Reduced Precious Metal Catalysts for Methane and NOx Emission Control of Natural Gas Vehicles

Mike Harold (PI), Lars Grabow (University of Houston)
Ru-Fen Liu (CDTi)
Bill Epling (University of Virginia)
Bill Partridge, Josh Pihl (Oak Ridge National Laboratory)

June 23, 2021

ACE128

Overview

Timeline

- Start: May 1, 2018
- End: April 30, 2022
- 75% complete

Budget

- Total project funding:
  - DOE: $1,640k (excl. ORNL)
  - UH & partners: $525k
- 3/31/2021 expenditure update:
  - $1435k federal (excl. ORNL)
  - $554k cost share

R1

Barriers/Targets

- Methane is greenhouse gas (25x CO_2); CH_4 GHG emissions above the 30 mg/mi light- duty vehicle cap count against fuel economy
- U.S. EPA mandates tailpipe methane emissions at 0.1 g/bhp-h for heavy-duty vehicles (95% reduction) & NOx emissions at 0.2 g/bhp-h
- State-of-art three-way catalyst (TWC) ineffective for methane oxidation at < 400 °C

Need for low cost emission catalyst for stoichiometric NG vehicles

Partners

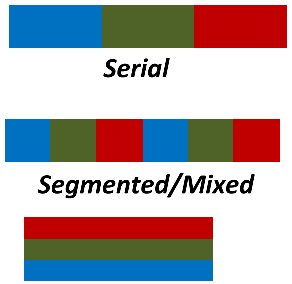
- U. Houston (lead)
- CDTi Advanced Materials, Inc.
- University of Virginia
- Oak Ridge National Lab

Relevance: Project Premise and Hypothesis

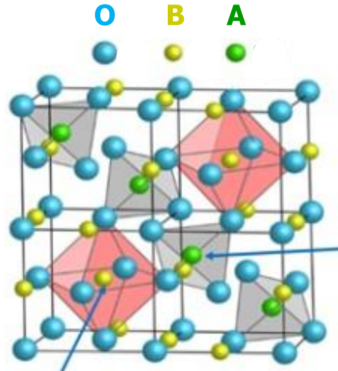
Develop the: ***FWC = Four Way Catalyst***

to enable reduced emissions of CH_4 in addition to CO, NOx & NMHCs from CNG-fueled vehicles

Material	**OSM**	+	**OXYCAT**	+	**N-RC**	**? =**	
	AB_2O_4 /Al_2O_3		**Pt/Pd /Al_2O_3**		**Pt/Rh/Al_2O_3**		
Function(s)	**O_2 storage & release**		**CH_4 + HC + CO oxidation**		**NO_x reduction**		



Spinel in combination with low levels of precious metals are cost-effective solution for coupled methane, CO and NO_x conversion in stoichiometric natural gas vehicle exhaust.



A Site – one metal with 4 nearest-neighbor O's **Tetrahedral Site**

B Site – one metal with 6 nearest-neighbor O's **Octahedral Site**

Spinel AB_2O_4

From 2020 AMR: Remaining Challenges & Barriers: Defining Future Work

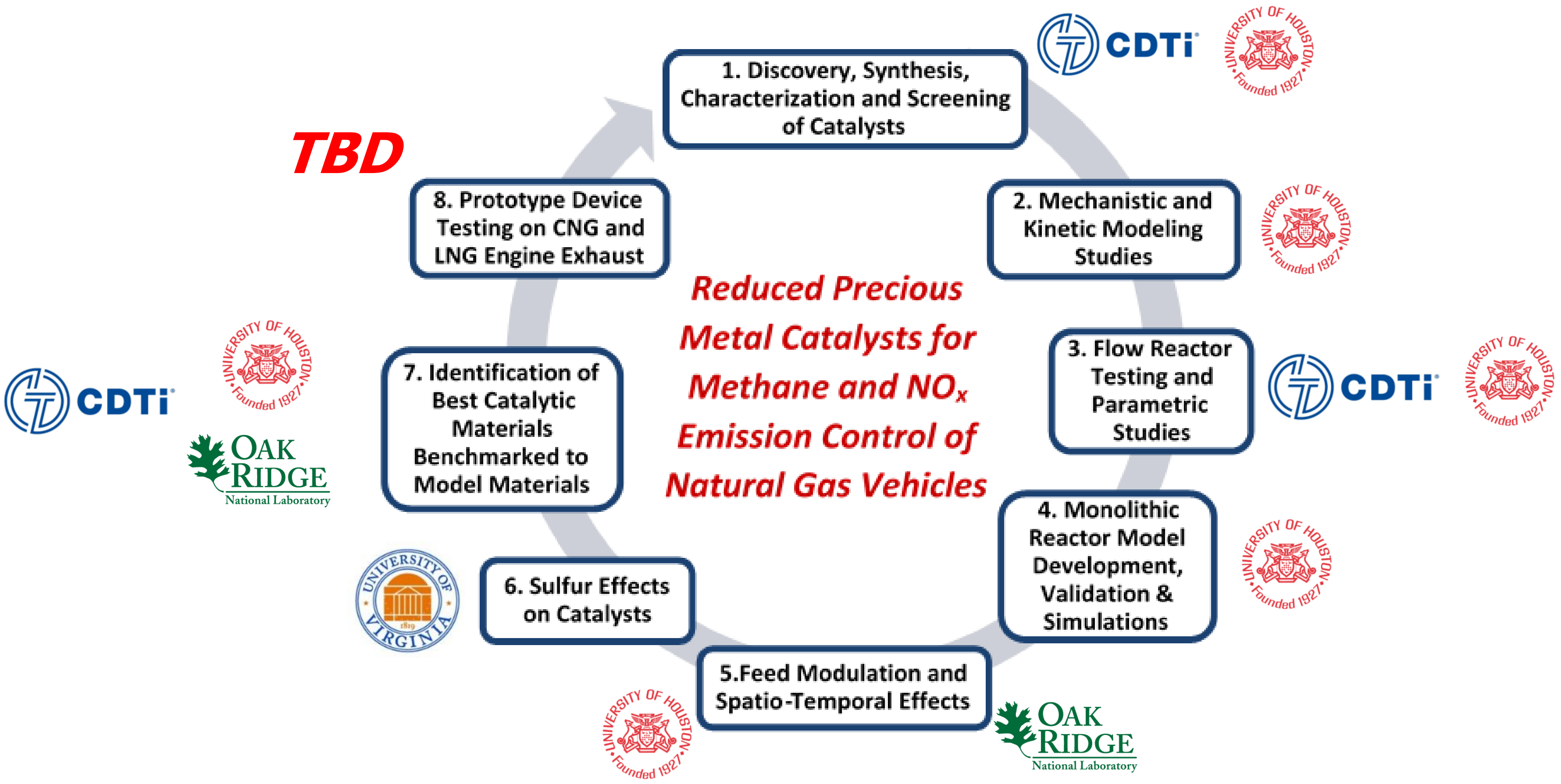
BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:

  Direct (methane oxidation) and/or Indirect (oxygen storage/release)

  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

Project Approach and Collaborations



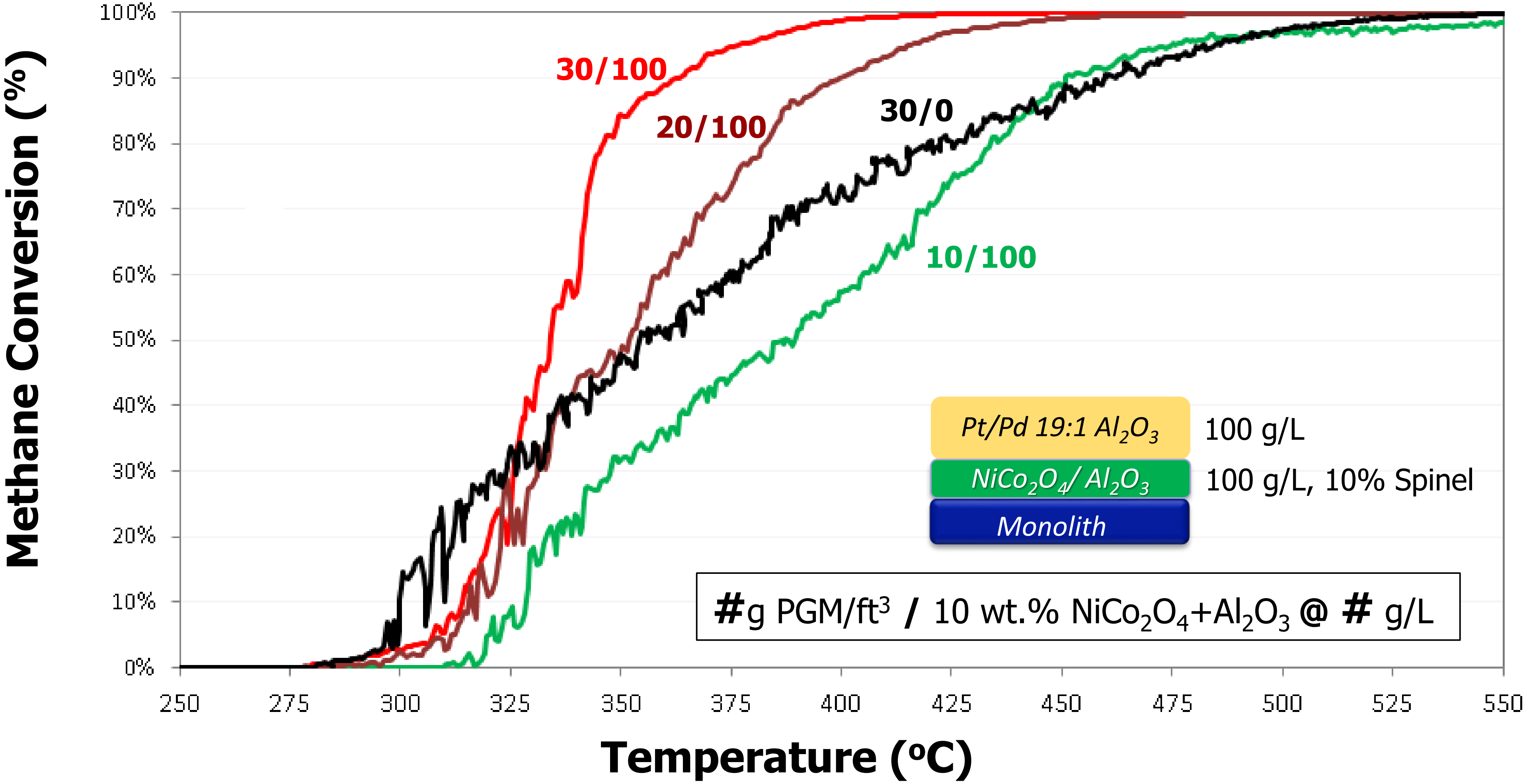
Comprehensive program spanning discovery, development, evaluation, and technology transfer will help to bring down cost barriers and accelerate the deployment of NGVs in the medium- and heavy-duty sectors

From 2020 AMR: Remaining Challenges & Barriers: Defining Future Work

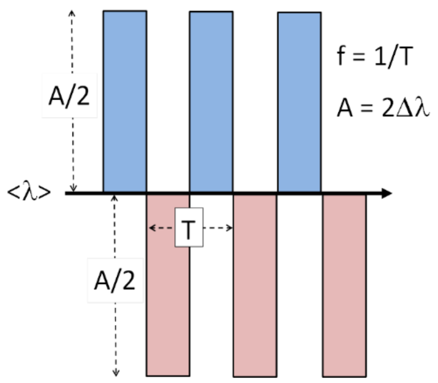
BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:
  Direct (methane oxidation) and/or Indirect (oxygen storage/release)
  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

PGM Thrifting with $NiCo_2O_4$ Spinel Addition



GHSV =90 hr^{-1}
<λ> = 0.996
f = 1 Hz
A = 0.028



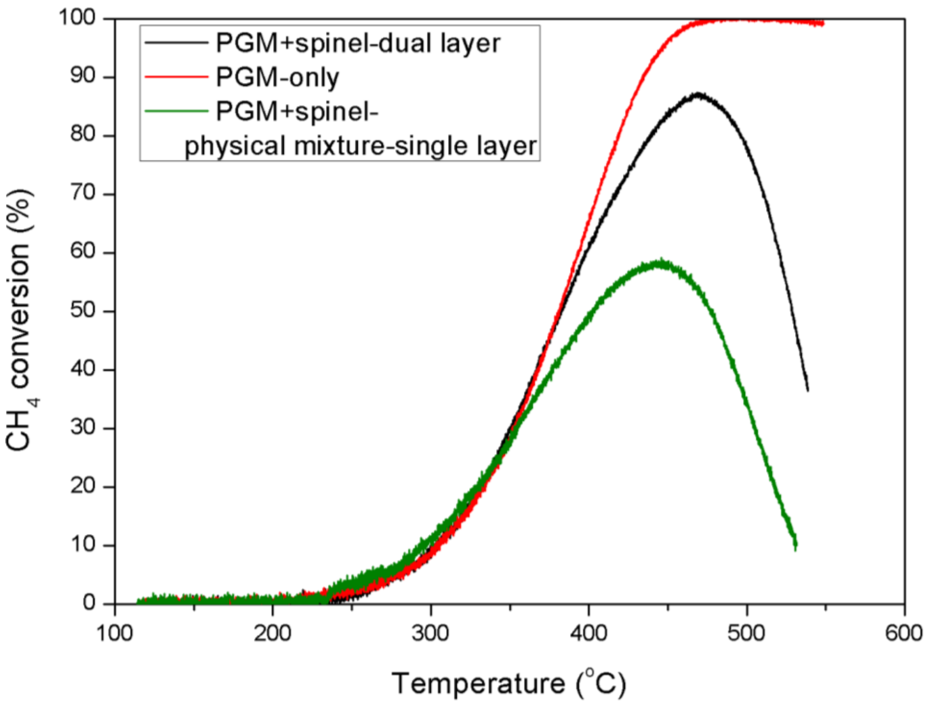
$NiCo_2O_4$ spinel addition equivalent to 10 - 15 g PGM/ft³

Catalyst Durability Findings

- Hydrothermal stability
  - Baseline catalyst shows activity loss under 900 ^{o}C + 12% H_2O exposure for 5 hours
  - Addition of CeO_2/ZrO_2 to Al_2O_3 support increases durability
- Sulfur poisoning
  - Spinel mitigates detrimental S poisoning of PGM at selected modulation frequencies
  - S degrades oxygen storage capacity of spinels
  - Desulfation strategies under investigation
- Metals migration
  - Evidence for Fe migration to PGM layer at high temperature and O_2 depletion
  - Leads to some loss of activity

Spinel Migration During Methane Steam Reforming

Steam reforming experiment:

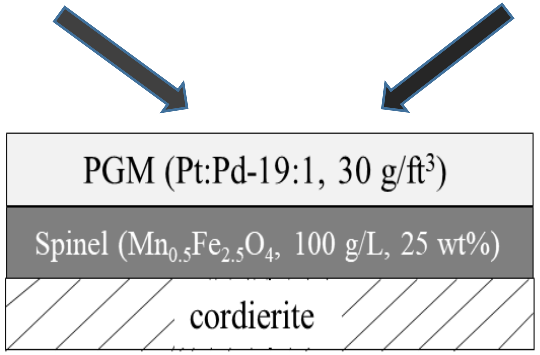


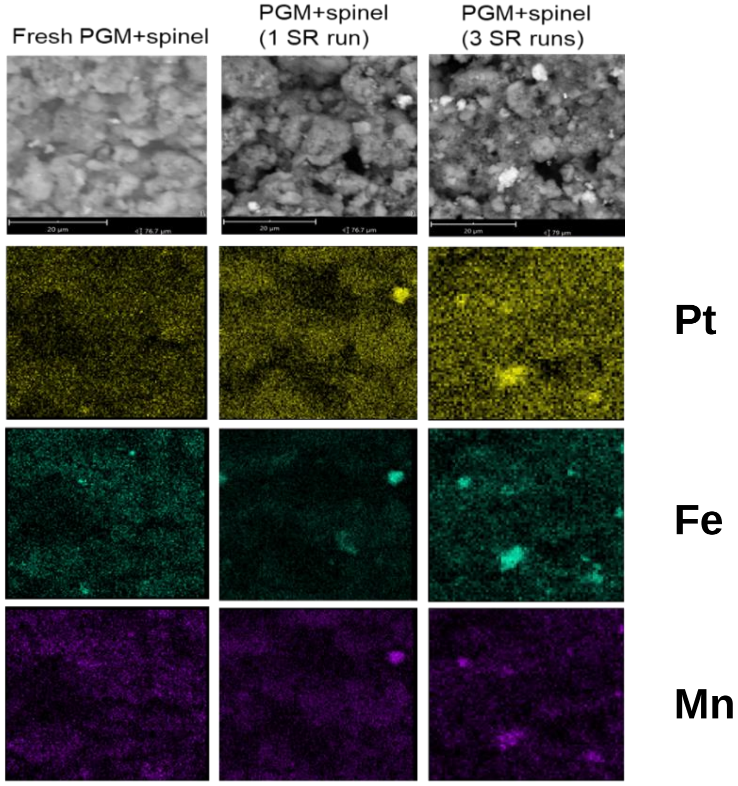
Amount of Fe and Mn species increased on PGM layer with prolonged SR run times

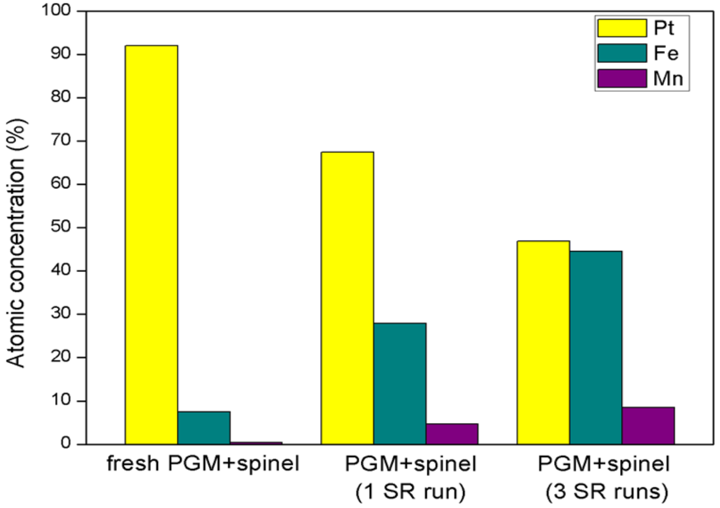
Hypothesis:

PGM site loss by elemental migration of Mn, Fe species from spinel layer to PGM layer during anaerobic conditions

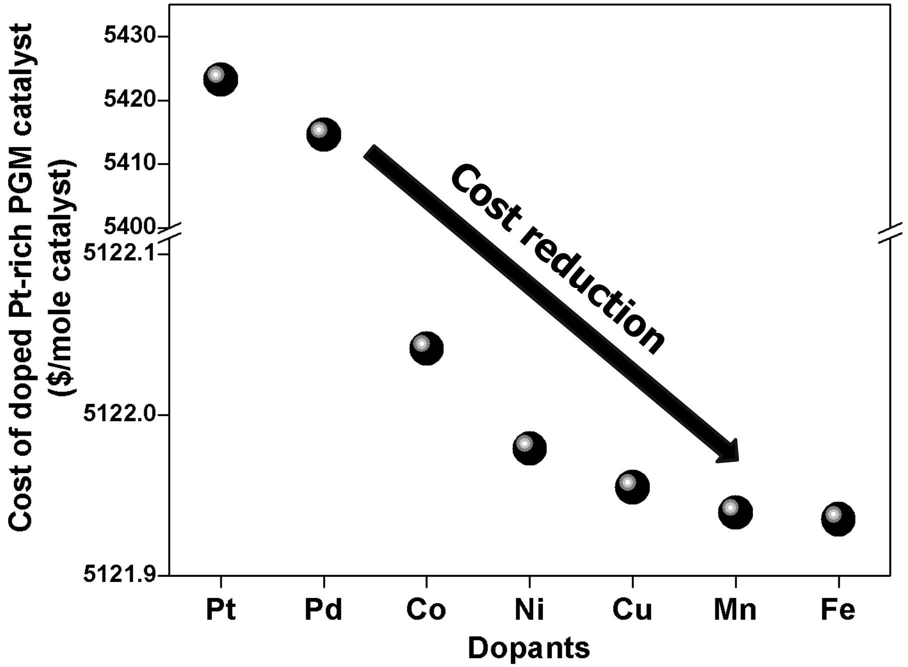
Pre-SR & post-SR catalyst characterization (CO-DRIFTS, SEM/EDS)



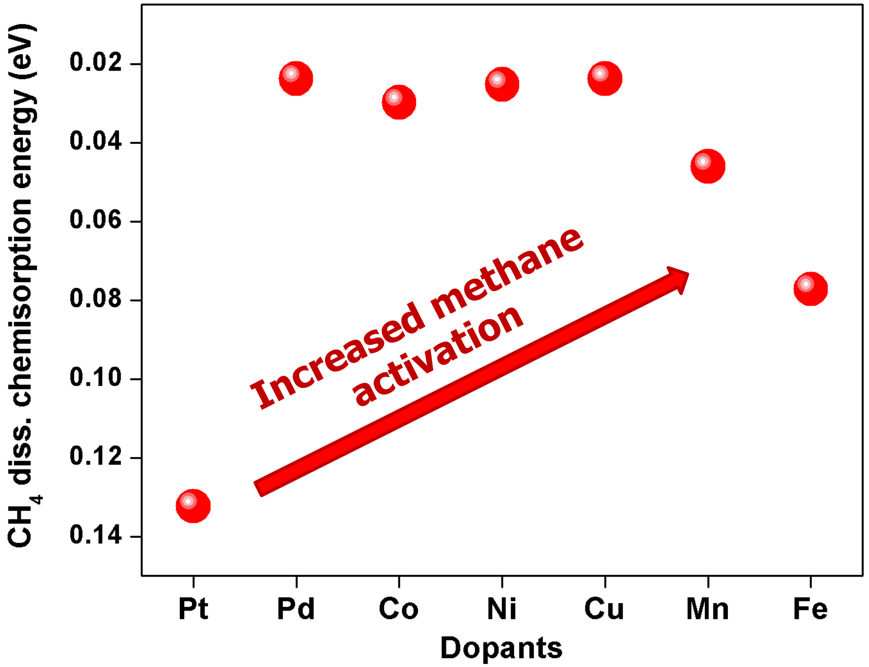




CH_4 Activation on Lower Cost PGM Catalysts



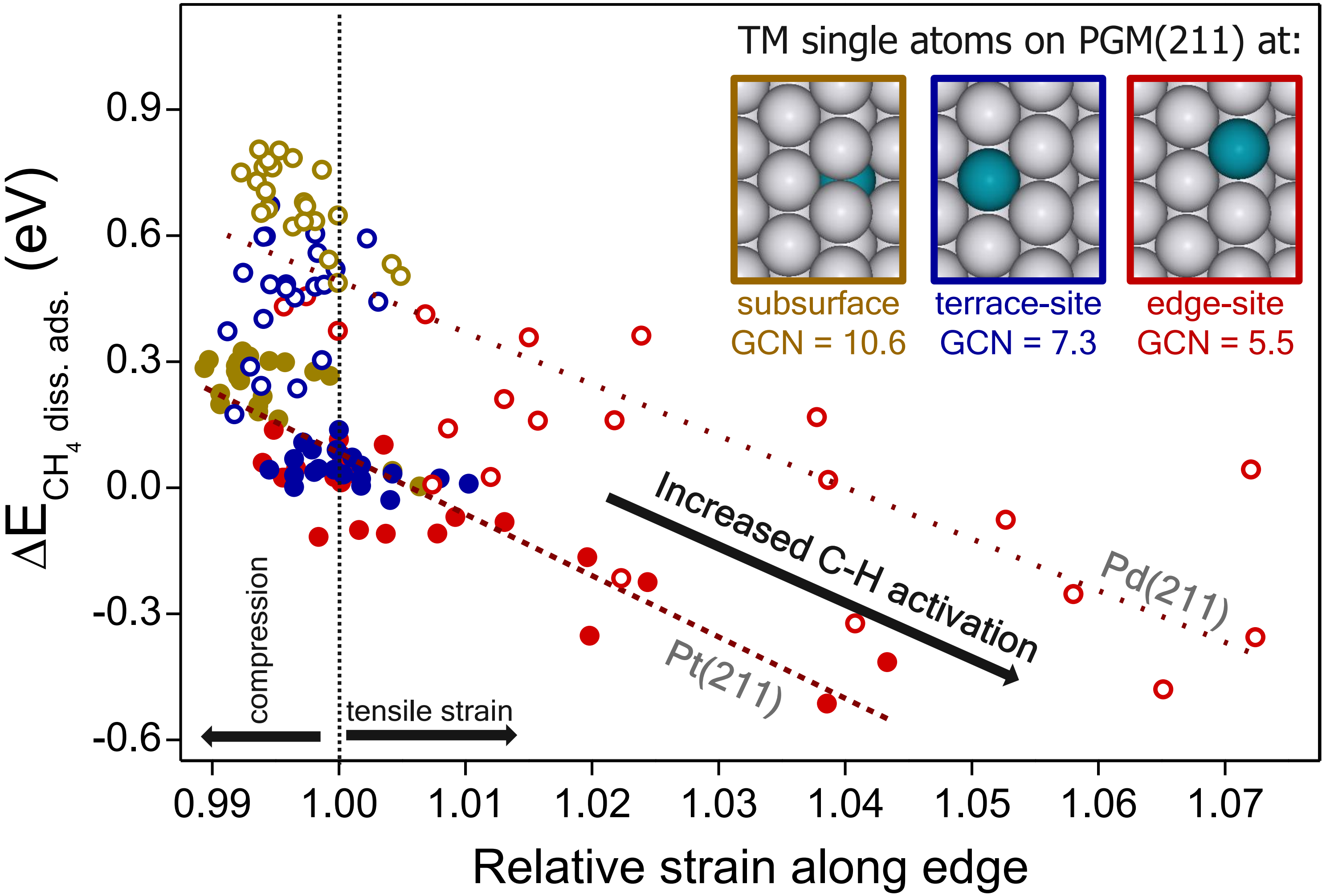
catalyst composition (Pt:dopants = 17:1)



catalyst composition (Pt:dopants = 17:1)

The CH_4 dissociation energy (a descriptor for CH_4 activation) on Pt modified with Co, Ni, or Cu is comparable to Pt-Pd alloys at considerably lower cost.

Promotion by Surface Strain



For the investigated dilute surface alloys, the effect of surface strain outweighs the modification of the electronic structure by alloying.

Promoters that induce a large expansive/tensile strain at undercoordinated sites are most effective.

From 2020 AMR: Remaining Challenges & Barriers: Defining Future Work

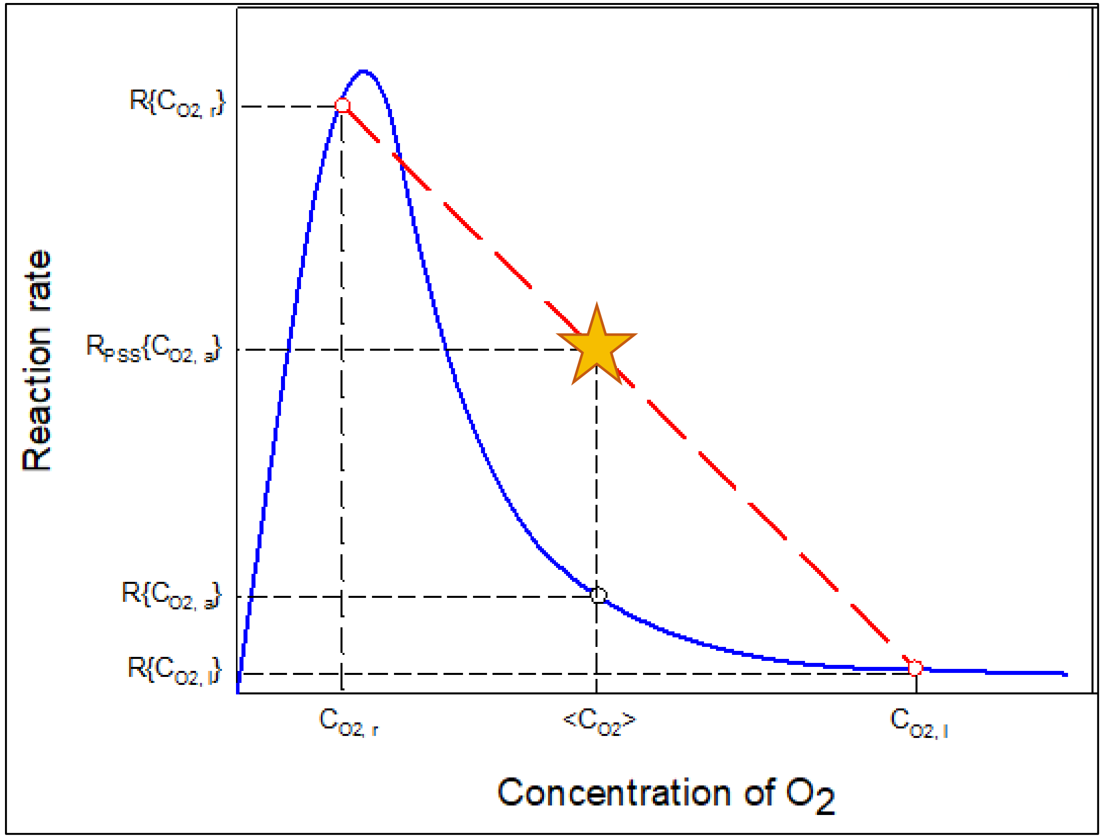
BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

