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

Tired of hearing about our energy future from movie stars, journalists, and politicians?
Sources of Energy through Time

Predictions, projections, and “postjections”
Sources of Energy through Time

Predictions, projections, and “postjections”
Sources of Energy through Time

- wood
- Coal
- Oil
- Gas

Graph showing the fraction of total energy market over the years.
Sources of Energy through Time

- wood
- Coal
- Oil
- Gas
- photons
- neutrons

![Graph showing the fraction of total energy market over time for wood, coal, petroleum, and natural gas.](image-url)
Sources of Energy through Time

wood

Coal

Oil

Gas

$H_2$, e$^-$, neutrons

energy carriers
Sources of Energy through Time

..... increasing H/C content ....
.... decreasing heteroatom content (O, N, S,...)
Sources of Energy through Time

wood
Coal
Oil
Gas
$H_2$
photons, neutrons

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
- Coal
- Oil
- Gas
- H₂
- e⁻
- photons
- neutrons
- pipelines
- LNG

P↑

T↓
Transporting Natural Gas to Markets

- wood
- Coal
- Oil
- Gas
- H₂
- neutrons
- photons
- pipelines
- convert
- LNG
- chemical liquefaction

- convert to liquid fuels and large volume petrochemicals
- a remote “methane refinery”
Transporting Natural Gas to Markets

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 = -(\text{CH}_2)- + \text{H}_2\text{O}
\]

- CH\textsubscript{4} should be burned ... chemical conversion decreases energy content
Methane Routes to Fuels and Petrochemicals

CH₄ → olefins, diesel gasoline
         → oligomers polymers
         → methanol
dimethylether
         → wax olefins
diesel gasoline
         → light olefins,
oxxygenates
         → methanol
gasoline
diesel
         → light paraffins
Methane Routes to Fuels and Petrochemicals

CH₄

- Selective partial oxidation
- Oxidative coupling
- Pyrolysis

methanol, formaldehyde
ethylene
ethylene, acetylene, benzene

olefins, diesel gasoline
oligomers, polymers
methanol
dimethyl ether

wax olefins, diesel gasoline
light olefins, oxygenates

methanol
gasoline, diesel
light paraffins

direct routes
a few products
Methane Routes to Fuels and Petrochemicals

direct routes

a few products
Methane Routes to Fuels and Petrochemicals

direct routes  
a few products

sequential conversion  
to other products
Methane Routes to Fuels and Petrochemicals

A Methane Refinery
Strategies for chemical conversion of natural gas

- theoretical efficiency set by products not by route

(diesel) \( \text{CH}_4 + \frac{1}{2} \text{O}_2 = -(\text{CH}_2)- + \text{H}_2\text{O} \quad \Delta H_R = -175 \text{ kJ/mol CH}_4 \)

(gasoline) \( \text{CH}_4 + \frac{3}{4} \text{O}_2 = -(\text{CH})- + 1.5 \text{H}_2\text{O} \quad \Delta H_R = -275 \text{ kJ/mol CH}_4 \)

.... unless \( \text{H}_2 \) or power can be exported
## Strategies for chemical conversion of natural gas

<table>
<thead>
<tr>
<th>Products</th>
<th>Theoretical Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>88</td>
</tr>
<tr>
<td>-(CH₂)-</td>
<td>78</td>
</tr>
<tr>
<td>-(CH₁.5)-</td>
<td>75</td>
</tr>
</tbody>
</table>
### Strategies for chemical conversion of natural gas

<table>
<thead>
<tr>
<th>Products</th>
<th>Theoretical Efficiency (%)</th>
<th>Actual Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>88</td>
<td>72</td>
</tr>
<tr>
<td>-(CH$_2$)-</td>
<td>78</td>
<td>~ 63</td>
</tr>
<tr>
<td>-(CH$_{1.5}$)-</td>
<td>75</td>
<td>~ 58</td>
</tr>
</tbody>
</table>

- Economics and actual efficiency set by “complexity” and capital costs
Strategies for chemical conversion of natural gas

<table>
<thead>
<tr>
<th>Products</th>
<th>Theoretical Efficiency (%)</th>
<th>Actual Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>88</td>
<td>72</td>
</tr>
<tr>
<td>-(CH$_2$)-</td>
<td>78</td>
<td>~ 63</td>
</tr>
<tr>
<td>-(CH$_{1.5}$)-</td>
<td>75</td>
<td>~ 58</td>
</tr>
</tbody>
</table>

- economics and actual efficiency set by "complexity" and capital costs

Diesel via synthesis gas

Syngas 60  Synthesis 25  Separation 15

recycle

Heat input  Heat recovery
Strategies for chemical conversion of natural gas

<table>
<thead>
<tr>
<th>Products</th>
<th>Theoretical Efficiency (%)</th>
<th>Actual Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>88</td>
<td>72</td>
</tr>
<tr>
<td>-(CH$_2$)-</td>
<td>78</td>
<td>~ 63</td>
</tr>
<tr>
<td>-(CH$_{1.5}$)-</td>
<td>75</td>
<td>~ 58</td>
</tr>
</tbody>
</table>

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

Diesel via synthesis gas

- pressure cycles
- temperature cycles
- yield per pass
Strategies for chemical conversion of natural gas

- Theoretical efficiency set by products not by route
- Economics and actual efficiency set by “complexity” and capital costs
Strategies for chemical conversion of natural gas

- theoretical efficiency set by products not by route

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

Strategies for chemical conversion of natural gas

- theoretical efficiency set by products not by route
- economics and actual efficiency set by "complexity" and capital costs

Direct routes are great ... as long as they are simple

.............. difficult separations and expensive oxidants hurt

Challenges in bringing CH$_4$ to markets by chemical means

Direct Routes

$\text{CH}_4 \rightarrow -(\text{CH}_x) \rightarrow (\text{C},$ 

- overcome thermodynamic constraints
Challenges in bringing CH$_4$ to markets by chemical means

Direct Routes

\[
\text{CH}_4 \xrightarrow{\chi} -(\text{CH}_x)- \xrightarrow{} (\text{C}, \text{CO}_x)
\]

- overcome thermodynamic constraints
- protect products with weaker C-H bonds
Challenges in bringing CH₄ to markets by chemical means

