Chemistry in the Center for Catalytic Hydrocarbon Functionalization: Fundamental Studies Relevant to Catalysts for C-H Functionalization

Center for Catalytic Hydrocarbon Functionalization

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Fuels

CO_2

Energy

Energy Security

O_2

H_2O

Sustainability

Commodity Chemicals

CH_4

N_2

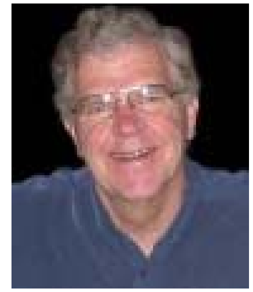
Fertilizer

CCHF
Center for Catalytic Hydrocarbon Functionalization

Team


Vedernikov/UM


Periana/TSRI


Groves/Princeton


Trewyn/Ames


Gunnoe/UVA

Homogeneous catalysis and organometallic chemistry

Electrochemistry and electrocatalysis

Bioinorganic chemistry and enzymatic chemistry

Computational chemistry and quantum mechanics

Materials chemistry (nanomaterials, electrodes surfaces, etc.)


Meyer/UNC


Crabtree/Yale


Ess/BYU


Goddard/Caltech


Cundari/UNT

An Economy Based on Natural Gas

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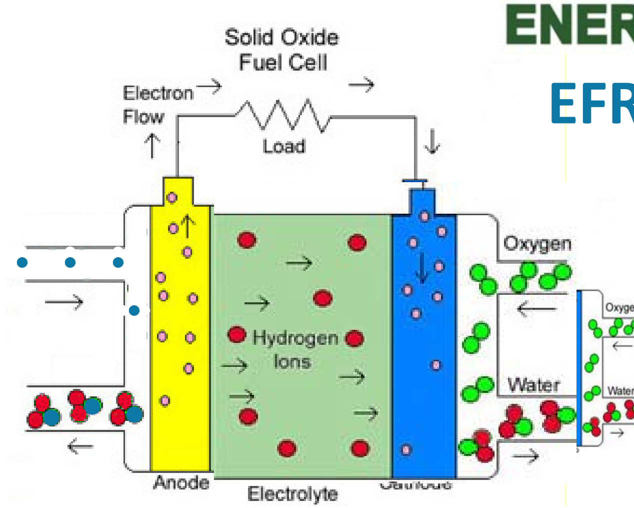
Fuels

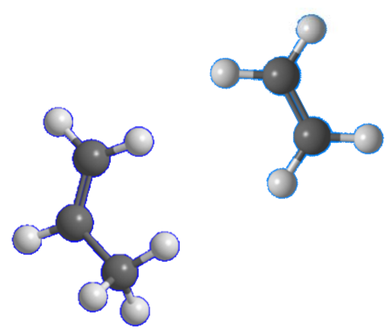
Natural Gas (CH_4)

$CH + \frac{1}{2} O_2 \rightarrow COH$

Next Generation Catalysts



Electricity



Materials

Why natural gas?

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Extensive Natural Gas Reserves

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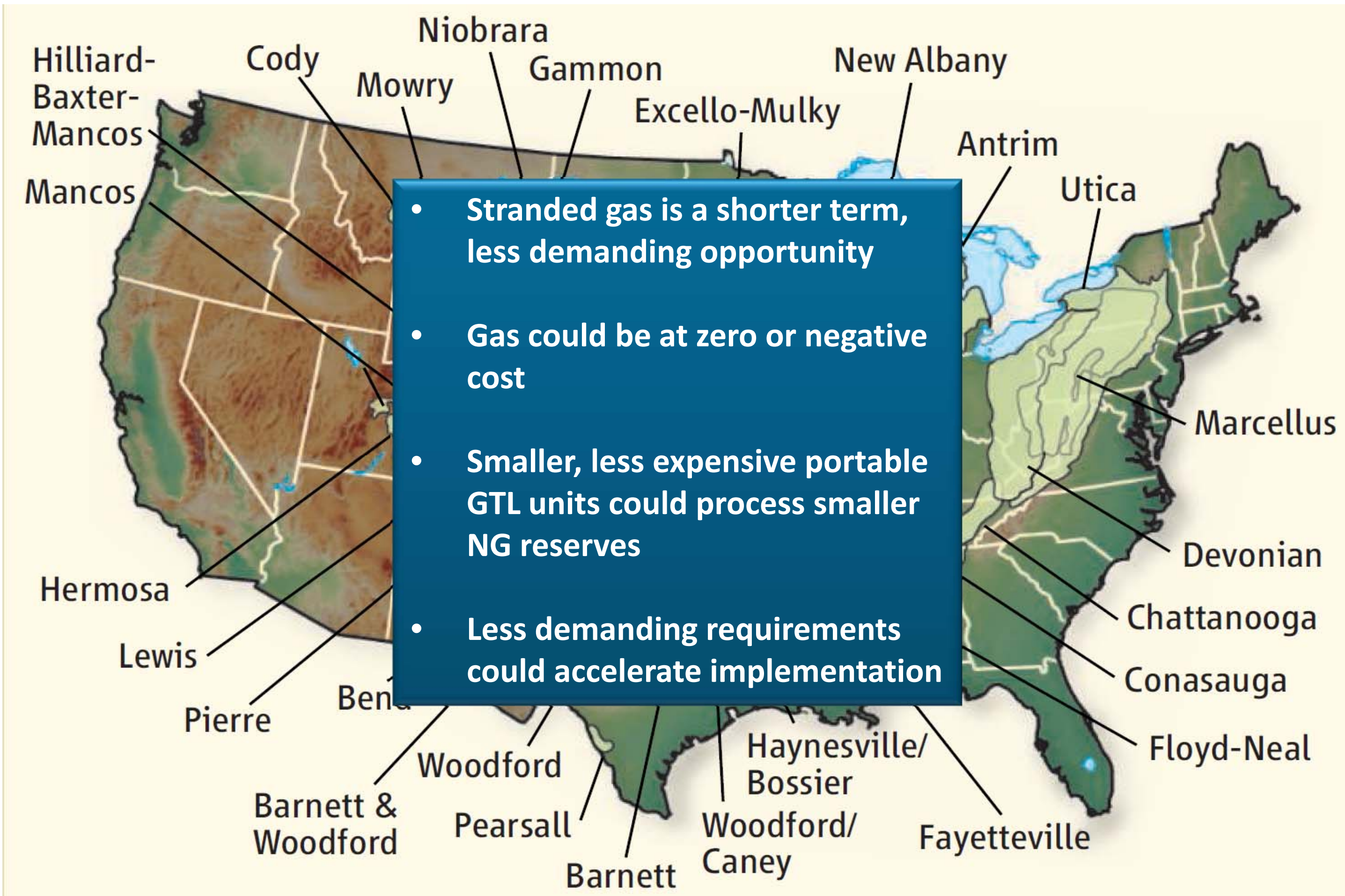

- **Stranded gas is a shorter term, less demanding opportunity**
- **Gas could be at zero or negative cost**
- **Smaller, less expensive portable GTL units could process smaller NG reserves**
- **Less demanding requirements could accelerate implementation**

Flared Gas is an Immediate Need

- Gas at negative value
- Require small Inexpensive GTL Units

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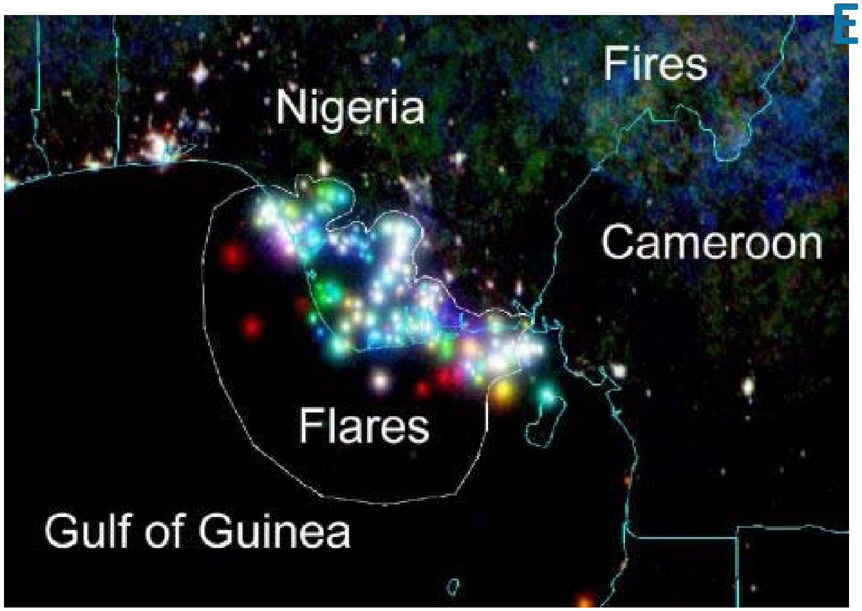

- ~25% of US needs is flared
- Current high Temperature, syngas technology too expensive and complex for these applications

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Implementing the Natural Gas Economy

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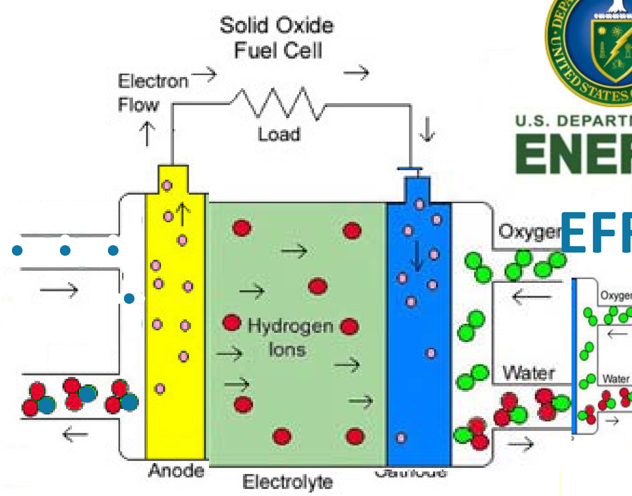
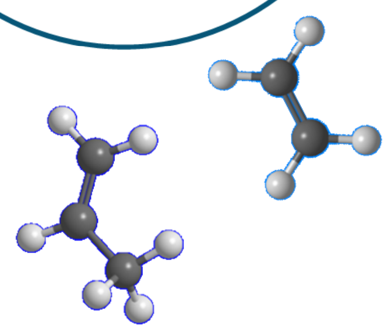
CH_4

CH_3OH
The future
Intermediate
Feedstock

Fuels



Electricity



Why Methanol (DME)?

