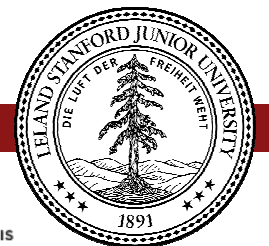




joint **NGI-SUNCAT** workshop  
14 September 2016

From methane to liquid  
fuels and beyond:  
**opportunities and  
challenges for a natural  
gas-powered future**





# objectives

Bring Stanford PIs and companies together

Understand the state-of-the-art

Fuel collaborations

Bridge the interests of PIs and companies



57 participants

25% from industry

60% students-postdocs

2 people from government (NSF)



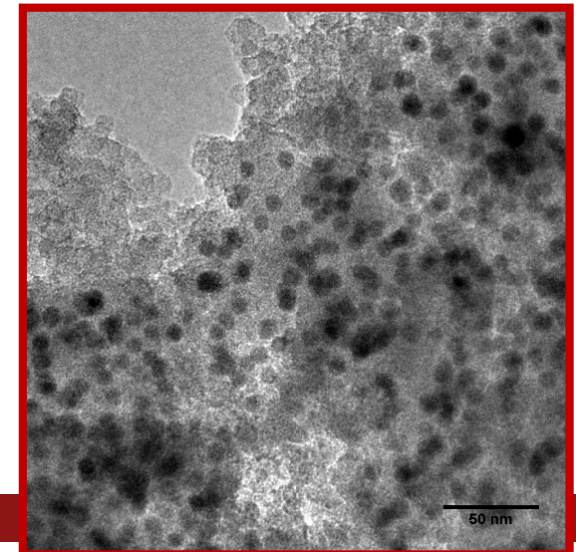
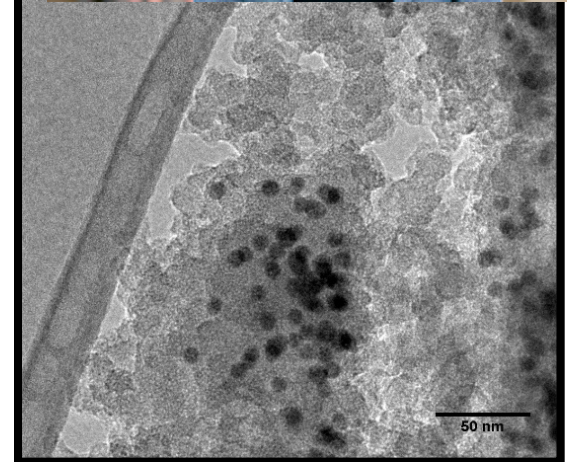
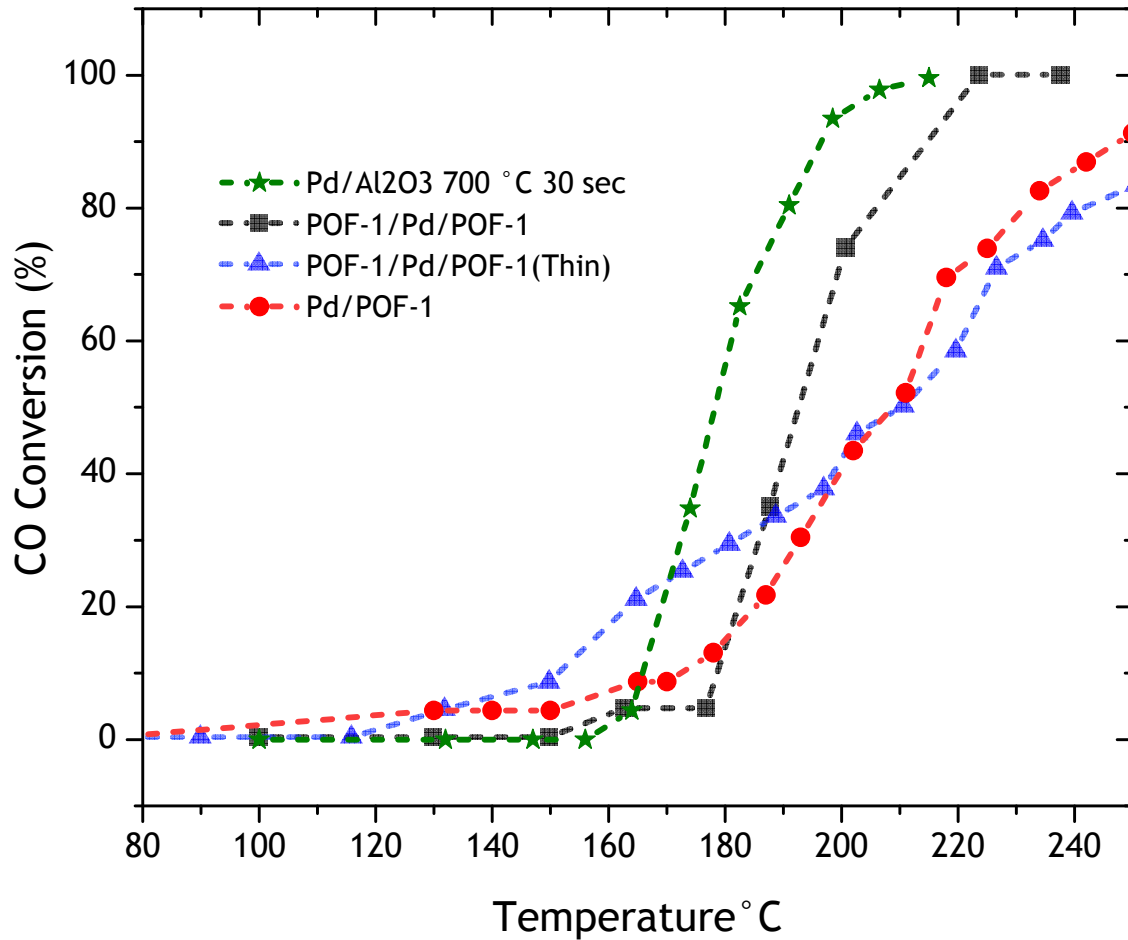
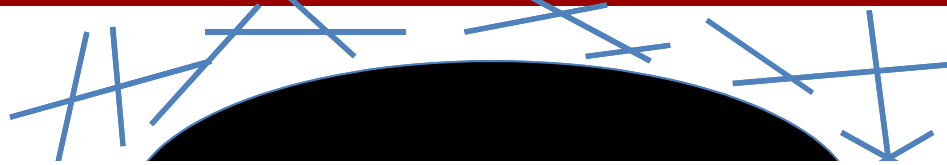
- 9.00 am – *Methane conversion: general discussion*
- 9.00 am – Paul Ayoub, Shell, “**The role of NG in transitioning toward tighter carbon constraints**”
- 9.20 am – Jim Bielenberg, ExxonMobil, “**Key issues for direct conversion routes**”
- 9.40 am – Ron Smith, IHS Energy, “**Markets for methane and derived products**”
- 10.00 am – Robert McCabe and Triantafillos John Mountziaris, NSF, “**An overview of federal funding opportunities for natural gas conversion**”
- 10.20 am – Discussion
- 10.50 am – Coffee break
- 11.20 am – *Biological methane conversion*
- 11.20 am – Craig Criddle, Stanford University, “**Challenges and opportunities for bioconversion of methane**”
- 11.40 am – Alfred Spormann, Stanford University, “**Microbial Life around Methane**”
- 12.00 pm – Discussion
- 12.30 pm – Lunch
- 2.00 pm – *Unconventional processes to convert or produce methane and related products*
- 2.00 pm – Ron Kent, SoCalGas, “**Conversion of renewable power to gas**”
- 2.20 pm – Pete Johnson, Monolith Materials, “**Natural gas conversion to carbon black**”
- 2.40 pm – Matt Kanan, Stanford University, “**Conversion of CO<sub>2</sub> to chemicals**”
- 3.00 pm – Discussion
- 3.30 pm – Coffee break
- 4.00 pm – *Poster session & reception*