**Direct Routes**

\[ CH₄ \xrightarrow{X} -(CHₓ)\rightarrow (C, COₓ) \]

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

**Indirect Routes**

\[ CH₄ \xrightarrow{X} I₁ \rightarrow I₂ \rightarrow -(CHₓ) \]

\[ (H₂/CO, CH₃OH, ..) \]

- couple endothermic-exothermic steps
- form the first carbon-carbon bond
Challenges in bringing CH₄ to markets by chemical means

**Direct Routes**

\[ CH_4 + X \rightarrow -(CH_x)\rightarrow (C, CO_x) \]

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

**Indirect Routes**

\[ CH_4 \rightarrow I_1 \rightarrow I_2 \rightarrow -(CH_x) \]

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

$X \xrightarrow{\text{CH}_4} -(\text{CH}_x)\rightarrow (\text{C, CO}_x)$

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

- avoid process complexity
- provide routes to products with large markets
Non-Oxidative Conversion of CH$_4$ to Larger Hydrocarbons

Non-Oxidative Conversion
(Pyrolysis)

\[ \text{CH}_4 \xleftrightarrow{H_2} \text{C}_2\text{H}_4 \xleftrightarrow{H_2} \text{(structure)} \xleftrightarrow{H_2} \text{(structure)} \]
Non-Oxidative Conversion of \( \text{CH}_4 \) to Larger Hydrocarbons

Non-Oxidative Conversion (Pyrolysis)

\[ \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{C}^* \]

\( \sim 1000 \text{ K} \)

\[ \Delta G, \text{kJ/mol H}_2 \]

\[ \text{CH}_4 = \frac{1}{2} \text{C}_2\text{H}_4 + \text{H}_2 \]

\[ \frac{2}{3} \text{CH}_4 = \frac{1}{9} \text{C}_6\text{H}_6 + \text{H}_2 \]

\( \Delta G = 0 \)

\[ T, \text{K} \]

200 400 600 800 1000 1200 1400
Non-Oxidative Conversion of CH₄ to Larger Hydrocarbons

**Non-Oxidative Conversion (Pyrolysis)**

\[ \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{HC} \rightarrow \text{C}_2 \text{H}_6 \]

\[ \text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{C}^* \]

((~ 1000 K))

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

\[ \Delta G, \text{kJ/mol H}_2 \]

\[ \text{CH}_4 = 1/2\text{C}_2\text{H}_4 + \text{H}_2 \]

\[ 2/3\text{CH}_4 = 1/9\text{C}_6\text{H}_6 + \text{H}_2 \]

\[ \Delta G = 0 \]

\[ T, \text{K} \]

\[ 200 \ 400 \ 600 \ 800 \ 1000 \ 1200 \ 1400 \]

“MoCₓ”

H⁶⁺

Si⁴⁺

Al³⁺

O⁶⁻

Si⁴⁺

H-ZSM5

“M”
Non-Oxidative Conversion of CH$_4$ to Larger Hydrocarbons

Non-Oxidative Conversion (Pyrolysis)

CH$_4$ $\rightarrow$ C$_2$H$_4$ $\rightarrow$ Benzene $\rightarrow$ Napth $\rightarrow$ C$_2$H$_6$

H$_2$ $\rightarrow$ H$_2$ $\rightarrow$ H$_2$

(~ 1000 K)

CH$_4$ conversion (%)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_4$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/H-ZSM5</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Selectivity (carbon basis %)

<table>
<thead>
<tr>
<th>Component</th>
<th>C$_2$H$_4$</th>
<th>Benzene</th>
<th>Napth</th>
<th>C$_{11+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>67</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

C$_2$-C$_{10}$ Yield (%)

<table>
<thead>
<tr>
<th>Component</th>
<th>C$<em>2$-C$</em>{10}$ Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.1</td>
</tr>
</tbody>
</table>
Non-Oxidative Conversion of CH$_4$ to Larger Hydrocarbons

Non-Oxidative Conversion (Pyrolysis)

\[ \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{C}_x \text{H}_y \rightarrow \text{C}^* \]

\[ \Delta G, \text{kJ/mol H}_2 \]

\[ \text{CH}_4 = \frac{1}{2} \text{C}_2\text{H}_4 + \text{H}_2 \]

\[ \frac{2}{3} \text{CH}_4 = \frac{1}{9} \text{C}_6\text{H}_6 + \text{H}_2 \]

\[ \Delta G = 0 \]

(~ 1000 K)

- deactivation and carbon: controlled addition of CO$_2$ (or H$_2$)
  ... kinetic coupling between CH$_x$ formation and removal
Non-Oxidative Conversion of CH₄ to Larger Hydrocarbons

Non-Oxidative Conversion (Pyrolysis)

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C}_2\text{H}_4 \\
& \rightarrow \text{H}_2 \\
& \rightarrow \text{H}_2 \\
& \rightarrow \underline{\text{C}^*} \\
& \rightarrow \text{H}_2
\end{align*}
\]

\(~1000 \text{ K}\)

\[
\Delta G, \text{kJ/mol H}_2
\]

\[
\begin{align*}
\text{CH}_4 &= 1/2\text{C}_2\text{H}_4 + \text{H}_2 \\
2/3\text{CH}_4 &= 1/9\text{C}_8\text{H}_8 + \text{H}_2 \\
\Delta G &= 0
\end{align*}
\]

- **Deactivation and Carbon**: Controlled addition of CO₂ (or H₂) ... kinetic coupling between CHₓ formation and removal
- **Thermodynamics**: Remove H₂ as it forms
CH₄ Pyrolysis with Continuous H₂ Removal

~ 1000 K

Diagram showing the pyrolysis process with CH₄ reacting to form CH₃, C₂H₄, and H₂, with continuous hydrogen removal.
CH₄ Pyrolysis with Continuous H₂ Removal

~ 1000 K

Diagram showing the chemical reactions involved in CH₄ pyrolysis, including the conversion of CH₄, CH₃, C₂H₄, H₂O, and O₂ to H₂ and other products. The diagram also includes a cross-section image labeled "dense film" and "porous substrate."
CH$_4$ Pyrolysis with Continuous H$_2$ Removal

~ 1000 K

Mo/HZSM5
SrCeYO$_x$
SrZrO$_x$

dense film
porous substrate

SrCe$_{0.95}$Yb$_{0.05}$O$_3$ thin films 20 $\mu$m, 950 K
Pd metal membranes 20 $\mu$m, 673 K
O$_2$ membranes, 1 mm

Permeability
CH₄ Pyrolysis with Continuous H₂ Removal

~ 1000 K

modest improvements in C₂-C₁₀ yields (8% → 14%)
... limited by low driving force for H₂ permeation

CH$_4$ Pyrolysis with Continuous H$_2$ Removal

~ 1000 K

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

SrCeYO$_x$

modest improvements in C$_2$-C$_{10}$ yields (8% $\rightarrow$ 14%)
... limited by low driving force for H$_2$ permeation

How else could we remove $H_2$?
Oxidative routes to avoid thermodynamic hurdles

How else could we remove $H_2$?