Technologies known or in development

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Current technology to convert CH_4 to Liquids

- ❑ 70% yield!

Selectivity of any new process must be >~80 – 90%!

- ❑ Mature technology!
- ❑ Practiced at fuel scale!
- ❑ Uses only AIR as the co-reagent!

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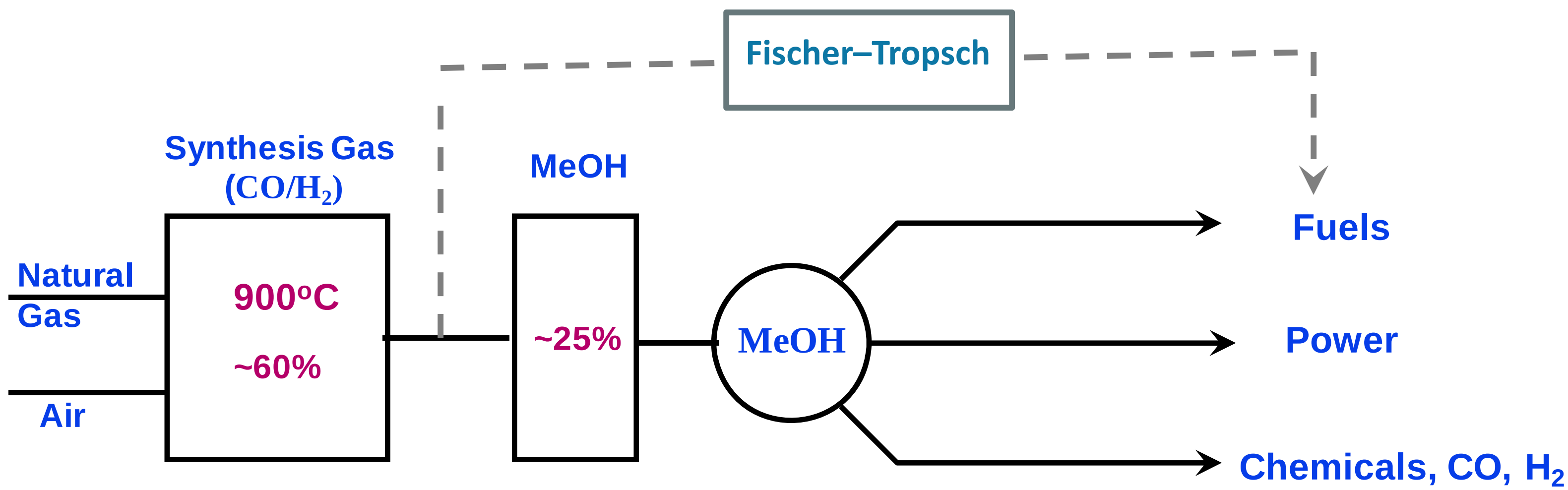
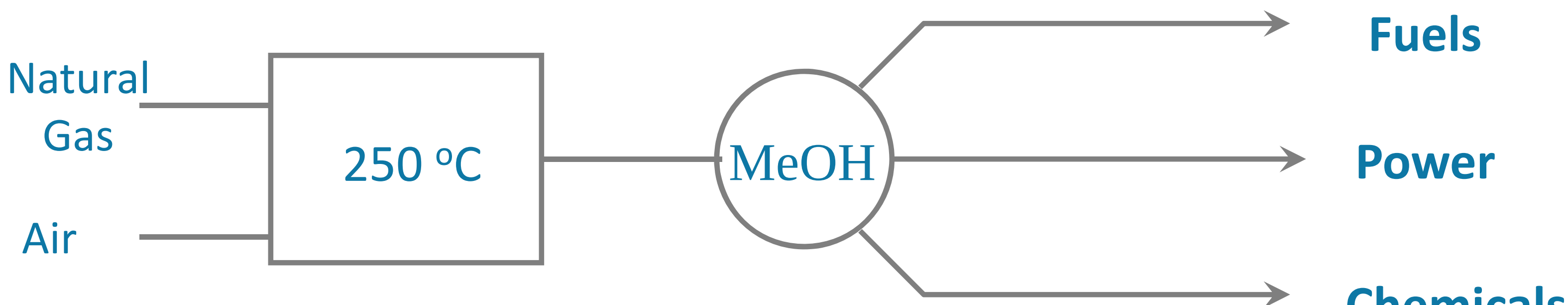
Key to cost reduction is lower capital cost!



Technology Needed

Direct, Selective, Lower Temperature Methane Oxidation



$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$

Goal: >50% reduction in cost relative to existing technology

The Challenge

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Utilize catalyst to activate (increase reactivity) of RH

Minimize

$$H_3C\text{-}H + \tfrac{1}{2}\,O_2 \longrightarrow H\text{-}CH_2\text{-}OH \not\longrightarrow CO_2 + H_2O$$

Utilize catalyst to activate (increase reactivity) of O_2

High Selectivity by Minimizing Product Oxidation

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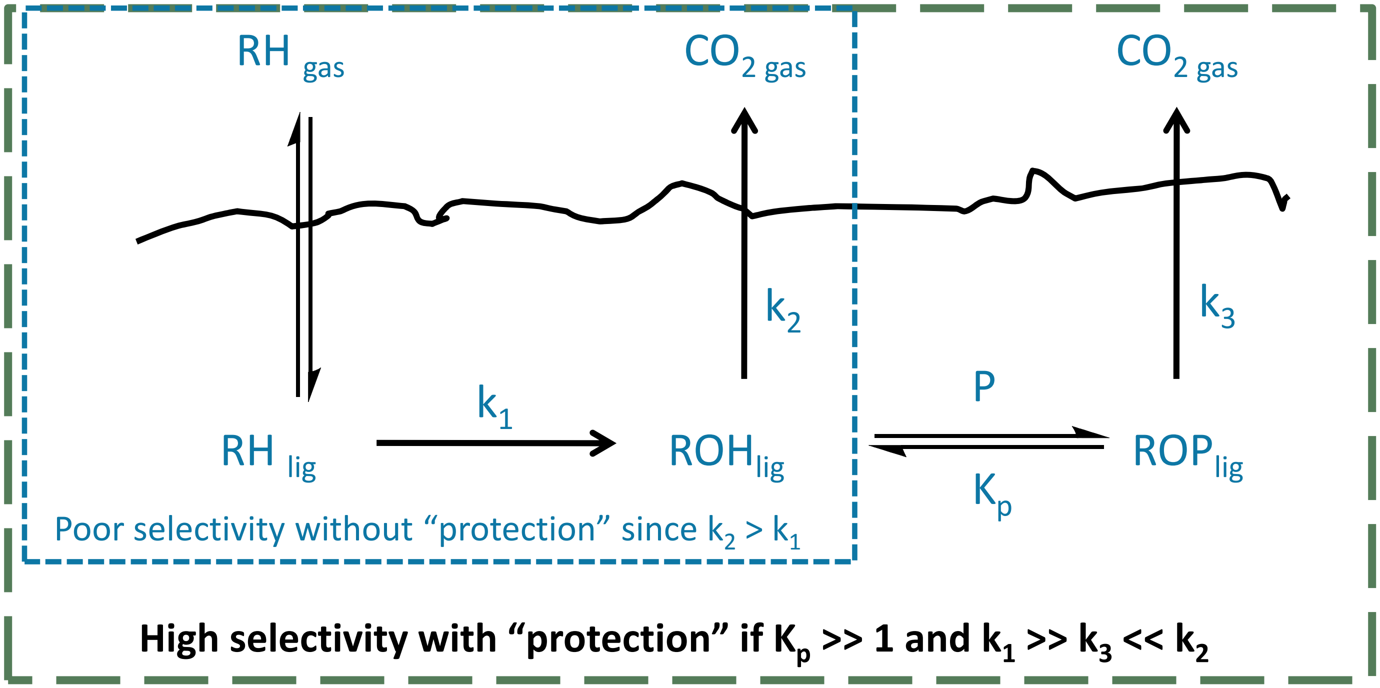
Product protection strategy

The strategy capitalize on reactivity of OH group



P group needs to be <u>inexpensive</u>, <u>stable</u> and <u>easily</u> recycled

Commercial Wacker Process for Partial Oxidation of Ethylene

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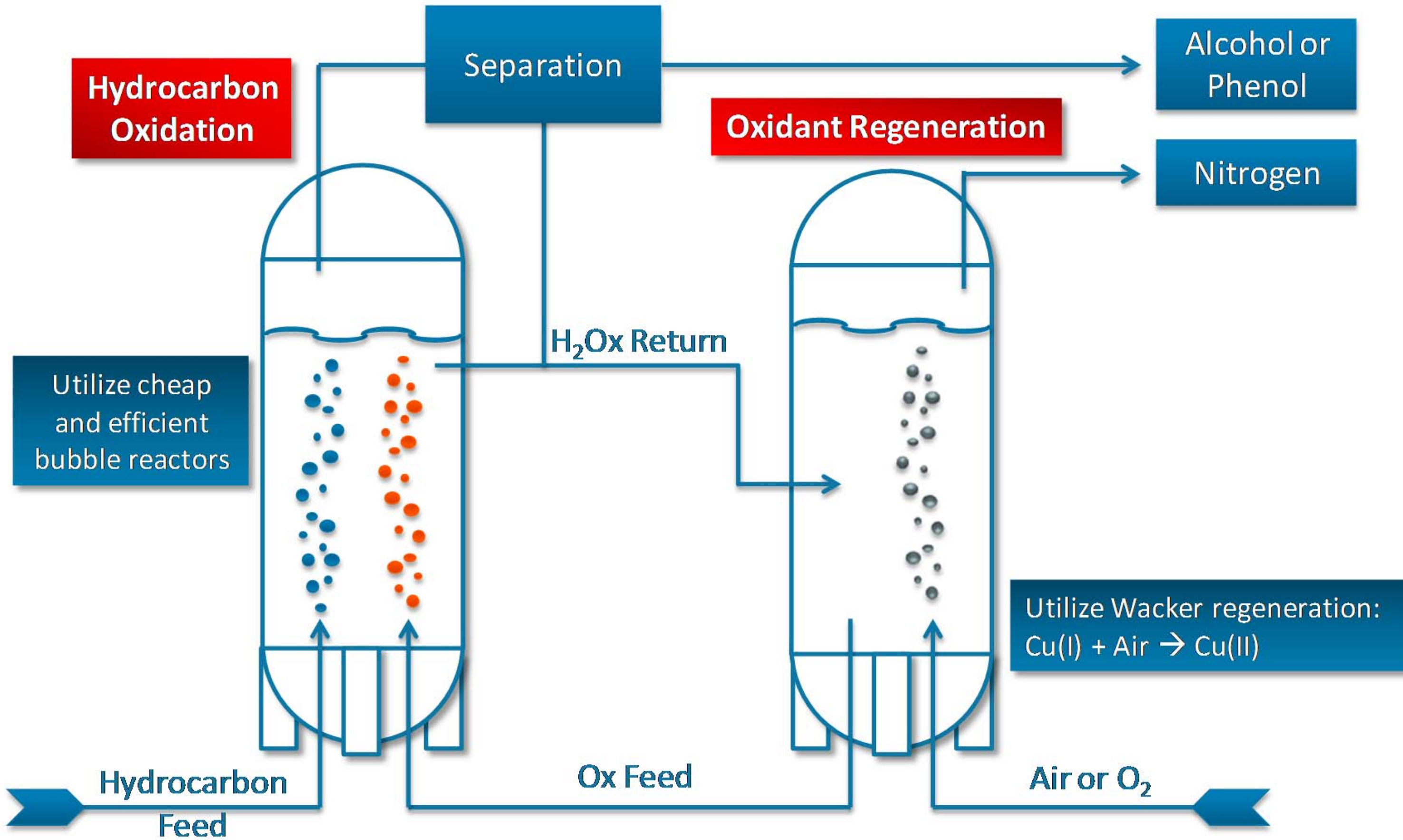