# thermochemical pathways

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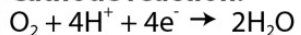


# electrochemical pathways

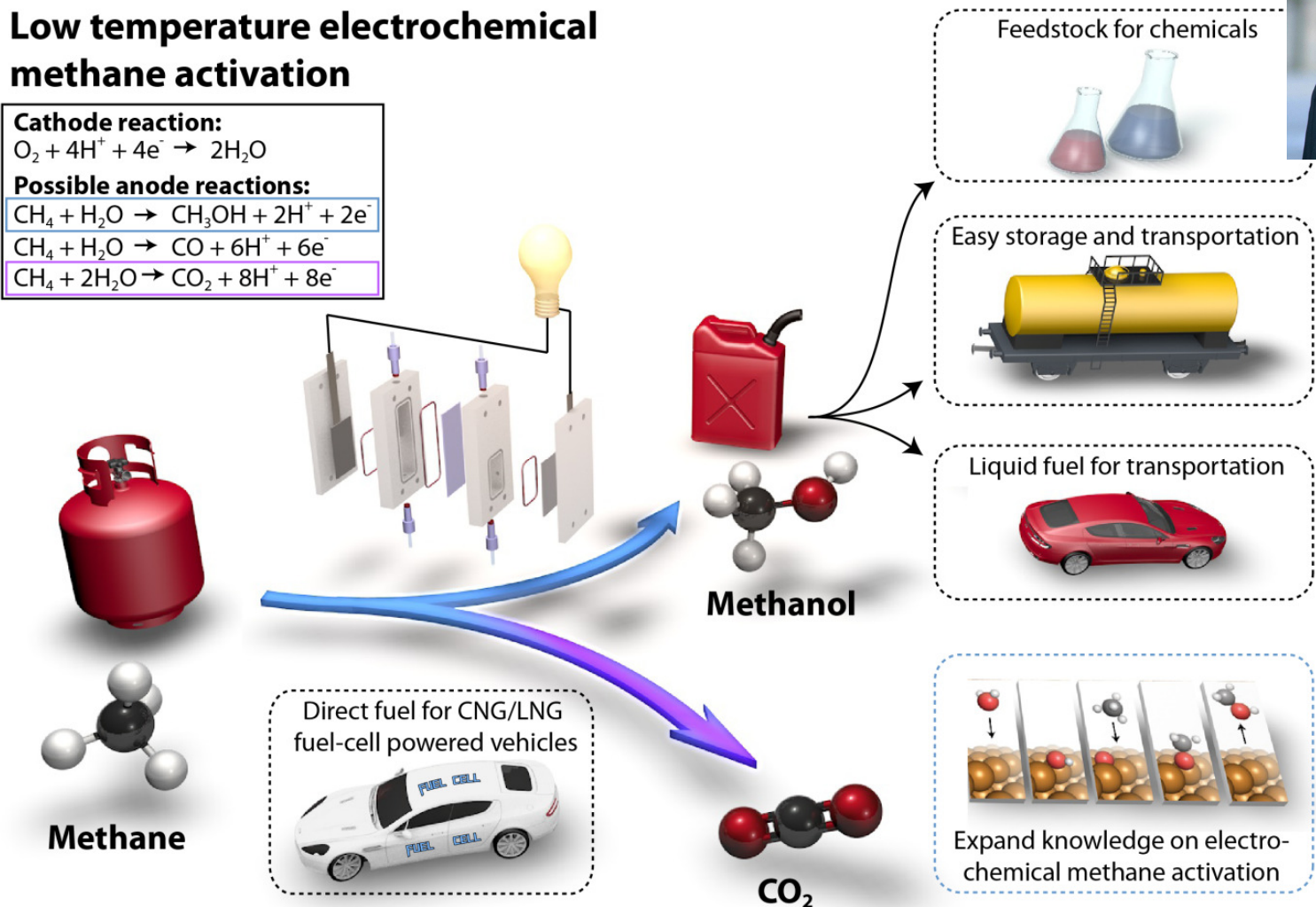


## Low temperature electrochemical methane activation

**Cathode reaction:**

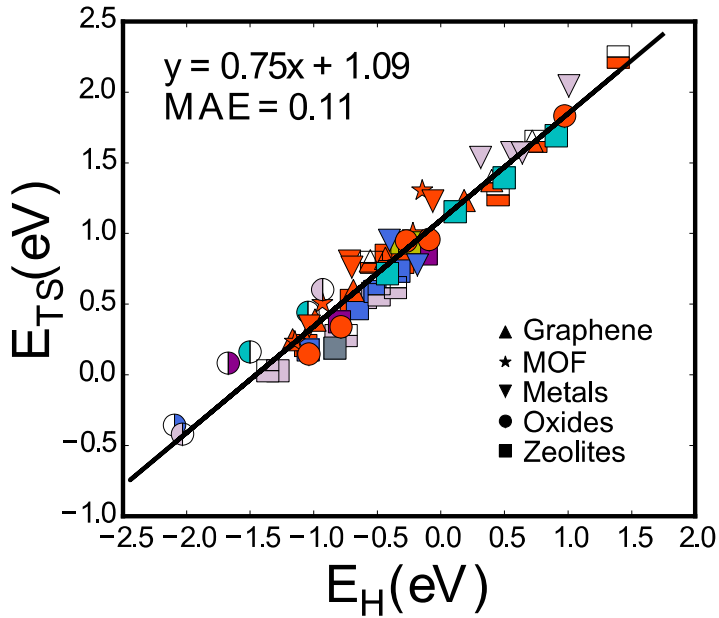


**Possible anode reactions:**

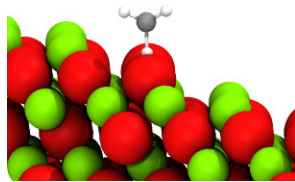
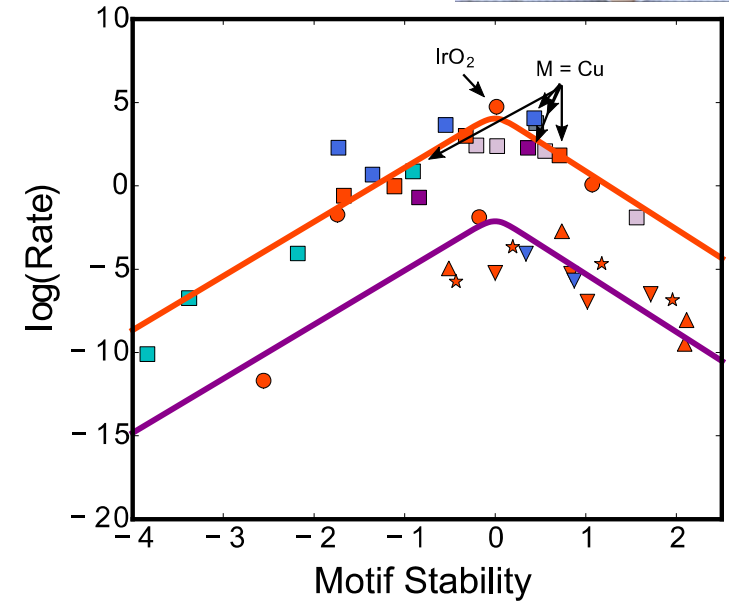
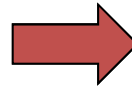




