Methane Partial Oxidation over Multifunctional 2-D Materials

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U.S. Department of Energy, NETL
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Goals and objectives

1) Design, synthesize, and evaluate highly selective, active, and stable multifunctional catalysts for the low temperature (< 500 K) partial oxidation of methane to methanol (MTM) with molecular oxygen:

$$CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(g).$$

2) As a materials platform, we investigate single atom catalysts embedded and stabilized in 2-D materials such as graphene and "supported" on Group VIII and IB transition metals such as Ni.

Funding, Performance Dates, Participants

DOE Funding: $1,000,000 Cost Share: $261,624

Performance Dates: March 20, 2020 – March 19, 2023

Project Participants:

University of South Carolina: Andreas Heyden
– Project management and planning
– Computational design of doped GR-based catalysts for the low temperature MTM

Pajarito Powder LLC: Barr Zulevi (resigned from PP in Sept. 2022), Geoff McCool
– Synthesis and characterization of computationally predicted actives and powder catalysts
– Process design and TEA of the MTM catalyst system (potential commercialization)

CU Boulder: Will Medlin
– Characterization (and minimal synthesis) of active sites and powder catalysts
– Experimental evaluation of catalysts for partial oxidation of MTM

Current CH_4 valorization: energy- and capital-intensive

B. Wang et al. / *Catalysis Today* 285 (2017) 147–158

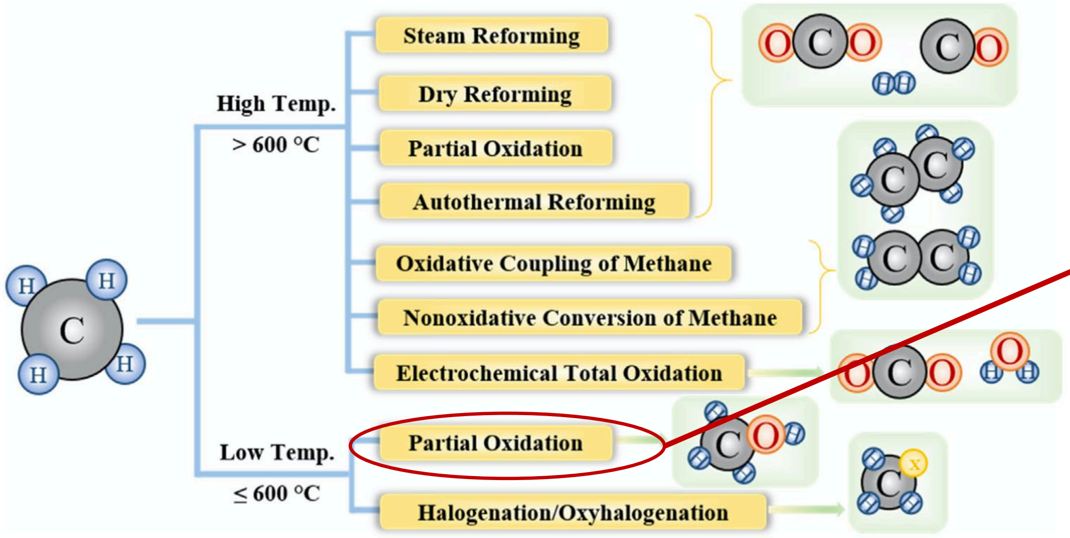


Fig. 1. Schematic of selected methane conversion processes at high- and low-temperatures.

Reforming $CH_4 + CO_2 \text{ -> } 2CO + 2H_2$ (>640 °C)

$CH_4 + H_2O \text{ -> } CO + 3H_2$ (815-925°C, 200-600psi)

Methanol production $2H_2 + CO \text{ -> } CH_3OH$ (200-315°C, 600-1700psi)

Fischer–Tropsch $(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

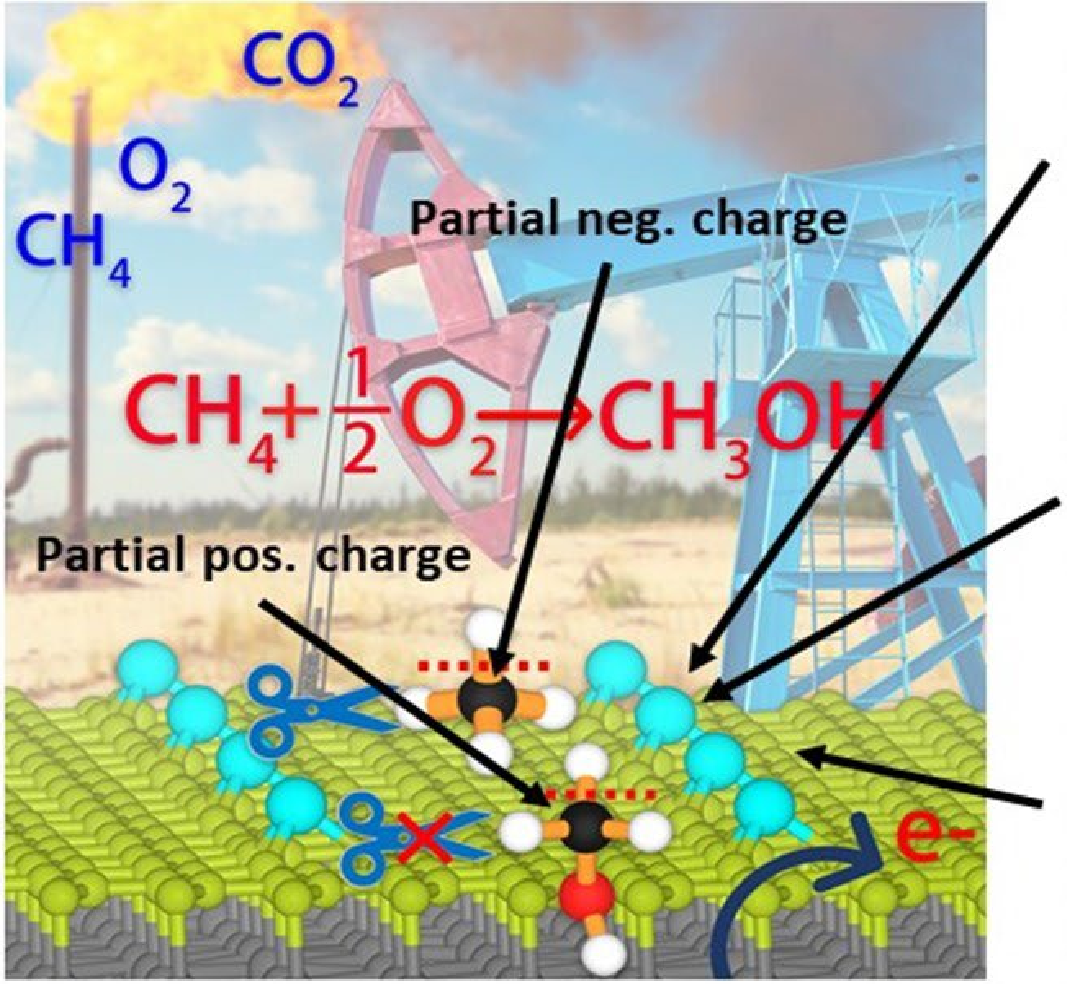
Challenges:

- Only large-scale methanol production is economically feasible
- Methane storage and transportation
- Distributed methane production

$2CH_4 + O_2 \text{ -> } 2CH_3OH$

Side reactions:
Oxidation of CH_4 to CO, CO_2, H_2O
Coupling reactions to C_2H_6

Idea for Goals and Objectives – Technology Background



MTM concept for catalyst design

Single metal site that strongly interacts with CH_3-group during C-H bond activation in CH_4 to enable surface-stabilized versus radical mechanism

Single metal site with pos. partial charge to create electrostatic driving force for distinguishing C-H activation in CH_4 and CH_3OH

Single metal site embedded in GR that can activate O_2 close to metal site due to interaction with metal support and e^- donation to GR leading to adsorbed $O_2^{\delta-}$

Computational design

Novel synthesis methods

Catalyst characterization & evaluation

Big Picture – Technology Background

- Use novel materials and methods previously not available to solve flaring problem (*catalyst development guided by computational design*)
- Process intensification at the macroscale: moving away from two-step methanol synthesis based on syngas; eliminating need for pure oxygen
- Process intensification at the nano-scale: engineering of reaction pathways on catalyst surface
- Liquid product, no oxygen plant, one reactor, relatively mild operating conditions, high selectivity => applicable to remote flare sites
- Methanol is a potential future H_2 carrier to decarbonize natural gas

Project risks and mitigation strategies

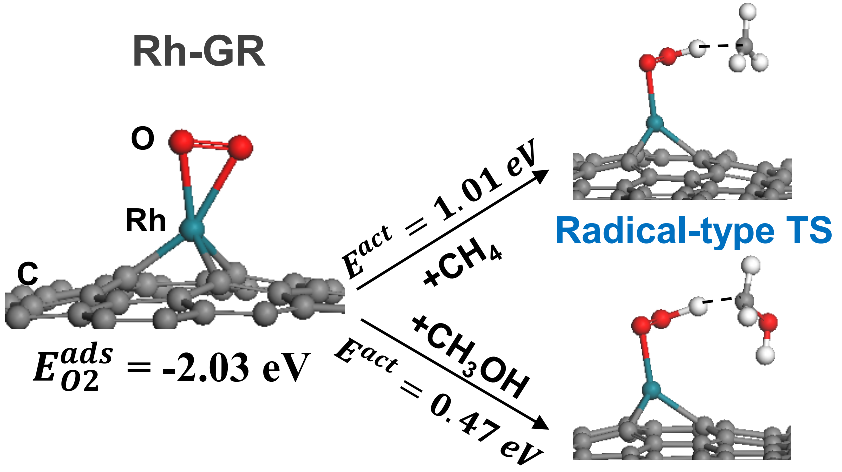
Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	(Low, Med, High)			
Technical/Scope Risks:				
Computational predictions significantly overestimate active site performance due to modeling accuracy issues and neglect of kinetically relevant reaction pathways	Medium	Medium	Medium	While it might be possible that the computational methodology slightly overestimates active site performance, the errors are likely small enough that interesting materials can still be identified. Also, due to the application of the proposed feedback loop, the reaction network under investigation can be extended during the project to ensure consideration of all kinetically relevant reaction pathways.
Difficulty in synthesis of computationally predicted most interesting catalysts	High	Medium	High	While it might be challenging to synthesize the best computationally predicted active site structures, by using a feedback loop in our computations that considers the experimental synthesizability of active sites, it should be possible to synthesize active site structures with interesting catalytic properties for the MTM.
Low site density of active sites in the synthesized powder catalysts	Medium	Low	Low	A low site density would require a larger amount of catalyst and a larger reactor which might affect the process economics. Nevertheless, this risk should not determine the success of this three-year project but might instead lead to future research aimed at increasing the site density.
Catalyst stability is too low for practical utilization in an industrial process	Medium	Low	Low	Dependent on the severity of catalyst deactivation, this could become a research topic for a follow-up study if otherwise the performance is excellent. By studying many active site models, we expect that some display good stability in the reaction environment.