$Ox = 2Cu^{2+}$

$$C_2H_4 + Ox + H_2O \xrightarrow{Pd^{2+}} CH_3CHO + H_2Ox$$

$$H_2Ox + \tfrac{1}{2} O_2 \rightarrow Ox + H_2O$$

Homogeneous catalysis

Wacker Process Design can be Utilized for Partial Oxidation of CH_4

$$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$$

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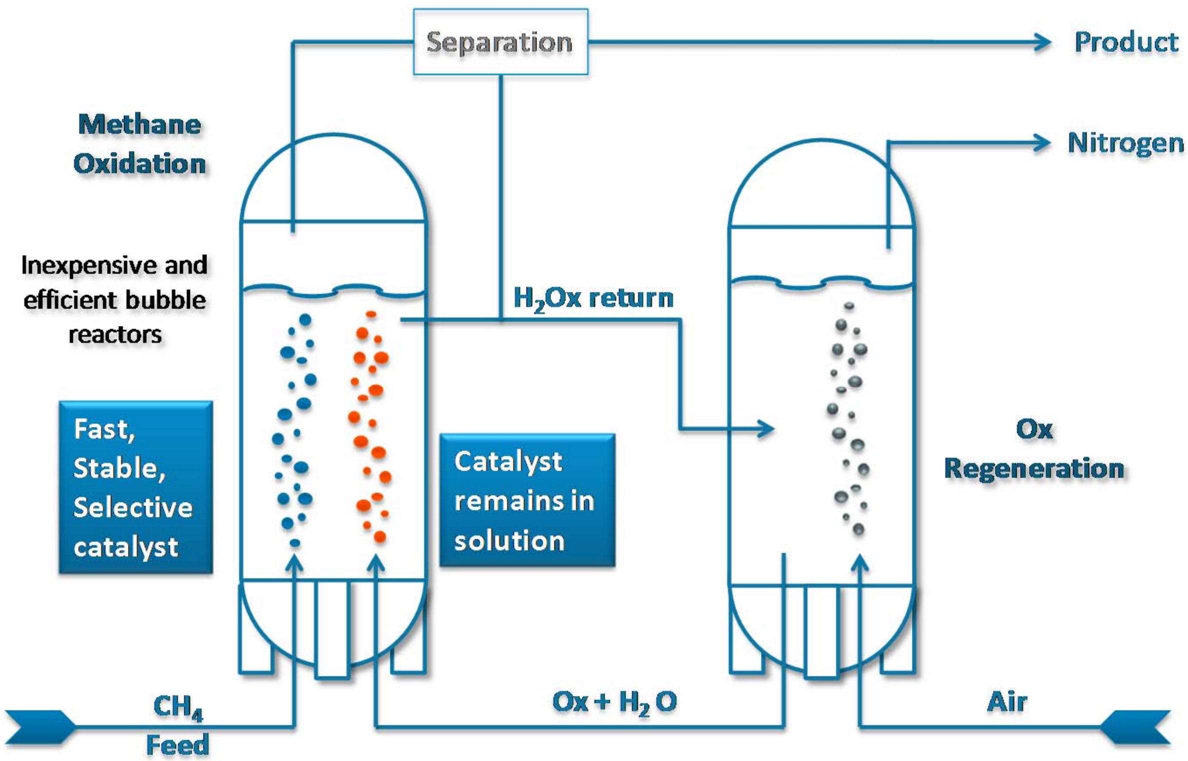

- Selective Partial oxidation
- **Lower capital and operating costs**
- Lower temperature
- Gas/Liquid system
- **No air separation**
- Inherently safer
- **Easily scalable**

- Pd^{II} is not effective
- **New homogeneous (molecular) catalyst design**

$CH_4 + Ox + H_2O \rightarrow CH_3OH + H_2Ox$

$H_2Ox + \frac{1}{2} O_2 \rightarrow Ox + H_2O$

Minimum Metrics for Measure Success

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Key engineering guidelines

- ❑ >90% Product Selectivity
- ❑ >20% Methane conversion per pass
- ❑ Temperature >200°C but < 300°C
- ❑ Reactor volumetric productivity (STY) ~10^{-6} mol/cc.sec
- ❑ Inexpensive product separation

Key Catalyst Guidelines

- ❑ TOF ~1 s^{-1}
- ❑ TON >10^3

Can molecular catalysts meet these targets??

Metrics to Measure Success

<u>Engineering Guidelines</u>

- ❑ Avoid explosive mixtures
- ❑ >20% Methane conversion <u>per pass</u>
- ❑ >90% Product Selectivity
- ❑ >20% Oxidant conversion <u>per pass</u>
- ❑ Non-corrosive materials for inexpensive reactor construction
- ❑ Facile product isolation
- ❑ Pressure <500 psig
- ❑ Temperature <u>>200°C</u> but < 300°C
- ❑ Reactor volumetric productivity (STY) ~10^{-6} mol/cc.sec = [cat] x TOF

<u>Key Catalyst Guidelines</u>

- ❑ TOF ~1 s^{-1}
- ❑ TON >10^3
- ❑ Catalyst concentration of <u>1 mM</u> at TOF = 1 s^{-1} to be cost effective
- ❑ At 1:1 gas:liquid should generate 2M MeOH in ~1.5 hr

Periana, J. Mol. Cat., 2004, *22*, 7

Molecular Catalyst Design

The Challenge

Utilize catalyst to activate (increase reactivity) of RH

Need to minimize

$$H_3C\text{-}H + \tfrac{1}{2}\,O_2 \longrightarrow H\text{-}CH_2\text{-}OH \nrightarrow CO_2 + H_2O$$

Utilize catalyst to activate (increase reactivity) of RH

Basis for Focus on Molecular Catalysts

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Emerging

Gas-Liquid or Gas-Solid

Expensive

Unstable above 250°C

Poor Catalyst Separation

Inexpensive Heat Transfer

Inexpensive Reactors

Very Selective

Fast below 250°C

Well Defined

Low Operating Costs

"Rational" Design

Full Molecular Model

Full synthetic Control

Can Integrate Modern Tools to Reduce time to Market

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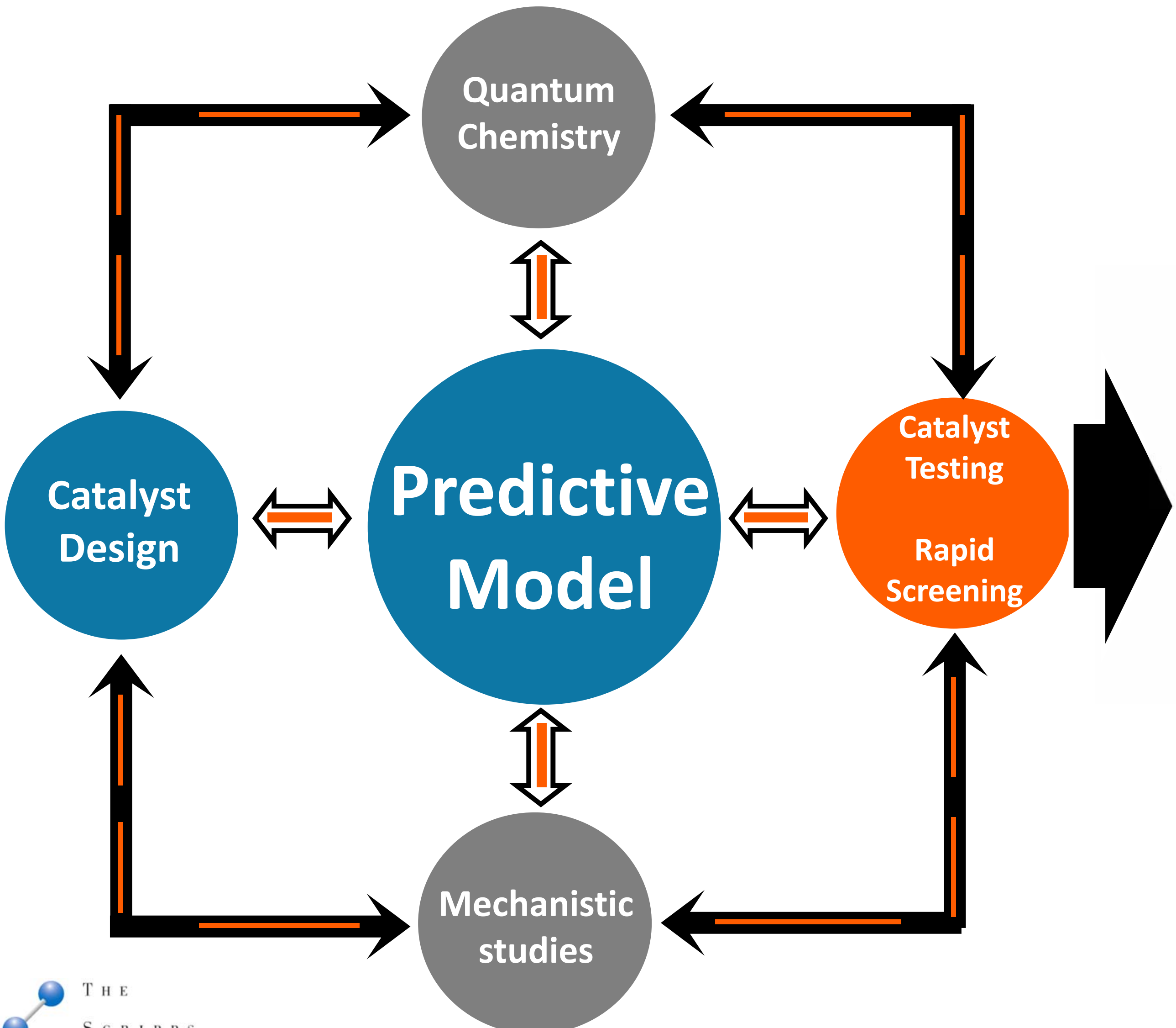

