## Methane Partial Oxidation Over Multifunctional 2-D Materials

FE0031878

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#### **Presentation Outline**

- Goals and Objectives
- Big Picture
- Technical Status
- Accomplishments to Date
- Lessons Learned
- Synergy Opportunities
- Project Summary

#### **Goals and Objectives**

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

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

• 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.

#### Idea for Goals and Objectives



MTM concept for catalyst design

Single metal site that strongly interacts with CH<sub>3</sub>-group during C-H bond activation in CH<sub>4</sub> to enable <u>surface-stabilized</u> versus radical <u>mechanism</u>

Single metal site with pos. partial charge to create electrostatic driving force for distinguishing C-H activation in CH<sub>4</sub> and CH<sub>3</sub>OH

Single metal site embedded in <u>GR that can activate O<sub>2</sub> close to</u> metal site due to interaction with metal support and e<sup>-</sup> donation to GR leading to adsorbed  $O_2^{\delta^-}$ 

## **Big Picture**

- Use novel materials and methods previously not available to solve flaring problem (catalyst development guided by computational design)
- Process intensification at the macro-scale: 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



#### **Technical Status**

#### Computational design of doped GR-based MTM catalysts



- $\blacktriangleright$  Adsorption of only one O<sub>2</sub> is favored on Rh-GR
- Overall free energy barrier for MTM is 2.02  $eV \Rightarrow low activity$
- Radical-type TS affects the selectivity towards CH<sub>3</sub>OH production (C-H activation barrier of CH<sub>3</sub>OH is 0.54 eV lower than that of  $CH_{4}$ )
- Ni support enables adsorption of additional O<sub>2</sub> molecule on Rh
- > Surface-stabilized TS was found at Rh/C interface and overall free energy barrier for MTM is 1.37 eV  $\Rightarrow$  improved activity
- $\blacktriangleright$  Free energy barrier of CH<sub>4</sub> C-H activation is ~0.2 eV lower than  $CH_3OH \Rightarrow Electronic$ atomic monolayer-metal support interaction promotes the (EAMSI) activity and selectivity towards methanol formation

#### Computational design of doped GR-based MTM catalysts



#### **Rh-dimer supported on graphene**

- Dissociative adsorption of single O<sub>2</sub> is favored on Rh<sub>2</sub>-GR
- CH<sub>4</sub> dissociation barrier is lower than Rh<sub>1</sub>-GR (0.61 vs. 1.01 eV)
- Radical-type TS affects the selectivity towards CH<sub>3</sub>OH production
- Ni support enables adsorption of additional O atoms at Rh/C interface
- Surface-stabilized TS is possible at the interface
- CH<sub>4</sub> dissociation barrier is higher than Rh<sub>1</sub>-GR/Ni(111) (1.36 vs. 0.76 eV)

 ❑ Adding second Rh atom does not improve the performance of Rh-GR catalyst
❑ Formation of Rh<sub>1</sub>-GR is preferred over Rh<sub>2</sub>-GR in the presence of double C vacancy ⇒ Rh<sub>2</sub>-GR is not a stable active site

#### Computational design of doped GR-based MTM catalysts



- At 473 K, Fe and Ru exhibit strong preference for M-O-O, Ir and Pt prefer M-O, Pd prefers M-2O<sub>2</sub>, and both M-O and M-O-O configurations could be stable for Rh
- > CH<sub>4</sub> 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<sub>2</sub>  $\Rightarrow$  (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- $O_2 \Rightarrow$  Pt and Ir-doped GR/Ni(111) catalysts could exhibit similar activity to Rh-GR/Ni(111) 9