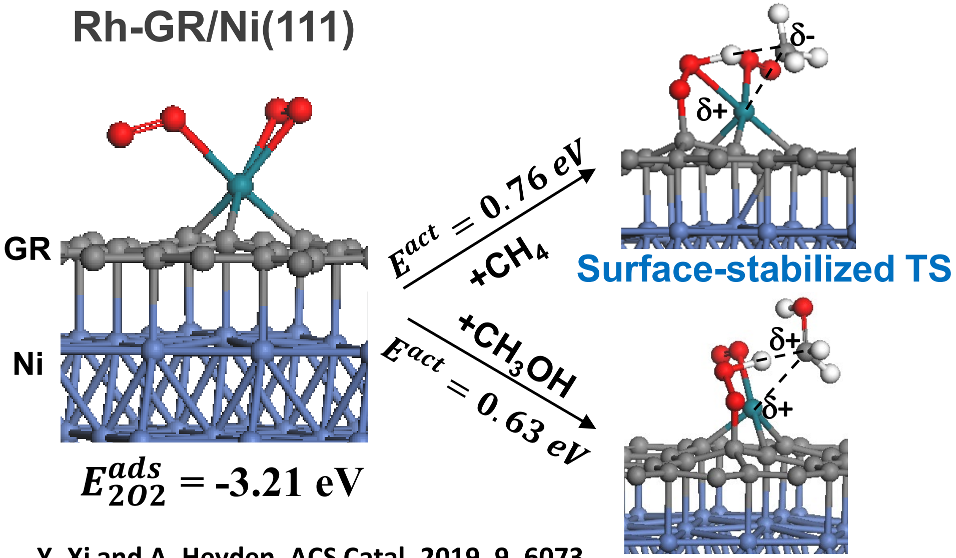
Products/success criteria

Several reports will be submitted to DOE that describe progress towards achieving the following success criteria:

1) A series of active site structures with desirable activity and selectivity characteristic for the MTM will be computationally predicted for experimental synthesis and evaluation.
2) A series of catalysts containing 2-D carbon-based, nitrogen- and metal-doped materials interfaced with metal nanoparticles will be generated. To demonstrate the capability to prepare designed materials, at least four different types of metals will be incorporated into the interfacial structures.
3) Large (at least five-fold) differences in methanol production rates will be observed for structures with nanoparticle/2-D material interfaces compared to structures containing only one component, demonstrating the hypothesized bifunctional mechanism.
4) At least one of the prepared catalysts will achieve a methanol selectivity of > 50% at conversion values of at least 20% during gas-phase MTM reactions.
5) Process design and TEA of proposed MTM catalyst system that suggests economic feasibility of the process at remote locations near shale oil sites.

Computational design of doped GR-based MTM catalysts





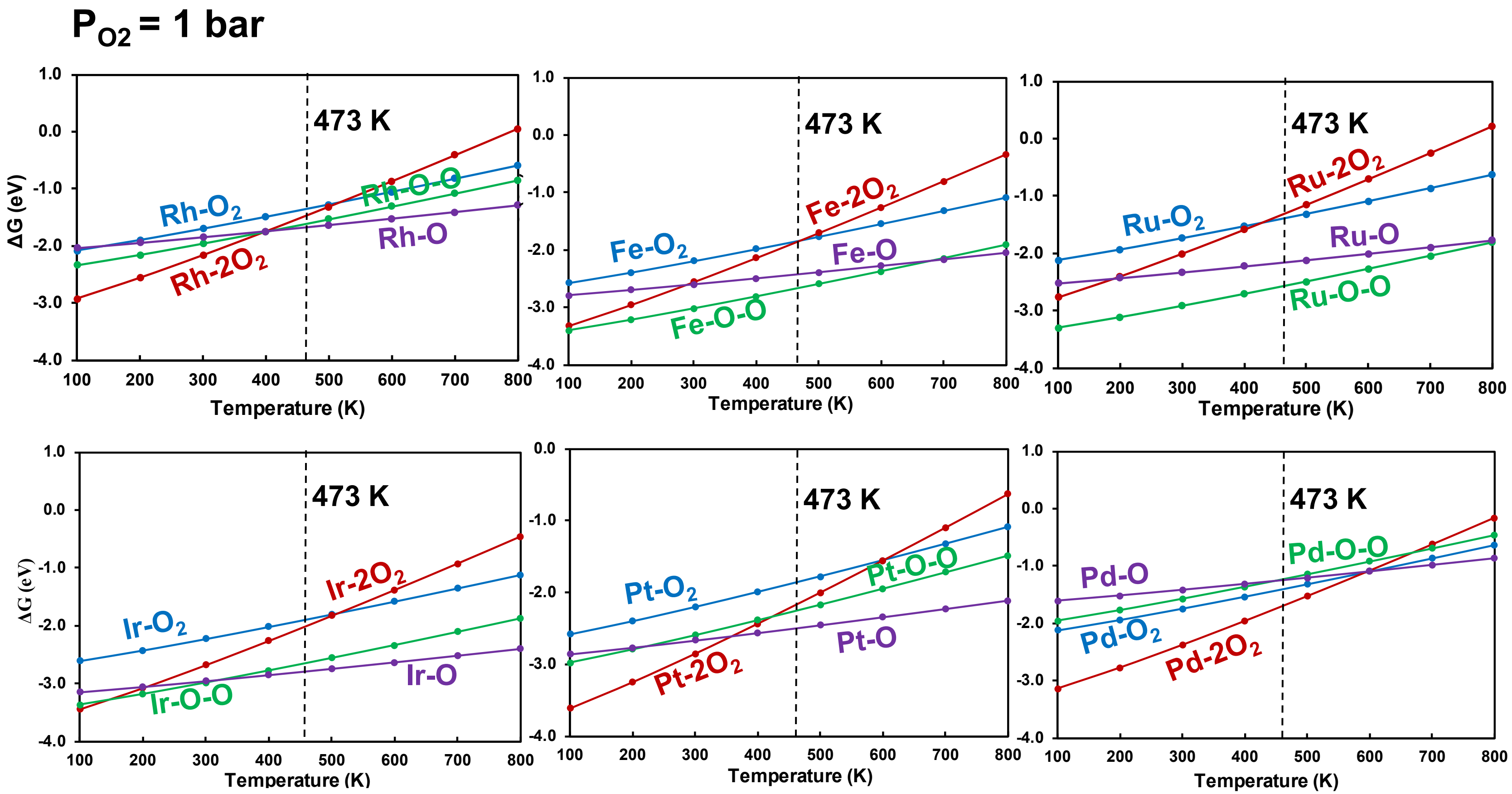
Y. Xi and A. Heyden, ACS Catal. 2019, 9, 6073

Rh-doped graphene catalysts for MTM

- Adsorption of only one O_2 is favored on Rh-GR
- Overall free energy barrier for MTM is 2.02 eV ⇒ low activity
- Radical-type TS affects the selectivity towards CH_3OH production (C-H activation barrier of CH_3OH is 0.54 eV lower than that of CH_4)

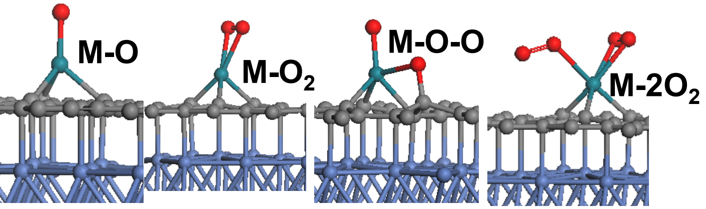
- Ni support enables adsorption of additional O_2 molecule on Rh
- Surface-stabilized TS was found at Rh/C interface and overall free energy barrier for MTM is 1.37 eV ⇒ improved activity
- Free energy barrier of CH_4 C-H activation is ~0.2 eV lower than CH_3OH ⇒ Electronic atomic monolayer-metal support interaction (EAMSI) promotes the activity and selectivity towards methanol formation

Computational design of single metal-doped graphene supported on Ni(111)



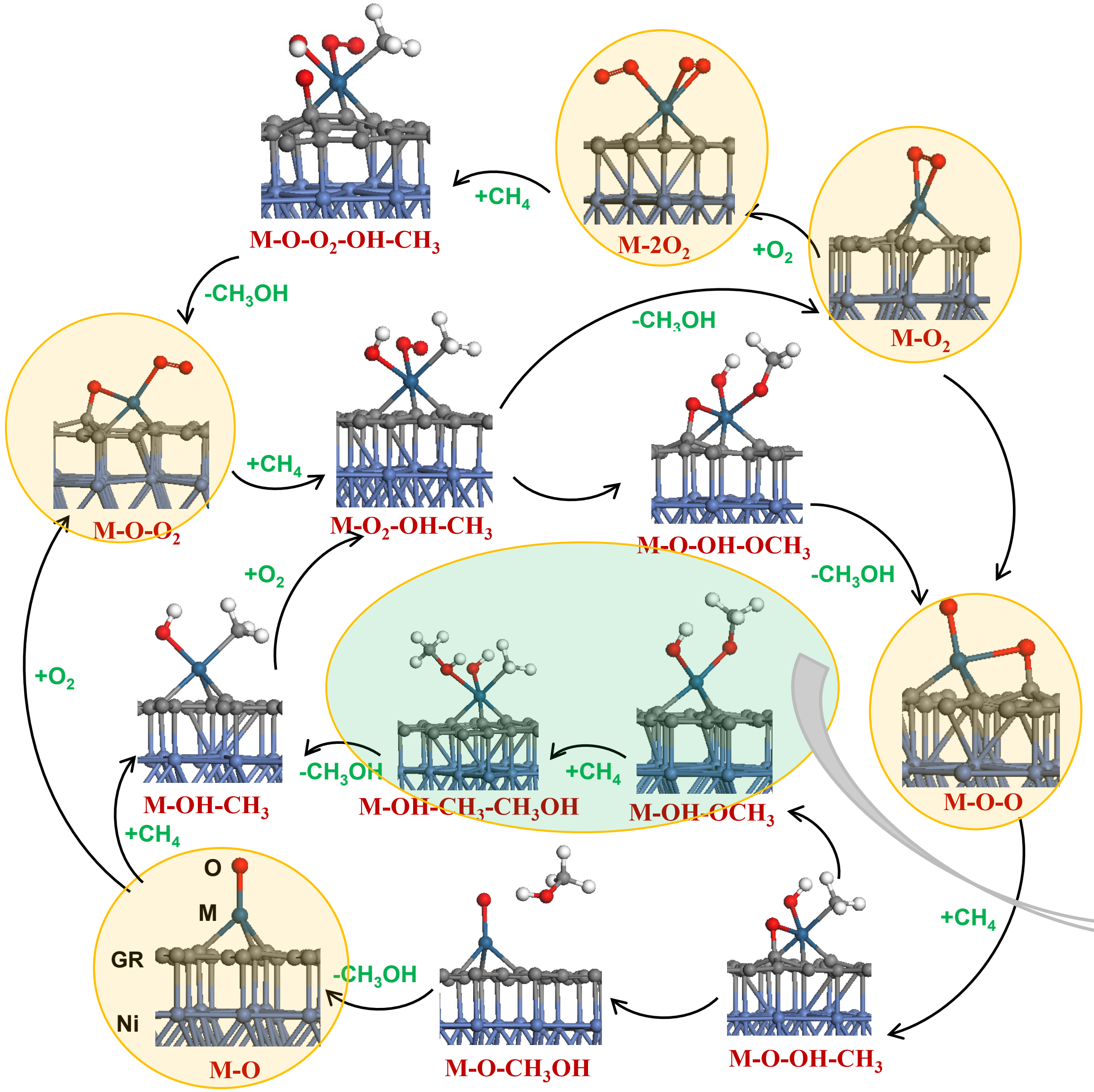
- At 473 K, Fe and Ru exhibit strong preference for M-O-O, Ir and Pt prefer M-O, Pd prefers M-2O$_2$, and both M-O and M-O-O configurations could be stable for Rh

- CH$_4$ dissociation barriers are in the range of 1.2-1.3 eV over M-O-O and 0.8-0.9 eV over M-2O$_2$ **⇒ (Fe&Ru)-GR/Ni(111) might not be active for MTM and Pd-GR/Ni(111) could exhibit some activity**

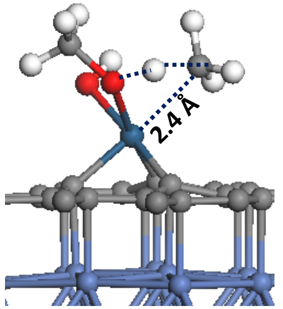


- CH$_4$ dissociation barriers are >1.3 eV over M-O, however additional O$_2$ can adsorb at the interface and the dissociation barriers are ~0.6-0.7 eV over M-O-O$_2$ **⇒ Pt and Ir-doped GR/Ni(111) catalysts could exhibit similar activity to Rh-GR/Ni(111)**

MTM reaction over M-GR/Ni(111) (M = Rh, Pt, Pd, Ir)