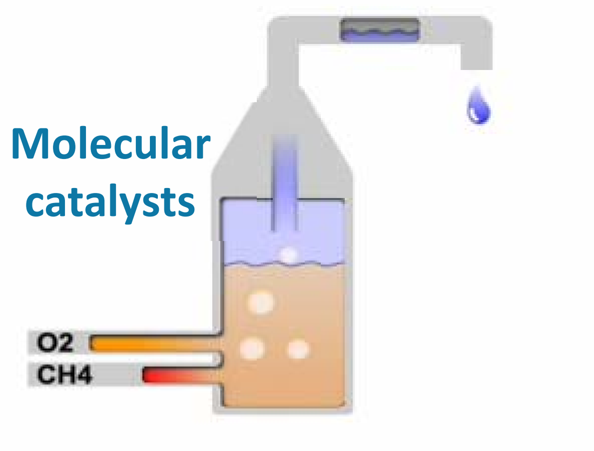

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Approaches to Catalyst Design

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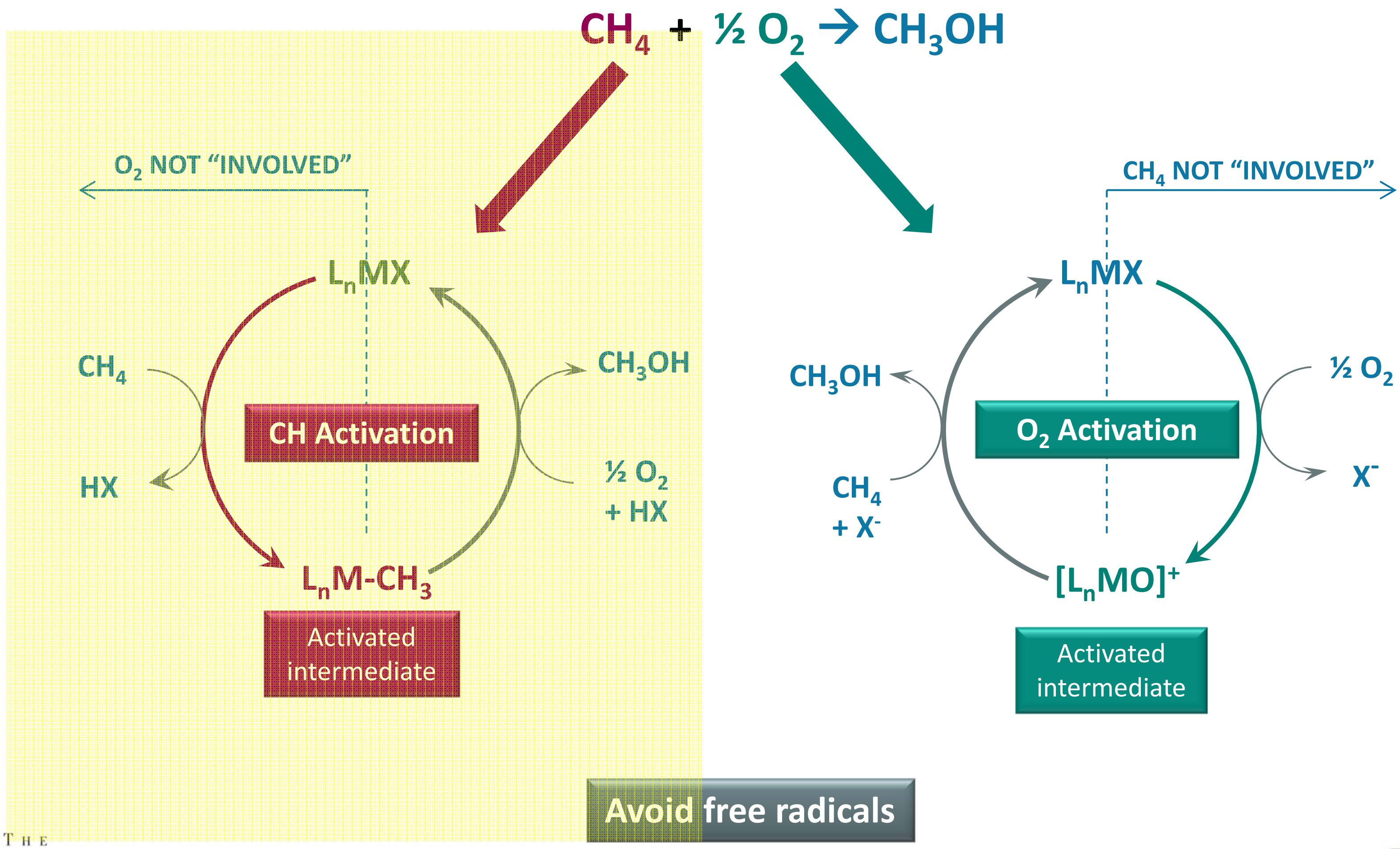
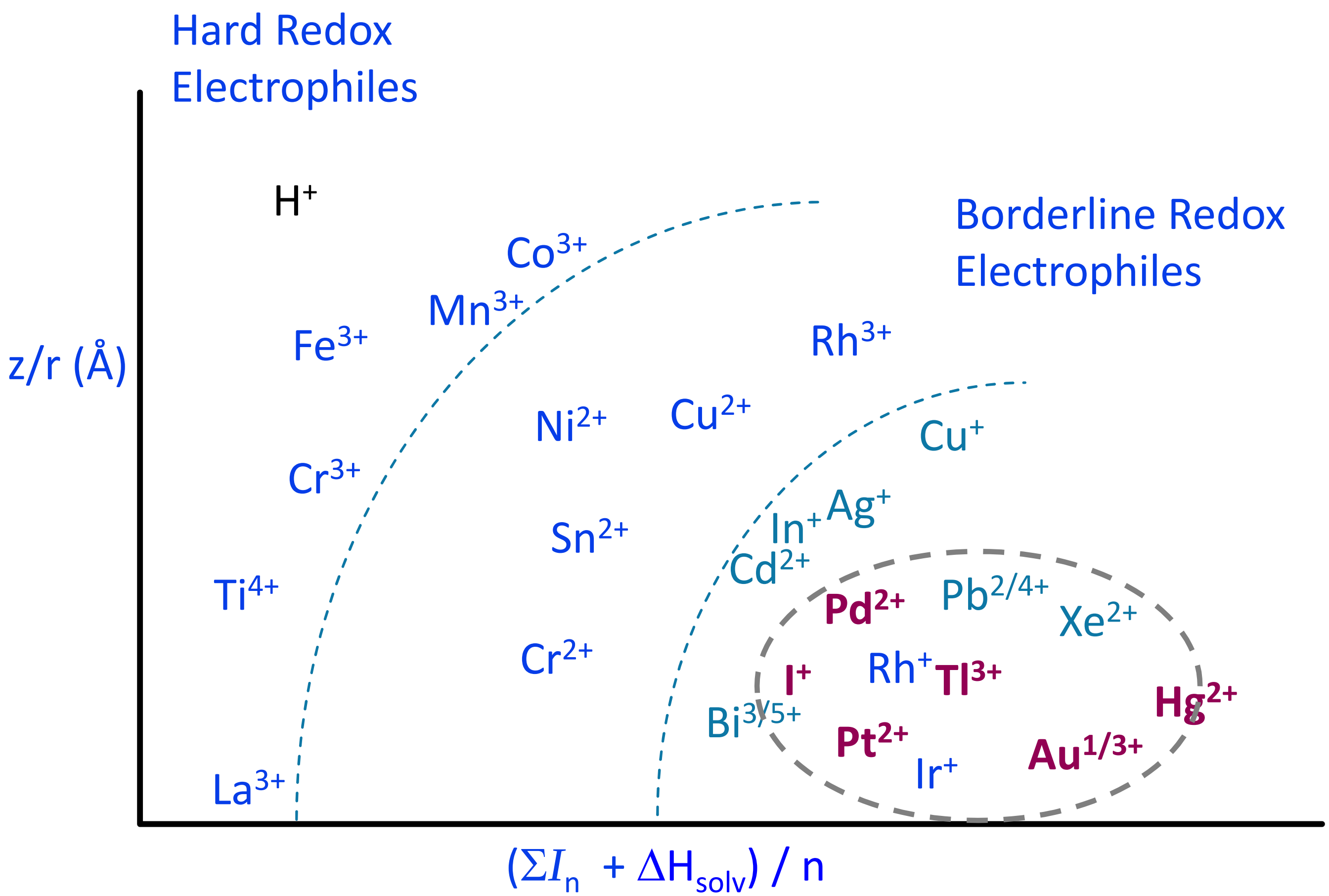


LMX Catalysts Identified by "Theoretical Chemistry"



Several Effective Electrophilic Catalysts Operate by Electrophilic CH Activation

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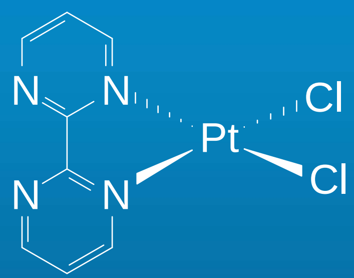
Soft, Redox active electrophiles

$Hg(II)/H_2SO_4$		I^+/H_2SO_4	$Pd(II)/H_2SO_4$	$Au(III)/H_2SeO_4$
Science, 1993	*Science*, 1998	*Chem Commun* 2002	*Science*, 2003	*Angew Chem. E.* 2004

- ❑ STY ~ 10^{-7} mol/cc.sec
- ❑ ~1M methanol
- ❑ Stable
- ❑ >90% Selectivity
- ❑ ~80% methane conversion
- ❑ All Catalysts operate by CH Activation

$$CH_4 + H_2SO_4 \xrightarrow[\text{220}^o\text{C, 2.5 hrs; 150 ml 98\% } H_2SO_4]{\text{Cat}} CH_3OH + H_2O + SO_2$$

CH_4: 500 psig; CH_3OH: ~ 1M

Acid solvent is essential!!