#### MTM reaction network over Pt-GR/Ni(111) model

- Different active sites such as Pt-O, Pt-O, Pt-O<sub>2</sub>, and Pt-2O<sub>2</sub> are included the reaction network
- Surface-stabilized transition states were found for CH<sub>4</sub> activation at these active sites
- Free energy barriers for the C-H bond cleavage of  $CH_3OH$  are about 0.1-0.2 eV higher than that of  $CH_4 \Rightarrow$  Pt-GR/Ni(111) can be selective towards methanol formation
  - Methoxy formation was found to be highly favored and  $Pt-OH-OCH_3$ structure is the dominant intermediate at 473 K. Surface coverages of Pt-O and Pt-O-O increase above 573 K.
  - Catalytic cycle including Pt-OH-OCH<sub>3</sub> (shown in green arrows) was found to be the dominant pathway



#### MTM reaction over Pt-GR/Ni(111) model

TOF at 573 K =  $4.84 \times 10^{-2}$  s<sup>-1</sup>

TOF at 623 K =  $1.96 \times 10^{-1} \text{ s}^{-1}$ 

Apparent activation barrier = 1.02 eV (473 K – 623 K)



Reaction orders  $\Rightarrow O_2 = 0.5$ ; CH<sub>4</sub> = 1

Pt-GR/Ni(111) catalyst system can be active and selective for MTM above 573 K

#### Catalysts Made and Characterized

- 4 N-C@Ni materials made
  - Variations in N content, Ni content, and carbon types
- Rh or Pt deposited on all 4
- Heat treated to improve interactions



#### Catalysts Made and Characterized

#### • Rh or Pt deposited on 4 N-C@Ni materials



- Raman and XRD show
  - Presence of Rh nanoparticles at 700 °C
  - Presence of Pt nanoparticles above 700 °C
- Type of support changes Rh and Pt nanoparticles sintering
  - Indicates different interactions between Rh or Pt and 4 N-C@Ni

#### **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 Rh catalyst



100mg 1%Rh/Ni-graphene 500 HT Rh1, H<sub>2</sub> reduction 200C, 690 psi, CH<sub>4</sub> 9.5ml/min, O<sub>2</sub> 0.5ml/min

Low ethane production (<0.001%) only at high temperatures</li>

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#### Other Rh catalysts

GC Chromatograph



100mg catalyst, H<sub>2</sub> reduction 200C, 690 psi, CH<sub>4</sub> 9.5ml/min, O<sub>2</sub> 0.5ml/min

• Ethane production (<0.001% yield) on 5%Rh/Al<sub>2</sub>O<sub>3</sub> and 0.5%Rh/ZrO<sub>2</sub> at 200C

# Non-oxidative coupling of methane to ethane



	5%Rh/C	5%Rh/Al <sub>2</sub> O <sub>3</sub>	5%Pt/C	5%Pt/Al <sub>2</sub> O <sub>3</sub>
Ethane yield	0.062%	0.035%	0.006%	0.006%

Significant ethane production from methane at mild temperature

## Transient methanol production on Pt catalyst



100mg catalyst, H<sub>2</sub> reduction 200C, 690 psi, CH<sub>4</sub> 9.5ml/min, O<sub>2</sub> 0.5ml/min

 Multiple cycles of transient methanol production on 1%Pt/NiMNC-6 after pressure release of CH<sub>4</sub> and O<sub>2</sub> and repressurize with CH<sub>4</sub> at 350C

### Accomplishments to Date

- Initial Techno-Economic Analysis
- Identification of Pt-GR/Ni(111) as second active and selective site beyond Rh-GR/Ni(111)
- Synthesized Rh-N-C@Ni and Pt-N-C@Ni catalysts
- Construction of new bench-scale reactor system for highpressure MTM
- Observing transient but selective methanol production over Pt-GR/Ni catalyst
- Steady state non-oxidative ethane production at 350°C over Rh/C catalyst

#### Lessons Learned

- Key challenge is difficulty in synthesis of computationally predicted most interesting active sites
- Likely there is only a very low density of active sites in the synthesized powder catalysts
- Conversion is still too low and no steady-state operation yet for methanol production
- It is essential to better characterize catalytic materials and optimize reaction conditions
- Stable, steady state non-oxidative ethane production at 350°C over Rh/C catalyst possible

