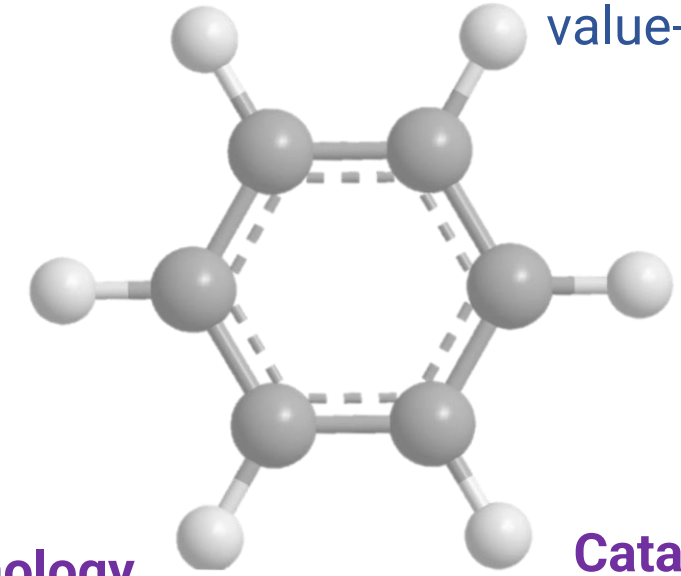
Benzene, **T**oluene, **X**ylene (**BTX**)



Industrial Applications
Solvent



Precursor to
value-added chemicals



Global Production (2010)
100 million metric tons

Projection (2050)
200 million metric tons (BTX)

Current Production Technology
Catalytic reforming of naphtha

Catalyst
Precious metals supported by high surface area materials with acidity

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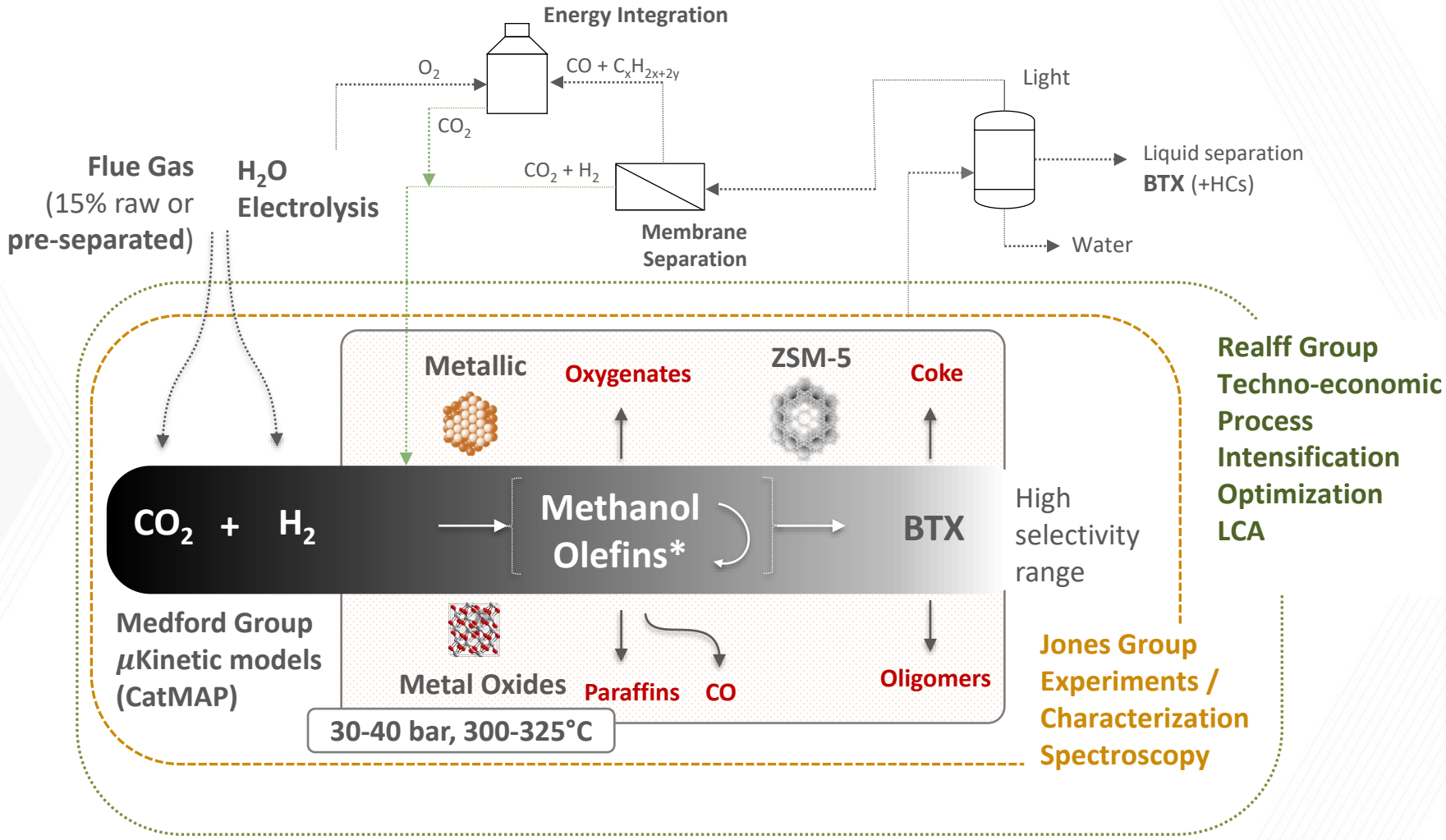
Direct conversion of CO_2 to BTX

Advantages

- Low-volatility products
- Simpler downstream separation trains

Challenges

- CO_2 separation costs vs. Increased CAPEX due to N_2 purges
- Reduce RWGS activity



*2-step route 1st order analysis: ***Fischer-Tropsch (Olefins) has performance advantages***

Research Focus (Experimental+Theoretical): **MeOH/ZSM-5 together**

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Technical Approach (Exp/Comp)

(i) Synthesis and testing of **composite catalytic materials** that include known methanol and hydrocarbon synthesis catalysts mixed with a known aromatization catalyst (**ZSM5**);

(ii) Varying material and reaction properties such as catalyst domain size or reactant composition to investigate effects on **measured rates and selectivities**;

(iii) Developing a **microkinetic computational model** on baseline systems and extending to various alloys and reactant compositions;

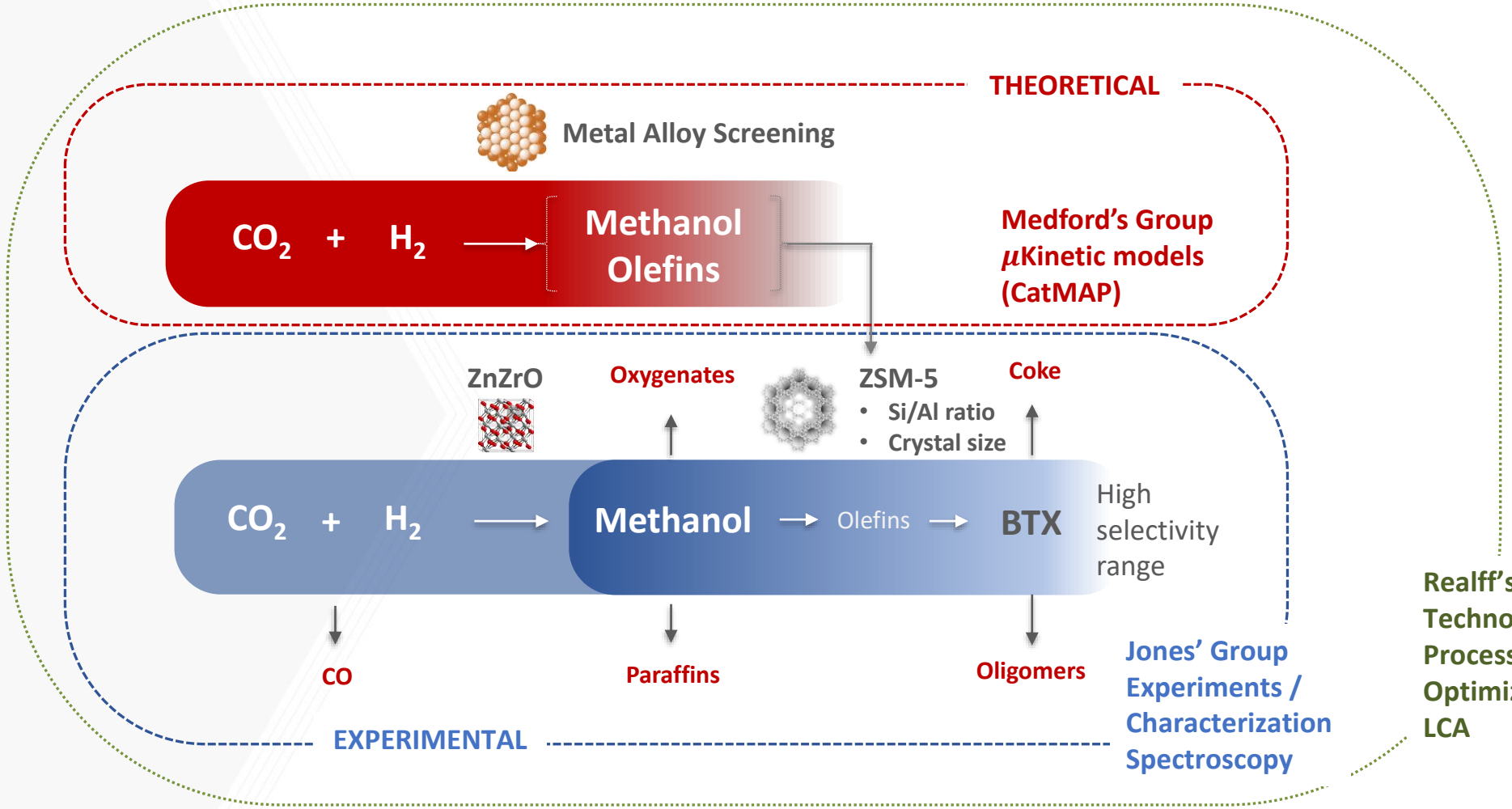
(iv) Refining computational mechanism(s) based on experimental data and including product interactions and subsequent reactions into the model for more realistic surface coverage effects;