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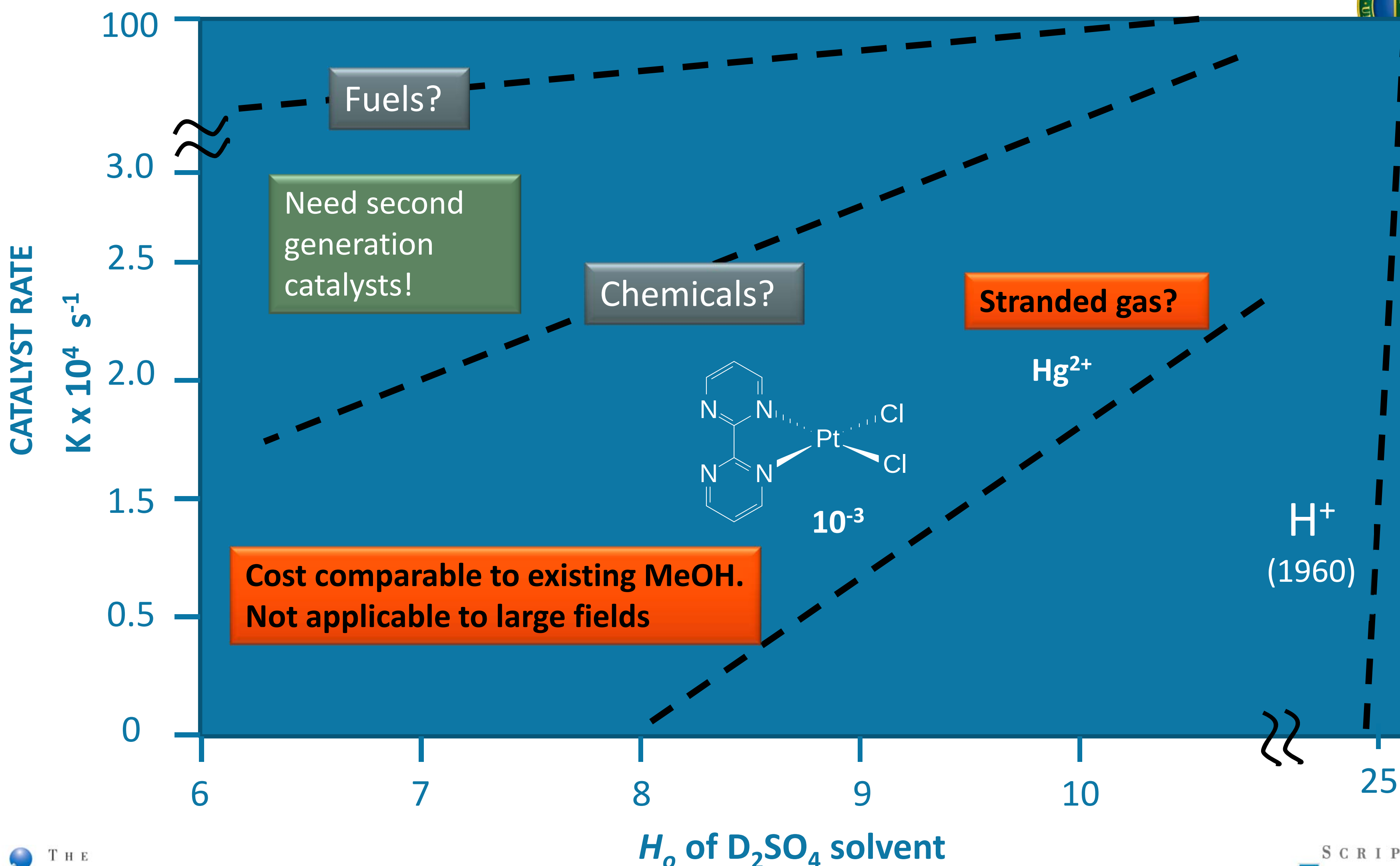
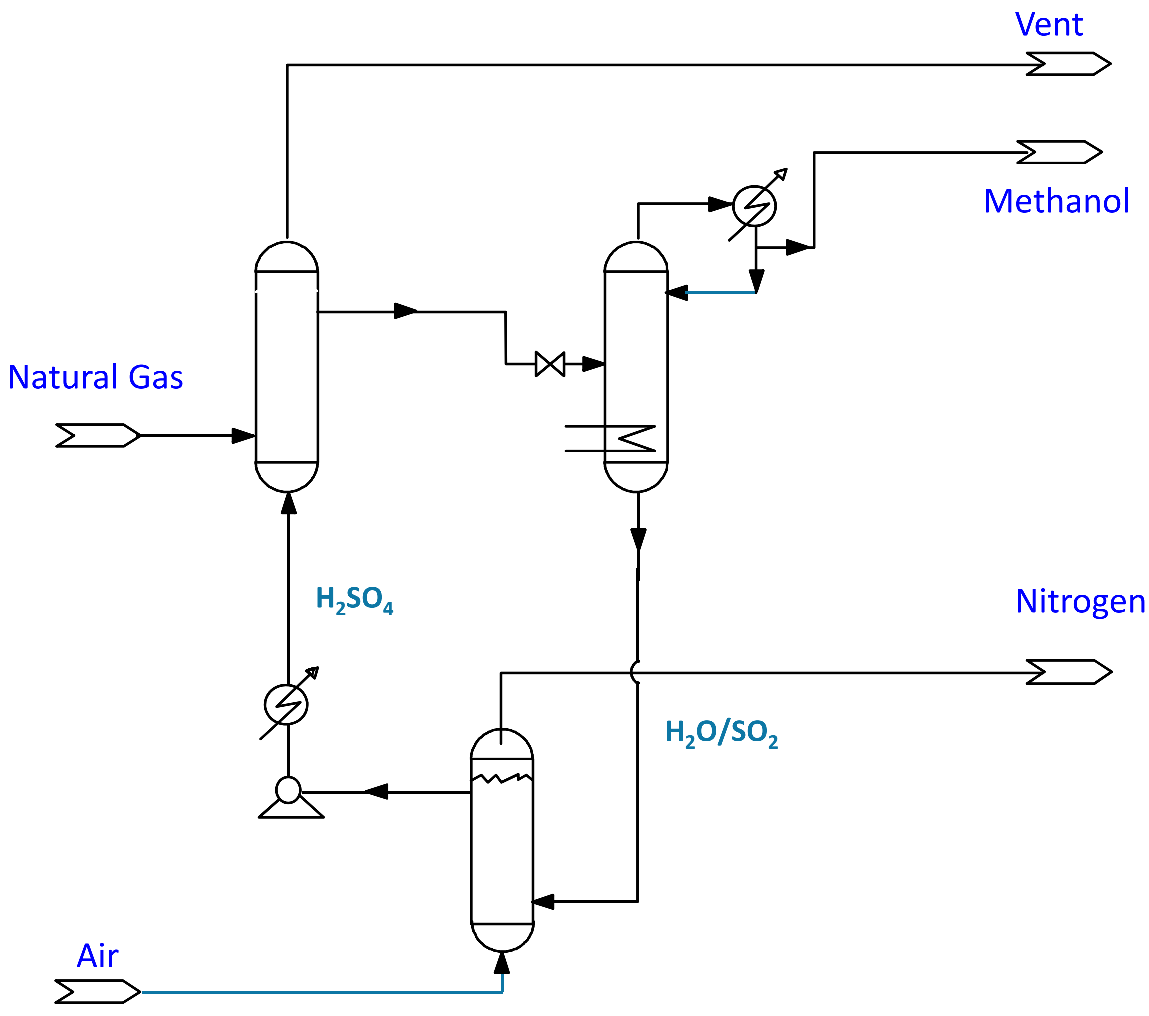
Catalysts inhibited by Products in Strong Acid Solvents



