Catalysis for Methane Conversion:

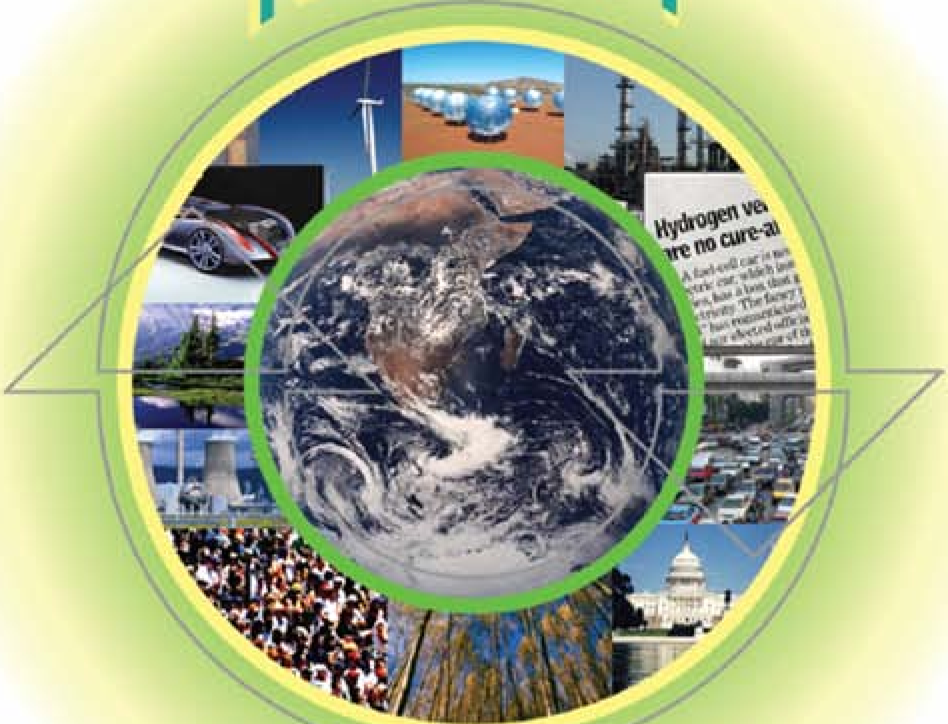
Chemical Processes and Heterogeneous Catalysts

Enrique Iglesia

Department of Chemical Engineering
University of California at Berkeley

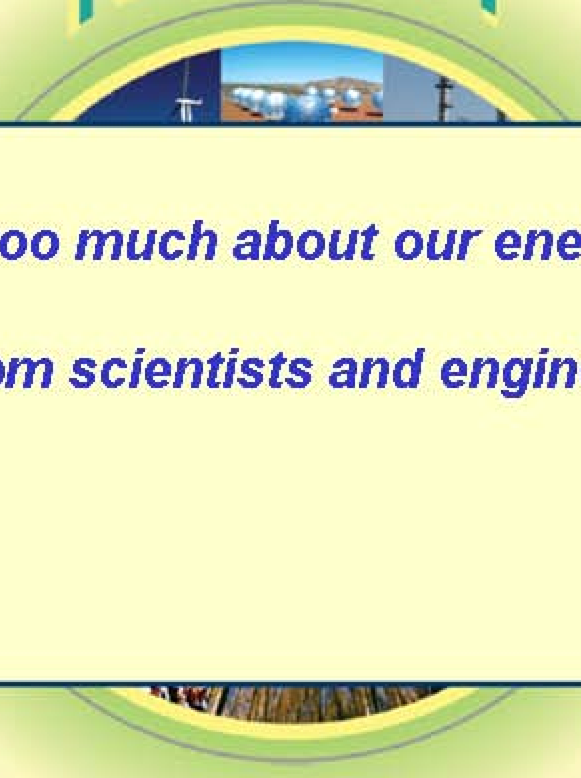
California Institute of Technology
22 February 2008

NRG 0.1



Tired of hearing about our energy future from movie stars, journalists, and politicians?

NRG 0.1



Heard too much about our energy future from scientists and engineers?

Tired of hearing about our energy future from movie stars, journalists, and politicians?

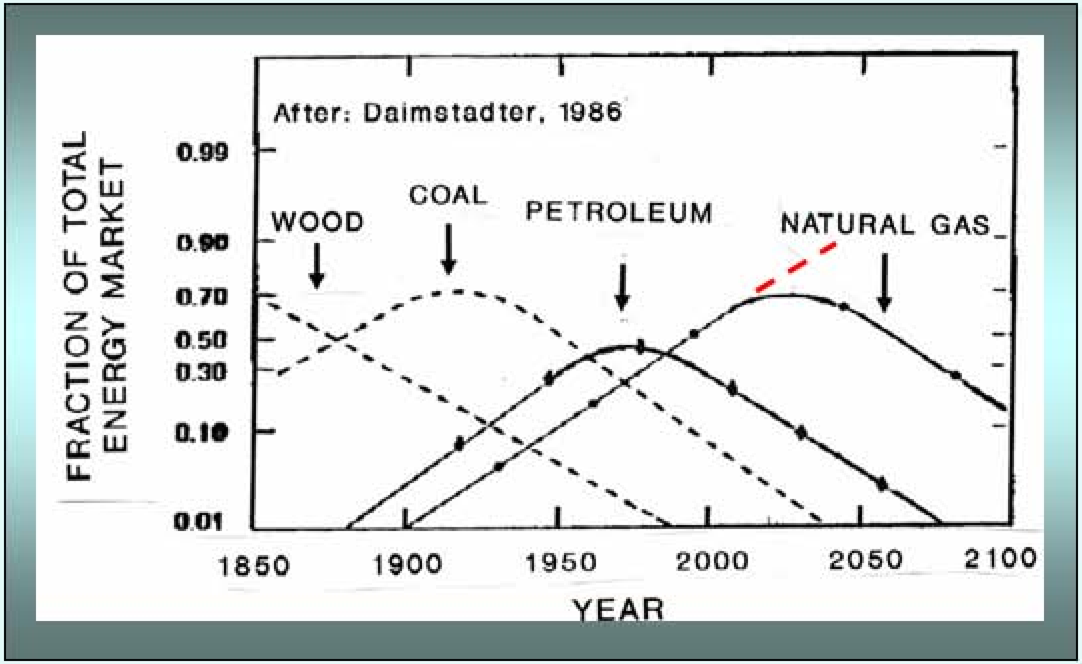
Heard too much about our energy future

from scientists and engineers?

Both?

Sources of Energy through Time

Predictions, projections, and "postjections"



Sources of Energy through Time

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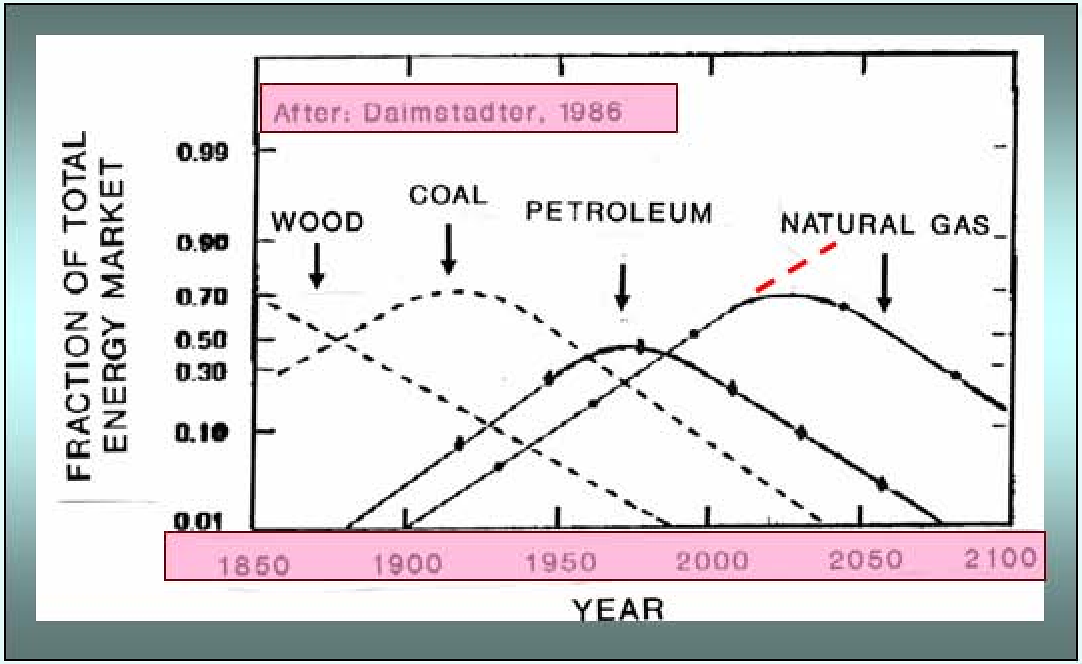
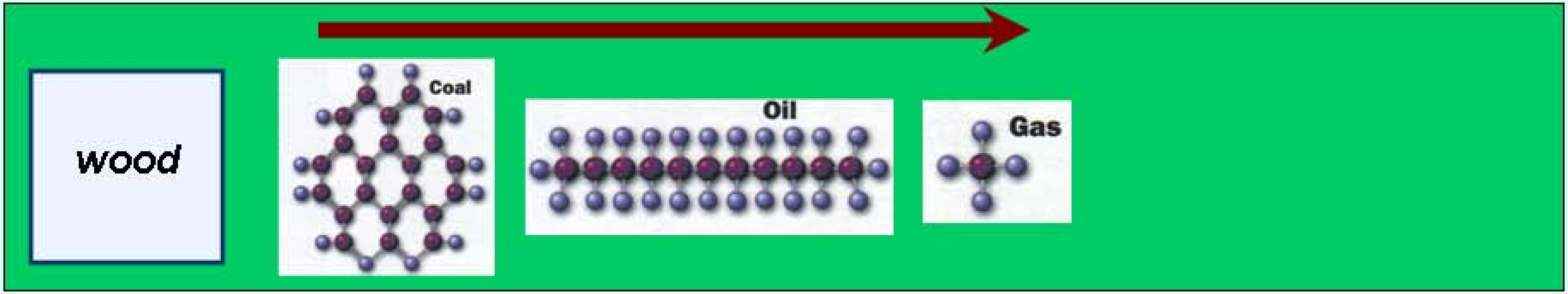
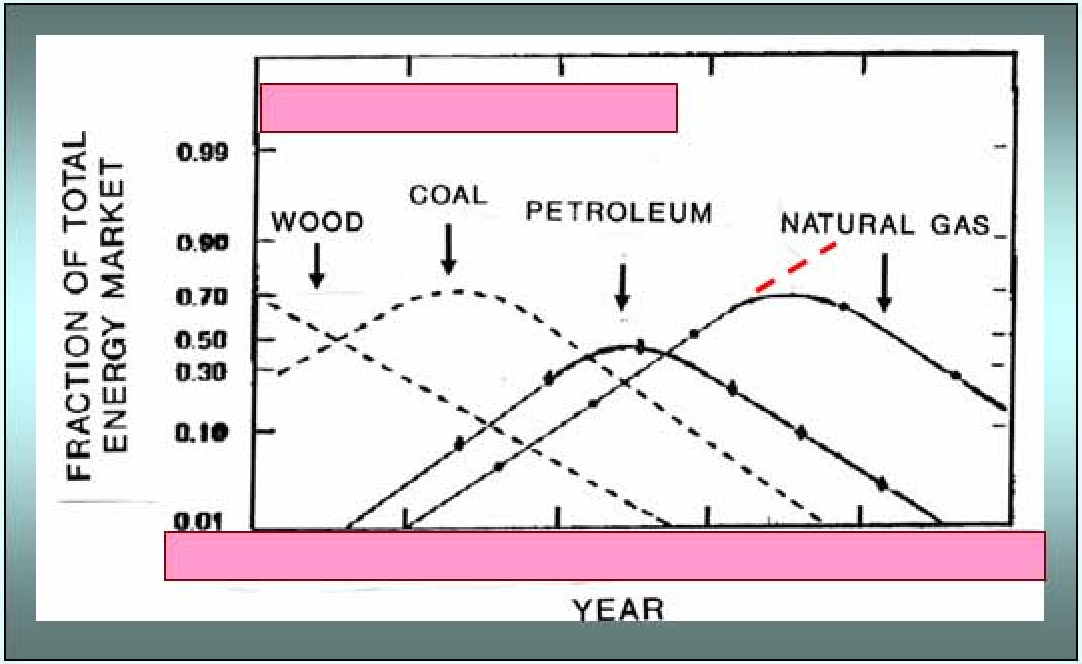


Sources of Energy through Time





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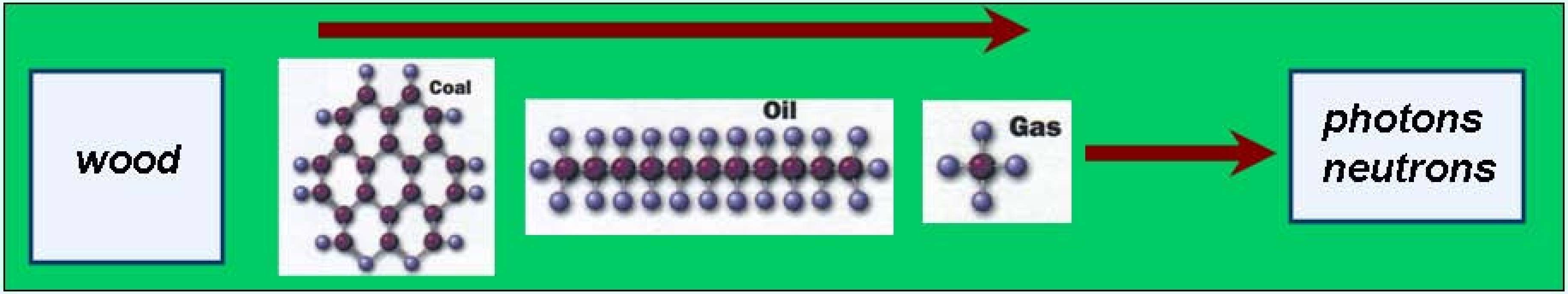
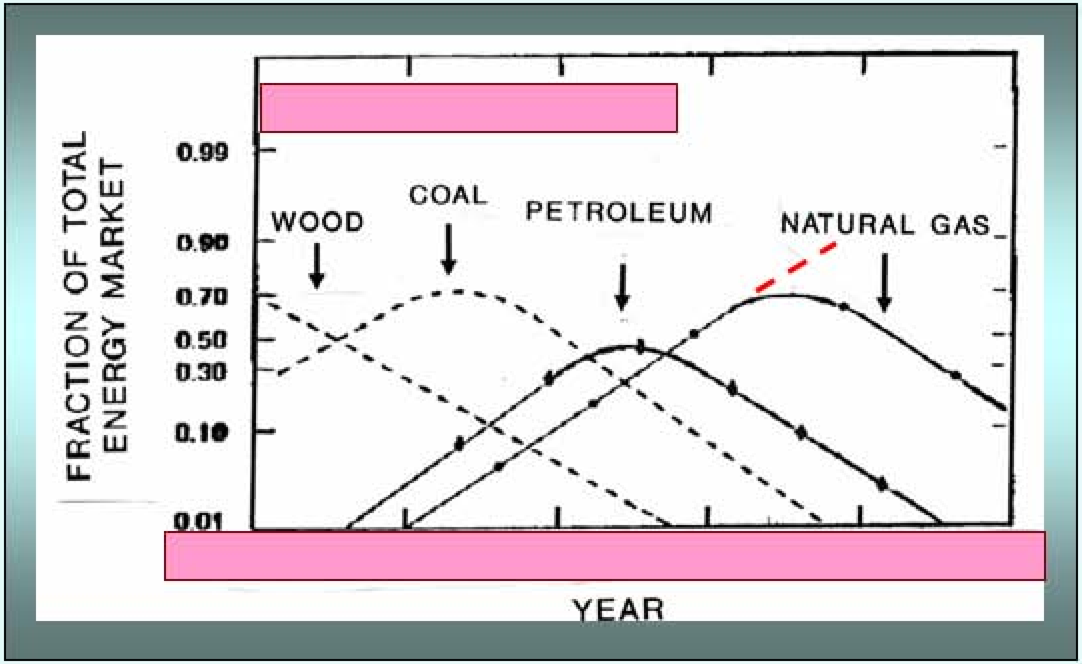


wood

photons
neutrons



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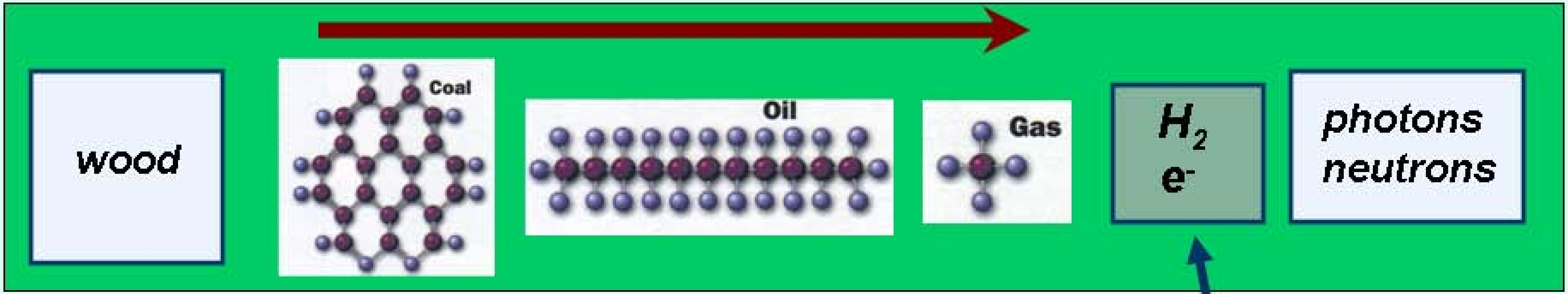
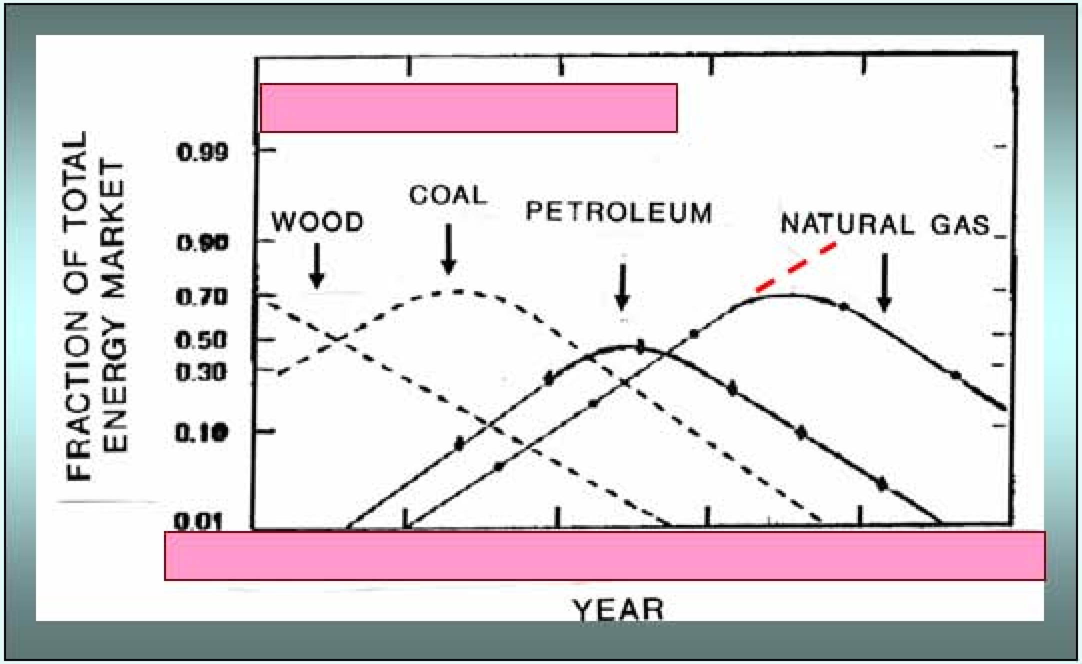
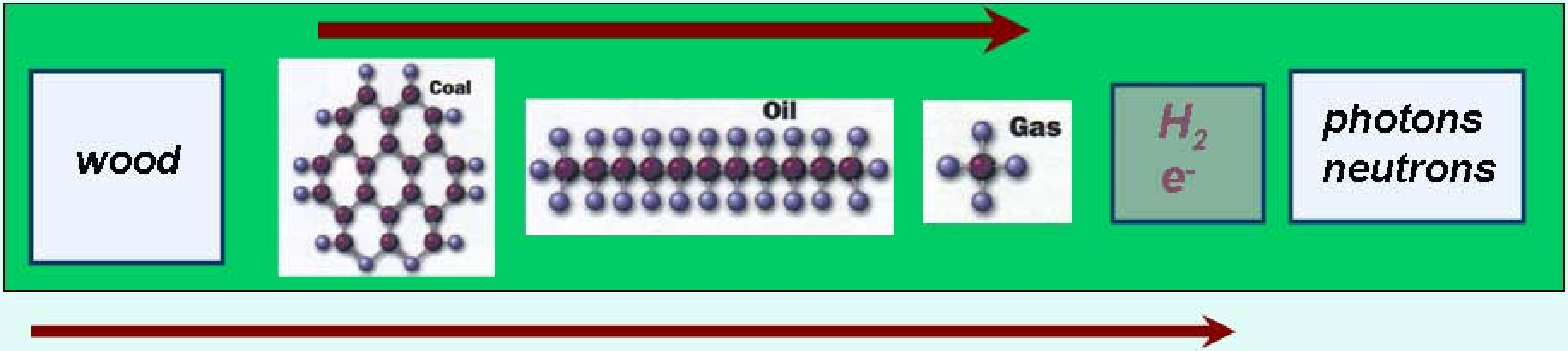




energy carriers

Sources of Energy through Time



wood

Coal

Oil

Gas

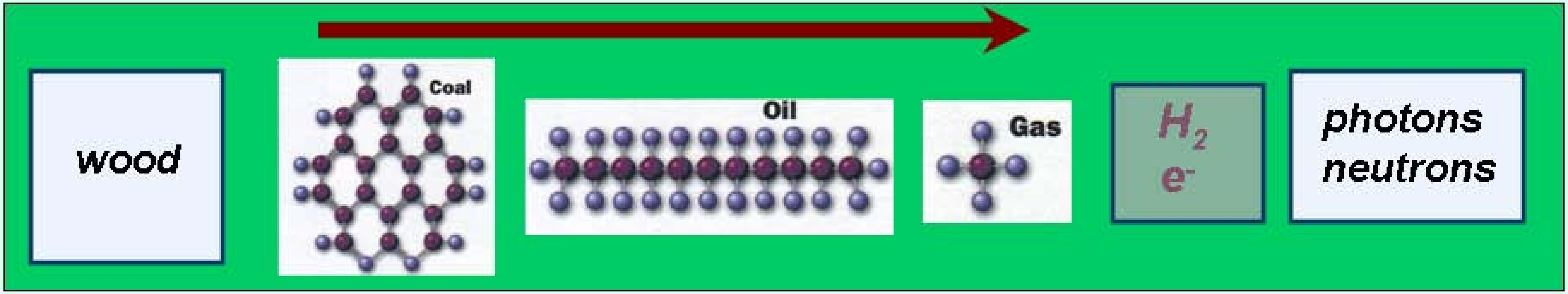
H_2
e^-

photons
neutrons

….. increasing H/C content ….

…. decreasing heteroatom content (O, N, S,…)

Sources of Energy through Time

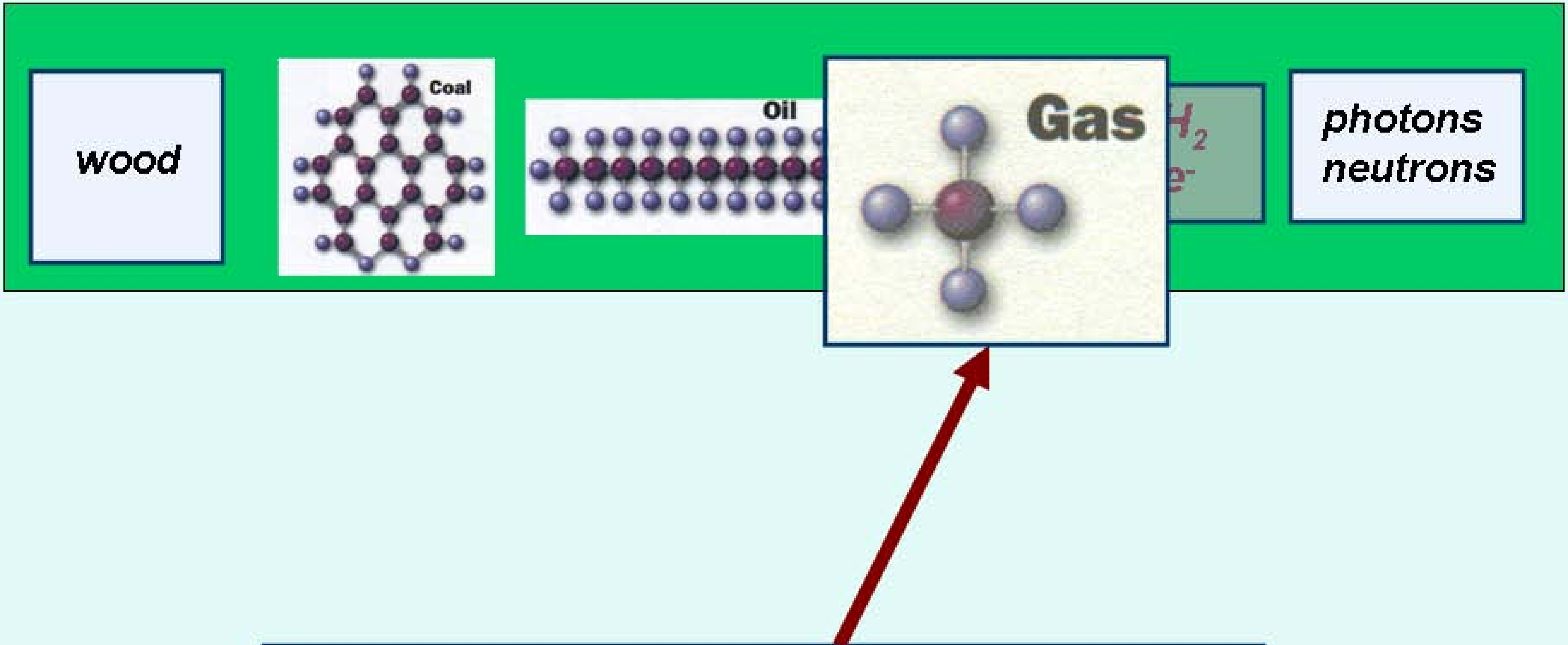


….. increasing H/C content ….

…. decreasing heteroatom content (O, N, S,…)

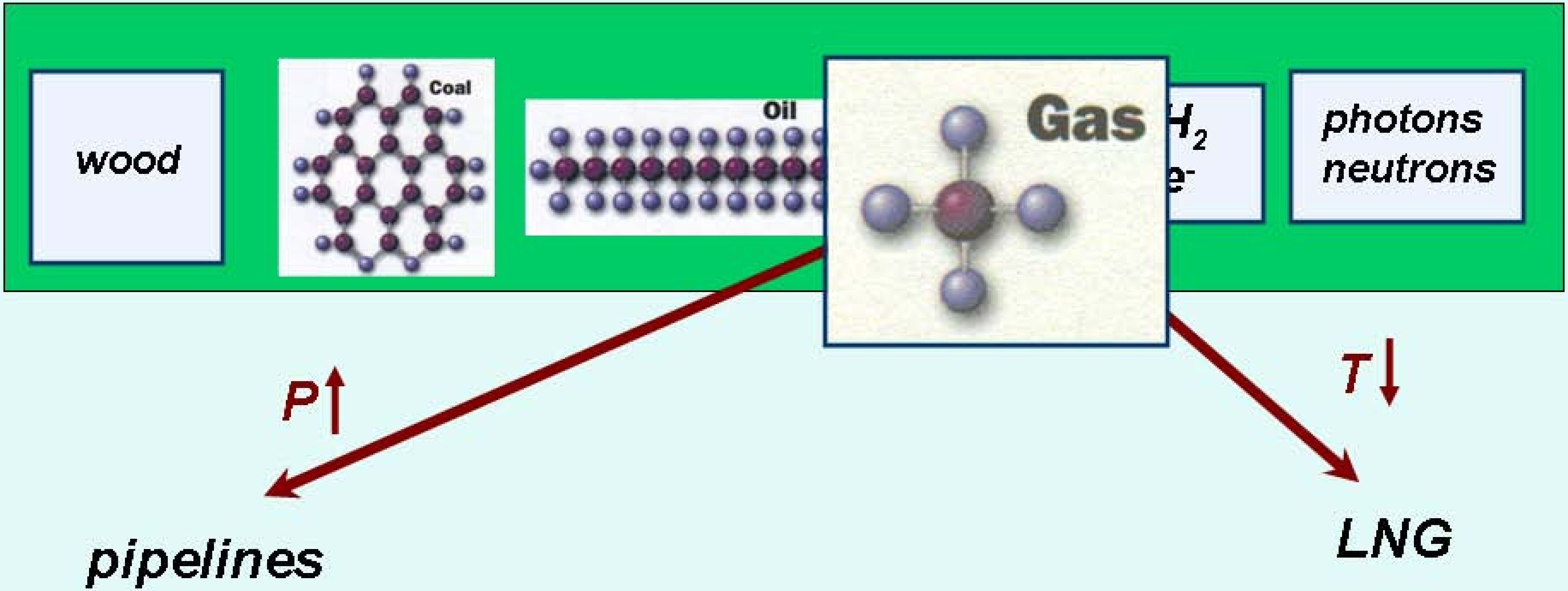
…. less complex molecules ***… no molecules***

Sources of Energy through Time



- ***natural gas is not where it is needed***
- ***it is spread more broadly than oil***
- ***… and it is awkward to transport***

Transporting Natural Gas to Markets



wood

H_2

e^-

photons
neutrons

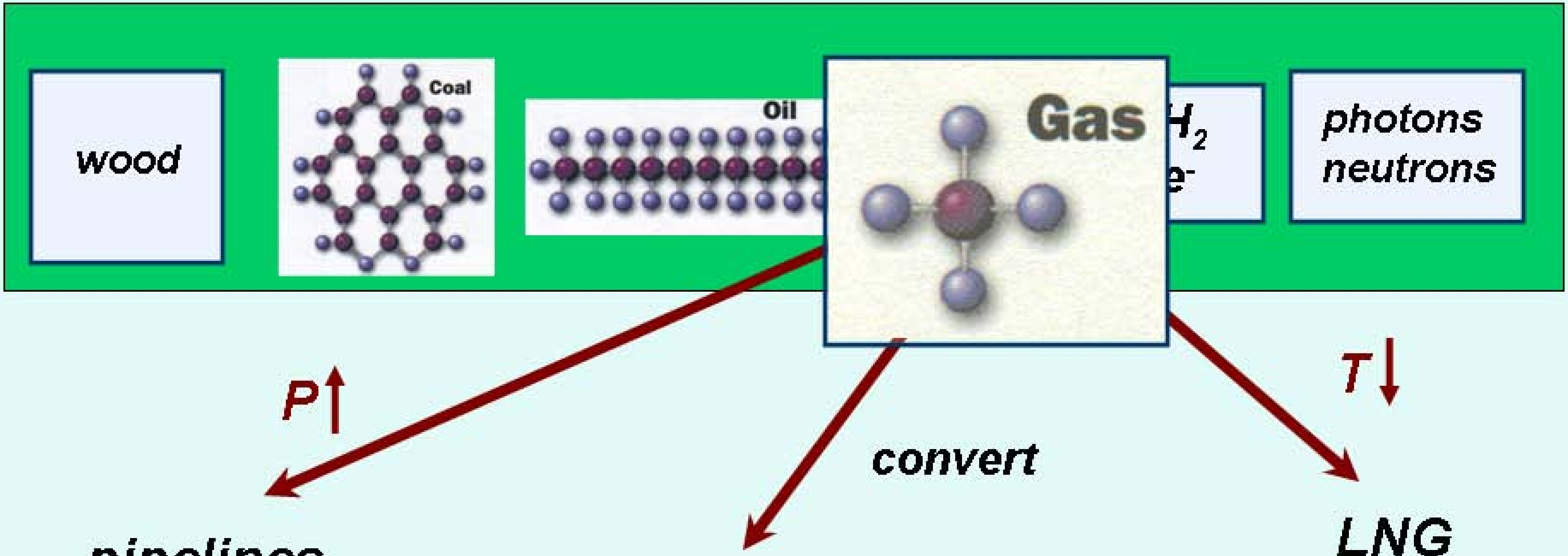
P ↑

T ↓

pipelines

LNG

Transporting Natural Gas to Markets



wood

H_2
e^-

photons
neutrons

P↑

pipelines

convert

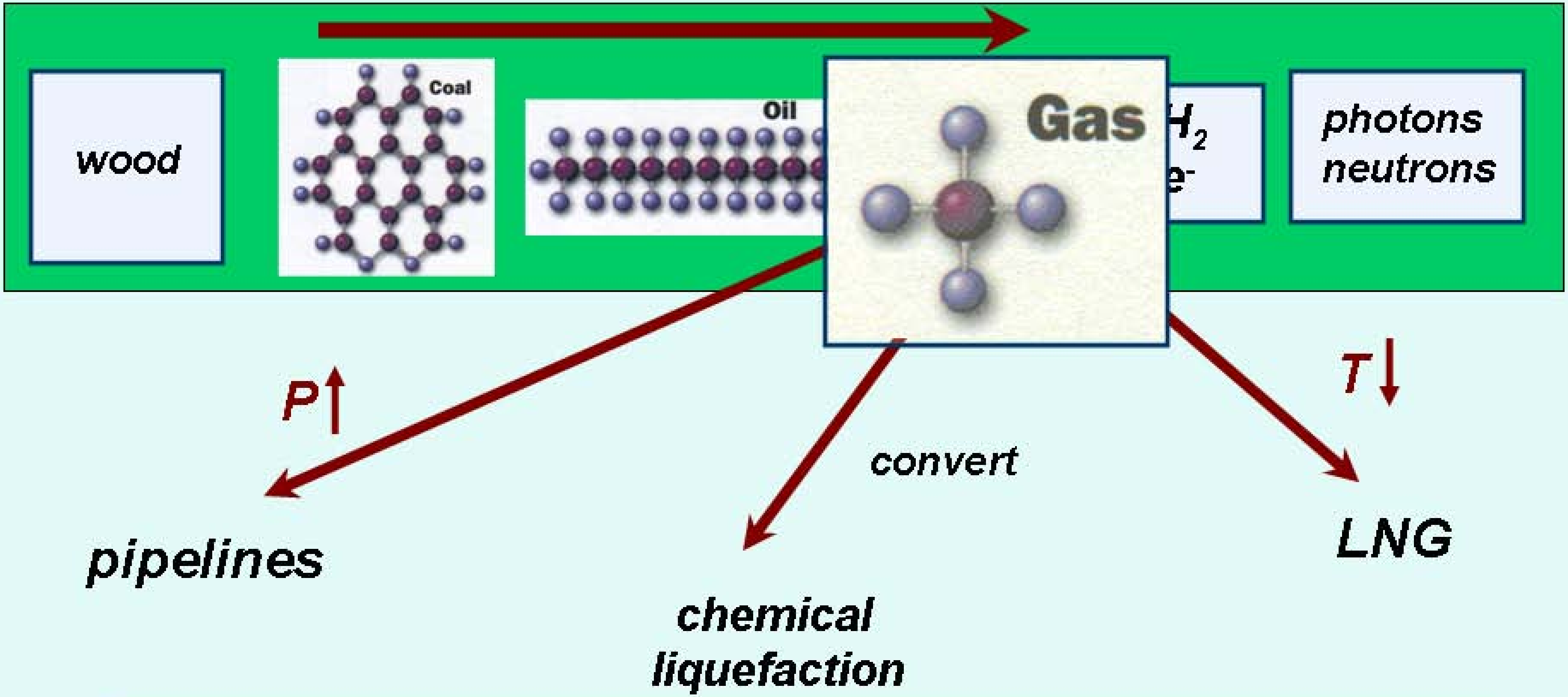
chemical
liquefaction

T↓

LNG

- convert to liquid fuels and large volume petrochemicals
- a remote "methane refinery"

Transporting Natural Gas to Markets



wood

H_2
e^-

photons
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convert

T↓

pipelines

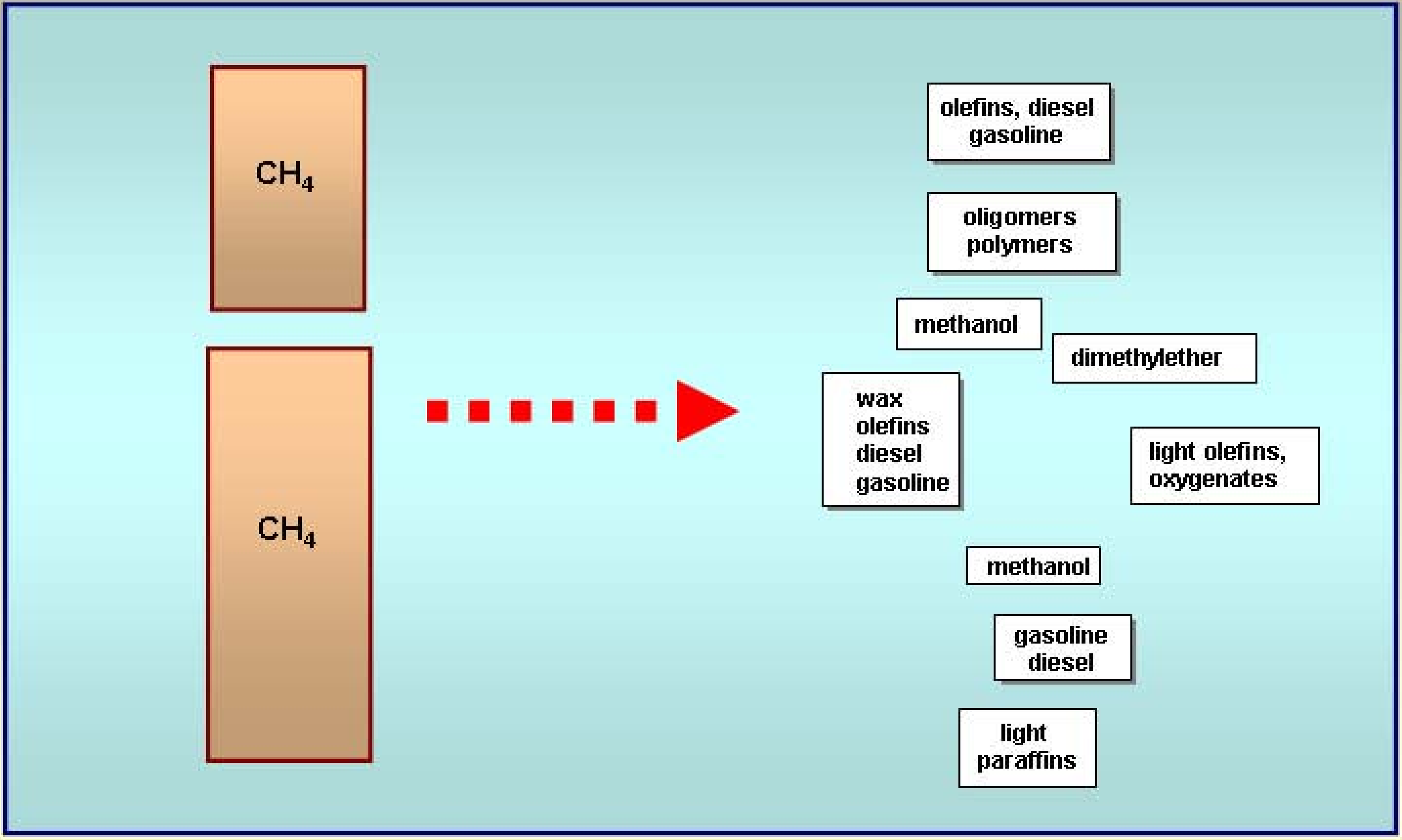
chemical
liquefaction

LNG

$$CH_4 + \tfrac{1}{2} O_2 = -(CH_2)- + H_2O$$

- *CH_4 should be burned … chemical conversion decreases energy content*

Methane Routes to Fuels and Petrochemicals



CH_4

CH_4

olefins, diesel
gasoline

oligomers
polymers

methanol

dimethylether

wax
olefins
diesel
gasoline

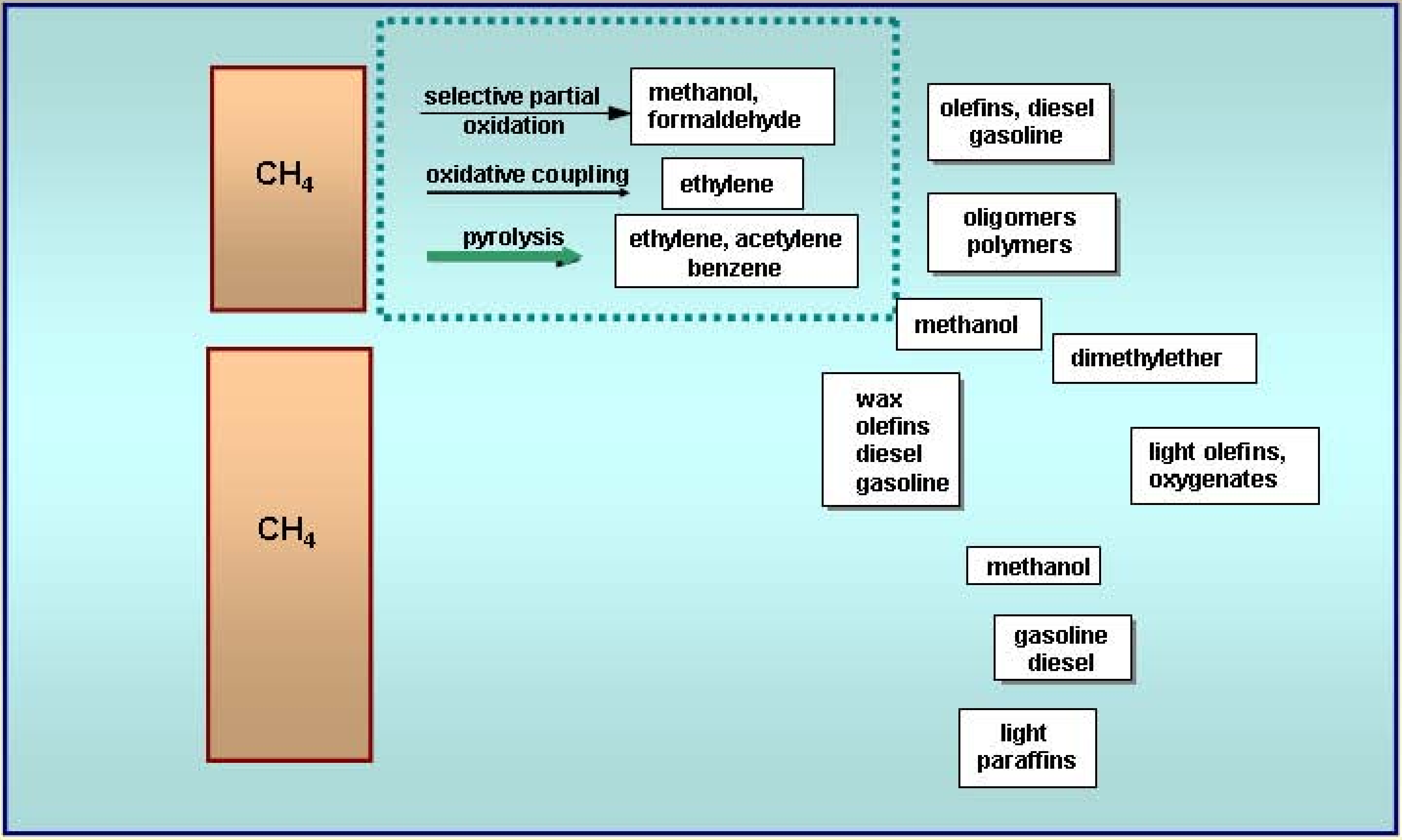
light olefins,
oxygenates

methanol

gasoline
diesel

light
paraffins

Methane Routes to Fuels and Petrochemicals



CH_4

selective partial oxidation → methanol, formaldehyde

oxidative coupling → ethylene

pyrolysis → ethylene, acetylene benzene

olefins, diesel gasoline

oligomers polymers

methanol

dimethylether

wax
olefins
diesel
gasoline

light olefins, oxygenates

CH_4

methanol

gasoline diesel

light paraffins

direct routes
a few products

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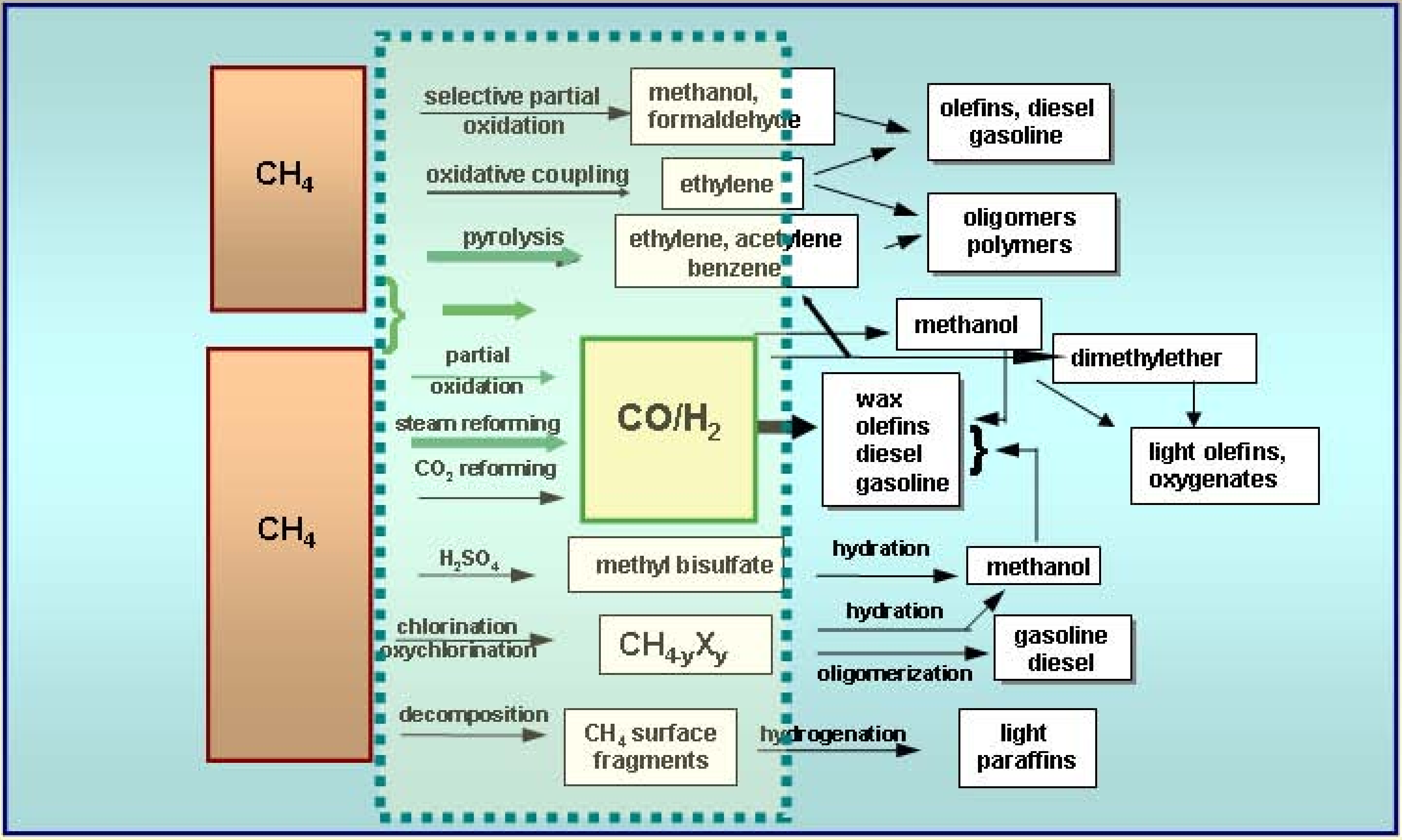