(v) Synthesis of alloys based on computational models to improve selectivities to BTX species.

Milestones Achievements

M #	Year	(Sub) Task #	Milestone Description	Planned Completion	Actual Completion	Verification Method
1	1	1.0	Project Management Plan	1/31/2019	1/31/2019	Project Management Plan File
2	1	4.2	Synthesis, characterization, reactor testing of physical mixtures	12/31/2019	10/15/2019	Y1, Q4 report
3	2	4.3	Experimental evaluation of impact of CO_2/H_2 ratio	11/30/2020	11/30/2020	Y2, Q4 report
4	1	5.3	Calculate rates under varied conditions	12/31/2019	03/09/2020	Y1, Q4 report
5	3	6.2	Experimental evaluation of impact of crystallite size	2/28/2021	2/28/2021	Y3, Q1 report
6	2	7.1	DFT Calculations of other TMs	09/30/2020	09/01/2020	Y2, Q3 report
7	3	7.3	Screening model under various conditions	03/31/2021	04/30/2021	Y3, Q2 report
8	3	10.2	Experimental evaluation of impact intimate mixing of acid and metal domains	09/30/2021		Y3, Q3 report
9	3	11.3	Predict performance under observed conditions	12/31/2021		Y3, Q4 report

Strategy


THEORETICAL
Metal Alloy Screening
CO_2 + H_2
Methanol Olefins
Medford's Group
μKinetic models
(CatMAP)
ZnZrO
Oxygenates
ZSM-5
• Si/Al ratio
• Crystal size
Coke
CO_2 + H_2
Methanol
Olefins
BTX
High selectivity range
CO
Paraffins
Oligomers
EXPERIMENTAL
Jones' Group
Experiments / Characterization
Spectroscopy
Realff's Group
Techno-economic
Process Intensification
Optimization
LCA

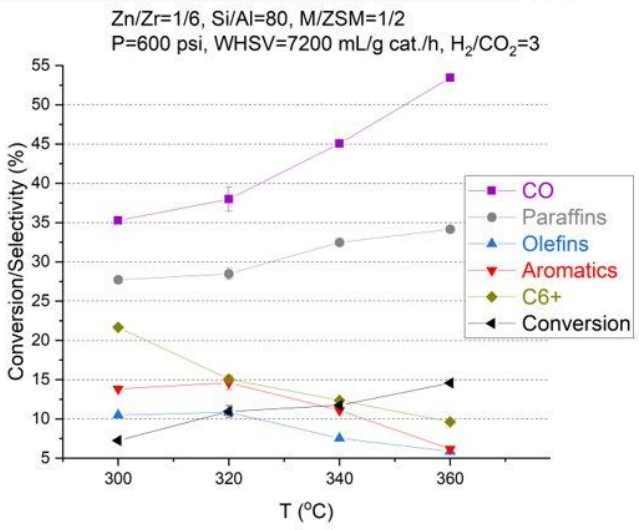
Risks

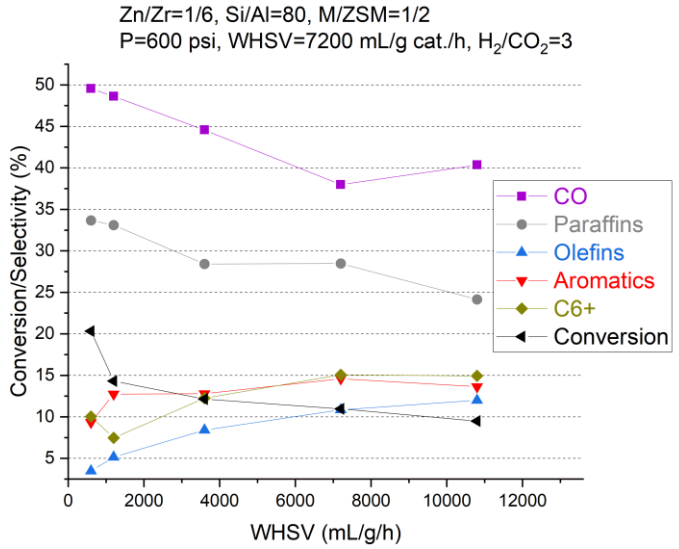
Perceived Risk	Risk Rating (Low, Med, High)			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
COVID-19 shutdown extends beyond July 1st 2020, or similar shutdown situation happens again	Med	High	Med	Experimental tasks (that need on-site presence) will be re-scheduled/prioritized to obtain critical required data in a timely manner.
				Laboratory shutdown is unlikely based on GT experience in summer 2020 with safe research operation. If shutdown were to occur, we would likely request a No-Cost-Extension.
Technical/Scope Risks:				
CatMAP screening fails	Low	Med	Med	CatMAP screening has been used for numerous reactions, but not CO_2 to aromatics. Initial failure will require more detail be incorporated into screening, which could delay the project progression. This will be mitigated by using models that have proven successful for syngas hydrogenation to alcohols as a starting point, and by employing uncertainty quantification to improve robustness.
Screening of only [211] surfaces does not produce insight	Low	Med	Low	Additional metal surfaces, likely [111], need to be considered. This is unlikely since previous screening models of similar reactions have been successful with [211] model surfaces. This risk can easily be mitigated by adding approximately 3 months to the timeline to complete DFT calculations on the [111] surfaces.
Coupling of reaction/transport between zeolite and catalyst cannot be approximated with proposed screening approach	Med	Med	Med	Spatial gradients in reactant/product concentration may play an important role in selectivity patterns. This will make it difficult to directly predict selectivity from existing models. This risk will be mitigated by the use of probabilistic screening that is more robust to errors, and if necessary, a PFR reactor model can be implemented in CatMAP to better account for transport issues.
Predicted alloy unable to be synthesized experimentally as small, bimetallic nanoparticles	Med	Med	Med	Some metals are not stable as bimetallic nanoparticles or are not accessible via traditional synthesis routes. Alternative, more advance routes can be taken or alternative alloys can be attempted.
				Close communication between experiment and theory researchers critical. Begin synthesizing new alloys as soon as preliminary data suggest a possible “hit” from computational screening. Err on side of having too many samples vs too few.

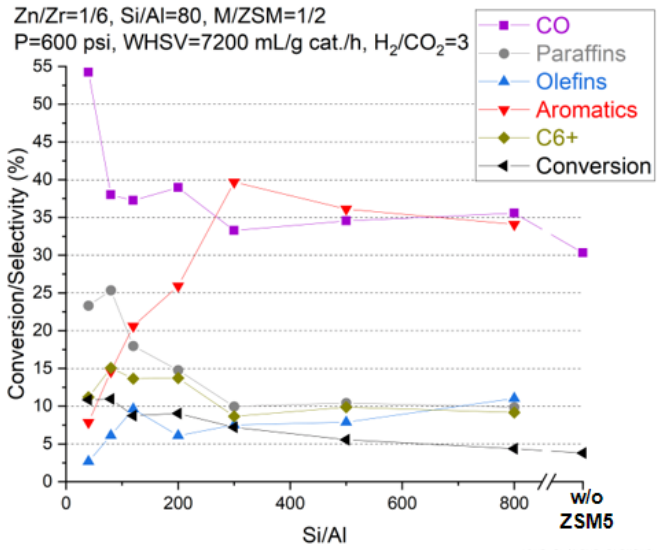
Progress and Current Status

Task 4. Experimental Testing of Baseline Systems **(Accomplished)**

- ZnZrOx: Higher alcohol selectivity at comparable conditions with $ZnGa_2O_4$ vs. CuZnAl catalysts
- Lower contact times, higher conversion of CO_2; Max aromatics selectivity at Si/Al = 300
- Optimum H_2/CO_2 ratio = 3/1
    - Higher H_2/CO_2 ratios: higher CO_2 conversion and lower aromatics selectivity amongst HCs
    - Lower H_2/CO_2 ratios: higher CO selectivity