Process Economics Show that this is not applicable to Large Fields



Mechanistic Studies Show that Systems Operate by CH Activation

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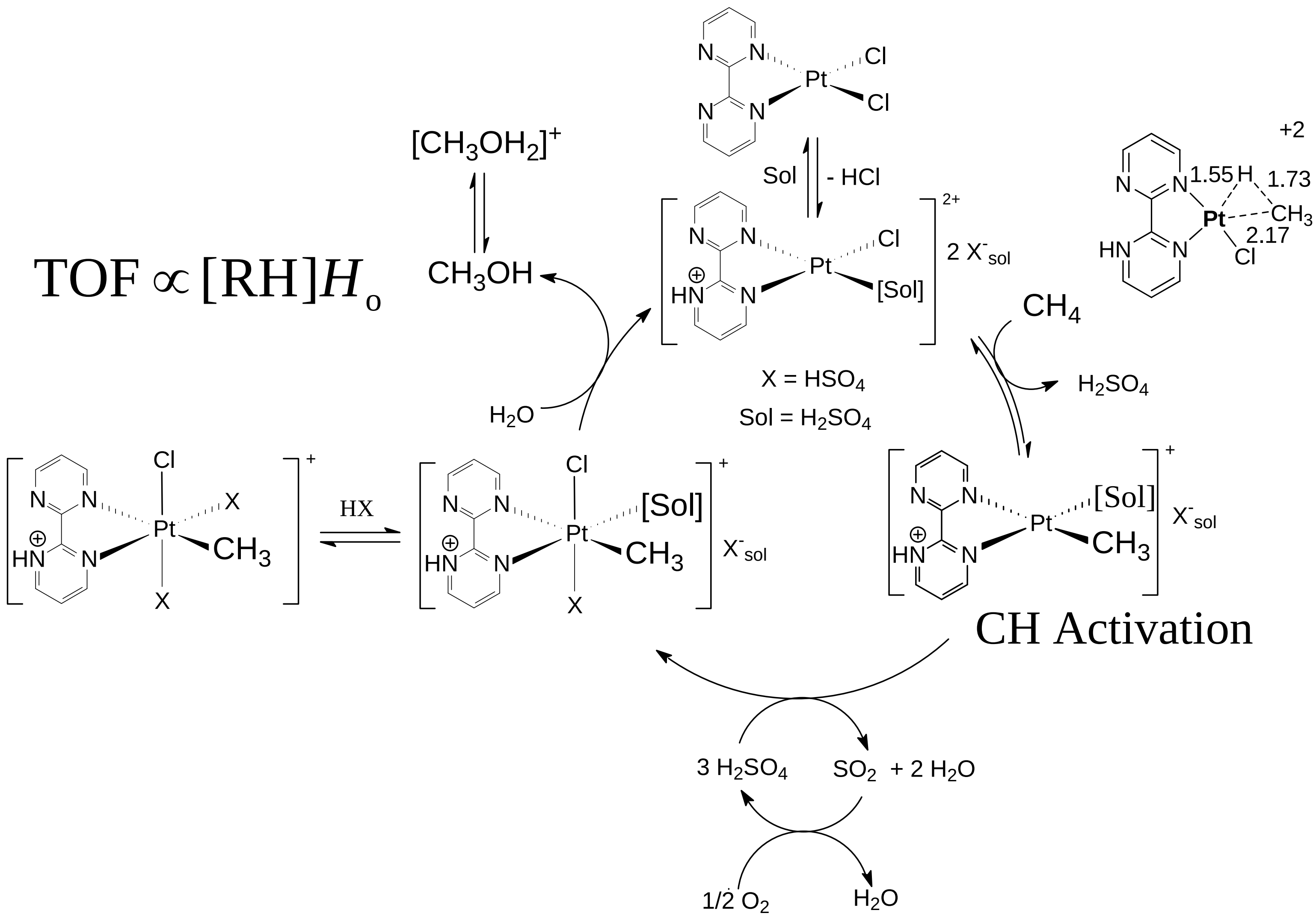
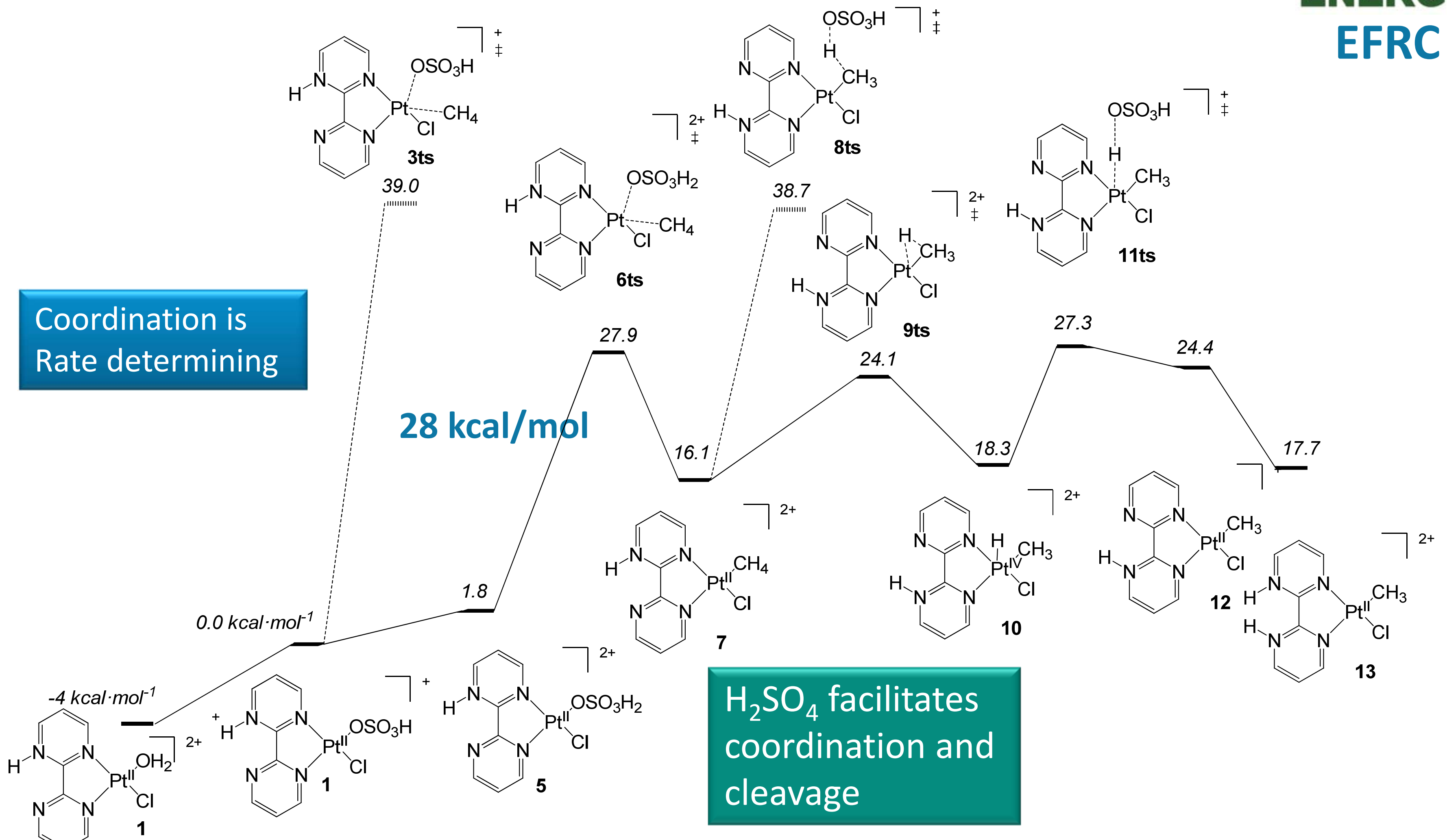
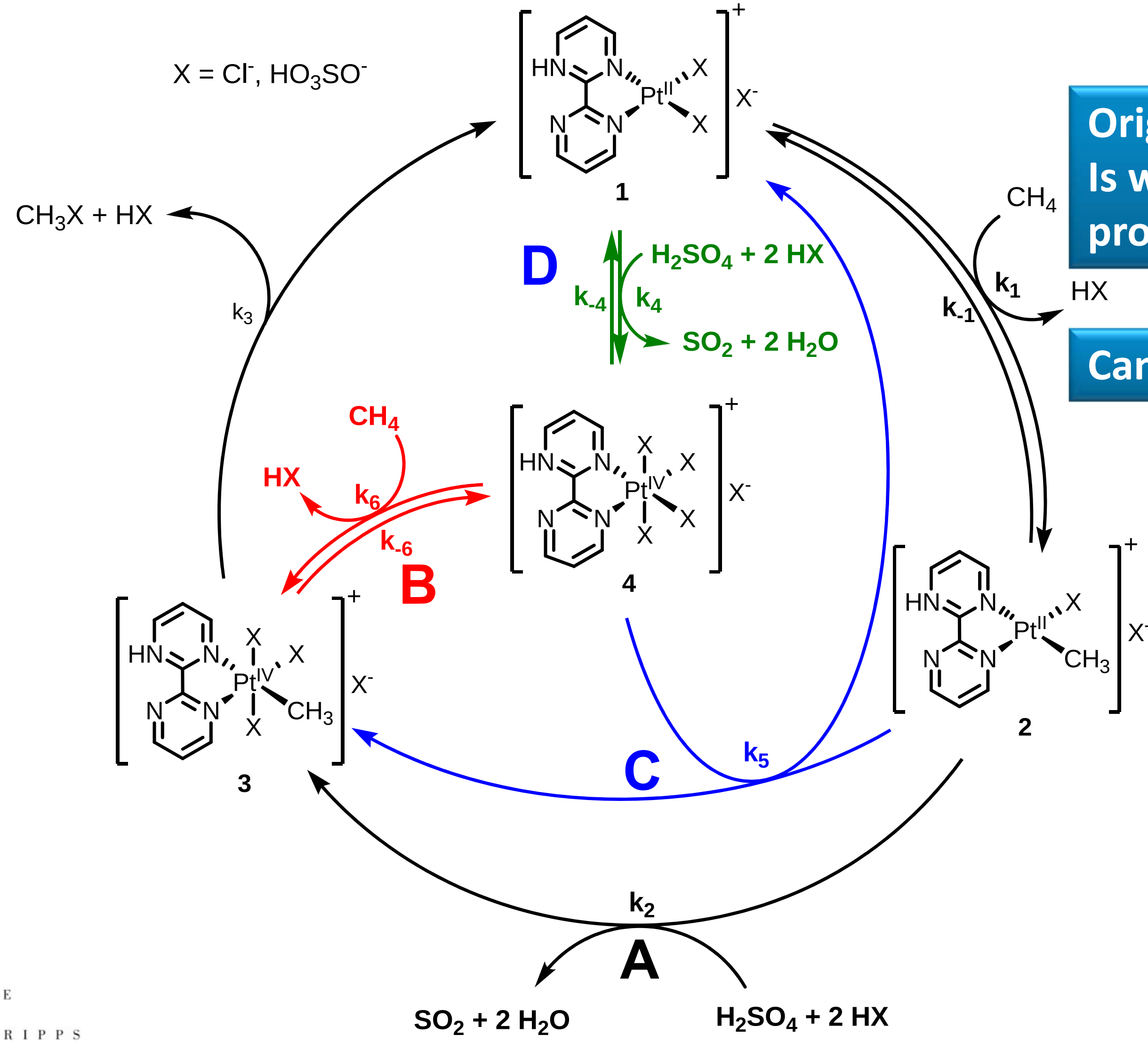
$$\mathrm{TOF} \propto [\mathrm{RH}]H_o$$