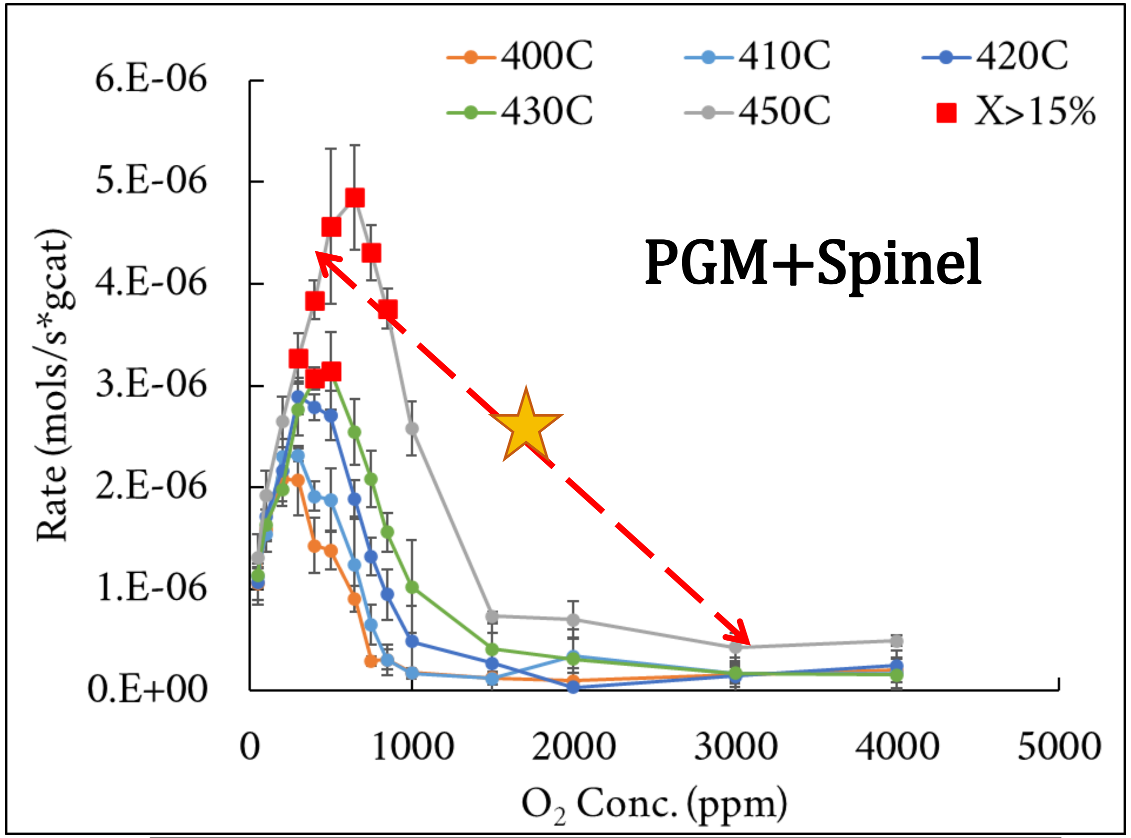
- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:

  Direct (methane oxidation) and/or Indirect (oxygen storage/release)

  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

CH_4 Oxidation Kinetics: O_2 Inhibition





Modulation achieves more active Pt+Pd for activating CH_4

O_2 + Pt + Pt → O-Pt + O-Pt

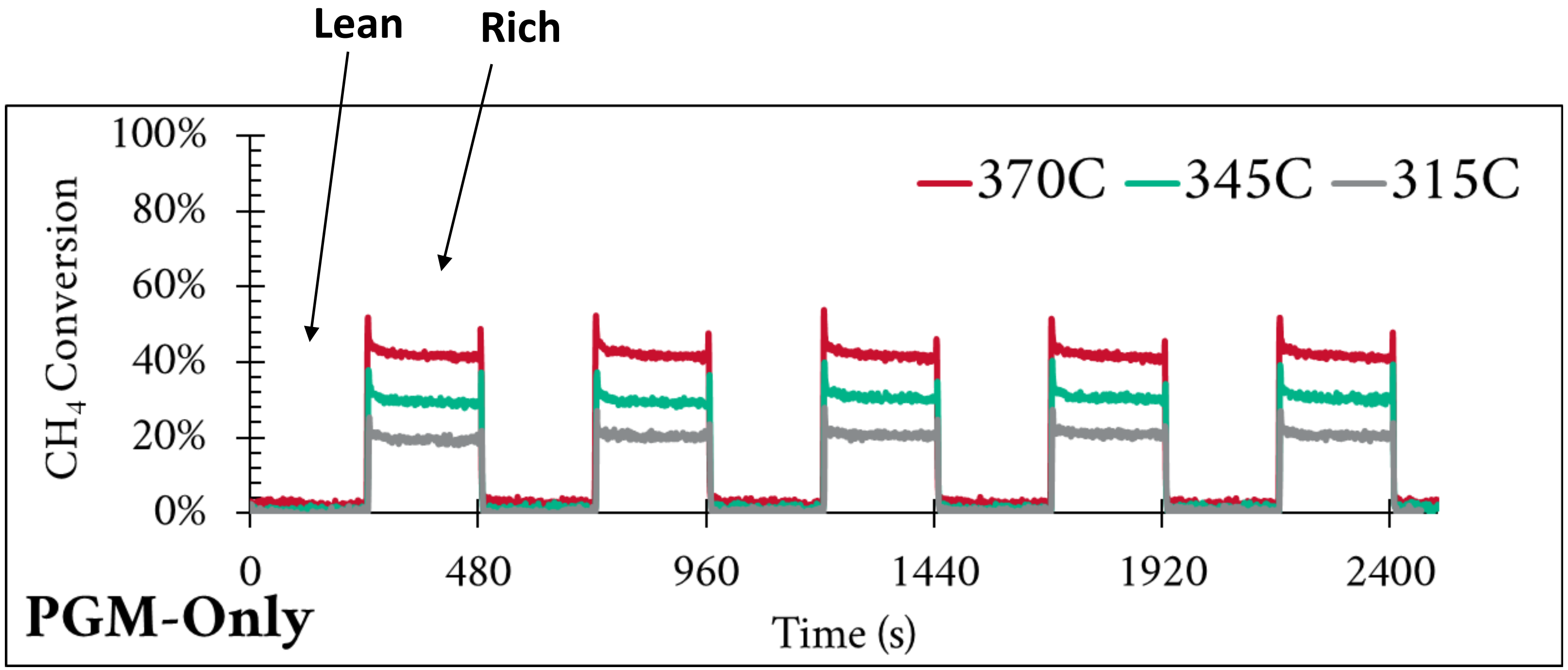
CH_4 + Pt + O-Pt → CH_3-Pt + OH-Pt

CH_3-Pt + n(O-Pt) → CO + H_2 + (n+1)Pt

Partially oxidized Pt is key to activating CH_4

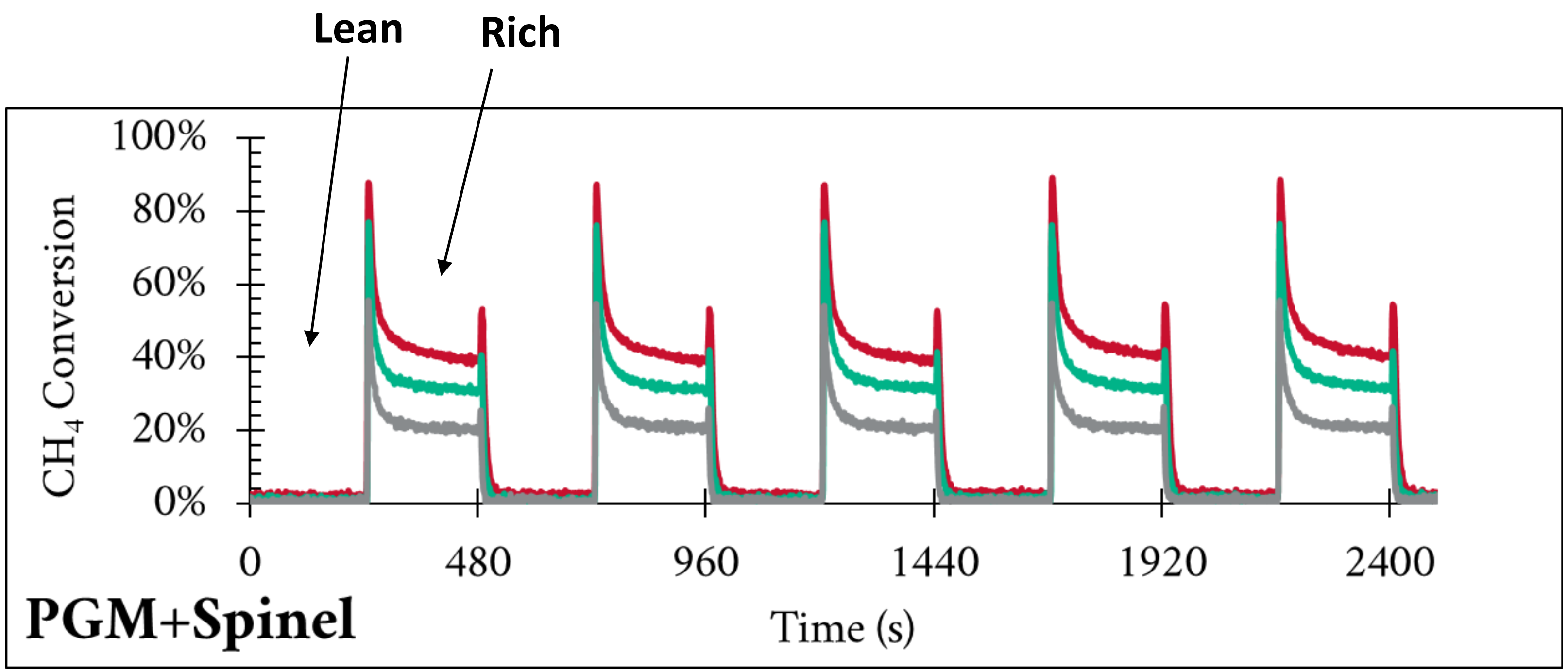
Modulation Impact: PGM-Only Catalyst

- *240s Lean/240s Rich*
- *Negligible conversion spike with PGM-only*

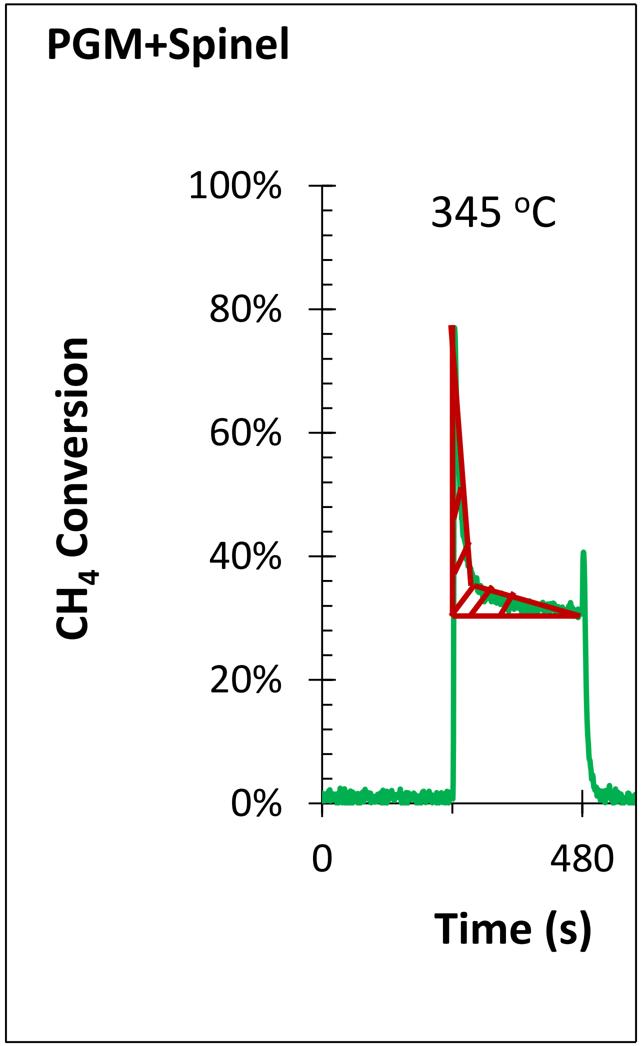


Modulation Impact: PGM-Spinel Catalyst

- *240s Lean/240s Rich*
- *Lean to Rich transition results in large transient spike in CH_4 conversion*
- *Role of spinel indicated*