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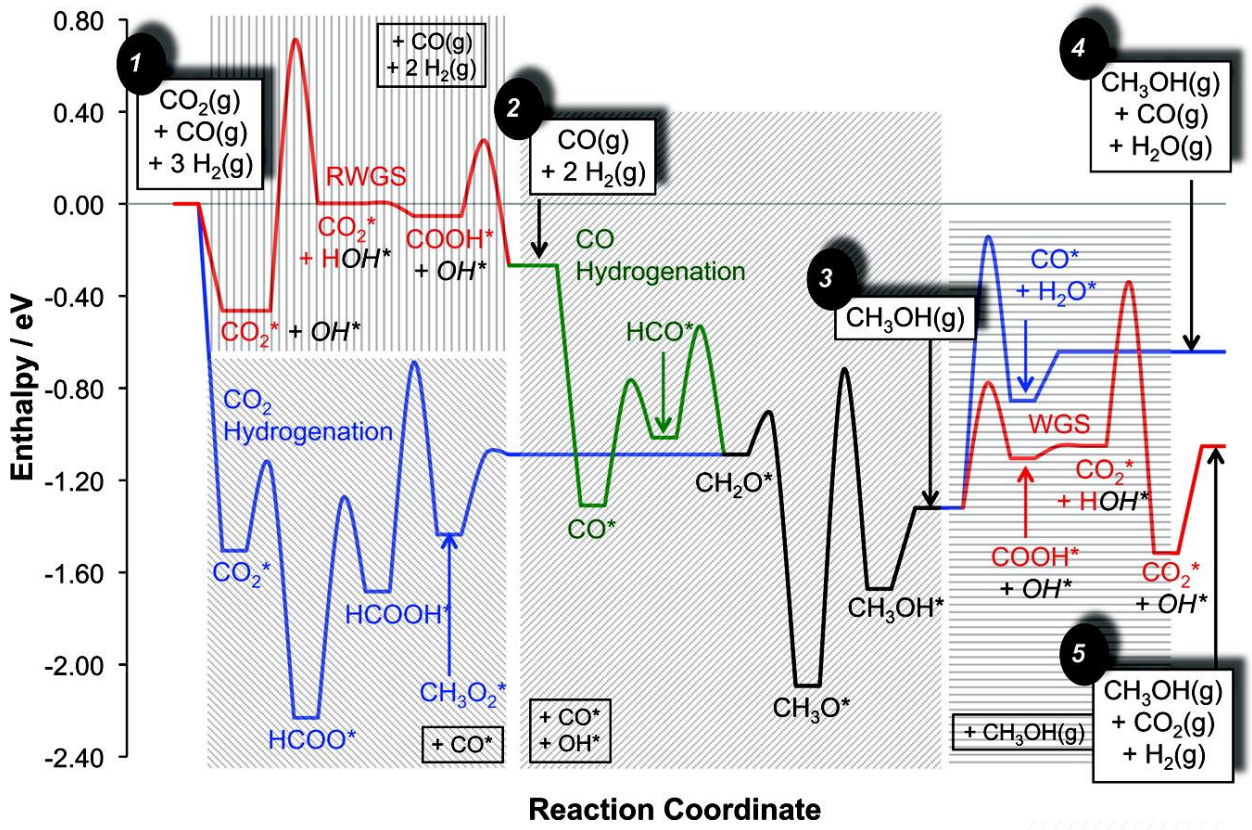
Progress and Current Status

Tasks 5. Microkinetic Model Development **(Accomplished)**

Baseline model

Grabow's MKM CO/CO_2 hydrogenation to methanol + WGS reaction

- Cu(111) surface
- 49 elementary reactions
- 30 chemical species
- DFT ground-state energies
- Vibrational frequencies and Shomate correlation parameters.
- Analyzed temperature range < 540K



Grabow, L. C. & Mavrikakis, M. Mechanism of Methanol Synthesis on Cu through CO_2 and CO Hydrogenation. *ACS Catal*. **2011**, 1, 365–384.

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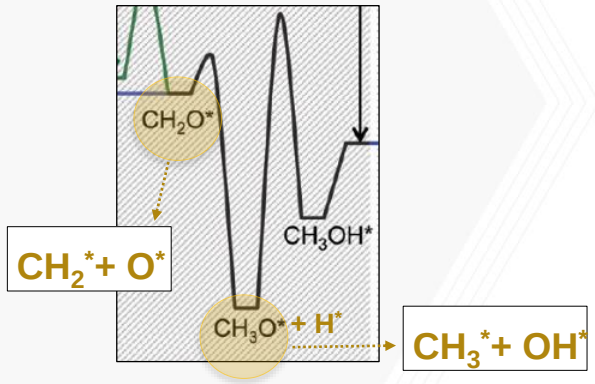
Tasks 5. Microkinetic Model Development **(Accomplished)**

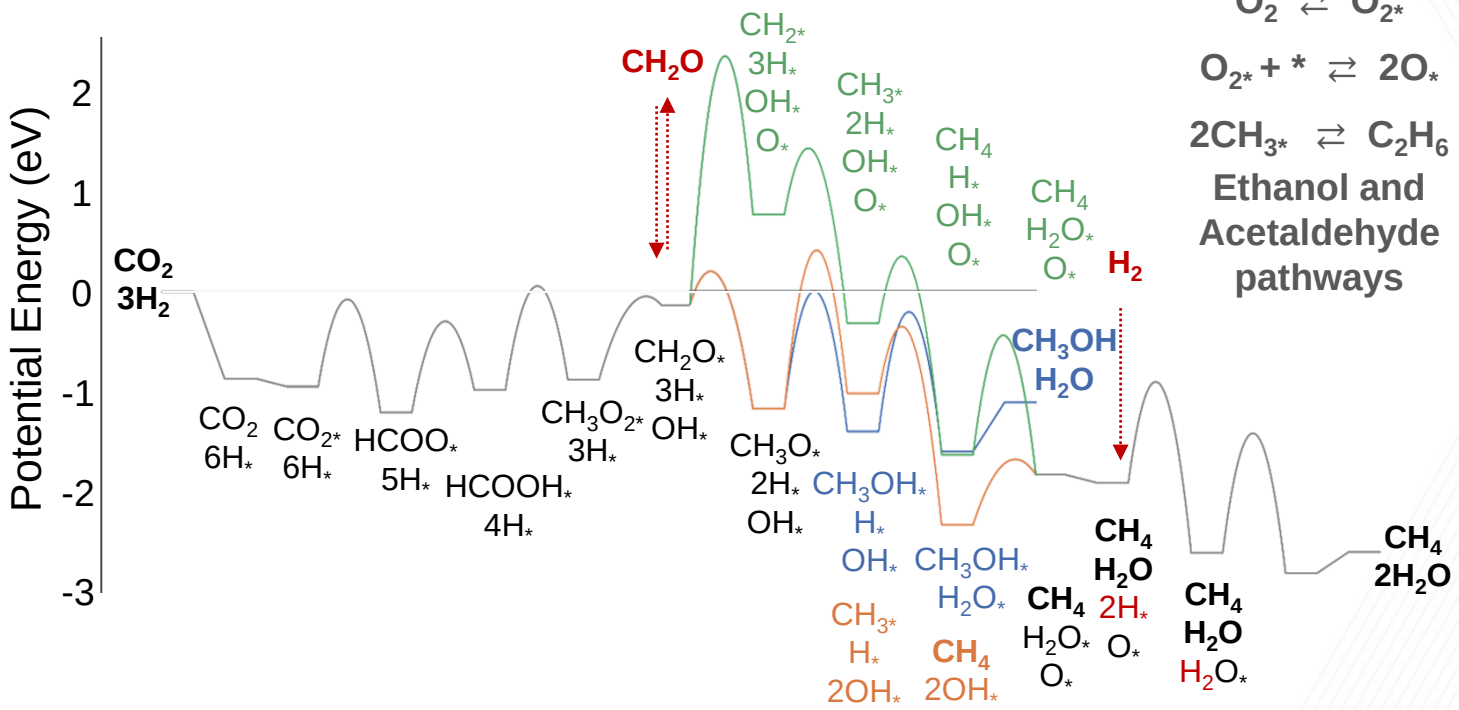
Extended MKM

Added missing routes

- C-O cleavage (hydrocarbons)



- Hydrocarbons associated routes (methane, ethane)
- Higher alcohols route (ethanol, acetaldehyde)



Grabow, L. C. & Mavrikakis, M. Mechanism of Methanol Synthesis on Cu through CO_2 and CO Hydrogenation. *ACS Catal*. **2011**, 1, 365–384.