Current Proposed Reaction Mechanism



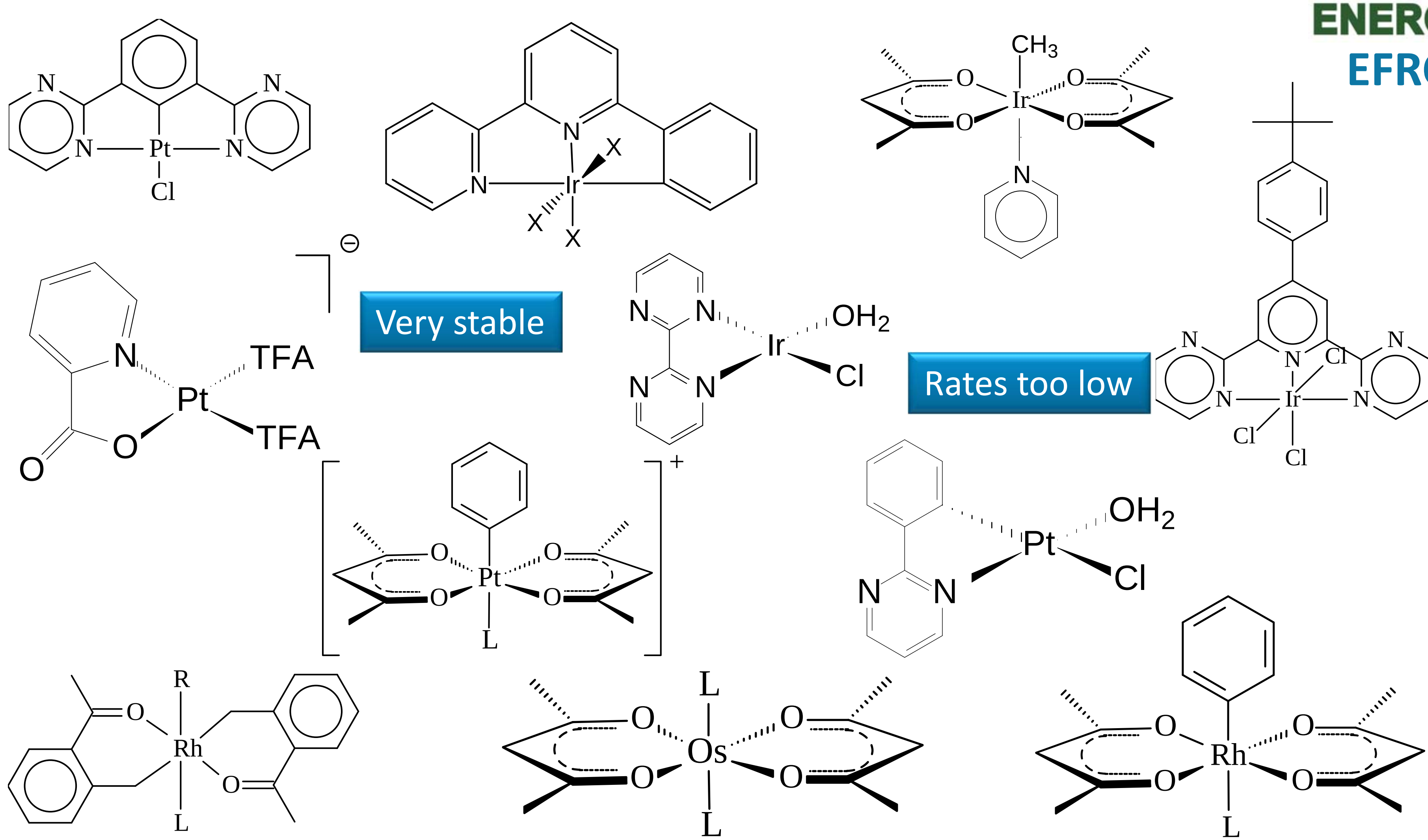
Several Possible Mechanisms: A, B, C and D



Original mechanism, A, Is wrong. Reactions proceeds by pathway D.

Can we get 10^3 increase?

New Catalyst Designs



Approaches to Catalyst Design

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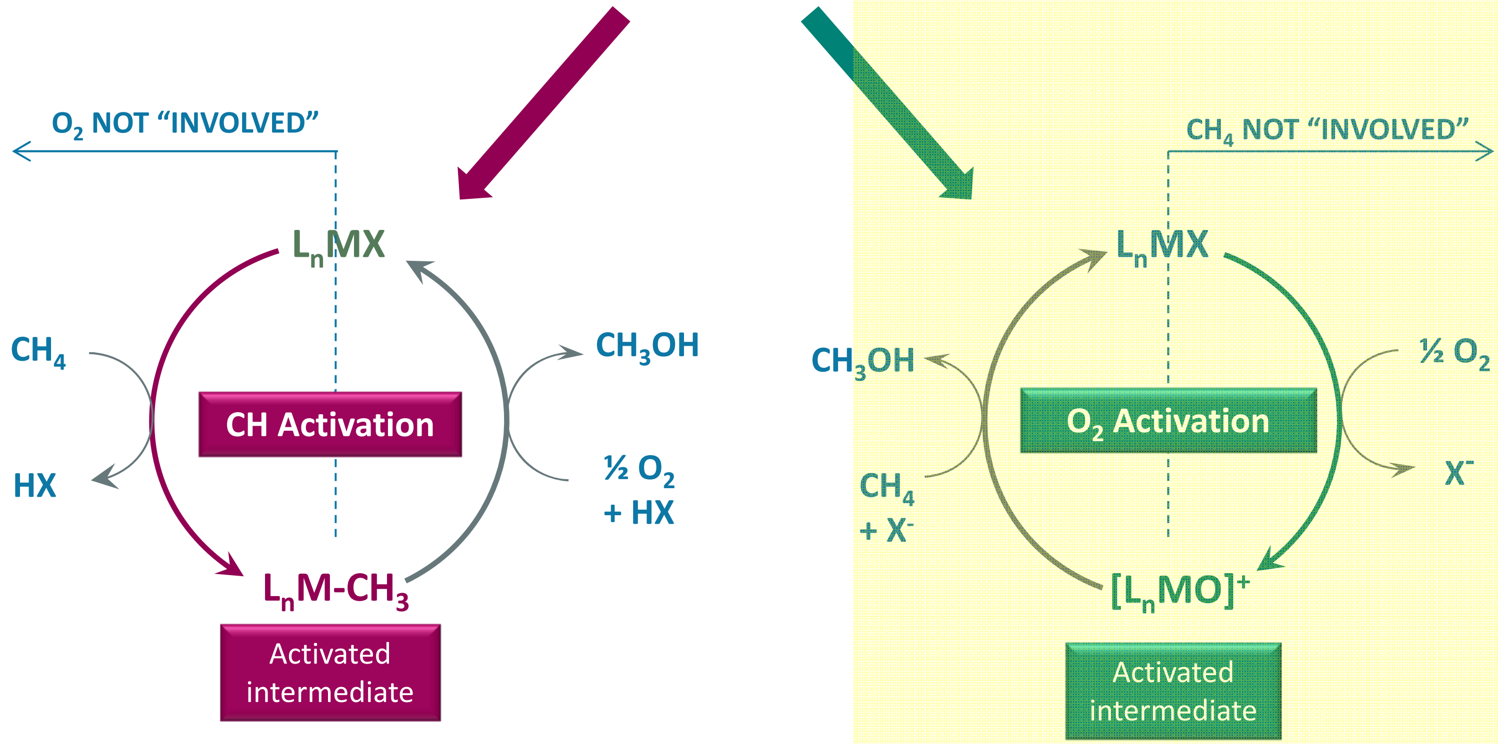
$CH_4 + ½\ O_2 \rightarrow CH_3OH$