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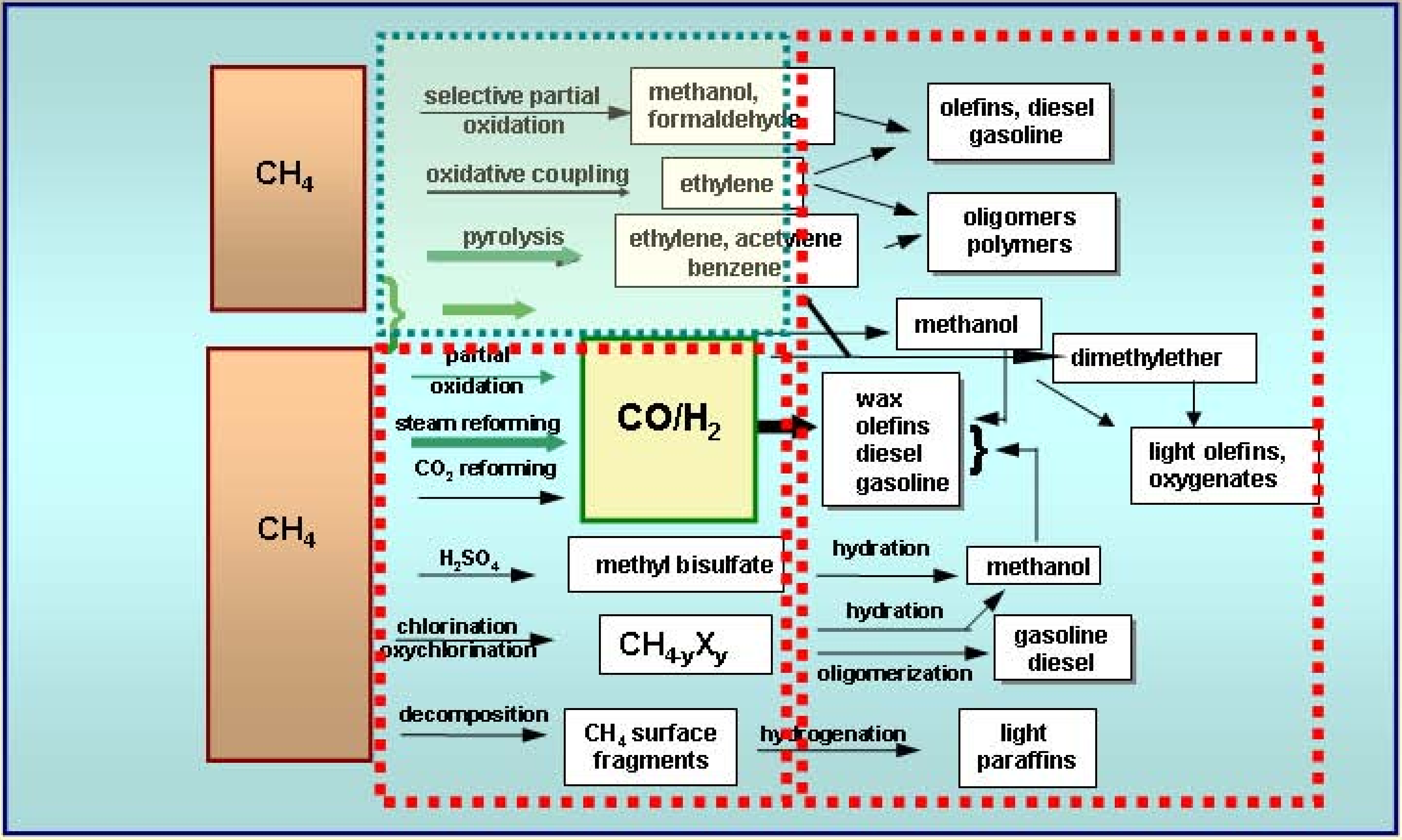


CH_4

selective partial oxidation

methanol, formaldehyde

oxidative coupling

ethylene

pyrolysis

ethylene, acetylene benzene

olefins, diesel gasoline

oligomers polymers

methanol

dimethylether

light olefins, oxygenates

CH_4

partial oxidation

steam reforming

CO_2 reforming

CO/H_2

wax olefins diesel gasoline

H_2SO_4

methyl bisulfate

hydration

methanol

chlorination oxychlorination

$CH_{4-y}X_y$

hydration

oligomerization

gasoline diesel

decomposition

CH_4 surface fragments

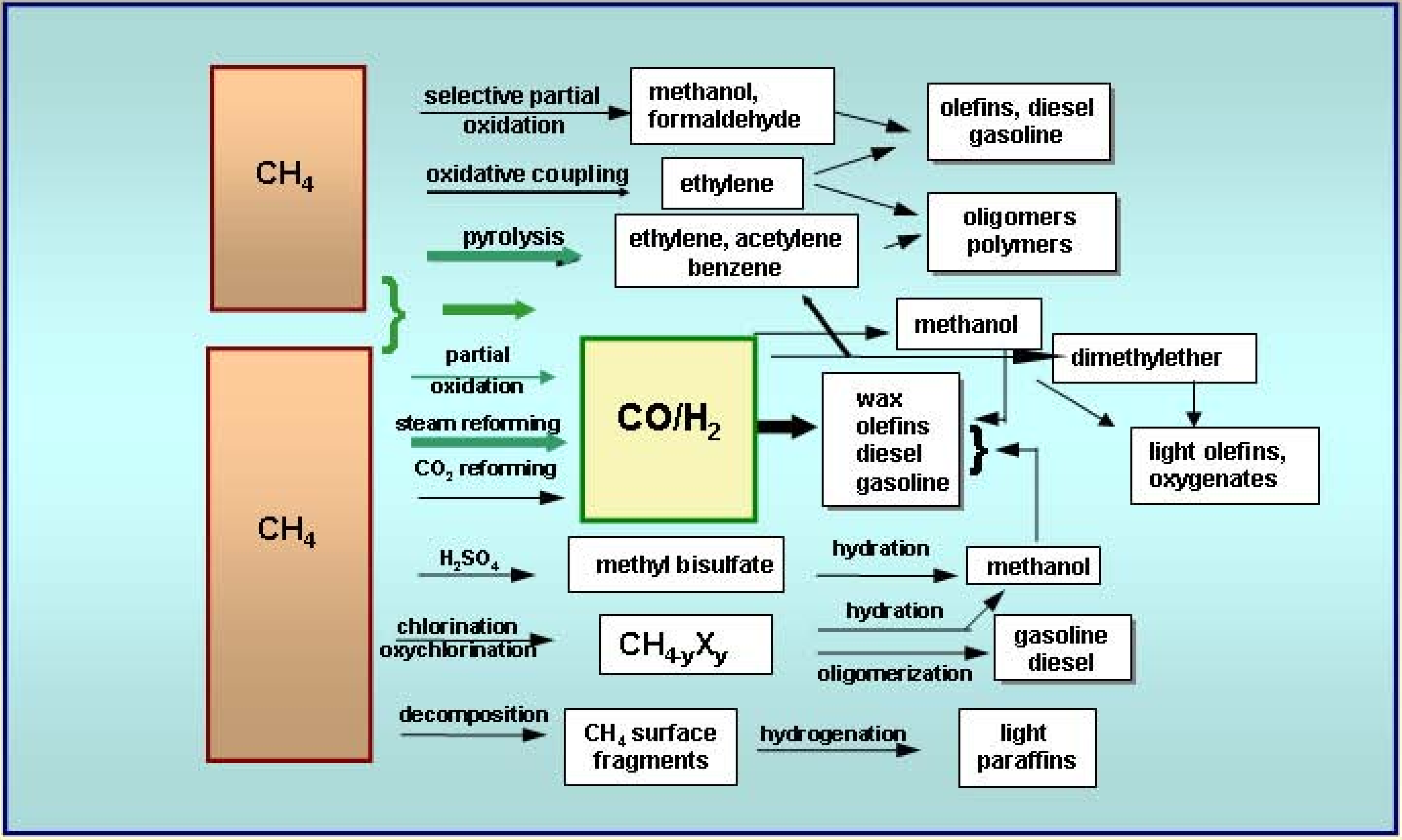
hydrogenation

light paraffins

direct routes
a few products

sequential conversion
to other products

Methane Routes to Fuels and Petrochemicals



CH_4

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methanol, formaldehyde

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ethylene, acetylene benzene

methanol

dimethylether

CH_4

partial oxidation

steam reforming

CO_2 reforming

CO/H_2

wax olefins diesel gasoline

light olefins, oxygenates

H_2SO_4

methyl bisulfate

hydration

methanol

chlorination oxychlorination

$CH_{4-y}X_y$

hydration

oligomerization

gasoline diesel

decomposition

CH_4 surface fragments

hydrogenation

light paraffins

A Methane Refinery

Strategies for chemical conversion of natural gas

- *theoretical efficiency set by products not by route*

(diesel) $CH_4 + \frac{1}{2} O_2 = \text{-}(CH_2)\text{-} + H_2O \quad \Delta H_R = -175\ \text{kJ/mol}\ CH_4$

(gasoline) $CH_4 + \frac{3}{4} O_2 = \text{-}(CH)\text{-} + 1.5\ H_2O \quad \Delta H_R = -275\ \text{kJ/mol}\ CH_4$

…. unless H_2 or power can be exported

Strategies for chemical conversion of natural gas

Products		Theoretical Efficiency (%)	
CH_3OH		88	
$-(CH_2)-$		78	
$-(CH_{1.5})-$		75	

Strategies for chemical conversion of natural gas

Products		Theoretical Efficiency (%)	Actual Efficiency (%)
CH_3OH		88	72
$-(CH_2)-$		78	~ 63
$-(CH_{1.5})-$		75	~ 58

- economics and actual efficiency set by “complexity” and capital costs

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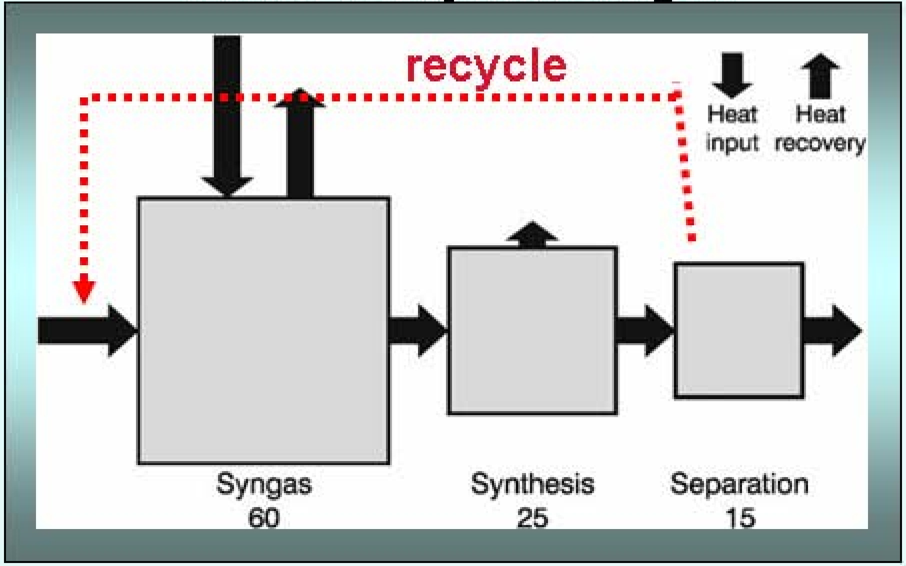
Diesel via synthesis gas



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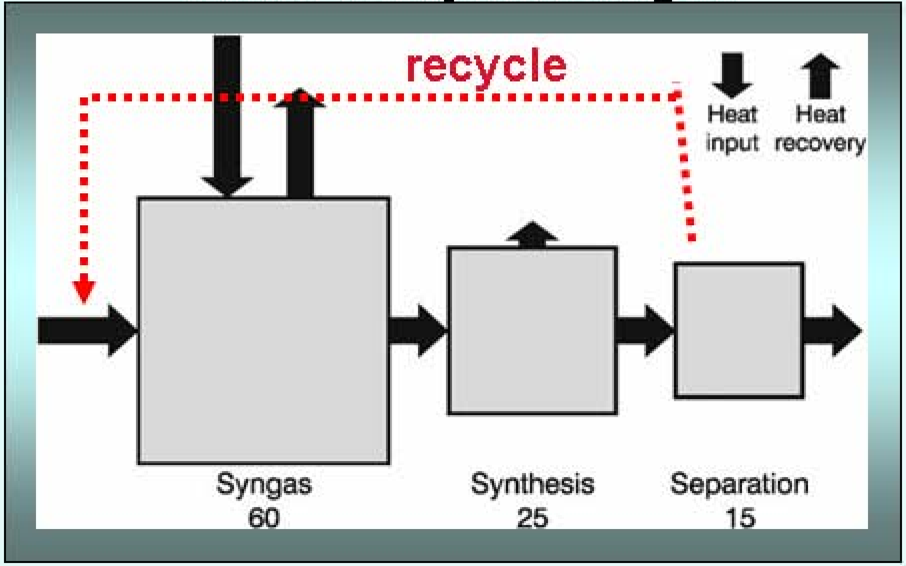

- *pressure cycles*
- *temperature cycles*
- *yield per pass*

Strategies for chemical conversion of natural gas

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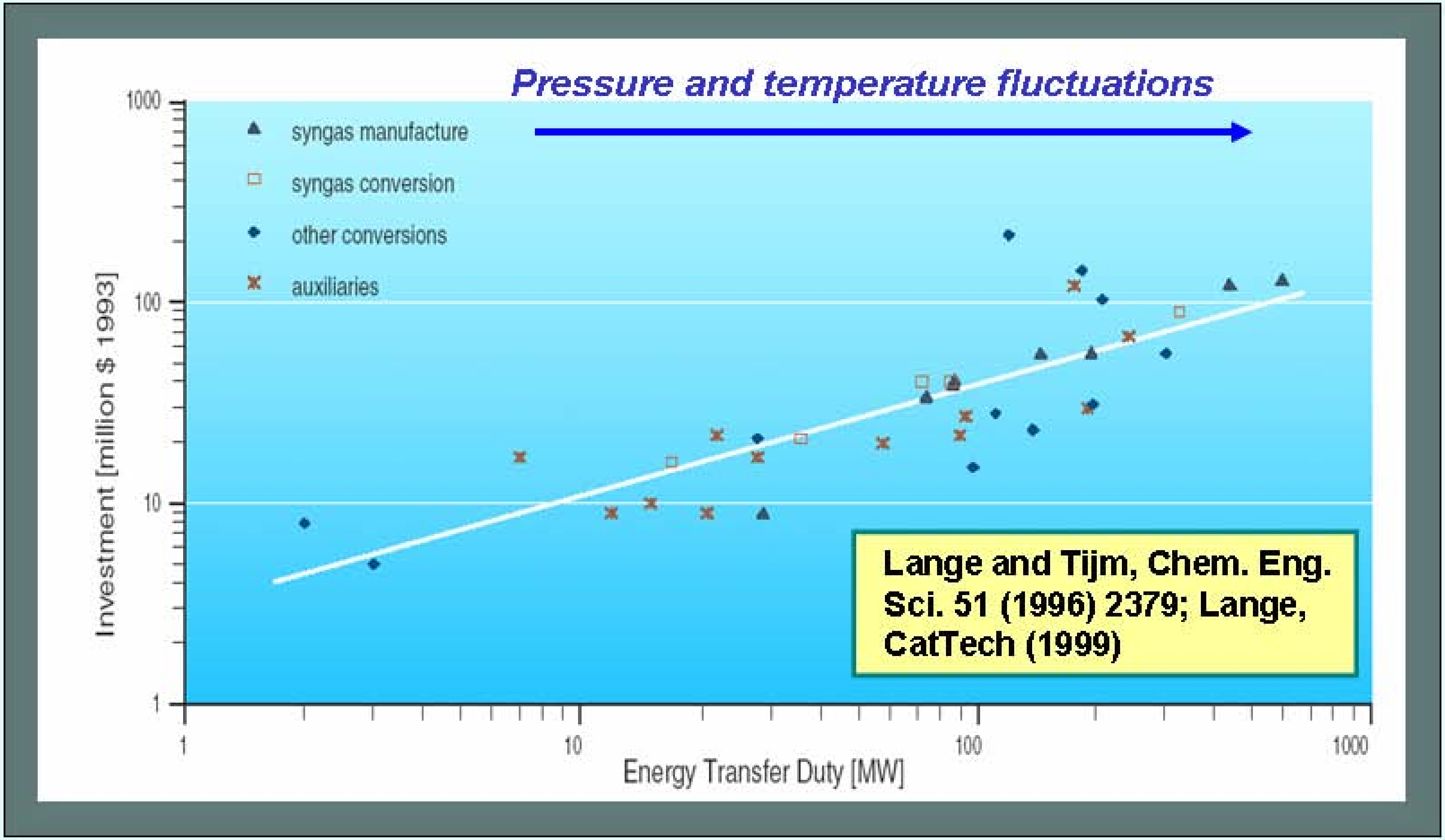

Lange and Tijm, Chem. Eng. Sci. 51 (1996) 2379; Lange, CatTech (1999)

Strategies for chemical conversion of natural gas

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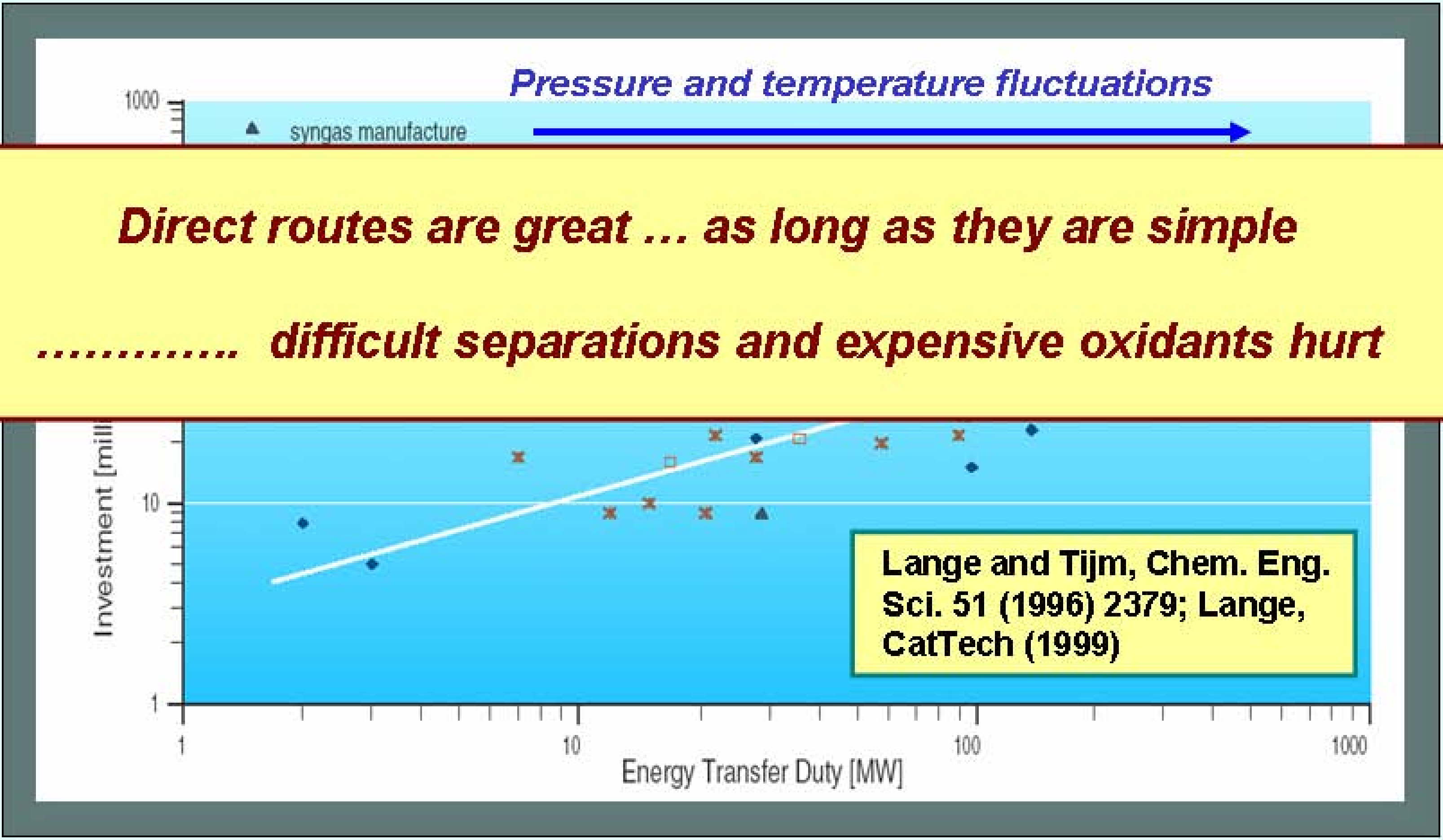

Direct routes are great … as long as they are simple

…………. difficult separations and expensive oxidants hurt

Lange and Tijm, Chem. Eng. Sci. 51 (1996) 2379; Lange, CatTech (1999)

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \longrightarrow -(CH_x)- \longrightarrow (C,$$

- *overcome thermodynamic constraints*

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} -(CH_x)- \longrightarrow (C, CO_x)$$

- overcome thermodynamic constraints
- protect products with weaker C-H bonds

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- *overcome thermodynamic constraints*
- *protect products with weaker C-H bonds*

Indirect Routes

$$\begin{tikzcd} CH_4 \arrow[r, "X"] & I_1 \arrow[r] & I_2 \arrow[r] & -(CH_x)- \\ & (H_2/CO,\ CH_3OH,\ ..) \arrow[u] \arrow[ur] & & \end{tikzcd}$$

- *couple endothermic-exothermic steps*
- *form the first carbon-carbon bond*

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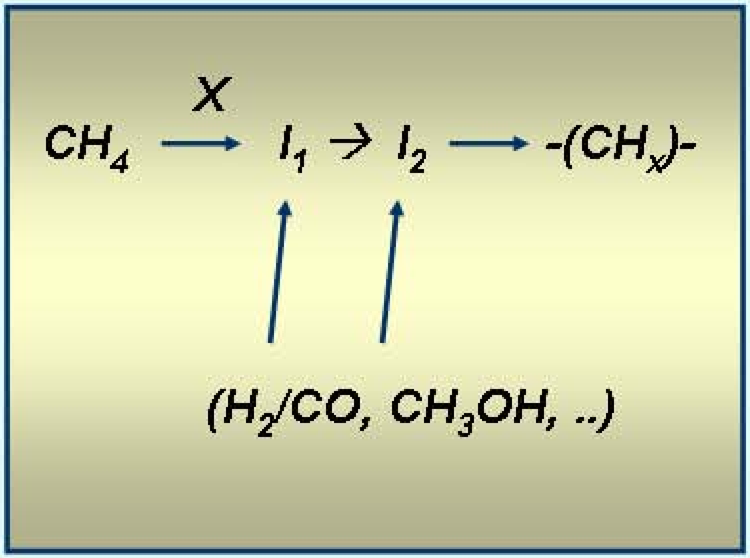
Indirect Routes



$$CH_4 \xrightarrow{X} I_1 \rightarrow I_2 \longrightarrow \text{-}(CH_x)\text{-}$$

$(H_2/CO,\ CH_3OH,\ ..)$

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- form the first carbon-carbon bond

- avoid process complexity
- provide routes to products with large markets

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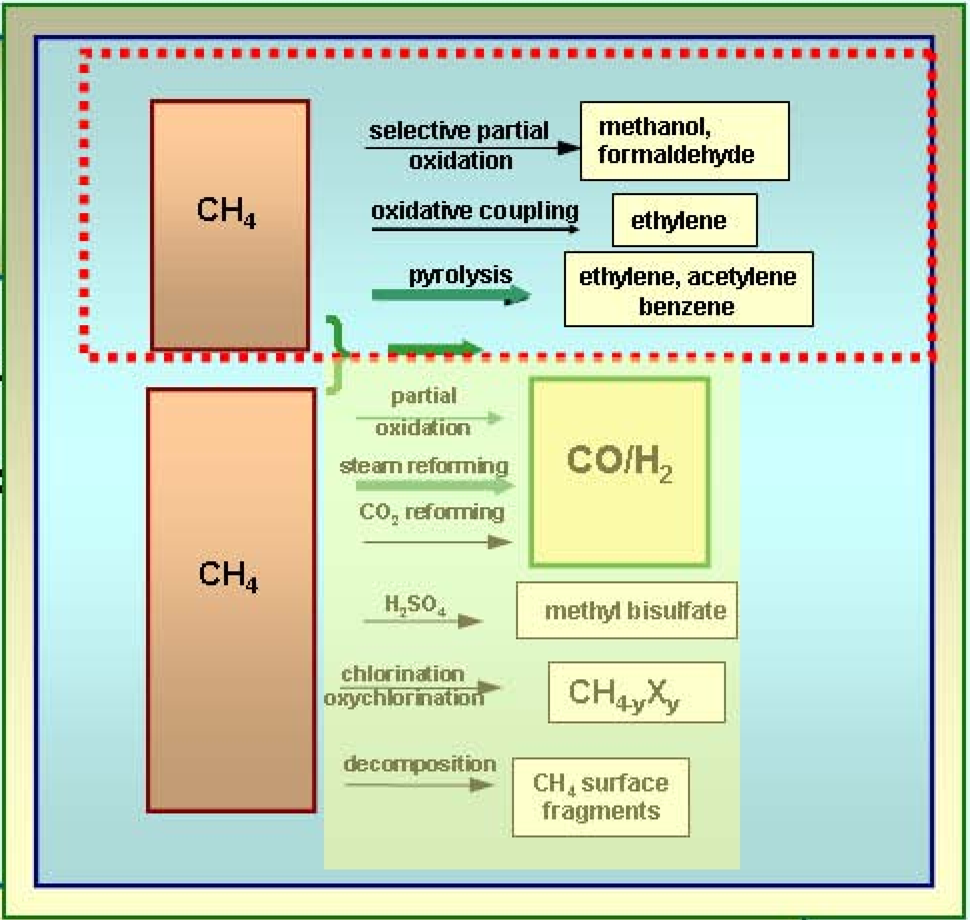
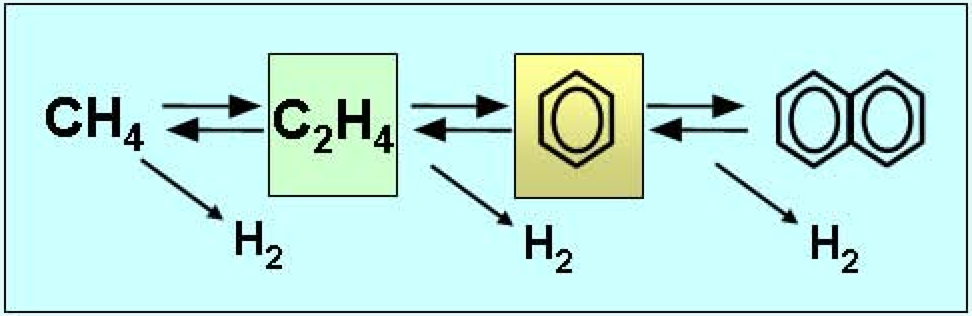


- ***avoid process complexity***
- ***provide routes to products with large markets***

Non-Oxidative Conversion of CH_4 to Larger Hydrocarbons

Non-Oxidative Conversion
(Pyrolysis)



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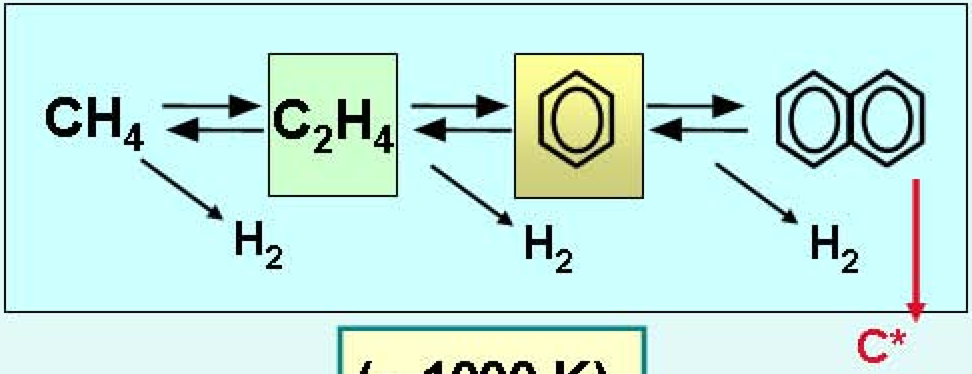
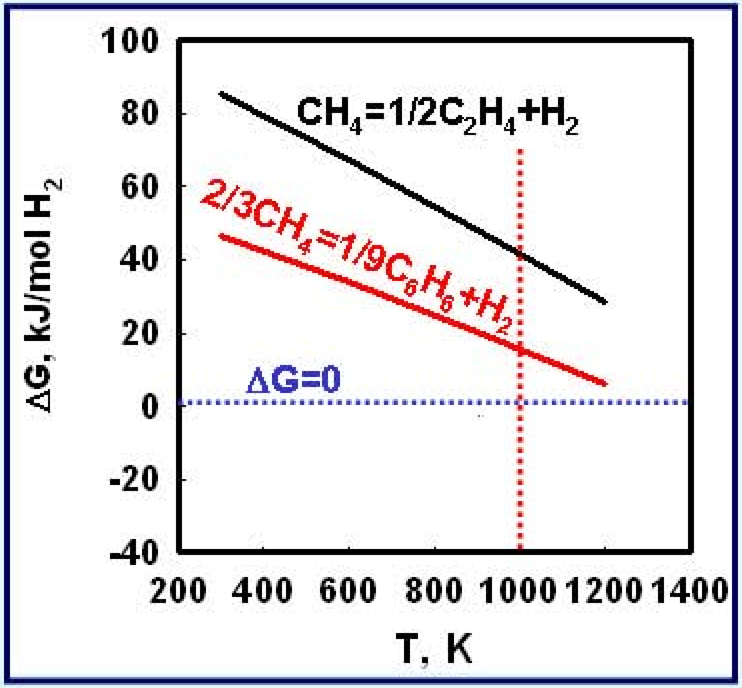


(~ 1000 K)



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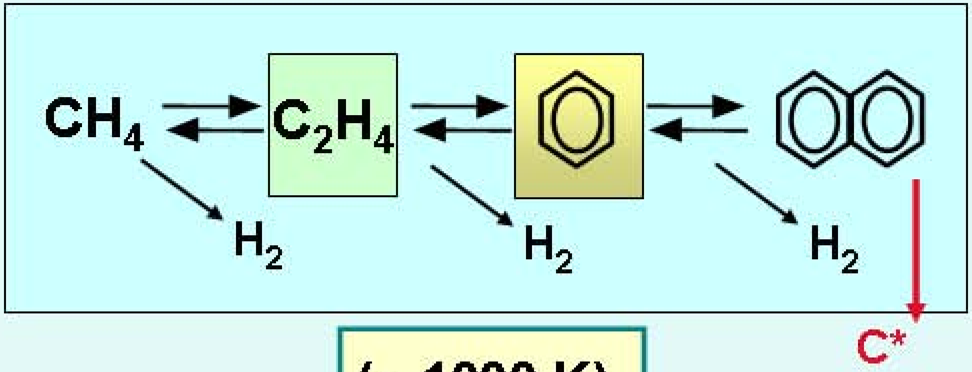

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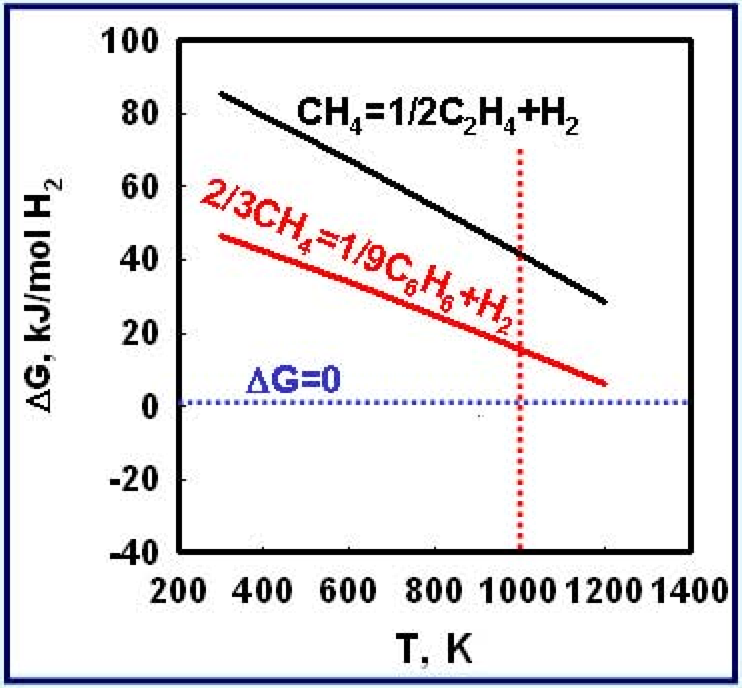
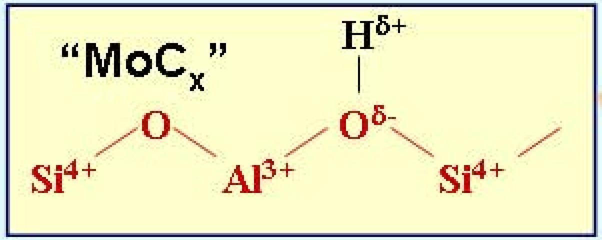
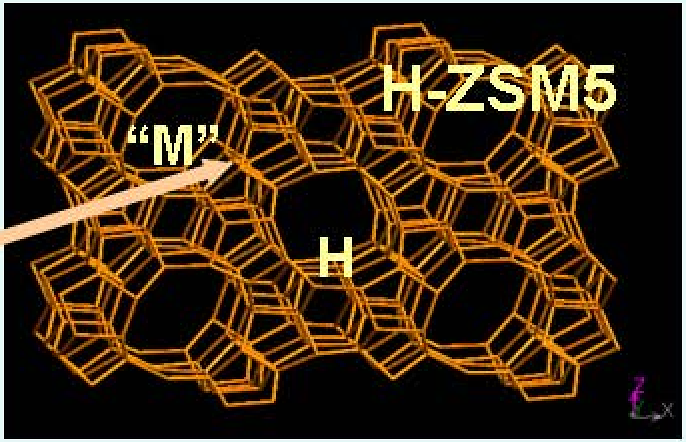


Encapsulated Re and Mo clusters (active sites within constrained microporous environments)





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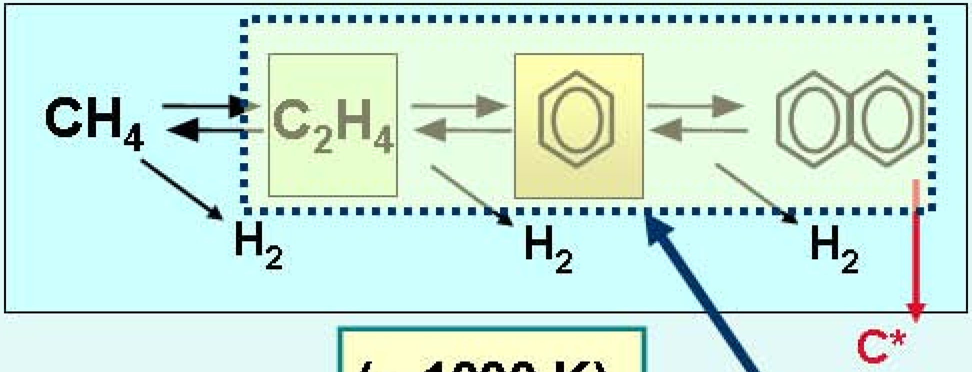

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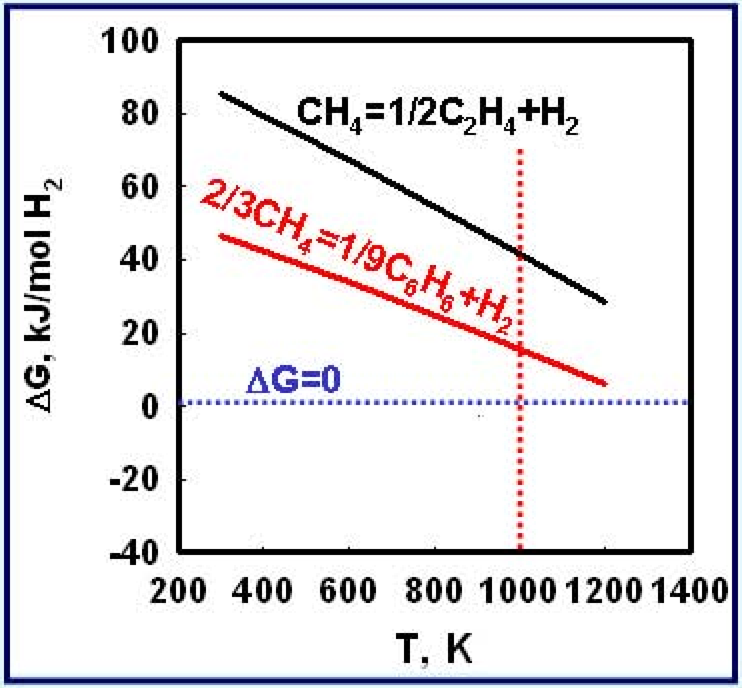
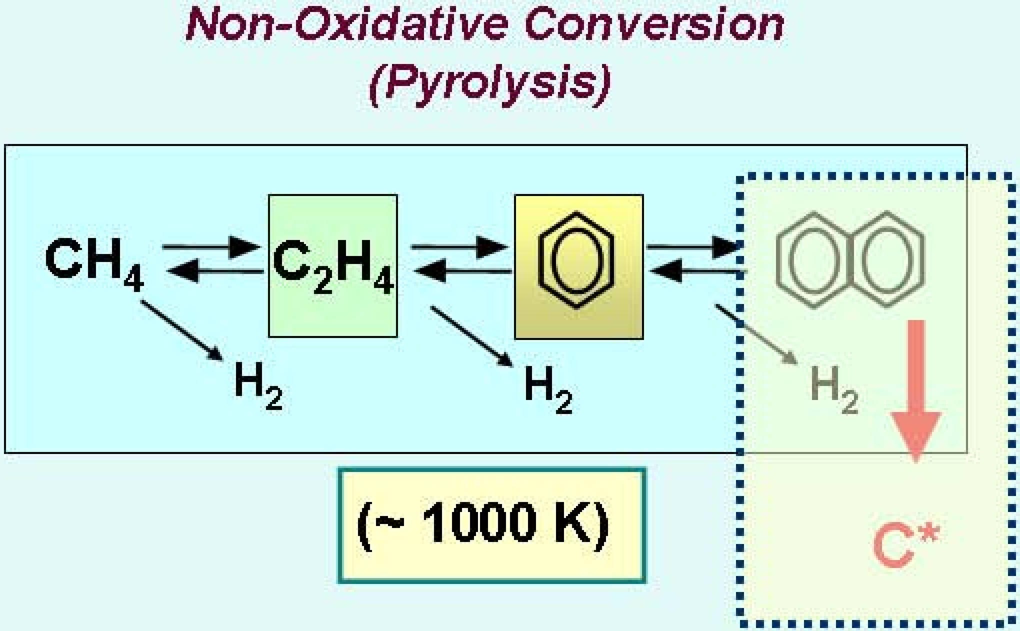
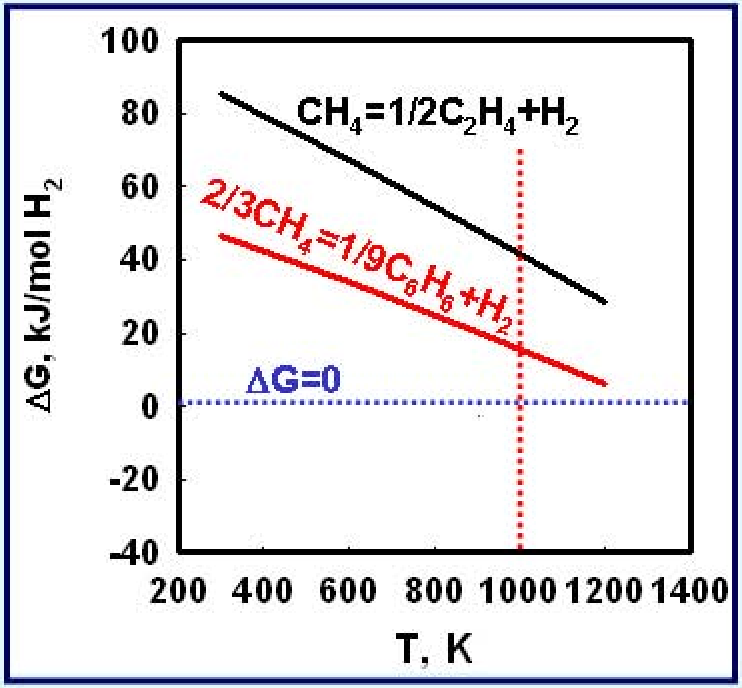


	CH_4 conversion (%)	Selectivity (carbon basis %)				C_2-C_{10} Yield (%)
		C_2H_4	Benzene	Napth	C_{11+}	
Mo/H-ZSM5	10.1	3	67	20	10	9.1

Non-Oxidative Conversion of CH_4 to Larger Hydrocarbons





- ***<u>deactivation and carbon</u>: controlled addition of CO_2 (or H_2)***
  … kinetic coupling between CH_x formation and removal