- $CO, CO_2, H_2O$ to $CH_4$
- $CH_4$ to $C_2H_6, C_2H_4$
- $O_2$ to $H^*$, $CH_x$, $CH_3^*$
- Oxide

Thermodynamic plot:

- $CH_4 = 1/2C_2H_4 + H_2$
- $2/3CH_4 = 1/9C_6H_6 + H_2$
- $H_2 + 1/2O_2 = H_2O$ (x 0.1)

ΔG, kJ/mol $H_2$

Temperature, T, K
Oxidative routes to avoid thermodynamic hurdles

\[ \text{CH}_4 = \frac{1}{2} \text{C}_2\text{H}_4 + \text{H}_2 \]

\[ \frac{2}{3} \text{CH}_4 = \frac{1}{9} \text{C}_6\text{H}_6 + \text{H}_2 \]

\[ \Delta \text{G} = 0 \]

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} \quad (x \ 0.1) \]
Oxidative routes to avoid thermodynamic hurdles

\[ \text{CH}_4 \rightarrow \text{C}_2\text{H}_{4,6} \]

\[ \frac{k_3}{k_1} > 1 \]

\[ \Delta G, \text{kJ/mol H}_2 \]

\[ \text{CH}_4 = \frac{1}{2\text{C}_2\text{H}_4 + \text{H}_2} \]

\[ \frac{2}{3}\text{CH}_4 = \frac{1}{9\text{C}_6\text{H}_6 + \text{H}_2} \]

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \]

Staged \( \text{O}_2 \) introduction and air purification
Oxidative routes to avoid thermodynamic hurdles

- Use more reactive "oxidants" to abstract H-atoms
- Extract and recover C₂ via separation and recycle
Encourage reactions with OH radicals instead of surfaces.

Surface (O*) mediated

\[ \text{CH}_4 \rightarrow \text{CH}_3^\cdot \rightarrow \text{C}_2\text{H}_6 \]

\[ \text{O}_2 \rightarrow \text{H}_2\text{O} \]

\[ \text{O}^* \rightarrow \text{O}^* \]

\[ \text{Mn/Na}_2\text{WO}_4/\text{SiO}_2 \rightarrow \sim 1000 \text{ K} \]

\[ \text{CH}_4 \rightarrow \text{O}_2 \rightarrow \text{CO}_x \]

\[ \text{CH}_4 + \text{CH}_3^\cdot \rightarrow \text{C}_2\text{H}_4,6 \]
Encourage reactions with OH radicals instead of surfaces

Surface (O*) mediated

\[
\begin{align*}
\text{CH}_4 & \quad \text{CH}_3^* \\
\text{O}_2 & \quad \text{O}^* & \quad \text{O}^* \\
\text{H}_2\text{O} & \quad \text{OH}^* \\
\text{Mn/Na}_2\text{WO}_4/\text{SiO}_2 & \quad \sim 1000 \text{ K}
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{H}_6 & \quad + \text{CH}_3^* \\
\text{CO}_x & \quad \text{C}_2\text{H}_{4,6}
\end{align*}
\]
Encourage reactions with OH radicals instead of surfaces

![Chemical reaction diagram]

**Surface (O*) mediated**

\[ \text{CH}_4 + \text{O}^* \rightarrow \text{CH}_3^* \]

\[ \text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}^* \]

\[ \text{C}_2\text{H}_6 + \text{CH}_3^* \rightarrow \text{C}_2\text{H}_4,6 \]

**OH- mediated**

\[ \text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3^* \]

\[ \text{H}_2\text{O} + \text{OH} \rightarrow \text{H}_2\text{O}_2^* \]

**Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2}**

\[ \sim 1000 \text{ K} \]
Encourage reactions with OH radicals instead of surfaces

Surface (O*) mediated

\[ \text{C}_2\text{H}_4 \]
\[ \text{C}_2\text{H}_6 \]
\[ \text{CH}_4 \]

OH· mediated

\[ \text{C}_2\text{H}_4 \]
\[ \text{C}_2\text{H}_6 \]
\[ \text{CH}_4 \]

Water is a co-catalyst

\[ \text{C}_2\text{H}_4,6 \]
\[ \text{CO}_x \]

\[ \text{CH}_4 \]
\[ \text{O}_2 \]

Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2}

\[ \sim 1000 \text{ K} \]
Encourage reactions with OH radicals instead of surfaces

**Surface (O*) mediated**
- $\text{C}_2\text{H}_4$
- $\text{C}_2\text{H}_6$
- $\text{CH}_4$

**OH· mediated**
- $\text{C}_2\text{H}_4$
- $\text{C}_2\text{H}_6$
- $\text{CH}_4$

$\text{CH}_4$ $\rightarrow$ $\text{C}_2\text{H}_4,6$

$\text{O}_2$ $\rightarrow$ $\text{O}^*$

$\text{O}^*$ $\rightarrow$ $\text{O}^*$

$\text{H}_2\text{O}$ $\rightarrow$ $\text{OH}$

$\text{H}^*$ $\rightarrow$ $\text{H}$

$\text{Mn/Na}_2\text{WO}_4/\text{SiO}_2$

$\sim 1000 \text{ K}$

**$k_i / k_{\text{CH}_4}$ vs C-H bond energies**

- $\text{C}_2\text{H}_6$
- $\text{CH}_4$
- $\text{C}_2\text{H}_4$

**Surface O* mediated**
Encourage reactions with OH radicals instead of surfaces.

Surface (O*) mediated:
- \(C_2H_4\)
- \(C_2H_6\)
- \(CH_4\)