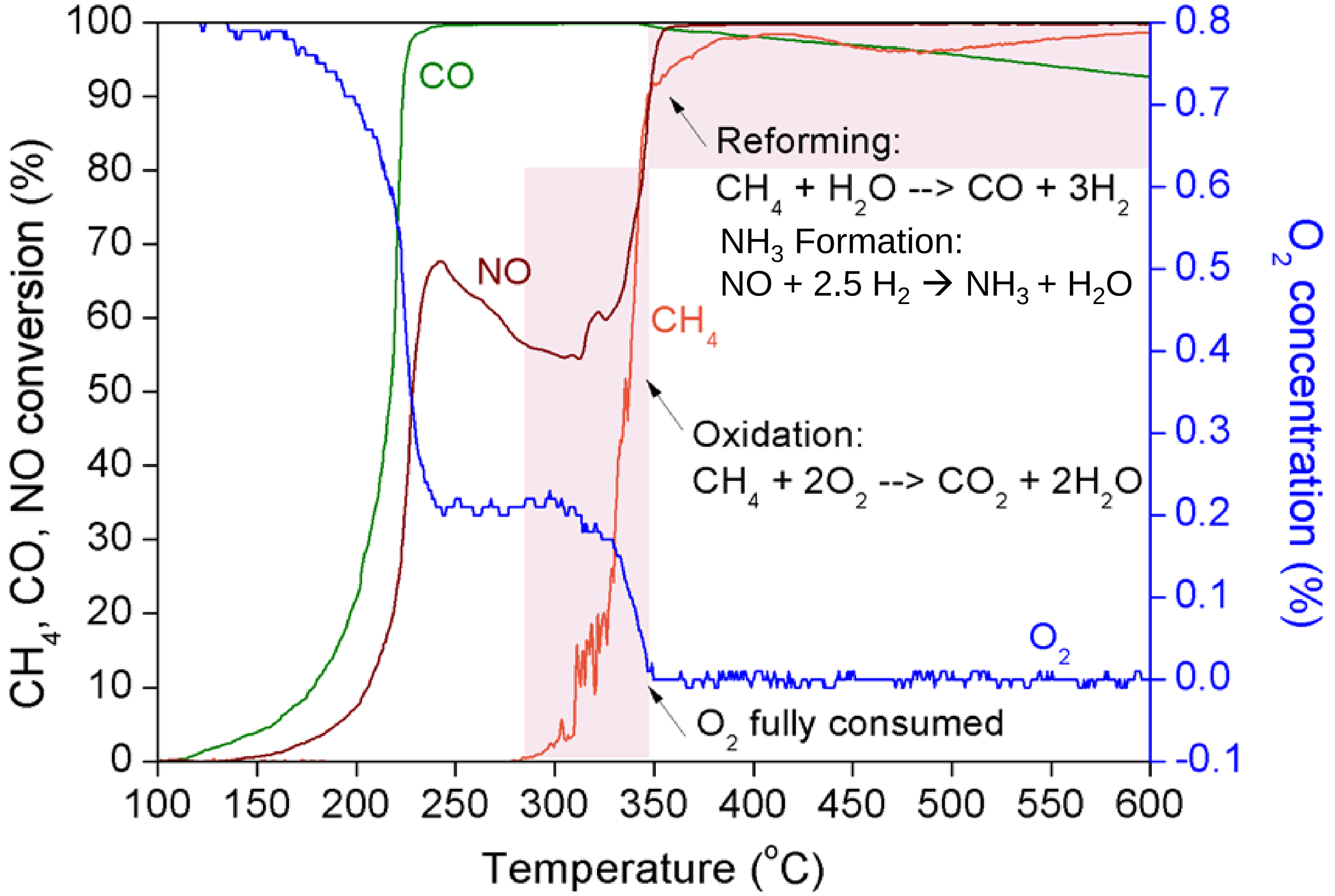


Lean to Rich Switch: Root Cause for Enhancement

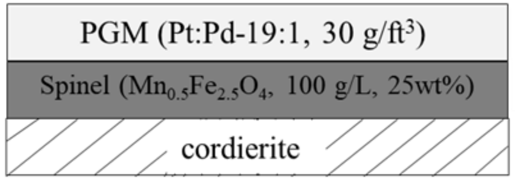


- *~75% of the incremental increase in CH_4 conversion with spinel addition due to conversion spike*
- *Suggests prominent root cause for enhancement*

CH_4 Conversion Light-off: $Pt+Pd/Al_2O_3$ + $Mn_{0.5}Fe_{2.5}O_4/Al_2O_3$ Dual Layer



PGM+Spinel (30/100)



0.15% CH_4, 0.8% CO, 0.1% NO, 0.2% H_2, 10% CO_2,10% H_2O
GHSV = 90k h^{-1}

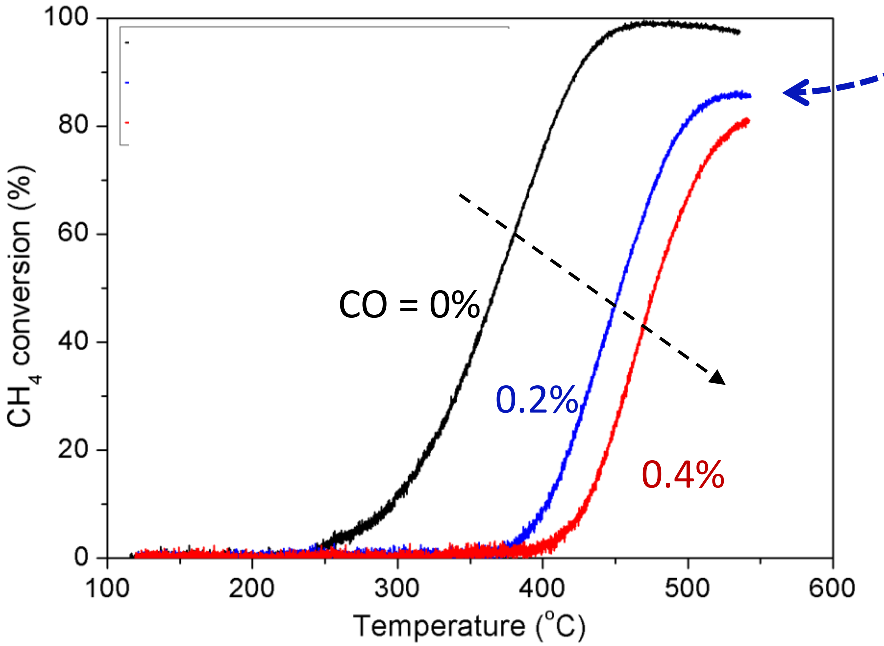
Without modulation:
λ_{avg} = **0.996**
0.565% O_2

With modulation:
λ_{avg} = **0.996**
0.34% $O_{2\ main}$
0.45% $O_{2\ add}$

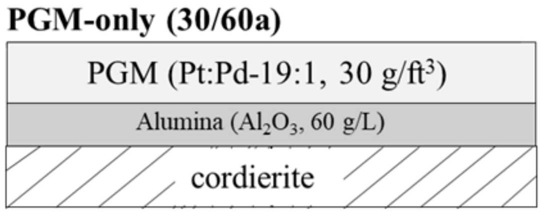
- *Most (~80%) CH_4 conversion by O_2; remainder (20%) by H_2O/CO_2*

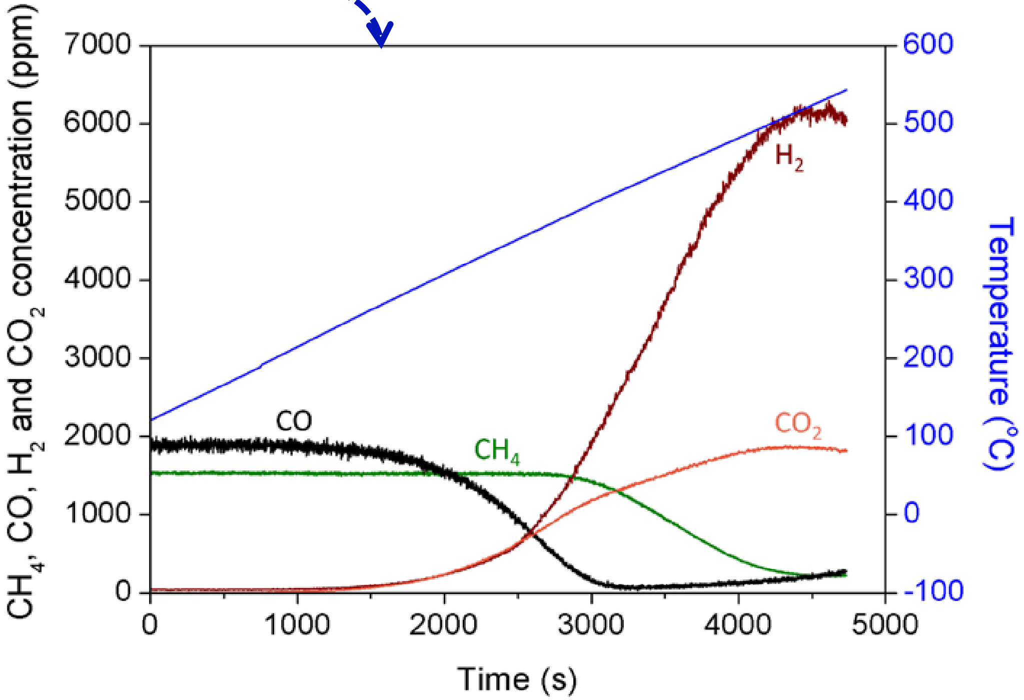
Steam Reforming of CH_4 on Pt-Pd/Al_2O_3

Conditions:
GHSV =40 hr^{-1}
1500 ppm CH_4, 10% H_2O
0.2% & 0.4% CO added



SR+0.2%CO:



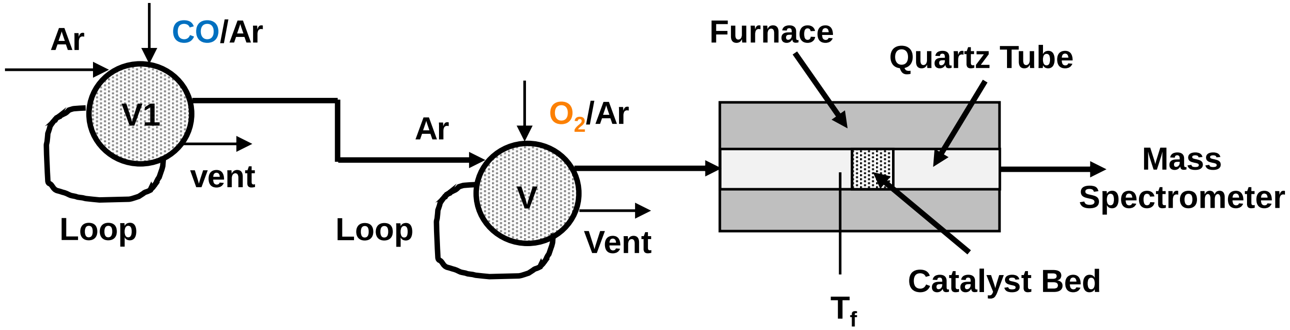


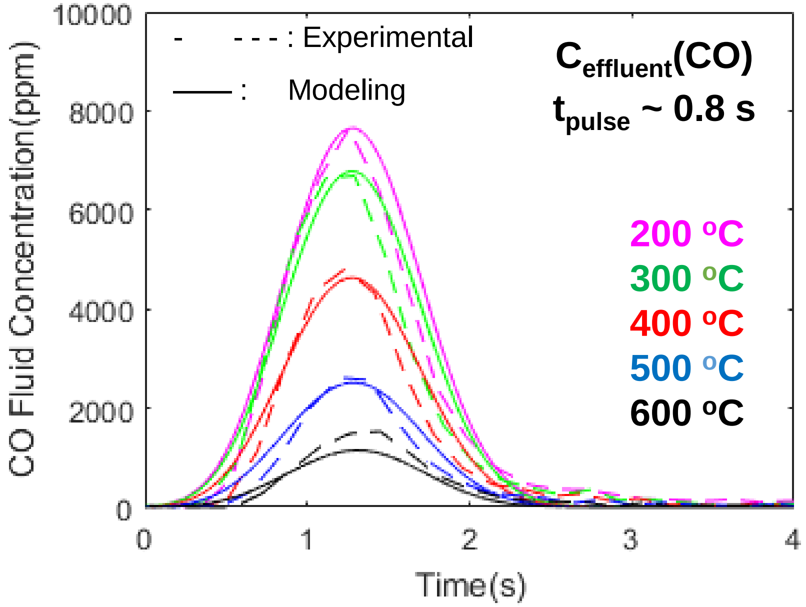
Rate (MSR) ~ $(CO)^n (H_2)^m$

$n < m < 0$

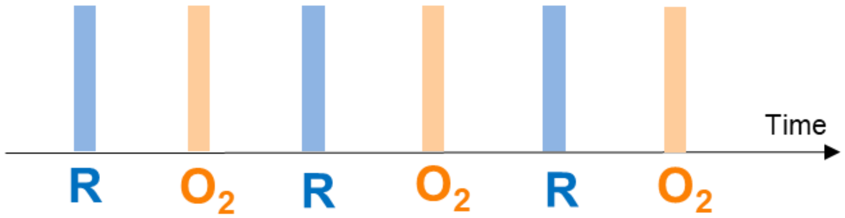
Addition of CO has inhibiting effect on reforming activity

DOSC of MFO Spinel with CO as Reductant





Periodic Pulsing of R (CO, H_2, CH_4) & O_2:

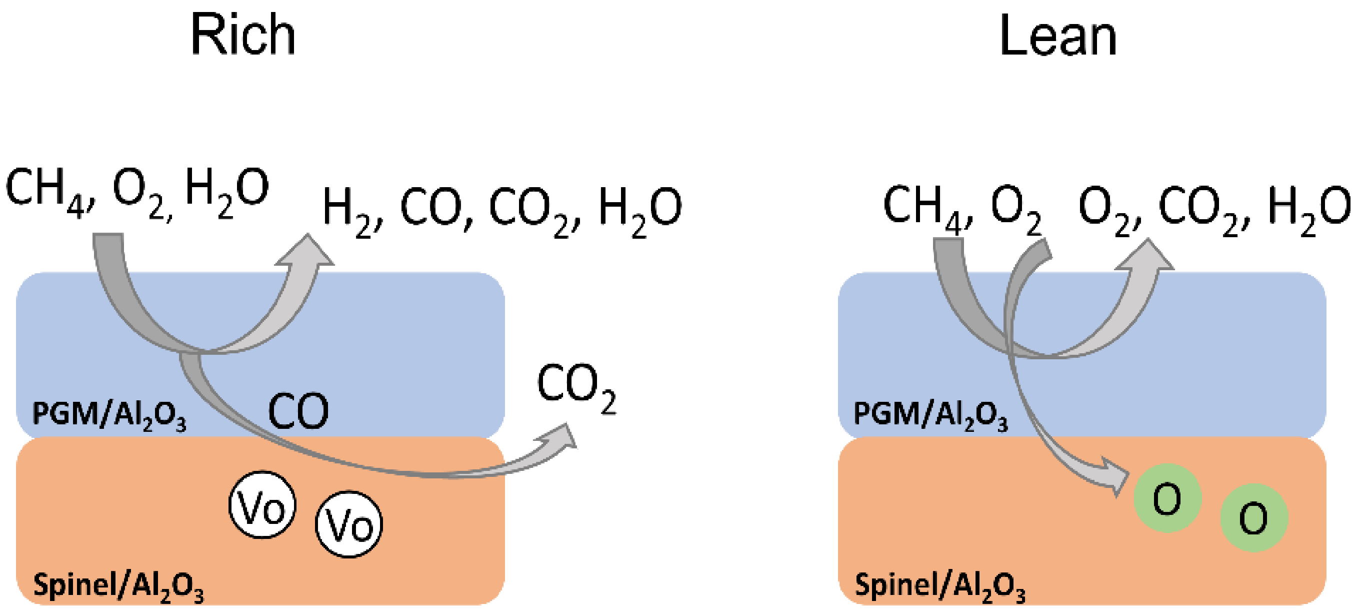


Conditions:
1.0% CO/Ar, 0.9% O_2/Ar, 0.8s/0.8s,
15 mg MFO/Al_2O_3, 150 sccm

- *Short-pulse CO-DOSC on MFO spinel shows excellent activity*
- *Analysis shows only first layer of O utilized during first several seconds*