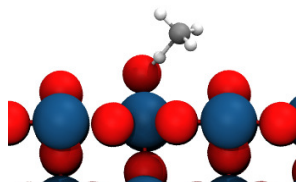
# universal scaling pathways



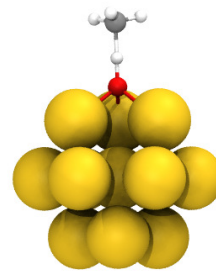
$$R_{CH_4 \text{ activation}} = \vartheta_{motif} \frac{k_b T}{h} \exp\left(\frac{-\Delta G_{TS}}{k_b T}\right)$$



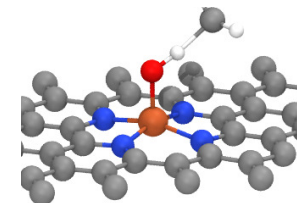
Non-reducible Oxides (MgO)



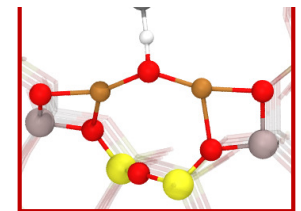
O-Promoted Reducible Oxides (IrO<sub>2</sub>)



O-Promoted Noble Metals (Au-O)



Decorated Graphene Nanosheets (Fe-O)



Zeolites (Mordenite Cu-O-Cu)

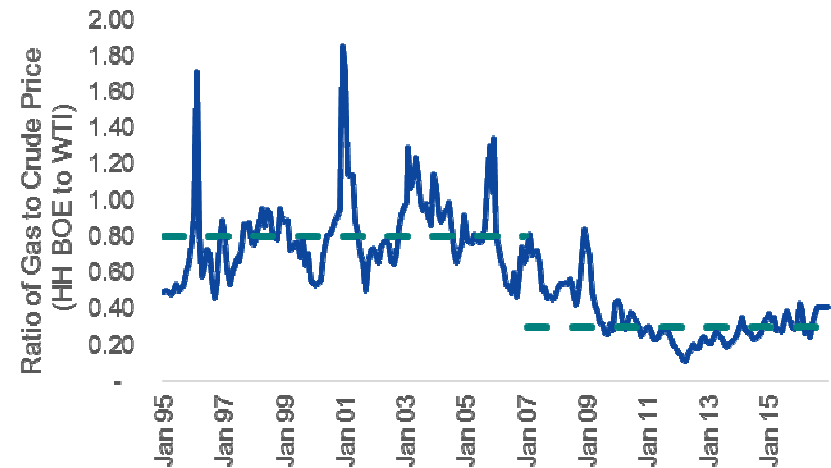
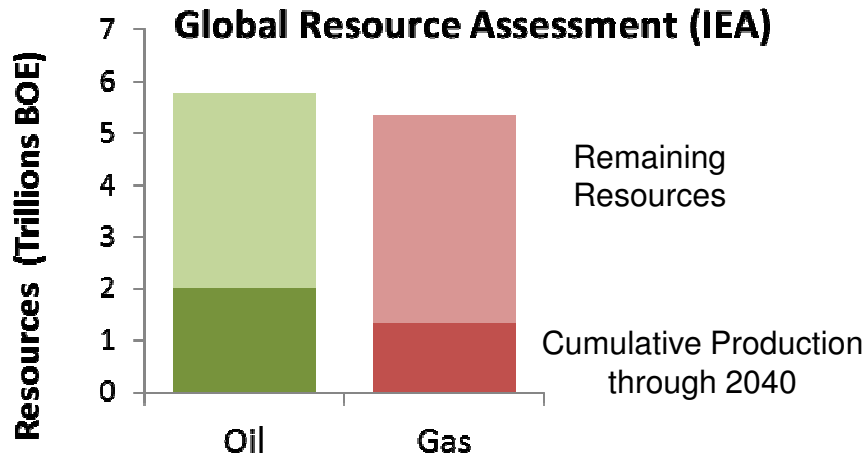
Latimer, Kulkarni *et al.* *Nature Materials* (accepted 2016)



# methane conversion: general discussion



Paul Ayoub, Shell; Jim Bielenberg, ExxonMobil







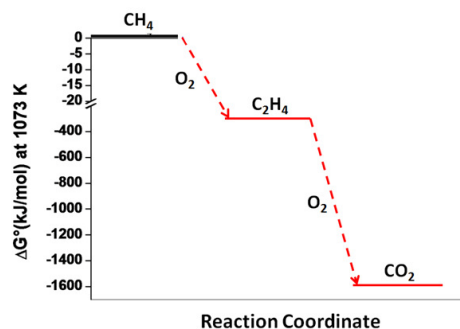
# methane conversion: general discussion

