Precision Combustion, Inc.
New Haven, Connecticut

- Privately-held small business ~50 FTE employees. Est 1986.
- High performance engineering team:
  - 12 PhDs, 38 engineers/technicians/admin., large/small co backgrounds
  - $35 MM SBIR awards, 75+ U.S. patents
- Focus on Innovation and product development
- Catalytic reactors/systems for Energy sector
  - Novel architectures, enhanced performances, systems implications
    - Ultra-compact, efficient
    - Resolves heat / mass transport issues
  - Fuel reformers/Processors/Fuel cells
  - Combustors/Burners
  - Air Cleaners
  - CO2 Capture / Processing
- Customers/partners: U.S. Govt., large & small companies, universities

PCI Precision Combustion, Inc.

PCI company vision and strategy

- Create, develop, commercialize novel high value added component/system solutions
- Innovative, close-knit and highly skilled engineering and development team
- Current product focus: catalytic reactor/system solutions to Energy sector challenges
- Customer focus: DoD, NASA, Energy industry
- Product-specific market entry plans.
  - PCI core catalytic component manufacture and sale, with potential system level license
  - PCI system sale and manufacture (supply chain for most of manufacture beyond core component)
  - License
- Bootstrapped financing:
  - SBIR for early stage tech and product development
  - Government and corporate partner/customer funding for later stage development
  - Commercial entry targeted to the product
- Leverage/risk strategies: Tech/product diversity. Defensible IP. Strategic relationships.
- Commercialization returns support stakeholders and further development

Commercialization Principles

- Committed customer with secured funding seeking a solution
  - Typically DoD, NASA or industrial companies
- Focusing on opportunities where weight, volume, efficiency or economics matter
- Vertically integrating to the level that makes “sense”
- Partnering with appropriate technology solution providers and system integrators
- Manufacturing what we can, buying what we can’t make, licensing to supply volumes we cannot provide
- Keeping PCI as a core R&D small business
- Spinning out product specific and manufacturing companies when they are required

PCI
Precision Combustion, Inc.

Multiple Military and Commercial Applications

Power & Propulsion

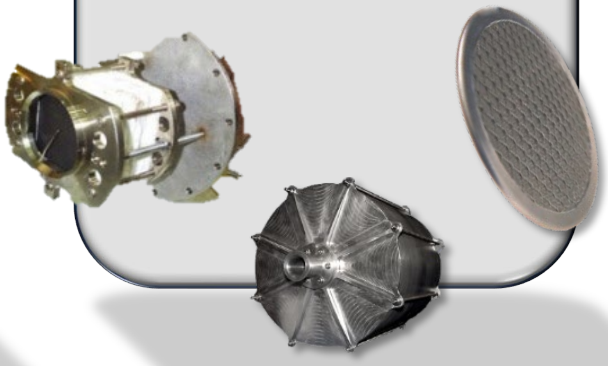
- Fuel Cell Systems
- IC Engine Systems
- Soldier Power Gensets
- Vehicle APU's
- UXV Power/ Propulsion

Combustion

- Catalytic Burners
  - Stirling, TPV, TEG
- Catalytic Combustors
  - Gas Turbines
  - Steam Generators
- Catalytic Glow Plugs

Purification

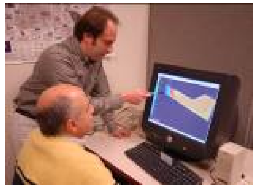
- **Carbon Capture**
- Oxidizers
- Adsorbers
- Desulfurization
- Catalytic Conversion



Reactors & Sensors

- CO2 Upgrading
- Hydrogen Generation
- Sabatier Reactors
- Gas Conversion
- Cetane Sensor

PCI Core Competencies



Low volume manufacturing
Prototype/product manufacture
Established supply chain
Automated catalyst manufacture