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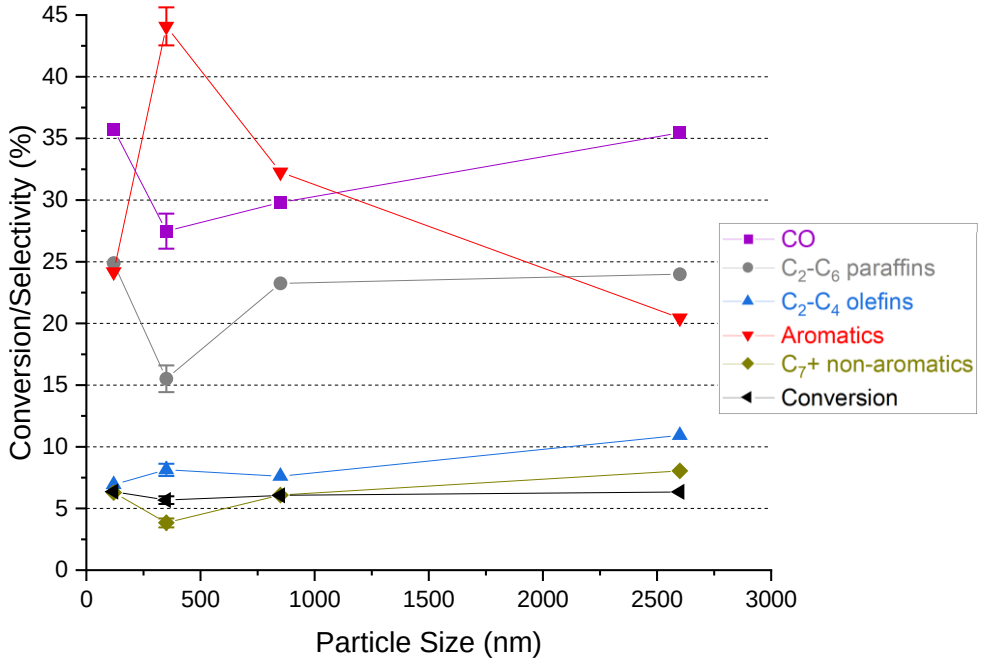
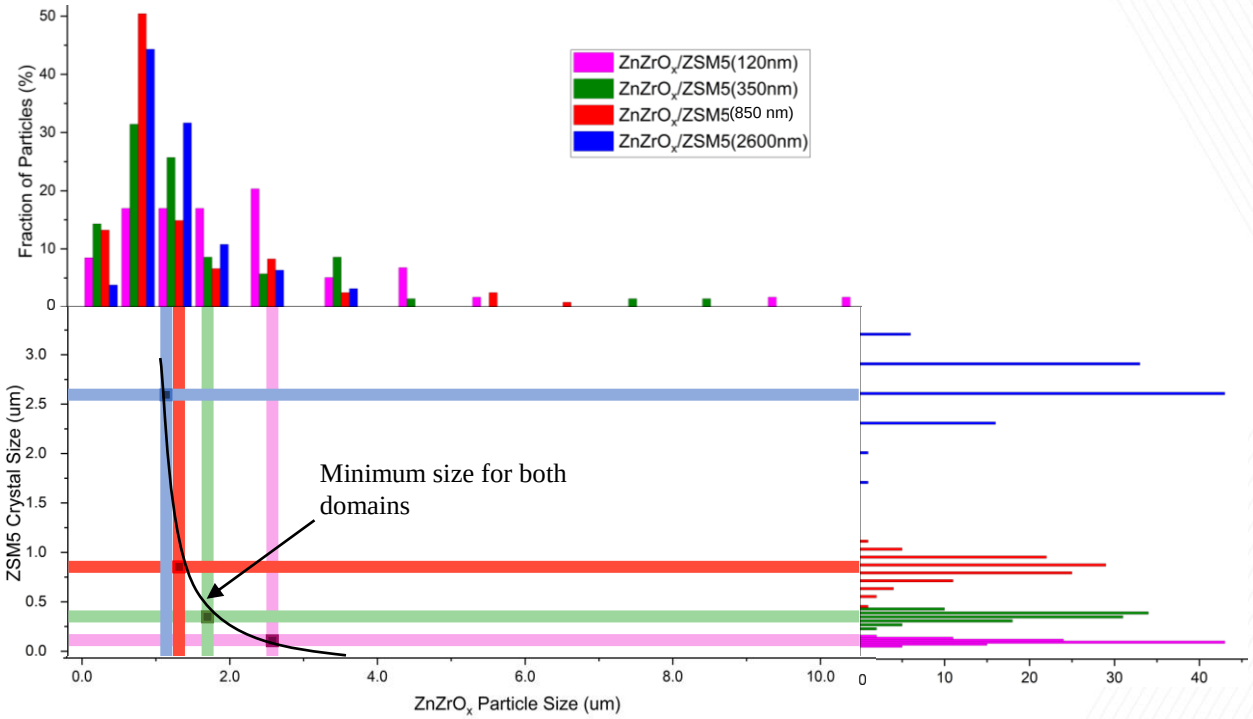
Task 6. Experimental testing of different zeolite crystallite structure sizes **(Accomplished)**

Zn/Zr=1/6, $ZnZrO_x$/ZSM5=1/2, P=600psi,
T=320°C, WHSV=7200mL/g/h, H_2/CO_2=3





- Smaller ZSM5 crystal sizes: shorter diffusion path length for intermediate compounds: better aromatization performance
- Very small ZSM5 crystal sizes: larger $ZnZrO_x$ particles: smaller interfacial surface area between active sites: lower rate of aromatization

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Tasks 7. DFT on Different Transition Metals **(Accomplished)**

Potential Energy Diagram

Baseline Model

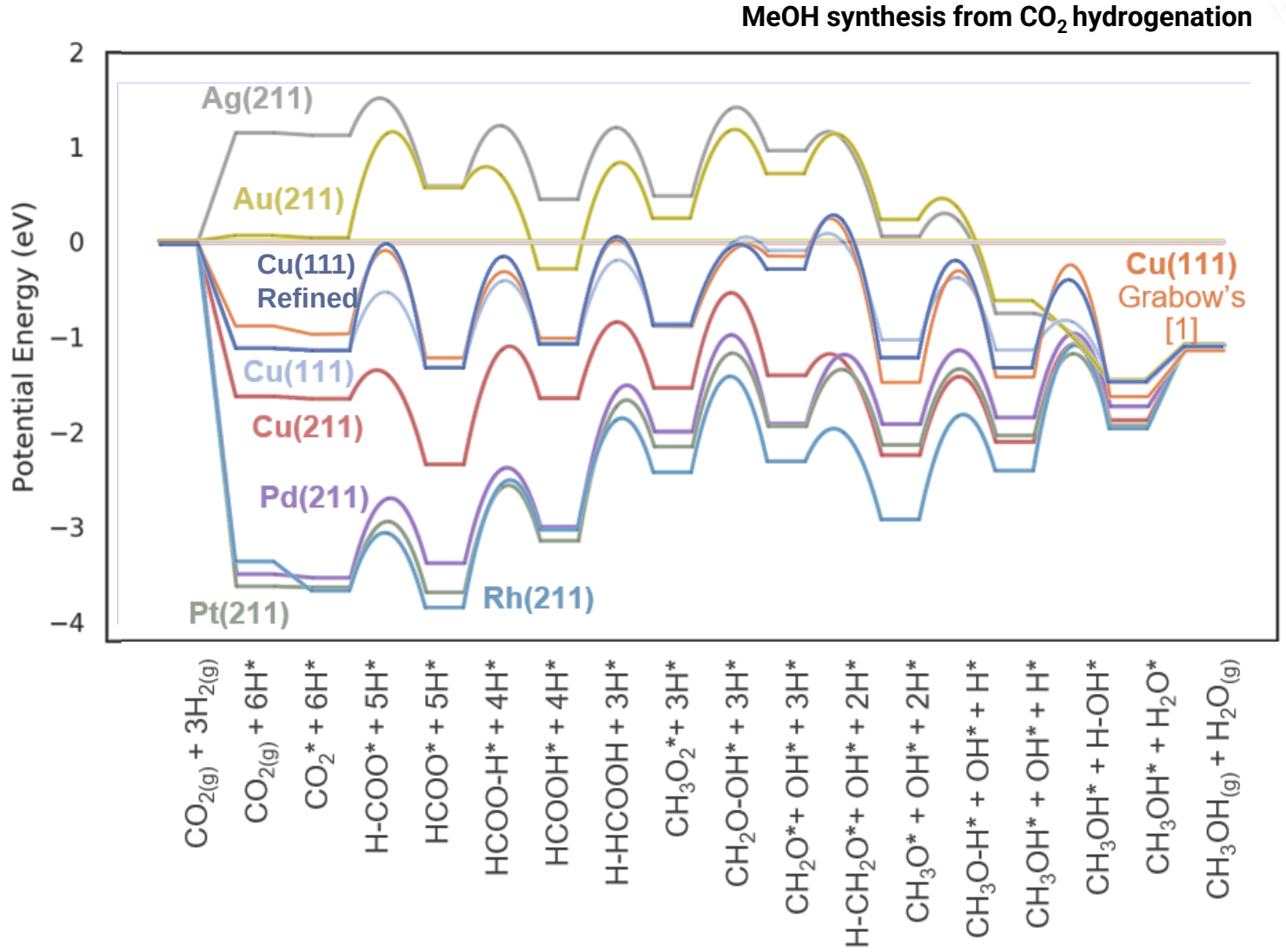
Grabow's Cu(111)