Avoid free radicals

Ni-CoM-dependent Methanogenesis

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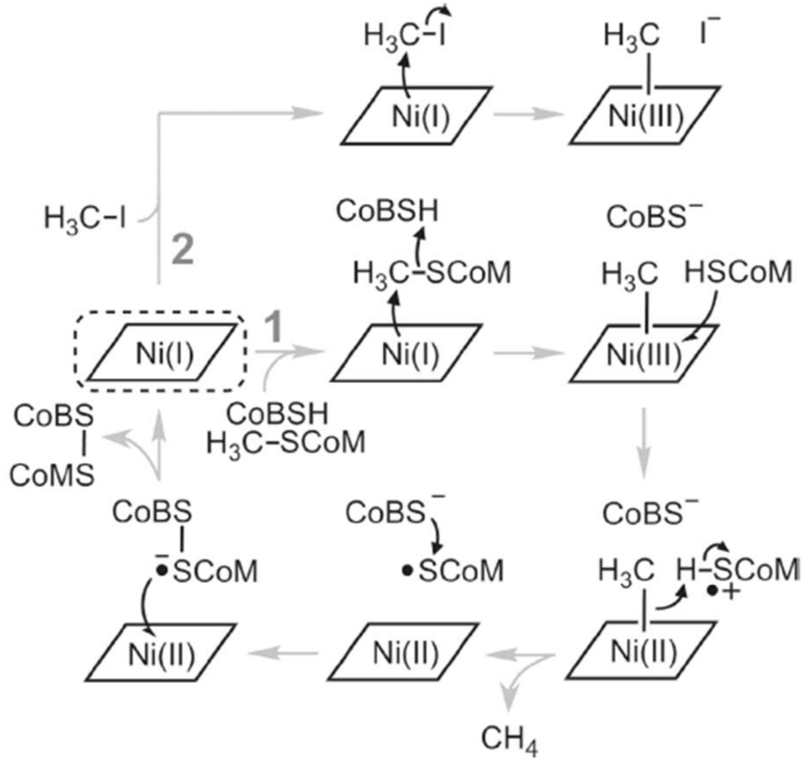
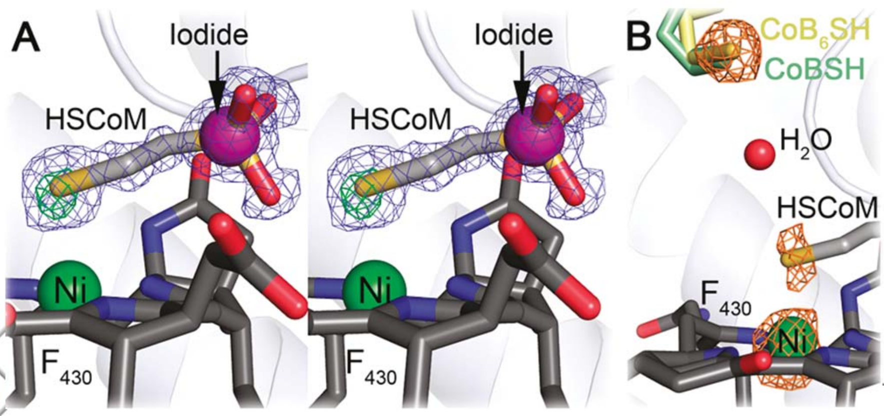
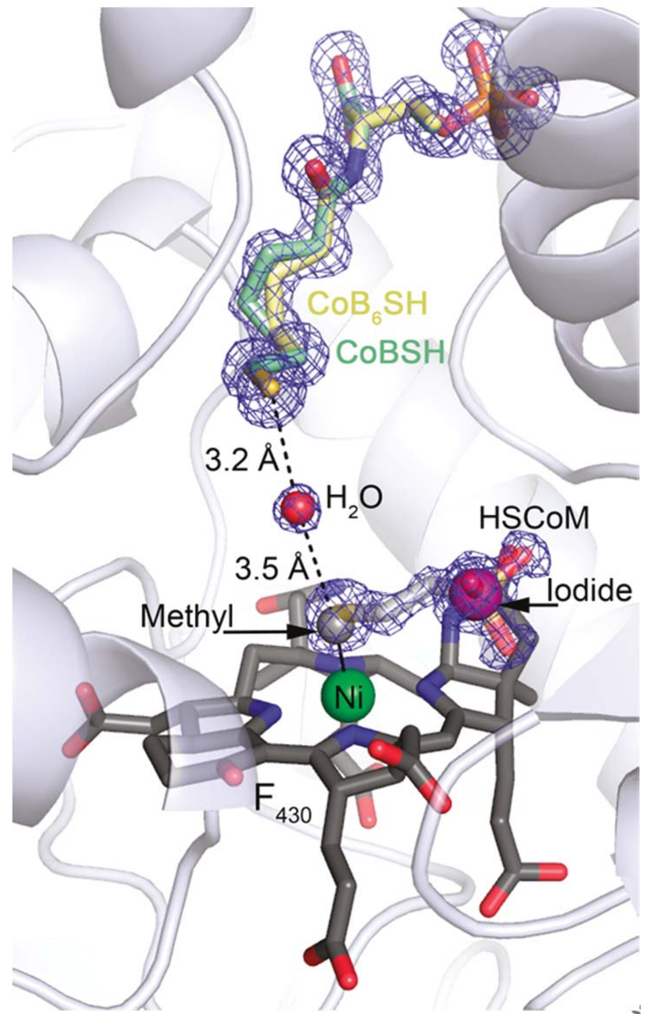
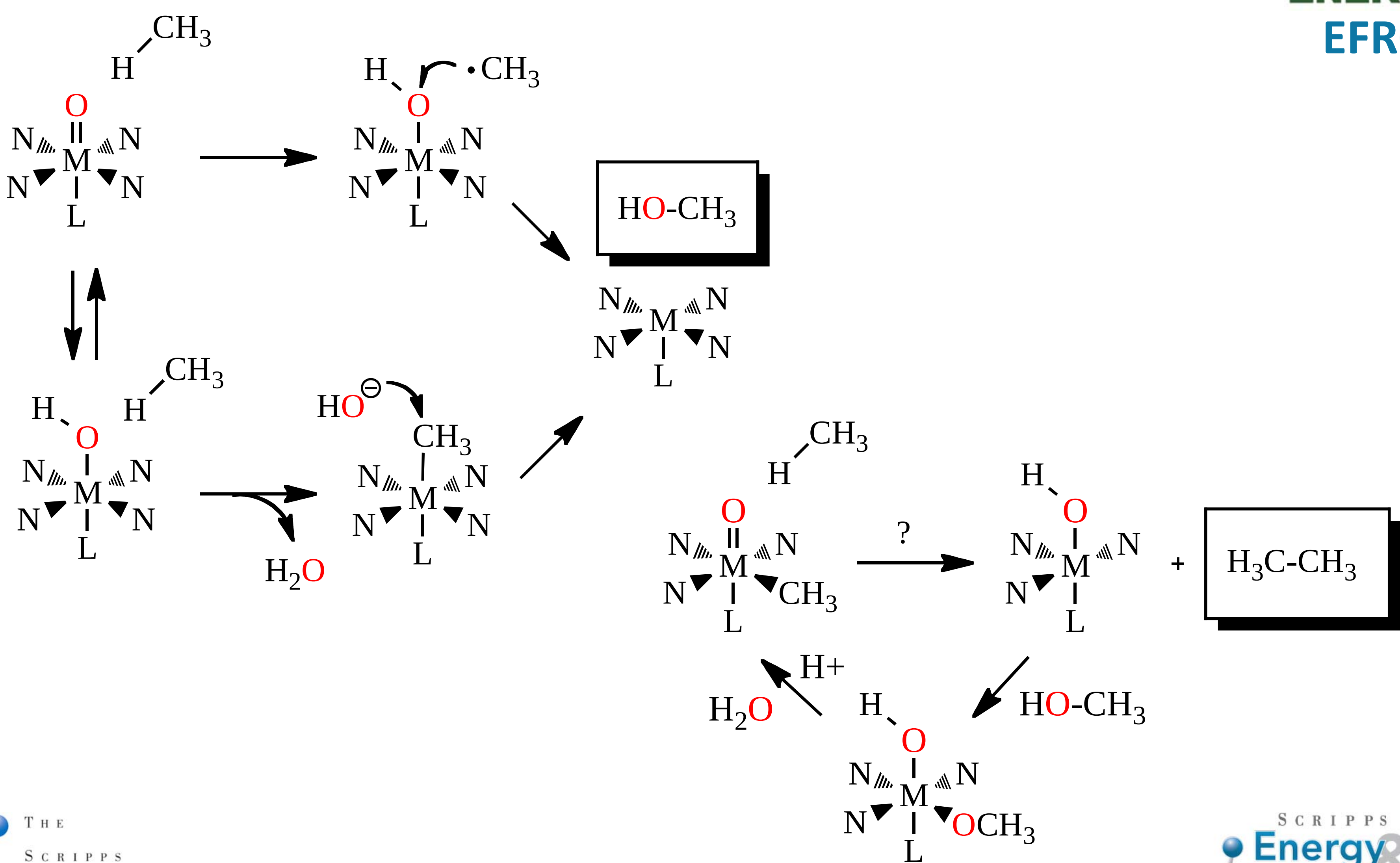






S. W. Ragsdale and C. Wilmot
J. Am. Chem. Soc. 2011, 133, 5626

Strategies for the oxygenation of strong C-H bonds



Methane Activation by Rhodium Porphyrins

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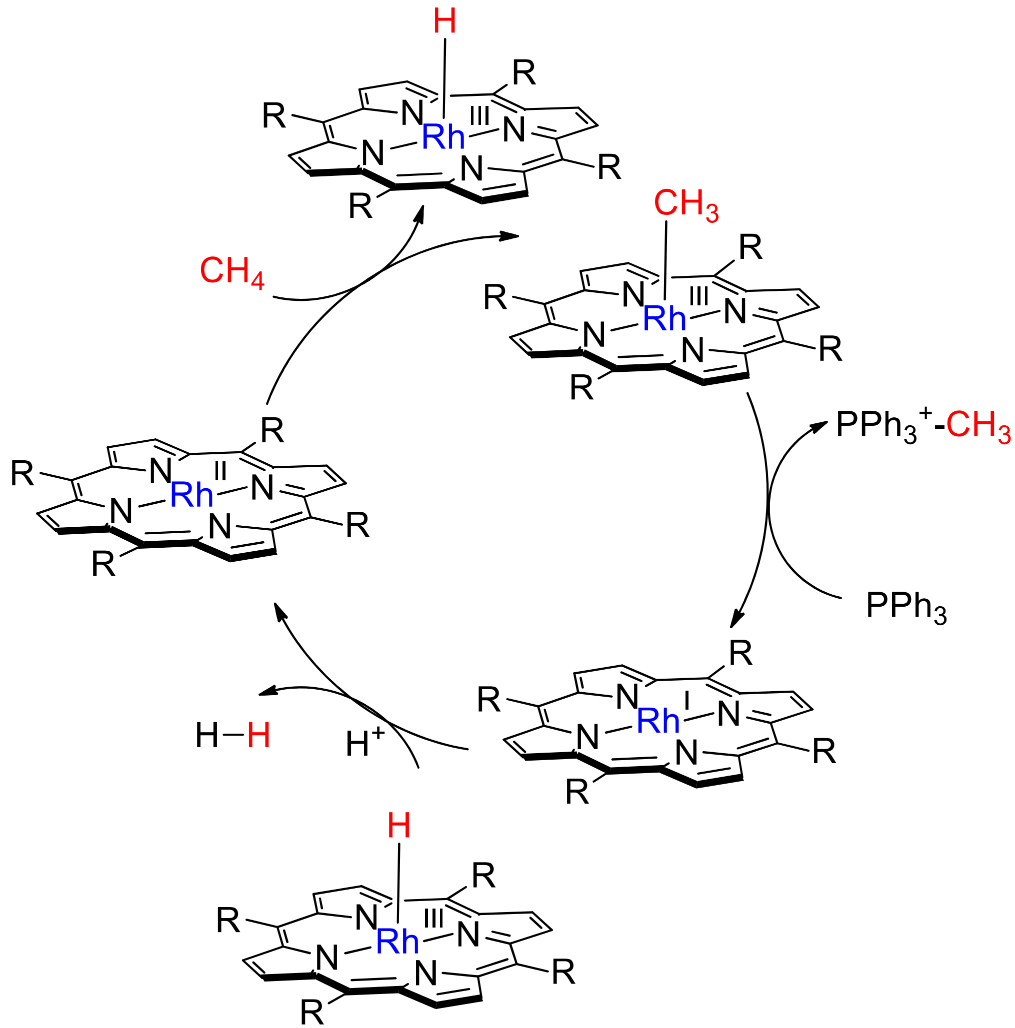

Wayland B. JACS, 1990; DiMagno, S. G. *J. Am. Chem. Soc.* **2000**; Han, Y. Z.; Sanford, M. S.; England, M. D.; Groves, J. T. *Chem. Comm.* **2006**, 549-551; Sanford, M.S.; Groves, J.T. *Angew. Chemie* **2004,** *116*, 598-600.

Several Effective Electrophilic Catalysts Operate by Electrophilic CH Activation

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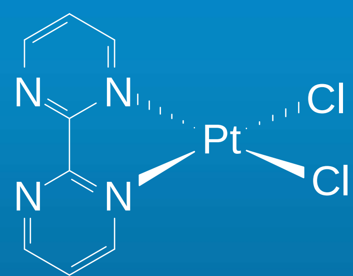
Applicable to flared gas?

Hg(II)/H_2SO_4		I^+/H_2SO_4	Pd(II)/H_2SO_4	Au(III)/H_2SeO_4
Science, 1993	*Science*, 1998	*Chem Commun* 2002	*Science*, 2003	*Angew Chem. E.* 2004

- STY ~ 10^{-7} mol/cc.sec
- ~1M methanol
- Stable
- >90% Selectivity
- ~80% methane conversion
- All catalysts operate by CH Activation

$$CH_4 + H_2SO_4 \xrightarrow[\text{220°C, 2.5 hrs; 150 ml 98\% } H_2SO_4]{\text{Cat}} CH_3OH + H_2O + SO_2$$

500 psig (for CH_4); ~ 1M (for CH_3OH)

Summary and Future Directions

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- Molecular catalysts that operate in solution at lower temperature by CH activation has been shown to be effective and potential practical for conversion of methane to methanol
- High selectivity observed in these systems can be attributed to fast reaction at lower temperatures and reaction without the involvement of free-radicals, and reversible protection
- Issues such as cost, stability, separations, etc. can be addressed through catalyst modifications, changes in solvents, oxidants, etc.
- A key basis for effectiveness of molecular catalysts is that detailed atomistic models can be obtained that together with a wide variety of synthetic tools utilized to "rationally" design improved catalysts.
- An important focus is increasing catalyst rate by ~10^3
- To speed up discovery, the iterative loop of synthesis, characterization, testing and study must be accelerated
- An important strategy to accelerating progress while minimizing risk is to leverage efforts directed at the other small molecules, O_2 ,N_2, CO_2 and H_2O