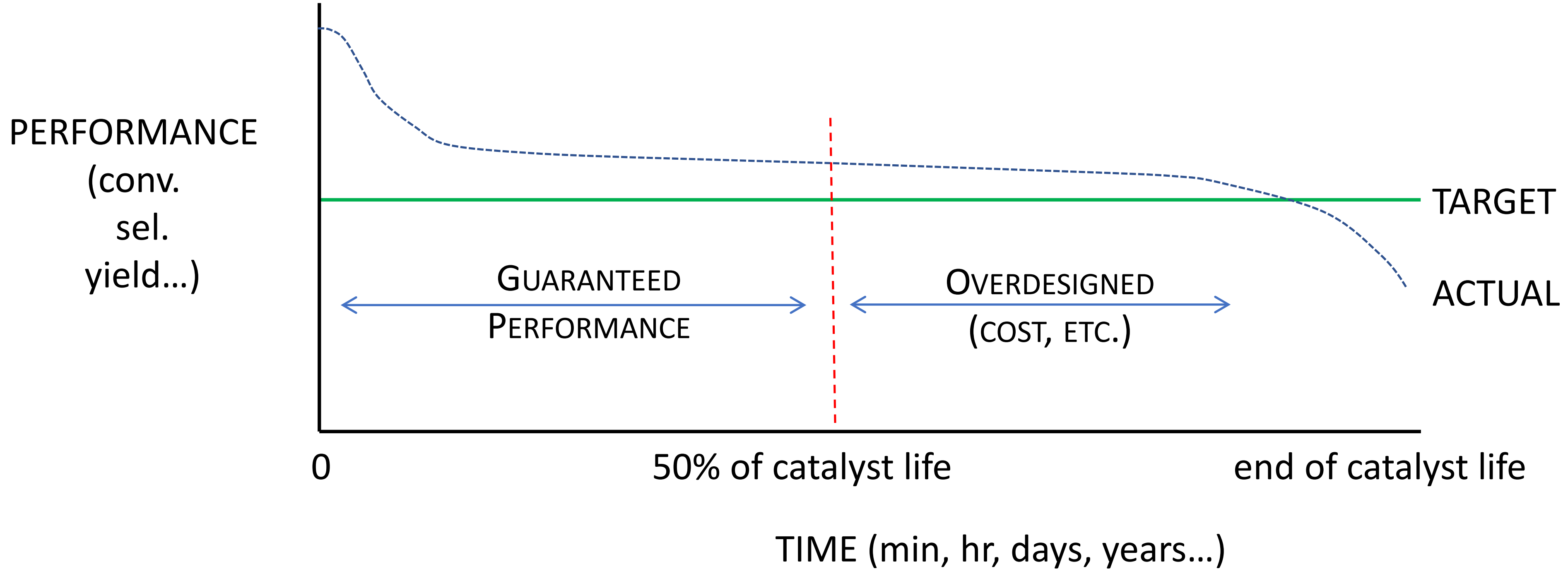
Catalytic reactor/system design/testing
New applications/reactor designs
Advanced system/reactor modeling
Product development

Catalyst design and coating
Materials analysis & processing
Substrate design & specification
Catalyst formulation, prep, coating