OH* mediated:
- \(C_2H_4\)
- \(C_2H_6\)
- \(CH_4\)

OH* mediated:

\[\frac{k_i}{k_{CH_4}} \text{ vs } C-H \text{ bond energies}\]

\(E_{C-H} (kJ \text{ mol}^{-1})\)
- \(C_2H_6\)
- \(CH_4\)
- \(C_2H_4\)

Mn/Na\(_2\)WO\(_4\)/SiO\(_2\)
~1000 K

\(k_1\) and \(k_3\)
Encourage reactions with OH radicals instead of surfaces

Surface (O*) mediated

\[ \text{C}_2\text{H}_4 \]
\[ \text{C}_2\text{H}_6 \]
\[ \text{CH}_4 \]

OH· mediated

\[ \text{C}_2\text{H}_4 \]
\[ \text{C}_2\text{H}_6 \]
\[ \text{CH}_4 \]

\[ \text{H}_2\text{O} \]
\[ \text{OH}^- \]

\[ \text{O}^* \]
\[ \text{O}^* \]

O\(_2\) \rightarrow \text{Mn/Na}_2\text{WO}_4/\text{SiO}_2 \sim 1000 \text{ K}

\[ k_1 \]
\[ k_3 \]

\[ \text{C}_2\text{H}_4,6 \]

\[ \text{CH}_4 \rightarrow \text{O}_2 \]

\[ k_i / k_{\text{CH}_4} \text{ vs C-H bond energies} \]

\[ E_{\text{C-H}} \text{ (kJ mol}^{-1} \text{)} \]

Surface O* mediated

OH mediated
Encourage reactions with OH radicals instead of surfaces

\[
\Delta H \text{ (kJ mol}^{-1}\text{)} \ R + H \rightarrow R-H
\]

Diagram showing the reaction pathways involving \( \text{CH}_4 \) and \( \text{O}_2 \) leading to \( \text{CO}_x \) with rate constants \( k_1 \), \( k_2 \), and \( k_3 \).
Encourage reactions with OH radicals instead of surfaces

\[ \Delta H \text{ (kJ mol}^{-1}\text{)} \quad \text{R + H} \rightarrow \text{R-H} \]

- \( k_{\text{OH}} \)
- \( k_{\text{C}_2\text{H}_6} \)

- \( \text{CH}_4 \)
- \( \text{O}_2 \)
- \( \text{C}_2\text{H}_{4,6} \)

- 29% max.

Surface (O*) mediated

\( k_1 \)
\( k_3 \)
Oxidative Coupling: extracting C\textsubscript{2} products as they form


Stage O\textsubscript{2} Remove C\textsubscript{2}H\textsubscript{4}
Oxidative Coupling: extracting $C_2$ products as they form


Stage $O_2$  Remove $C_2H_4$

with $C_2$ removal
**Oxidative Coupling: extracting C₂ products as they form**


[Diagram showing a process flow with key points:
- Stage O₂
- Remove C₂H₄
- 1000 K
- 200-300 K
- ~ 90% C₂ yield with C₂ removal]

- CH₄ feed
- (Electro-)catalytic reactor
- Molecular sieve trap
- Pump
- NV
- F₁
- GC

- B[chart showing relationship between CH₄ conversion and C₂ yield]
Oxidative Coupling: extracting C\textsubscript{2} products as they form


\[ \text{Mn/Na}_2\text{WO}_4\cdot\text{SiO}_2 \ (1073 \text{ K}) \]

OCM reactor

H-ZSM-5 reactor (550 K)

Convert C\textsubscript{2} to C\textsubscript{4+} hydrocarbons

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

\[ \text{\sim 90\% C}_2 \text{ yield with C}_2 \text{ removal} \]
Challenges in bringing CH₄ to markets by chemical means

**Direct Routes**

\[
CH_4 \xrightarrow{X} -(CH_x)- \rightarrow (C, CO_x)
\]

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

**Indirect Routes**

\[
CH_4 \xrightarrow{X} I_1 \rightarrow I_2 \rightarrow -(CH_x)\]

\((H_2/CO, CH_3OH, \ldots)\)

- 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**

\[ \text{CH}_4 \xrightarrow{X} -(\text{CH}_x)- \rightarrow (\text{C, CO}_x) \]

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

**Indirect Routes**

\[ \text{CH}_4 \xrightarrow{X} I_1 \rightarrow I_2 \rightarrow -(\text{CH}_x)- \]

- (H\(_2\)/CO, CH\(_3\)OH, ..)

- 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.

\[ \text{CH}_3\text{OSO}_3\text{H} \]

\[ \text{H}_2/\text{CO} \]
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

Keep it simple!

A “protected” form of methane is used as an intermediate. Protection can be kinetic or thermodynamic.
Methane “Oxidation” to Synthesis Gas
Methane "Oxidation" to Synthesis Gas
Methane “Oxidation” to Synthesis Gas

CH₄

O=CO, O-H₂, O=O

H₂

C*

O*

CO

(Rh, Ni, Pt, Ir, Ru, Pd)
Methane “Oxidation” to Synthesis Gas

Challenges

- couple endothermic and exothermic reactions in space and time
- minimize temperature gradients... avoid carbon formation
- lower costs of oxidant (O₂)
Methane “Oxidation” to Synthesis Gas

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \]

\[ + 250 \text{ kJ/mol} \]

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \]
Methane “Oxidation” to Synthesis Gas

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \]
\[ + 250 \text{ kJ/mol} \]

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \]

Requires high temperatures ...

......... catalyst sintering and carbon formation

\[ \text{CO} + 2\text{H}_2 \rightarrow -(\text{CH}_2)- + \text{H}_2\text{O} \]
Small metal clusters are more “active”, inhibit carbon formation.
Small metal clusters are more “active”, inhibit carbon formation

[873 K, 20 kPa CH₄]
Small metal clusters are more “active”, inhibit carbon formation.

[Graph showing the forward rate vs. metal dispersion for different catalysts: Pt, Ir, Rh, Ni, Ru. The graph includes data points and trend lines for 10 nm and 1.5 nm cluster sizes.]

[Rh, Ni, Pt, Ir, Ru, Pd]

[Diagram showing the reaction pathways for CH₄ and H₂O, leading to CO₂, H₂O, CH₄, H₂, and CO. Carbon filaments are indicated.]
Small metal clusters are more “active”, inhibit carbon formation.