MeOH + RWGS

Extended Model

DFT: Ground-state Energies

Transition State: BEP Scaling relations



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Tasks 7. Screening Model **(Accomplished)**

Binding Energies Screening Model

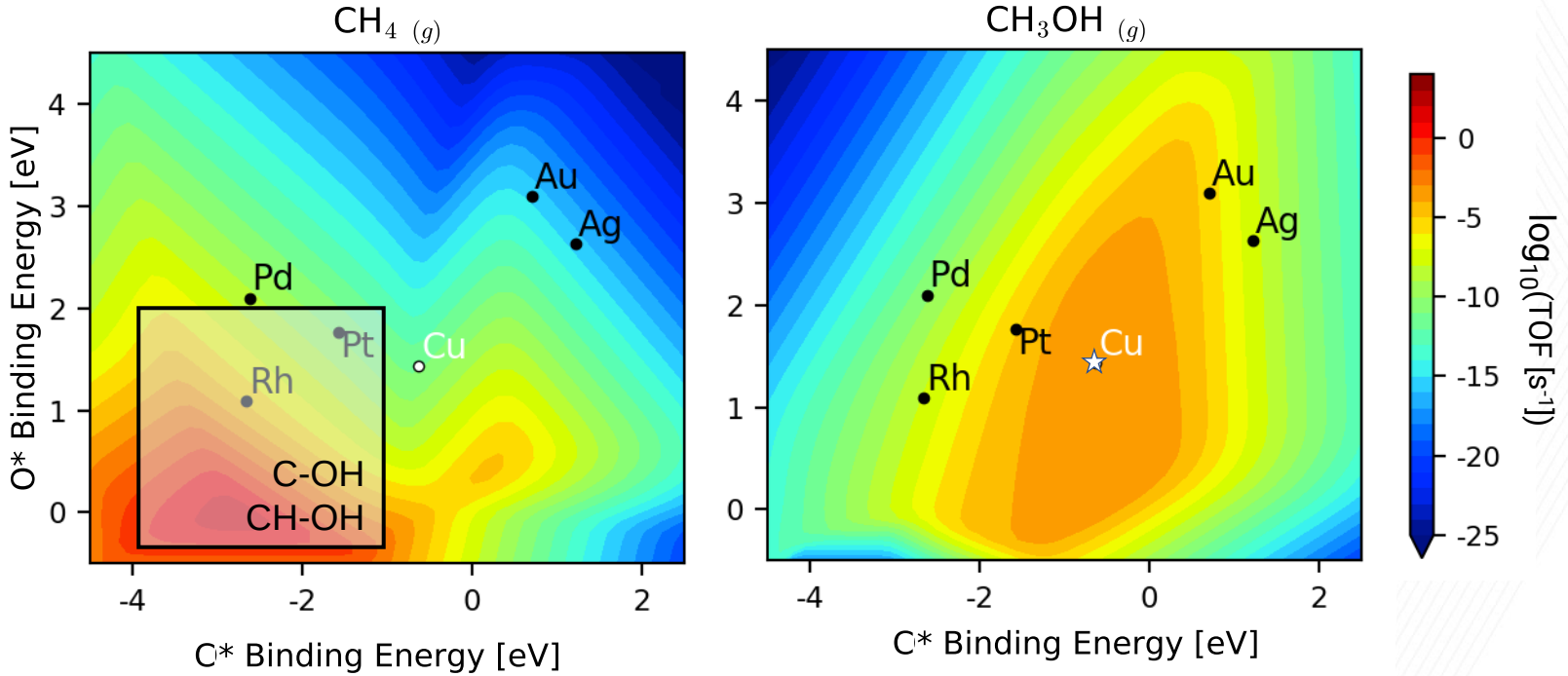
*Provides **trends** in **catalytic activity** as a function of metallic **catalyst binding energies**.*

Extended Model

Four-fold active sites

Cu(211) C-O dissociation pathways

Benchmark against literature results.
TOF: turn-over frequency



T = 593 K, p_{CO} = 30 bar, p_{H2} = 60 bar (0.01 bar H_2O)
as in Syngas to higher alcohols

Medford, A. J. et al. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. J. Catal. 328, 36–42 (2015).

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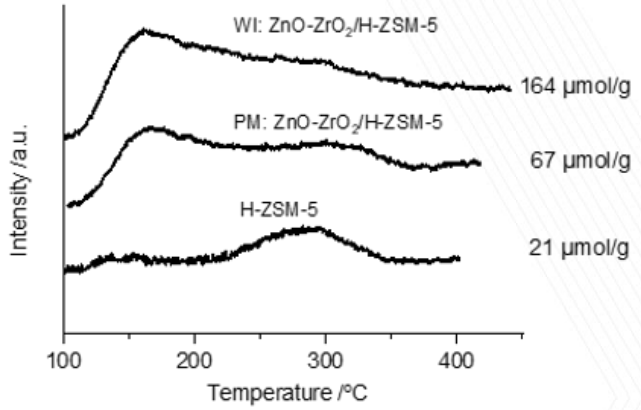
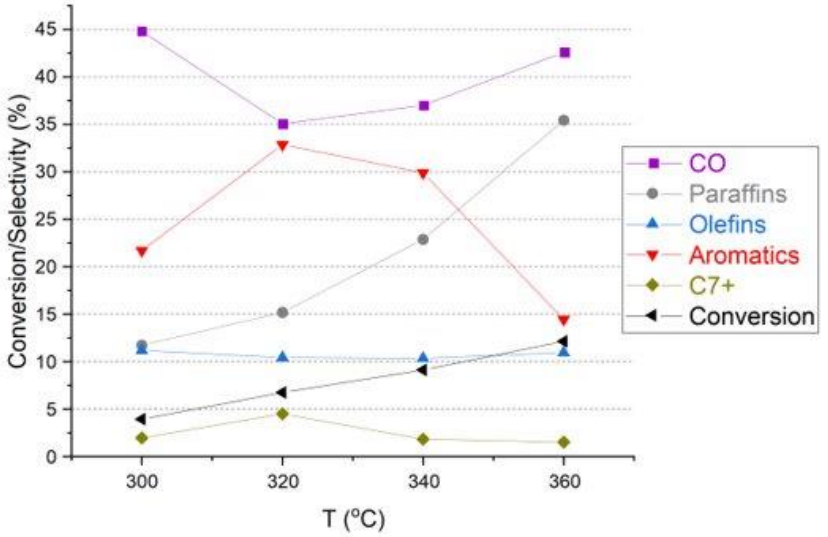
Task 8. Experimental testing of chemical mixtures **(Accomplished)**

- **Goal**: Minimizing the reaction-diffusion length scales (minimizing the chances of intermediates side-reactions)
- NH_3 TPD and XRD results indicate similar types of active sites for the wetness impregnated (WI) and physically mixed (PM) catalysts, while quantified EDS and NH_3 TPD results suggest higher density of metal oxide active sites in the WI catalyst

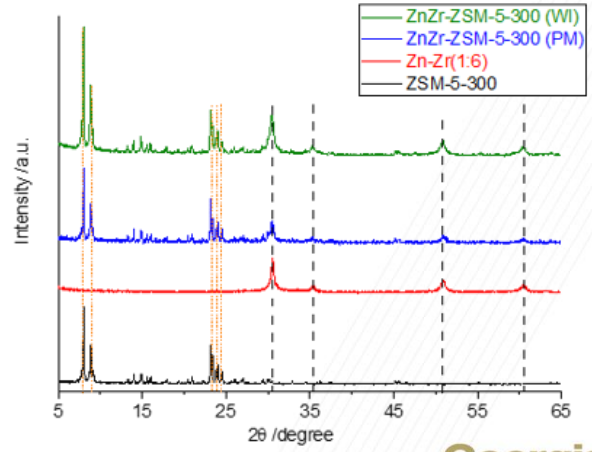
NH_3 TPD



- The WI and PM catalysts show similar behavior at different temperatures: Similar reaction pathways for both catalysts
- Higher CO selectivity for the WI catalyst could be due to a more effective coverage of aromatization active sites by metal oxides in the WI catalyst