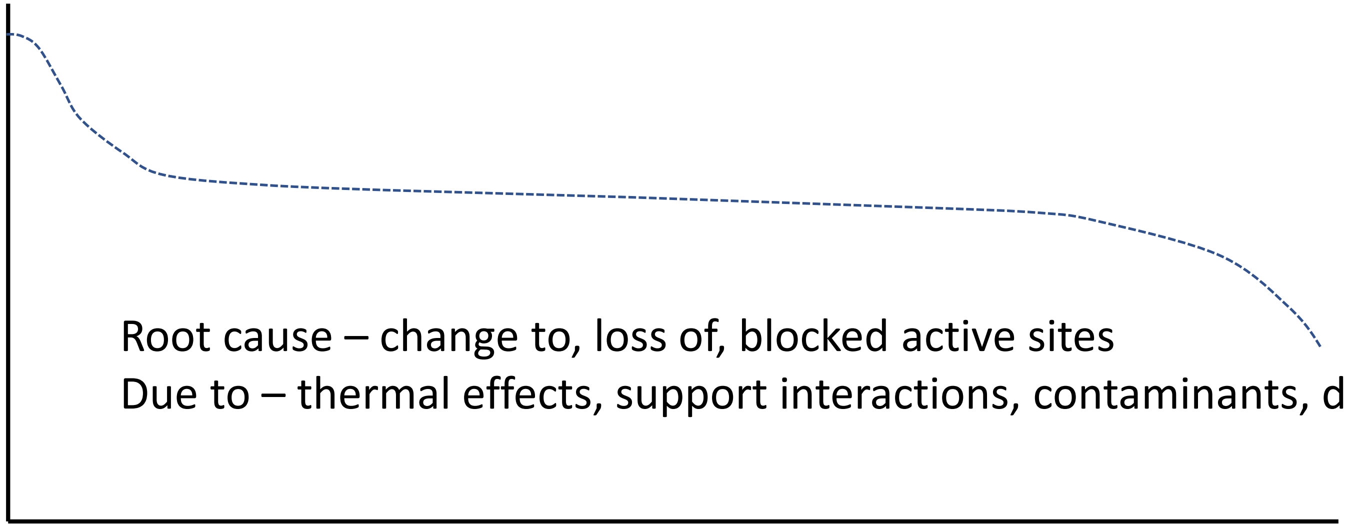
Innovative design

Systems approach

Catalyst Challenge



Catalyst Questions



What are the active sites?

How to identify them?

How to modify or protect them?

Enhance their numbers?

Current Challenges in Heterogeneous Catalysis

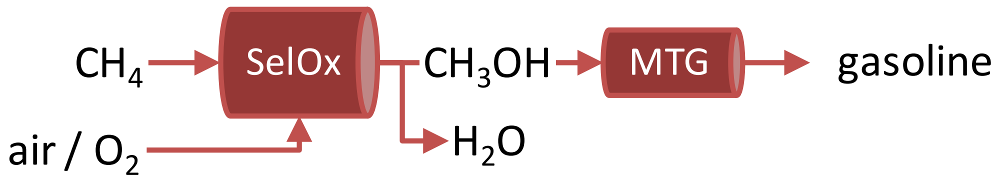
- C-O bond breaking (electrolysis)
  - application - CO2 utilization
    - product - CO
- C-H bond formation
  - application - CO2 utilization
    - also, H2 generation (HT/LT electrolysis)
  - product – CH4 mostly

- C-C bond formation
  - application - CH4 utilization (and CO2 valorization)
    - rational - Petroleum/crude oil replacements
    - FT – high pressure, challenging to scale
    - alcohol synthesis – high pressure, low yields
  - Desired – low pressure high yield process

Shale / Natural Gas to Liquids

Currently No Good Options

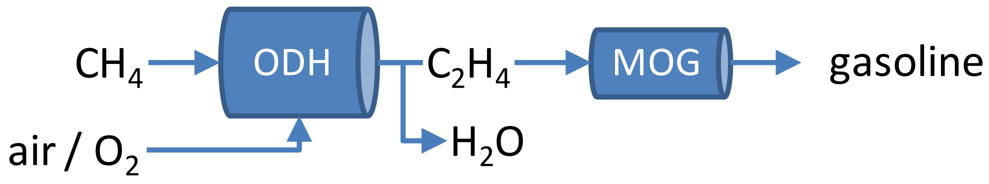
- Indirect processes (w/intermediate product separations) – large, energy intensive
  - Methane-steam reforming – WGS - Fischer Tropsch
  - Methane-steam reforming – WGS – methanol synthesis – methanol-to-gasoline



- Direct processes – low efficiency, not viable

- Oxidative Coupling of Methane ($2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$)
  - Heat of reaction drives combustion
  - Trade-offs between CH_4 conv. and C_2H_4 selectivity limits C_2H_4 yield to < 28 %
  - At current and projected NG and C_2H_4 wholesale values, 28 % is not economic
  - est. 35-40% $C2^+$ yield for commercially viable process
  - similar Oxidative Dehydrogenation of Ethane