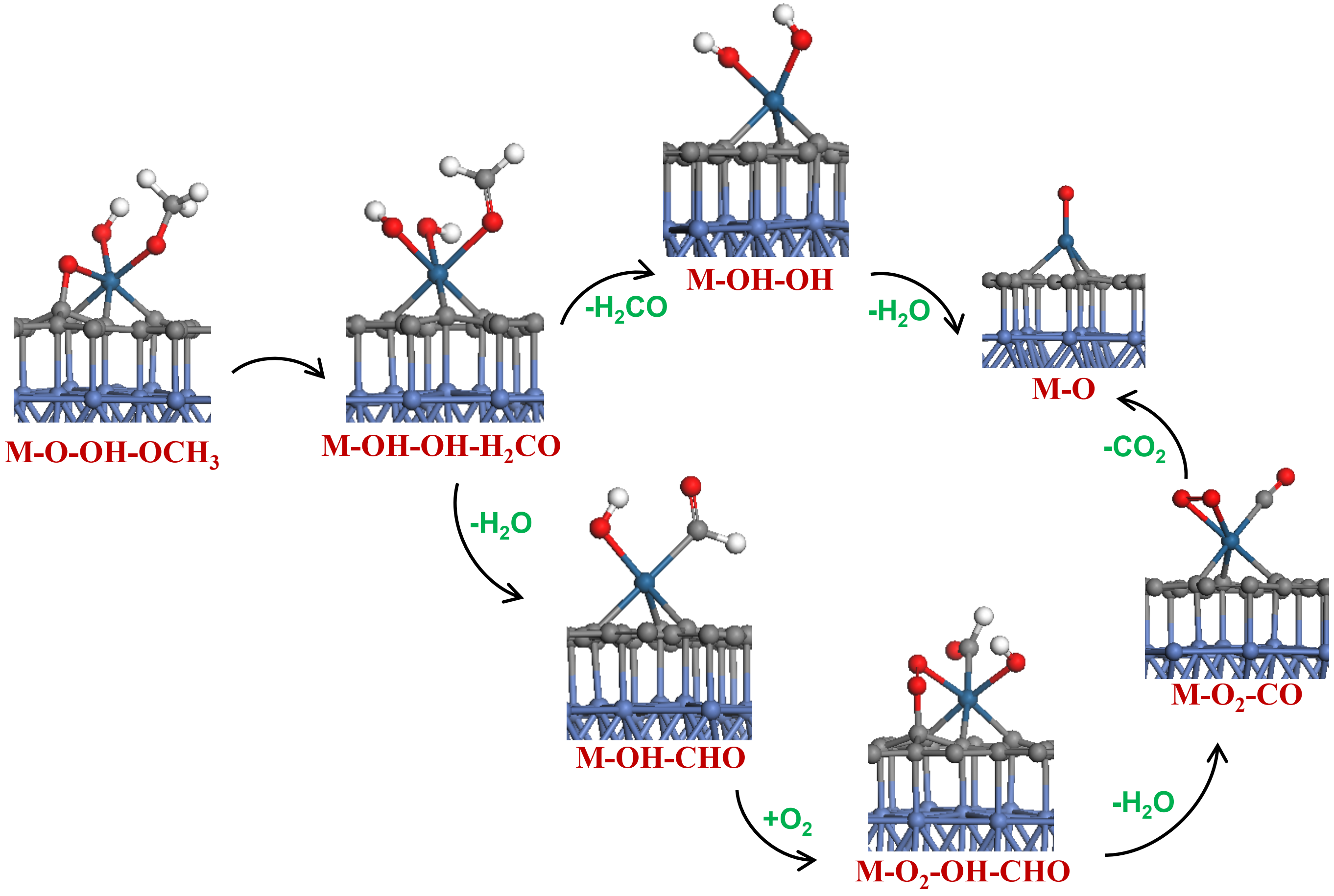
- Larger reaction network for MTM was generated including all the stable states of oxygen adsorbed structures
- Methoxy (-OCH_3) species were found to be stable on these active sites
- Stable methoxy species can be removed as methanol by direct dissociation of CH_4 over -OCH_3 via surface-stabilized transition state (highlighted in green)



TS for CH_4 dissociation on –OCH_3

MTM reaction over M-GR/Ni(111) (M = Rh, Pt, Pd, Ir)

Conversion of methoxy species to H_2CO and CO_2



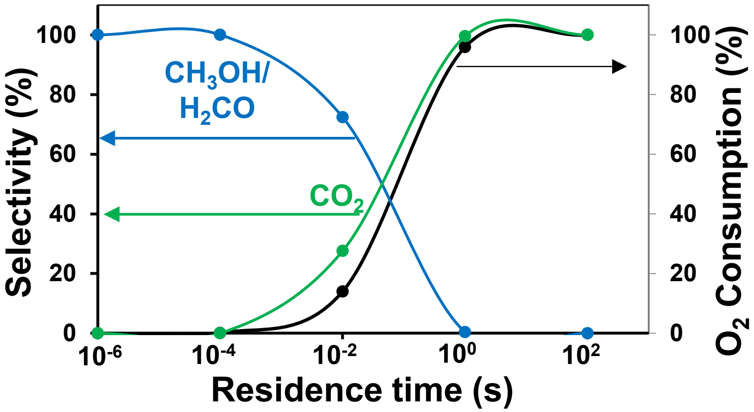
- ➢ Methoxy ($-OCH_3$) species can easily dissociate by transferring a H atom to the adsorbed O atom forming H_2CO with activation barriers ranging from 0.4–0.7 eV
- ➢ H_2CO can further dissociate to form CO with activation barriers of < 1 eV
- ➢ CO oxidation to CO_2 is preferred over CO desorption over all metal dopants

MTM reaction over M-GR/Ni(111) (M = Rh, Pt, Pd, Ir)

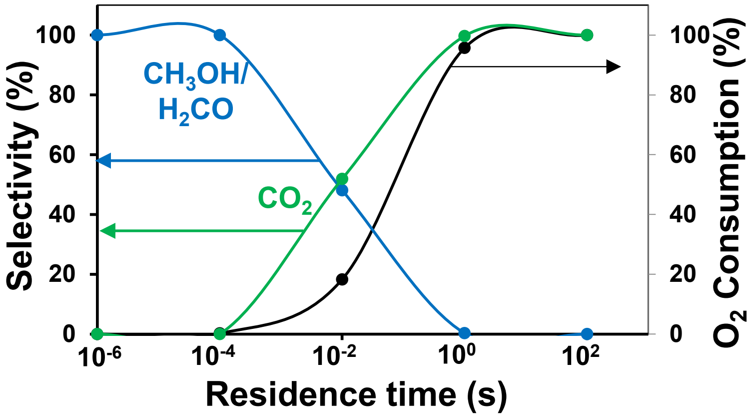
Microkinetic CSTR Model

T = 400 °C; P_{O2} = 2.4 bar; P_{CH4} = 45 bar

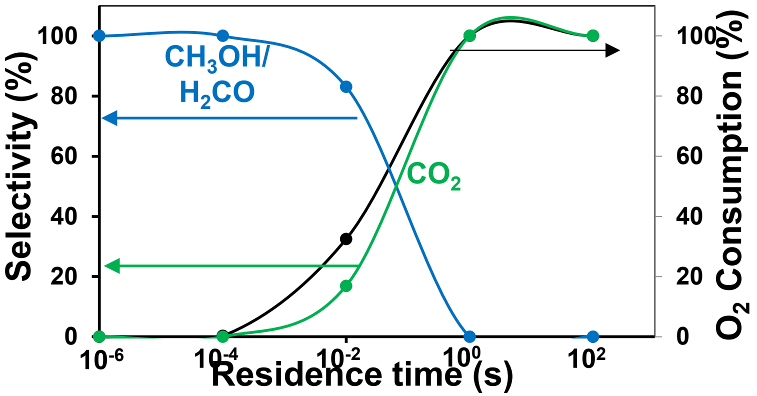
Rh-GR/Ni(111)



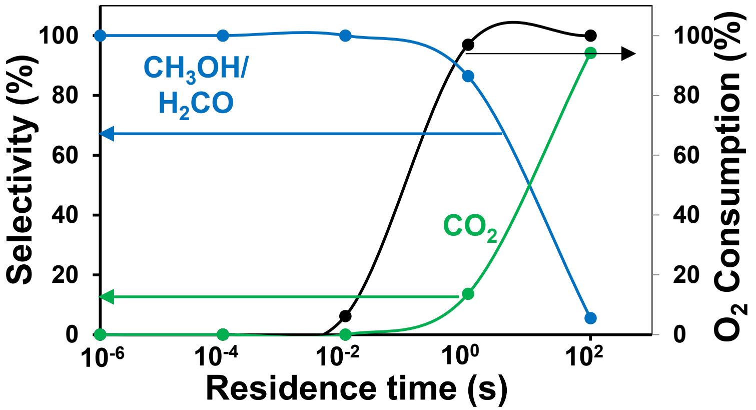
Pt-GR/Ni(111)



Pd-GR/Ni(111)



Ir-GR/Ni(111)



At low consumption of oxygen (<40%)

- CH_3OH and H_2CO are the main products (TOFs in the range of 10^{-1} s^{-1})

At higher consumption (longer residence times)

- CO_2 is the main product

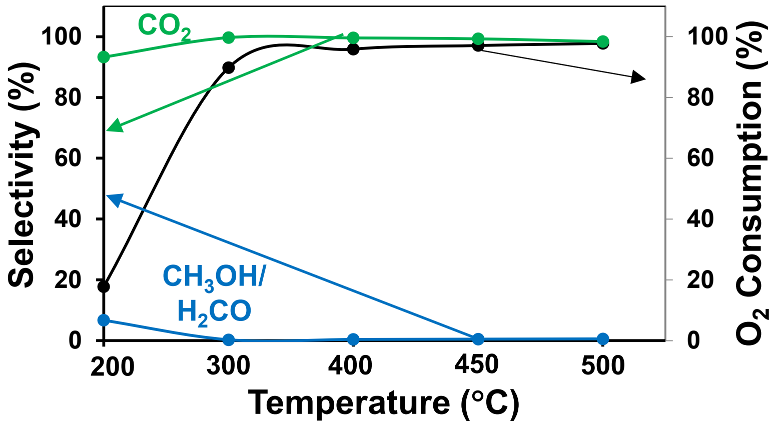
Conversion of CH_4 reaches a maximum of around 2.6% on all the metal dopants except for Ir which exhibits a slightly higher conversion of 4.6%

MTM reaction over M-GR/Ni(111) (M = Rh, Pt, Pd, Ir)

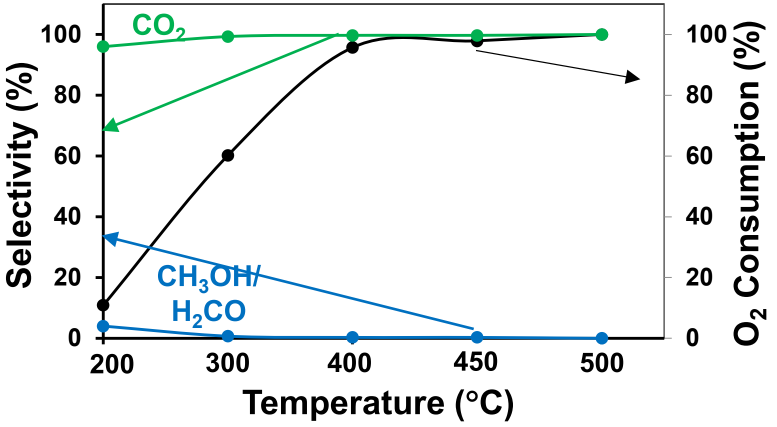
Microkinetic CSTR Model

$(\tau \times \alpha)$ = 1 s; P_{O2} = 2.4 bar; P_{CH4} = 45 bar

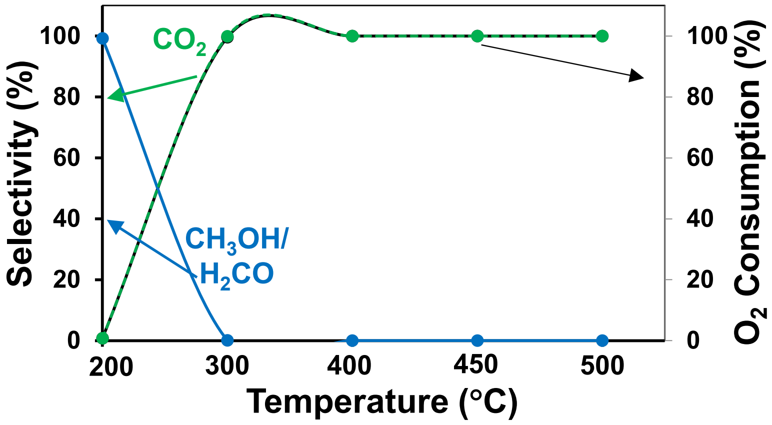
Rh-GR/Ni(111)