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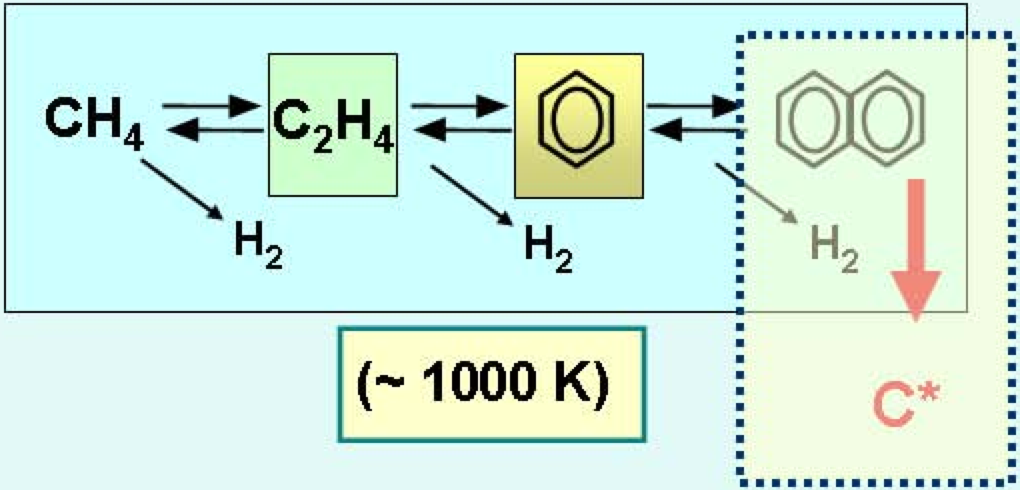
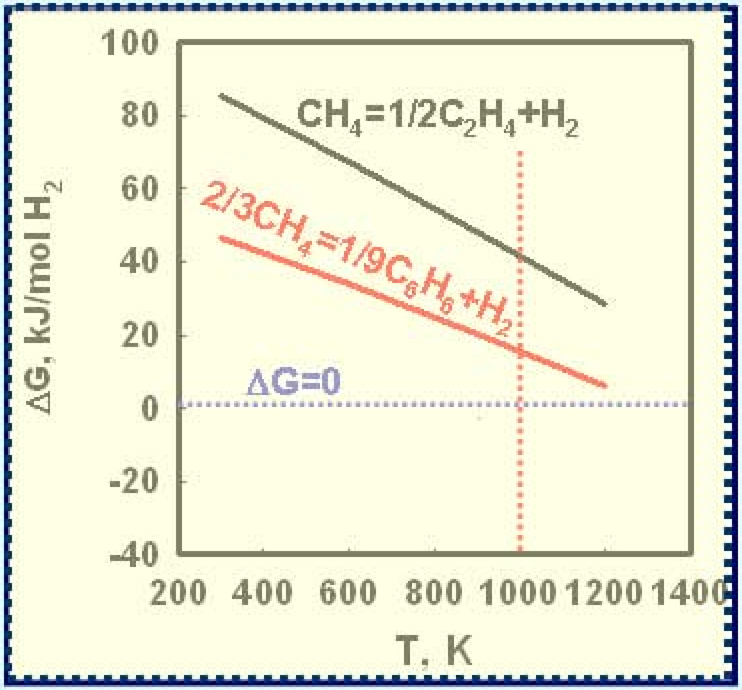


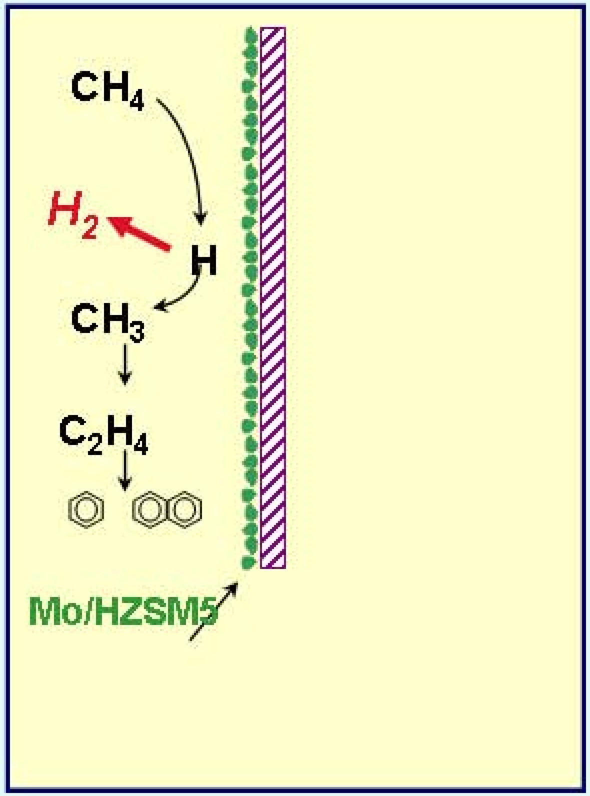


- ***deactivation and carbon**: controlled addition of CO_2 (or H_2)*
  … kinetic coupling between CH_x formation and removal

- ***thermodynamics**: remove H_2 as it forms*

CH_4 Pyrolysis with Continuous H_2 Removal

~ 1000 K



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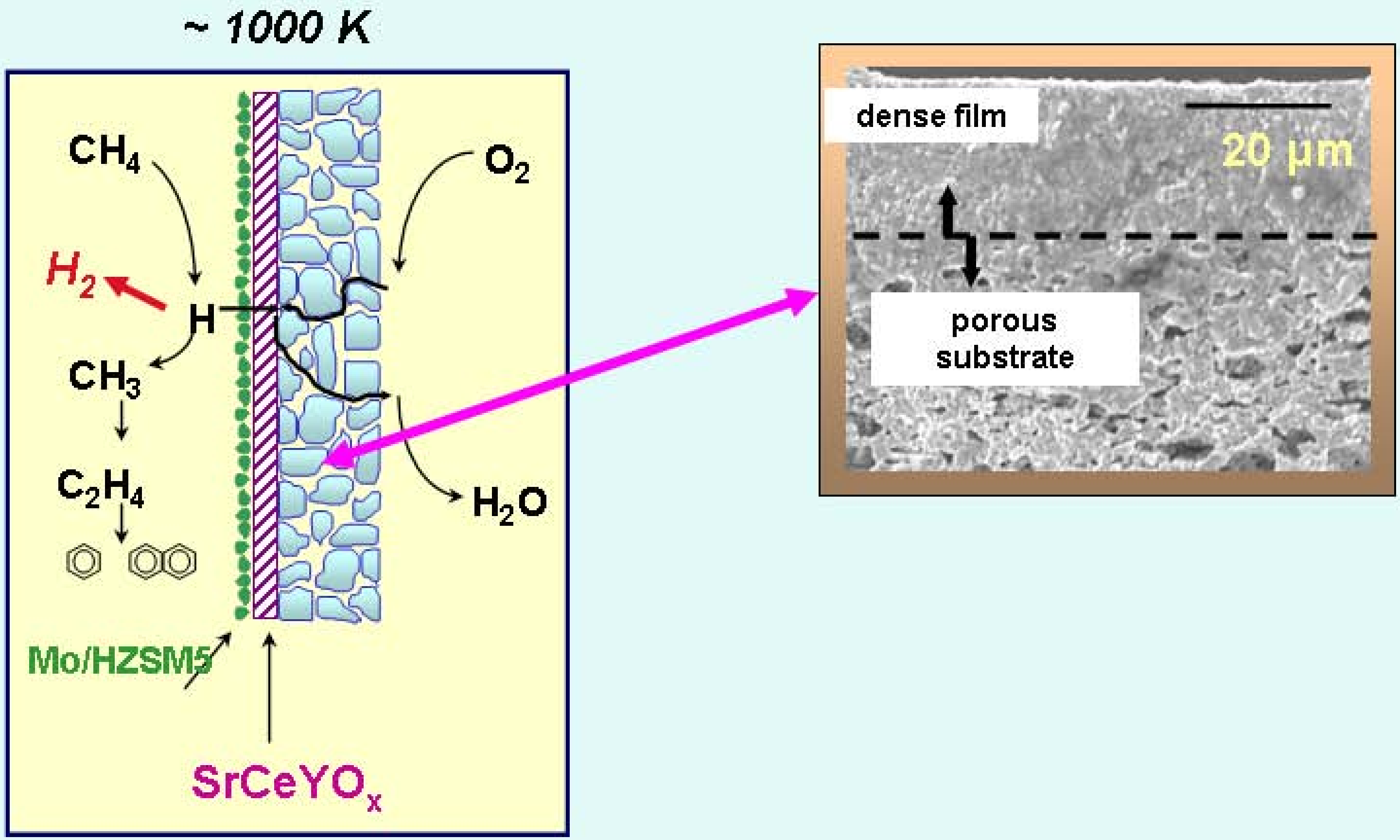

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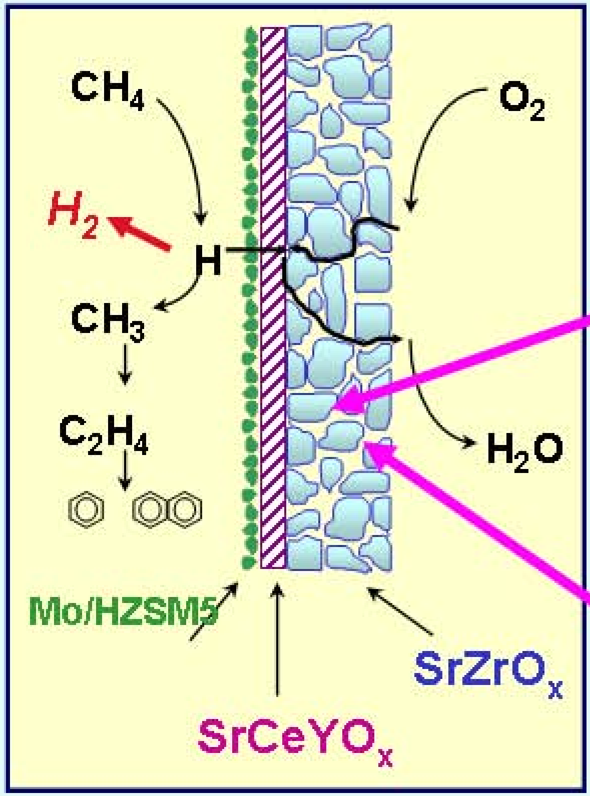
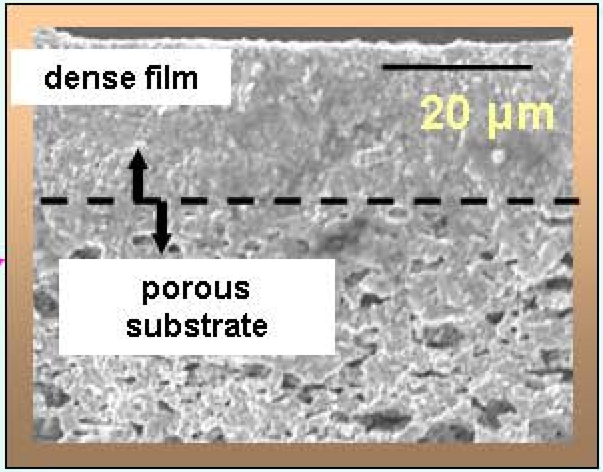
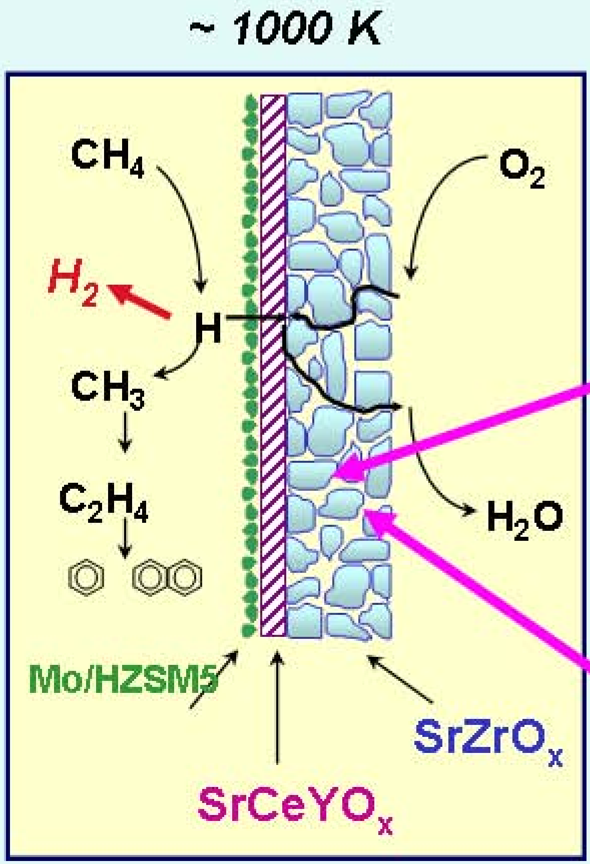
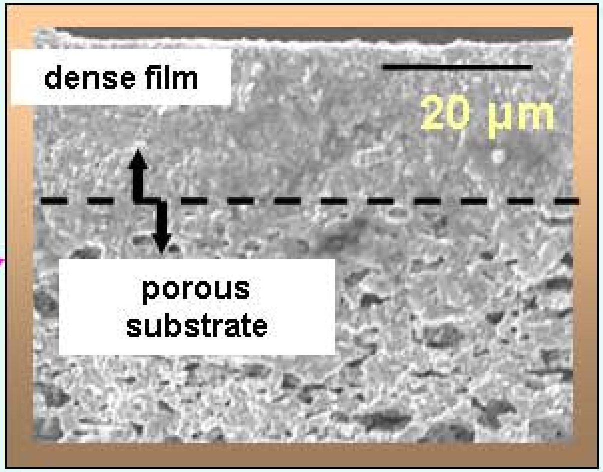


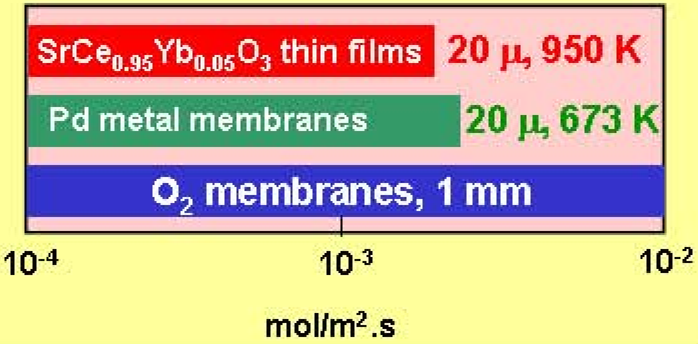


Permeability

CH_4 Pyrolysis with Continuous H_2 Removal





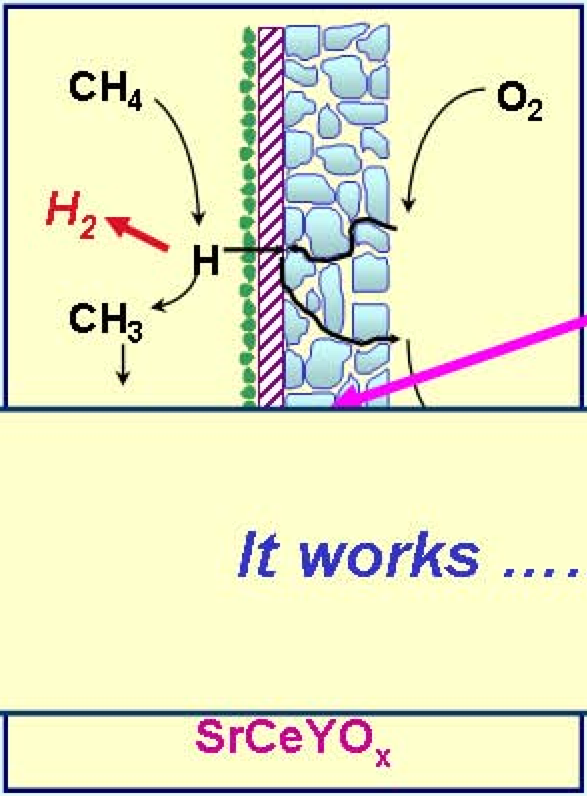


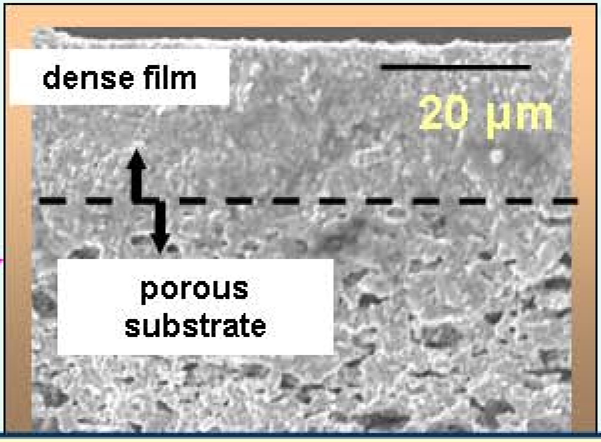
modest improvements in C_2-C_{10} yields (8% → 14%)
… limited by low driving force for H_2 permeation

Catal. Lett. 82, 175 (2002); Chem. Eng. Sci. 57, 4595 (2002)

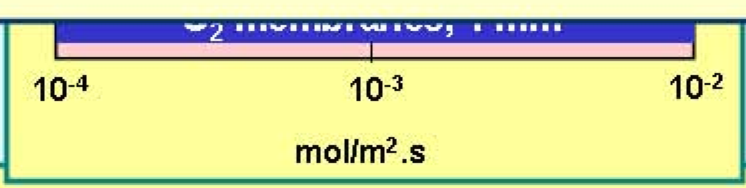
CH_4 Pyrolysis with Continuous H_2 Removal

~ 1000 K





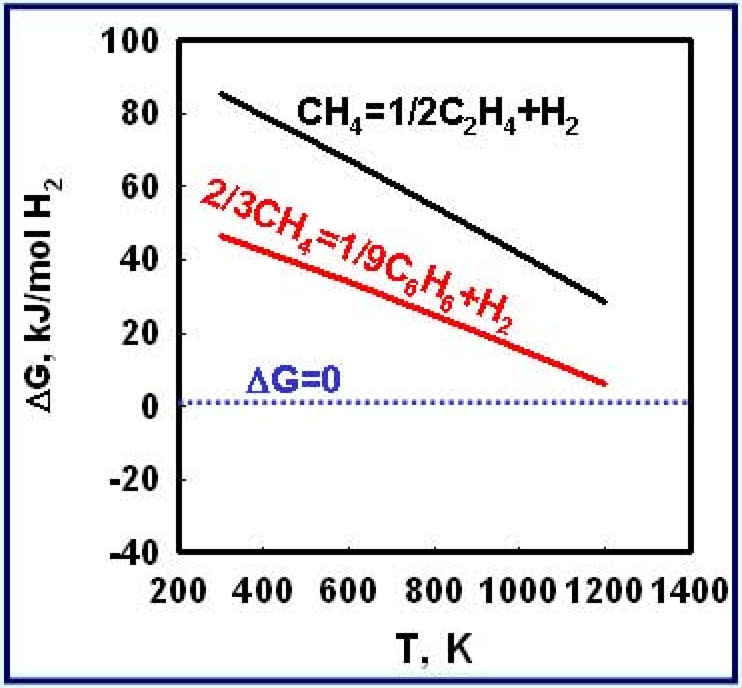
It works .... but it is not simple!

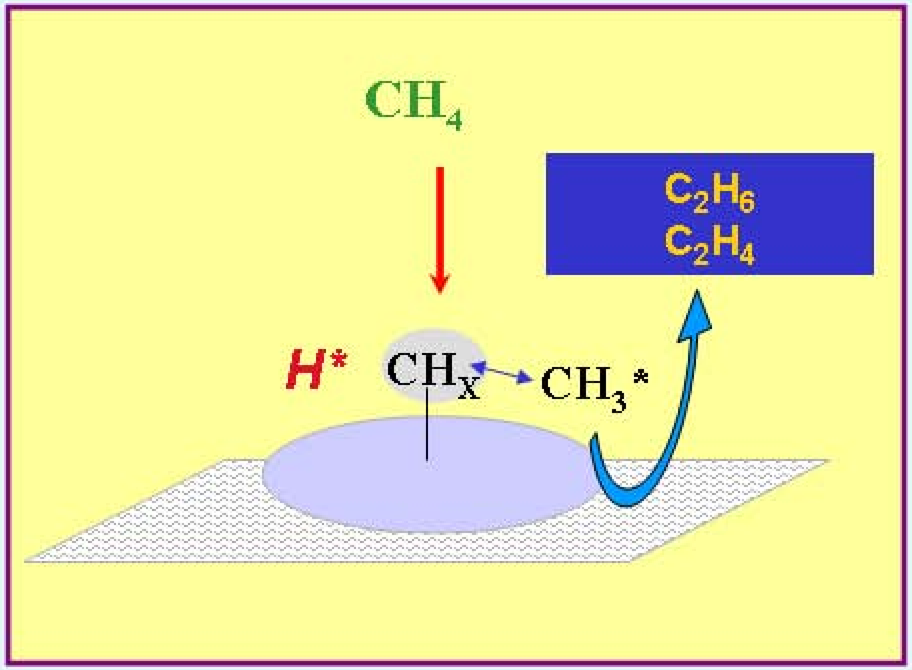


modest improvements in C_2-C_{10} yields (8% → 14%)
… limited by low driving force for H_2 permeation

Catal. Lett. 82, 175 (2002); Chem. Eng. Sci. 57, 4595 (2002)

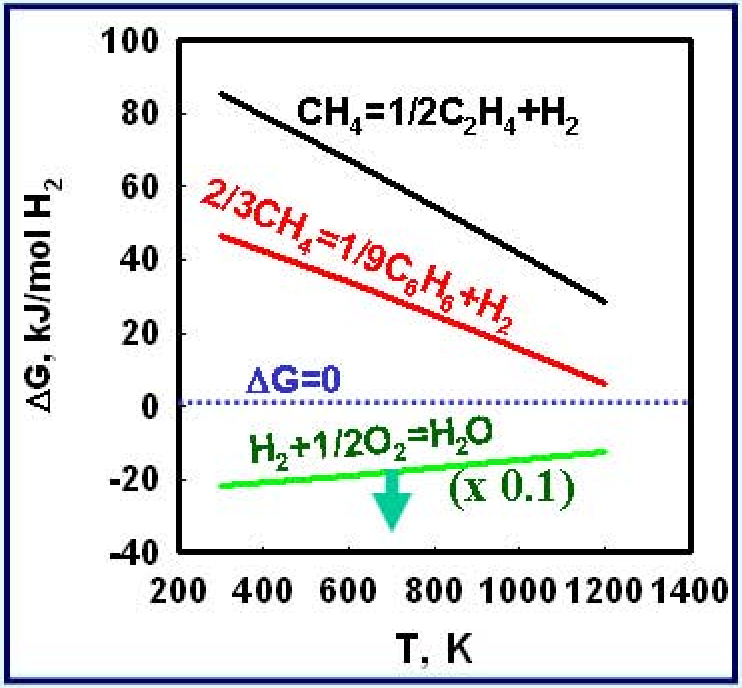
How else could we remove H_2?

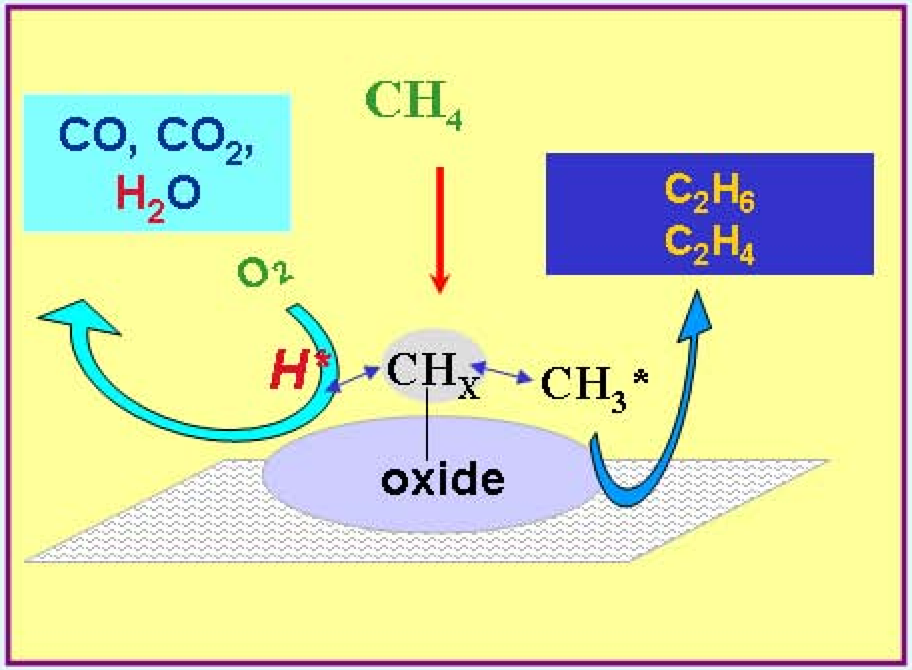




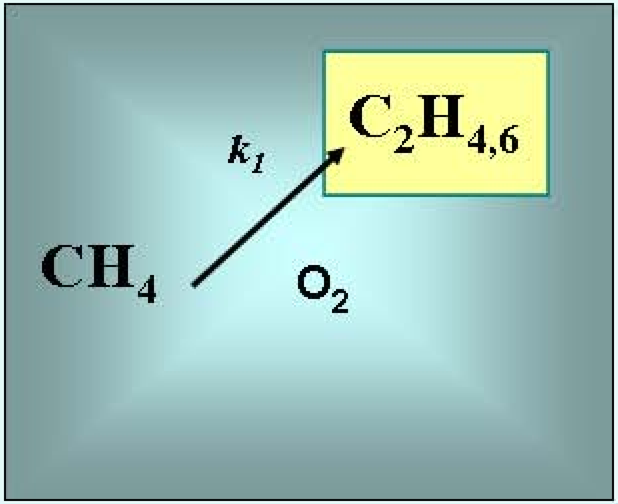
Oxidative routes to avoid thermodynamic hurdles

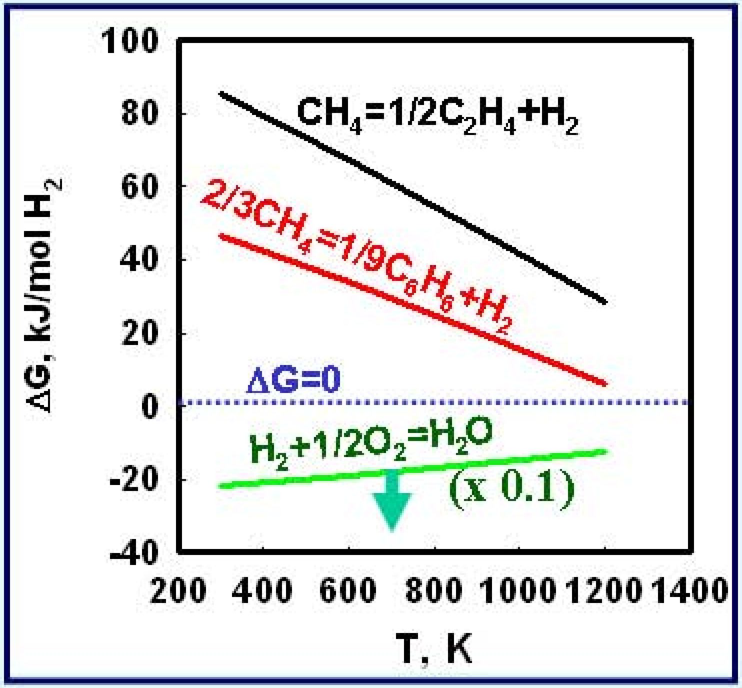
How else could we remove H_2?

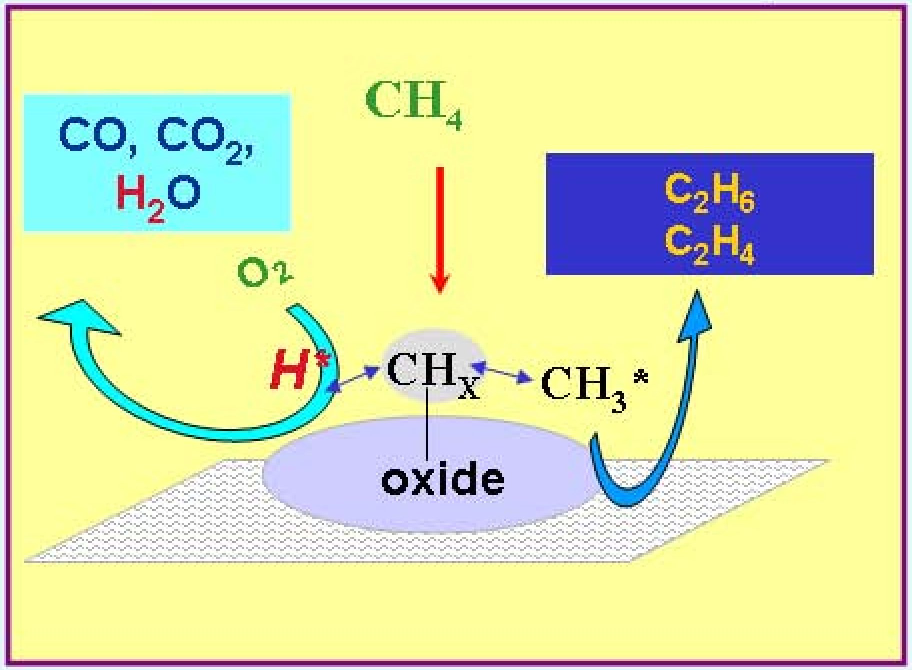




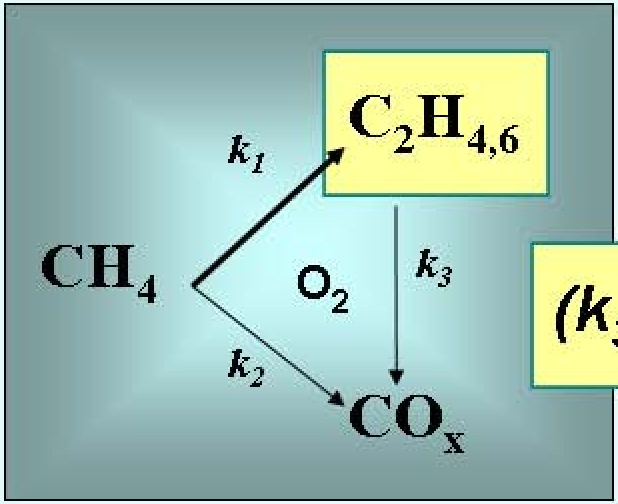
Oxidative routes to avoid thermodynamic hurdles



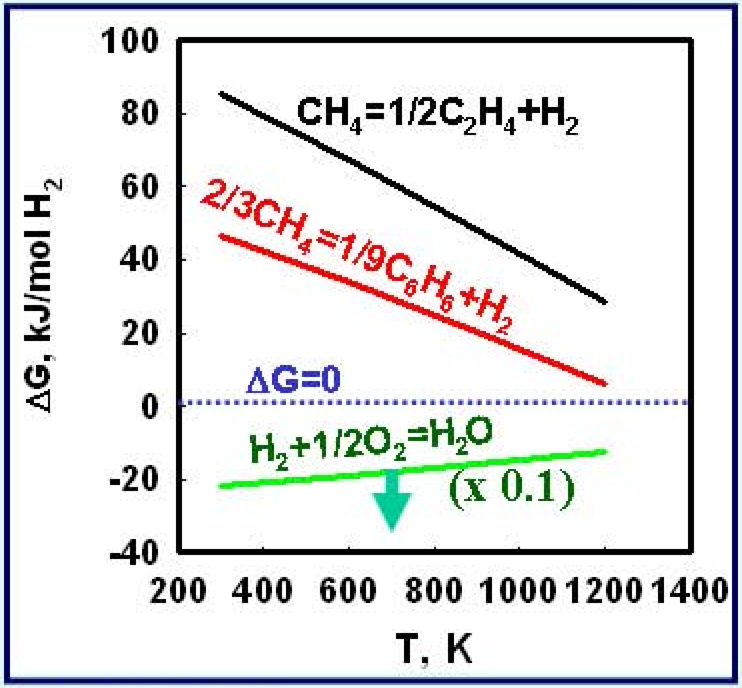




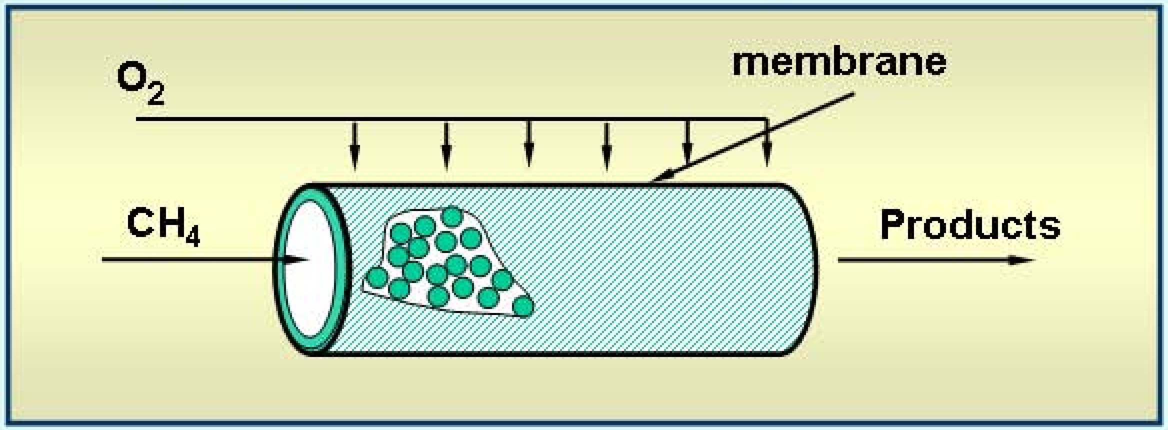
Oxidative routes to avoid thermodynamic hurdles



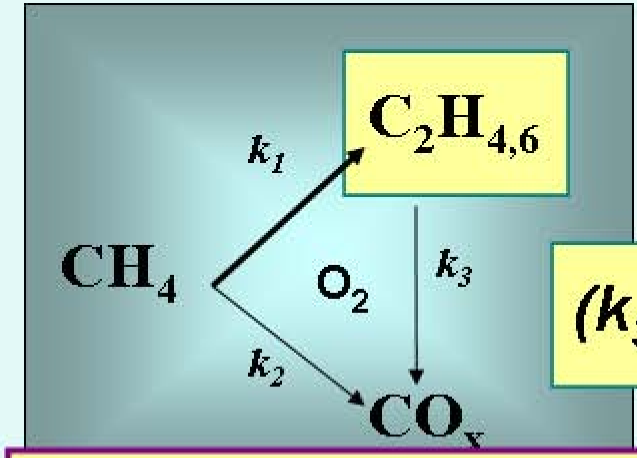
$(k_3/k_1) > 1$



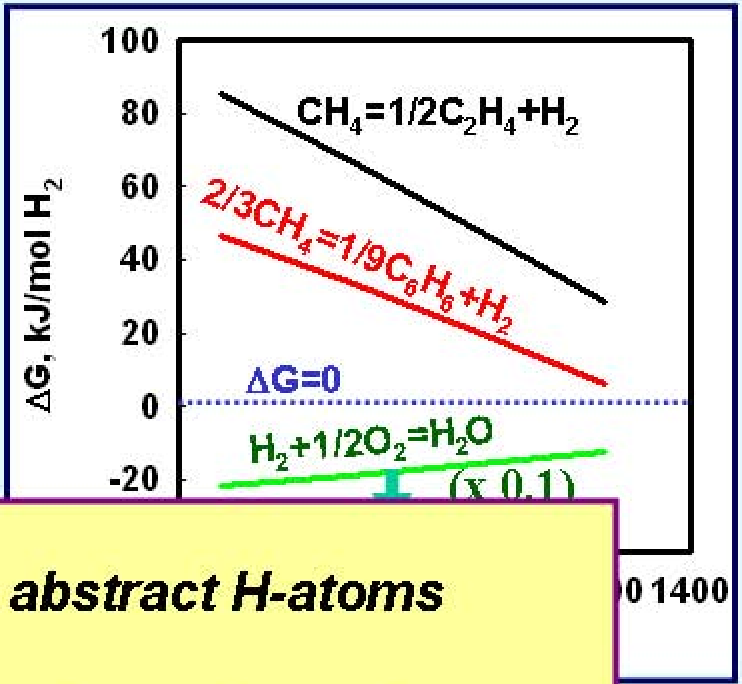
Staged O_2 introduction and air purification



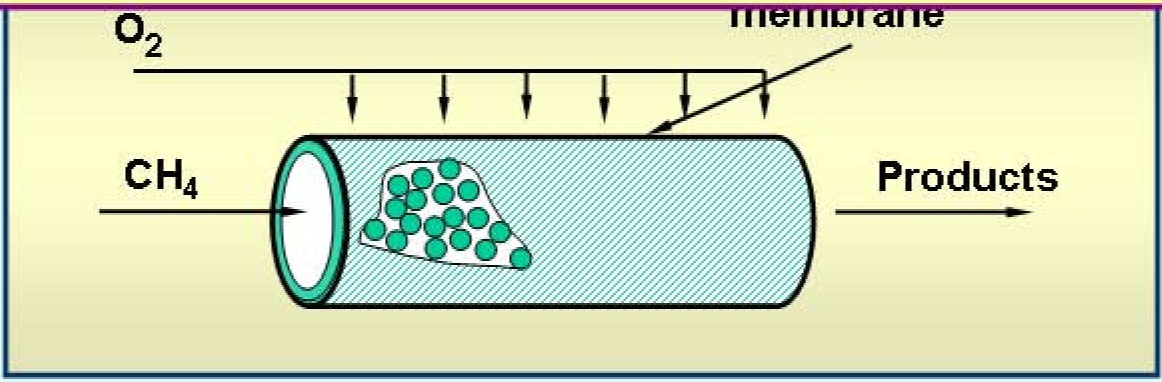
Oxidative routes to avoid thermodynamic hurdles



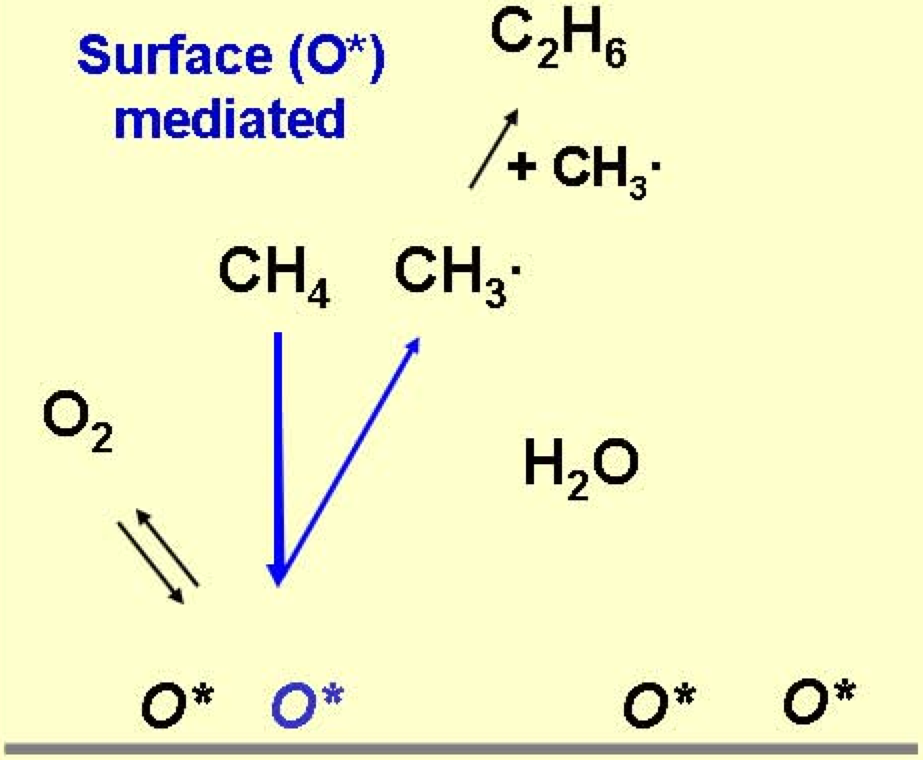
$(k_3/k_1) > 1$



- ***Use more reactive "oxidants" to abstract H-atoms***
- ***Extract and recover C_2 via separation and recycle***



Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

C_2H_6

$+ CH_3\cdot$

CH_4 $CH_3\cdot$

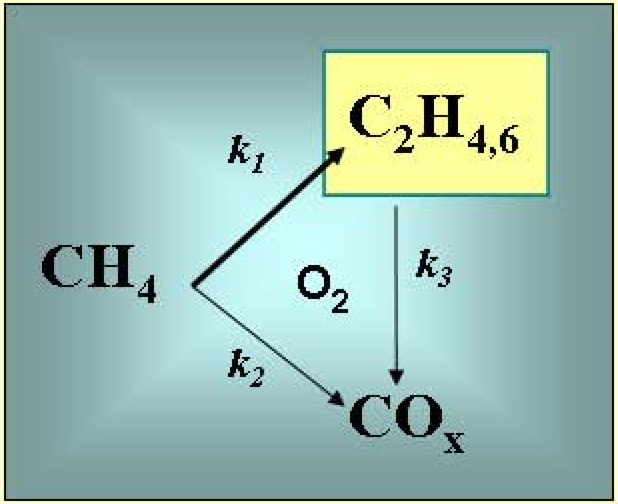
O_2

H_2O

*O** *O** *O** *O**

$Mn/Na_2WO_4/SiO_2$

~1000 K

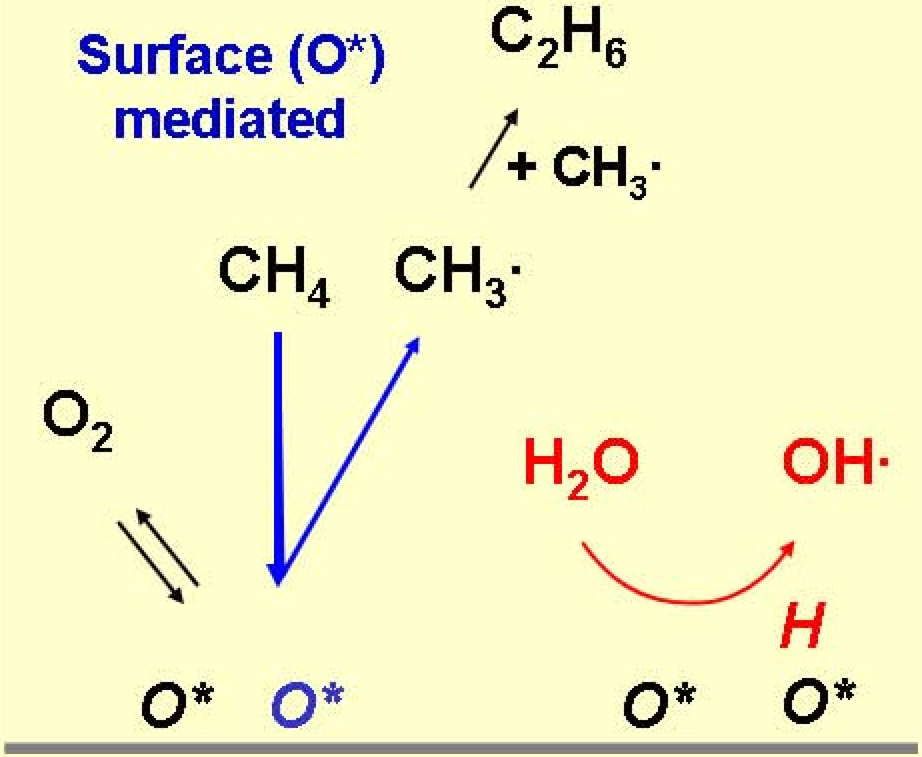


$$CH_4 \xrightarrow{k_1} C_2H_{4,6} \xrightarrow{k_3} CO_x$$

$$CH_4 \xrightarrow{k_2} CO_x$$

O_2

Encourage reactions with OH radicals instead of surfaces



Surface (O^*) mediated

C_2H_6

$+ CH_3\cdot$

CH_4 $CH_3\cdot$

O_2

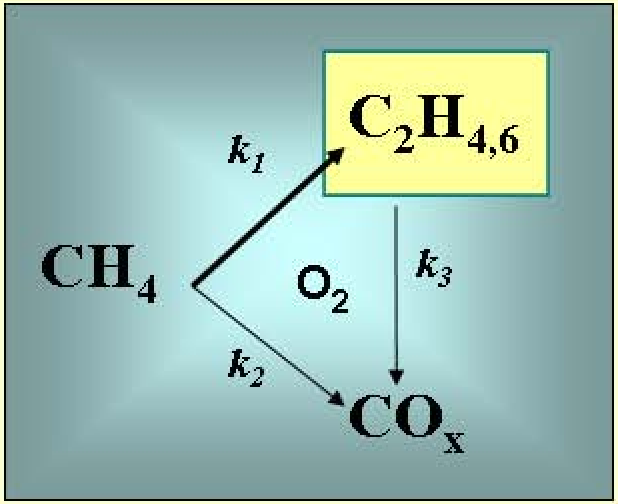
H_2O $OH\cdot$

H

O^* *O^** *O^** *O^**

$Mn/Na_2WO_4/SiO_2$

~1000 K



$C_2H_{4,6}$

CH_4

k_1

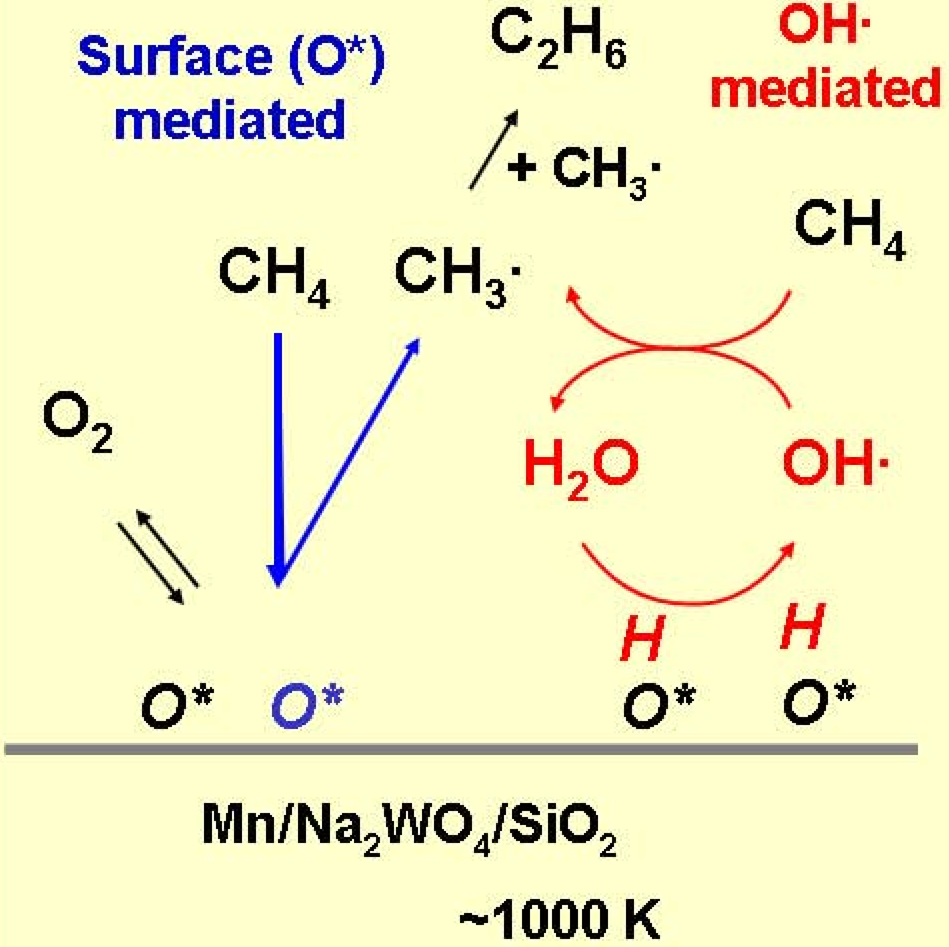
O_2

k_3

k_2

CO_x

Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

C_2H_6

OH· mediated

$+ CH_3·$

CH_4 $CH_3·$

CH_4

O_2

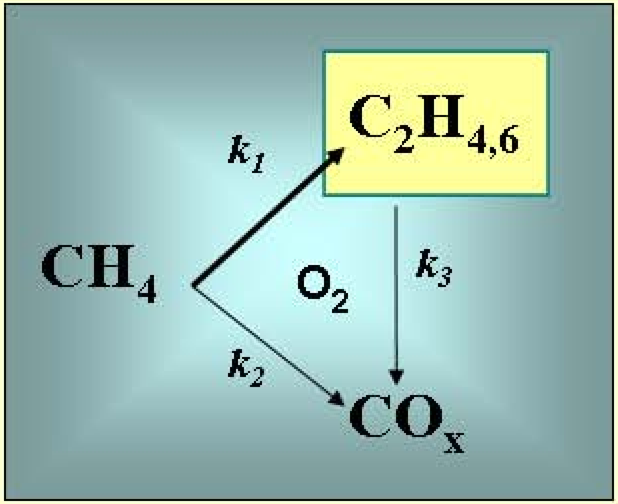
H_2O OH·

H *H*

*O** *O** *O** *O**

$Mn/Na_2WO_4/SiO_2$

~1000 K



$C_2H_{4,6}$

CH_4

k_1

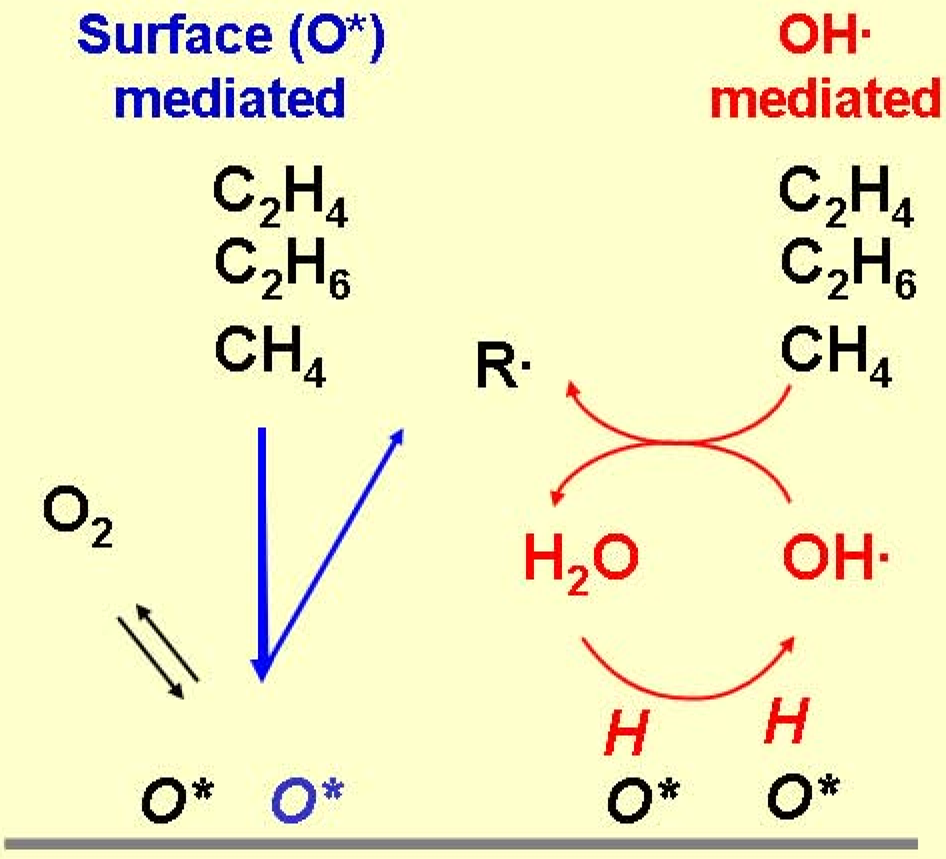
O_2

k_3

k_2

CO_x

Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

C_2H_4
C_2H_6
CH_4

O_2

*O** *O**

OH· mediated

C_2H_4
C_2H_6
CH_4

R·

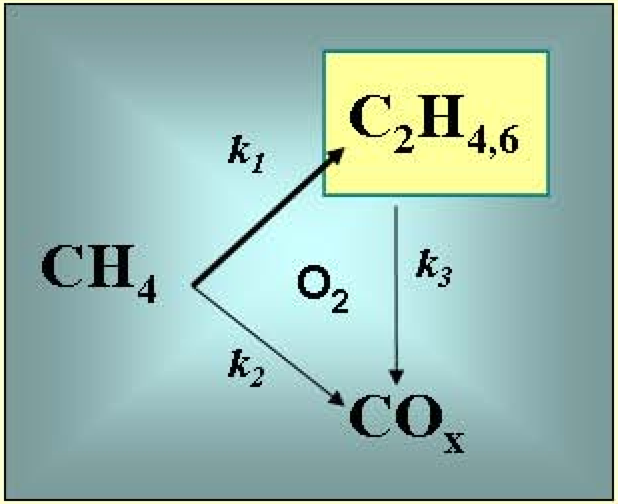
H_2O OH·

H *H*

*O** *O**

$Mn/Na_2WO_4/SiO_2$

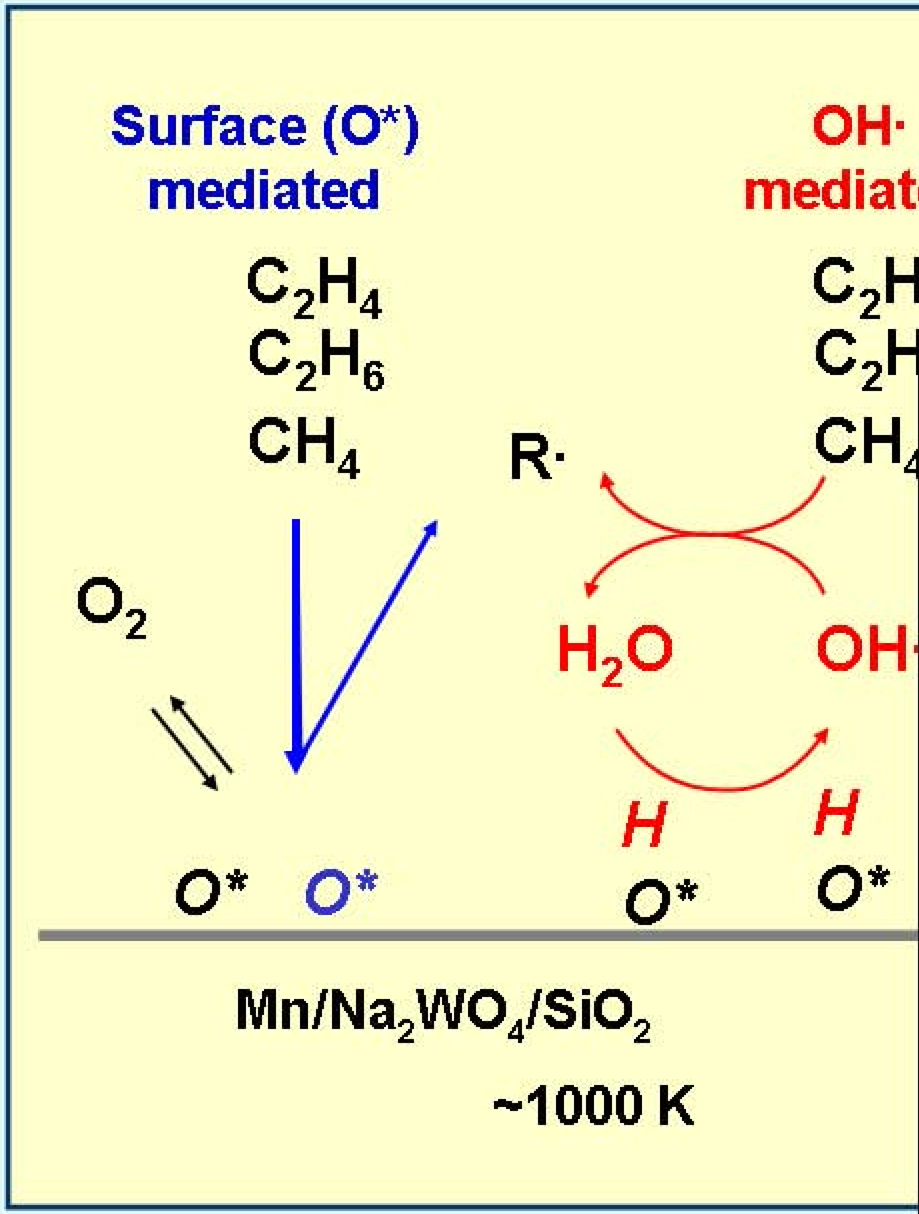
~1000 K



$$CH_4 \xrightarrow{k_1} C_2H_{4,6} \xrightarrow{k_3} CO_x, \quad CH_4 \xrightarrow{k_2} CO_x \quad (O_2)$$

Water is a co-catalyst

Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

C_2H_4
C_2H_6
CH_4

O_2

O* O*

OH· mediated

C_2H_4
C_2H_6
CH_4

R·

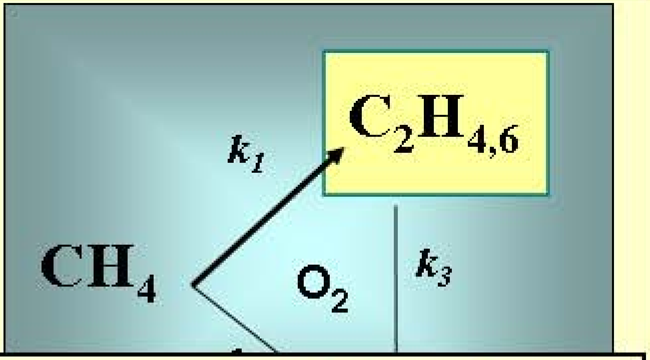
H_2O OH·

H H

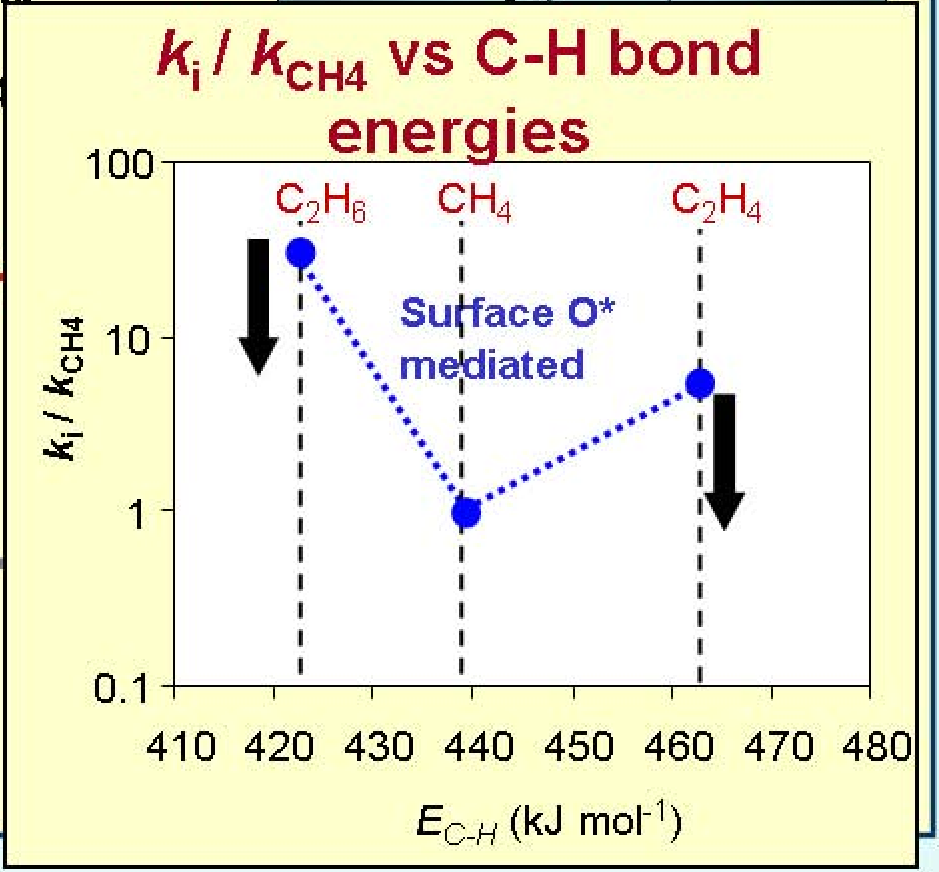
O* O*

$Mn/Na_2WO_4/SiO_2$

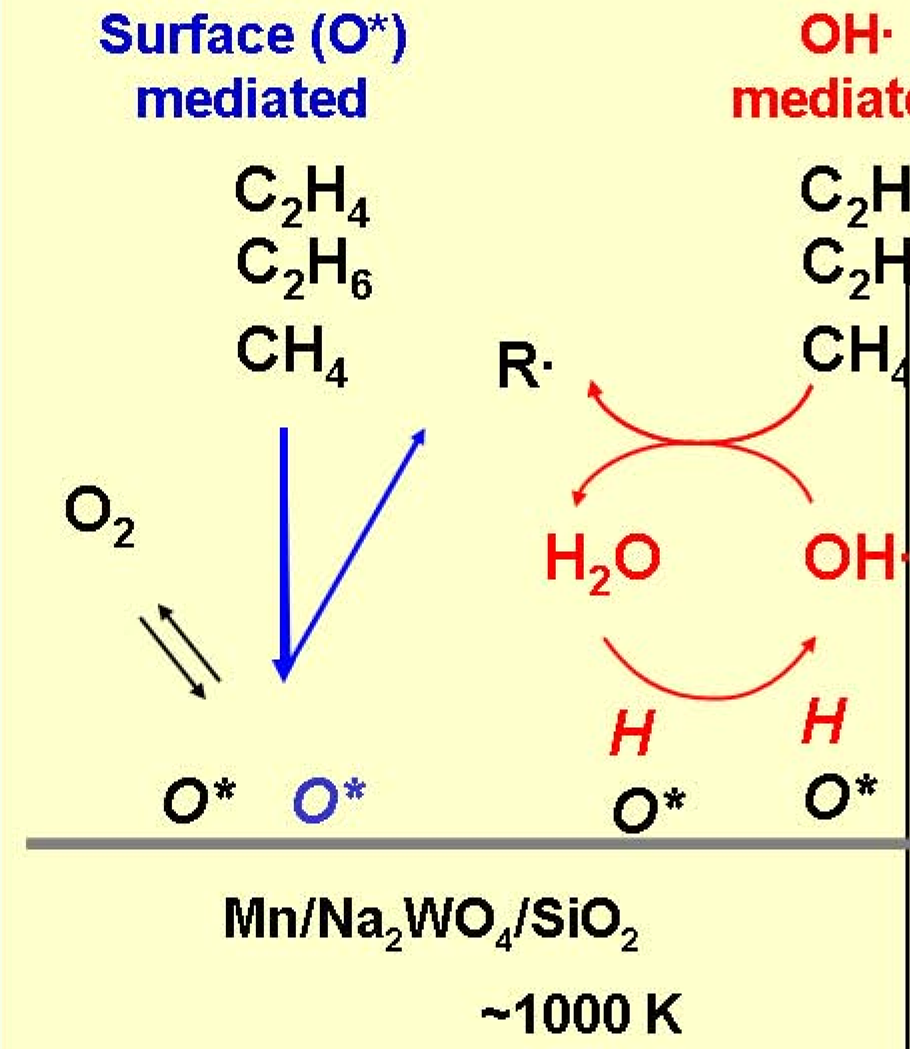
~1000 K



k_i / k_{CH4} vs C-H bond energies



Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

OH· mediated

C_2H_4

C_2H_6

CH_4

R·

O_2

H_2O

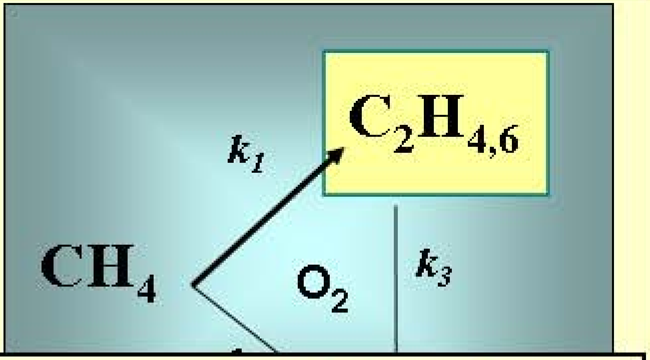
OH·

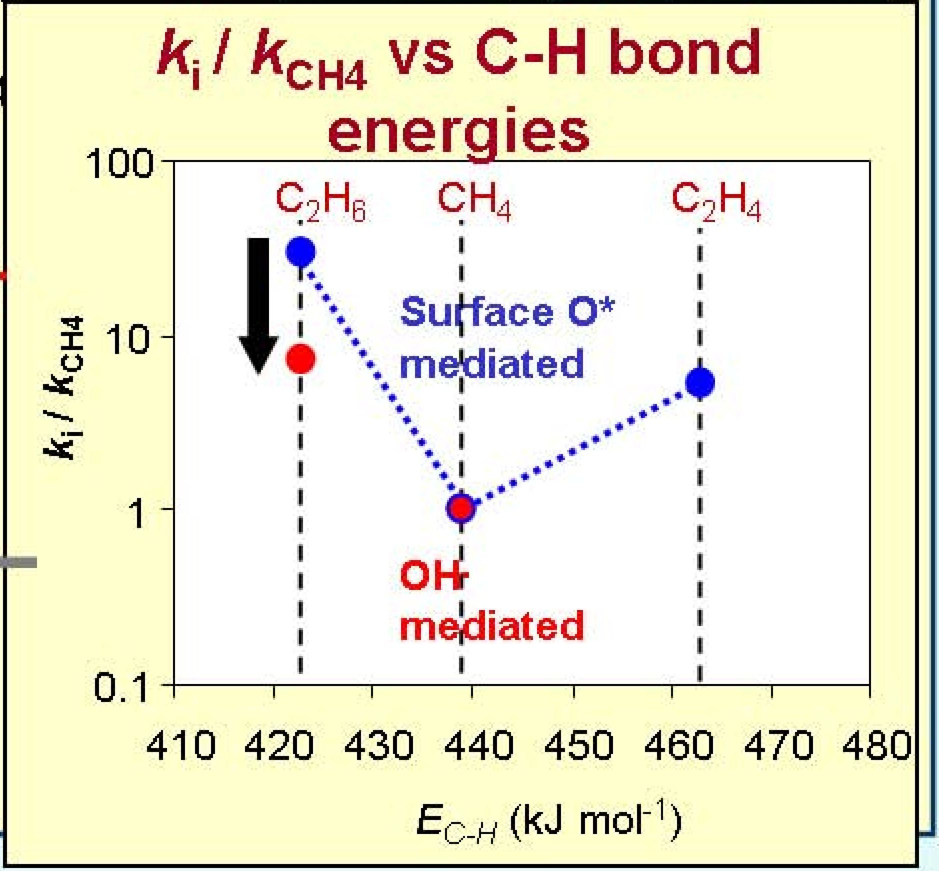
H

*O**

$Mn/Na_2WO_4/SiO_2$

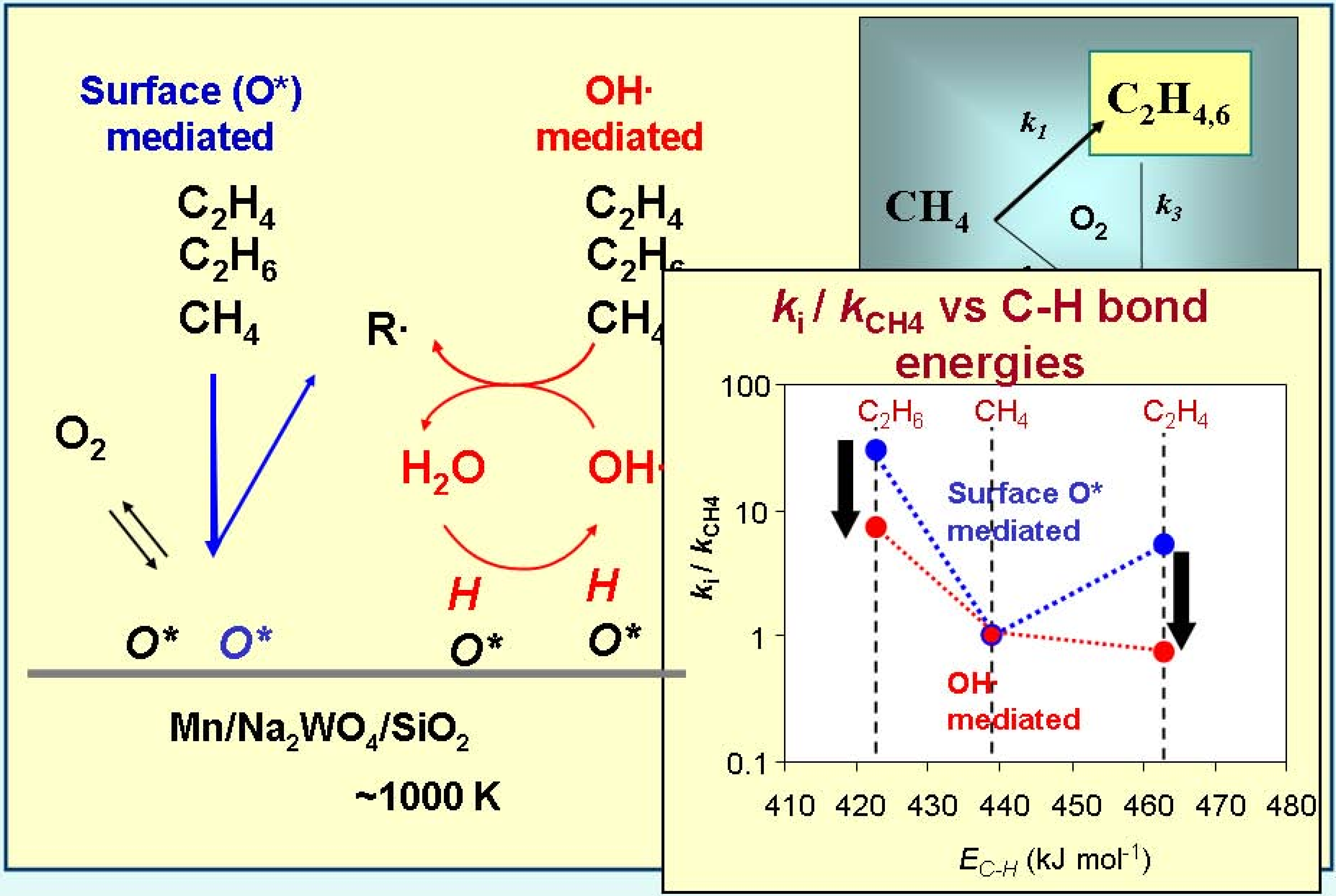
~1000 K





k_i / k_{CH4} vs C-H bond energies

Encourage reactions with OH radicals instead of surfaces



Surface (O*) mediated

OH· mediated

C_2H_4
C_2H_6
CH_4

$R\cdot$

O_2

H_2O

$OH\cdot$

H *H*

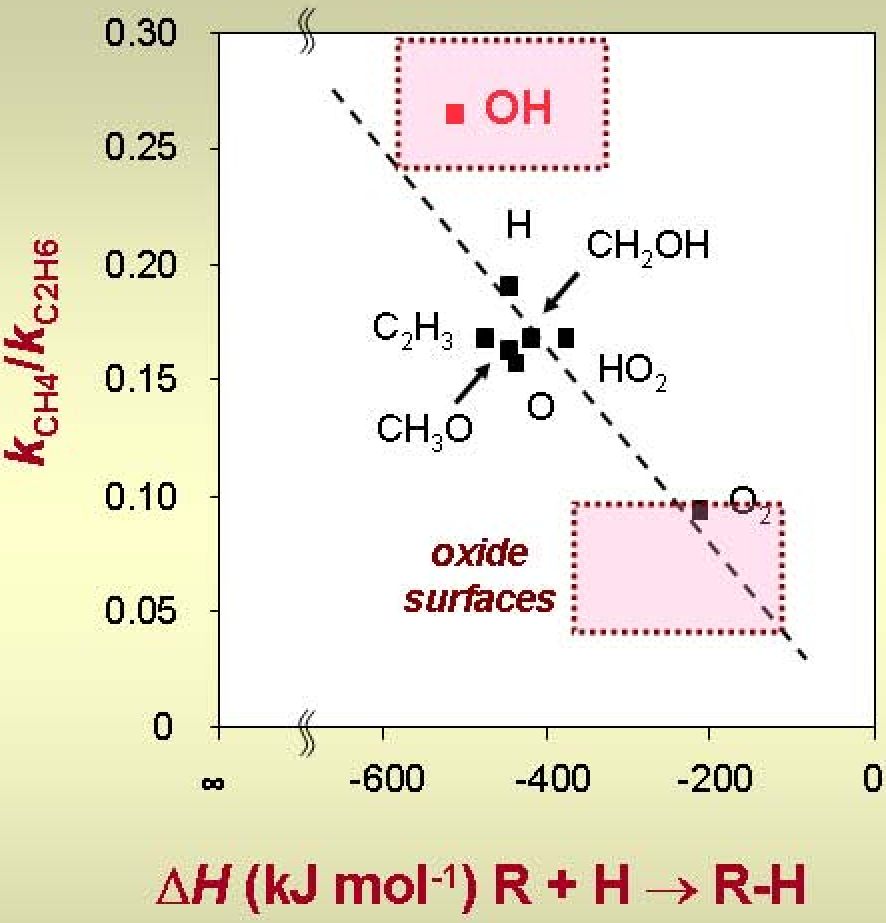
*O** *O** *O** *O**

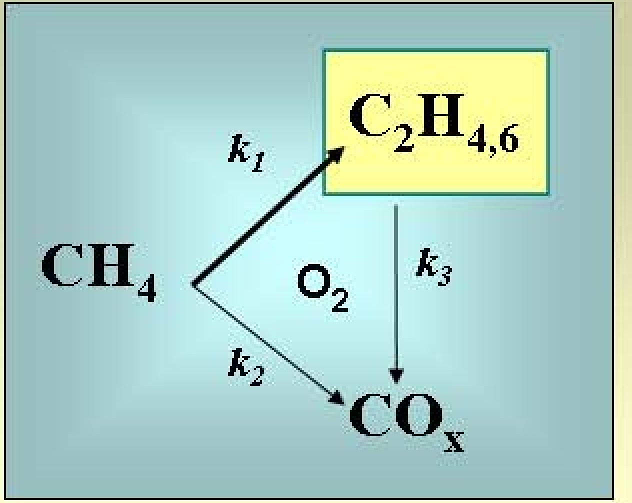
$Mn/Na_2WO_4/SiO_2$

~1000 K

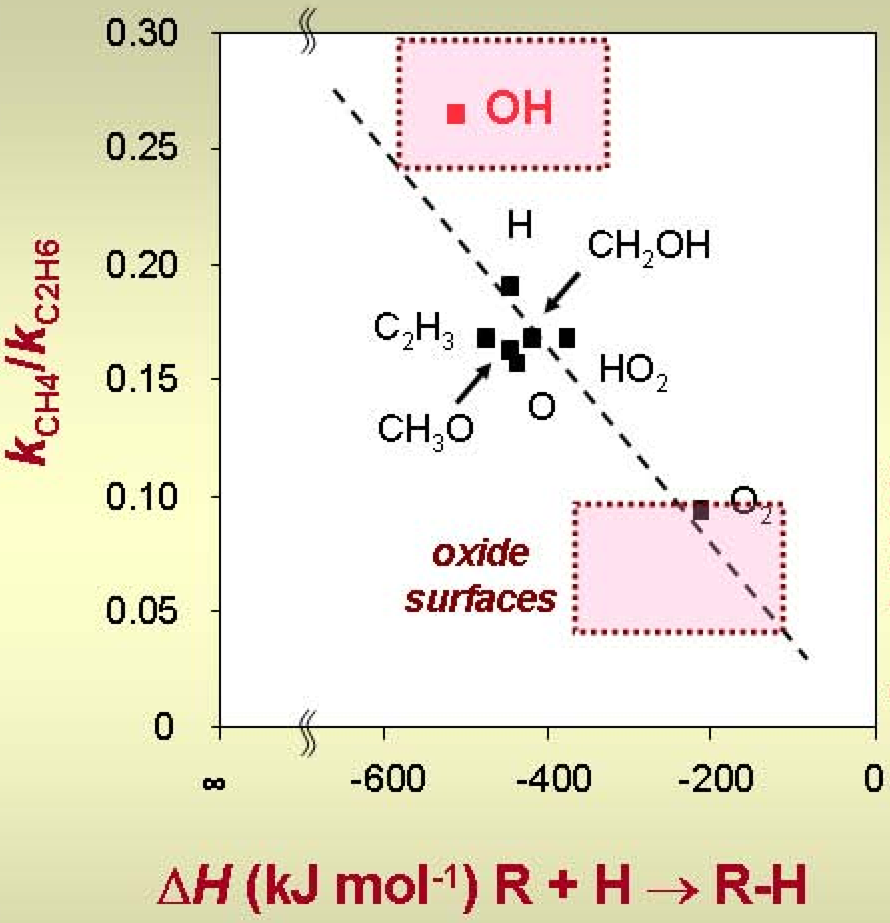
k_i / k_{CH4} vs C-H bond energies

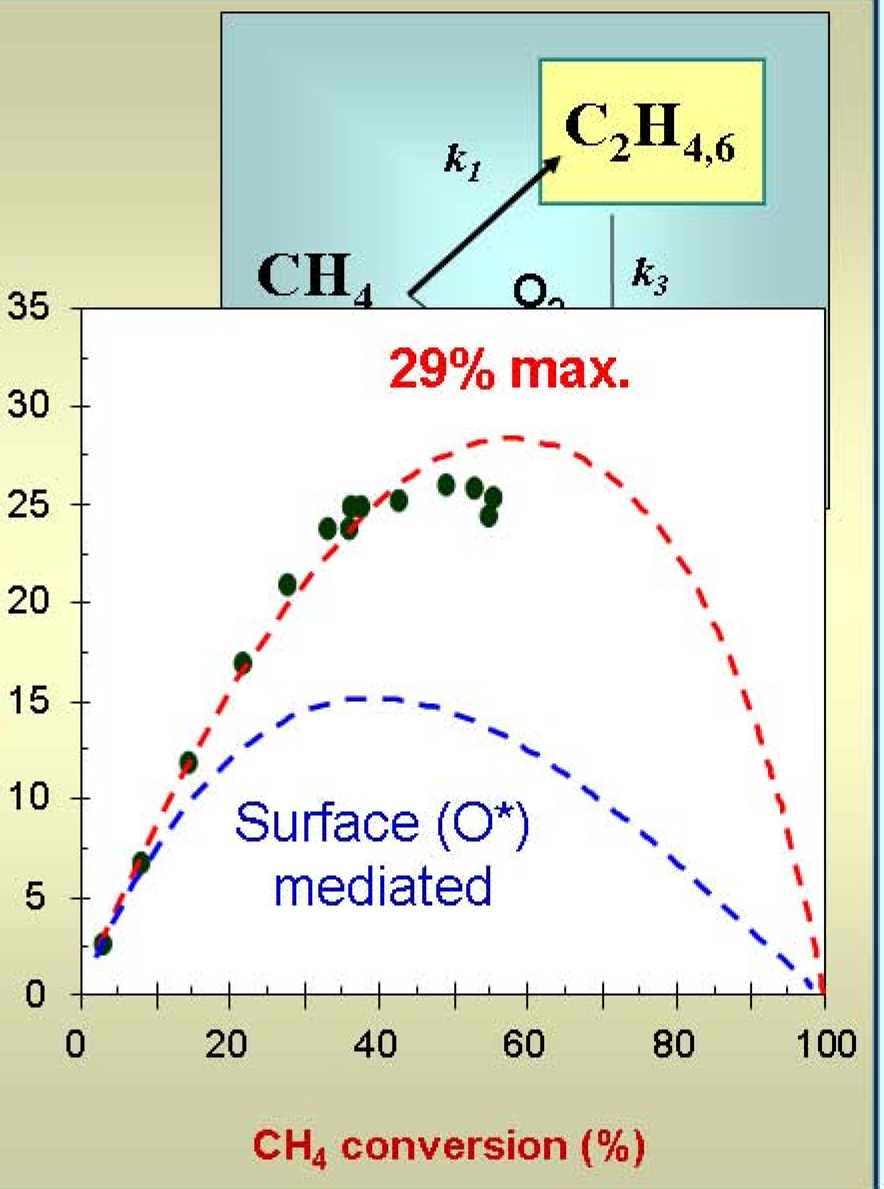
Encourage reactions with OH radicals instead of surfaces





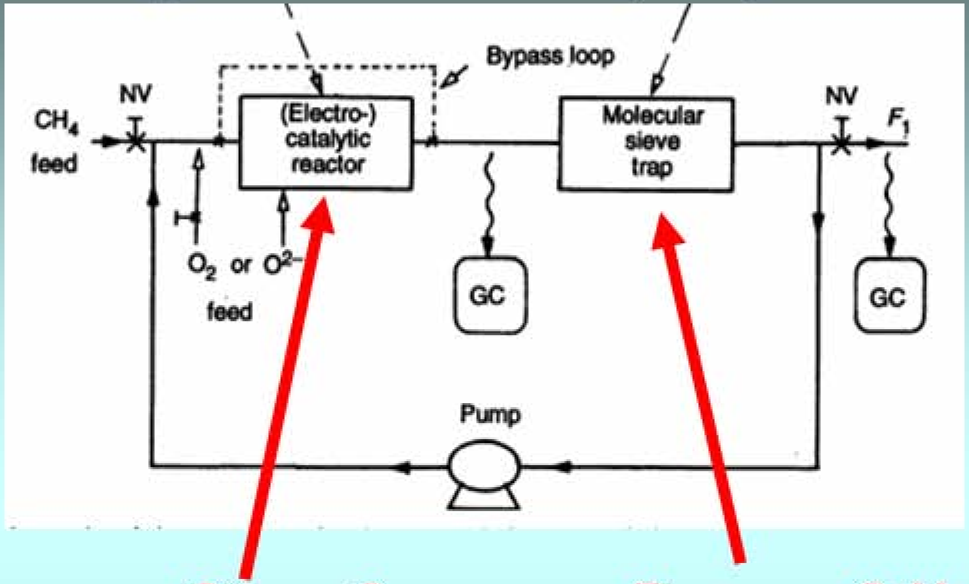
Encourage reactions with OH radicals instead of surfaces





Oxidative Coupling: extracting C_2 products as they form

Jiang, et al., Science 264 (1994) 1563

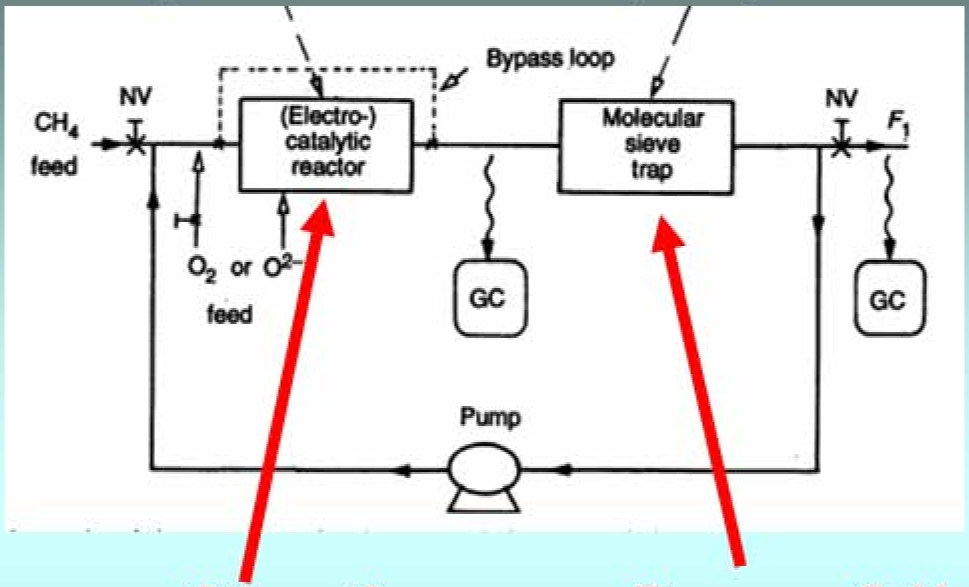


Stage O_2

Remove C_2H_4

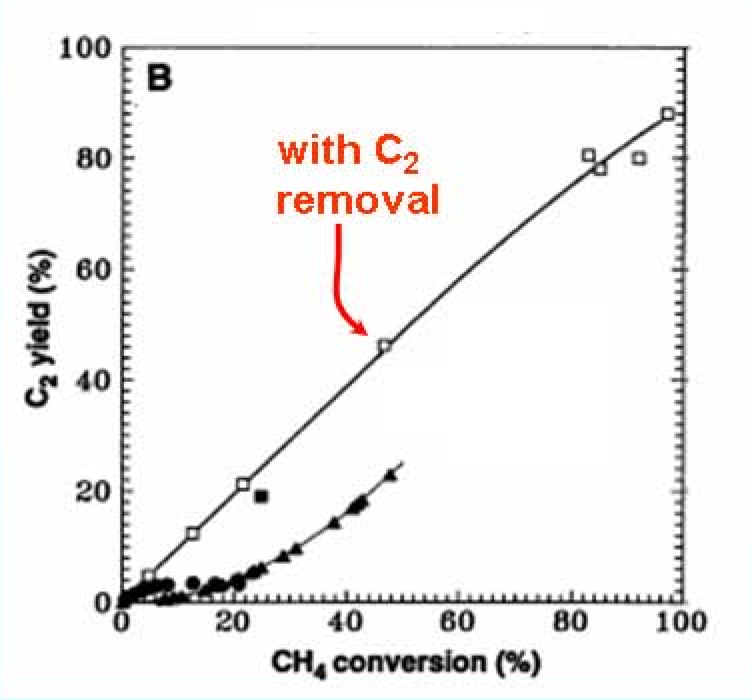
Oxidative Coupling: extracting C_2 products as they form