    DOE SBIR Phase I/II/IIA + I/II

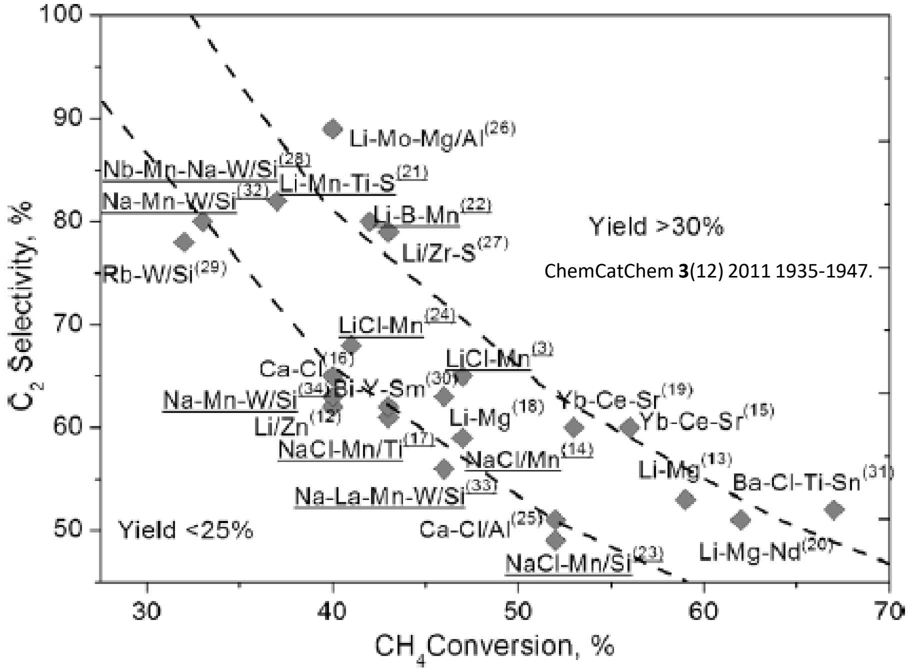


Methane to Ethylene Reaction is Self Limiting and Non-Economic

- Multi-step reaction proceeding through CH_3 radical intermediate
  - elementary steps may be both gas- or surface-phase
  - basic (non-acidic) catalysts work best
- Overall: $CH_4 + ½O_2 \rightarrow ½C_2H_4 + H_2O$ ($\Delta H°_{rxn}$ = -141 kJ/mol)
  - $CH_4 \rightarrow CH_3\cdot + H\cdot$ (surface reaction – rate limiting step)
  - $2CH_3\cdot \rightarrow C_2H_6$ (gas-phase)
  - $C_2H_6 \rightarrow C_2H_5^* + H\cdot$ (surface)
  - $C_2H_5^* \rightarrow C_2H_4 + H\cdot$ (gas-phase)
  - $2H\cdot + ½O_2 \rightarrow H_2O$ (gas phase)

- Major side reactions
  - C_2H_4 combustion to $CO_2 + H_2O$ ($\Delta H°_{rxn}$ = -1323 kJ/mol)
  - CH_4 combustion to $CO_2 + H_2O$ ($\Delta H°_{rxn}$ = -803 kJ/mol)
  - CH_4 partial oxidation to $CO + H_2$ ($\Delta H°_{rxn}$ = -36 kJ/mol)

- Side reactions catalyzed by:
  - metals – including catalytic metals and materials of construction
  - acidic ceramics – including catalyst supports, substrates, and materials

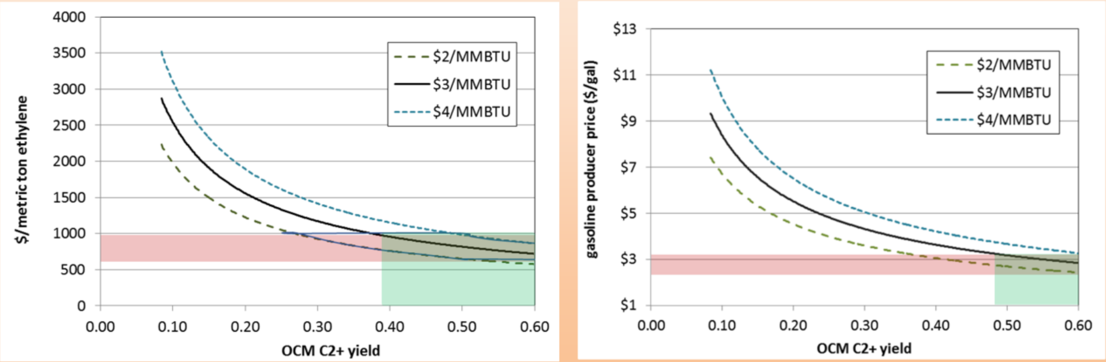


Plot represents synthesis of data over wide range of reactor types and operating conditions