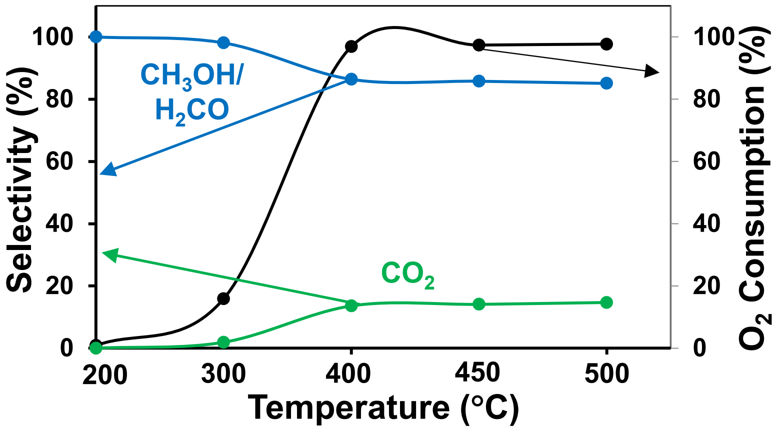
Pt-GR/Ni(111)



Pd-GR/Ni(111)



Ir-GR/Ni(111)



At an effective residence time of 1s

- CH_4 conversion ranges from 0.3 – 2.7% on Rh & Pt between 200 – 500 °C and CO_2 is the main product
- Pd exhibits preference for CH_3OH/ H_2CO products at 200 °C, but CH_4 conversion is only 0.04%
- Ir exhibits preference for CH_3OH/ H_2CO products at all the temperatures with CH_4 conversion ranging from 0.005 – 4.6%

Overall activity and selectivity towards CH_3OH/H_2CO products could be higher on the Ir dopant

Microkinetic CSTR Model of MTM reaction over Ir-GR/Ni(111)

$(\tau \times \alpha) = 1$ s; $P_{CH4} = 45$ bar

P_{O2} (bar)	**Temperature [°C]**						
			200	**300**	**400**	**450**	**500**
2.4	CH_4 conversion (%)		5×10^{-3}	0.8	4.6	4.6	4.6
	O_2 consumption (%)		9×10^{-2}	15.9	96.9	97.4	97.8
	Selectivity (%)	CH_3OH/H_2CO	**100.0**	**98.1**	**86.4**	**85.9**	**85.3**
		CO_2	0.0	1.9	13.6	14.1	14.7
10	CH_4 conversion (%)		6×10^{-3}	0.8	15.1	15.1	15.0
	O_2 consumption (%)		3×10^{-2}	3.7	96.7	97.9	98.2
	Selectivity (%)	CH_3OH/H_2CO	**100.0**	**98.4**	**57.3**	**55.7**	**54.5**
		CO_2	0.0	1.6	42.8	44.3	45.5
20	CH_4 conversion (%)		7×10^{-3}	0.9	26.1	26.4	26.3
	O_2 consumption (%)		2×10^{-2}	1.9	95.5	98.1	98.4
	Selectivity (%)	CH_3OH/H_2CO	100.0	98.4	37.1	34.8	33.5
		CO_2	0.0	1.6	62.9	65.2	66.4

At an effective residence time of 1s

- CH_4 conversion increases with increasing O_2 partial pressure
- At P_{O2} = 10 bar, a maximum CH_4 conversion of 15.1% was achieved at 400 °C and significant selectivity for CH_3OH/H_2CO products was observed at all the temperatures
- Although CH_4 conversion increased to 26% at P_{O2} = 20 bar, more CO_2 production was observed above 400 °C

Catalyst Synthesis - Overview

1. Support materials
   A. “Nano-porous” 3-D structured Ni- and N-doped Graphene synthesized
   B. Graphene/Nickel synthesis
   C. Ni Addition
2. Rh, Pt, Ir addition
3. Iterative refinement of materials with feedback from reactor and computation
5. Over 30 samples made, delivered, and characterized

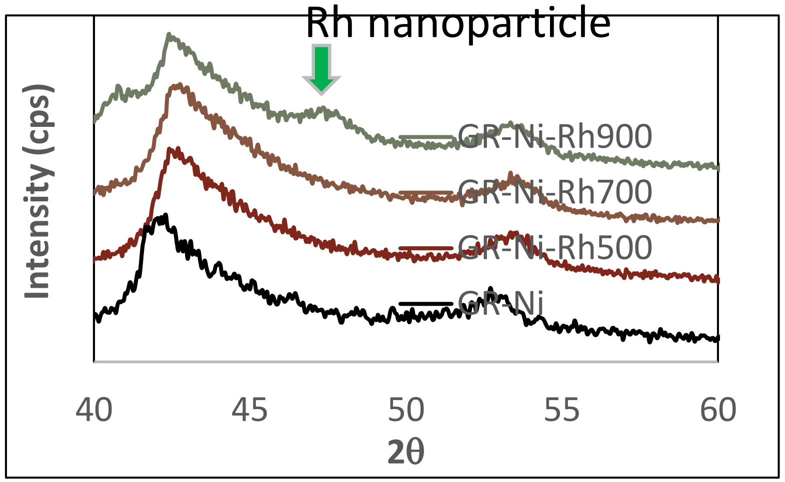
Precursors & structuring agents

Mixing

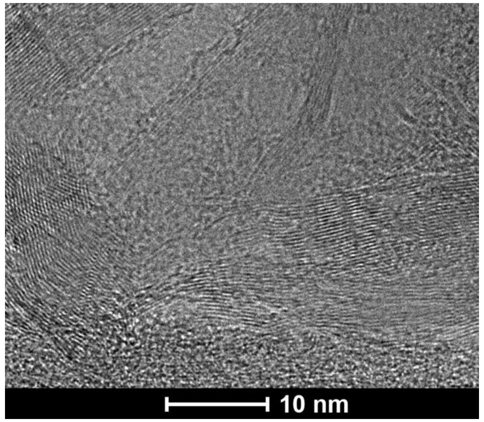
Graphitization

Doping

XRD- 1wt% Rh/Ni/Gr



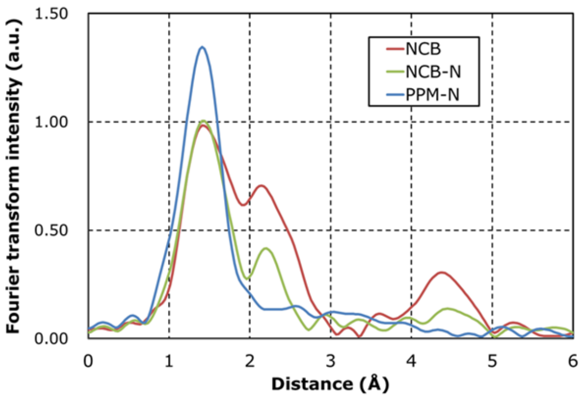
HRTEM illustrating graphene overlayers on Nickel nanoparticles

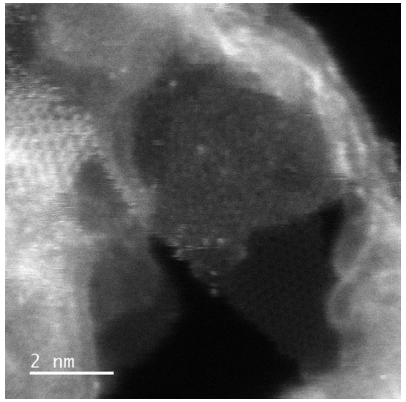


Catalyst Characterization

- Characterization of Rh-N-C@Ni is in process
  - In-lab(PP) XRD, Raman, ICP-OES
  - Advanced: XPS (CU@CU), AC-TEM (PP@UNM)
  - In development(PP): CO/H_2/CH_3OH adsorption, chemisorption
  - "Beamline": XAS

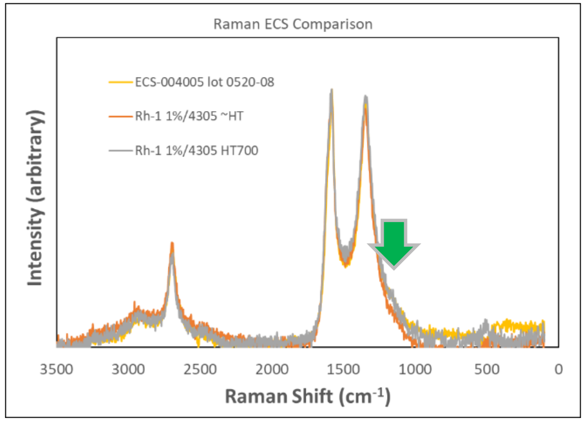
Single Atom Active Sites

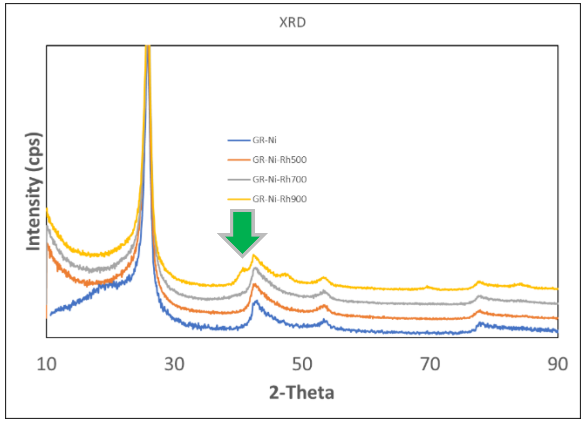




Left: X-Ray Absorption Spectroscopy shows atomic (Fe-N) bonds only, indicating atomic dispersion. Figure from Tanaka et al[7] Right: Abberation Corrected Transmission Electron Microscopy by ORNL Dr. Dave Cullen showing atomically dispersed iron sites.