[Graph showing forward rate vs. metal dispersion for different catalysts (Pt, Ir, Rh, Ni, Ru) at 10 nm and 1.5 nm particle sizes.]

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

[Diagram showing the reaction of CH₄/H₂O to CO₂, H₂O with CO formation and carbon filaments.]

[Equation: [873 K, 20 kPa CH₄]]

.. but tend not to stay small
CH$_4$-O$_2$ REACTIONS: Partial Oxidation and Combustion

catalytic partial oxidation

- 22 kJ/mol
CH$_4$-O$_2$ REACTIONS: Partial Oxidation and Combustion

- 22 kJ/mol

2CH$_4$ + O$_2$ $\rightarrow$ 2CO + 4H$_2$
**CH₄-O₂ REACTIONS: Partial Oxidation and Combustion**

- **Partial Oxidation**
  - $\text{CH}_4 \rightarrow \text{H}_2, \text{CO}$
  - $-22 \text{ kJ/mol}$

- **Combustion**
  - $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
  - $-800 \text{ kJ/mol}$

**Axial Temperature Profiles**

$2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$
CH$_4$-O$_2$ REACTIONS: Partial Oxidation and Combustion

Catalytic partial oxidation

$\text{H}_2, \text{CO}$

- 22 kJ/mol

Catalytic combustion

$\text{CO}_2, \text{H}_2\text{O}$

- 800 kJ/mol

Axial Temperature Profiles

$\text{CH}_4 / \text{O}_2$ → $T$

Chemical Reactions:

\[2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\]

\[\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}\]
**CH₄-O₂ REACTIONS: Partial Oxidation and Combustion**

- **Catalytic partial oxidation**
  - **CH₄** → **O₂** → **H₂, CO**
  - **- 22 kJ/mol**

- **Catalytic combustion**
  - **CO₂, H₂O**
  - **- 800 kJ/mol**

**Axial Temperature Profiles**

- **2CH₄ + O₂ → 2CO + 4H₂**

**Chemical Reactions**

- **CH₄ + 2O₂ → CO₂ + 2H₂O**
- **CH₄ → CO + H₂**
**CH₄-O₂ REACTIONS: Partial Oxidation and Combustion**

Catalytic partial oxidation

- **CH₄**
- **O₂**
  - **H₂, CO**
  - **CO₂, H₂O**

- 22 kJ/mol
- 800 kJ/mol

**Axial Temperature Profiles**

- **CH₄/O₂**
  - Combustion
- **CH₄/O₂**
  - Reforming

**Chemical Reactions**

- 2CH₄ + O₂ → 2CO + 4H₂
- CH₄ + 2O₂ → CO₂ + 2H₂O

**Catalytic Combustion**
"Partial Oxidation" and Autothermal Reforming

Feedstock + Steam → Synthesis Gas

Oxygen (or Enriched Air)

\[ \text{CH}_4/\text{O}_2 \rightarrow \text{CO}_2/\text{H}_2\text{O} \]

\[ \text{CO}/\text{H}_2 \]

(combustion reforming)

(813 K, 5 kPa \text{CH}_4, 5 \text{kPa O}_2)
"Partial Oxidation" and Autothermal Reforming

Combustion

Adiabatic Reforming

$\text{CH}_4/\text{O}_2 \rightarrow \text{CO}_2/\text{H}_2\text{O}$

$\text{CO}/\text{H}_2$

$(813 \text{ K}, 5 \text{ kPa} \text{ CH}_4, 5 \text{ kPa} \text{ O}_2)$
"Partial Oxidation" and Autoothermal Reforming

- Feedstock + Steam
- Oxygen (or Enriched Air)
- Combustion
- Adiabatic Reforming

\[
\begin{align*}
\text{CH}_4/O_2 & \rightarrow \text{CO}_2/H_2O \\
\text{CO}/H_2 & \rightarrow \text{combustion} \quad \text{reforming}
\end{align*}
\]

\[(813 \text{ K}, 5 \text{ kPa CH}_4, 5 \text{ kPa O}_2)\]
COUPLING ENDOThERMIC AND EXOTHERMIC REACTIONS..
.......... continuous removal (and combustion) of H₂

membranes allow heat and mass transfer

CH₄ + H₂O + CH₄/H₂O

H₂ + CO

H₂O

N₂/O₂

dense oxide conductors

porous substrate

Combustion catalyst

Reforming catalyst

(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

with Hengyong Xu
COUPLING ENDO THERMIC 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

- couple within short thermal conduction distances

(with Hengyong Xu)
COUPLING ENDO THERM IC AND EXOTHERMIC REACTIONS ..

.......... across a thin plate without boundary layers

Heat integration in catalytic plate reactors

- couple within short thermal conduction distances
- short monolith reactors

(with Hengyong Xu)
Challenges in bringing CH₄ to markets by chemical means

Direct Routes

CH₄ → -(CHₓ)- → (C, COₓ)

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

Indirect Routes

CH₄ → I₁ → I₂ → -(CHₓ)-

(H₂/CO, CH₃OH, ..)

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

- avoid process complexity
- provide routes to products with large markets
CO + H₂ → diesel (Co, Fe)

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

Mo₂C, MoS₂, Rh, Co-Cu,
C-C Bond Formation Bottlenecks in Synthesis Gas Conversion

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

\[ CO + H_2 \rightarrow C_1^* \rightarrow C_2^* \rightarrow \ldots \rightarrow C_n^* \]
C-C Bond Formation Bottlenecks in Synthesis Gas Conversion

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

Alcohol synthesis

<table>
<thead>
<tr>
<th>CH₃OH</th>
<th>C₂H₅OH</th>
<th>CₙH₂n+1OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁⁺</td>
<td>C₂⁺</td>
<td>Cₙ⁺</td>
</tr>
</tbody>
</table>

Fischer-Tropsch

<table>
<thead>
<tr>
<th>CH₄</th>
<th>C₂H₄,6</th>
<th>CₙH₂n, 2(n+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁⁺</td>
<td>C₂⁺</td>
<td>Cₙ⁺</td>
</tr>
</tbody>
</table>
C-C Bond Formation Bottlenecks in Synthesis Gas Conversion

- monomer synthesis and CO activation (assisted by H*?)
- \( \text{C}_1 \) bottleneck ... formation of initial C-C bond

**Alcohol synthesis**

- \( \text{CH}_3\text{OH} \) \( \text{C}_2\text{H}_5\text{OH} \) \( \text{C}_n\text{H}_{2n+1}\text{OH} \)

**Fischer-Tropsch**

- \( \text{CH}_4 \) \( \text{C}_2\text{H}_{4,6} \) \( \text{C}_n\text{H}_{2n, 2(n+1)} \)
Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H₂) ----> CH₃OH, DME
Catalytic conversion of methanol and dimethylether

Synthesis gas \((\text{CO/H}_2)\) \(\rightarrow\) \(\text{CH}_3\text{OH}, \text{DME}\)

- acetic acid, methyl acetate
- gasoline
- olefins
- polymers, oxygenates, nitriles, ...