XRD



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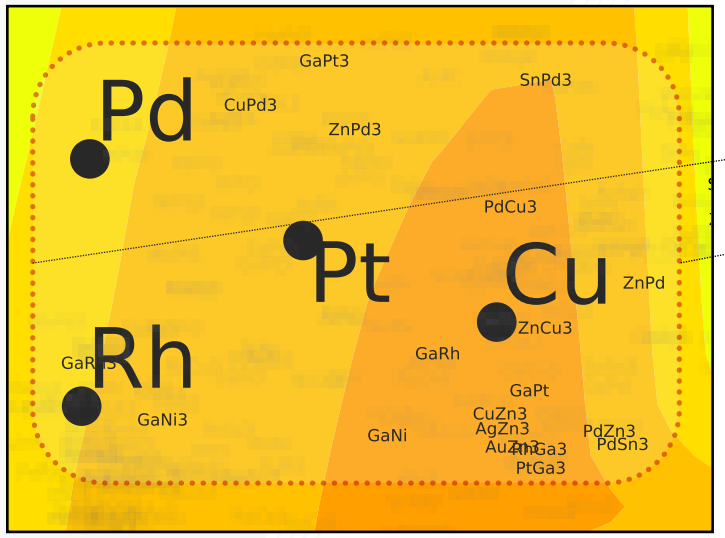
Tasks 9. Alloy Screening **(Accomplished)**

Binding Energies Screening Model

Extended Model

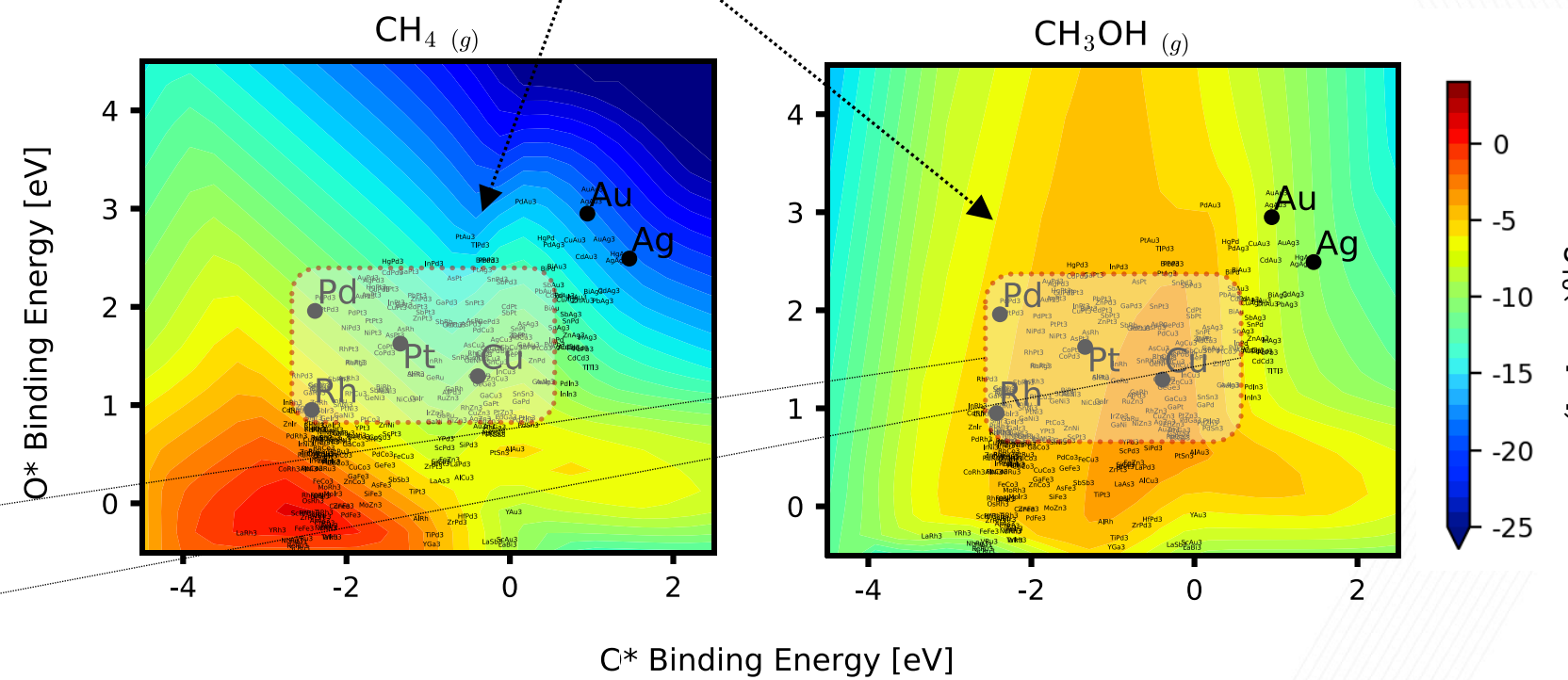
@ equilibrated rWGS

Potential Alloy Candidates



High MeOH
Low CH_4
activity

rWGS-equilibrated conditions



Selectivity: Pd+(Zn/Sn/Cu)

Activity: Zn+(Au/Ag/Cu)

Intermediate: Ga+(Ni/Rh/Pt)

T = 593 K, P = 40 bar;
p_{H2} :p_{CO2}= 3:1
y_{CO} = y_{H2O} = 0.031
y_{CH3OH} = 0. (inlet)

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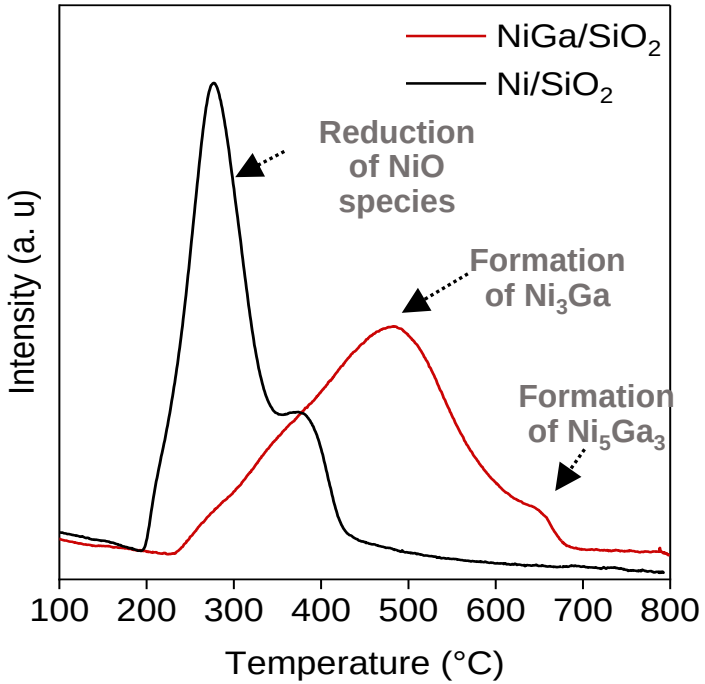
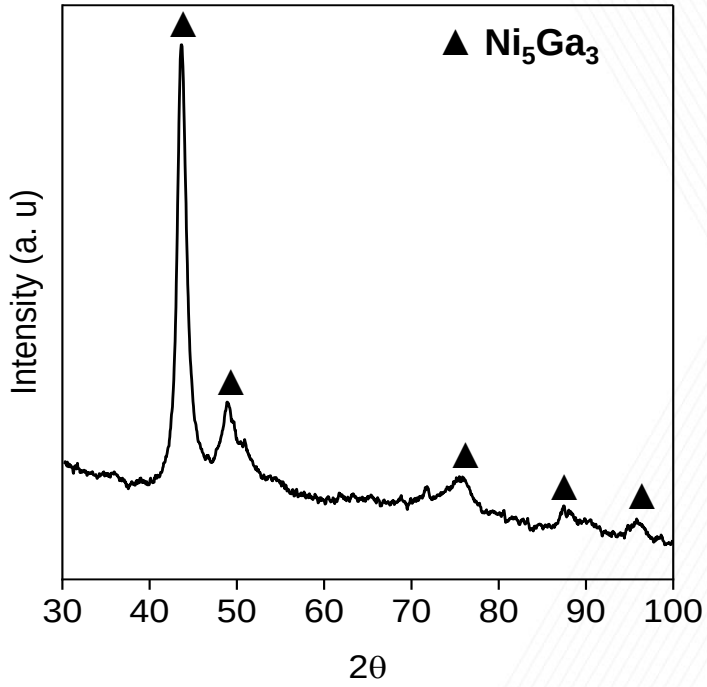
Task 10. Experimental testing of new alloy compositions **(Ongoing)**

Subtask 10.1 – Establish synthesis procedures

- $NiGa/SiO_2$ catalyst synthetized via incipient wetness impregnation.
- Temperature programmed reduction in H_2 evidenced formation of alloys with different stoichiometry
- Incipient wetness impregnation is suitable for Ni-Ga alloy synthesis





XRD pattern of $NiGa/SiO_2$ catalyst after reduction at 700 °C for 2 h in 10% H_2/N_2

Progress and Current Status

Goal: Regression / Inverse Problem

adjust the 5 T-dependent rate parameters based on our experimental data and assume the chemical equilibrium-parameters and prefactors remain the same.

Tasks 11. Macroscale Model **(Ongoing)**

CO_2 to Methanol LHHW-model [1]

($Cu/ZnO/Al_2O_3$) Devised by [2] with eq. constants from [4], further refined by [3].