Jiang, et al., Science 264 (1994) 1563



Stage O_2

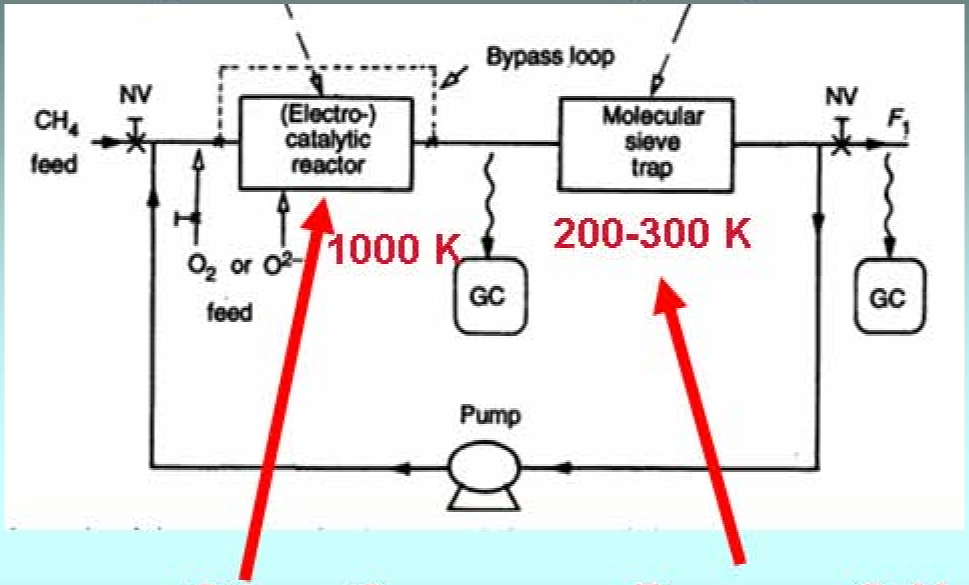
Remove C_2H_4



with C_2 removal

Oxidative Coupling: extracting C_2 products as they form

Jiang, et al., Science 264 (1994) 1563

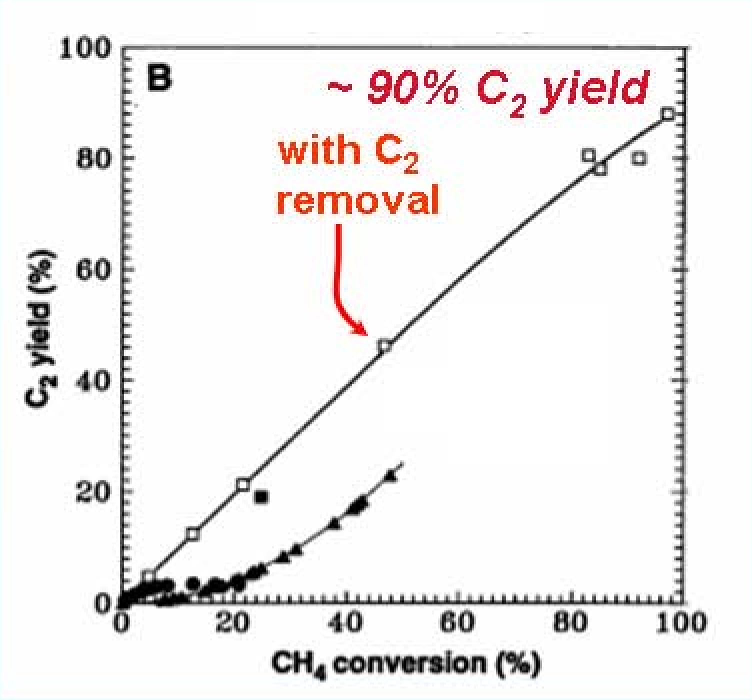


1000 K

200-300 K

Stage O_2

Remove C_2H_4

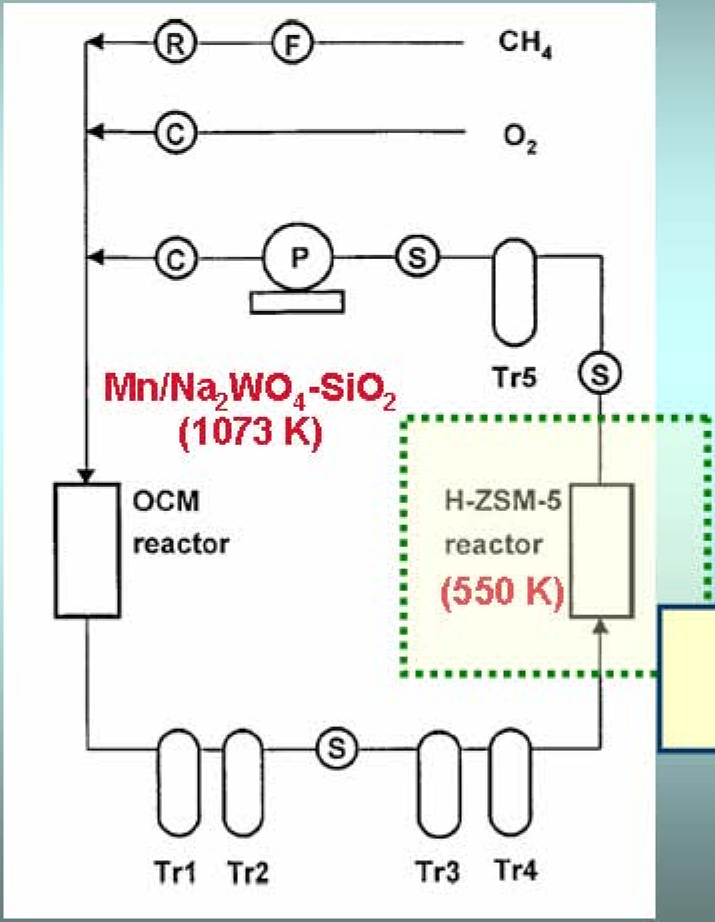


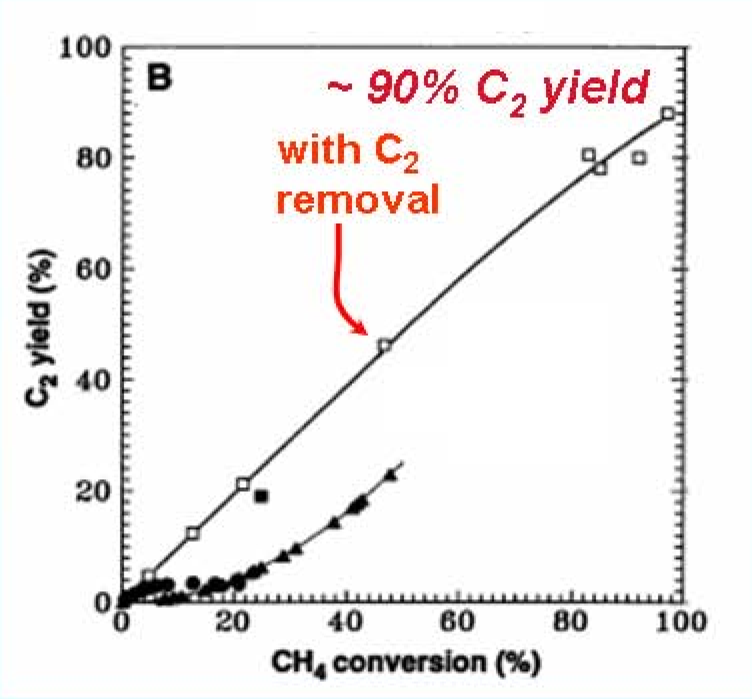
~ 90% C_2 yield

with C_2 removal

Oxidative Coupling: extracting C_2 products as they form

Jiang, et al., Science 264 (1994) 1563





Convert C_2 to C_{4+} hydrocarbons

Pak, et al., Catal. Lett. 66 (2000) 1

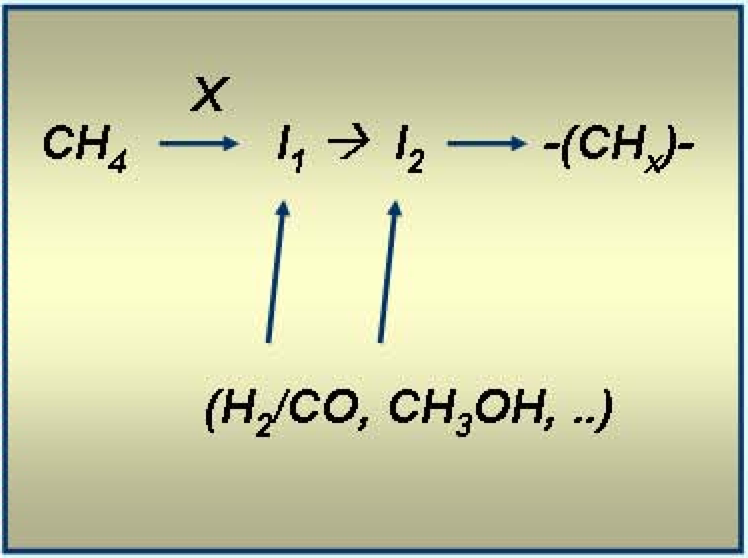
Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} \text{-}(CH_x)\text{-} \longrightarrow (C, CO_x)$$

- *overcome thermodynamic constraints*
- *protect products with weaker C-H bonds*

Indirect Routes



$$CH_4 \xrightarrow{X} I_1 \rightarrow I_2 \longrightarrow \text{-}(CH_x)\text{-}$$

$(H_2/CO, CH_3OH, ..)$

- *couple endothermic-exothermic steps*
- *form the first carbon-carbon bond*

- ***avoid process complexity***
- ***provide routes to products with large markets***

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} -(CH_x)- \longrightarrow (C, CO_x)$$

- *overcome thermodynamic constraints*
- *protect products with weaker C-H bonds*

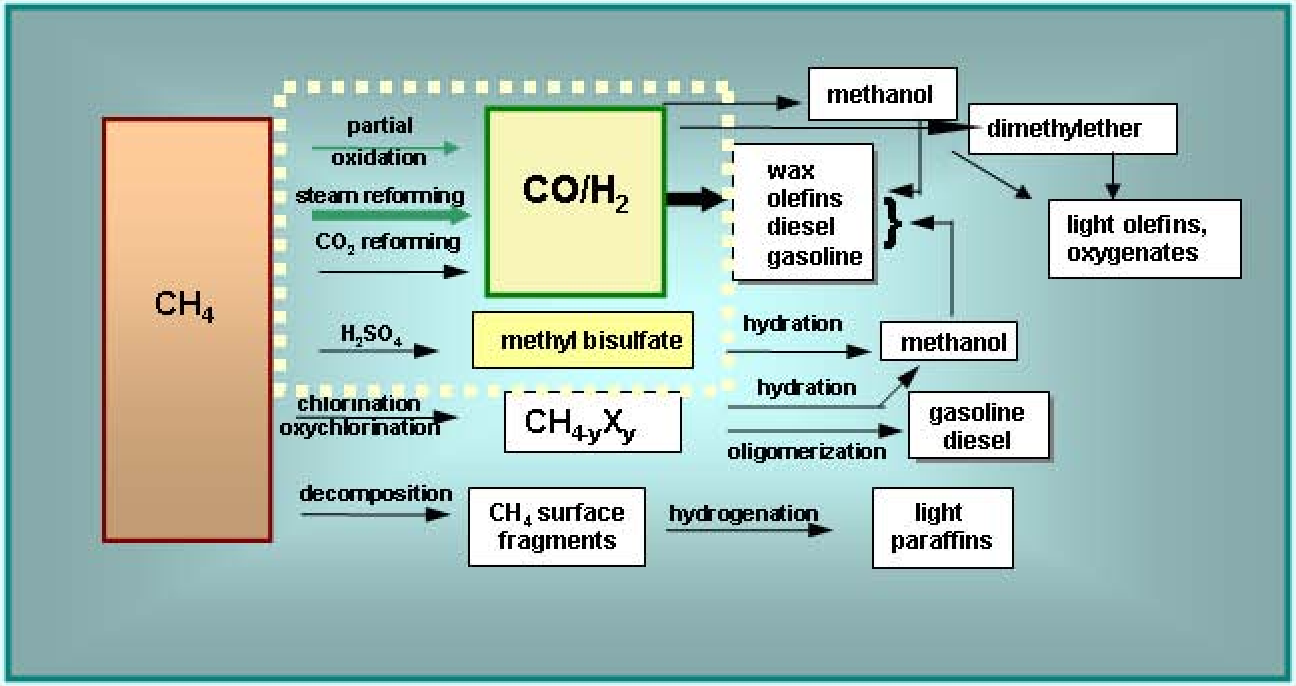
Indirect Routes

$$\begin{tikzcd}
CH_4 \arrow[r, "X"] & I_1 \arrow[r] & I_2 \arrow[r] & -(CH_x)- \\
& (H_2/CO, CH_3OH, ..) \arrow[u] \arrow[ur] & &
\end{tikzcd}$$

- *couple endothermic-exothermic steps*
- *form the first carbon-carbon bond*

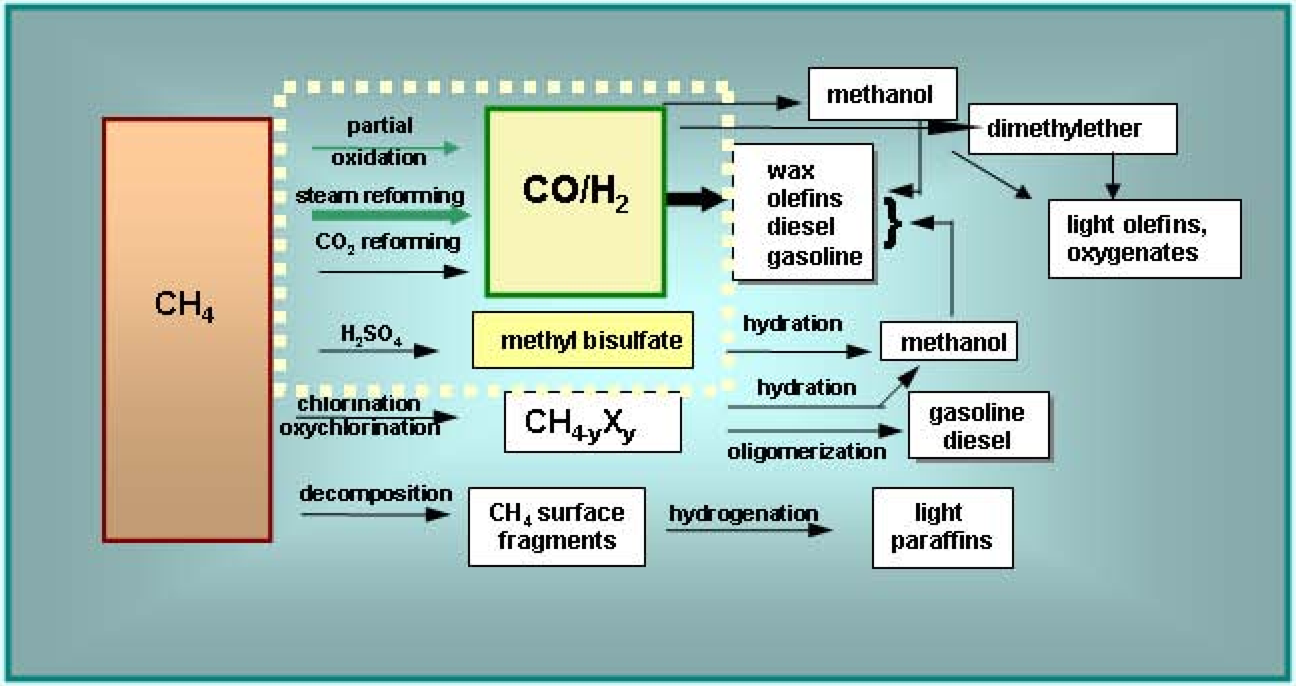
- ***avoid process complexity***
- ***provide routes to products with large markets***

Converting Methane to Fuels and Chemicals …. Indirectly



a "protected" form of methane is used as an intermediate

Converting Methane to Fuels and Chemicals …. Indirectly



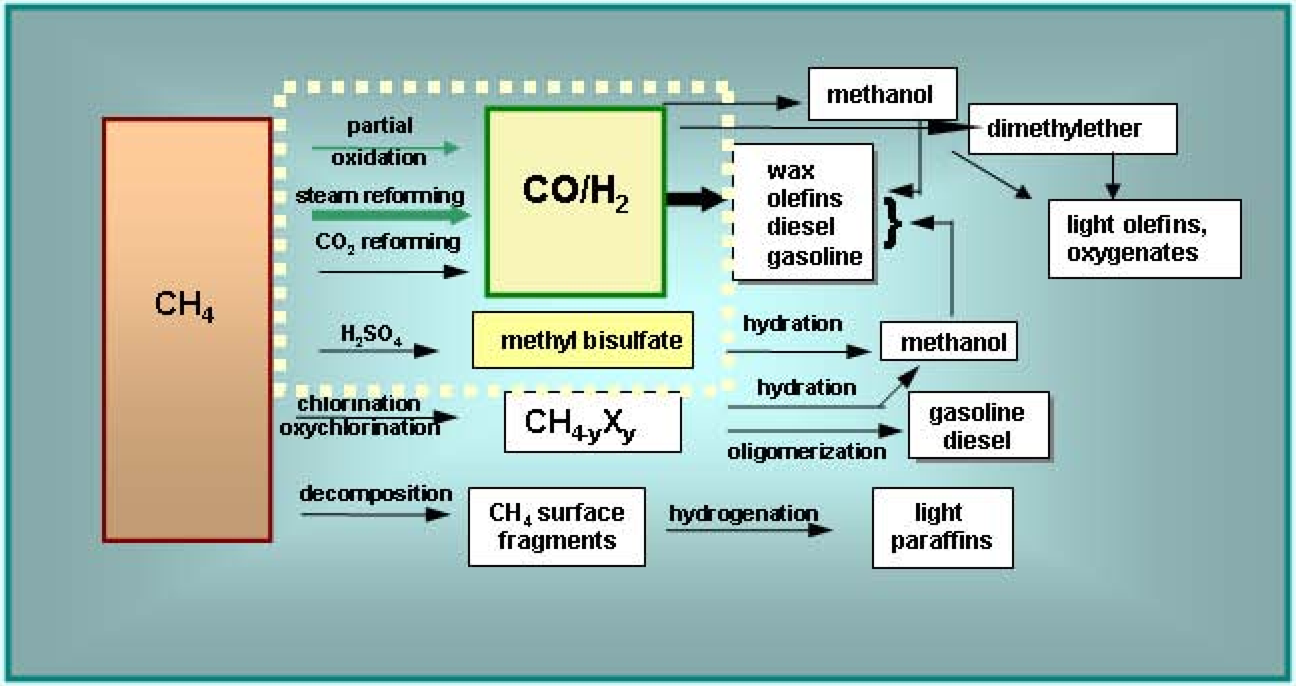
a "protected" form of methane is used as an intermediate

protection can be kinetic or thermodynamic

CH_3OSO_3H

H_2/CO

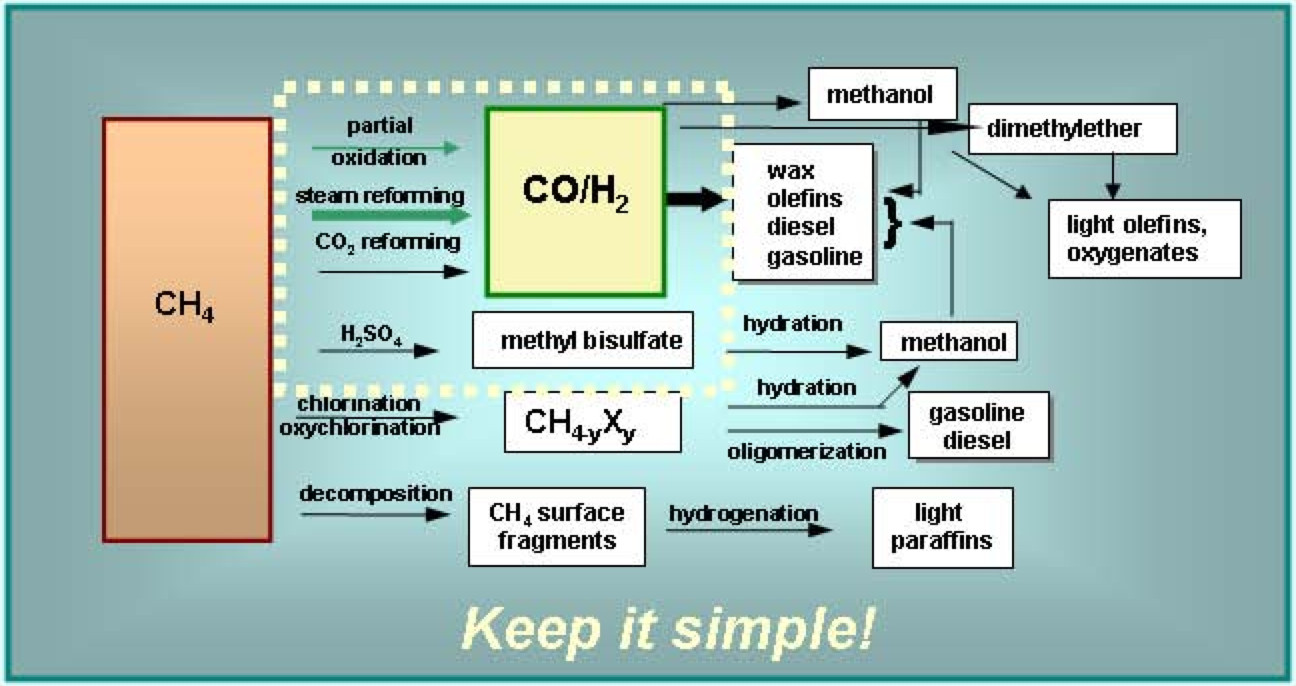
Converting Methane to Fuels and Chemicals …. Indirectly



a “protected” form of methane is used as an intermediate

protection can be kinetic or thermodynamic

Converting Methane to Fuels and Chemicals …. Indirectly



CH_4

partial oxidation

steam reforming

CO_2 reforming

CO/H_2

methanol

dimethylether

wax
olefins
diesel
gasoline

light olefins, oxygenates

H_2SO_4

methyl bisulfate

hydration

methanol

chlorination
oxychlorination

$CH_{4-y}X_y$

hydration

oligomerization

gasoline
diesel

decomposition

CH_4 surface fragments

hydrogenation

light paraffins

Keep it simple!

a “protected” form of methane is used as an intermediate

protection can be <u>kinetic</u> or <u>thermodynamic</u>

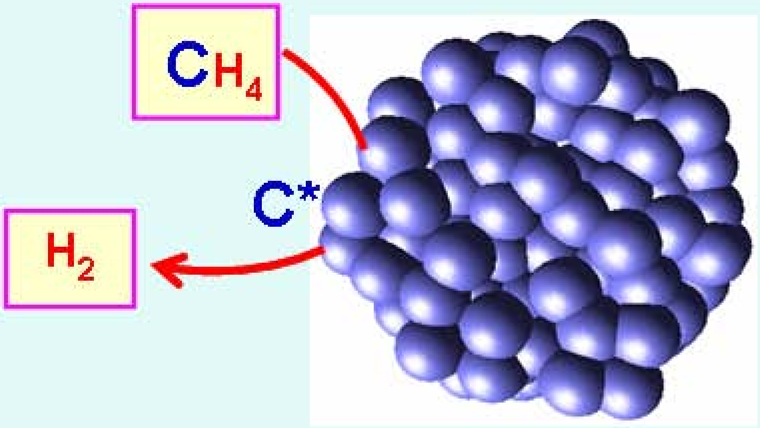
H_2SO_4

CH_3OSO_3H

H_2/CO

O_2
H_2O
CO_2

Methane “Oxidation” to Synthesis Gas

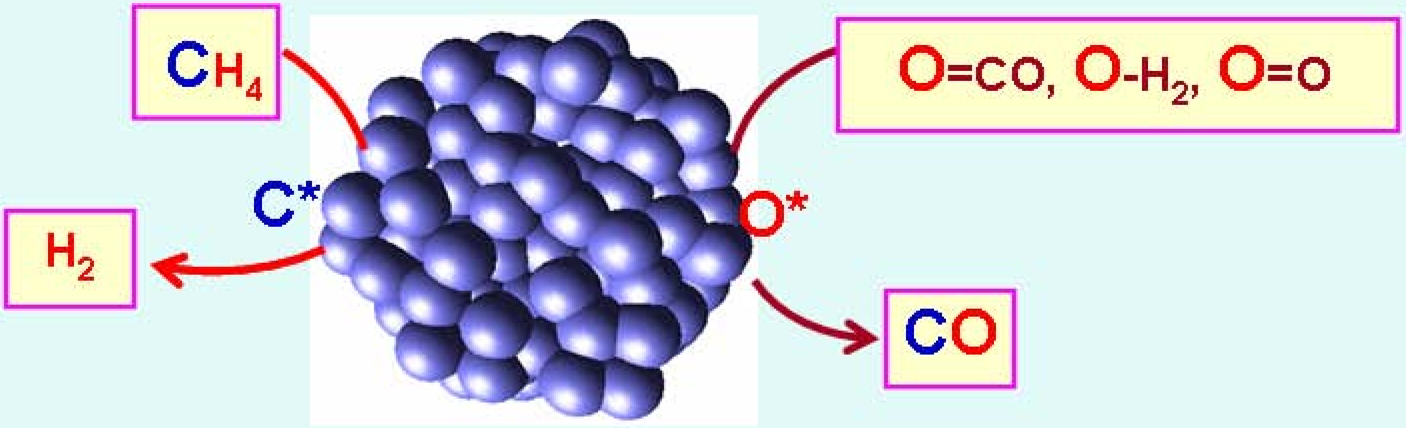


CH_4

C^*

H_2

Methane "Oxidation" to Synthesis Gas



CH_4

C*

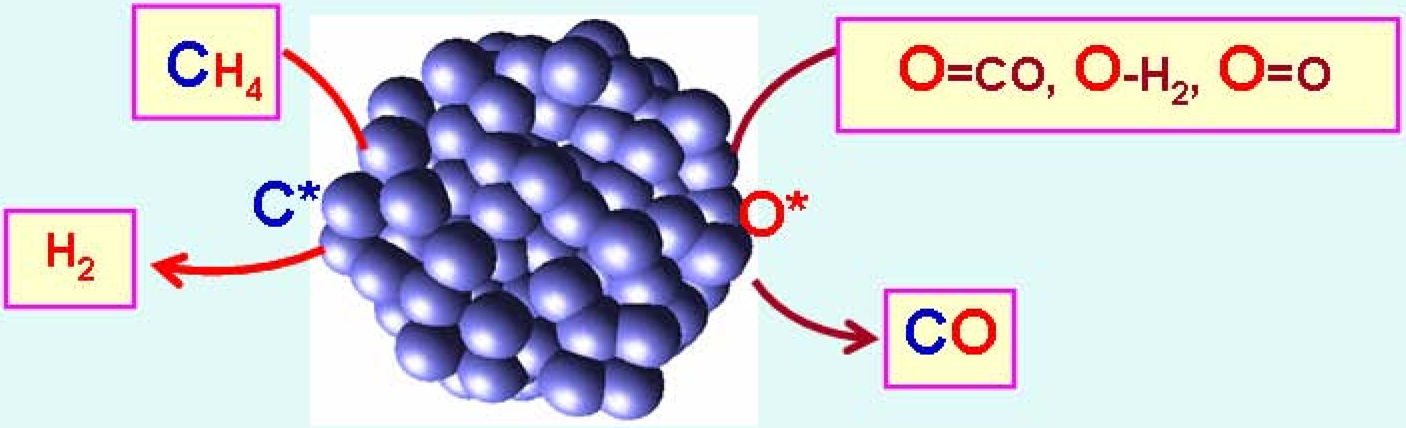
H_2

O=CO, O-H_2, O=O

O*

CO

Methane "Oxidation" to Synthesis Gas



CH_4

C^*

H_2

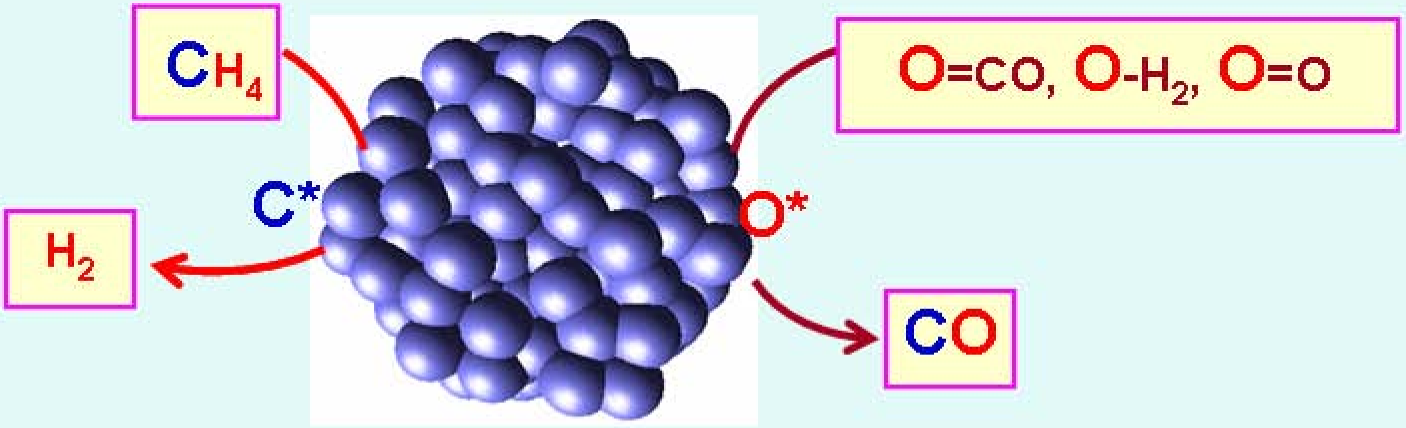
$O{=}CO$, $O{-}H_2$, $O{=}O$

O^*

CO

(Rh, Ni, Pt, Ir, Ru, Pd)

Methane "Oxidation" to Synthesis Gas



CH_4

C^*

H_2

O^*

$O{=}CO$, $O{-}H_2$, $O{=}O$

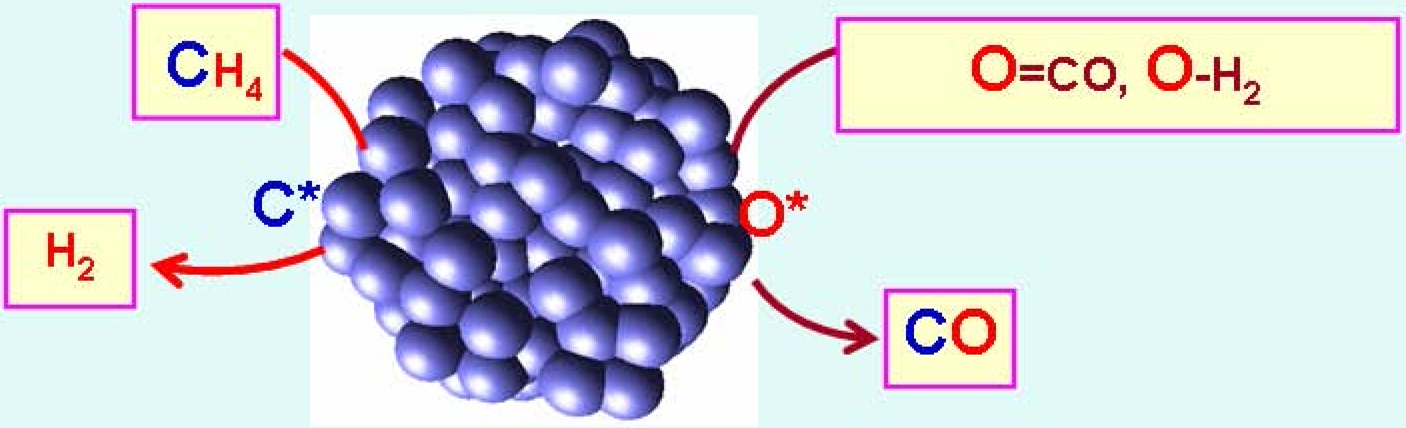
CO

(Rh, Ni, Pt, Ir, Ru, Pd)

Challenges →

- *couple endothermic and exothermic reactions in space and time*
- *minimize temperature gradients… avoid carbon formation*
- *lower costs of oxidant (O_2)*

Methane “Oxidation” to Synthesis Gas



CH_4

C^*

H_2

$O{=}CO$, $O{-}H_2$

O^*

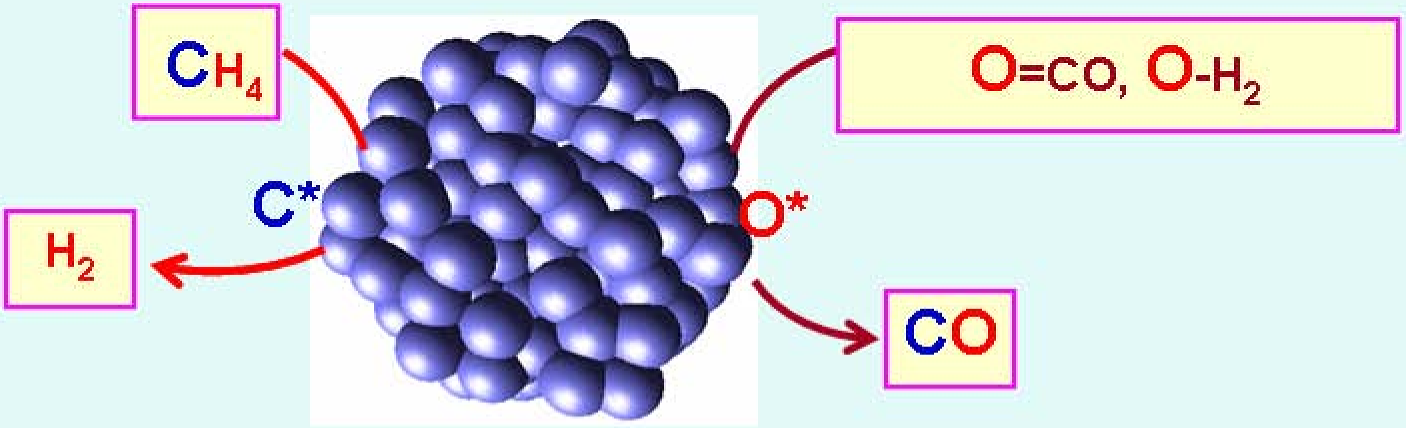
CO

$$CH_4 + H_2O \rightarrow 3\,H_2 + CO$$

$$CH_4 + CO_2 \rightarrow 2\,H_2 + 2\,CO$$

+ 250 kJ/mol

Methane "Oxidation" to Synthesis Gas



$$CH_4 + H_2O \rightarrow 3\,H_2 + CO$$

$$CH_4 + CO_2 \rightarrow 2\,H_2 + 2\,CO$$

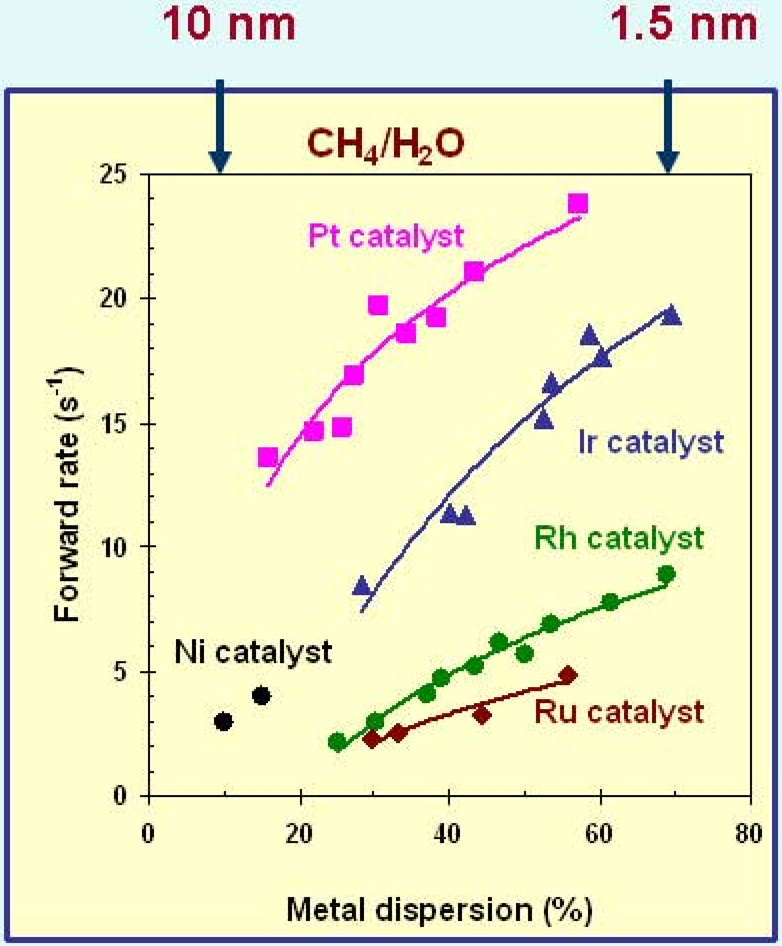
+ 250 kJ/mol

Requires high temperatures …

…….. catalyst sintering and carbon formation

$$CO + 2\,H_2 \rightarrow -(CH_2)- + H_2O$$

Small metal clusters are more "active", inhibit carbon formation



[873 K, 20 kPa CH_4]

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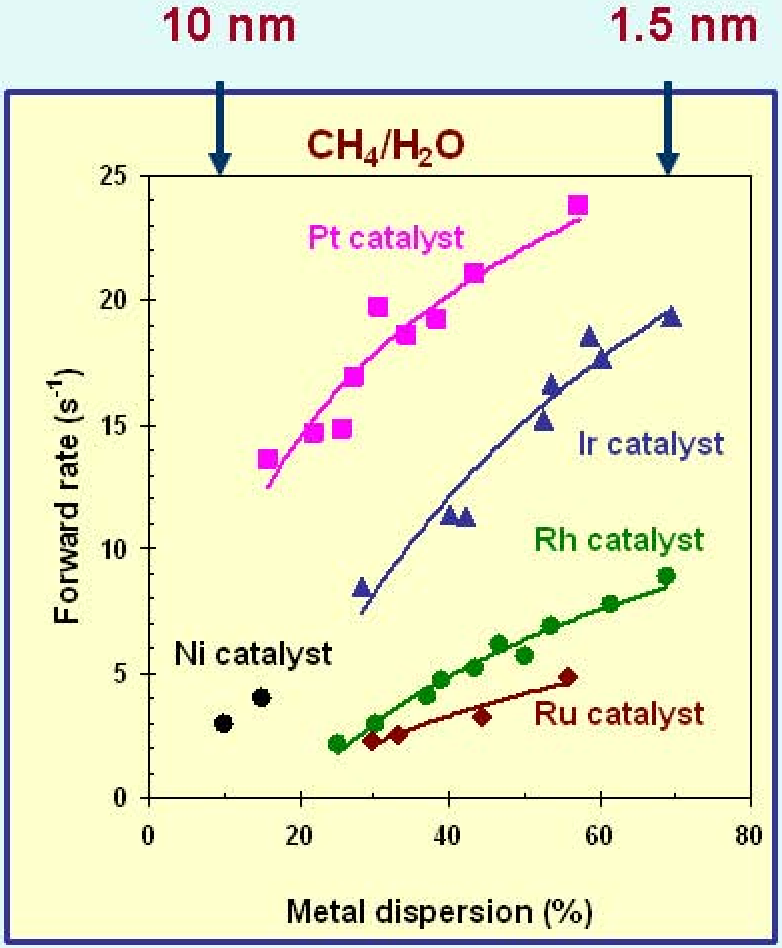

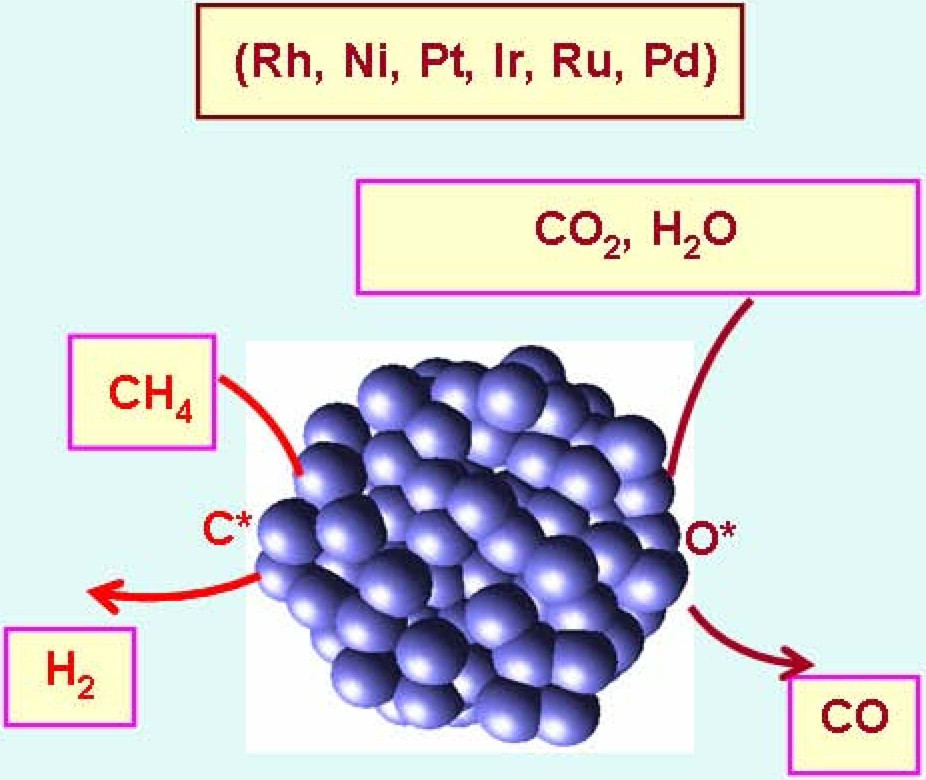

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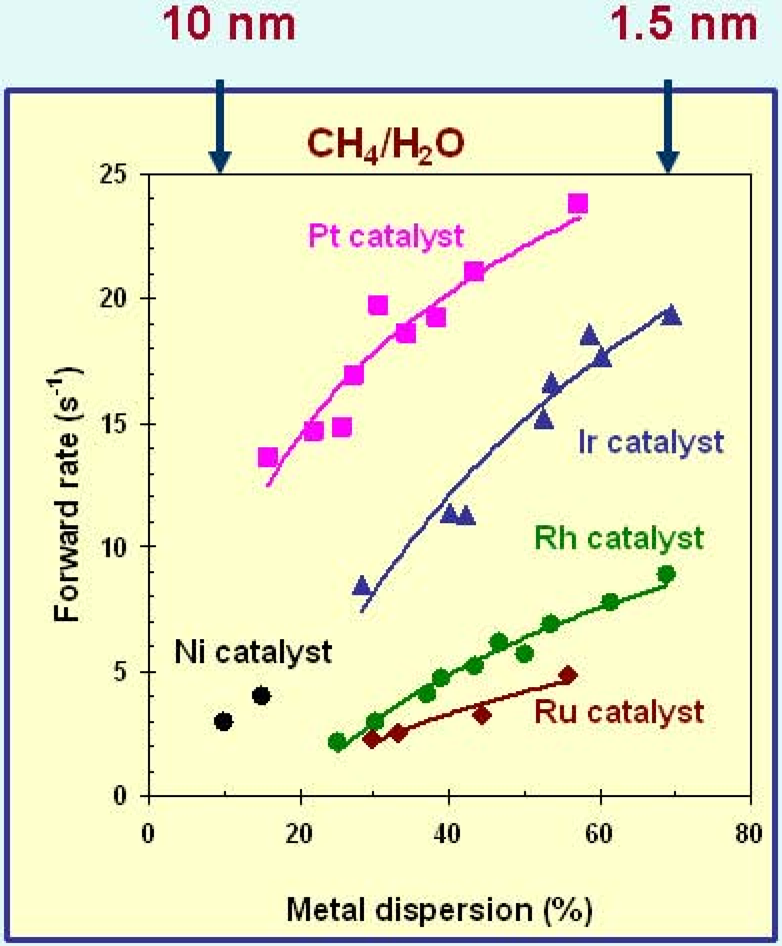

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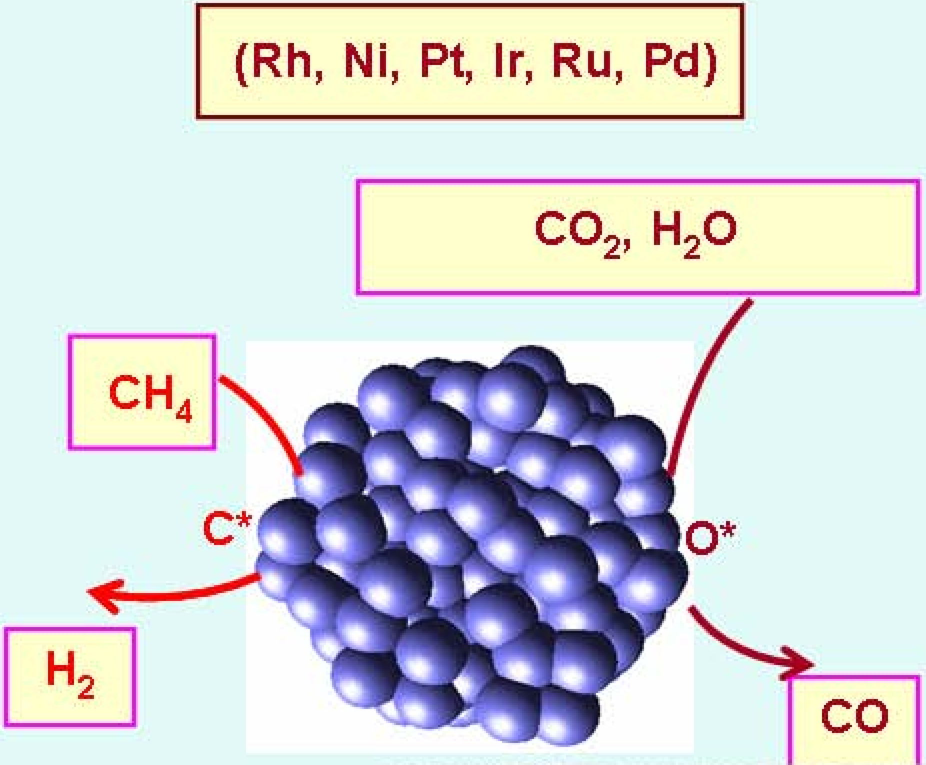


(Rh, Ni, Pt, Ir, Ru, Pd)