Perspectives on OCM (and ODH)

Process Economics

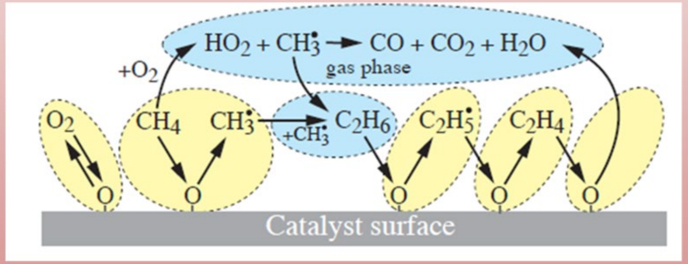
- Value of products depends on C_2H_4 yield and natural gas cost
- Cost model accounts for all major process steps:
  - OCM, cracking, separation, olefin processing, etc.



Cost of producing product as functions of OCM yield and natural gas values
red shaded areas – target product values; green shaded areas – target C_2^+ yields

Lunsford model captures most major features of isothermal-based reaction mechanism

Yellow – catalytic pathways
Blue – gas phase reactions



J. H. Lunsford, Angew. Chem. Int. Ed. 34, 970-980 (1995)

OCM : $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$
ODH : $C_2H_6 + ½O_2 \rightarrow C_2H_4 + H_2O$

MUTIPLE SURFACE REACTIONS UNKNOWN:

TOF's

ACTIVE SITE(S) ID

Reaction Mechanism / Implications

GAS-PHASE REACTIONS

1.	$CH_4 + O_2 \leftrightarrow CH_3^* + HO_2^*$	**21.**	$C_2H_5^* + M \leftrightarrow C_2H_4 + H^* + M$
2.	$CH_4 + H^* \leftrightarrow CH_3^* + H_2$	**22.**	$C_2H_5^* + O_2 \leftrightarrow C_2H_4 + HO_2^*$
3.	$CH_4 + O^* \leftrightarrow CH_3^* + OH^*$	**23.**	$C_2H_4 + O_2 + M \leftrightarrow C_2H_3^* + HO_2^* + M$
4.	$CH_4 + OH^* \leftrightarrow CH_3^* + H_2O$	**24.**	$C_2H_4 + H^* \leftrightarrow C_2H_3^* + H_2$
5.	$CH_4 + HO_2^* \leftrightarrow CH_3^* + H_2O_2$	**25.**	$C_2H_4 + OH^* \leftrightarrow C_2H_3^* + H_2O$
6.	$CH_3^* + O_2 \leftrightarrow CH_3O^* + O^*$	**26.**	$C_2H_4 + CH_3^* \leftrightarrow C_2H_3^* + CH_4$
7.	$CH_3^* + O_2 \leftrightarrow CH_2O + OH^*$	**27.**	$C_2H_4 + OH^* \leftrightarrow CH_3^* + CH_2O$
8.	$CH_3^* + HO_2^* \leftrightarrow CH_3O^* + OH^*$	**28.**	$C_2H_3^* + M \leftrightarrow C_2H_2 + H^* + M$
9.	$CH_3^* + CH_3^* + M \leftrightarrow C_2H_6 + M$	**29.**	$C_2H_3^* + O_2 \leftrightarrow C_2H_2 + HO_2^*$
10.	$CH_3O^* + M \leftrightarrow CH_2O + H^* + M$	**30.**	$C_2H_3^* + O_2 \leftrightarrow CH_2O + HCO^*$
11.	$CH_2O + OH^* \leftrightarrow HCO^* + H_2O$	**31.**	$C_2H_5^* + CH_3^* \leftrightarrow C_3H_8$
12.	$CH_2O + HO_2^* \leftrightarrow HCO^* + H_2O_2$	**32.**	$C_3H_8 + H^* \leftrightarrow C_3H_7 + H_2$
13.	$CH_2O + CH_3^* \leftrightarrow HCO^* + CH_4$	**33.**	$C_2H_4 + CH_3^* \leftrightarrow C_3H_7^*$
14.	$HCO^* + M \leftrightarrow CO + H^* + M$	**34.**	$C_3H_7^* \leftrightarrow C_3H_6 + H^*$
15.	$HCO^* + O_2 \leftrightarrow CO + HO_2^*$	**35.**	$O_2 + H^* \leftrightarrow OH^* + O^*$
16.	$CO + HO_2^* \leftrightarrow CO_2 + OH^*$	**36.**	$O_2 + H^* + M \leftrightarrow HO_2^* + M$
17.	$C_2H_6 + H^* \leftrightarrow C_2H_5^* + H_2$	**37.**	$HO_2^* + HO_2^* \leftrightarrow O_2 + OH^* + OH^*$
18.	$C_2H_6 + OH^* \leftrightarrow C_2H_5^* + H_2O$	**38.**	$H_2O_2 + M \leftrightarrow OH^* + OH^* + M$
19.	$C_2H_6 + CH_3^* \leftrightarrow C_2H_5^* + CH_4$	**39.**	$C_2H_6 \leftrightarrow C_2H_5^* + H^*$
20.	$C_2H_5^* + HO_2^* \leftrightarrow CH_3^* + CH_2O + OH^*$		