Z. Zhou, M.P. Harold, D. Luss, Ind. Eng. Chem. Res. (2021).

Oxidation Enhancement Mechanism



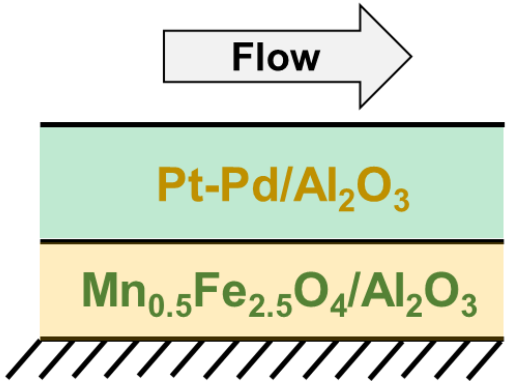
Conversion enhancement due to removal of MSR inhibitors CO & H_2 through their oxidation by spinel

From 2020 AMR: Remaining Challenges & Barriers: Defining Future Work

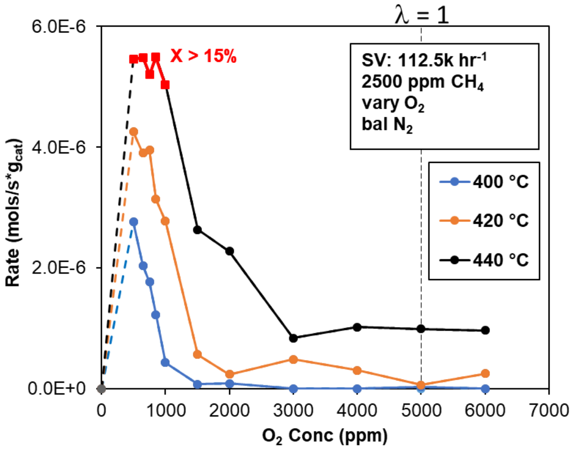
BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:
  Direct (methane oxidation) and/or Indirect (oxygen storage/release)
  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

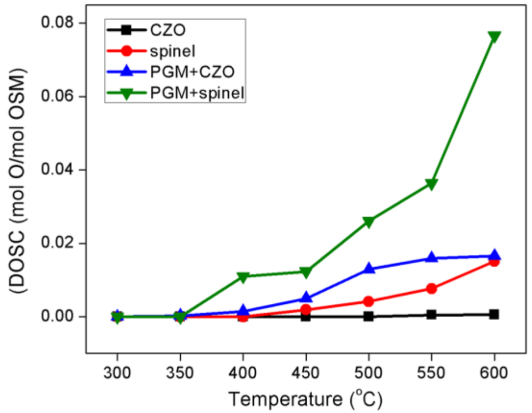
Monolith Reactor Model Elements



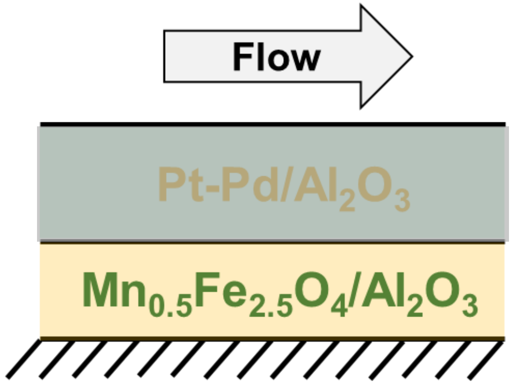
- Pt + Pd /Al_2O_3
  - CH_4 oxidation kinetics



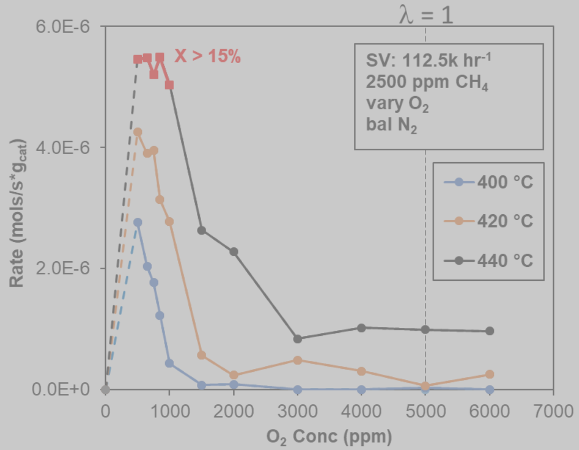
- Spinel/Al_2O_3
  - O_2 storage & release kinetics



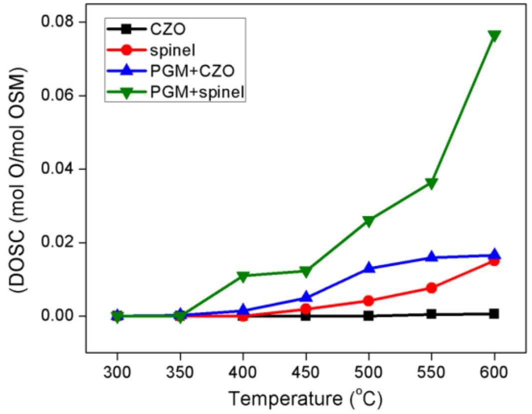
Monolith Reactor Model Elements



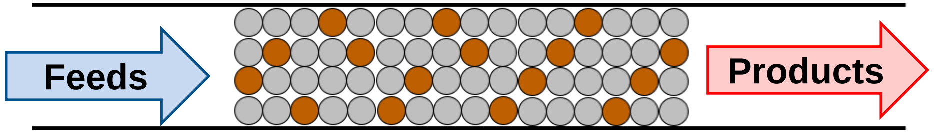
- Pt + Pd /Al_2O_3
  - CH_4 oxidation kinetics



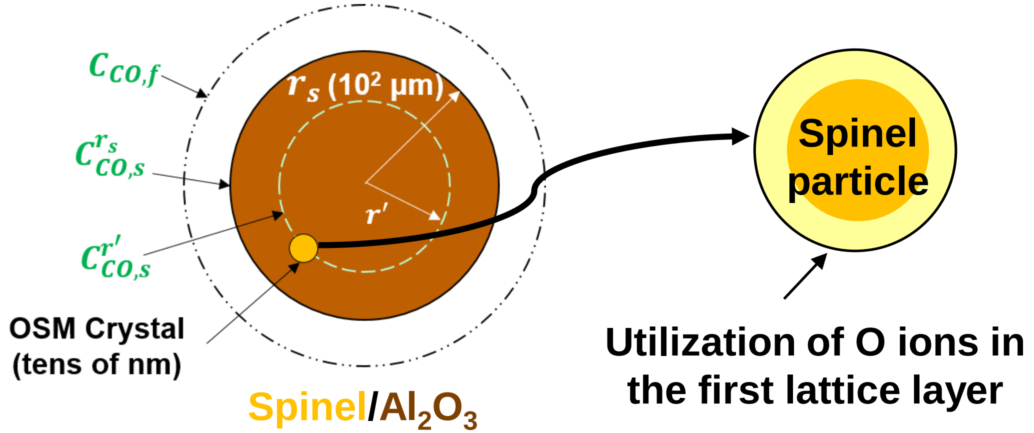
- Spinel/Al_2O_3
  - O_2 storage & release kinetics



Spinel O_2 Uptake & Release DOSC Model



Diluent Pellet (Silica)   OSM Pellet (MFO spinel)



- **Species balances in heterogeneous model:**

Fluid Phase	$\frac{\partial x_{f,i}}{\partial t} + \frac{u_f}{\varepsilon_b}\frac{\partial x_{f,i}}{\partial z} = -k_{c,i}a_s\frac{\varepsilon_p}{\varepsilon_b}(x_{f,i} - x_{s,i})$
Solid Phase	$\frac{\partial x_{s,i}}{\partial t} = D_{e,i}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial x_{s,i}}{\partial r}) + \frac{1}{C_0}\sum_{j=1}^{r}\upsilon_{nj}r_j$
Site Balance	$\frac{\partial \vartheta_i}{\partial t} = \frac{1}{\Omega_{MFO_4}}\sum_{j=1}^{r}\upsilon_{nj}r_j$

- **Boundary conditions:**

at z = 0	$x_{f,i}(t) = x^{in}_{f,i}(t)$
at r = 0	$\left.\frac{\partial x_{s,i}}{\partial r}\right\rvert_{r=0} = 0$
at r = r_s	$k_{c,i}(x_{f,i} - x_{s,i}) = -D_{e,i}\left.\frac{\partial x_{s,i}}{\partial r}\right\rvert_{r=r_s}$

- **Reaction Steps**

1) $MFO_4 \underset{O_2}{\overset{CO/H_2}{\rightleftharpoons}} MFO_3 + O$

2) $MFO_3 \underset{O_2}{\overset{CO/H_2}{\rightleftharpoons}} MFO_{0.5} + 2.5\ O$

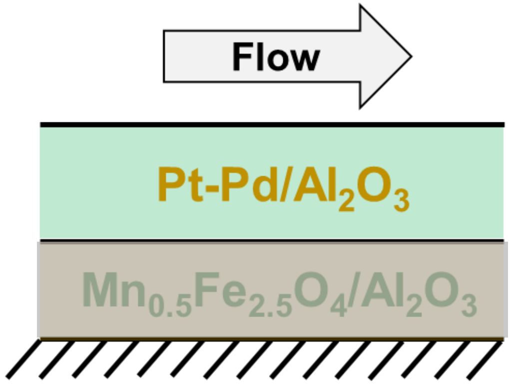
MFO_4: $Mn_{0.5}Fe_{2.5}O_4$

- **Rate Expression**

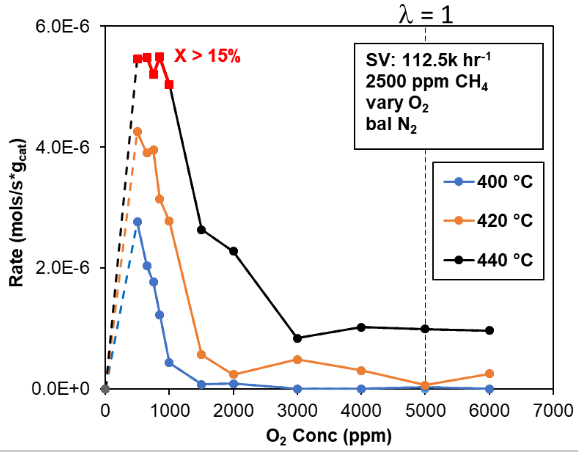
$$r_{1,red.} = k_{1,r}C_{CO}\Omega_{MFO_4}\vartheta_{MFO_4}$$
$$r_{1,oxi} = k_{1,o}C_{O_2}\Omega_{MFO_4}\vartheta_{MFO_3}$$
$$r_{2,red.} = k_{2,r}C_{CO}\Omega_{MFO_4}\vartheta_{MFO_3}$$
$$r_{2,oxi} = k_{2,o}C_{O_2}\Omega_{MFO_4}\vartheta_{MFO_{0.5}}$$

$$\vartheta_{MFO_x} = \frac{N_{MFO_x}}{N_{MFO_4} + N_{MFO_3} + N_{MFO_{0.5}}}$$

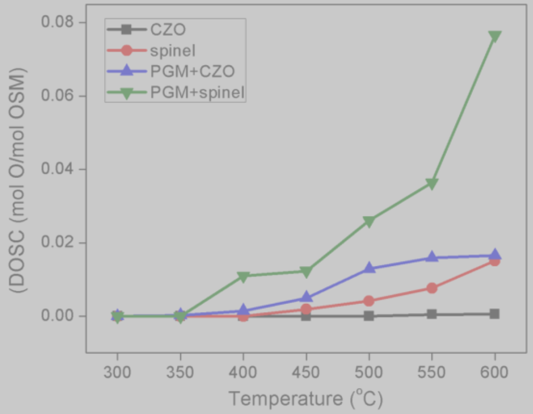
Monolith Reactor Model Elements



- Pt + Pd /Al_2O_3
  - CH_4 oxidation kinetics



- Spinel/Al_2O_3
  - O_2 storage & release kinetics



UNIVERSITY OF HOUSTON • Founded 1927 •

Overview | Milestones | Relevance | **Approach** | Progress | Future Work | Collaborations

Methane Oxidation on Pt/Pd/Al_2O_3: Monolith Model

- 1 + 1 D monolith model
- Global kinetics approach
  - Use 1 - 3 reactions from the set

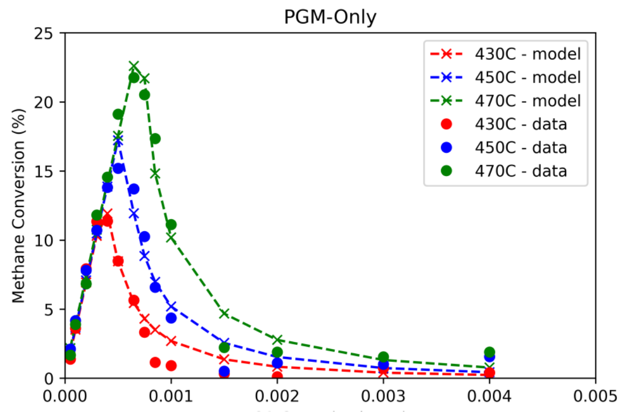
Total oxidation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

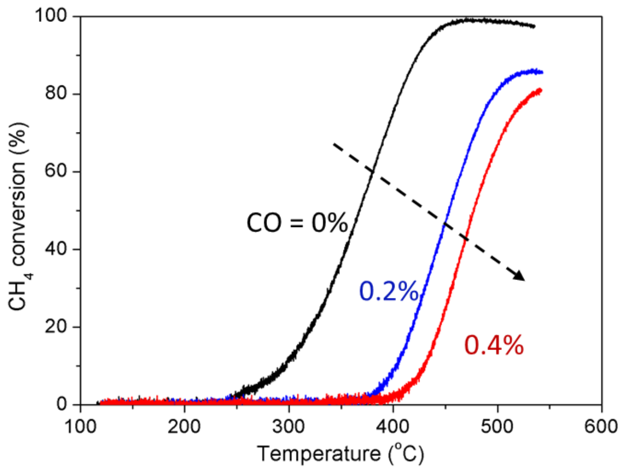
Partial oxidation: $CH_4 + 0.5\ O_2 \leftrightarrow CO + 2H_2$

Water gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$

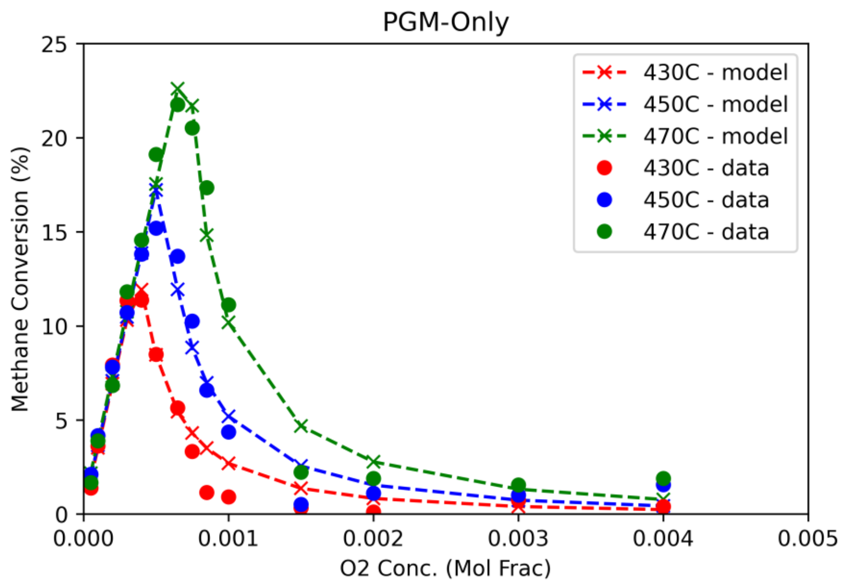
Steam reforming: $CH_4 + 0.5\ O_2 \leftrightarrow CO + 2H_2$