CO_2, H_2O

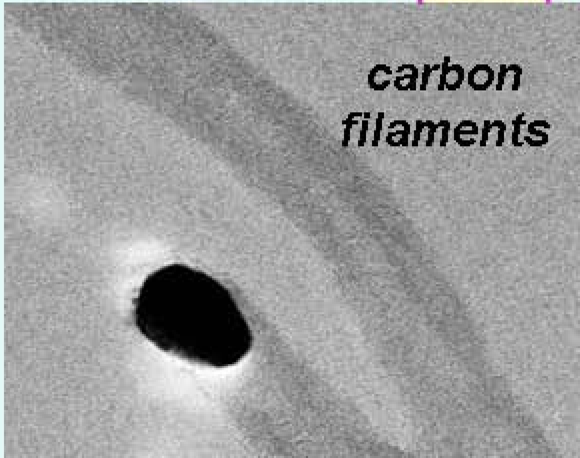
CH_4

C*

O*

H_2

CO



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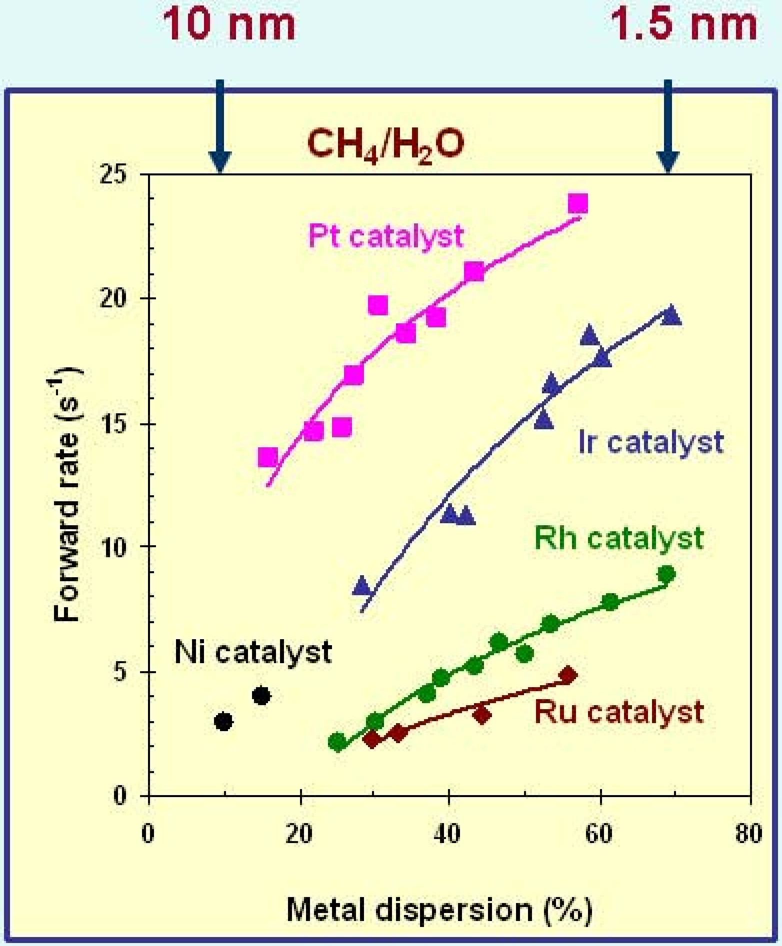

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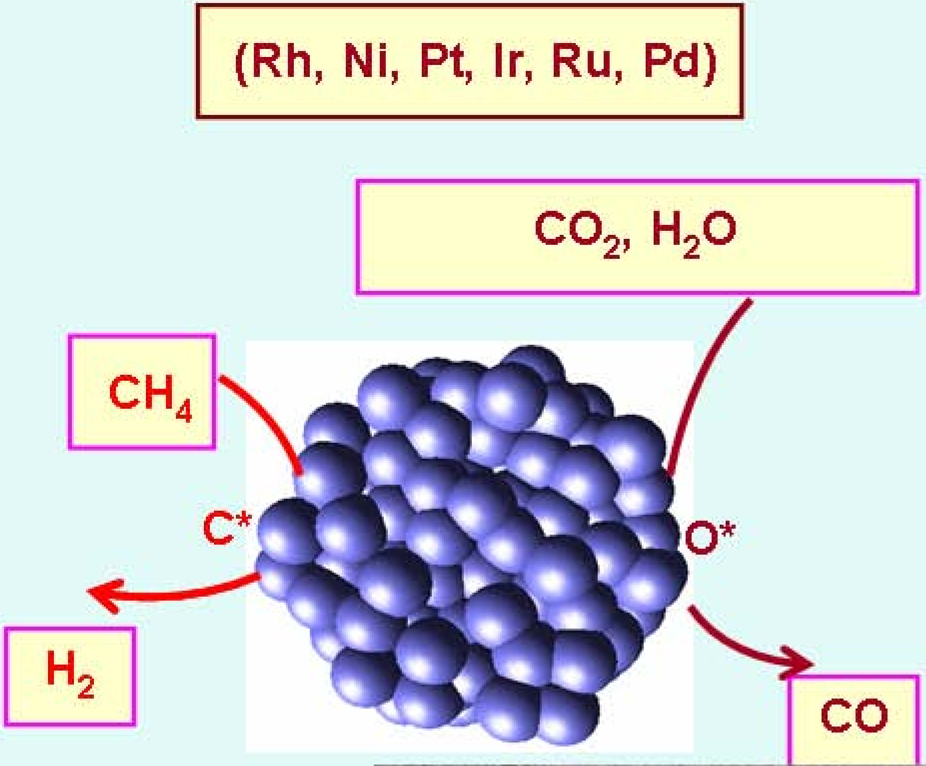

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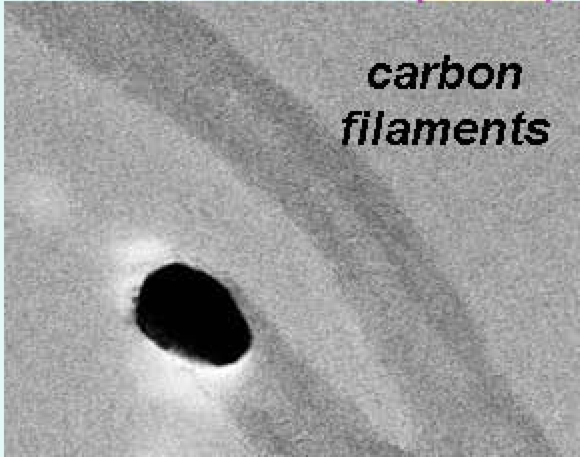
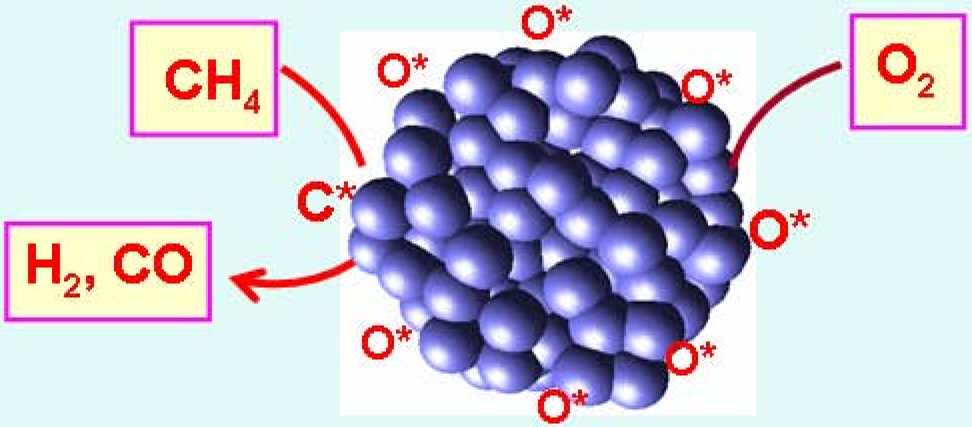


.. but tend not to stay small

CH_4-O_2 REACTIONS: Partial Oxidation and Combustion

catalytic partial oxidation



CH_4

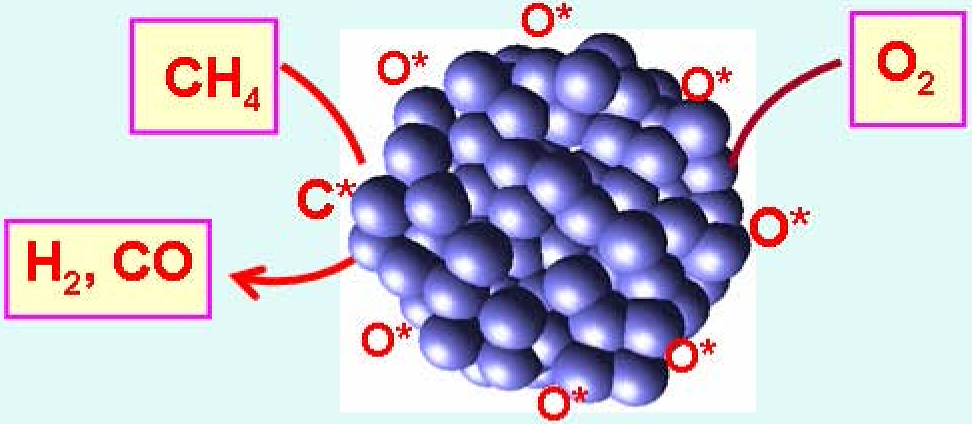
O_2

H_2, CO

- 22 kJ/mol

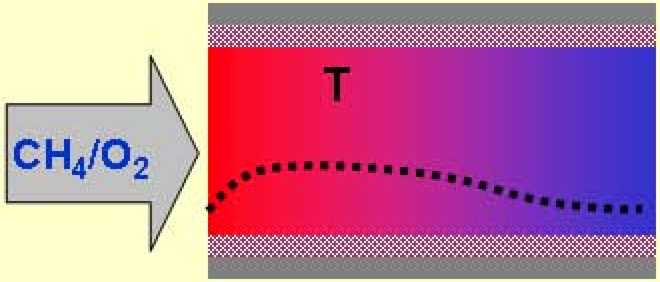
CH_4-O_2 REACTIONS: Partial Oxidation and Combustion

catalytic partial oxidation



- 22 kJ/mol

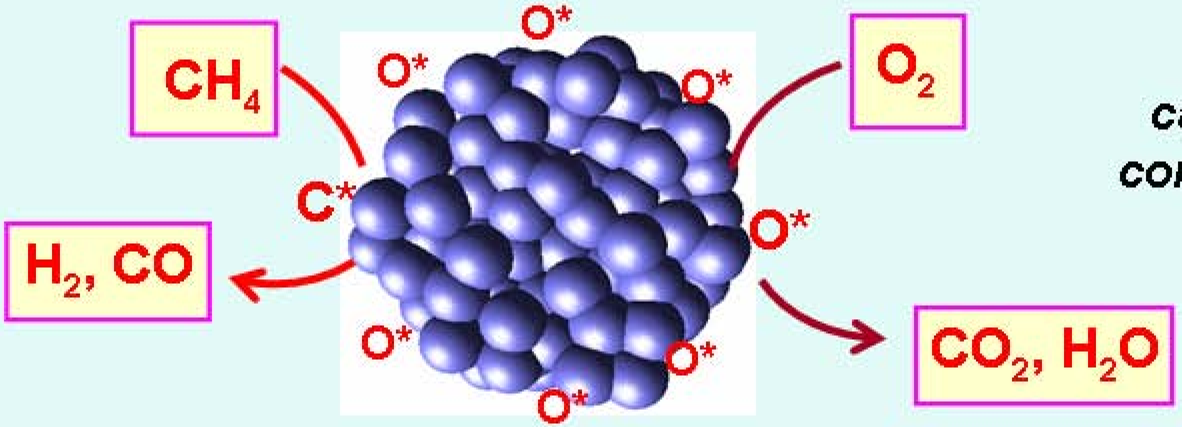
Axial Temperature Profiles



$$2CH_4 + O_2 \longrightarrow 2CO + 4H_2$$

CH_4-O_2 REACTIONS: Partial Oxidation and Combustion

catalytic partial oxidation



CH_4

C^*

H_2, CO

O^*

O_2

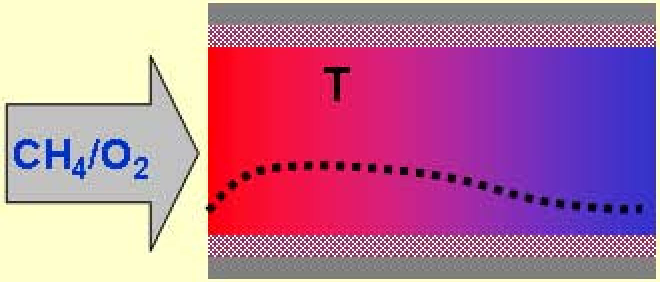
CO_2, H_2O

catalytic combustion

- 22 kJ/mol

- 800 kJ/mol

Axial Temperature Profiles



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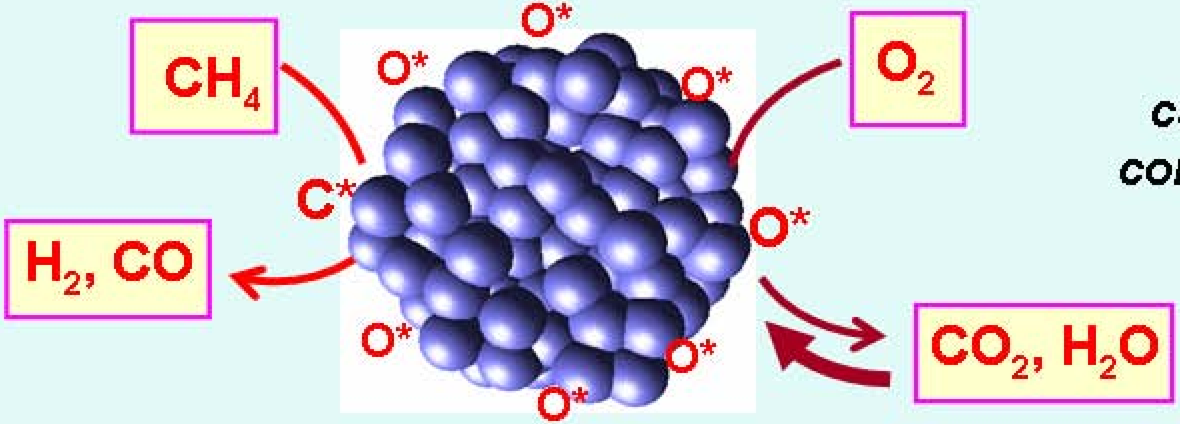

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O_2

H_2, CO

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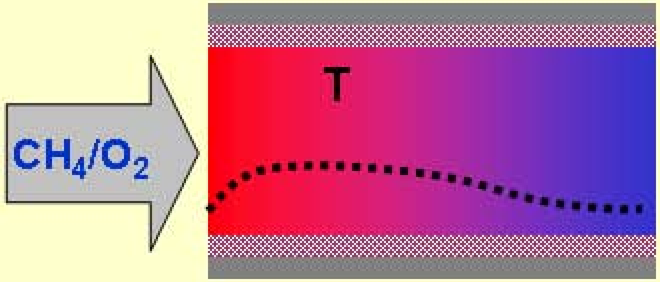

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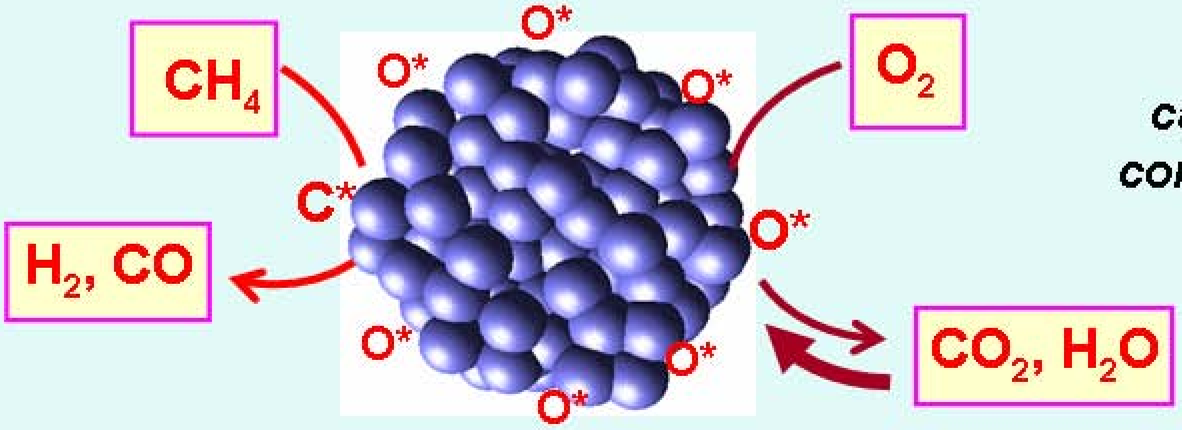

catalytic partial oxidation

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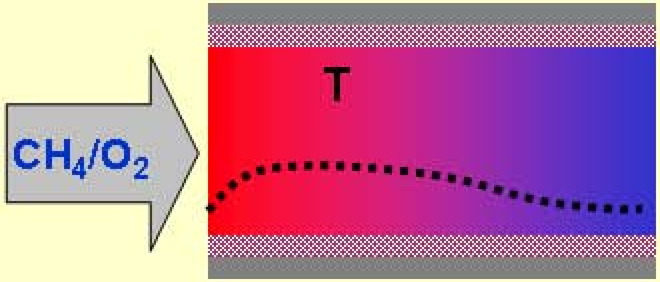
Axial Temperature Profiles



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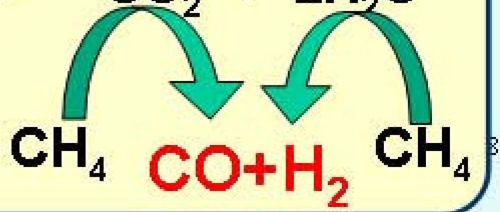
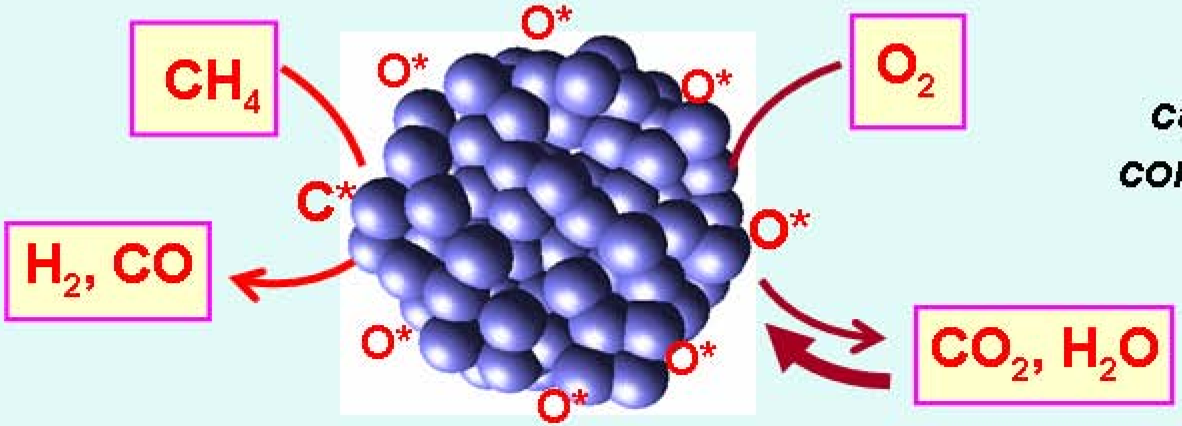


CH_4-O_2 REACTIONS: *Partial Oxidation and Combustion*

catalytic partial oxidation



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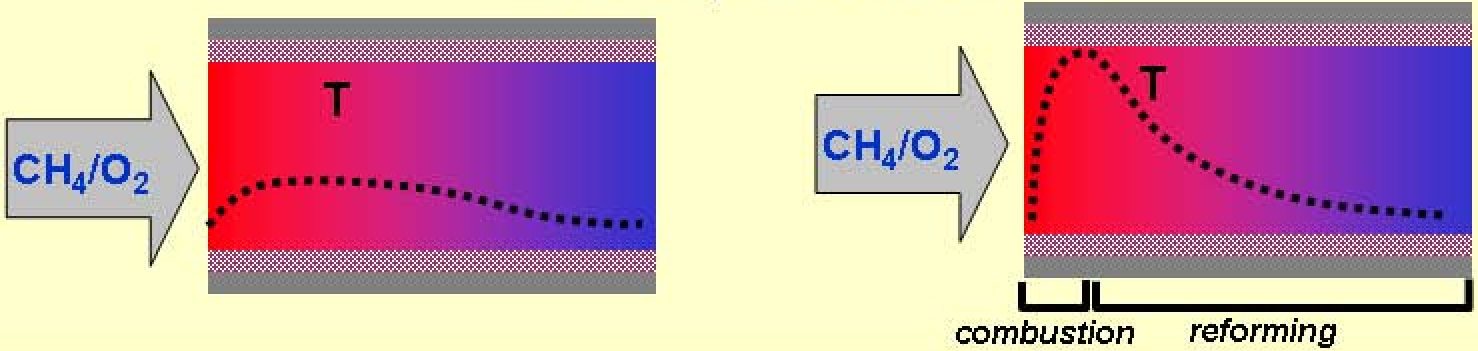
Axial Temperature Profiles



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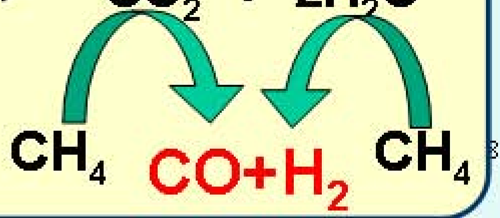
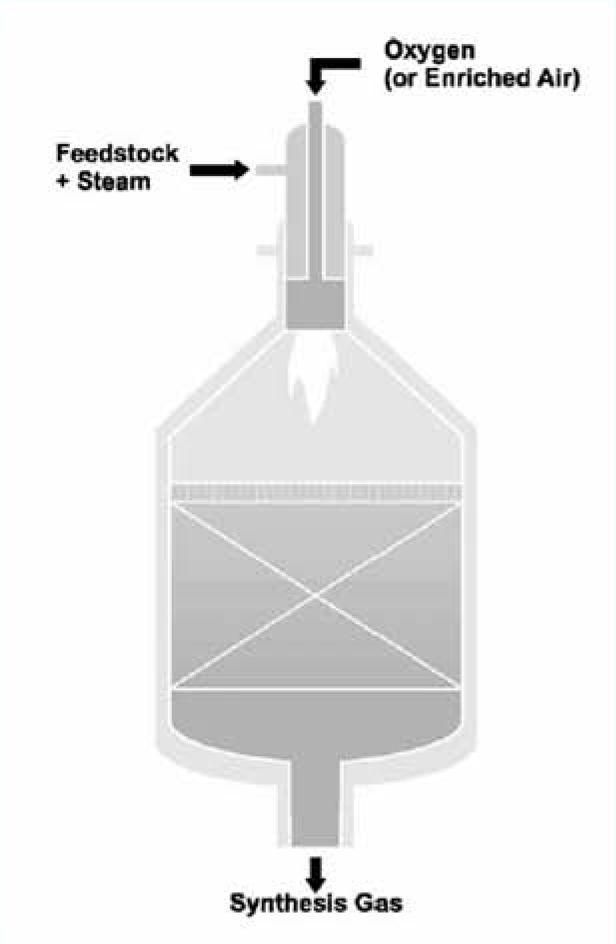
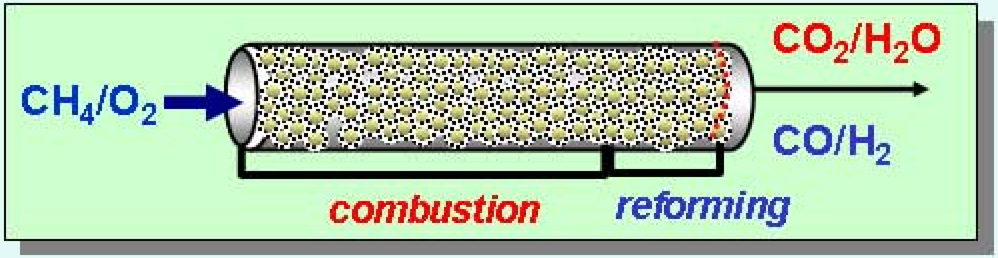


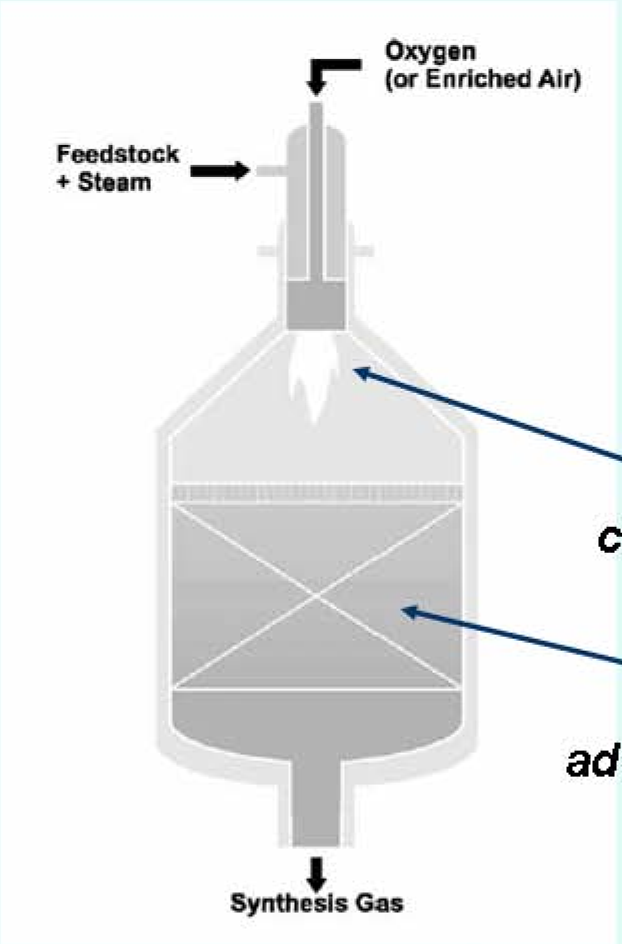
"Partial Oxidation" and Authothermal Reforming





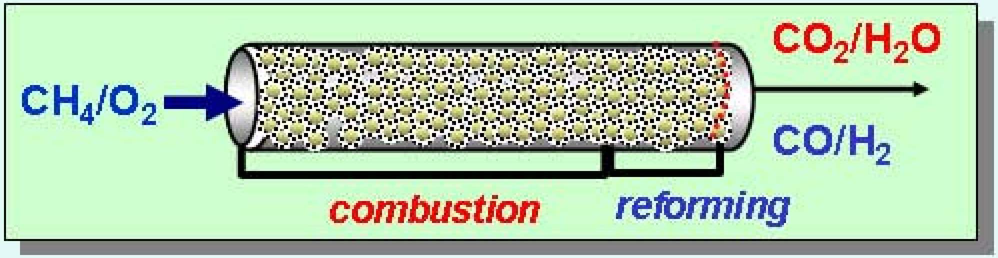
(813 K, 5 kPa CH_4, 5 kPa O_2)

“Partial Oxidation” and Authothermal Reforming



combustion

adiabatic reforming



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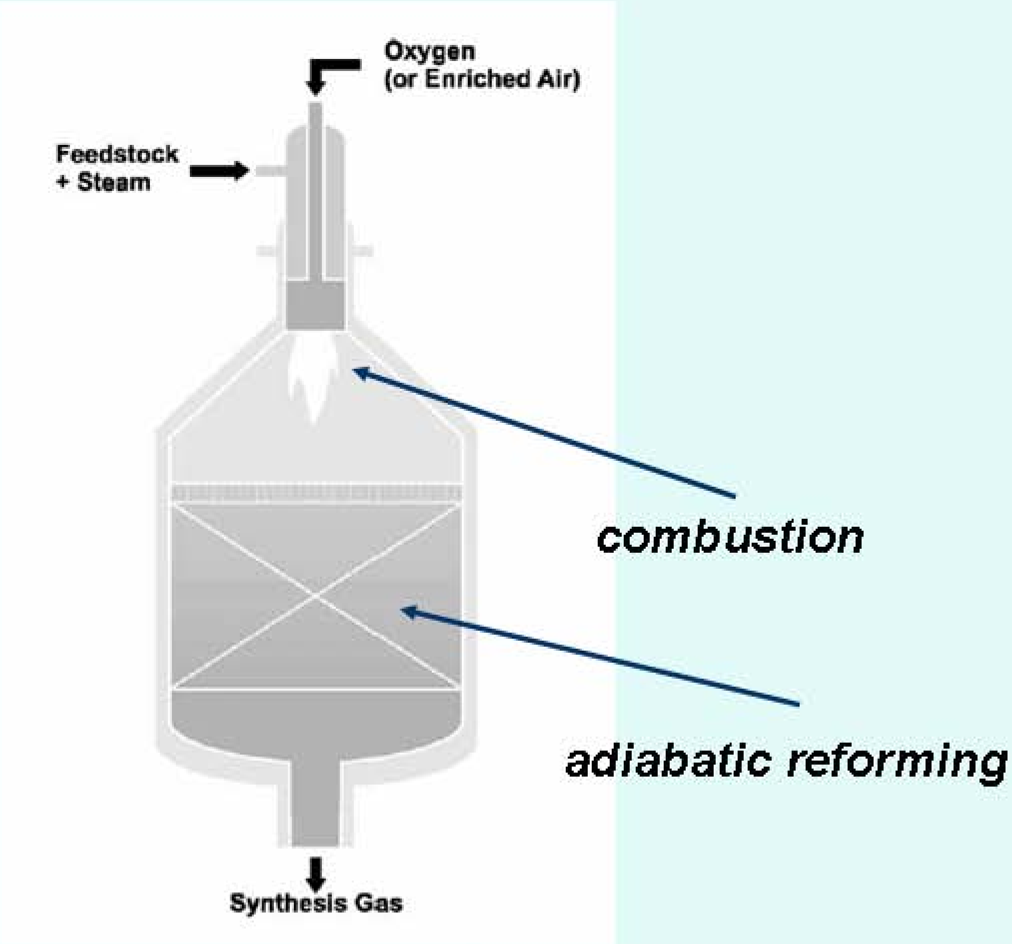
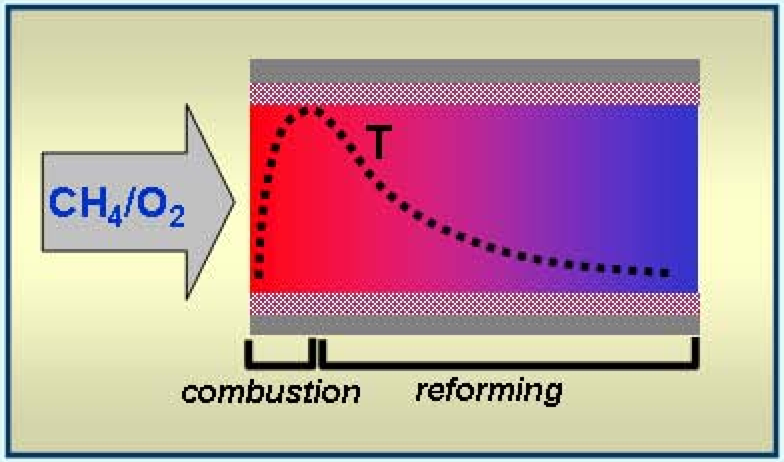
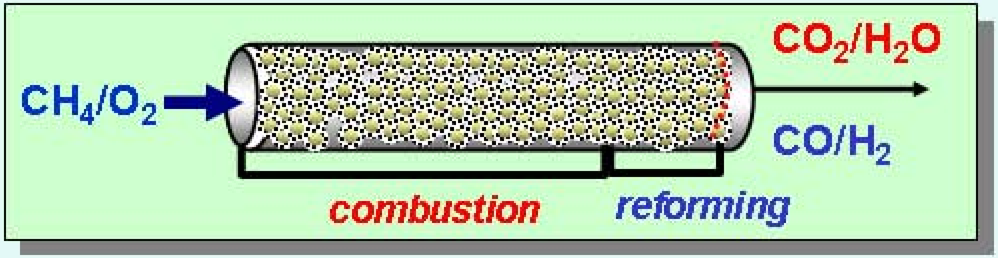


combustion

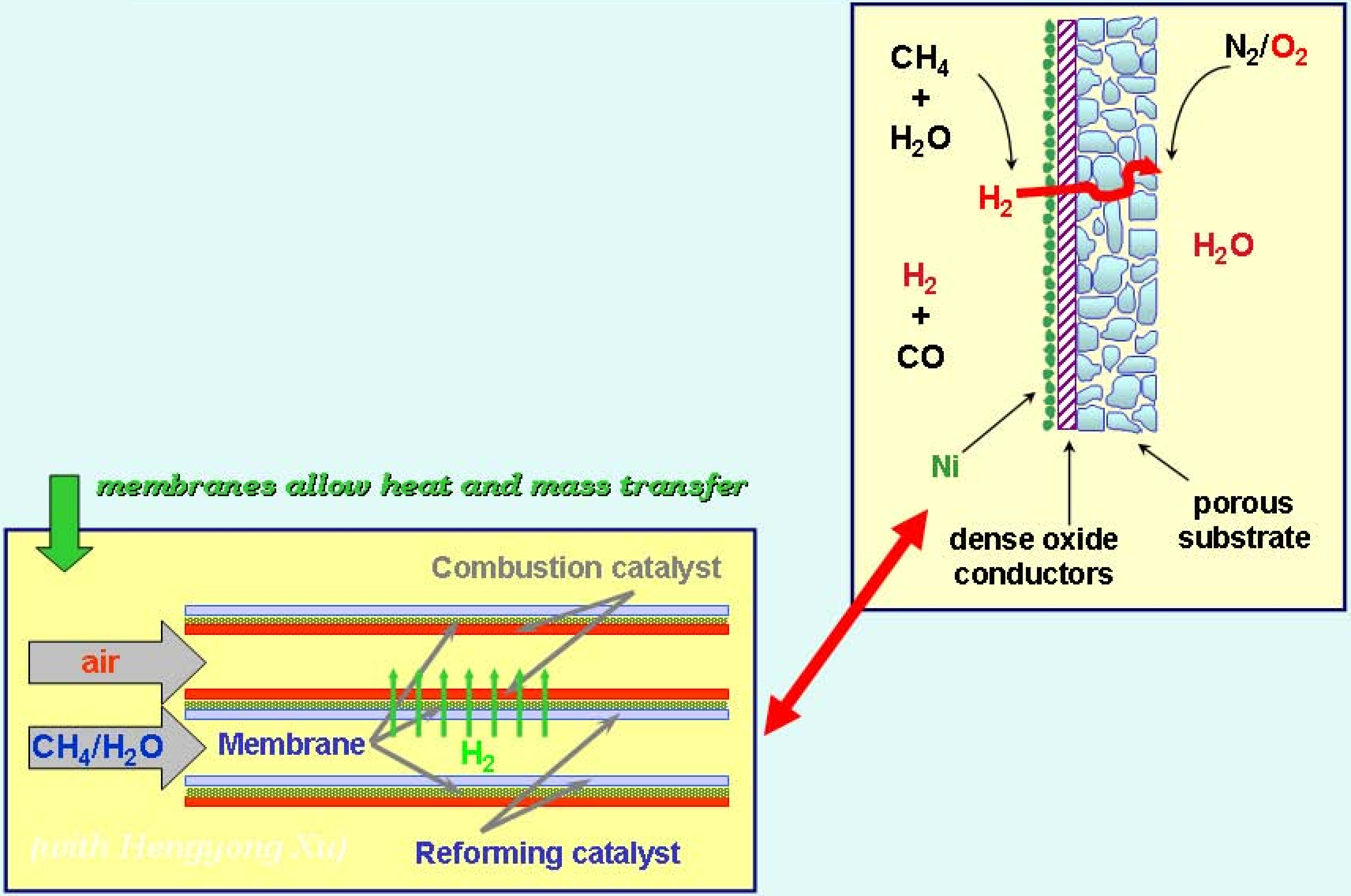
adiabatic reforming





(813 K, 5 kPa CH_4, 5 kPa O_2)

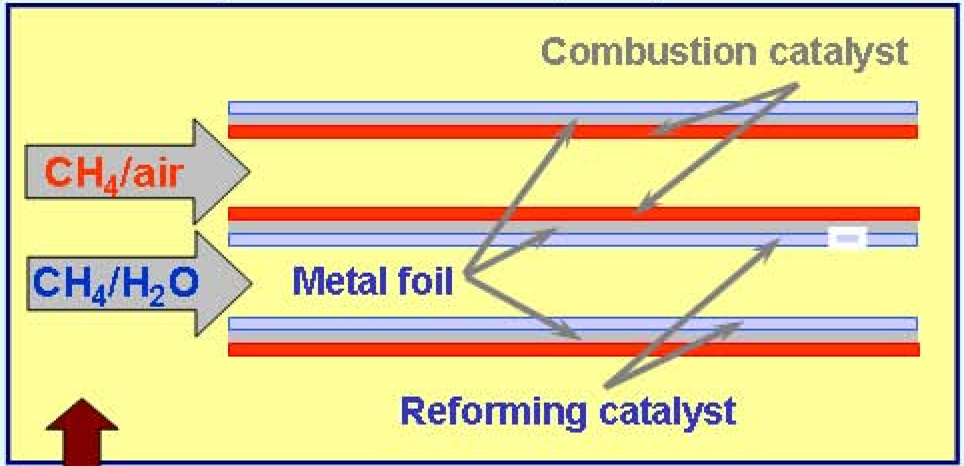
COUPLING ENDOTHERMIC AND EXOTHERMIC REACTIONS ..
………. continuous removal (and combustion) of H_2



(with Hengyong Xu)

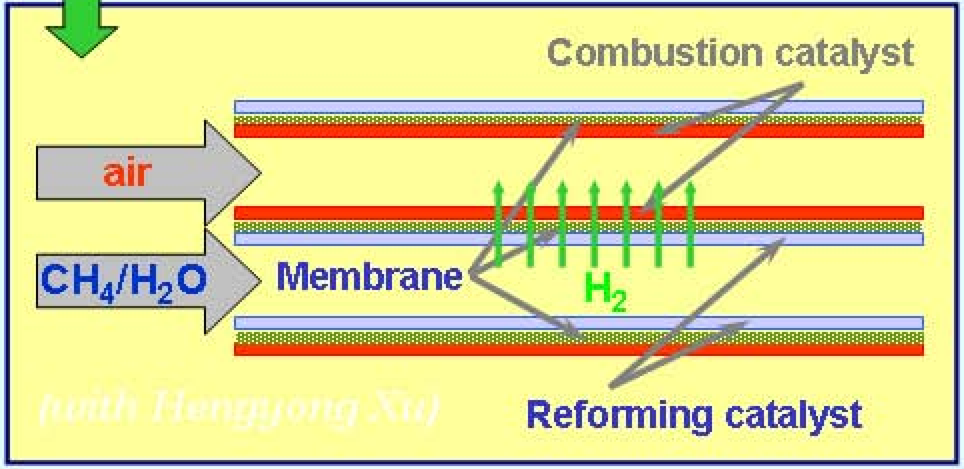
COUPLING ENDOTHERMIC AND EXOTHERMIC REACTIONS ..
………. across a thin plate without boundary layers

Heat integration in catalytic plate reactors



plates allow heat transfer only

membranes allow heat and mass transfer



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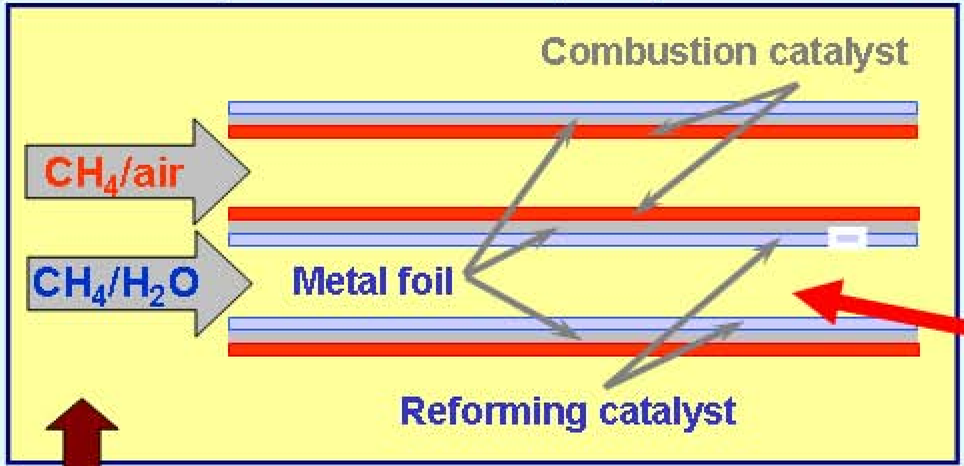

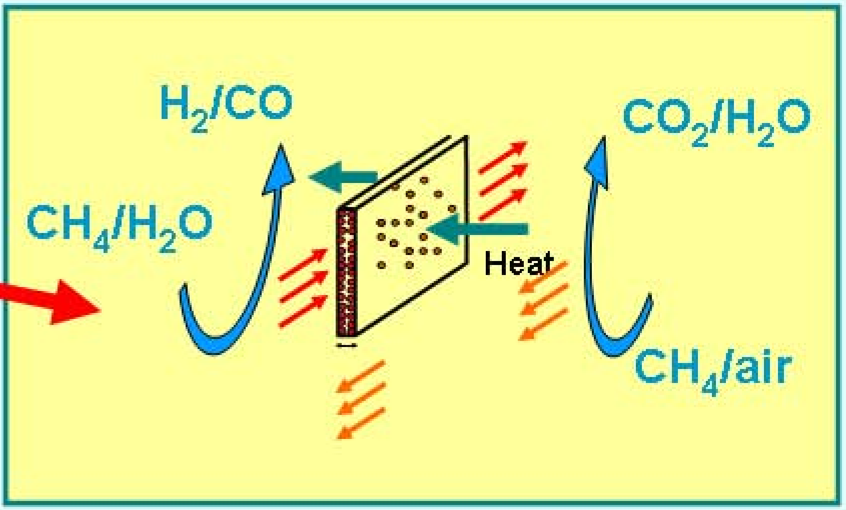

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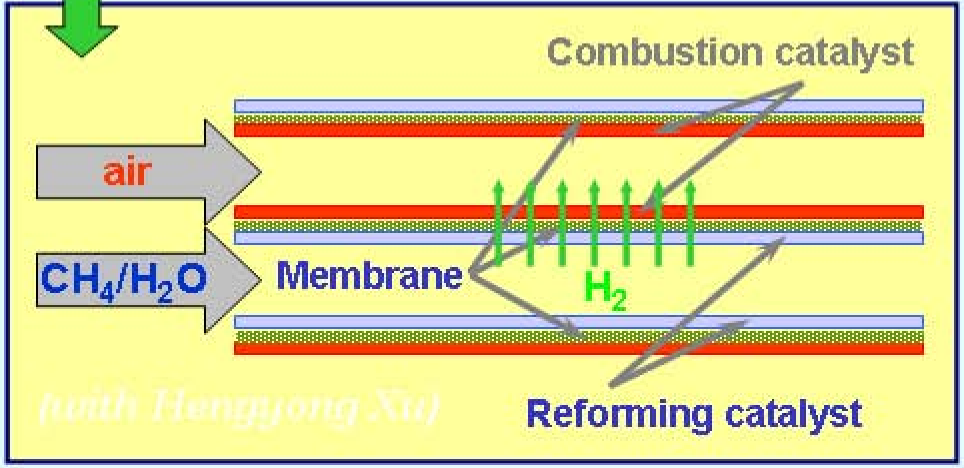
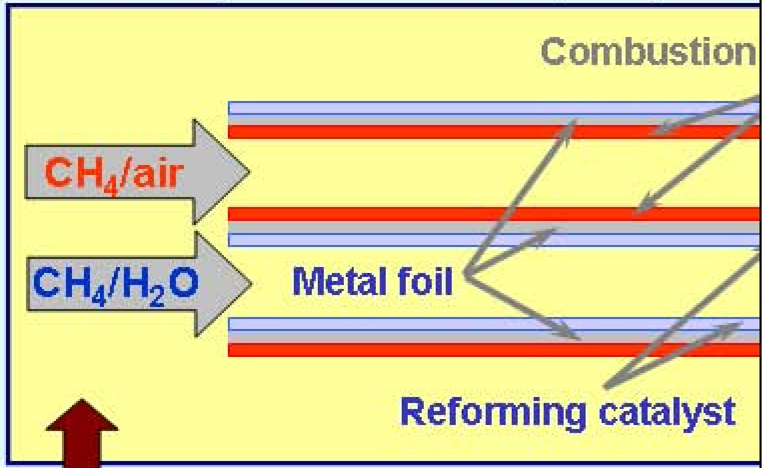
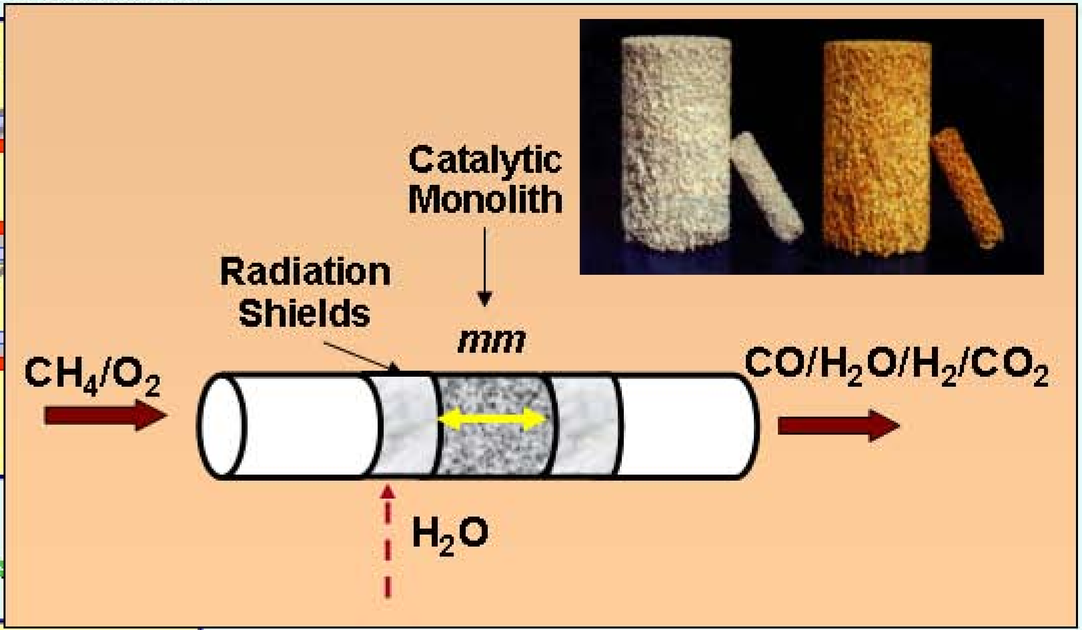