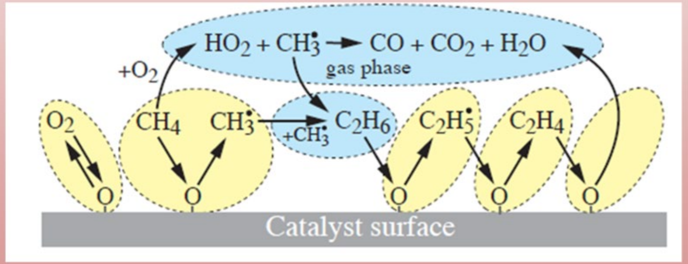
SURFACE REACTIONS

S40.	$O_2 + X(s) + X(s) \rightarrow O(s) + O(s)$	**S54.**	$CH_3O(s) + O(s) \rightarrow CH_2O(s) + OH(s)$
S41.	$O(s) + O(s) \rightarrow O_2 + X(s) + X(s)$	**S55.**	$CH_2O(s) + OH(s) \rightarrow CH_3O(s) + O(s)$
S42.	$CH_4 + O(s) \rightarrow CH_3^* + OH(s)$	**S56.**	$CH_2O(s) + O(s) \rightarrow CHO(s) + OH(s)$
S43.	$CH_3^* + OH(s) \rightarrow CH_4 + O(s)$	**S57.**	$CHO(s) + OH(s) \rightarrow CH_2O(s) + O(s)$
S44.	$C_2H_4 + O(s) \rightarrow C_2H_3^* + OH(s)$	**S58.**	$CHO(s) + O(s) \rightarrow CO(s) + OH(s)$
S45.	$C_2H_3^* + OH(s) \rightarrow C_2H_4 + O(s)$	**S59.**	$CO(s) + OH(s) \rightarrow CHO(s) + O(s)$
S46.	$C_2H_6 + O(s) \rightarrow C_2H_5^* + OH(s)$	**S60.**	$CO(s) + O(s) \rightarrow CO_2(s) + X(s)$
S47.	$C_2H_5^* + OH(s) \rightarrow C_2H_6 + O(s)$	**S61.**	$CO_2(s) + X(s) \rightarrow CO(s) + O(s)$
S48.	$2OH(s) \rightarrow H_2O(s) + O(s)$	**S62.**	$CO + X(s) \rightarrow CO(s)$
S49.	$H_2O(s) + O(s) \rightarrow 2OH(s)$	**S63.**	$CO(s) \rightarrow CO + X(s)$
S50.	$H_2O(s) \rightarrow H_2O + X(s)$	**S64.**	$CO_2 + X(s) \rightarrow CO_2(s)$
S51.	$H_2O + X(s) \rightarrow H_2O(s)$	**S65.**	$CO_2(s) \rightarrow CO_2 + X(s)$
S52.	$CH_3^* + O(s) \rightarrow CH_3O(s)$	**S66.**	$4HO_2^* \rightarrow 3O_2 + 2H_2O$
S53.	$CH_3O(s) \rightarrow CH_3^* + O(s)$		