Non-Oxidative Coupling

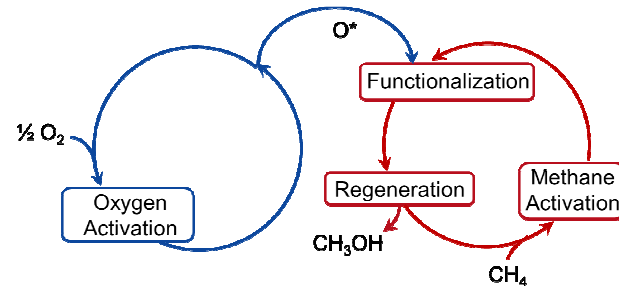
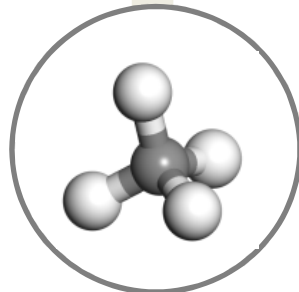
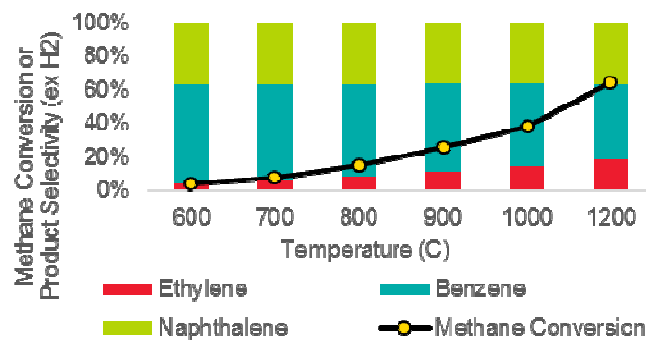
Oxidative Coupling

Low Temp Direct Oxidation

Conversion via Syngas



Non-Oxidative Methane Coupling







# methane conversion: general discussion

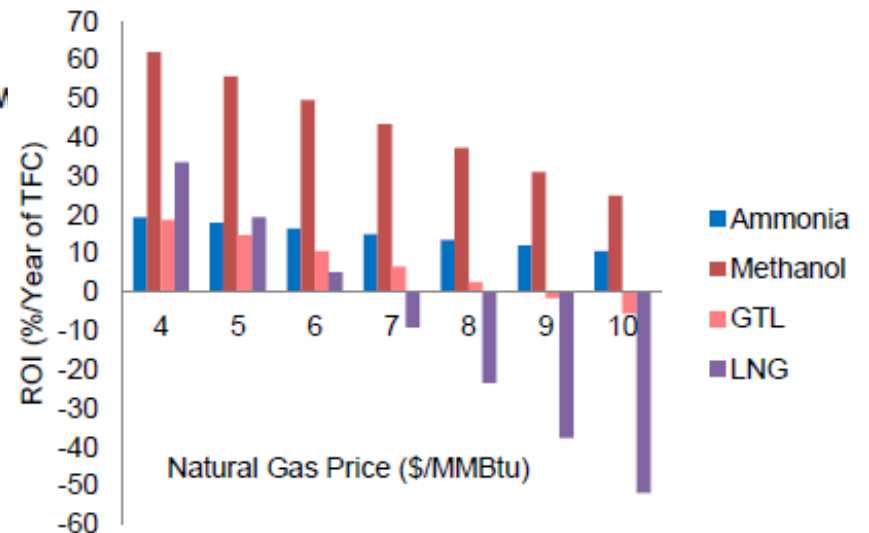


Ron Smith, IHS

## Overall Economics for Natural Gas Products

Product	Plant Capacity	Total Capital Investment <sup>a</sup>	Capital Intensity <sup>b</sup>	Return-on-Investment	Annual Return <sup>c</sup>	Payback Period
Ammonia	3,300 MTPD <sup>d</sup>	1.56	427,727	9.2%	142.2	14.2 Yrs
GTL Product	35,000 BPD <sup>e</sup>	2.76	78,857	8.2%	227.0	16.4 Yrs
LNG	19,436 MTPD <sup>d</sup>	2.51	129,142	15.9% <sup>f</sup>	399.1 <sup>g</sup>	8.1 Yrs
Methanol	5,000 MTPD <sup>d</sup>	0.94	188,000	51.2%	438.6	3.2 Yrs

- a. Billion of US dollars
- b. US dollars per daily installed capacity
- c. Annual return (\$ in millions) is based on the difference betw product market price
- d. MTPD: Metric Tons/Day
- e. BPD: Barrels/Day
- f. Calculated for UK at a local LNG price of \$10.00/MMBtu
- g. LNG profitability is increased when it is exported to Japan





# methane conversion: general discussion

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Bob McCabe, Lakis Mountziaris, NSF



**Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen**

Xiaoguang Guo *et al.*

*Science* **344**, 616 (2014);

DOI: 10.1126/science.1253150

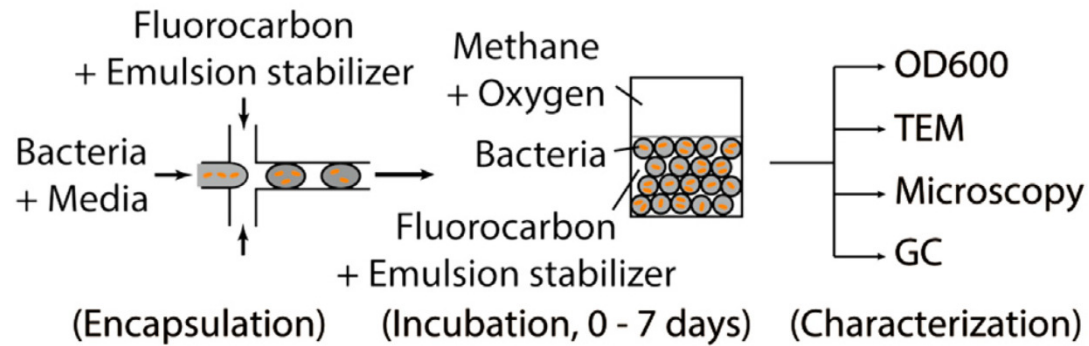
## Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen