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} \left(1 - \frac{1}{K_{eq1}} \frac{P_{H_2O} P_{CH_3OH}}{P_{H_2}^3 P_{CO_2}}\right)}{\left(1 + k_2 \frac{P_{H_2O}}{P_{H_2}} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}\right)^3} \quad \left[\frac{\text{mol}}{\text{kg}_{\text{cat}}\ \text{s}}\right] \quad (5)$$

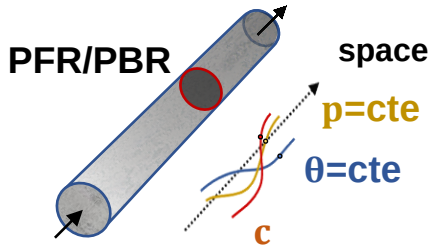
Reverse water gas shift reaction

$$r_{RWGS} = \frac{k_5 P_{CO_2} \left(1 - K_{eq2} \frac{P_{H_2O} P_{CO}}{P_{CO_2} P_{H_2}}\right)}{\left(1 + k_2 \frac{P_{H_2O}}{P_{H_2}} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}\right)} \quad \left[\frac{\text{mol}}{\text{kg}_{\text{cat}}\ \text{s}}\right] \quad (6)$$

$$k_i = A_i \exp\left(\frac{B_i}{RT}\right) \quad (7)$$

$$\log_{10} K_{eq1} = \frac{3066}{T} - 10.592 \quad (8)$$

$$\log_{10} \frac{1}{K_{eq2}} = -\frac{2073}{T} + 2.029 \quad (9)$$



$$\frac{d}{dw}\dot{n} = -f(n)$$

Experimental Data

$ZnZrO_x$: Conversion and Selectivity as a function of WHSV and Temperature

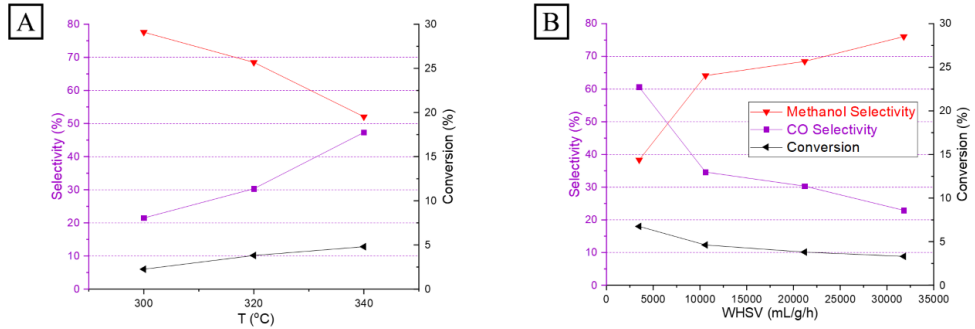


Figure 1. Experimental studies over the $ZnZrO_x$ catalyst. (A) temperature, and (B) WHSV study.

[1] Van-Dal, É. S. & Bouallou, C. Design and simulation of a methanol production plant from CO2 hydrogenation. J. Clean. Prod. 57, 38–45 (2013).
[2] Vanden Bussche, K. M. & Froment, G. F. A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al2O3 catalyst. J. Catal. 161, 1–10 (1996).
[3] Mignard, D. & Pritchard, C. On the use of electrolytic hydrogen from variable renewable energies for the enhanced conversion of biomass to fuels. Chem. Eng. Res. Des. 86, 473–487 (2008).
[4] Graaf, G. H., Sijtsema, P. J. J. M., Stamhuis, E. J. & Joosten, G. E. H. Chemical equilibria in methanol synthesis. Chem. Eng. Sci. 41, 2883–2890 (1986).

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Future Plans

Current Project

Assess the performance of bimetallic catalysts for CO_2-MeOH-BTX in conjunction with ZSM-5.

Develop/adjust the MeOH to BTX macroscale model based on $ZnZrO_x$:ZSM-5 experimental results

Finalize LCA and carbon footprint studies (AspenPlus) based on the final macroscale model

Future Projects and Scale-up Potential

Preliminary Results: Hydrogen input (as electricity from electrolysis) contributes largely to the OPEX

Pure CO_2 feed is preferred to reduce N_2 purge losses.

rWGS reaction still prevails (faster) in most CO_2 and CO to MeOH catalytic routes. FT routes fare better.

Equilibrating the rWGS reaction would lead to higher yield to species in (CO/CO_2-MeOH-BTX);

However, it requires CO recycle and, thus, selective downstream separation trains

Thank you!

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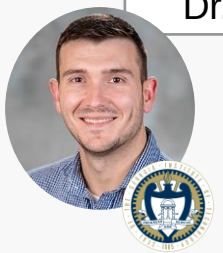
Organizational Chart

DOE Award #: DE-FE003171

Project Director
Dr. C. W. Jones

NETL Program Manager
Mariah Richardson

Contributing Principal Investigator
Dr. Andrew Medford



Senior/Key Investigator
Dr. Matthew Realff

Direct Contributing Personnel

Dr. I. Nezam

Gabriel Gusmao

Indirect and Past Contributors

Dr. K. Golub

Wei Zhou

Gantt Chart

Task	Team Member	Description	Project Year 1				Project Year 2				Project Year 3				M	S	Start Date	End Date
			Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12				
1	CWJ; AJM	Project Management Plan													M1		1/1/2019	12/30/2021
2	CWJ; AJM; MJR	Technology Maturation Plan															2/1/2019	6/30/2019
3	CWJ	Retrofitting Reactor															4/1/2019	8/30/2019
4.1	CWJ	Synthesis, characterization, reactor testing of separate metal catalysts and ZSM5															2/1/2019	8/30/2020
4.2		Synthesis, characterization, reactor testing of physical mixtures													M2		4/1/2019	9/30/2020
4.3		Experimental evaluation of impact of CO2/H2 ratio													M3	S1	5/1/2020	11/30/2020
5.1	AJM	Develop microkinetic model															2/1/2019	5/15/2019
5.2		Calculate DFT-based rates															2/1/2019	10/15/2019
5.3		Calculate rates under varied conditions													M4	S2	8/1/2019	12/31/2019
6.1	CWJ	ZSM5: Establish synthesis procedures															5/15/2019	10/15/2019
6.2		Experimental evaluation of impact of crystallite size													M5		11/1/2020	2/28/2021
7.1	AJM	DFT calculations of other TMs													M6		10/15/2019	9/30/2020
7.2		CatMAP screening model															4/1/2020	12/30/2020
7.3		Screening model under various conditions													M7		5/1/2020	3/30/2021
8.1	CWJ	Chemical Mixtures: Establish synthesis procedures															8/1/2020	12/30/2020
8.2		Experimental evaluation of intimate mixing of acid and metal domains															12/1/2020	4/30/2021
9.1	AJM	Compute descriptors on binary alloys															4/1/2020	3/30/2021
9.2		Predict alloy catalysts															10/1/2020	6/30/2021
10.1	CWJ	New Alloy Composition: Establish synthesis procedures															3/1/2021	6/30/2021
10.2		Experimental evaluation of impact intimate mixing of acid and metal domains													M8		3/1/2021	9/30/2021
11.1	AJM	Macroscale model development															1/1/2021	3/30/2021
11.2		Model combination/Integration with CatMAP															1/1/2021	9/30/2021
11.3		Extend CatMAP to varid conversion prediction														S3	10/1/2021	12/30/2021
12	CWJ	Experimental optimization of conditions for best alloy															7/1/2021	12/30/2021
13.1	CWJ; AJM	Calculate carbon footprint of this process based on the collected data															7/1/2021	12/30/2021
13.2		Determine if using raw flue gas (15% CO2) or concentrated CO2 improves techno-economics															7/1/2021	12/30/2021