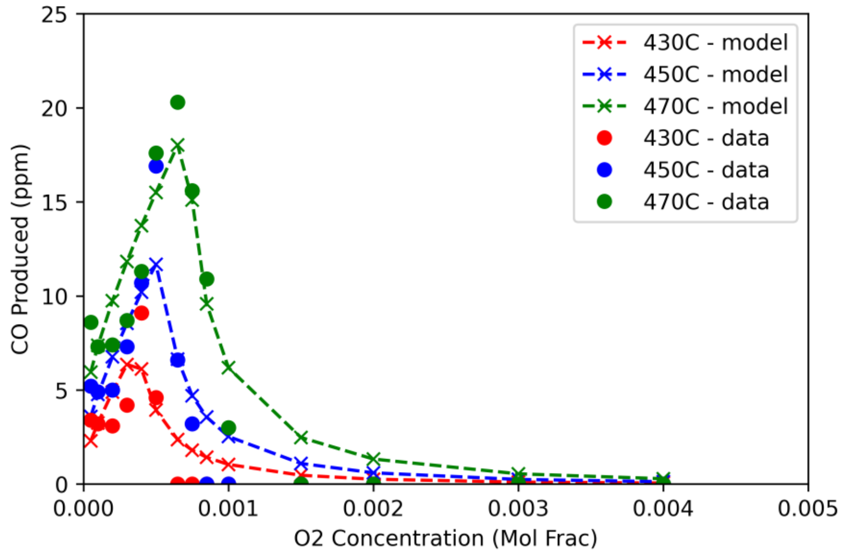
- Combine kinetics for
  - CH_4 oxidation
  - Water gas shift
  - Steam reforming: Incorporate CO& H_2 inhibition
- Validate complete model





Methane Oxidation on $Pt/Pd/Al_2O_3$: Monolith Model





$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$$r_{TO} = k_1 * K_{in_1} * \frac{Y_{CH4} * Y_{O2}}{\left(1 + K_{in_1} Y_{O2}\right)^3}$$

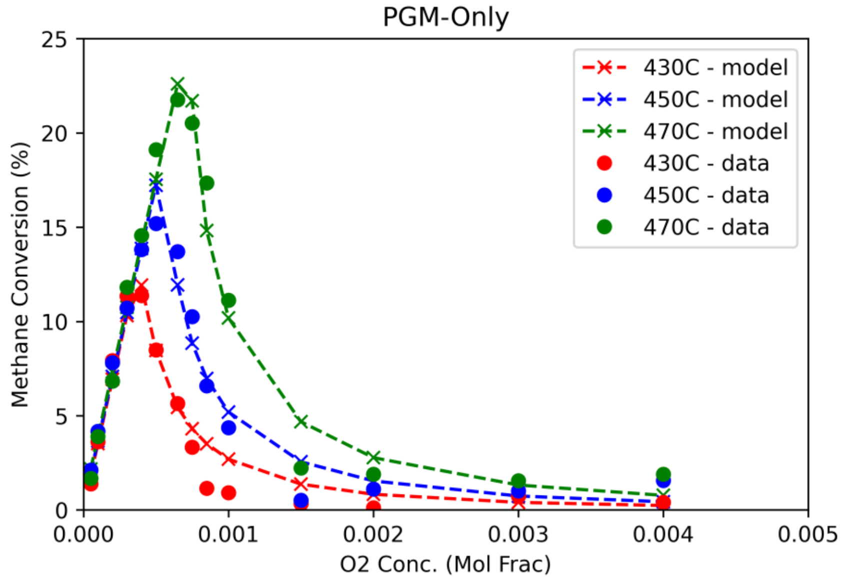
$CH_4 + 0.5\ O_2 \leftrightarrow CO + 2H_2$

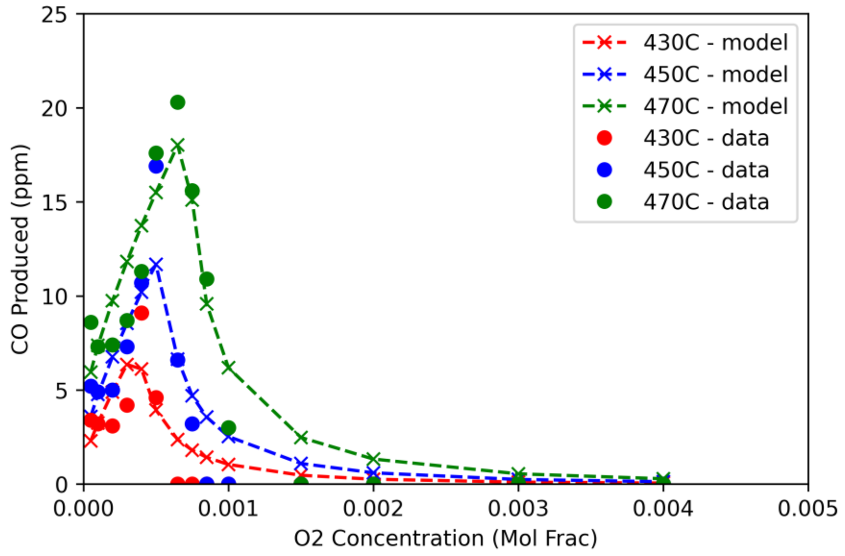
$$r_{PO} = k_2 * K_{in_2} * \frac{Y_{CH4} * Y_{O2}^{0.5} - \frac{1}{K_{e,PO}} * Y_{CO} * Y_{H2}^2}{\left(1 + K_{in_2} Y_{O2}\right)^3}$$

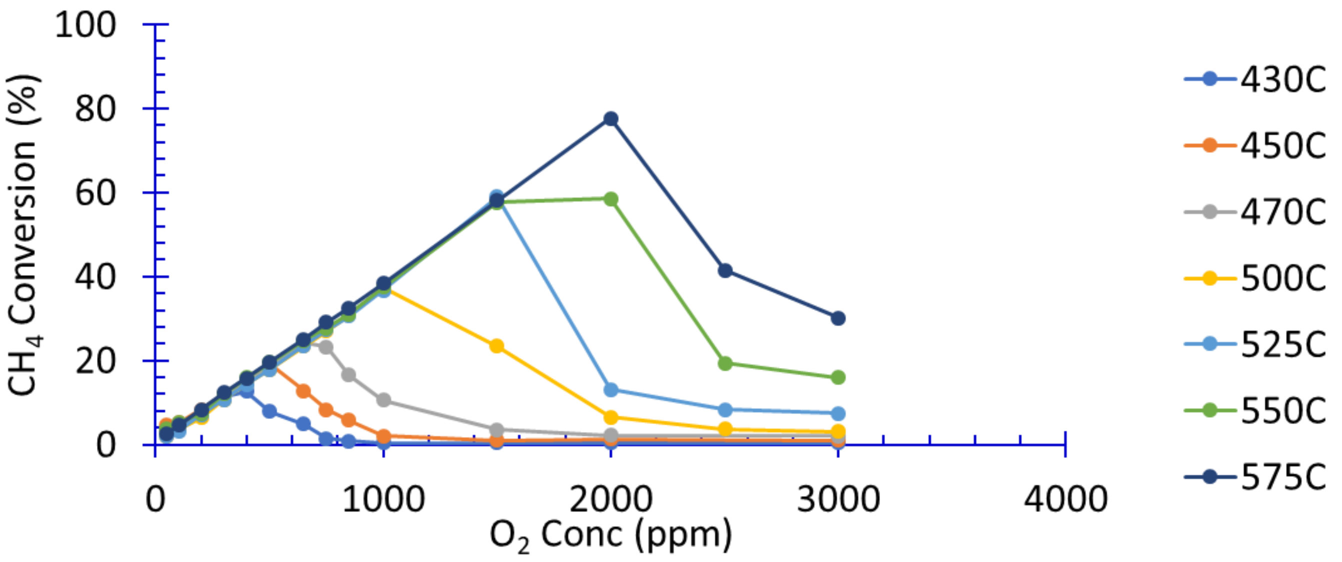
$CO + H_2O \leftrightarrow CO_2 + H_2$

$$r_{WGS} = k_3 * \left(Y_{CO} * Y_{H2O} - \frac{1}{K_{e,WGS}} * Y_{CO2} * Y_{H2}\right)$$

Methane Oxidation on Pt/Pd/Al_2O_3: Monolith Model







From 2020 AMR: Remaining Challenges & Barriers: Defining Future Work

BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:

  Direct (methane oxidation) and/or Indirect (oxygen storage/release)

  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

Approach for Resolving Transient Lambda-Modulation Distribution

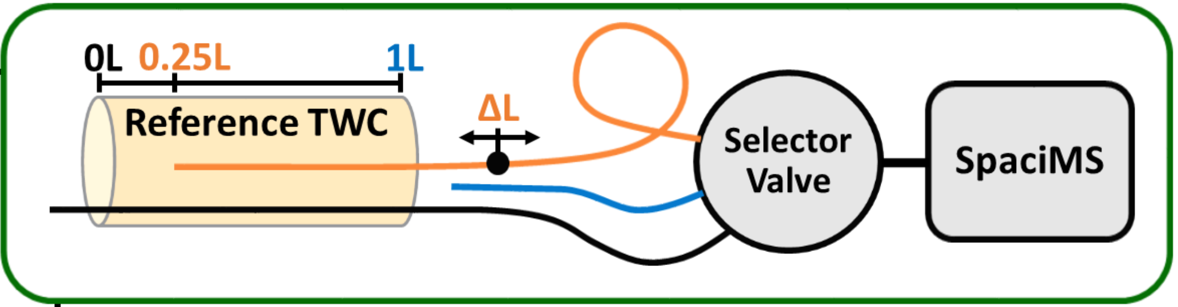
Species	Conc.
H_2O	18.5%
CO_2	9.5%
CH_4	0.42%
CO	0.45%
H_2	0.15%
NO	0.10%
O_2	varies

Variable	Values
GHSV (h^{-1})	40,000
T (°C)	400
Centerpoint λ	1.000
Amplitude	0.10
frequency	0.25

λ	O_2
1.05	2.038%
0.95	0.331%

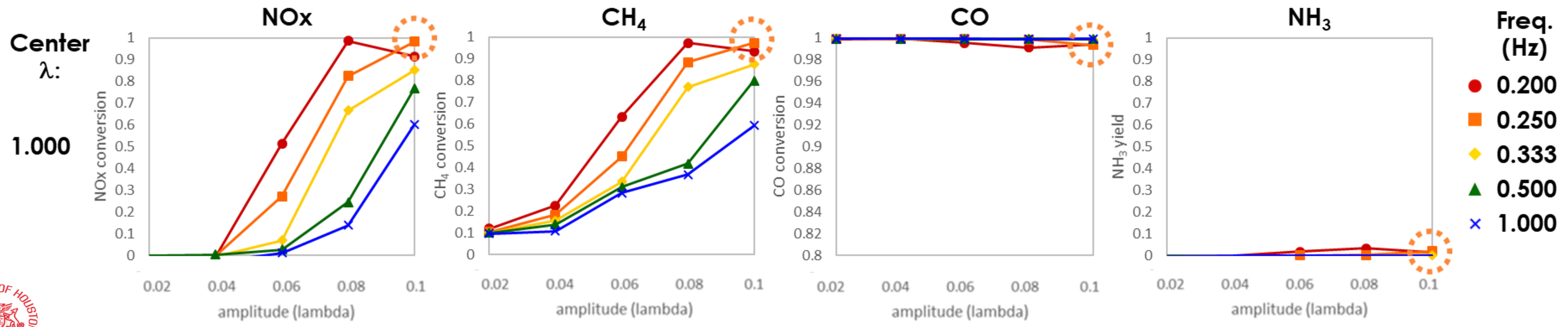
Reference TWC

- Commercial, Pd based
- PGM: 90 g/ft^3
- Support: $CeZrO_x$ & Al_2O_3
- 400cpsi cordierite monolith
- Gong et al., Catal. Today, V360, p294-304, 2021



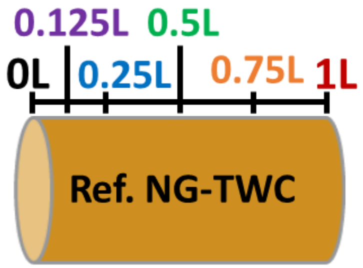
Integral Conversion & Yield

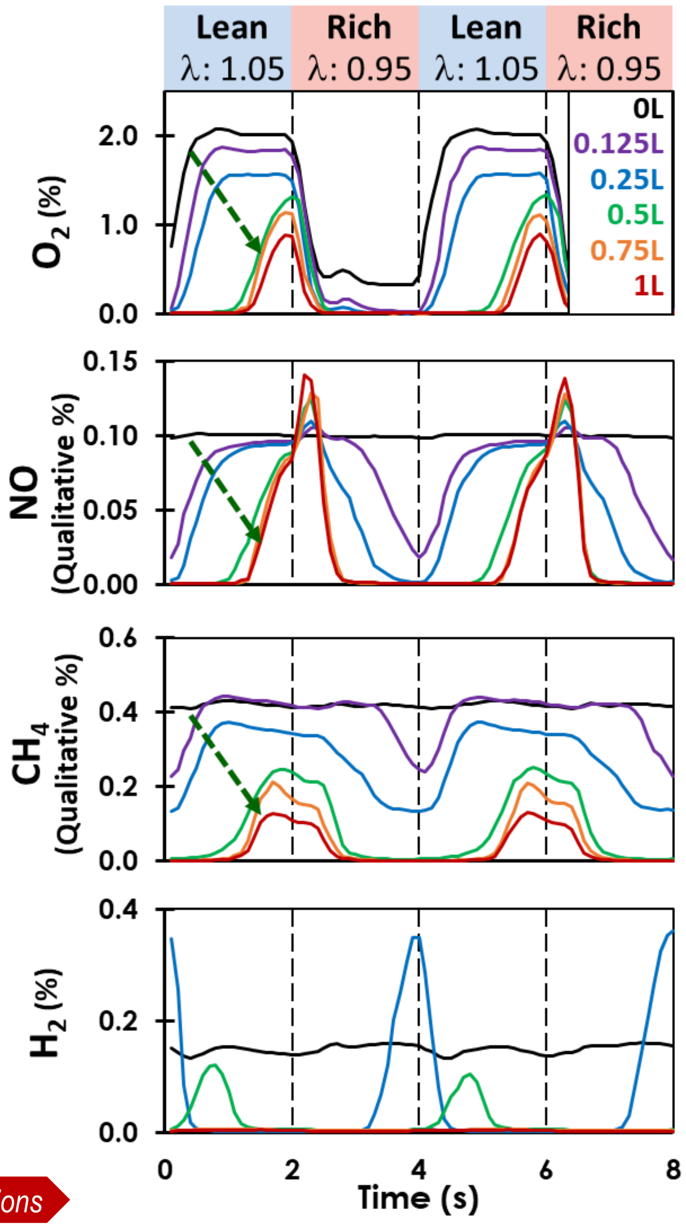
- Reference TWC, 400°C, broad Lambda-dither sweep
- High for NO_x, CH_4, and CO
- Negligible NH_3 yield