DME

- \(\text{HCHO}\)
- \(\text{HCOOCH}_3\)
- \(\text{HCOOH}_3\) (methyl formate) (MF)
- \(\text{CH}_3\text{OCH}_2\text{OCH}_3\) (dimethoxymethane) (DMM)
- \((\text{CH}_3\text{O})_2\text{CO}\) (DMC)
Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H₂) ----> CH₃OH, DME

dimethoxymethane (DMM)
CH₃OCH₂OCH₃
(methyl formate) (MF)

no C-C bonds formed
Catalytic conversion of methanol and dimethylether

Synthesis gas (CO/H₂) ----> CH₃OH, DME

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

- acetic acid, methyl acetate
- gasoline, olefins
- polymers, oxygenates, nitriles, ...
- DME
- (CH₃O)₂CO (DMC)
- HCHO
- CH₃OCH₂OCH₃ (dimethoxymethane) (DMM)
- HCOOCH₃ (methyl formate) (MF)

no C-C bonds formed
Refining Methane into Useful Products

........ in a Methane “Refinery”
Challenges in bringing CH₄ to markets by chemical means

Direct Routes

CH₄ \xrightarrow{\text{X}} -(CH_x)- \rightarrow (C, CO_x)

- overcome thermodynamic constraints
- protect products with weaker C-H bonds
Challenges in bringing CH₄ to markets by chemical means

**Direct Routes**

\[
\text{CH}_4 \xrightarrow{X} -(\text{CH}_x)- \rightarrow (\text{C, CO}_x)
\]

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

**Indirect Routes**

\[
\text{CH}_4 \xrightarrow{X} \text{I}_1 \rightarrow \text{I}_2 \rightarrow -(\text{CH}_x)
\]

\[
(\text{H}_2/\text{CO, CH}_3\text{OH, ..})
\]

- couple endothermic-exothermic steps
- form the first carbon-carbon bond
Challenges in bringing CH₄ to markets by chemical means

Direct Routes

\[ \text{CH}_4 \xrightarrow{X} -(\text{CH}_x) \xrightarrow{} (\text{C, CO}_x) \]

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

Indirect Routes

\[ \text{CH}_4 \xrightarrow{X} I_1 \xrightarrow{} I_2 \xrightarrow{} -(\text{CH}_x) \]

\[ (\text{H}_2/\text{CO, CH}_3\text{OH, ..}) \]

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

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

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow{[\text{Ni}] \text{ heat}} \text{CO}(g) + 3 \text{H}_2(g) \]

\[ \Delta H^\circ = 49.3 \text{ kcal/mol} \]

“Syngas” (CO + nH\textsubscript{2}) is currently used to produce methanol, Fischer-Tropsch’d to hydrocarbons and water, and is water-gas shifted to pure H\textsubscript{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. \[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow{[\text{Ni}] \text{ heat}} \text{CO}(g) + 3 \text{H}_2(g) \quad \Delta H^\circ = 49.3 \text{ kcal/mol} \]

2. \[ \text{CO}(g) + 2 \text{H}_2(g) \xrightarrow{\text{[Cu/ZnO/Al}_2\text{O}_3]} \text{80 atm, 250 °C} \rightarrow \text{CH}_3\text{OH}(g) \quad \Delta H^\circ = -21.7 \text{ kcal/mol} \]

3. \[ \text{CH}_3\text{OH}(g) + \text{CO}(g) \xrightarrow{\text{[Rh or Ir] homogeneous}} \text{[I}^\cdot\text{], 35 atm, 180 °C} \rightarrow \text{CH}_3\text{COOH}(g) \quad \Delta H^\circ = -29.4 \text{ kcal/mol} \]

4. \[ 2 \text{CO}(g) + 4 \text{H}_2(g) \xrightarrow{\text{catalyst?}} \rightarrow \text{CH}_3\text{CH}_2\text{OH}(g) \quad \Delta H^\circ = -61.2 \text{ kcal/mol} \]

5. \[ 2 \text{CO}(g) + 3 \text{H}_2(g) \xrightarrow{\text{catalyst?}} \rightarrow \text{HOCH}_2\text{CH}_2\text{OH}(g) \quad \Delta H^\circ = -55.8 \text{ kcal/mol} \]

6. \[ 2 \text{CO}(g) + 4 \text{H}_2(g) \xrightarrow{\text{catalyst?}} \rightarrow \text{CH}_2=\text{CH}(g) + 2 \text{H}_2\text{O}(g) \quad \Delta H^\circ = -50.3 \text{ kcal/mol} \]

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

\[ \text{CH}_3\text{OH} \xrightarrow{\text{ZnI}_2 \text{ or InI}_3 \text{ 200 °C}} \text{H}_2\text{O} + \text{hydrocarbons (} \sim 20\% \text{ triptane = } \text{octane rating = 102}} \]
Direct methane conversion: what is possible?

indirect routes
reform CH₄ to CO + H₂; use syngas to produce methanol, acetic acid, FT to HC's, etc:

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow{\text{[Ni]}\ \text{heat}} \text{CO}(g) + 3 \text{H}_2(g)
\]
\[\Delta H^\circ = 49.3 \text{ kcal/mol}\]

direct routes

\[
\begin{align*}
\text{CH}_4 + \text{CO} & \rightleftharpoons \text{CH}_3\text{CHO} & \text{uphill: } \Delta H^\circ = 4.6 \text{ kcal/mol} \\
\text{CH}_4 + \text{CO}_2 & \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} & \text{uphill: } \Delta H^\circ = 8.2 \text{ kcal/mol} \\
\text{CH}_4 + \text{CH}_2=\text{CH}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 & \text{downhill: } \Delta H^\circ = -19.4 \text{ kcal/mol}, \\
& & \text{but product less valuable than CH}_2=\text{CH}_2 \\
\text{CH}_4 + \text{CO} + \text{H}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{OH} & \text{downhill: } \Delta H^\circ = -11.9 \text{ kcal/mol}, \\
& & \text{but FT typically does not re-incorporate RH products}
\end{align*}
\]
Oxidative direct routes potentially offer many desirable products (thermodynamics are favorable for most):

\[
\text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{\text{catalyst?}} \text{CH}_3\text{OH}(g) \quad \Delta H^\circ = -30.7 \text{ kcal/mol}
\]

\[
2 \text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{\text{catalyst?}} \text{CH}_3\text{CH}_3(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ = -60.1 \text{ kcal/mol}
\]

\[
\text{CH}_4(g) + \text{CH}_3\text{CH}_3(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{\text{catalyst?}} \text{CH}_3\text{CH}_2\text{CH}_3(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ = -62.4 \text{ kcal/mol}
\]

\[
\text{etc.}
\]

\[
2 \text{CH}_4(g) + \text{O}_2(g) \xrightarrow{\text{catalyst?}} \text{CH}_2=\text{CH}_2(g) + 2 \text{H}_2\text{O} \quad \Delta H^\circ = -67.3 \text{ kcal/mol}
\]

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 O₂ are susceptible to an *autooxidation* mechanism
Methane monooxygenase manages to avoid over-oxidation by using a highly engineered binding pocket

\[
\text{CH}_4 + \text{O}_2 + 2e^- + 2\text{H}^+ \xrightarrow{[\text{MMO}]} \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

or

\[
\text{CH}_4 + \text{NADH} + \text{O}_2 + \text{H}^+ \xrightarrow{[\text{MMO}]} \text{CH}_3\text{OH} + \text{NAD}^+ + \text{H}_2\text{O}
\]

soluble MMO consists of (1) an Fe$_2$ hydroxylase (MMOH, 251 kD), (2) an Fe$_2$S$_2$-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 $\alpha$ and $\beta$ 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:

\[
\begin{align*}
\text{CH}_4 + Q\cdot & \xrightarrow{k_1} \text{CH}_3\cdot + \text{QH} (Q\cdot = \text{HO\cdot, MO, ...}) \\
\text{CH}_3\text{OH} + Q\cdot & \xrightarrow{k_2} \text{HOCH}_2\cdot + \text{QH}
\end{align*}
\]

\(k_2/k_1\) is typically 20 to 100, implying maximum yield \(\approx 4\%\); 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 organo-transition metal chemistry:

\[
\text{CH}_4 + [\text{L}_n\text{M}] \rightarrow \text{L}_n\text{M} - \text{CH}_3^+ + \text{H}^+ \\
\text{M} = \text{d-block transition metal} \\
\text{L} = \text{"ligand" group; controls reactivity of M} \\
\text{non radical pathways common} \\
\text{low T} \\
\text{[O], CO insertion} \\
\text{redox coupling} \\
\text{H}_2 \text{redox} \\
\text{olefins} \\
\text{higher alkanes}
\]
A particularly promising “electrophilic” system:

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

\[
\begin{align*}
\text{CH}_4 + \text{Pt}^{IV}\text{Cl}_6^{2-} + \text{H}_2\text{O} \quad \xrightarrow{120^\circ C} \quad [\text{Pt}^{II}\text{Cl}_4^{2-}] & \quad \text{CH}_3\text{OH} \ (\& \text{CH}_3\text{Cl}) + \text{Pt}^{II}\text{Cl}_4^{2-} + 2 \text{H}^+ + 2\text{Cl}^- \\
\end{align*}
\]

- 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 \equiv -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”

\[
\text{Cl} \cdot \text{Pt}^{II} \cdot \text{OH}_2 + \text{CH}_4 \xrightarrow{i} \left[ \text{Cl} \cdot \text{Pt}^{II} \cdot \text{CH}_3 \right]^- + \text{H}^+ \\
2 \text{Cl}^- + \text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{Cl} \\
\text{S}_N2 \text{ displacement} \\
\text{H}_2\text{O} \rightarrow \text{Cl}^- \\
\text{Cl}^- \\
\left[ \text{Pt}^{IV} \text{Cl}_6 \right]^{2-} \\
\text{electron transfer} \\
\left[ \text{Pt}^{II} \text{Cl}_4 \right]^{2-} \\
\text{net: } \text{CH}_4 + \left[ \text{Pt}^{IV} \text{Cl}_6 \right]^{2-} + \text{H}_2\text{O} \xrightarrow{[\text{Pt}^{III}]} \text{CH}_3\text{OH} + \left[ \text{Pt}^{II} \text{Cl}_4 \right]^{2-} + 2\text{HCl}
\]

**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\text{IV} oxidant with more practical one...O\text{2} best?

ii. Can we increase rate?

iii. If we succeed in making cycle catalytic with O\text{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\textsuperscript{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(CH₃)L]⁺ with arenes are clean models for methane activation step in Shilov oxidation system:

aqueous system relatively slow

solvent C-D bonds totally inert!!

non-aqueous system faster
High pressure NMR studies of methane activation in the forward direction:
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 $\text{C}_6\text{D}_6$ gives an approximately 7 M solution
Relative rates of C-H activation with [(diimine)Pt(CH₃)(TFE)]⁺, first generation model for Shilov system:

\[
\begin{align*}
\text{Ar} & \quad \text{Pt} & \quad \text{CH₃} & \quad \text{ODCD₂CF₃} \\
\text{D} & \quad \text{Ar} & \quad \text{R} & \quad \text{ODCD₂CF₃}
\end{align*}
\]

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

- \( H-\text{C}H \): 80
- \( H-\text{CMe}_3 \): 10
- \( H-\text{CF}_3 \): 200
- \( \text{C-H Oxidative Addition} \)
- \( \text{Order of strength of metal-ligand bond:} \)
  - Lone pair donation:  \( \text{C} \)  >  \( \text{C}π \)  >  \( \text{C}σ \)