Nanoparticles and Support



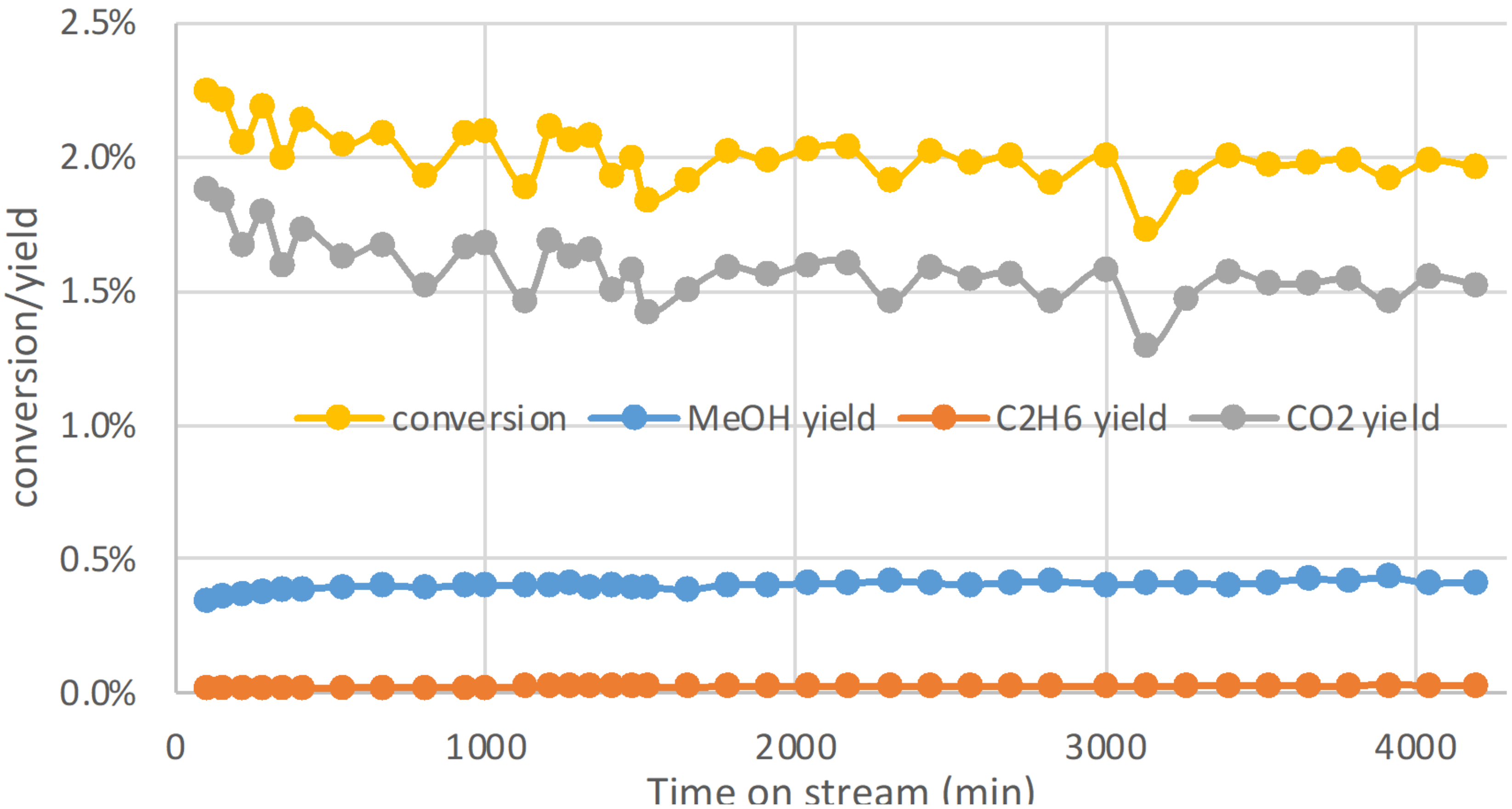


Characterization of Rh-N-C@Ni. Left, Raman spectroscopy showing small feature at 500 for heat treated samples. Right, XRD shows small amounts of rhodium nanoparticles evident by a small peak at 41 which evolve with increasing heat treatment of catalyst indicating sintering.

Reactor Setup

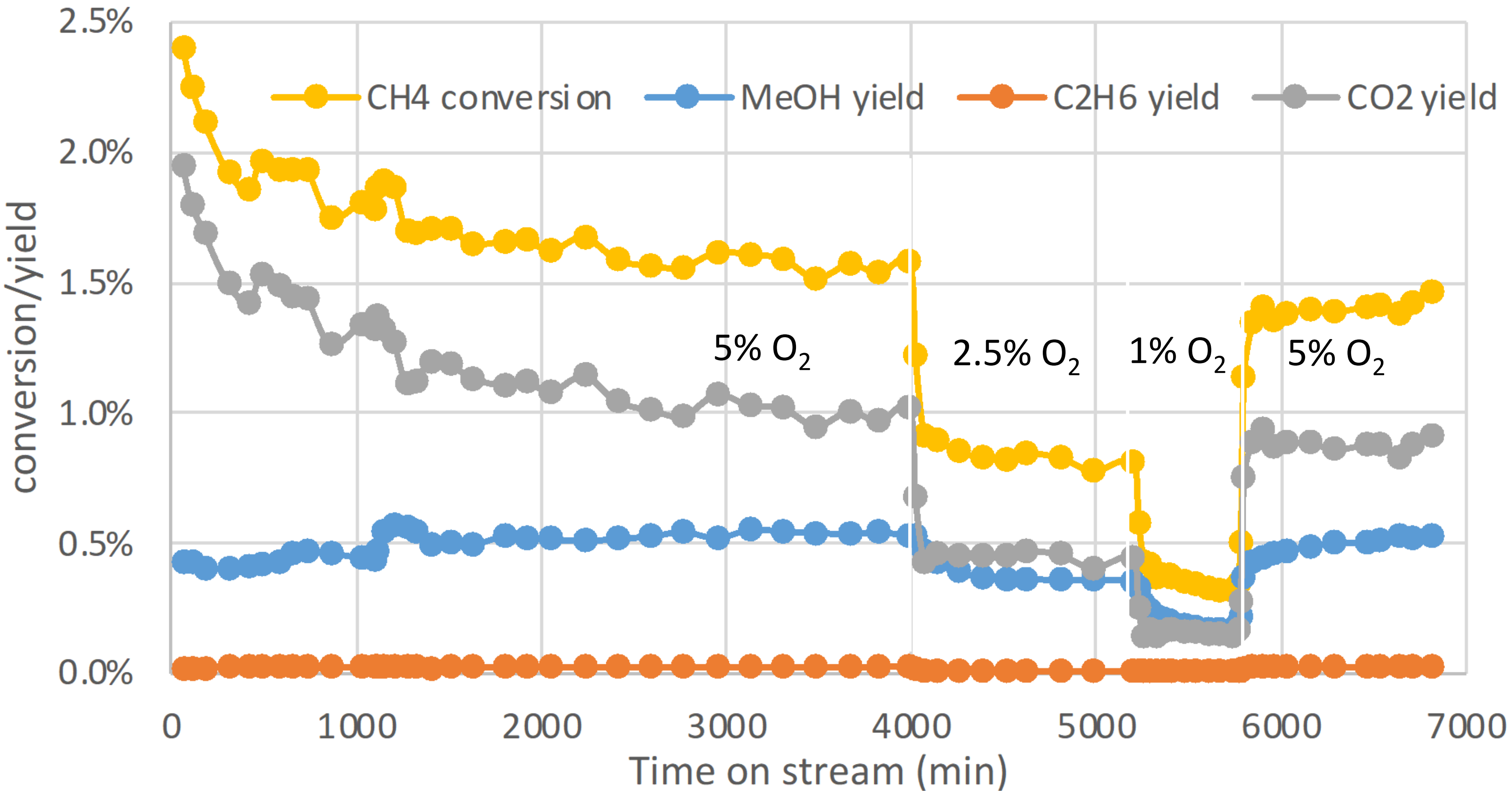
- High pressure (50bar) gas phase reactor with 4 MFCs for CH_4, O_2, H_2, and He
- Online GC with TCD and FID detectors for product quantification
- Stainless steel reactor for catalyst testing
- Electronic pressure gauge

Pajarito-made Pt catalyst exhibits acceptable activity and yield toward methanol at high temperature



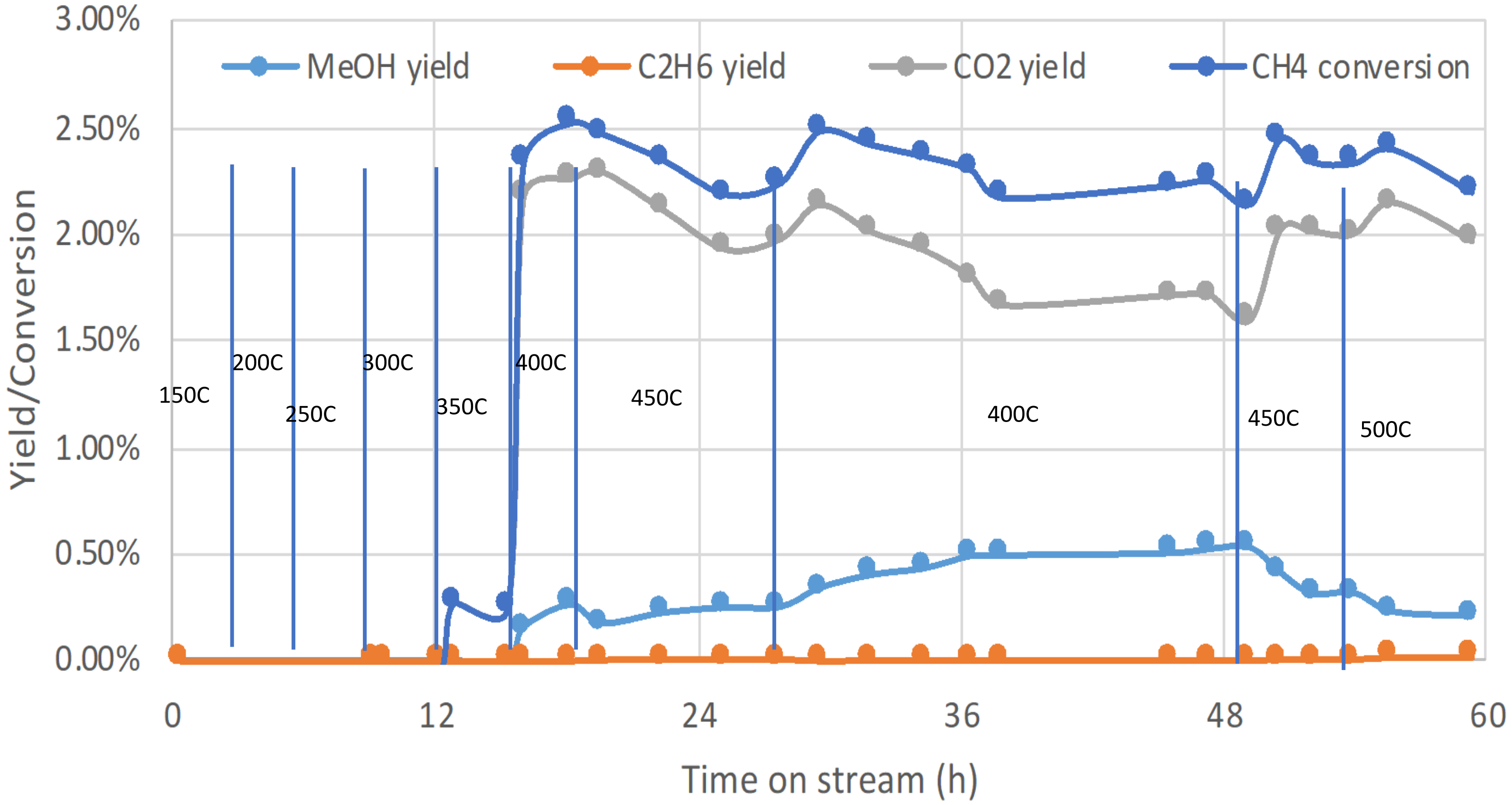
5 mg of catalyst,
CH_4 95 ml/min,
O_2 5 ml/min,
690 psi, **450°C**.

Higher O_2 partial pressure favors MeOH production on Pt-GR/Ni



5mg catalyst
450°C, 690 psi

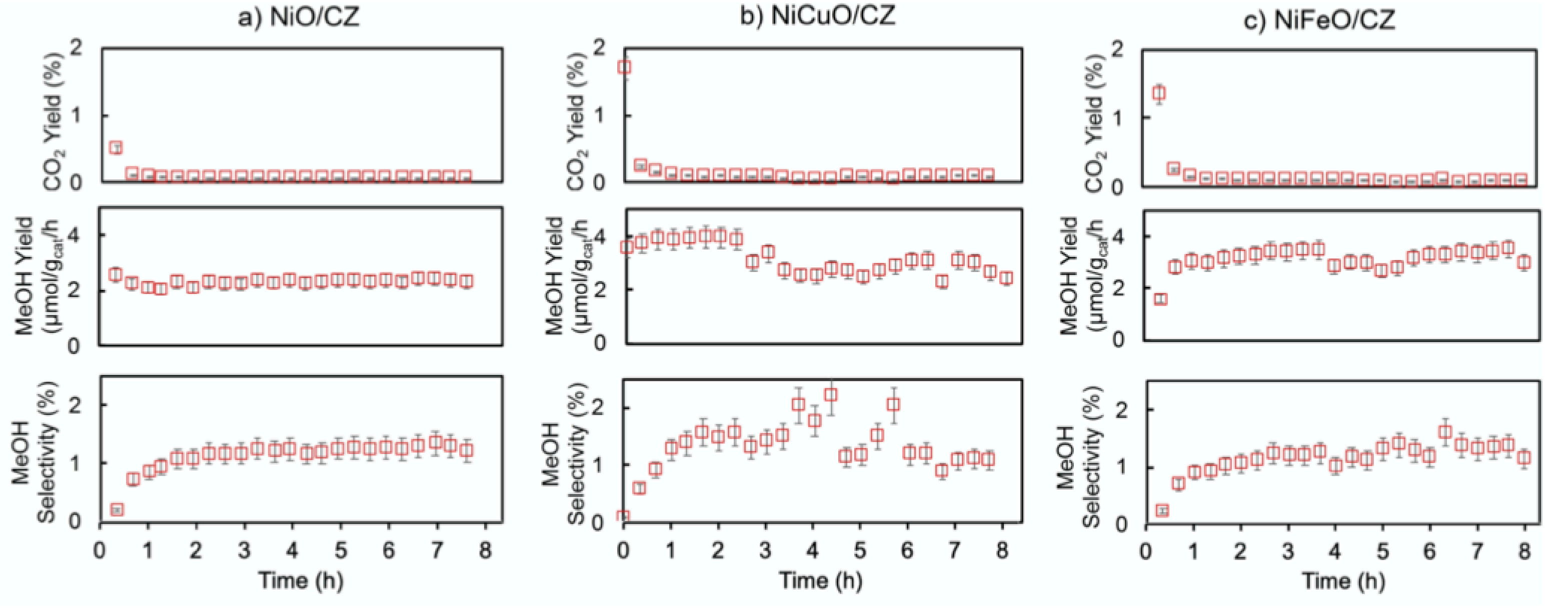
Pajarito-made Rh catalyst exhibits acceptable activity and yield toward methanol at 400ºC