Modulated Conversion Evolves Along Catalyst

- Lambda 0.95-1.05 wave travels along catalyst axis
  - Lambda modulated implemented by O_2 modulation
- O_2 consumed both at Lambda-wave front and body
  - Fully consumed at wave front – possibly replenishing OSC
  - Only tail of O_2 modulation remains at catalyst exit, 1L
- NO conversion mainly in rich phase
  - Onset and tail appears to follow OSC depletion & restoration dynamic
  - Generation pulse at Lean-Rich transition
- CH_4 conversion greatest when OSC most depleted (R-L transition)
  - Produces H_2 via steam reforming
- Intra-catalyst-generated H_2 consumed within the catalyst
- ***SpaciMS offers great insights for understanding fundamental chemistry and optimizing catalyst design and control***
  - Broadly sweep Lambda modulation and temperature conditions
  - Apply spatiotemporal data to guide and validate model development





Reviewer Comments from 2020 AMR

- **Technical Barriers (TB)**
  - **n/a**
- **Technical Accomplishments (TA)**

TA1: Not to nitpick, but the presentation of the budget period 2 (BP2) go/no-go decision is confusing (and probably a copy-and-paste error). The decision point is "Identification of a candidate material complete," and the description refers to modeling progress. It can be inferred that this was meant to refer to the modeling effort and that the Go/No-Go was answered in the affirmative.

- The Go/No-Go was indeed the modeling effort: "Develop and demonstrate predictive model that predicts performance of Baseline FWC within 15% and which can be used for optimization." The "milestone" is in error. We apologize for that.

TA2: New spinel is identified through screening. However, it is not obvious if the desired light-off and cost targets (that are not presented) can be achieved or were achieved with the identified formulations. Such estimations will be needed for evaluating the technical accomplishments; otherwise, the judgment would be based on qualitative interpretation.

- Desired light-off achieved with the baseline spinel and one of the new spinels. Cost targets based on PGM reduction, which has been demonstrated.

- **Collaboration (C)**

C1: The team of collaborators on the project is excellent at University of Houston, University of Virginia, ORNL, and Clean Diesel Technologies, Inc. (CDTI). They have good contacts with OEMS but might consider a direct interaction with a company making NG engines./

The reviewer commented that this is a good R&D collaborative effort. It would benefit from the inclusion of an LD OEM for guidance./ Collaboration appears good with commercial catalyst partner providing materials for evaluation. Further collaboration with a clear path toward commercialization would improve the likelihood of program success.

- Ways to test catalysts in final phase of work may involve NG engine manufacturer. Decision during 1Q of no-cost extension year.

Reviewer Comments from 2020 AMR

Collaboration (C), cont.

C3: The collaboration slide, while detailing well the various work components, did not delineate who did what, i.e., what were the specific contributions spread across the various partners. A separate slide showing a discrete example of how the team worked together on each component of the work would have been powerful in convincing reviewers the project team provides a sum greater than the parts./ The project appears to be well coordinated with cooperation across the participants. Some indication of which work was led by which party would be helpful. It looks like the heavy lifting was done primarily by the University of Houston.

- This slide has been included in 2021 AMR presentation.

Proposed Future Research (PFR)

PFR1: The inclusion of another Pt/Pd ratio than 19:1 could be considered, while being wary of the potential negative interactions between Pt and Pd. The important role of partially oxidized Pt could be studied further, along with how it is affected by S.

- While we did not vary the Pt/Pd ratio, we have evidence for spinel cation migration; thus, we investigated dilute surface alloys of Pt and Pd with 22 relevant promoters using DFT.
- Sulfur studies are underway to rank-order the several spinel candidates.

PFR2: With all of the project feeds having large amounts of water, one wonders if a few experiments, with very small amounts of water or no water, would comment on the mechanism in a useful way.

- Methane oxidation conducted with H_2O in performance studies, w/ & w/o H_2O in kinetics/mechanistic studies.

PFR3: With the importance of modulation determined, the Spaci-MS work can be very useful for understanding the mechanism of the reaction through the catalyst.

- SpaciMS studies were delayed by COVID, but currently underway.

Relevance (REL) & Resources (RES)

- **n/a**

Remaining Challenges: Proposed Future Research

BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Complete evaluation of new spinels:
  $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Evaluate catalyst durability
  - Quantify sulfur tolerance & develop mitigation strategies
  - Evaluate hydrothermal stability
  - Check for metals migration
- Quantify mechanism for conversion enhancement
  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Complete predictive monolith model to guide improvements
- Evaluate & rank-order catalysts with application-relevant feeds

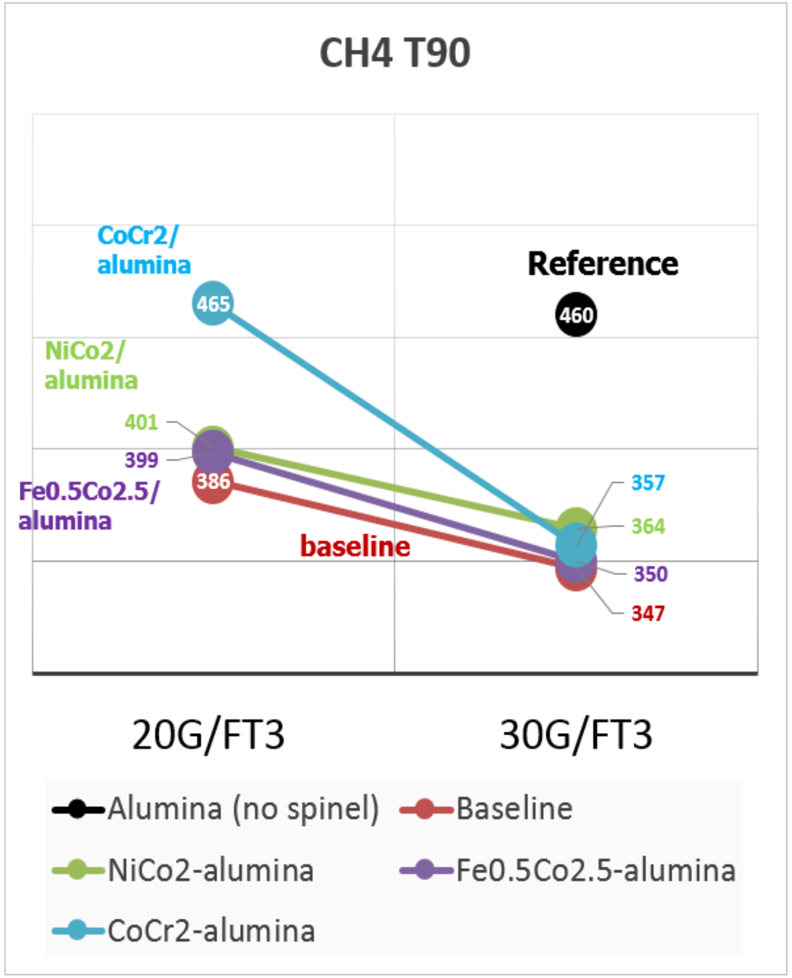
Summary

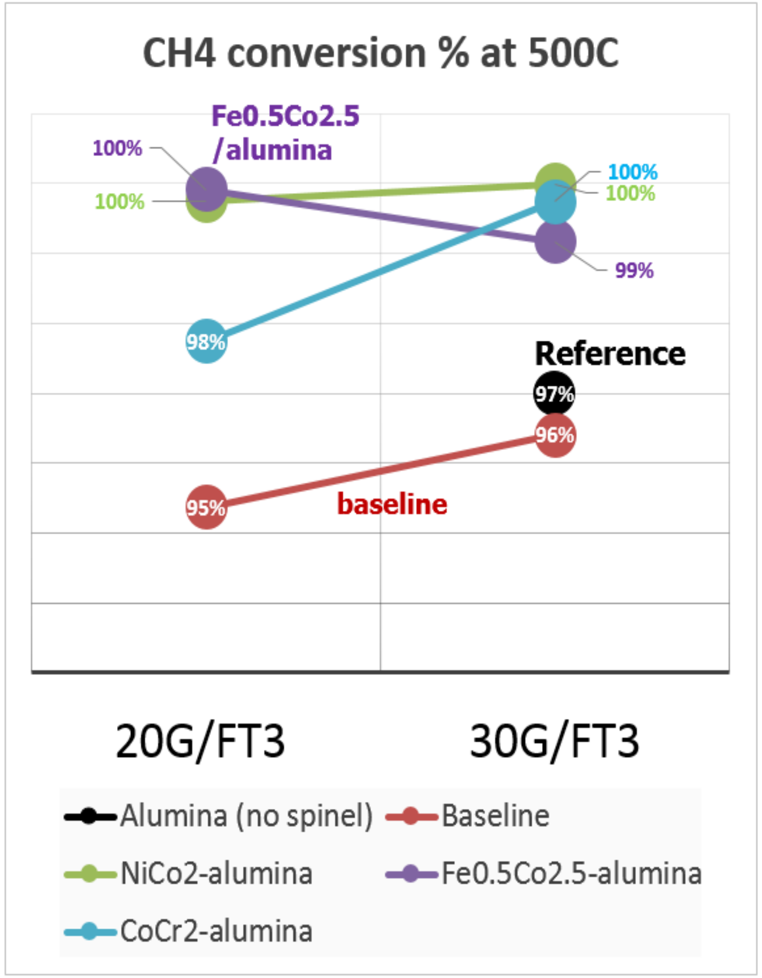
- **Relevance**
  - Enabling emergence of natural gas vehicles by removing emissions hurdle
- **Approach**
  - From molecular-level discovery & mechanism to development & demonstration
- **Technical Accomplishments & Progress**
  - Good progress on all fronts; BP2 milestones achieved
  - New spinels identified through screening
- **Collaborations & Coordination**
  - Cooperation: universities (UH+UVA), national lab (ORNL), industry (CDTi)
- **Proposed Future Research**
  - Converge on next-gen catalysts, integration, modeling, & optimization

Technical Backup Slides

PGM Thrifting: Comparison of Co- Spinels

PGM dependence over various spinels in comparison with the reference 30g/ft^3 PGM-only in terms of CH_4 conversion.



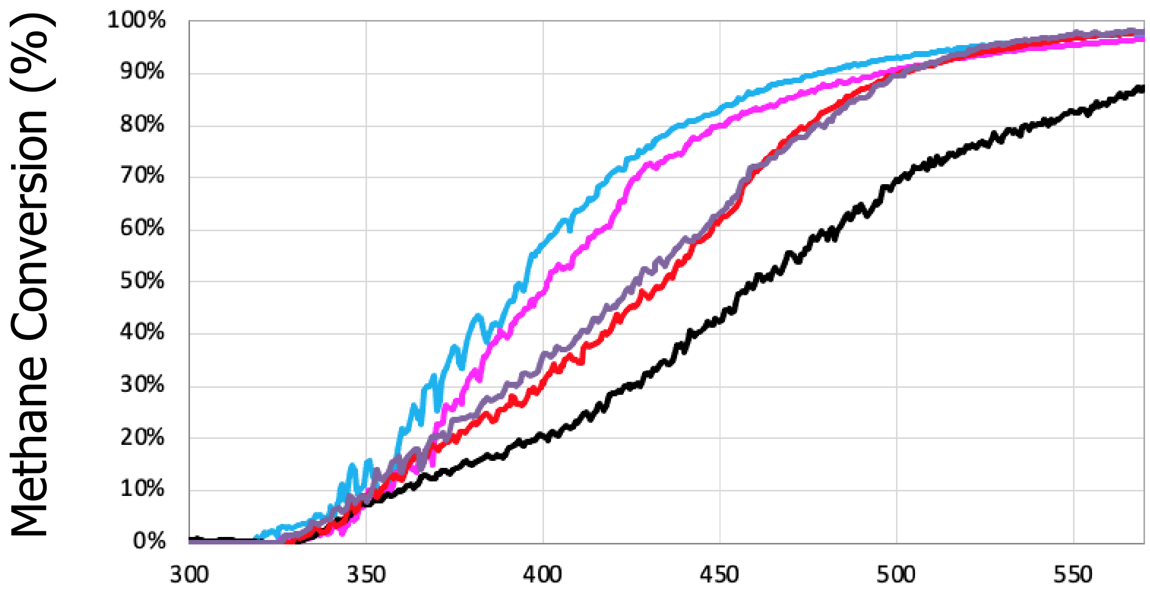


Impact of Hydrothermal Aging

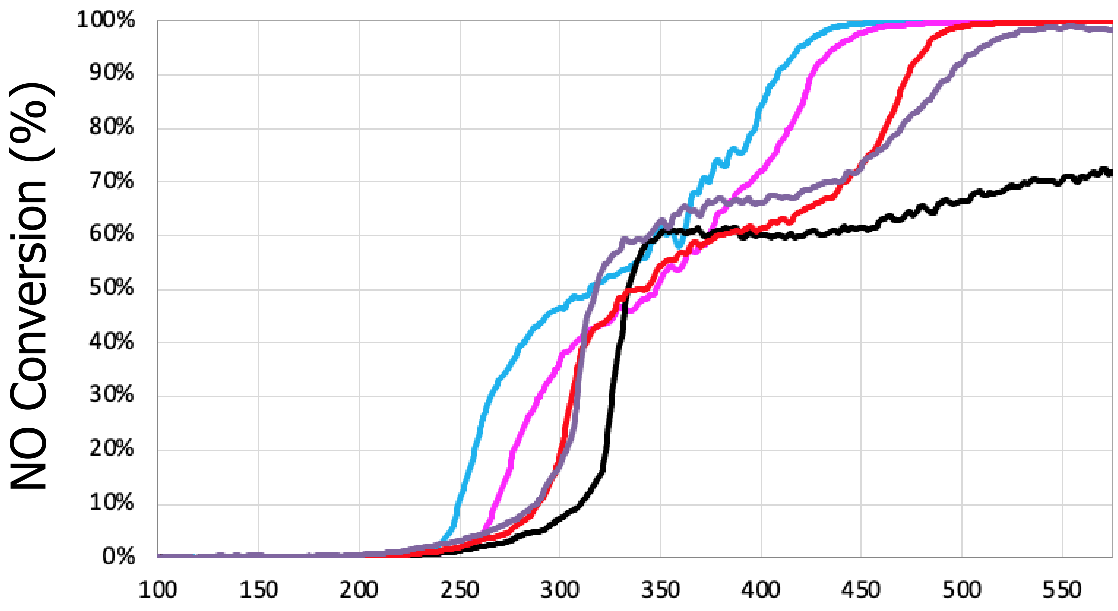
GHSV =90 hr^{-1}
40 °C/min
$\langle\lambda\rangle$ = 0.996
z
28