Risks

Perceived Risk	Risk Rating (Low, Med, High)			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
Existing equipment failure, replacement funds not in budget	Low	Med	Low	Much of the existing reactor will be retrofitted with new parts. Old GC will remain. GC failure after proper maintenance and only 10 yr use unlikely. Lab has >5 other GCs that might be used in its place.
Cost/Schedule Risks:				
Delayed hiring of personnel	Med	High	Med	PIs will seek applicants for project before notification of award. PIs will seek applicants already at Georgia Tech.
Delayed delivery of required analysis component(s) (gas tanks, materials)	Low	Med	Low	Spare parts will be available on-hand in most cases.
COVID-19 shutdown extends beyond July 1st 2020, or similar shutdown situation happens again	Med	High	Med	Experimental tasks (that need on-site presence) will be re-scheduled/prioritized to obtain critical required data in a timely manner.
Technical/Scope Risks:				
CatMAP screening fails	Low	Med	Med	CatMAP screening has been used for numerous reactions, but not CO_2 to aromatics. Initial failure will require more detail be incorporated into screening, which could delay the project progression. This will be mitigated by using models that have proven successful for syngas hydrogenation to alcohols as a starting point, and by employing uncertainty quantification to improve robustness.
Screening of only [211] surfaces does not produce insight	Low	Med	Low	Additional metal surfaces, likely [111], need to be considered. This is unlikely since previous screening models of similar reactions have been successful with [211] model surfaces. This risk can easily be mitigated by adding approximately 3 months to the timeline to complete DFT calculations on the [111] surfaces.
Suggested metal oxides do not provide satisfying results for aromatics production	Med	Med	Med	An up-to-date literature review will be conducted to identify and test alternative options.
Coupling of reaction/transport between zeolite and catalyst cannot be approximated with proposed screening approach	Med	Med	Med	Spatial gradients in reactant/product concentration may play an important role in selectivity patterns. This will make it difficult to directly predict selectivity from existing models. This risk will be mitigated by the use of probabilistic screening that is more robust to errors, and if necessary, a PFR reactor model can be implemented in CatMAP to better account for transport issues.
Zeolite MFI does not produce BTX	Low	Low	Low	MFI is the most commercially applied zeolite. It is highly effective at aromatization. If fails, other zeolites can be used from vendors, or synthesized by Jones.
Predicted alloy unable to be synthesized experimentally as small, bimetallic nanoparticles	Med	Med	Med	Some metals are not stable as bimetallic nanoparticles or are not accessible via traditional synthesis routes. Alternative, more advance routes can be taken or alternative alloys can be attempted.
Management Risks:				
Team collaboration and communication is poor	Low	Med	Low	Jones, Medford, Realff work together in the same building at Georgia Tech. Jones/Realff and have worked together before.
Planning and Oversight Risks:				
None perceived.				
ES&H Risks:				
Accident associated with experimental testing	Low	High	Low	Laboratory designed for high pressure catalytic reactions. Gas cabinets, CO monitors, and computer-controlled reactor already in place. Jones is Chair of Georgia Tech Institute Council on Environmental Health & Safety
External Factor Risks:				
None perceived.				

Risks

Perceived Risk	Risk Rating (Low, Med, High)			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
Existing equipment failure, replacement funds not in budget	Low	Med	Low	Much of the existing reactor will be retrofitted with new parts. Old GC will remain. GC failure after proper maintenance and only 10 yr use unlikely. Lab has >5 other GCs that might be used in its place.
Cost/Schedule Risks:				
Delayed hiring of personnel	Med	High	Med	PIs will seek applicants for project before notification of award. PIs will seek applicants already at Georgia Tech.
Delayed delivery of required analysis component(s) (gas tanks, materials)	Low	Med	Low	Spare parts will be available on-hand in most cases.
COVID-19 shutdown extends beyond July 1st 2020, or similar shutdown situation happens again	Med	High	Med	Experimental tasks (that need on-site presence) will be re-scheduled/prioritized to obtain critical required data in a timely manner.
Technical/Scope Risks:				
CatMAP screening fails	Low	Med	Med	CatMAP screening has been used for numerous reactions, but not CO_2 to aromatics. Initial failure will require more detail be incorporated into screening, which could delay the project progression. This will be mitigated by using models that have proven successful for syngas hydrogenation to alcohols as a starting point, and by employing uncertainty quantification to improve robustness.
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Coupling of reaction/transport between zeolite and catalyst cannot be approximated with proposed screening approach	Med	Med	Med	Spatial gradients in reactant/product concentration may play an important role in selectivity patterns. This will make it difficult to directly predict selectivity from existing models. This risk will be mitigated by the use of probabilistic screening that is more robust to errors, and if necessary, a PFR reactor model can be implemented in CatMAP to better account for transport issues.
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Management Risks:				
Team collaboration and communication is poor	Low	Med	Low	Jones, Medford, Realff work together in the same building at Georgia Tech. Jones/Realff and have worked together before.
Planning and Oversight Risks:				
None perceived.				
ES&H Risks:				
Accident associated with experimental testing	Low	High	Low	Laboratory designed for high pressure catalytic reactions. Gas cabinets, CO monitors, and computer-controlled reactor already in place. Jones is Chair of Georgia Tech Institute Council on Environmental Health & Safety
External Factor Risks:				
None perceived.				

Risks

Perceived Risk	Risk Rating (Low, Med, High)			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
COVID-19 shutdown extends beyond July 1st 2020, or similar shutdown situation happens again	Med	High	Med	Experimental tasks (that need on-site presence) will be re-scheduled/prioritized to obtain critical required data in a timely manner.
				Laboratory shutdown is unlikely based on GT experience in summer 2020 with safe research operation. If shutdown were to occur, we would likely request a No-Cost-Extension.
Technical/Scope Risks:				
CatMAP screening fails	Low	Med	Med	CatMAP screening has been used for numerous reactions, but not CO_2 to aromatics. Initial failure will require more detail be incorporated into screening, which could delay the project progression. This will be mitigated by using models that have proven successful for syngas hydrogenation to alcohols as a starting point, and by employing uncertainty quantification to improve robustness.
Screening of only [211] surfaces does not produce insight	Low	Med	Low	Additional metal surfaces, likely [111], need to be considered. This is unlikely since previous screening models of similar reactions have been successful with [211] model surfaces. This risk can easily be mitigated by adding approximately 3 months to the timeline to complete DFT calculations on the [111] surfaces.
Coupling of reaction/transport between zeolite and catalyst cannot be approximated with proposed screening approach	Med	Med	Med	Spatial gradients in reactant/product concentration may play an important role in selectivity patterns. This will make it difficult to directly predict selectivity from existing models. This risk will be mitigated by the use of probabilistic screening that is more robust to errors, and if necessary, a PFR reactor model can be implemented in CatMAP to better account for transport issues.
Predicted alloy unable to be synthesized experimentally as small, bimetallic nanoparticles	Med	Med	Med	Some metals are not stable as bimetallic nanoparticles or are not accessible via traditional synthesis routes. Alternative, more advance routes can be taken or alternative alloys can be attempted.
				Close communication between experiment and theory researchers critical. Begin synthesizing new alloys as soon as preliminary data suggest a possible “hit” from computational screening. Err on side of having too many samples vs too few.
Management Risks:				

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Success Criteria

S #	(Sub)Task #	Decision Point	Date	Success Criteria
1	4.3	Experimental evaluation of impact of CO_2/H_2 ratio	11/30/2020	Table of steady-state conversion and selectivity for physical mixtures with the minimum aromatics selectivity of 20% in total carbon or 50% in hydrocarbon products for at least one condition at different CO_2/H_2 ratios
2	5.3	Calculate rates under varied conditions	12/31/2019	Agreement between calculations of rate/selectivity from microkinetic model and experimental results for baseline system
3	11.3	Predict performance under observed conditions	12/31/2021	Agreement between calculation of rate/selectivity between microkinetic model and experimental results under optimal operating conditions for best catalyst

Planned Work

Ongoing Tasks:

Task 10.0 – Experimental testing of new alloy compositions

Subtask 10.1 – Establish synthesis procedures: The Recipient will carry out the synthesis and routine characterization of computationally predicted alloy nanoparticles on Al_2O_3. These catalysts will be physically mixed with ZSM5 crystals of size determined from Task 6.0 to have the optimal diffusion-reaction length scales. **June 2021**

Subtask 10.2 – Experimental evaluation of alloys: Steady-state conversion testing, measuring rates and selectivities, will be completed. **Sep. 2021**

Task 11.0 – Refine mechanism based on presence of aromatics

Subtask 11.1 – Macroscale model development: The Recipient will develop macro-scale kinetic model of conversion of methanol (COMPLETED) /alkanes to aromatics (LATE) based on experimental results. **Mar. 2021**

Planned Work

Future Tasks:

Task 11.0 – Refine mechanism based on presence of aromatics

Subtask 11.2 – Model combination/integration: The Recipient will integrate the macro-scale kinetic model with the micro-kinetic model in CatMAP. **Sep. 2021**

Subtask 11.3 – Extended CatMAP to varied conversion prediction: The Recipient will use the CatMAP model to evaluate activity/selectivity as a function of conversion to aromatics. **Dec. 2021**

Task 12.0 – Experimental optimization of conditions for best alloy

Steady-state conversion testing, measuring rates and selectivities as a function of CO_2/H_2 ratio, will be experimentally completed. **Dec. 2021**

Planned Work

Future Tasks:

Task 13.0 – Technology assessment of intensified reactor

Subtask 13.1 – Carbon footprint: The Recipient will calculate carbon footprint of this process based on the collected data. This will be a key component of a life cycle assessment (LCA) focused on the reactions proposed and the reactor. The recipient will consider the use of water by the process, and the derived measures of LCA from energy use such as contributions to eutrophication and acid rain using standard LCA tools. The boundary of the process will be the reactor system necessary to convert CO2 from coal into aromatic products and will not include separation, distribution and ultimate fate of those aromatics within a chemical complex. **Dec. 2021**

Subtask 13.2 – Assess need for CO_2 purification: The Recipient will determine if using raw flue gas (15% CO_2) is feasible for aromatics production, or whether use of concentrated CO_2 improves overall techno-economics. **Dec. 2021**

Thank you!

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