M represents third body interactions
X(s) is generic catalytic surface site
* denotes gas-phase free radical

Lunsford model captures most major features of isothermal-based reaction mechanism

Yellow – catalytic pathways
Blue – gas phase reactions



J. H. Lunsford, Angew. Chem. Int. Ed. 34, 970-980 (1995)

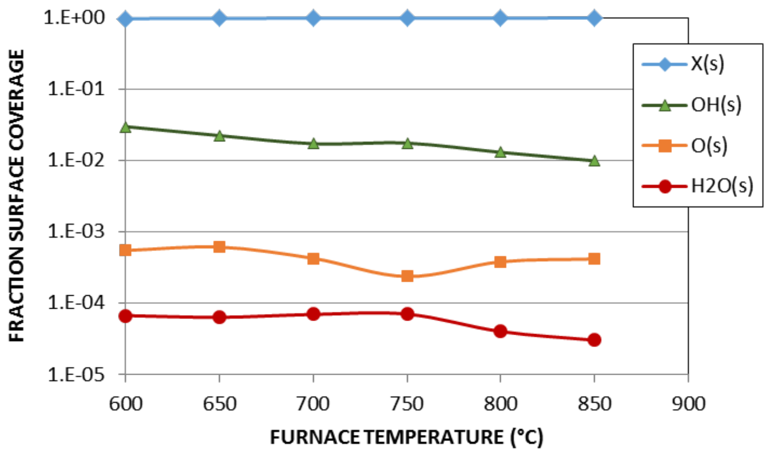
Modeled using 'mean-field approximation,'
- surface reactions on identical uniformly distributed sites

see: *"A detailed reaction mechanism for oxidative coupling of methane over $Mn/Na_2WO_4/SiO_2$ catalysts for non-isothermal conditions," C. Karakaya, H. Zhu, C. Loebick, J. G. Weissman and R. J. Kee, Catalysis Today 312, 10-22 (2018).*

Modeling Results

Goals:

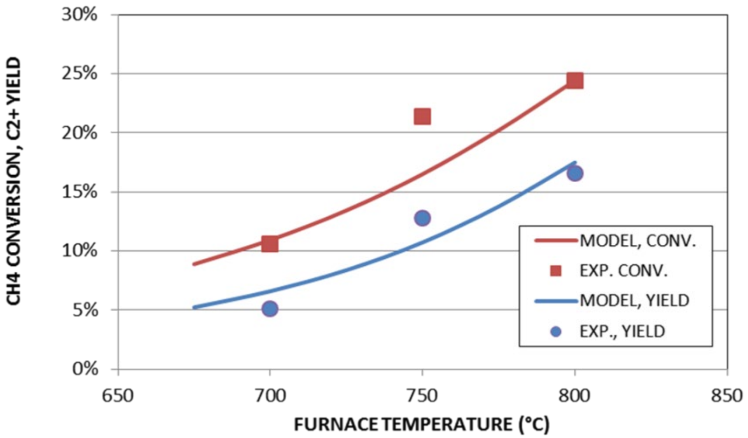
- Reactive CFD modeling to optimize reactor design
- Determine process conditions to enable economic C_2H_4 yields from OCM (and ODH)



Catalyst Active Site Coverage as Function of Temperature – at CH_4/O_2 5:1

Most surface sites are not covered by reactive species

Only important reactive surface species are O, OH, and H_2O



2-D Model vs. Experimentally Measured CH4 Conversion and C2+ Yields

Measured at CH_4/O_2 mole ratio of 5

Acknowledgement: This material is based upon work supported by the U.S. Department of Energy, Office of Science, under Award Numbers DE-SC0011353 and DE-SC0019711