Xiaoguang Guo,<sup>1</sup> Guangzong Fang,<sup>1</sup> Gang Li,<sup>2,3</sup> Hao Ma,<sup>1</sup> Hongjun Fan,<sup>2</sup> Liang Yu,<sup>1</sup> Chao Ma,<sup>4</sup> Xing Wu,<sup>5</sup> Dehui Deng,<sup>1</sup> Mingming Wei,<sup>1</sup> Dali Tan,<sup>1</sup> Rui Si,<sup>6</sup> Shuo Zhang,<sup>6</sup> Jianqi Li,<sup>4</sup> Litao Sun,<sup>5</sup> Zichao Tang,<sup>2</sup> Xiulian Pan,<sup>1</sup> Xinhe Bao<sup>1\*</sup>



# biological methane conversion

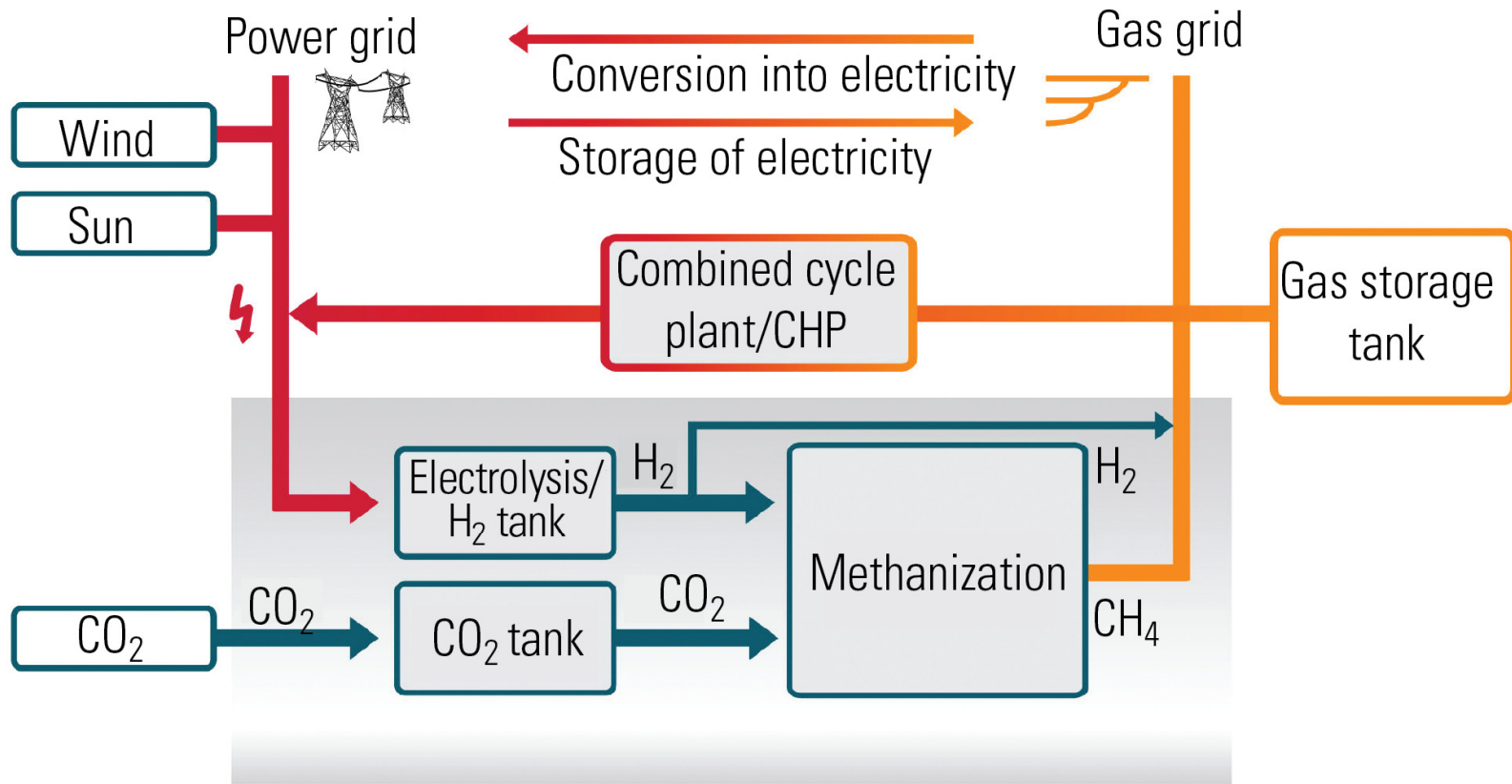
Craig Criddle, Alfred Spormann, Stanford