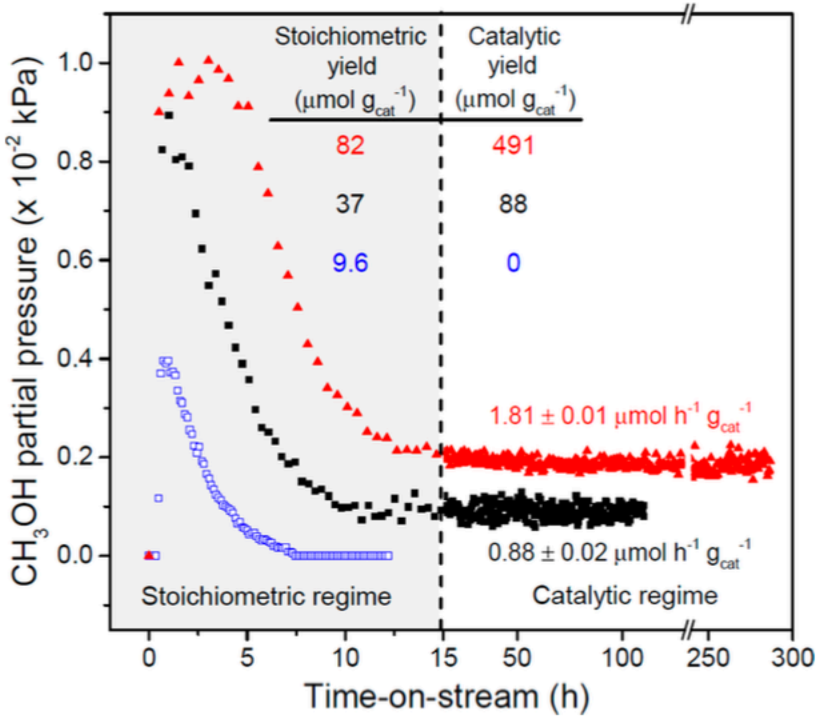
Temp (ºC)	Methanol yield	CO_2 yield	C_2H_6 yield
150	0	0	0
200	0	0	0
250	0	0	0
300	0	0	0
350	0	0.251%	0.001%
400	0.538%	1.601%	0.007%
450	0.323%	2.004%	0.012%
500	0.211%	1.971%	0.021%

5 mg of catalyst, CH_4 95 ml/min, O_2 5 ml/min, 690 psi

Comparison with literature shows activity is much higher for Rh catalyst, though temperature and pressure are also higher



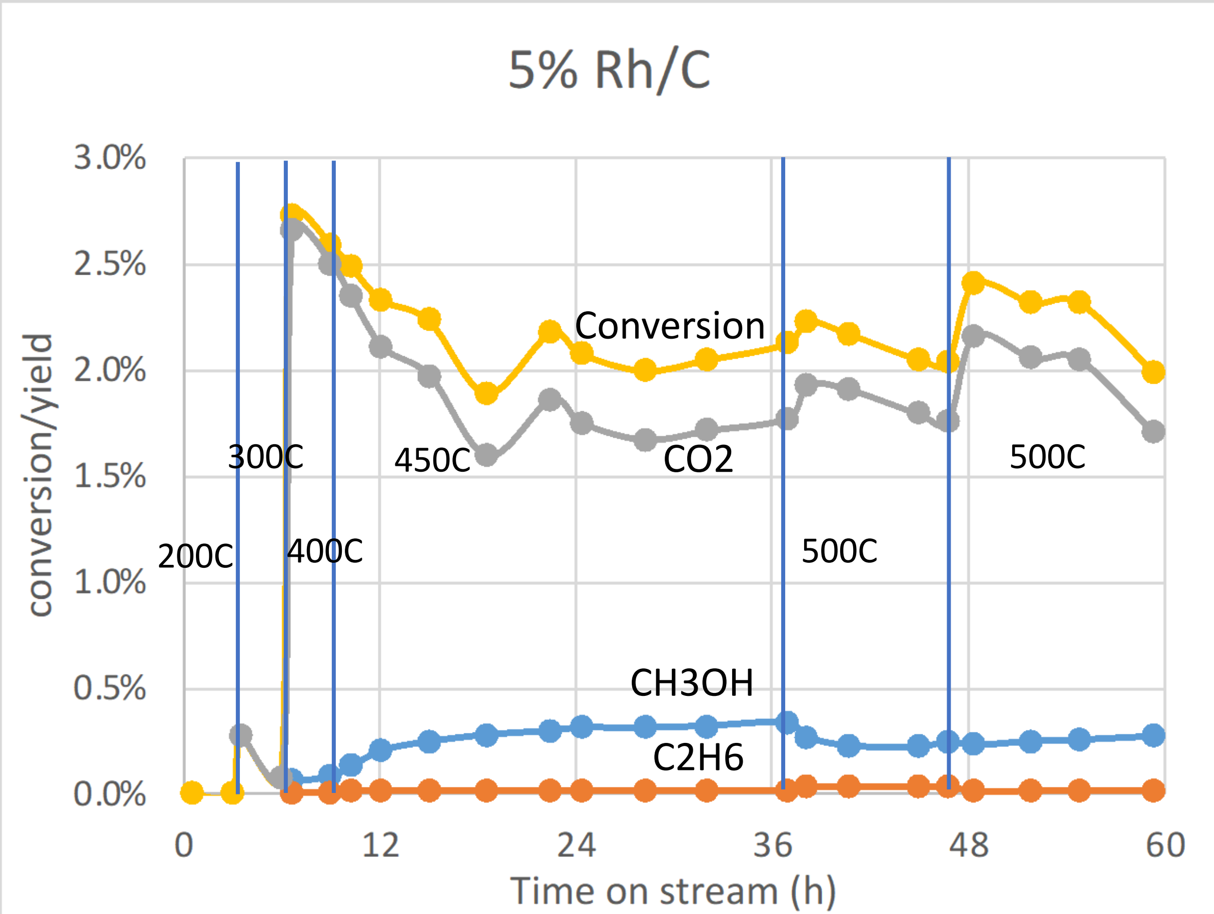
Sievers, C. *ChemCatChem* **2021,** *13* (12)



Roman-Leshkov, Y. *ACS Cent. Sci.* **2016,** *2* (6)

	Sievers' study[1]	Roman-Leshkov's study[2]	this study
Methanol yield ($\mu mol\ h^{-1}\ g_{cat}^{-1}$)	3.2	1.8	2.7 x 10^5
Temp (°C)	250	210	400
Pressure (psi)	15	15	690

Steady state methanol yield on other catalysts



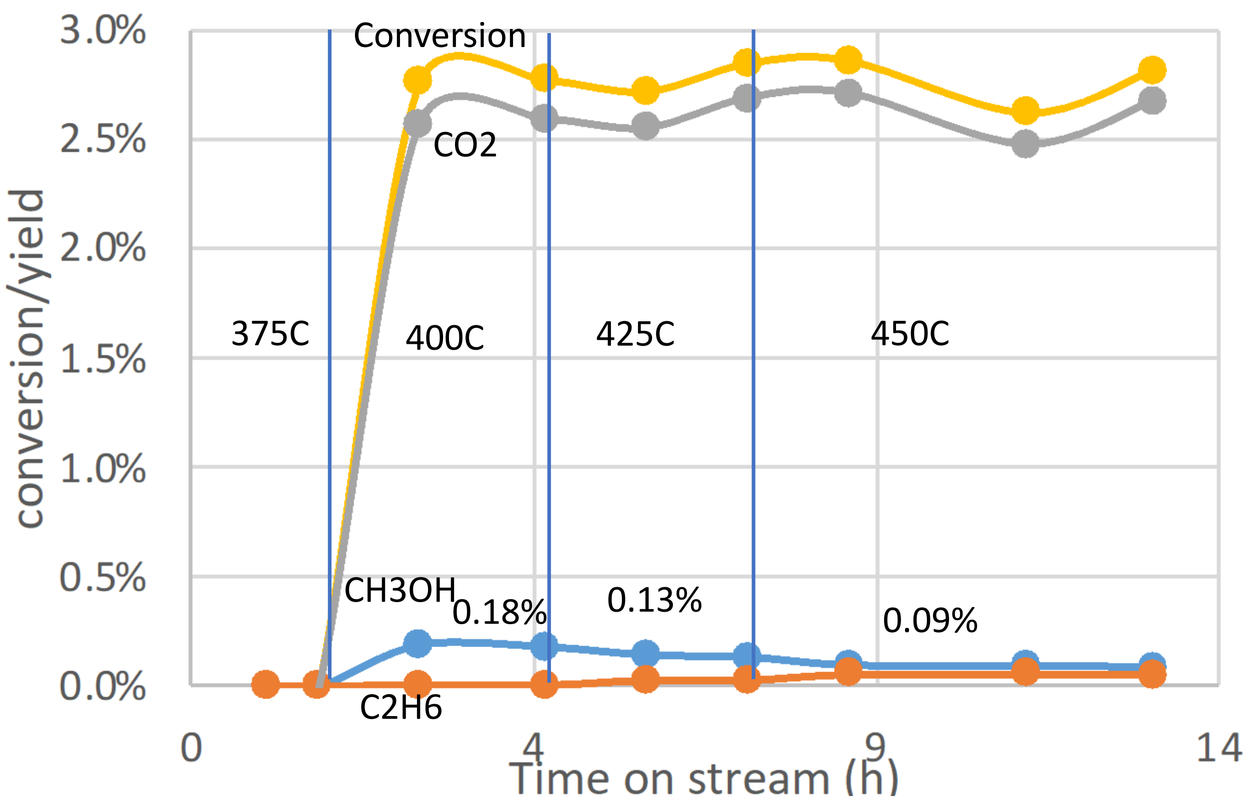
5% Rh/C catalyst possesses many more surface sites than Rh-GR/Ni catalyst but at 400°C hardly any activity

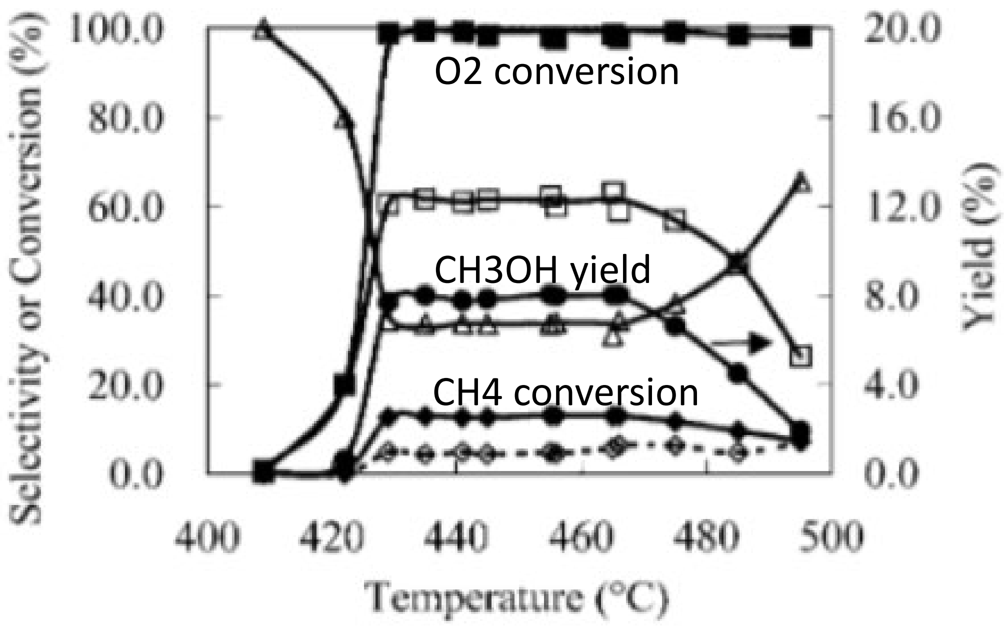
But also significant activity at 450°C.