Aging protocol: 900 °C in 10% H_2O for 5 hours

HC Light-Off Curves



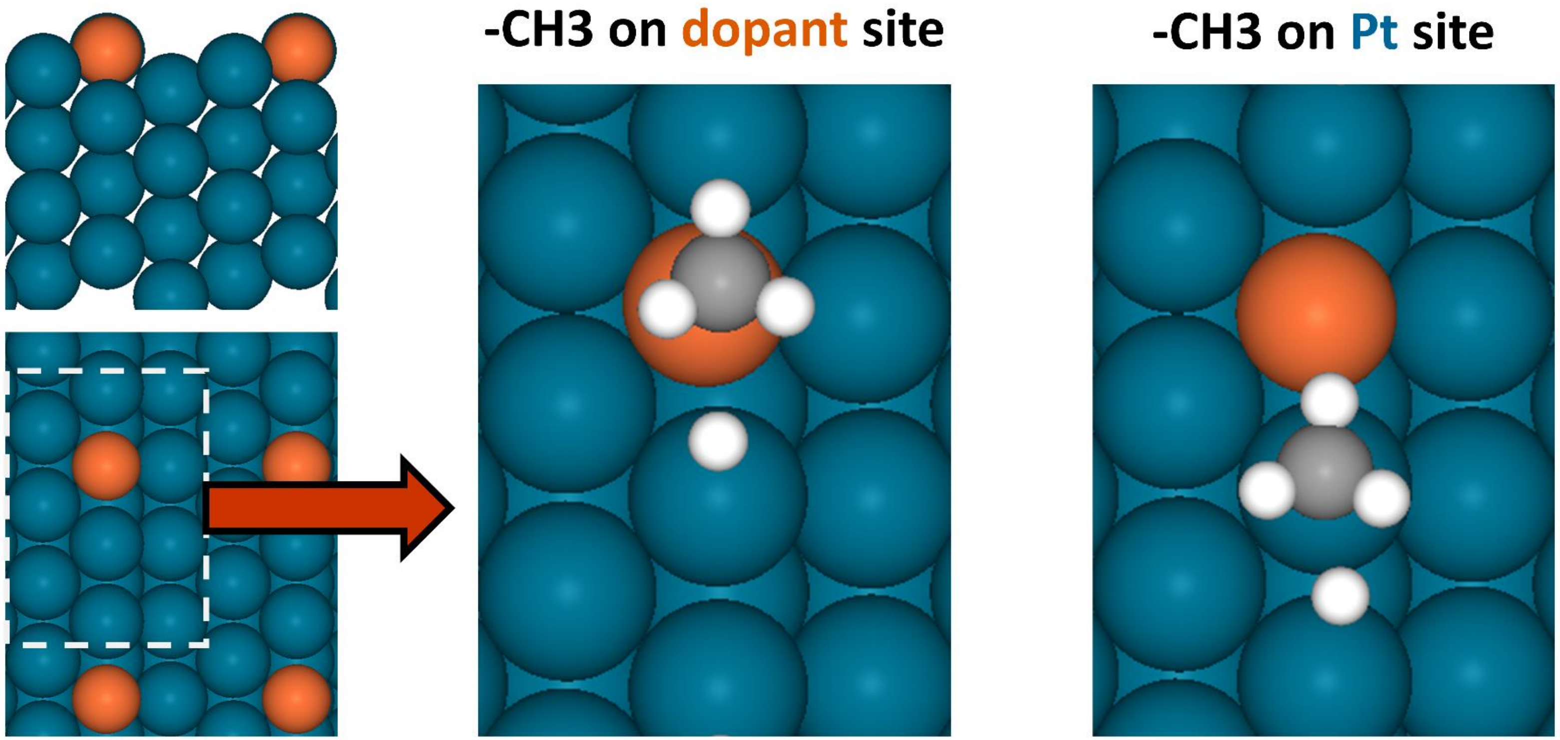
NOx Light-Off Curves



CeO_2 + ZrO_2 (CZO) as support boosts stability

Pt/Pd 19:1 Al_2O_3	100 g/L, 30 g PGM/ft^3
Spinel /Al_2O_3 or CZO	100 g/L, 20 – 25 wt.% Spinel
Monolith	

DFT Investigation of Promoted PGM Catalysts



Methane activation over earth abundant metal doped PGM catalysts

Doped Pt(211) surface

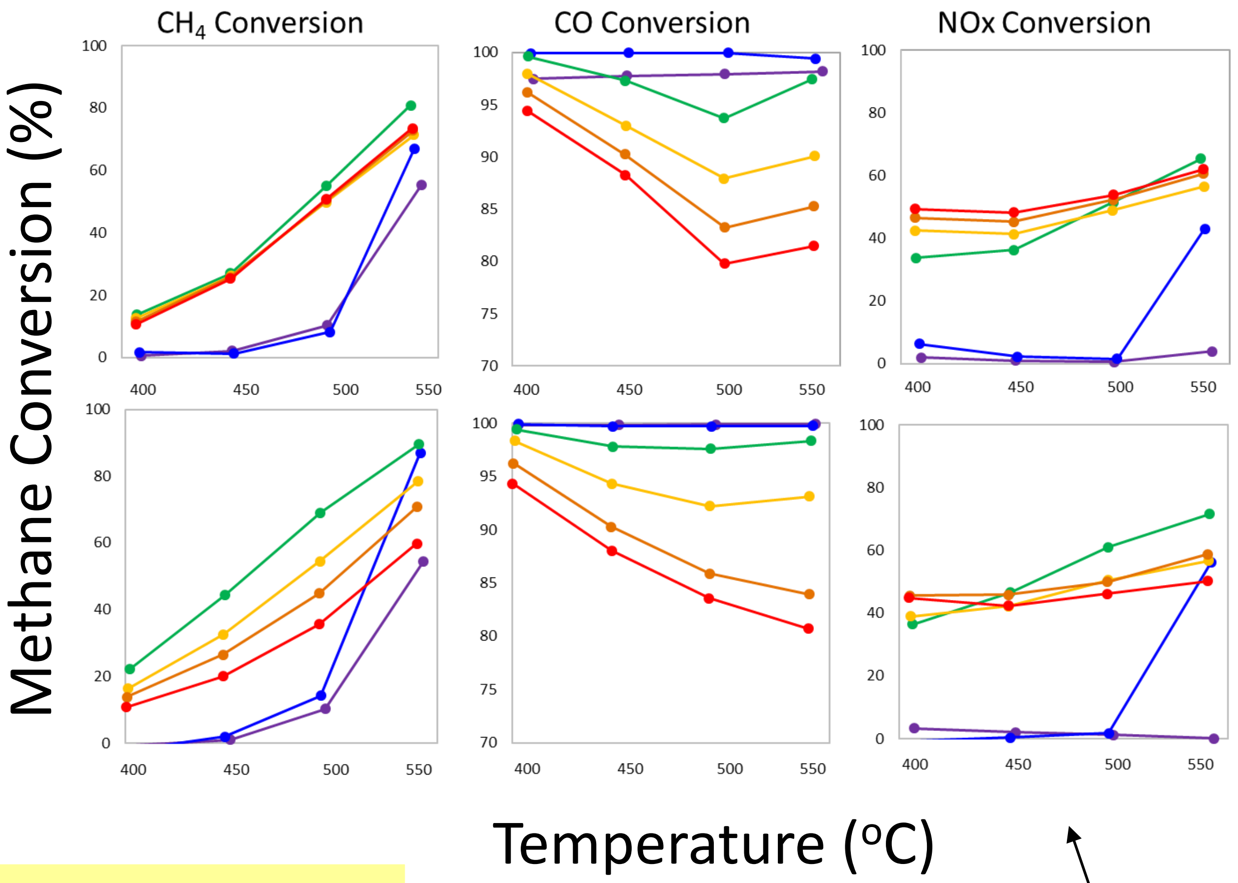
Impact of Sulfur

Evaluate effect of added SO_2 on modulated reactor performance

30/100 PGM/$Mn_{0.5}Fe_{2.5}O_4$

Flowrate (L/min)	1
GHSV (hr^{-1})	60,000
Temperatures (°C)	400, 450, 500, 550
Frequencies (Hz)	1, 0.5, 0.333, 0.25, 0.2

A	<λ> = 1; λ range	<O_2> (%)
0.10	0.95 - 1.05	1.12
0.06	0.97 - 1.03	1.12
0.02	0.99 - 1.01	1.12



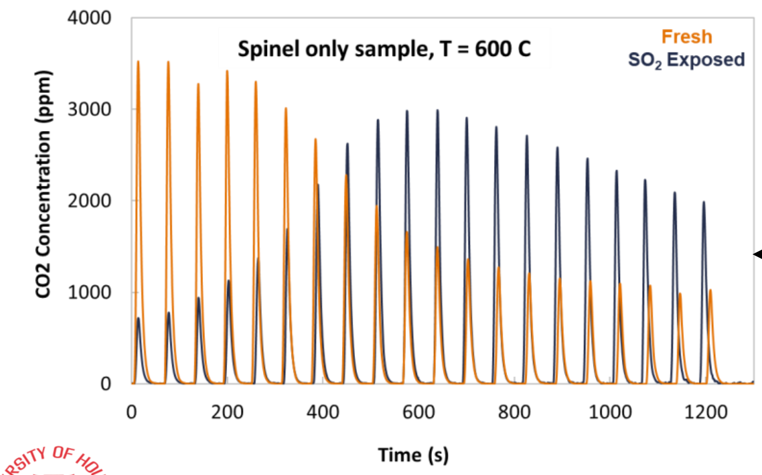
No Cycling

Freq. (Hz)
0.200
0.250
0.333
0.500
1.000

w/o SO_2

w/ SO_2

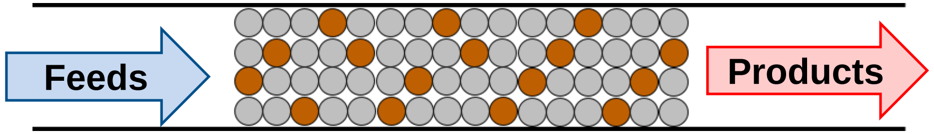
0/100 ($Mn_{0.5}Fe_{2.5}O_4$ Spinel Only)



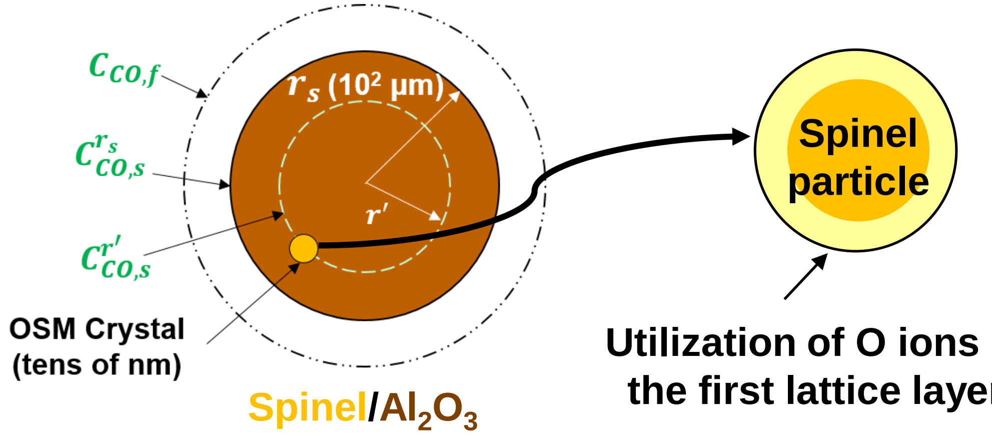
SO_2 exposure reduces OSC of spinel

Spinel mitigates SO_2 impact

Spinel O_2 Uptake & Release DOSC Model



Diluent Pellet (Silica) OSM Pellet (MFO spinel)



- **Species balances in heterogeneous model:**

Fluid Phase	$\frac{\partial x_{f,i}}{\partial t} + \frac{u_f}{\varepsilon_b}\frac{\partial x_{f,i}}{\partial z} = -k_{c,i}a_s\frac{\varepsilon_p}{\varepsilon_b}(x_{f,i} - x_{s,i})$
Solid Phase	$\frac{\partial x_{s,i}}{\partial t} = D_{e,i}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial x_{s,i}}{\partial r}) + \frac{1}{C_0}\sum_{j=1}^{r} \upsilon_{nj} r_j$
Site Balance	$\frac{\partial \vartheta_i}{\partial t} = \frac{1}{\Omega_{MFO_4}}\sum_{j=1}^{r} \upsilon_{nj} r_j$

- **Boundary conditions:**

at z = 0	$x_{f,i}(t) = x^{in}_{f,i}(t)$
at r = 0	$\left.\frac{\partial x_{s,i}}{\partial r}\right\vert_{r=0} = 0$
at r =r_s	$k_{c,i}(x_{f,i} - x_{s,i}) = -D_{e,i}\left.\frac{\partial x_{s,i}}{\partial r}\right\vert_{r=r_s}$

- **Reaction Steps**

1) $MFO_4 \underset{O_2}{\overset{CO/H_2}{\rightleftharpoons}} MFO_3 + O$

2) $MFO_3 \underset{O_2}{\overset{CO/H_2}{\rightleftharpoons}} MFO_{0.5} + 2.5\ O$

MFO_4: $Mn_{0.5}Fe_{2.5}O_4$

- **Rate Expression**

$$r_{1,red.} = k_{1,r}C_{CO}\Omega_{MFO_4}\vartheta_{MFO_4}$$

$$r_{1,oxi} = k_{1,o}C_{O_2}\Omega_{MFO_4}\vartheta_{MFO_3}$$

$$r_{2,red.} = k_{2,r}C_{CO}\Omega_{MFO_4}\vartheta_{MFO_3}$$

$$r_{2,oxi} = k_{2,o}C_{O_2}\Omega_{MFO_4}\vartheta_{MFO_{0.5}}$$

$$\vartheta_{MFO_x} = \frac{N_{MFO_x}}{N_{MFO_4} + N_{MFO_3} + N_{MFO_{0.5}}}$$