## Synergy Opportunities

- Exploring other synthesis approaches for isolated single metal atoms on various supports (Dongxia Liu, University of Maryland - FE0031877)
- Initial discussions with Jason Hicks, University of Notre Dame, on the possibility of plasma stimulation (FE0031862)
- Initial discussions with Fanxing Li, North Carolina State University, on their oxidative aromatization catalyst (FE0031869)

## **Project Summary**

- Pt-GR/Ni catalyst potential active site for MTM
- Methanol is selectively produced over Pt-GR/Ni catalyst (however currently no steady-state production)
- Rh/C catalyzes non-oxidative coupling of methane at low temperature
- It is essential to better characterize catalytic materials
- Need to optimize reaction conditions
- Need to synthesize catalysts with higher fraction of desired active site structures
- Continue computational catalyst design, i.e., study Ir and Pd

## Appendix

#### Benefit to the Program

AOI 2 – Process-Intensified Technologies for the Upcycling of Flare Gas into Transportable, Value-added Products

AOI 2A – Multi-Functional Catalysts for methane to liquid petrochemicals

- Project uses novel materials and methods previously not available to solve flaring problem (catalyst development guided by computations)
- Process intensification at the macro-scale: moving away from twostep methanol synthesis based on syngas; eliminating need for pure oxygen
- Process intensification at the nano-micro scale: engineering of reaction pathways on catalyst surface
- Liquid product, no oxygen plant, one reactor, relatively mild operating conditions, high selectivity => potentially applicable to remote flare sites

#### **Project Overview**

Goals and Objectives (shown on slide 3 focusing here on success criteria)

#### 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.

### **Organization Chart**



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





PAJARITO

FUEL CELL CATALYSTS

University of Colorado Boulder

- characterization Synthesis and 1) of computationally predicted active sites and powder catalysts
- 2) Process design and techno-economic analysis of the MTM catalyst system (potential commercialization)
- 1) Characterization (and minimal synthesis) of computationally predicted active sites and powder catalysts
- Experimental evaluation of the catalysts 2) for the partial oxidation of methane to methanol under relevant reaction conditions

#### **Gantt Chart**

Tasks	Assigned resource		Year 1		3		ear 2		Year 3						
		Q4	Q1	Q2	Q3	Q4	Q1	Q	2 Q	3 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 2 <sup>nd</sup> -generation of MTM catalysts	AH														

## Gantt Chart Approx. date today

Task 3.0 Synthesis and characterization of computationally predicted	BZ/WM												
active sites and powder catalysts													
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 2 <sup>nd</sup> -generation catalysts	BZ/WM							t					
Milestone 3.1: Synthesized <u>Rh-N-C@Ni</u> catalysts with detailed characterization	BZ/WM							T	•				
Milestone 3.0: Synthesis and characterization of 1st-generation of computationally predicted active sites and powder catalysts	BZ/WM							T		٠			
Milestone 3.0: Synthesis and characterization of 2 <sup>nd</sup> -generation of computationally predicted active sites and powder catalysts	BZ/WM							T				٠	
Task 4.0 Experimental evaluation of the catalysts for the partial oxidation of methane to methanol under relevant reaction conditions	WM							T					
Subtask 4.1 – Construction of new bench-scale reactor system for high-pressure MTM	WM							T					
Subtask 4.2 – Evaluation of catalysts for MTM activity and selectivity	WM							T					
Subtask 4.3 – Detailed kinetic studies of promising MTM catalysts	WM							Т					
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							Γ		٠			
Milestone 4.2: Experimental evaluation of 2 <sup>nd</sup> -generation of catalysts for the MTM under relevant conditions	WM							T				٠	
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							Τ					
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							T				٠	

## Bibliography

- List peer reviewed publications generated from the project per the format of the examples below.
- <u>Currently none to report</u>