- *couple within short thermal conduction distances*

COUPLING ENDOTHERMIC AND EXOTHERMIC REACTIONS ..
………. across a thin plate without boundary layers

Heat integration in catalytic plate reactors





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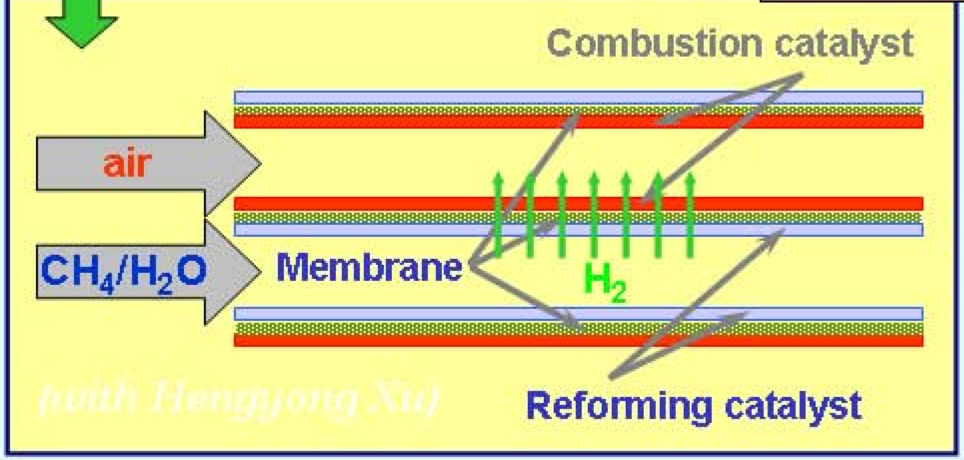


(with Hengyong Xu)

- *couple within short thermal conduction distances*

↓

short monolith reactors

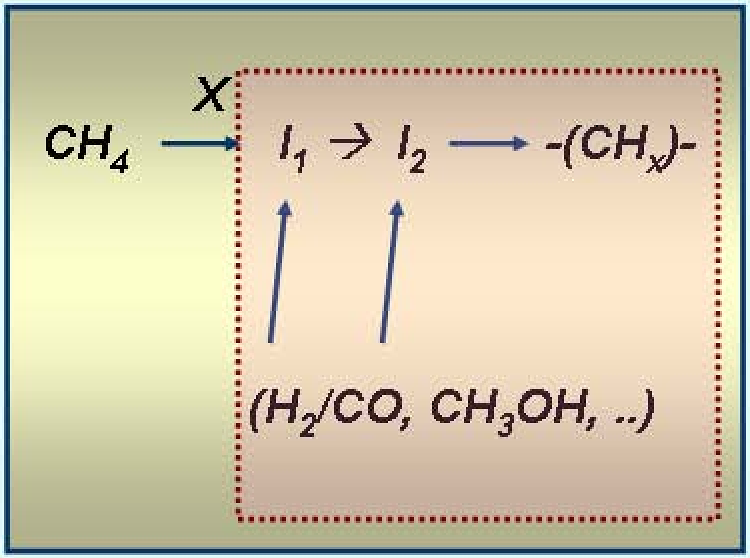
Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} \text{-}(CH_x)\text{-} \longrightarrow (C, CO_x)$$

- *overcome thermodynamic constraints*
- *protect products with weaker C-H bonds*

Indirect Routes



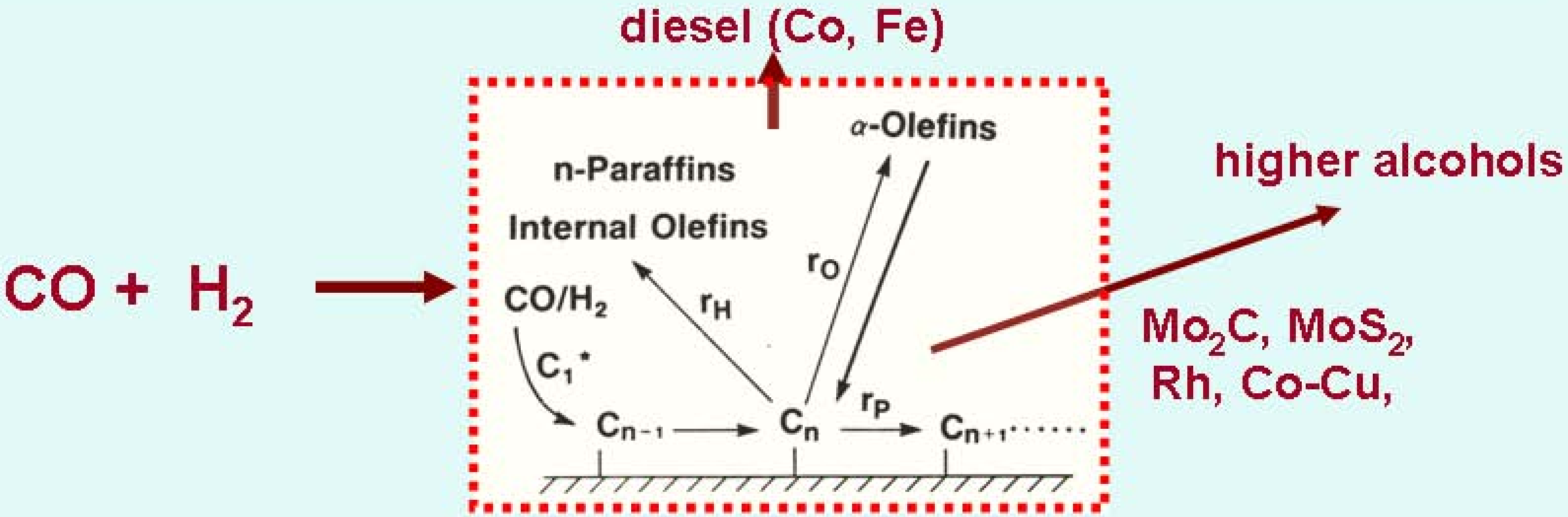
$$CH_4 \xrightarrow{X} I_1 \rightarrow I_2 \longrightarrow \text{-}(CH_x)\text{-}$$

$(H_2/CO, CH_3OH, ..)$

- *couple endothermic-exothermic steps*
- ***form the first carbon-carbon bond***

- ***avoid process complexity***
- ***provide routes to products with large markets***

C-C Bond Formation Bottlenecks in Synthesis Gas Conversion



diesel (Co, Fe)

$CO + H_2$

higher alcohols

Mo_2C, MoS_2, Rh, Co-Cu,

- monomer synthesis and CO activation (assisted by H*?)

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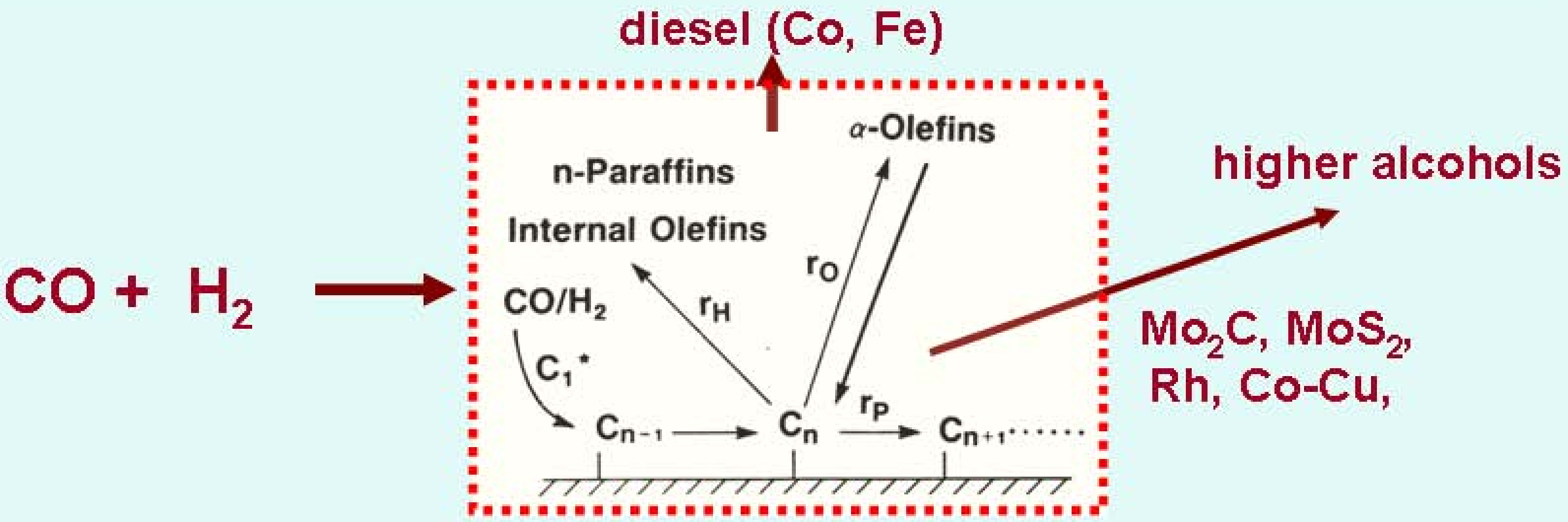
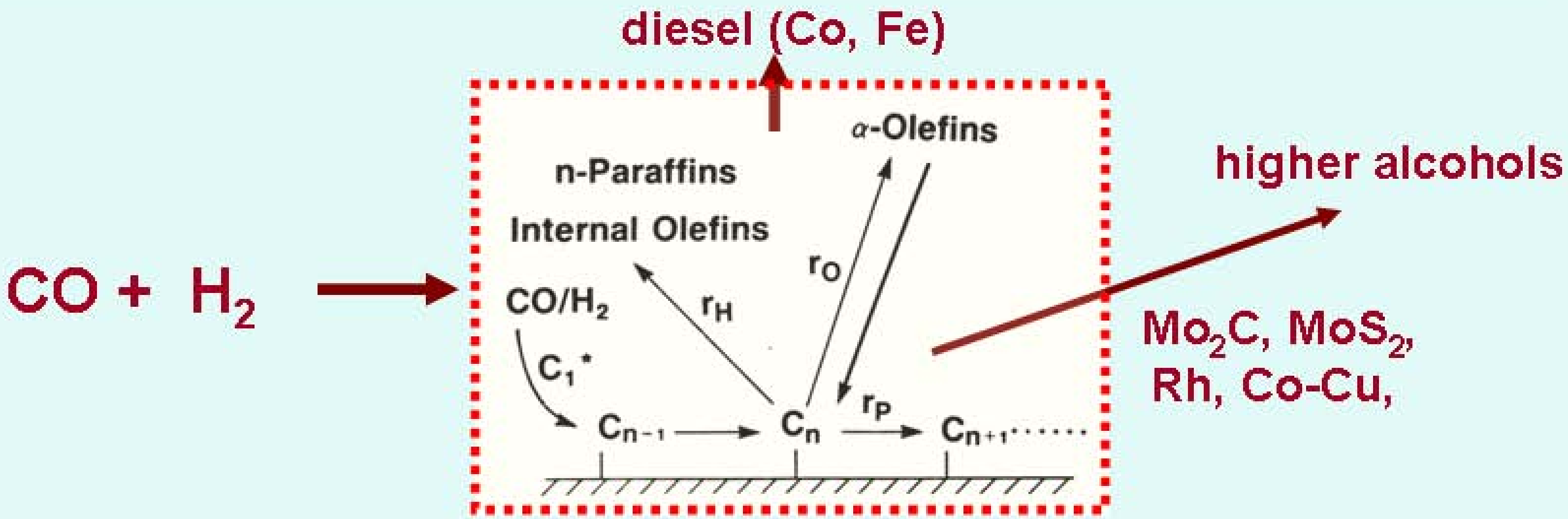


- monomer synthesis and CO activation (assisted by H*?)

$C_1^* \rightarrow C_2^* \rightarrow \ldots\ldots \rightarrow C_n^*$

C-C Bond Formation Bottlenecks in Synthesis Gas Conversion



diesel (Co, Fe)

$CO + H_2$

higher alcohols

Mo_2C, MoS_2, Rh, Co-Cu,

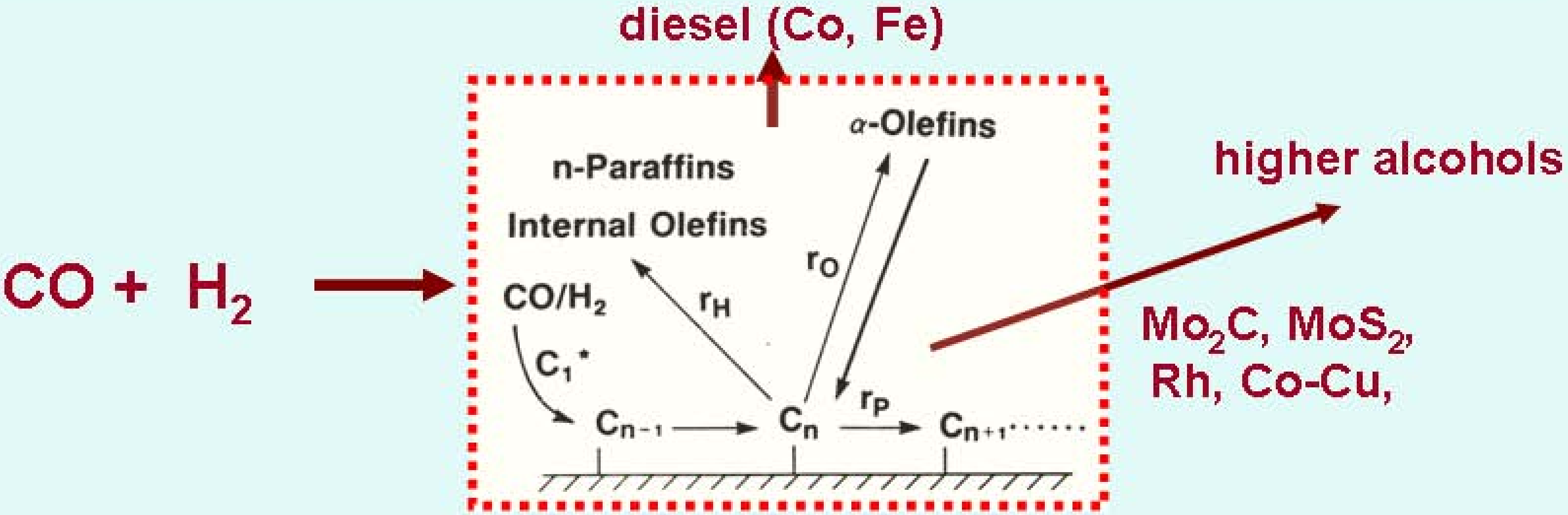
- monomer synthesis and CO activation (assisted by H*?)

Alcohol synthesis

Fischer-Tropsch

$$\begin{tikzcd}
CH_3OH & C_2H_5OH & & C_nH_{2n+1}OH \\
C_1^* \arrow[u] \arrow[r] \arrow[d] & C_2^* \arrow[u] \arrow[r] \arrow[d] & \ldots\ldots \arrow[r] & C_n^* \arrow[u] \arrow[d] \\
CH_4 & C_2H_{4,6} & & C_nH_{2n,\,2(n+1)}
\end{tikzcd}$$

C-C Bond Formation Bottlenecks in Synthesis Gas Conversion



$CO + H_2$

diesel (Co, Fe)

higher alcohols

Mo_2C, MoS_2, Rh, Co-Cu,

- monomer synthesis and CO activation (assisted by H*?)

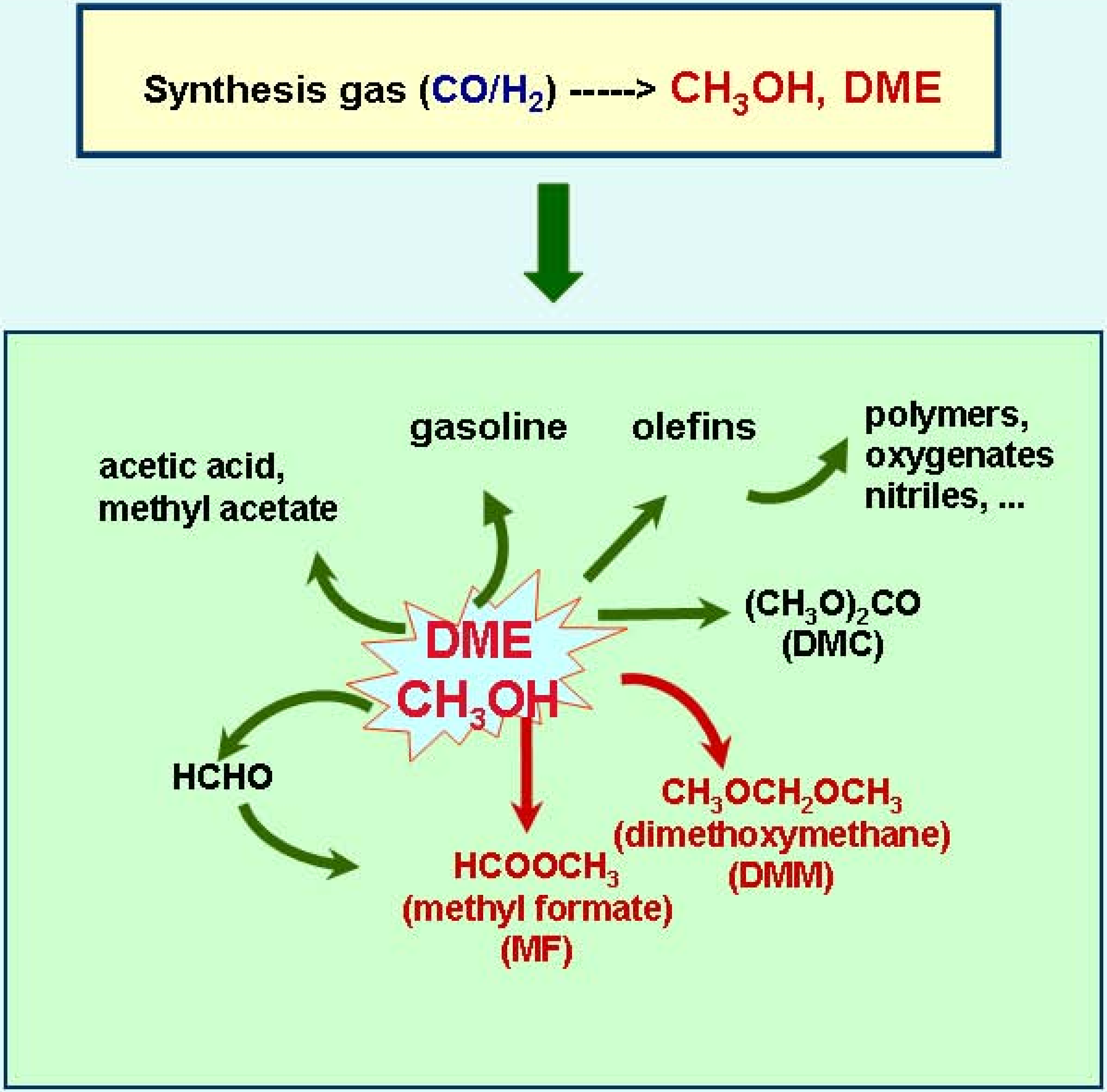
- C_1 bottleneck … formation of initial C-C bond

$$\begin{tikzcd}
& CH_3OH & C_2H_5OH & & & C_nH_{2n+1}OH \\
\text{Alcohol synthesis} & & & & & \\
& C_1^* \arrow[uu] \arrow[dd] \arrow[r] & C_2^* \arrow[uu] \arrow[dd] \arrow[r] & \text{……} \arrow[r] & & C_n^* \arrow[uu] \arrow[dd] \\
\text{Fischer-Tropsch} & & & & & \\
& CH_4 & C_2H_{4,6} & & & C_nH_{2n,\ 2(n+1)}
\end{tikzcd}$$

Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H_2) -----> CH_3OH, DME

Catalytic conversion of methanol and dimethylether



Synthesis gas (CO/H_2) -----> CH_3OH, DME

DME

CH_3OH

acetic acid,
methyl acetate

gasoline

olefins

polymers,
oxygenates
nitriles, ...

$(CH_3O)_2CO$
(DMC)

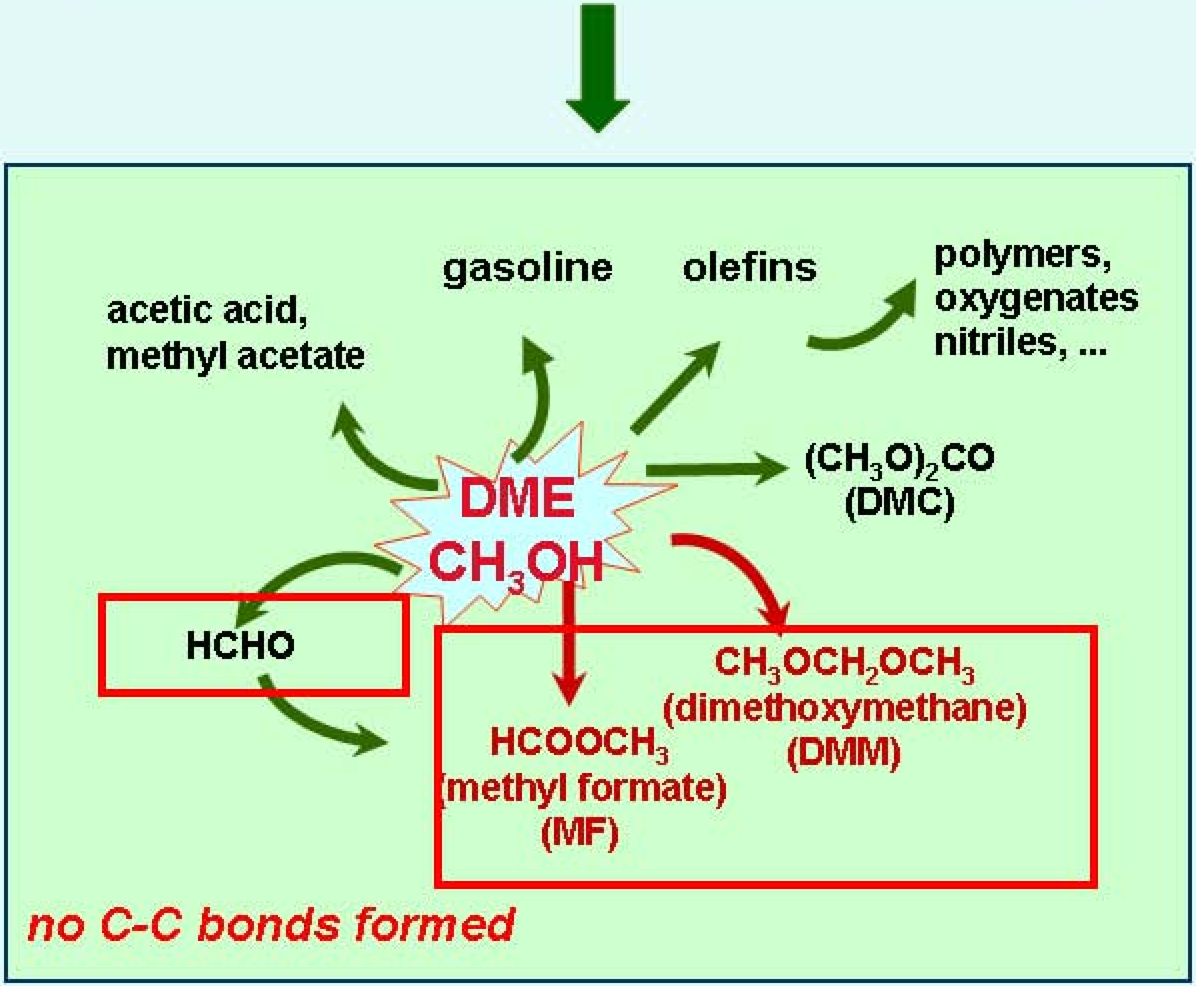
HCHO

$HCOOCH_3$
(methyl formate)
(MF)

$CH_3OCH_2OCH_3$
(dimethoxymethane)
(DMM)

Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H_2) -----> CH_3OH, DME



DME

CH_3OH

acetic acid,
methyl acetate

gasoline

olefins

polymers,
oxygenates
nitriles, ...

$(CH_3O)_2CO$
(DMC)

HCHO

$HCOOCH_3$
(methyl formate)
(MF)

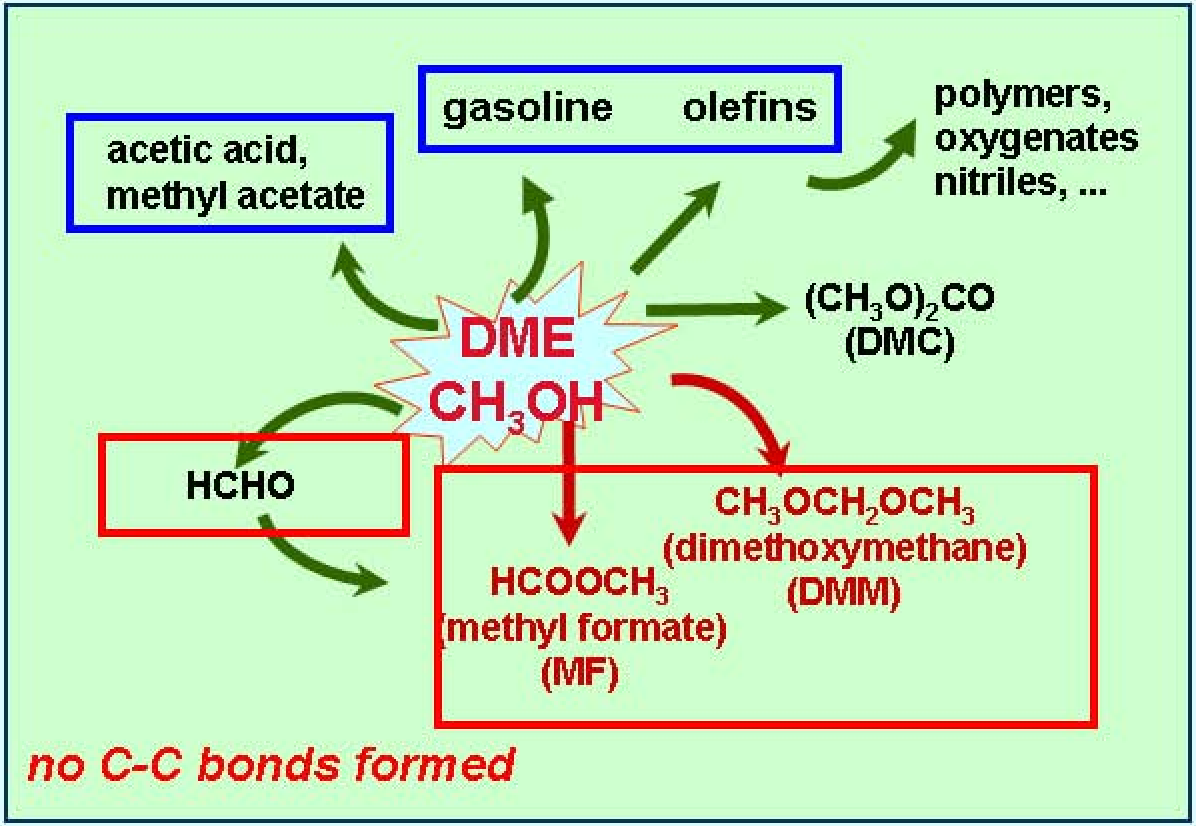
$CH_3OCH_2OCH_3$
(dimethoxymethane)
(DMM)

no C-C bonds formed

Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H_2) -----> CH_3OH, DME

Chemistry on solid acids limited by formation of the first C-C bond



DME

CH_3OH

acetic acid,
methyl acetate

gasoline olefins

polymers,
oxygenates
nitriles, ...

$(CH_3O)_2CO$
(DMC)

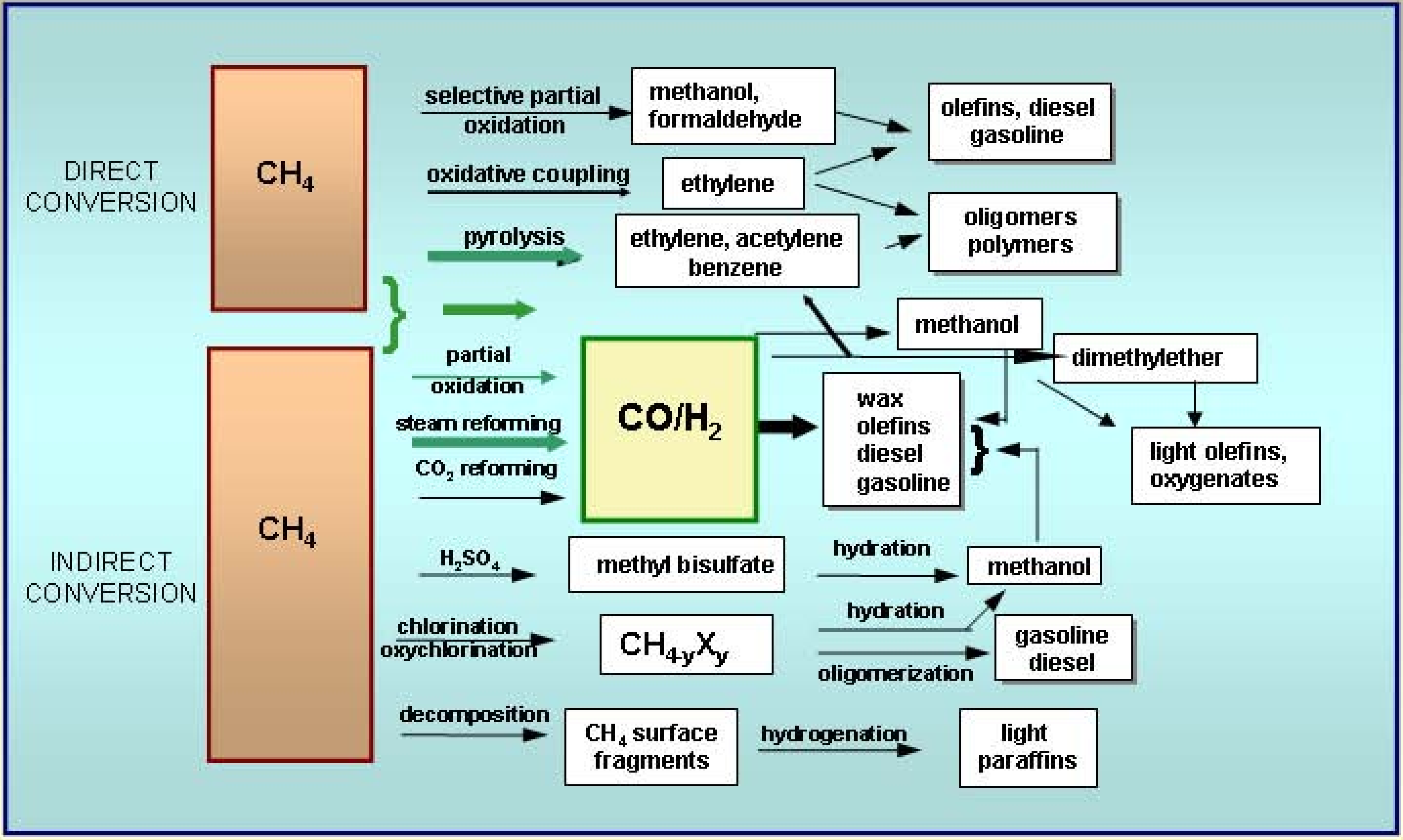
HCHO

$HCOOCH_3$
(methyl formate)
(MF)

$CH_3OCH_2OCH_3$
(dimethoxymethane)
(DMM)

no C-C bonds formed

Refining Methane into Useful Products



.... in a Methane "Refinery"

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} \text{-}(CH_x)\text{-} \longrightarrow (C,\ CO_x)$$

- *overcome thermodynamic constraints*
- *protect products with weaker C-H bonds*

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} -(CH_x)- \longrightarrow (C, CO_x)$$

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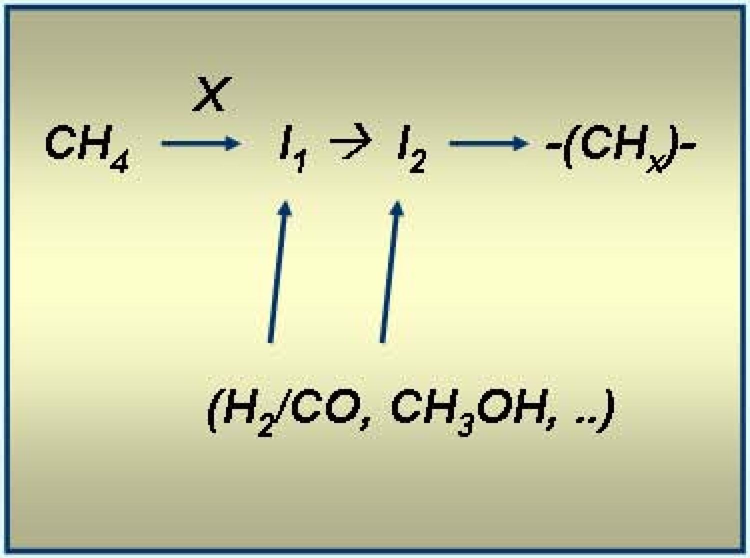
Indirect Routes



- *couple endothermic-exothermic steps*
- *form the first carbon-carbon bond*

Challenges in bringing CH_4 to markets by chemical means

Direct Routes

$$CH_4 \xrightarrow{X} -(CH_x)- \longrightarrow (C, CO_x)$$

- overcome thermodynamic constraints
- protect products with weaker C-H bonds

Indirect Routes

$$\begin{tikzcd}
CH_4 \arrow[r, "X"] & I_1 \arrow[r] & I_2 \arrow[r] & -(CH_x)- \\
 & (H_2/CO,\ CH_3OH,\ ..) \arrow[u] \arrow[ur] & &
\end{tikzcd}$$

- couple endothermic-exothermic steps
- form the first carbon-carbon bond

- **avoid process complexity**
- **decrease cost of oxidant (X)**

Using methane *indirectly*

$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[Ni]} CO(g) + 3\,H_2(g)$ $\Delta H° = 49.3$ kcal/mol

"Syngas" ($CO + nH_2$) is currently used to produce methanol, Fischer-Tropsch'd to hydrocarbons and water, and is water-gas shifted to pure H_2 for ammonia synthesis, *etc.*.

Indirect (*i.e.* via syngas) processes could provide very valuable products, but (except for methanol and acetic acid) catalysts are not currently known or not yet practical.

1. $CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[Ni]} CO(g) + 3\,H_2(g)$ $\Delta H^\circ = 49.3$ kcal/mol

2. $CO(g) + 2\,H_2(g) \xrightarrow[80\text{ atm, }250\ ^\circ C]{[Cu/ZnO/Al_2O_3]} CH_3OH(g)$ $\Delta H^\circ = -21.7$ kcal/mol

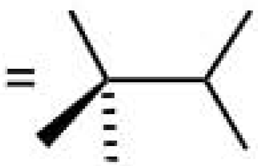
3. $CH_3OH(g) + CO(g) \xrightarrow[[I^-],\ 35\text{ atm, }180\ ^\circ C]{[Rh\text{ or }Ir]\ \textit{homogeneous}} CH_3COOH(g)$ $\Delta H^\circ = -29.4$ kcal/mol

4. $2\,CO(g) + 4\,H_2(g) \xrightarrow{\textit{catalyst ?}} CH_3CH_2OH(g)$ $\Delta H^\circ = -61.2$ kcal/mol

5. $2\,CO(g) + 3\,H_2(g) \xrightarrow{\textit{catalyst ?}} HOCH_2CH_2OH(g)$ $\Delta H^\circ = -55.8$ kcal/mol

6. $2\,CO(g) + 4\,H_2(g) \xrightarrow{\textit{catalyst ?}} CH_2{=}CH_2(g) + 2\,H_2O(g)$ $\Delta H^\circ = -50.3$ kcal/mol

There are plenty of opportunities for important developments in syngas catalysis.

$CH_3OH \xrightarrow[200\ ^\circ C]{ZnI_2\text{ or }InI_3} H_2O$ + hydrocarbons (~20% triptane = )

octane rating = 102

Direct methane conversion: what is possible?

indirect routes

reform CH_4 to CO + H_2; use syngas to produce methanol, acetic acid, FT to HC's, *etc*:

$$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[Ni]} CO(g) + 3\,H_2(g)$$

$\Delta H° = 49.3$ kcal/mol

direct routes

$CH_4 + CO \rightleftharpoons CH_3CHO$ *uphill*: $\Delta H° = 4.6$ kcal/mol

$CH_4 + CO_2 \rightleftharpoons CH_3CO_2H$ *uphill*: $\Delta H° = 8.2$ kcal/mol

$CH_4 + CH_2{=}CH_2 \longrightarrow CH_3CH_2CH_3$ *downhill*: $\Delta H° = -19.4$ kcal/mol, but product less valuable than $CH_2{=}CH_2$

$CH_4 + CO + H_2 \xrightarrow{??} CH_3CH_2OH$ *downhill*: $\Delta H° = -11.9$ kcal/mol, but FT typically does not re-incorporate RH products

Oxidative direct routes potentially offer many desirable products (thermodynamics are favorable for most):

$$CH_4(g) + 1/2\ O_2(g) \xrightarrow{\textit{catalyst?}} CH_3OH(g) \qquad \Delta H^\circ = -30.7\ \text{kcal/mol}$$

$$2\ CH_4(g) + 1/2\ O_2(g) \xrightarrow{\textit{catalyst?}} CH_3CH_3(g) + H_2O(g) \qquad \Delta H^\circ = -60.1\ \text{kcal/mol}$$

$$CH_4(g) + CH_3CH_3(g) + 1/2\ O_2(g) \xrightarrow{\textit{catalyst?}} CH_3CH_2CH_3(g) + H_2O(g) \qquad \Delta H^\circ = -62.4\ \text{kcal/mol}$$

etc.

$$2\ CH_4(g) + O_2(g) \xrightarrow{\textit{catalyst?}} CH_2{=}CH_2(g) + 2\ H_2O \qquad \Delta H^\circ = -67.3\ \text{kcal/mol}$$

Similarly, *selective* partial oxidations of alkanes to value-added products, alcohols, olefins, epoxides, *etc.*, would be much more efficient than currently used technologies.

but obtaining useful selectivity at high conversion is very difficult…
hydrocarbons and O_2 are susceptible to an *autoxidation* mechanism

Methane monooxygenase manages to avoid over-oxidation by using a highly engineered binding pocket

$$CH_4 + O_2 + 2e^- + 2H^+ \xrightarrow{[MMO]} CH_3OH + H_2O$$

or

$$CH_4 + NADH + O_2 + H^+ \xrightarrow{[MMO]} CH_3OH + NAD^+ + H_2O$$

soluble MMO consists of (1) an Fe_2 hydroxylase (MMOH, 251 kD),
(2) an Fe_2S_2-flavin reductase (MMOR, 39 kD),
(3) a regulatory protein (component B, 15 kD).

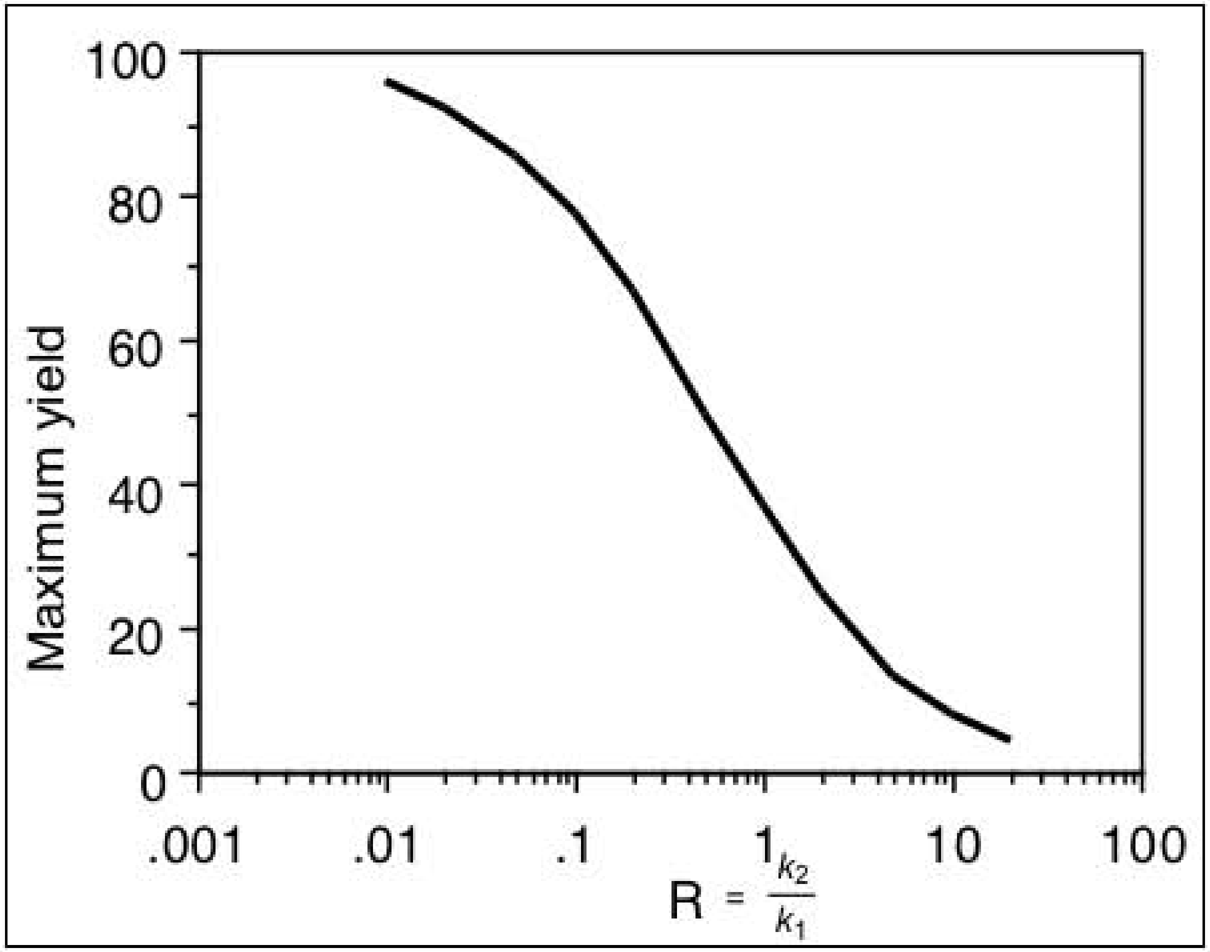
crystal structure (Lippard et al) reveals two juxtaposed canyon regions formed by α and β subunits, with the dinuclear iron centers residing just 12 Å above the canyon floor.

Methanol is expelled from highly hydrophobic binding pocket much faster than MMO “machinery is re-charged” with e^-’s, H^+’s and O_2.

Synthetic models will likely involve complex architecture…?

Constraints on maximum yield for conventional solid catalysts:

High temperature, *heterogeneously* catalyzed oxidations of methane are subject to severe constraints on selectivity/yield; products more reactive ⇒ not possible to obtain high yield and high selectivity together.

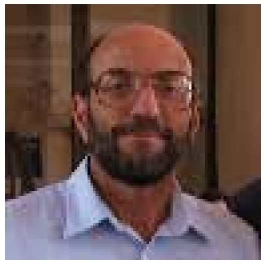


e.g. for oxidation of methane to methanol:

$$CH_4 + Q\bullet \xrightarrow{k_1} CH_3\bullet + QH \ (Q\bullet = HO\bullet, MO, ...)$$

$$CH_3OH + Q\bullet \xrightarrow{k_2} HOCH_2\bullet + QH$$

k_2/k_1 is typically 20 to 100, implying maximum yield ≈ 4%; agrees with (reproducible) literature.