5 mg of catalyst, CH_4 95 ml/min, O_2 5 ml/min, 690 psi

Blank reactor tests

CH_4 95 ml/min, O_2 5 ml/min, 690 psi





CH_4 / O_2 / N_2 =100/10/10 ml/min, 725psi

Zhang et.al. Appl. Catal. A. **2002**, *224*, 201 – 207

Blank reactor test reveals background MTM activity. However, at 400ºC Rh-GR/Ni ~3 times higher yield.

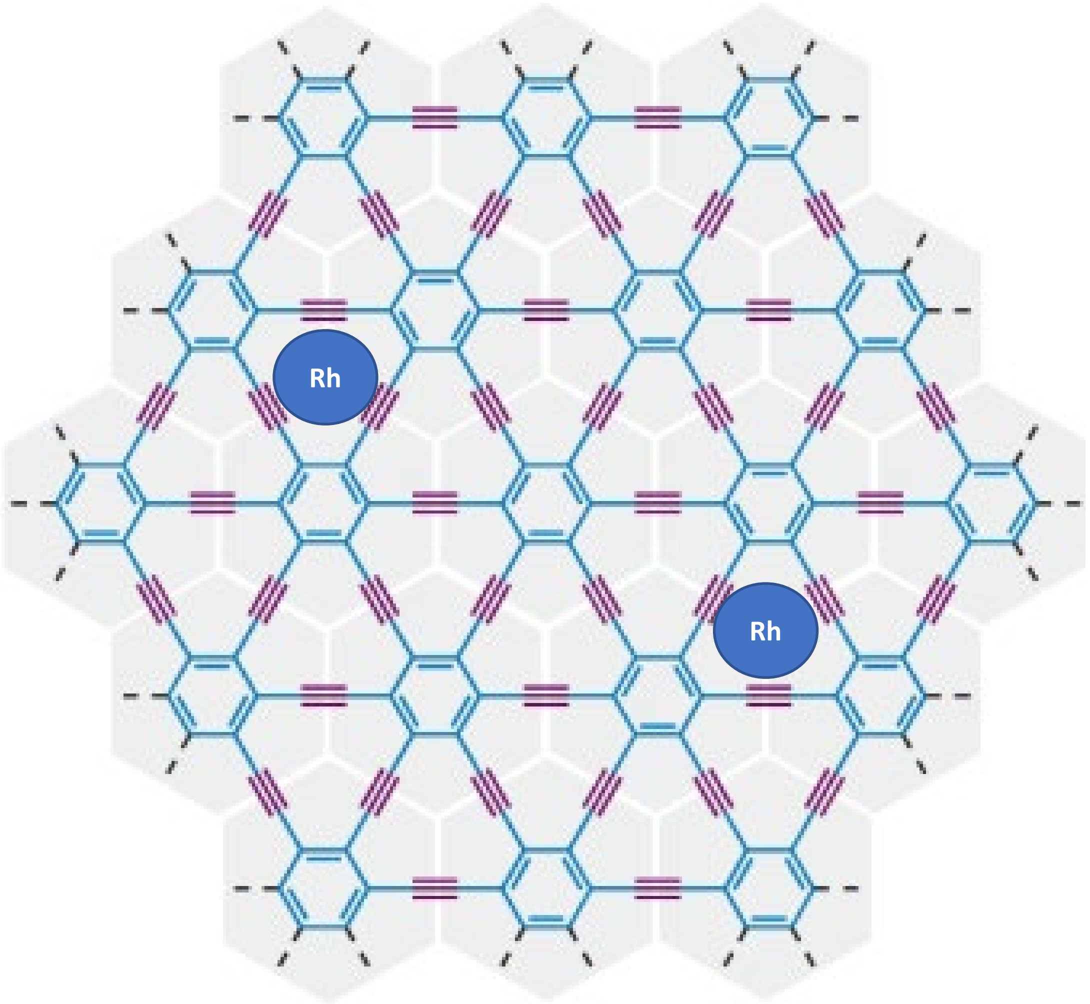
Summary and lessons learned

- ❑ (Rh, Pt, Pd, Ir)-GR/Ni catalysts potential active site for MTM
- ❑ Computationally, Ir- and Pd-GR/Ni catalyst appear best at low temperatures
- ❑ Experimentally, high methanol yield observed on Ni-modified graphene supported single atom metal catalysts
- ❑ High oxygen concentration, high pressure, and relatively high temperature (<450ºC) favors methanol production
- ❑ Background methanol yield presents problems in data interpretation
- ❑ Key challenge is difficulty in synthesis of computationally predicted most interesting active sites at high density

Next steps

- ☐ Lower-temperature activity would allow exclusion of background activity effects, promote catalyst durability
- ☐ Testing of Ir- and Pd-GR/Ni catalysts at low temperature and relatively high residence time
- ☐ Simplify support structure with similar properties desirable for low temperature activity and selectivity (metal-doped graphyne)

Wei Zhang (CU Boulder) produces graphyne while Medlin incorporates metal cation



γ-Graphyne

Nature Synthesis 1, 449–454 (2022)

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University of South Carolina

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Res. Ass. Prof.

Pajarito Powder, LLC

Dr. Barr Zulevi, coPI
CTO and President
Resigned Sept. 2022

Geoff McCool
Senior Chemist

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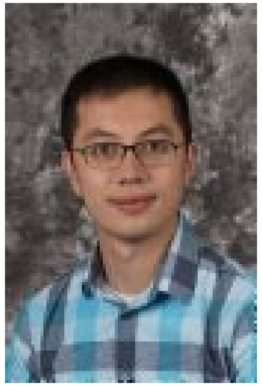
Dr. Will Medlin
Professor, coPI



Dr. Jiajie Huo
PostDoc

Appendix

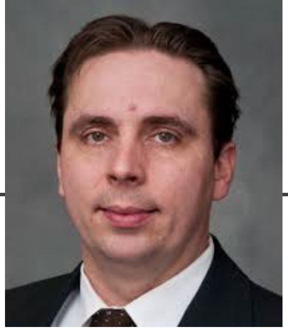
Organization Chart

Dr. Barr Zulevi
CTO and President
Pajarito Powder
Resigned Sept. 2022

Geoff McCool
Senior Chemist
Pajarito Powder

South Carolina

1) Project Management and Planning
2) Computational design of doped GR-based catalysts for the low temperature MTM



Dr. Andreas Heyden
UofSC

Dr. Will Medlin
CU Boulder

PAJARITO POWDER
FUEL CELL CATALYSTS

1) Synthesis and characterization of computationally predicted active sites and powder catalysts
2) Process design and techno-economic analysis of the MTM catalyst system (potential commercialization)

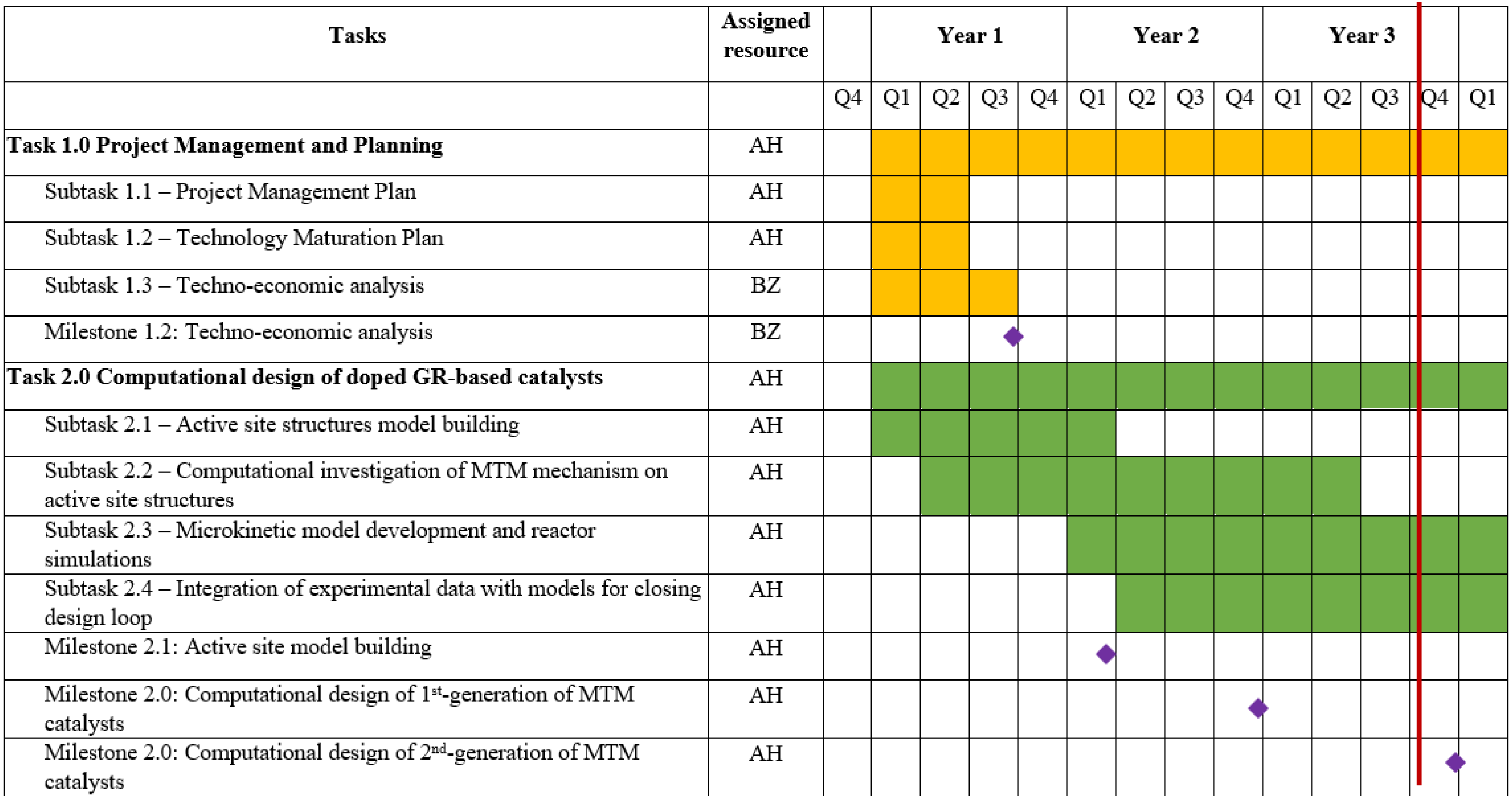
University of Colorado Boulder

1) Characterization (and minimal synthesis) of computationally predicted active sites and powder catalysts
2) Experimental evaluation of the catalysts for the partial oxidation of methane to methanol under relevant reaction conditions