# unconventional processes

Ron Kent, SoCalGas

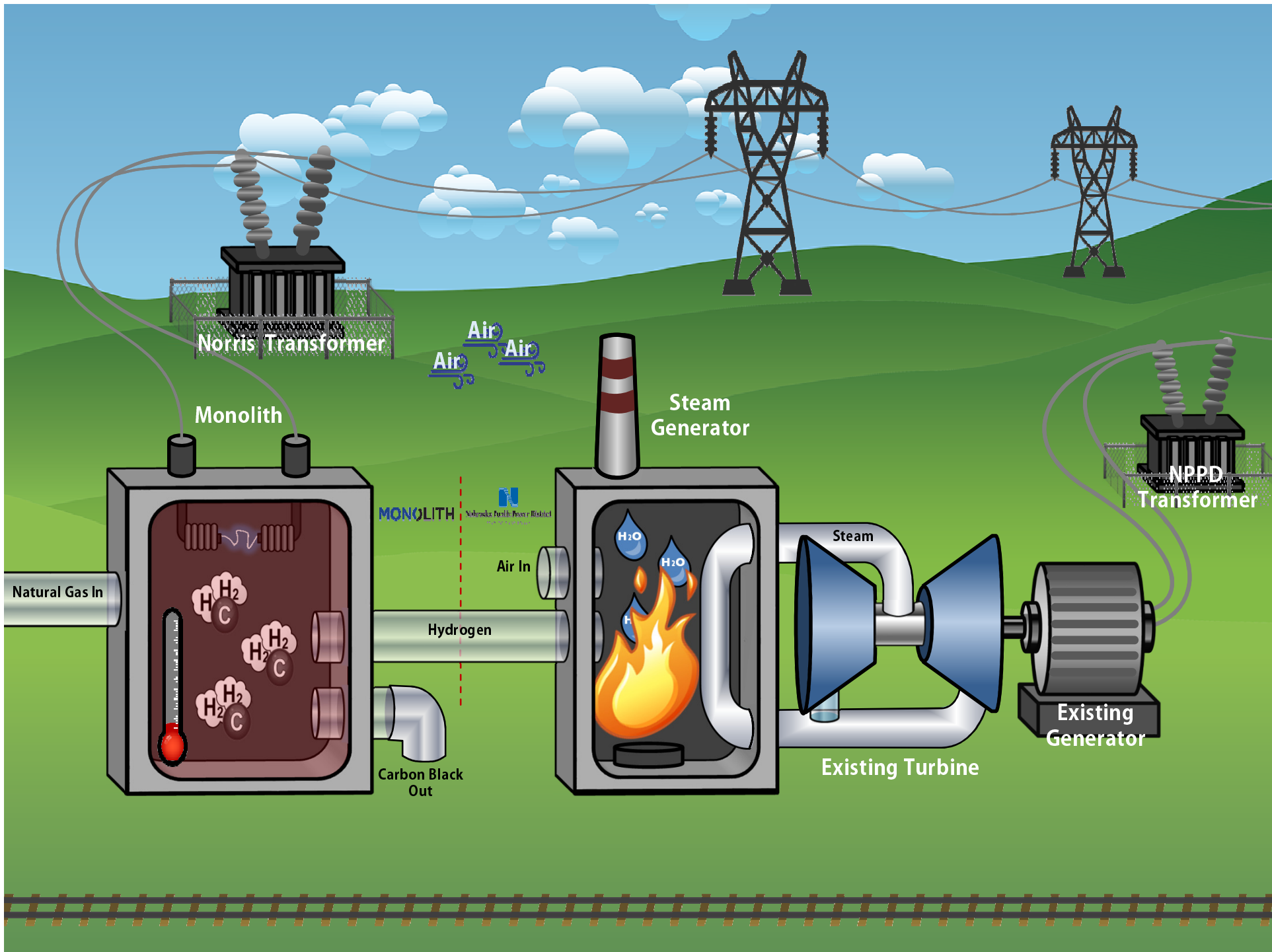




# unconventional processes

Pete Johnson, Monolith Materials

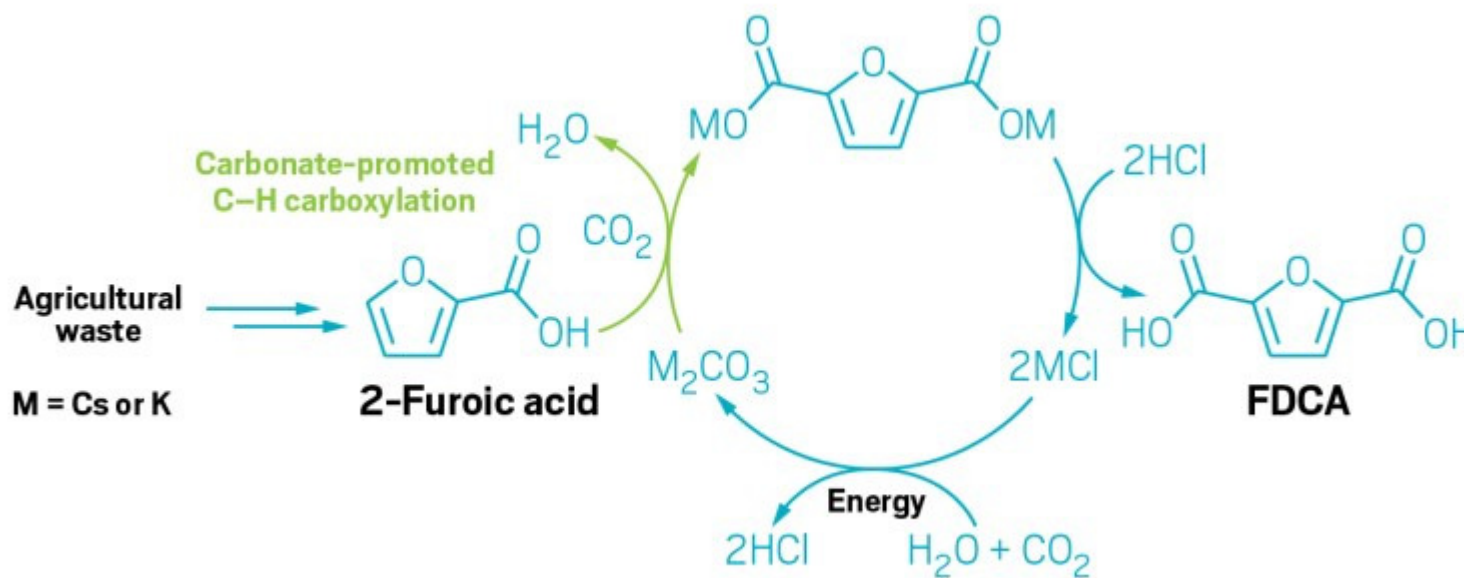
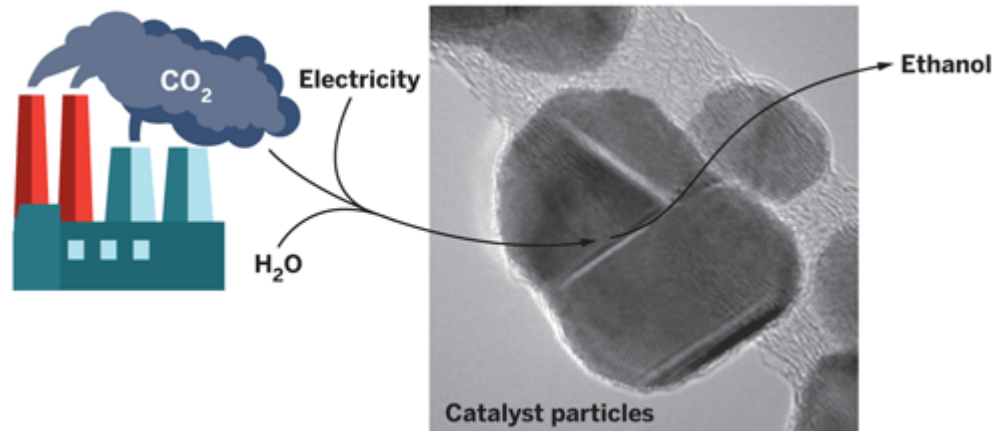






# unconventional processes

Matt Kanan,  
Stanford University

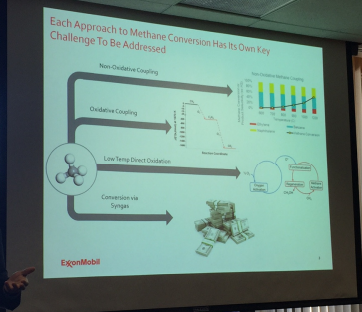




Shell

ExxonMobil

IHS



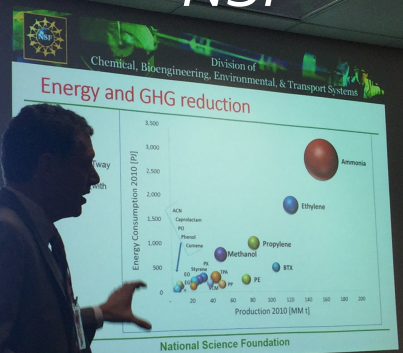
Technology options for monetization of natural gas - USGC  
monetization results (2014)

Product	Plant Capacity	Feed Cost	Production	Revenue	Operating Costs	Profit
CO <sub>2</sub> Product	1.5 Mtpa	1.10	1.5	2.0	1.5	0.5
Methanol	1.5 Mtpa	1.10	1.5	2.0	1.5	0.5
Ammonia	1.5 Mtpa	1.10	1.5	2.0	1.5	0.5

NSF

Stanford

Stanford



Thank you

Background

Methanotrophs = methane oxidizing bacteria

Aerobic methanotrophs oxidize methane oxidized with the enzyme methane monooxygenase (MMO).

To make CH<sub>3</sub>OH, MMO uses 1 mole of O<sub>2</sub> and 2 moles of electrons per mole of CH<sub>4</sub> oxidized. The requirement for 2 moles of reducing power is equivalent to an energy level of 5x more of CH<sub>4</sub>.

MMO is non-specific; many compounds are tetrahedrally oxidized besides methane. Examples include other alkanes and chlorinated molecules.

- From methane to liquid fuels and beyond: opportunities and challenges for a natural gas-powered future
- Microbial Life around Methane
- Microbial Metabolism of Methane
- 1) Microbial Processes using Methane - An Alternative Use
  - 2) Microbial Processes producing Methane: Conversion of Electricity plus CO<sub>2</sub> to CH<sub>4</sub> via Microbial Electrosynthesis (Green Methane)

SoCal Gas

Monolith Materials

Stanford