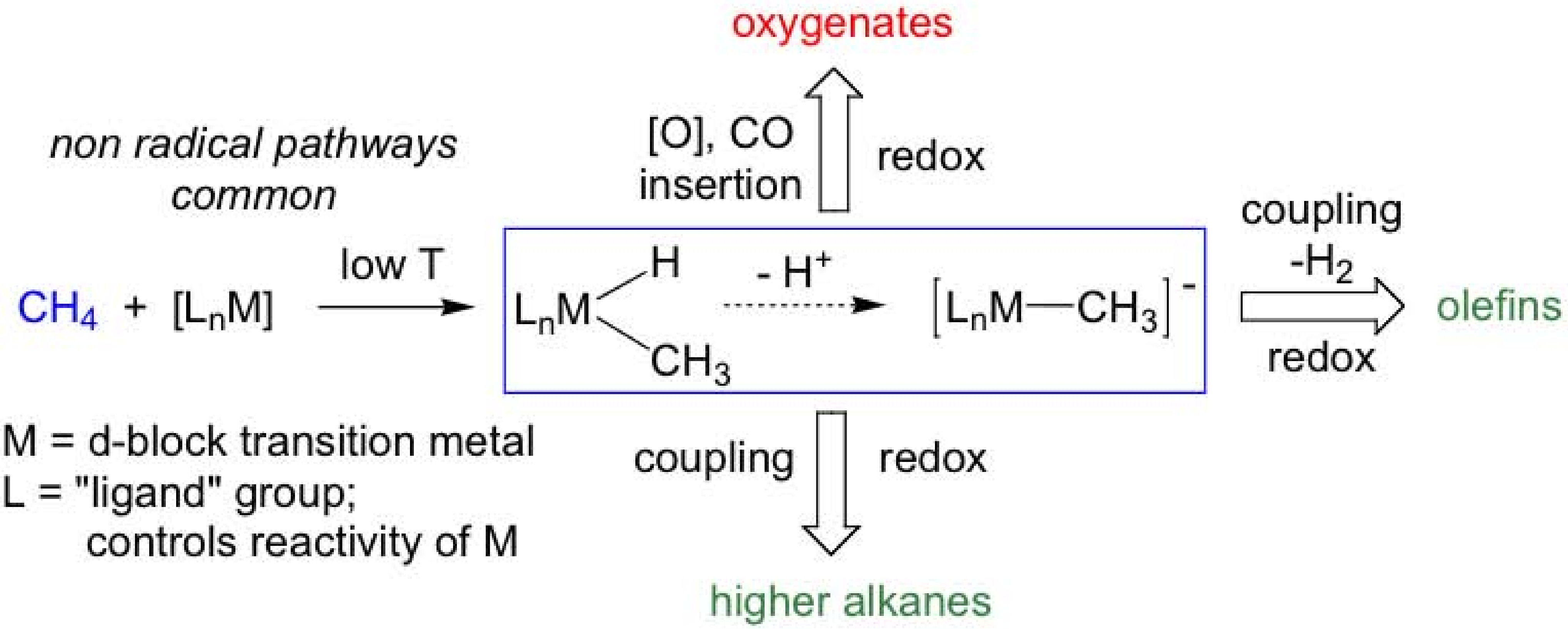


"Labinger Limit"

Homogeneously catalyzed reactions may proceed by non-radical pathways, and thus, potentially offer more desirable selectivity and yield.

Soluble (homogeneous catalytic) systems for CH_4 oxidations potentially offer a range of advantages:

approaches using organotransition metal chemistry:



non radical pathways common

CH_4 + $[L_nM]$ $\xrightarrow{\text{low T}}$ $L_nM(H)(CH_3)$ $\overset{-H^+}{\dashrightarrow}$ $[L_nM{-}CH_3]^-$

oxygenates: [O], CO insertion; redox

olefins: coupling, $-H_2$; redox

higher alkanes: coupling; redox

M = d-block transition metal
L = "ligand" group;
controls reactivity of M

A particularly promising “electrophilic” system:

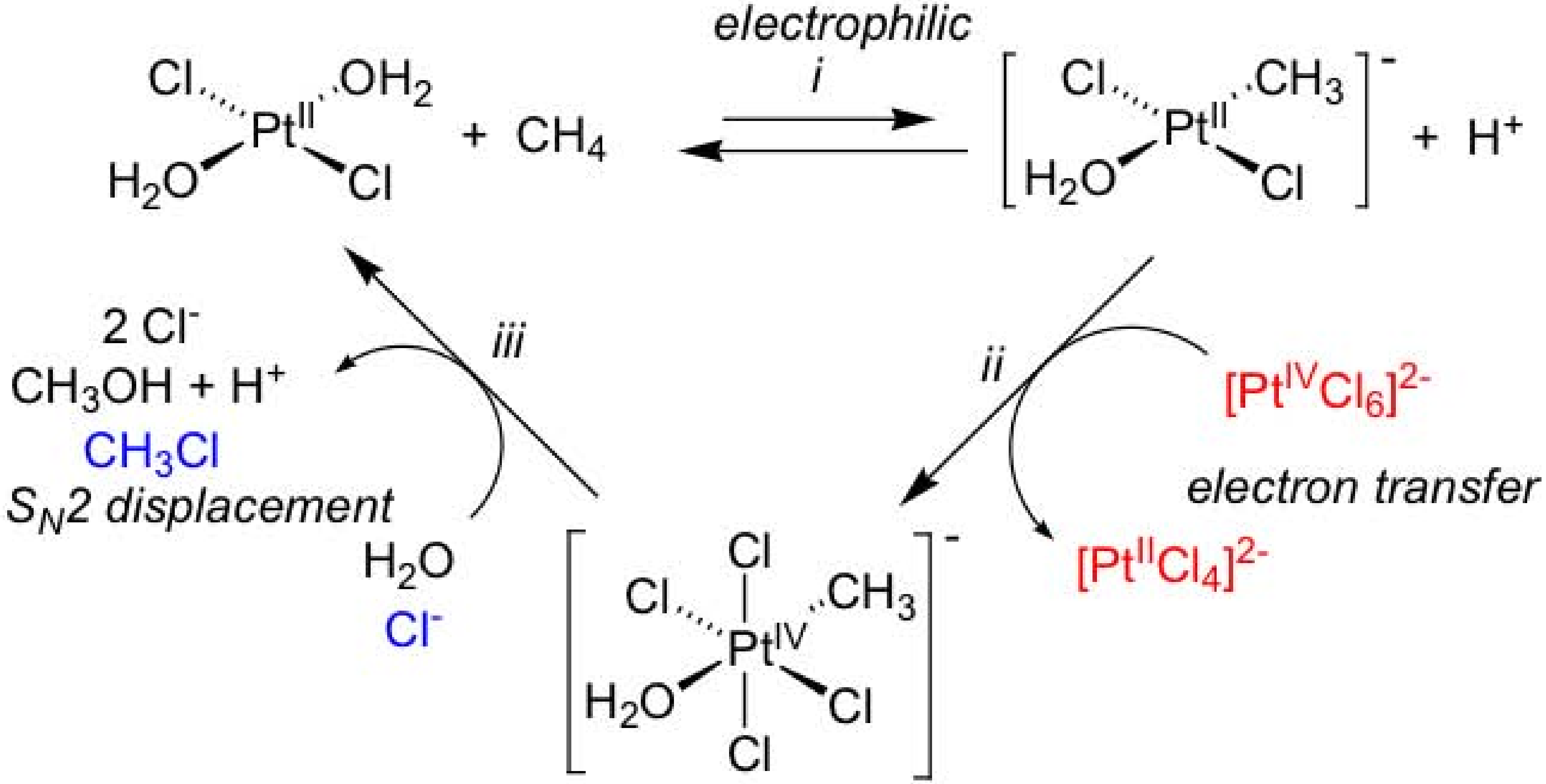
"Catalytic" oxidation of methane by Pt^{II}/Pt^{IV} salts in aqueous solution
(Shilov, 1972)

$$CH_4 + Pt^{IV}Cl_6^{2-} + H_2O \xrightarrow[120°C]{[Pt^{II}Cl_4^{2-}]} CH_3OH\ (\&\ CH_3Cl) + Pt^{II}Cl_4^{2-} + 2\,H^+ + 2Cl^-$$

- catalytic in Pt^{II} [but stoichiometric in Pt^{IV}]
- functions in aqueous solution in the presence of O_2
- unusual regioselectivity (for higher alkanes): 1° > 2° > 3°
- unusual oxidation selectivity $-CH_3 \cong -CH_2OH$
- at low $[Pt^{IV}]$, Pt^{II} (also) functions as stoichiometric oxidant; gives Pt^0, which catalyzes further, unwanted oxidations

- Preliminary studies reveal that mechanism does *not* involve radical intermediates.
- Although not practical as then constituted, perhaps an understanding of unusual (and encouraging) selectivity could lead to more practical analogs.

The “Shilov Cycle”



net: $CH_4 + [Pt^{IV}Cl_6]^{2-} + H_2O \xrightarrow{[Pt^{II}]} CH_3\text{-}OH + [Pt^{II}Cl_4]^{2-} + 2HCl$

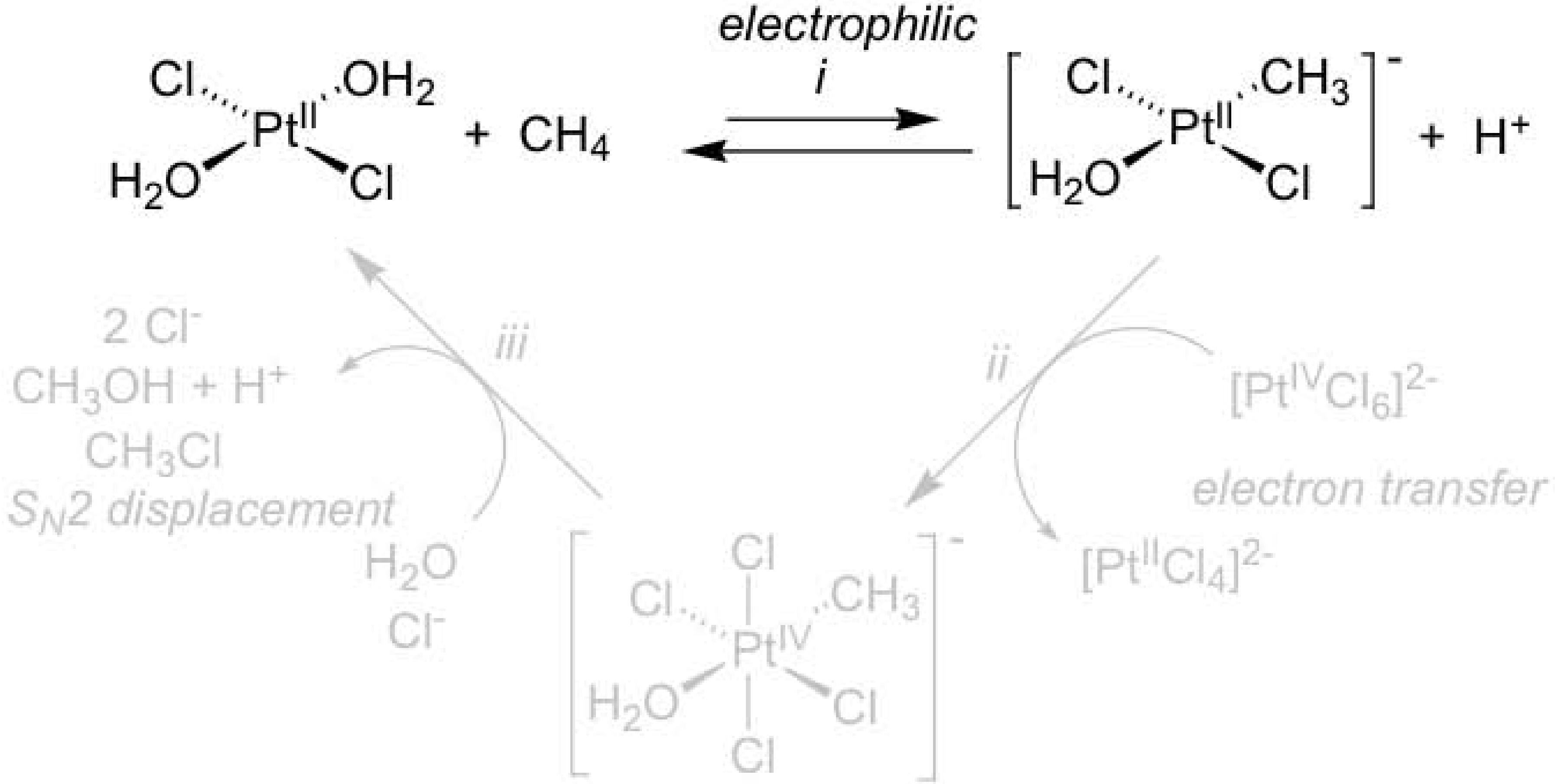
fundamental questions:

- *i.* What is slowest (rate-determining) step in cycle?
- *ii.* What is basis for remarkable selectivity for methane *vs.* products?

practical questions:

- *i.* Can we replace Pt^{IV} oxidant with more practical one...O_2 best?
- *ii.* Can we increase rate?
- *iii.* If we succeed in making cycle catalytic with O_2, can we transfer solution phase reaction to supported one: flow reactor mode?

The first step of Shilov Cycle: determines rate and selectivity

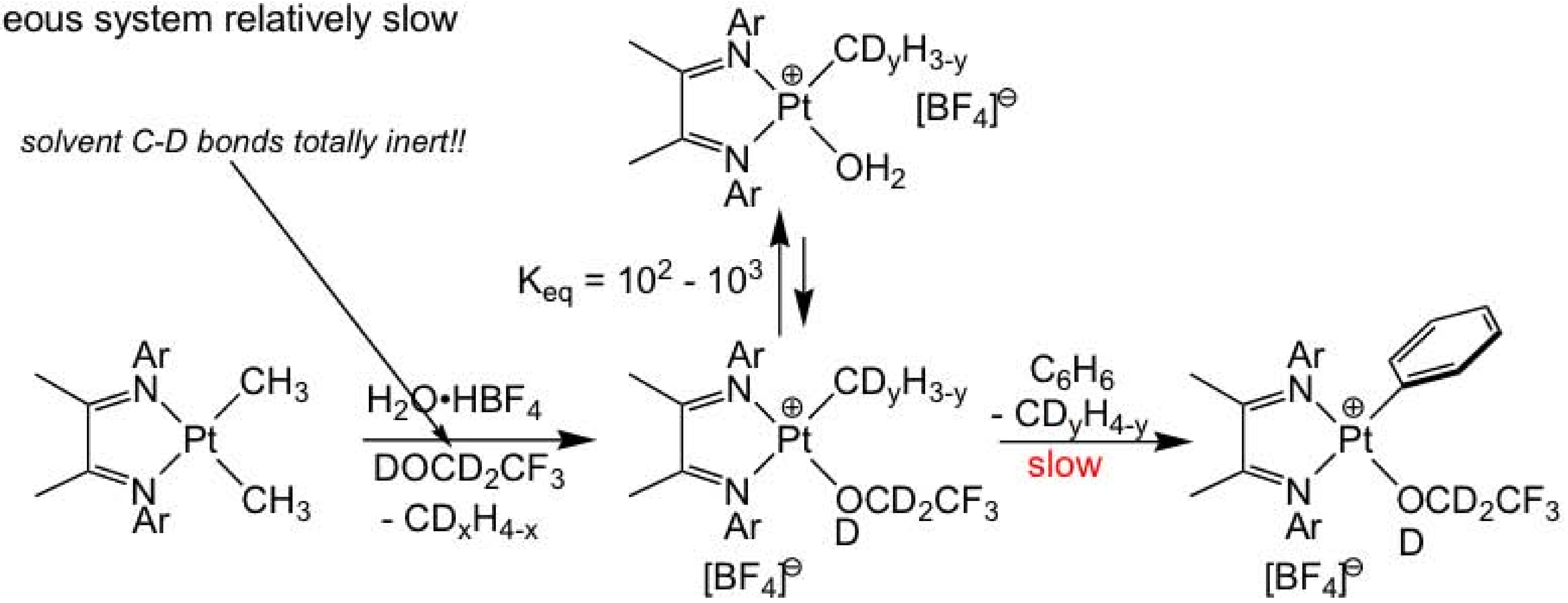


- what factors determine rate and selectivity of C-H bond activation at Pt^{II} centers?
- what are the elementary chemical reactions that comprise this step?

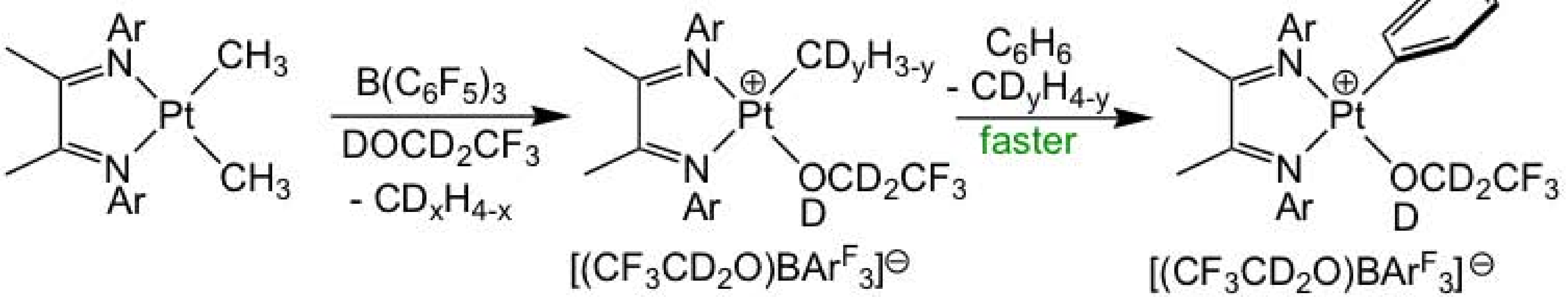
Kinetics of original Shilov system are too complex, even at low conversion
⇒ develop and investigate model systems

We have established that reactions of [(di-imine)Pt(CH_3)L]$^+$ with arenes are clean models for methane activation step in Shilov oxidation system:

aqueous system relatively slow

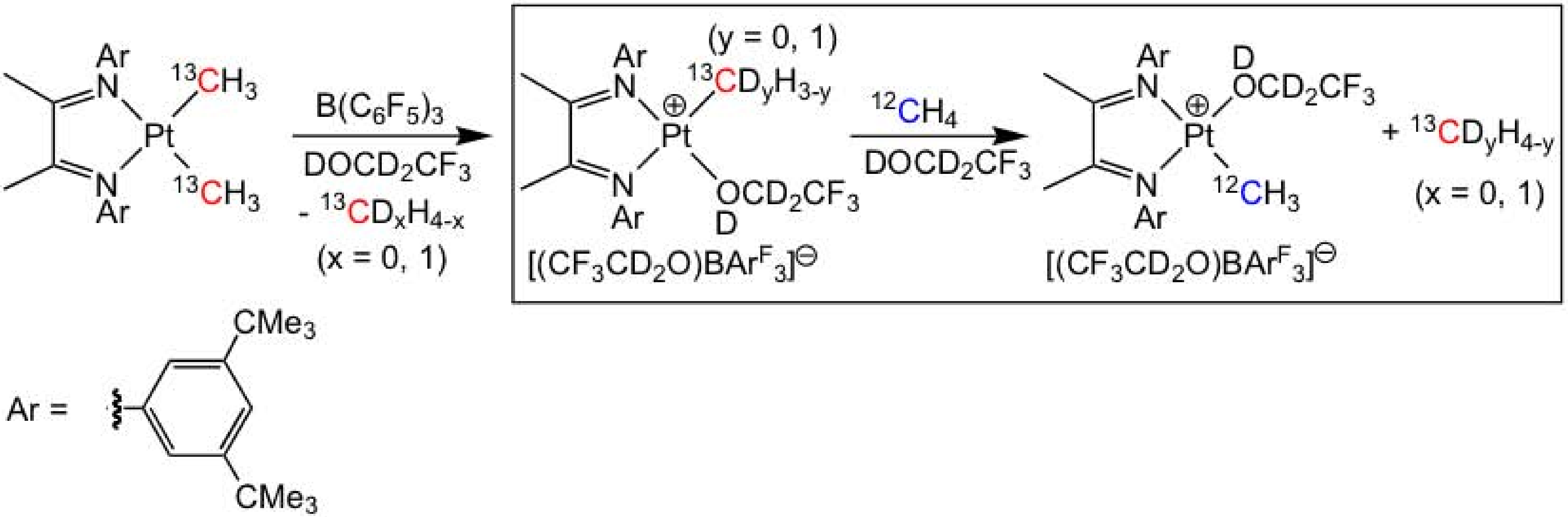


non-aqueous system faster



Tilset, Johansson, Zhong, van Eldik, Heyduk

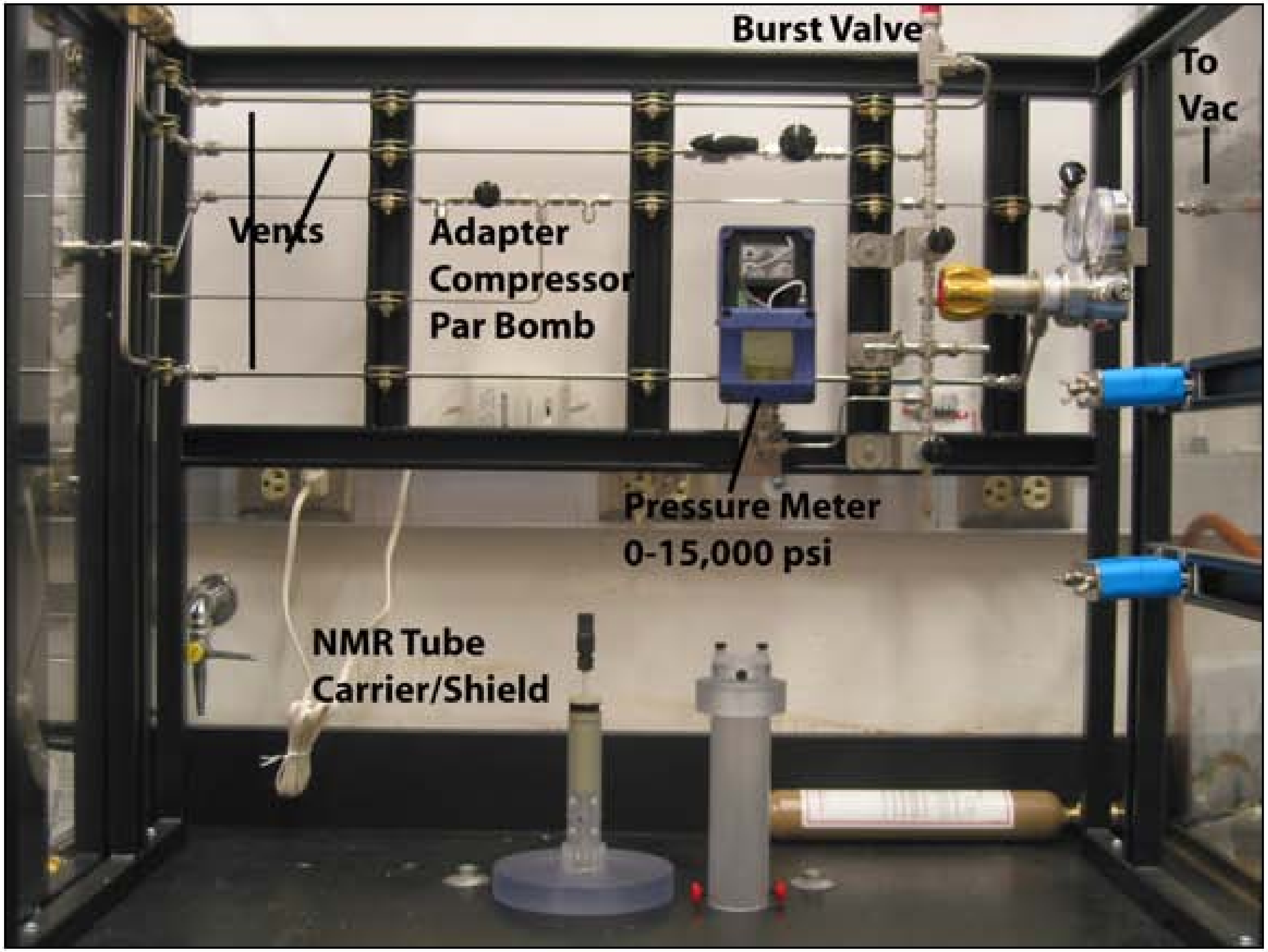
High pressure NMR studies of methane activation in the forward direction:



Owen

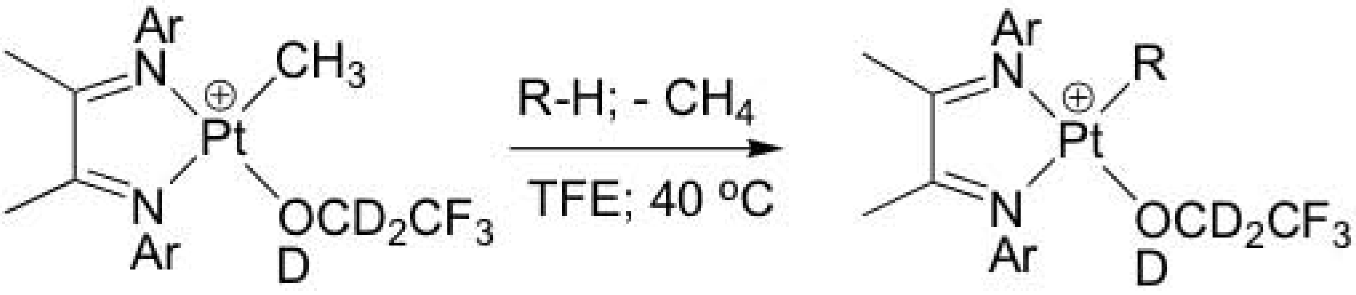
New high pressure NMR experiments: sapphire tube filling station

- tubes tested to 3000 psi nitrogen
- spectra recorded without spinning and with 0.4 mL sample
- 566 psi ethane in C_6D_6 gives an approximately 7 *M* solution

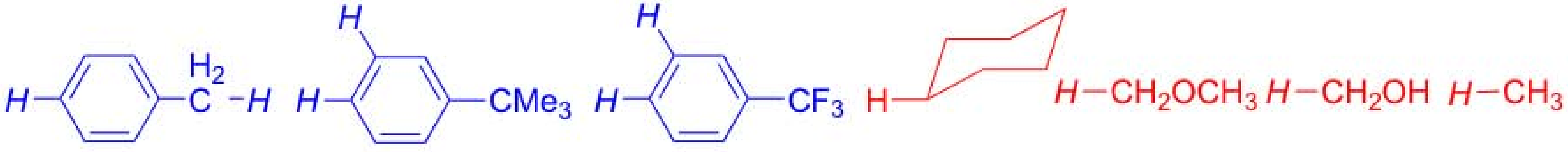


Owen

Relative rates of C-H activation with $[(\text{diimine})Pt(CH_3)(TFE)]^+$, first generation model for Shilov system:



approximate k^{rel} (methane = 1.0):



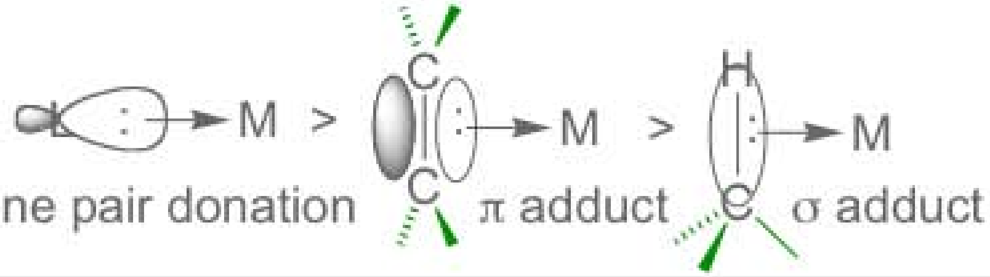
80 10 200 26 6 2 1.2 1.0

arene π coordination precedes (rate-determining)
C-H oxidative addition

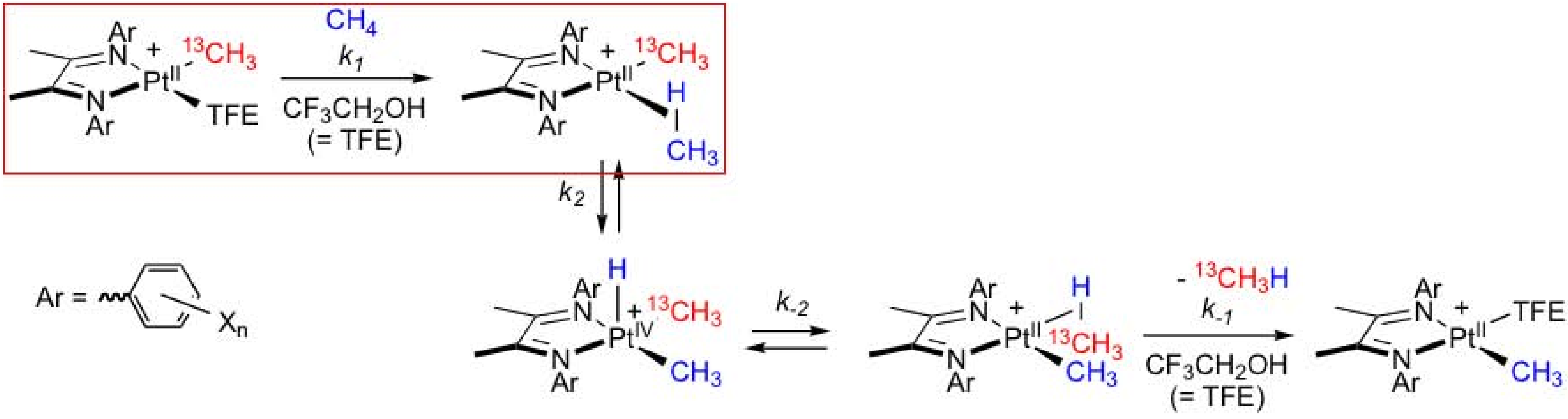
C-H σ bond coordination
rate determining

$H-CH(OH)CF_3$
$H-CHCl_2$
< 0.001

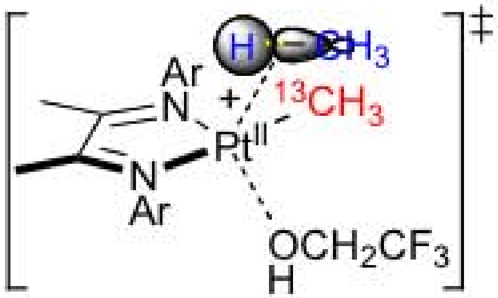
order of strength of metal-ligand bond:



Mechanistic studies (isotope effects, kinetics, *etc.*) of N-ligated model complexes: provide key insights into the basis for selectivity in Shilov System:



- C-H σ bond of hydrocarbon displaces solvent ligand: this step (k_1) controls rate and selectivity.

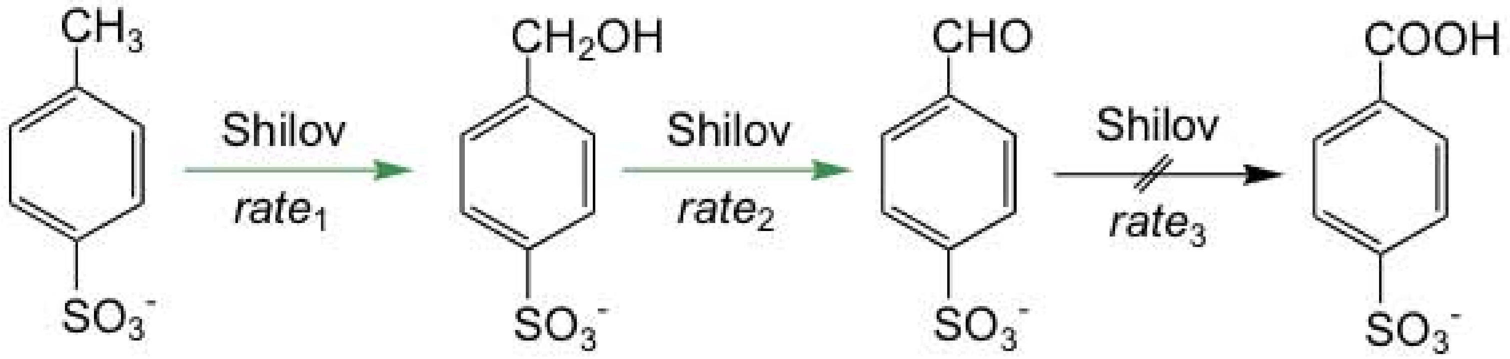


- Selectivity not particularly dependent on stereoelectronic effects for this organometallic system…model Shilov system is rather indiscriminate, unless electronic effects are very pronounced, as for example, with solvent (CH_2Cl_2, CF_3CH_2OH) C-H bonds, which are inert.

- Findings validate this approach to *selective* methane oxidation…rapid over oxidation of methanol will not be an inherently insurmountable problem (*cf*: CH_3OH reacts *ca.* 200 times faster than CH_4 with $Me_3COO\cdot$).

Zhong, Owen

Can estimate *rate*$_1$ *vs rate*$_2$ for some oxidations of the original Shilov system (Pt^{II}/Pt^{IV} aqueous chlorides), and related Pt system:



$$\frac{rate_1}{rate_2} \sim 1.5 \qquad \frac{rate_1}{rate_3} > 10^3!$$

$$HOCH_2CH_2OH \xleftarrow[rate_1]{\text{Shilov}} CH_3CH_2OH \xrightarrow[rate_2]{\text{Shilov}} CH_3CHO\ (\&\ CH_3COOH)$$

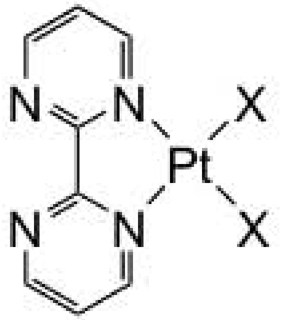
$$\frac{rate_1}{rate_2} \sim 1.5$$

Caltech

73% max one pass yield! ⇒ $\frac{rate_1}{rate_2} \sim 10^2$

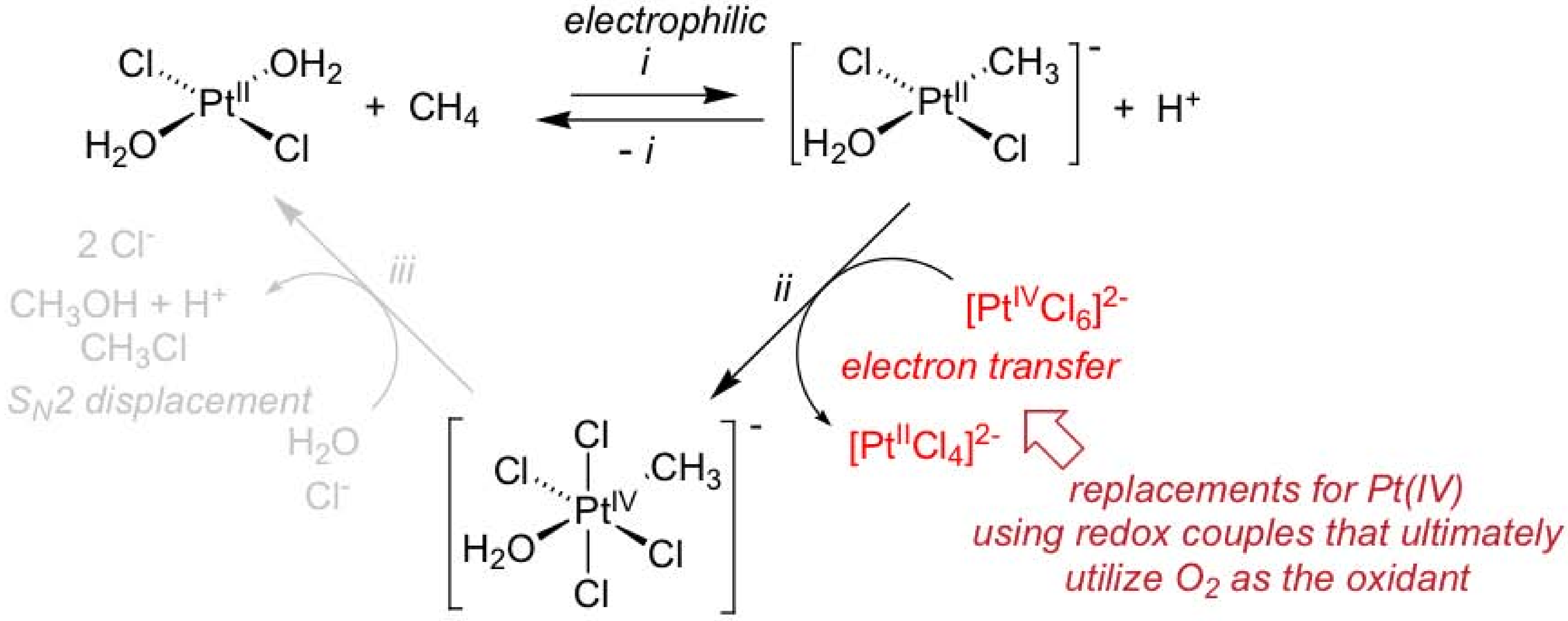
$$CH_4 + 2\ H_2SO_4 \longrightarrow CH_3OSO_3H + SO_2 + 2\ H_2O$$

catalyst based on



Catalytica

Improving the practicality of a Shilov-based alkane oxidation system



replacements for Pt(IV) using redox couples that ultimately utilize O_2 as the oxidant

Systematic studies of relative rates of step *ii* versus reverse of step *i* reveals:

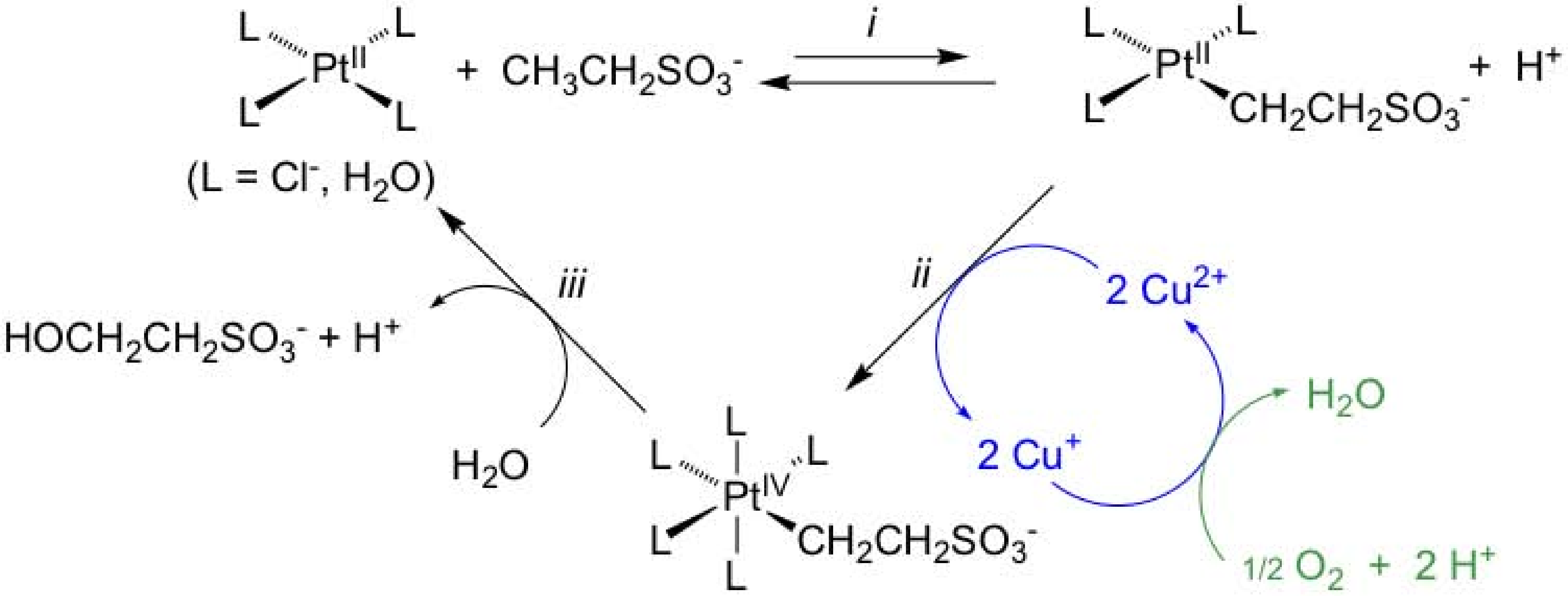
	$[Cu^{II}Cl_4]^{2-}$ >	$[Pt^{IV}Cl_6]^{2-}$ >	$[Fe^{III}Cl_4]^-$ ~	$[H_3PMo_9V_3O_{40}]^{3-}$
k_{ii}/k_{-i} =	8	2	1	1

(viable oxidant must not prematurely oxidize “inorganic” Pt^{II} before C-H activation by *i*)

Weinberg

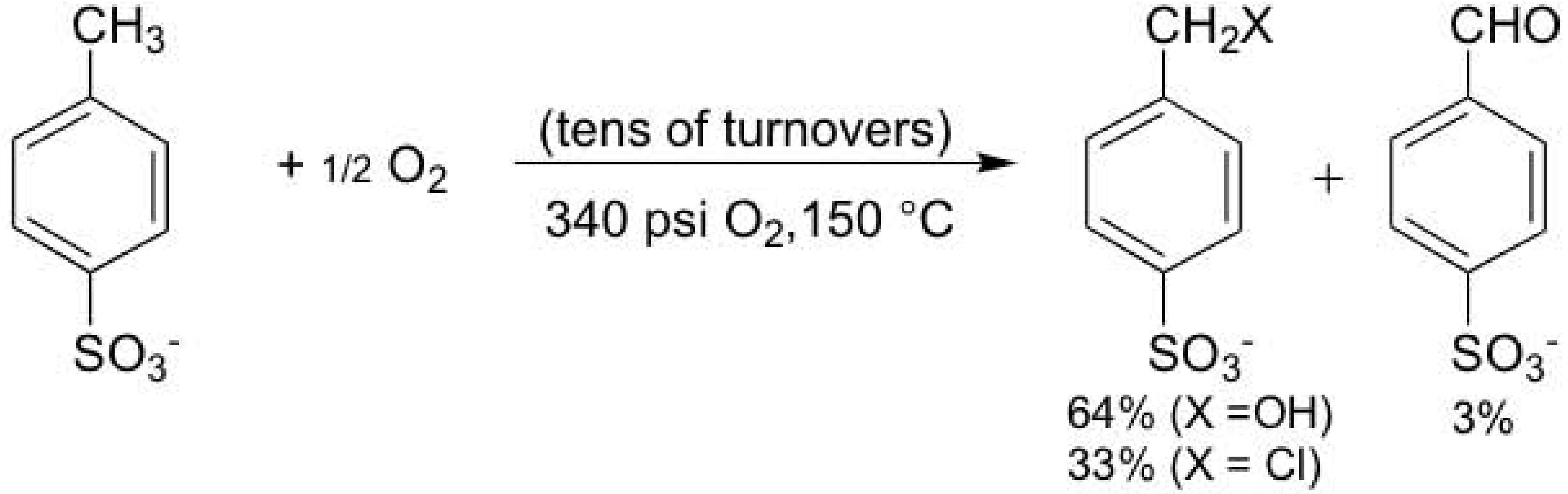
Use of Cu^{II}/Cu^{I} (as chlorides) and O_2 (*cf* Wacker oxidation of ethylene) to effect a catalytic version of the Shilov cycle

extending on Sen *et al* *JACS* **2001**, 1000:



net: $$CH_3CH_2SO_3^- + 1/2\ O_2 \xrightarrow[\text{340 psi } O_2\text{, 150 °C}]{\text{(tens of turnovers)}} XCH_2CH_2SO_3^-$$

75% (X =OH); 25% (X = Cl)



64% (X =OH)
33% (X = Cl)

3%

Weinberg,
Byers, Baker

Prospects for a homogeneous catalytic conversion of methane to methanol and other products

- C-H activation with Pt complexes resembles other late transition metal systems that oxidative add C-H bonds of hydrocarbons.
  - proceeds via rate limiting σ adduct formation for alkanes (and methanol)
  - Shilov system and models are not selective, except (not) for TFE & CH_2Cl_2.
  - lack of (unfavorable) selectivity allows for useful methane functionalization.

- Rapid oxidation following C-H activation is key to functionalization:
  - oxidant's potential and rate must select for Pt^{II}-CH_3 over Pt^{II}-solvento.
  - dioxygen capable of cleanly oxidizing dimethylplatinum(II) complexes, but not monomethylplatinum(II)-halides or -solvento cations.
  - Cu^{I}/Cu^{II} and O_2 work well, but catalyst lifetime too short.

- A truly practical homogeneous system for methane + dioxygen to methanol must use a supported version in a flow reactor; separating methanol from water too $.

- A practical system is *not* on the immediate horizon. System requires improved: (i) activity, (ii) stability, (iii) engineering to a supported mode.

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NSF
BP (Methane Conversion Consortium)

Methane Conversion Cooperative
MC^2