Milestones

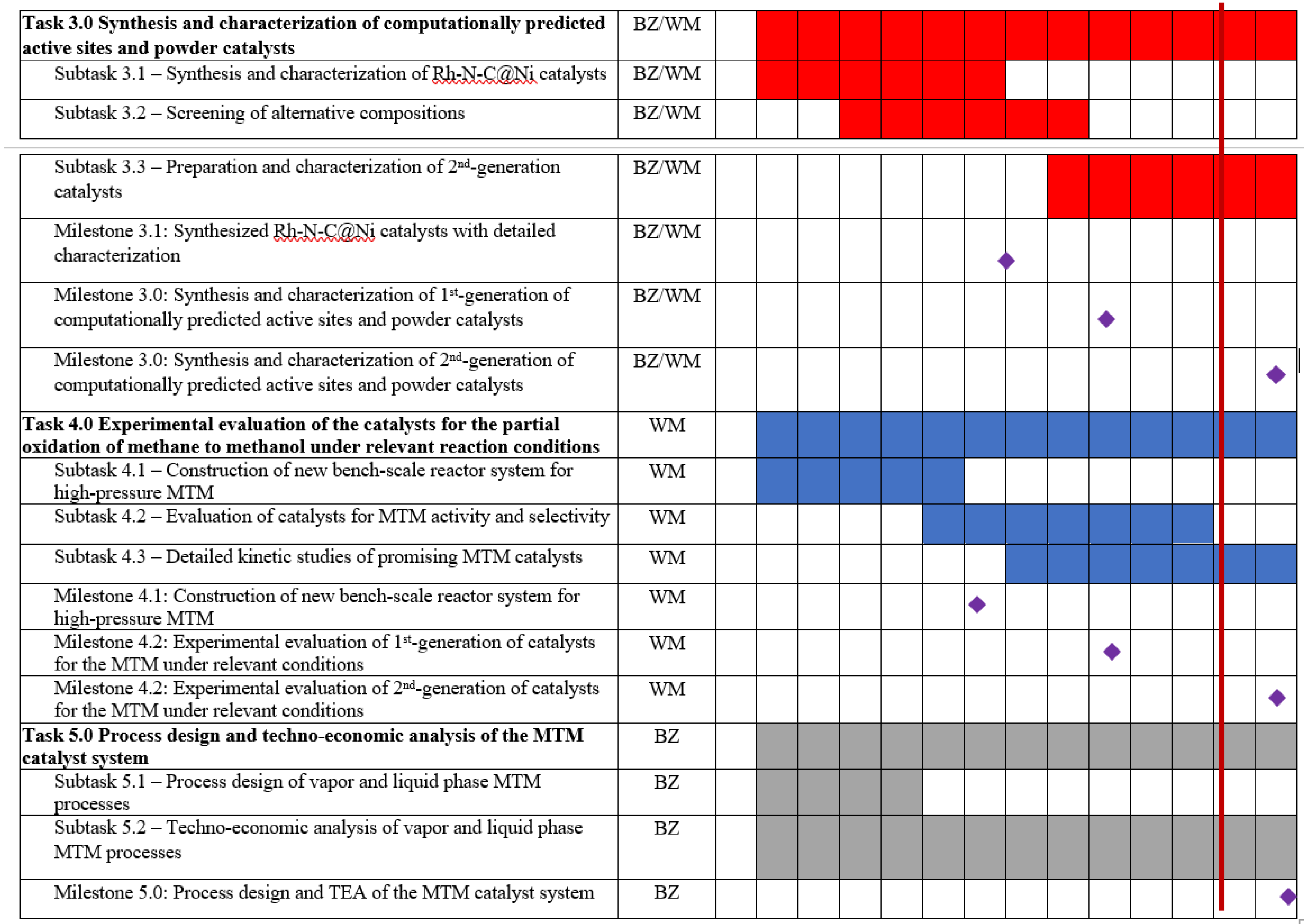
Task/Subtask	Milestone Title & Description	Planned Completion Date	Verification method
✓ **1.1**	Update of Project Management Plan	4/19/2020	PMP submitted to DOE
✓ **1.2**	Technology Maturation Plan	5/19/2020	Technology Maturation Plan submitted to DOE
✓ **1.3**	Initial Techno-Economic Analysis	9/16/2020	Initial TEA submitted to DOE
✓ **2.1**	Active site structures model building	2/15/2021	Report to DOE
✓ **4.1**	Construction of new bench-scale reactor system for high-pressure MTM	4/15/2021	Report to DOE & Reactor available for inspection
✓ **3.1**	Synthesized Rh-N-C@Ni catalysts	5/15/2021	Report to DOE
✓ **2.0**	Computational design of 1st-generation of MTM catalysts	11/15/2021	Report to DOE
✓ **3.0**	Synthesis and characterization of 1st-generation of computationally predicted active sites and powder catalysts	2/15/2022	Report to DOE
✓ **4.2**	Experimental evaluation of 1st-generation of catalysts for the MTM under relevant conditions	2/15/2022	Report to DOE
2.0	Computational design of 2nd-generation of doped GR-based catalysts	11/15/2022	Report to DOE
3.0	Synthesis and characterization of 2nd-generation of computationally predicted active sites and powder catalysts	2/15/2023	Report to DOE
4.2	Experimental evaluation of 2nd-generation of catalysts for the MTM under relevant conditions	2/15/2023	Report to DOE
5.0	Process design and TEA of the MTM catalyst system	3/15/2023	Report to DOE

Schedule/Gantt chart



Tasks	Assigned resource		Year 1				Year 2				Year 3				
		Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1
Task 1.0 Project Management and Planning	AH		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
Subtask 1.1 – Project Management Plan	AH		🟨	🟨											
Subtask 1.2 – Technology Maturation Plan	AH		🟨	🟨											
Subtask 1.3 – Techno-economic analysis	BZ		🟨	🟨	🟨										
Milestone 1.2: Techno-economic analysis	BZ				◆										
Task 2.0 Computational design of doped GR-based catalysts	AH		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Subtask 2.1 – Active site structures model building	AH		🟩	🟩	🟩	🟩	🟩								
Subtask 2.2 – Computational investigation of MTM mechanism on active site structures	AH			🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩			
Subtask 2.3 – Microkinetic model development and reactor simulations	AH						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Subtask 2.4 – Integration of experimental data with models for closing design loop	AH							🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Milestone 2.1: Active site model building	AH						◆								
Milestone 2.0: Computational design of 1st-generation of MTM catalysts	AH									◆					
Milestone 2.0: Computational design of 2nd-generation of MTM catalysts	AH													◆	

Schedule/Gantt chart



Task 3.0 Synthesis and characterization of computationally predicted active sites and powder catalysts	BZ/WM		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Subtask 3.1 – Synthesis and characterization of Rh-N-C@Ni catalysts	BZ/WM		🟥	🟥	🟥	🟥	🟥	🟥							
Subtask 3.2 – Screening of alternative compositions	BZ/WM				🟥	🟥	🟥	🟥	🟥	🟥					
Subtask 3.3 – Preparation and characterization of 2nd-generation catalysts	BZ/WM									🟥	🟥	🟥	🟥	🟥	🟥
Milestone 3.1: Synthesized Rh-N-C@Ni catalysts with detailed characterization	BZ/WM							◆							
Milestone 3.0: Synthesis and characterization of 1st-generation of computationally predicted active sites and powder catalysts	BZ/WM										◆				
Milestone 3.0: Synthesis and characterization of 2nd-generation of computationally predicted active sites and powder catalysts	BZ/WM														◆
Task 4.0 Experimental evaluation of the catalysts for the partial oxidation of methane to methanol under relevant reaction conditions	WM		🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Subtask 4.1 – Construction of new bench-scale reactor system for high-pressure MTM	WM		🟦	🟦	🟦	🟦	🟦								
Subtask 4.2 – Evaluation of catalysts for MTM activity and selectivity	WM						🟦	🟦	🟦	🟦	🟦	🟦	🟦		
Subtask 4.3 – Detailed kinetic studies of promising MTM catalysts	WM								🟦	🟦	🟦	🟦	🟦	🟦	🟦
Milestone 4.1: Construction of new bench-scale reactor system for high-pressure MTM	WM							◆							
Milestone 4.2: Experimental evaluation of 1st-generation of catalysts for the MTM under relevant conditions	WM										◆				
Milestone 4.2: Experimental evaluation of 2nd-generation of catalysts for the MTM under relevant conditions	WM														◆
Task 5.0 Process design and techno-economic analysis of the MTM catalyst system	BZ		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Subtask 5.1 – Process design of vapor and liquid phase MTM processes	BZ		▨	▨	▨	▨									
Subtask 5.2 – Techno-economic analysis of vapor and liquid phase MTM processes	BZ		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Milestone 5.0: Process design and TEA of the MTM catalyst system	BZ														◆

Project structure (Table 1 of PMP)

Team	PI	Task
University of South Carolina (USC)	Andreas Heyden	• Computationally screen and design doped GR-based catalysts supported on Ni and other Group VIII metals • Develop microkinetic reactor models based on DFT data and integrate experimental kinetic information into these models to enable a feedback loop between theory and experimentation • Coordinate all research efforts
University of Colorado, Boulder (CU)	Will Medlin	• Evaluate the catalysts for the gas-phase partial oxidation of methane to methanol. Reaction rates for methane and methanol oxidation will be measured at differential conversion in order to estimate activation energies and reaction orders that can be compared to kinetic modeling studies, helping to close the design loop • Promising catalytic materials will be thoroughly characterized before and after reaction using techniques including: static adsorption for total and metal-specific surface areas; temperature programmed reduction (TPR) for determining the reducibility of metal components (which is expected to be an important descriptor for turnover rates); aberration-corrected transmission electron microscopy (TEM) for imaging of catalyst nanostructure, and, where possible, infrared (FTIR) spectroscopy after CO adsorption to characterize binding sites
Pajarito Powder, LLC	Barr Zulevi	• Modify current VariPore™ manufacturing platform for the manufacture of PGM-free fuel cell catalysts based on atomically-dispersed metal-nitro-carbide active sites to produce the predicted structures as high surface area powders • Modify current Rh wet-chemistry deposition methods and/or chemical vapor, atomic layer, and physical vapor deposition methods to the atomically dispersed levels needed • Characterize materials by X-ray diffraction, Raman spectroscopy, Zeta-potential, and both physi- and chemisorption. For promising catalytic materials, atomic-resolution electron microscopy can also be carried out using the Los Alamos/Sandia National Laboratories Center for Integrated Nano-Technology, University of New Mexico, to confirm structures • Design and TEA of conceptual small scale MTM process to identify critical bottlenecks that inhibit future commercialization

Tasks and interrelationships

	Task/Subtask	Milestone Title & Description	
Independent	**1.0**	Project Management and Planning	
	1.1	Update of Project Management Plan	
Independent	**1.2**	Technology Maturation Plan	
	1.3	Initial Techno-Economic Analysis	Fairly independent; might need some more detailed reactor modeling based on published microkinetic model
	2.0	Computational design of doped GR-based MTM catalysts	
	2.1	Active site structures model building	Initially independent (after first meeting on catalyst synthesizability) later dependent on Task 3.0 and 4.0
Dependent on 2.1	**2.2**	Computational investigation of MTM mechanism on active site structures	
Dependent on 2.2	**2.3**	Microkinetic model development and reactor simulations	
	2.4	Integration of experimental data with models for closing design loop	Dependent on 2.3 and reactor parameters such as flowrate, reactor volume, number and type of active sites per volume, observed rate parameters, product distribution etc. (Task 3.0 and 4.0)
	3.0	Synthesis and characterization of computationally predicted active sites and powder catalysts	
	3.1	Synthesized Rh-N-C@Ni catalysts	Independent - goal is to reduce N-content & creation of homogenous sites – also, to identify other sites in these catalysts
	3.2	Screening of alternative compositions	Feedback primarily from Task 2.0
	3.3	Preparation and characterization of 2nd-generation catalysts	Feedback from both Task 2.0 and 4.0

Tasks and interrelationships

	Task/Subtask	Milestone Title & Description	
Dependent on 3.0	**4.0**	Experimental evaluation of the catalysts for the partial oxidation of methane to methanol under relevant reaction conditions	
independent	**4.1**	Construction of new bench-scale reactor system for high-pressure MTM	
	4.2	Evaluation of catalysts for MTM activity and selectivity	Dependent on 3.0 and currently 4.1 (currently debating how to make this task less dependent on 4.1)
Dependent on 3.0, 4.1, and 4.2	**4.3**	Detailed kinetic studies of promising MTM catalysts	
	5.0	Process design and techno-economic analysis of the MTM catalyst system	Fairly independent; might need some more detailed reactor modeling based on published microkinetic model
	5.1	Process design of vapor and liquid phase MTM process	
Dependent on 5.1	**5.2**	Techno-economic analysis of vapor and liquid phase MTM process	