- \( H-\text{CH(OH)CF}_3 \): 6
- \( H-\text{CHCl}_2 \): 2
- \( H-\text{CH₂OCH}_3 \): 1.2
- \( H-\text{CHOH} \): 1.0

\( \text{C-H σ bond coordination rate determining} \)
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$_2$Cl$_2$, CF$_3$CH$_2$OH) 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$_3$OH reacts ca. 200 times faster than CH$_4$ with Me$_3$COO·).
Can estimate $rate_1$ vs $rate_2$ for some oxidations of the original Shilov system ($\text{Pt}^{II}/\text{Pt}^{IV}$ aqueous chlorides), and related Pt system:

$$
\begin{align*}
\text{CH}_3 & \rightarrow \text{Shilov} \rightarrow \text{CH}_2\text{OH} \\
& \quad \text{rate}_1 \\
\text{CH}_2\text{OH} & \rightarrow \text{Shilov} \rightarrow \text{CHO} \\
& \quad \text{rate}_2 \\
\text{CHO} & \rightarrow \text{Shilov} \rightarrow \text{COOH} \\
& \quad \text{rate}_3 \\
\frac{\text{rate}_1}{\text{rate}_2} & \sim 1.5 \\
\frac{\text{rate}_1}{\text{rate}_3} & > 10^3!
\end{align*}
$$

$$
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{OH} & \rightarrow \text{Shilov} \rightarrow \text{CH}_3\text{CH}_2\text{OH} \\
& \quad \text{rate}_1 \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{Shilov} \rightarrow \text{CH}_3\text{CHO} (\& \text{CH}_3\text{COOH}) \\
& \quad \text{rate}_2 \\
\frac{\text{rate}_1}{\text{rate}_2} & \sim 1.5 \\
\text{Caltech}
\end{align*}
$$

$$
\begin{align*}
\text{CH}_4 + 2 \text{H}_2\text{SO}_4 & \rightarrow \text{CH}_3\text{OSO}_3\text{H} + \text{SO}_2 + 2 \text{H}_2\text{O} \\
\text{catalyst based on} & \\
\text{Catalytica}
\end{align*}
$$

73% max one pass yield!
Improving the practicality of a Shilov-based alkane oxidation system

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

\[ [\text{Cu}^{II}\text{Cl}_4]^{2-} > [\text{Pt}^{IV}\text{Cl}_6]^{2-} > [\text{Fe}^{III}\text{Cl}_4]^{-} \sim [\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}]^{3-} \]

\[ \frac{k_{ii}}{k_{-i}} = \frac{8}{2} \frac{2}{1} \frac{1}{1} \]

(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:

\[
\begin{align*}
\text{Pt}^{II}L_{2} & \quad + \quad \text{CH}_{3}\text{CH}_{2}\text{SO}_{3}^{-} \quad \xrightarrow{i} \quad \text{Pt}^{II}L_{2}L^{-} \quad + \quad \text{H}^{+} \\
\text{L} = \text{Cl}^{-}, \text{H}_{2}\text{O} & \quad \xrightarrow{iii} \quad \text{HOCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-} + \text{H}^{+} \quad + \quad \text{H}_{2}\text{O} \quad \xrightarrow{ii} \quad \text{Pt}^{IV}L_{2}L^{-} \quad + \quad 2\text{Cu}^{2+} \\
& \quad \xrightarrow{1/2\text{O}_{2} + 2\text{H}^{+}} \quad 2\text{Cu}^{+} \quad \xrightarrow{1/2\text{O}_{2},150^\circ\text{C}} \quad \text{XCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-} \\
& \quad \text{net: CH}_{3}\text{CH}_{2}\text{SO}_{3}^{-} + 1/2\text{O}_{2} \quad \xrightarrow{340\text{ psi }\text{O}_{2},150^\circ\text{C}} \quad \text{XCH}_{2}\text{CH}_{2}\text{SO}_{3}^{-} \\
& \quad 75\% (X = \text{OH}; 25\% (X = \text{Cl}) \\
& \quad \text{CH}_{3} + 1/2\text{O}_{2} \quad \xrightarrow{340\text{ psi }\text{O}_{2},150^\circ\text{C}} \quad \text{CH}_{2}X \quad + \quad \text{CHO} \\
& \quad 64\% (X = \text{OH}; 33\% (X = \text{Cl}; 3\%}
\end{align*}
\]

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 $\sigma$ adduct formation for alkanes (and methanol)
  - Shilov system and models are not selective, except (not) for TFE & $\text{CH}_2\text{Cl}_2$.
  - 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 $\text{Pt}^{\text{II}}$-$\text{CH}_3$ over $\text{Pt}^{\text{II}}$-solvento.
  - dioxygen capable of cleanly oxidizing dimethylplatinum(II) complexes, but not monomethylplatinum(II)-halides or -solvento cations.
  - $\text{Cu}^{\text{I}}$/Cu$^{\text{II}}$ and $\text{O}_2$ 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.
Acknowledgments

Dr. Jay A. Labinger
Dr. Andrew Herring (NREL)
Dr. David Lyon (Bend Research)
Dr. Gerrit Luinstra (BASF)
Dr. James Gilchrist
Dr. Lin Wang (DuPont)
Professor Shannon Stahl (U Wisconsin)
Dr. Matt Holtcamp (ExxonMobil)
Dr. Seva Rostovtsev (DuPont)
Dr. Antek Wong-Foy (U Michigan)
Dr. John Scollard (Testmark)
Professor Lars Johansson (Stockholm)
Dr. Annita Zhong (Yale Law School)
Dr. Christoph Balzarek (Celanese)
Dr. Joseph Sadighi (US Army)
Dr. Lily Ackerman (Symyx)
Professor Alan Heyduk (UC, Irvine)
Professor Tom Driver (U Illinois, Chicago)
Dr. Jonathan Owen (UC, Berkeley)
David Weinberg
Dr. Jeff Byers (MIT)
George Chen
Dr. Tom Baker (Los Alamos)
Professor Mats Tilset & M. Lersch (U Oslo)
Professor Travis Williams (USC)
Dr. Nilay Hizari
Valerie Scott
Paul Oblad
Professor Andrew Caffyn (University of the West Indies)