Is oxidative coupling the royal road for the valorization of methane to olefines?


Presentation at „Changing Landscape…“-Workshop, Washington, DC, March 7-8, 2016
The Scenario

**Indirect methods**

- CH$_3$OH
- Synthesis of methanol
- CO + H$_2$ production
- Fischer-Tropsch synthesis
  - Alkane, Olefin, Alcohol

**Direct methods**

- CH$_3$OH, CH$_2$O
- Synthesis of methanol and formaldehyde
- Oxidative coupling
- C$_2$H$_4$
- Without an oxidant
  - Aromatics, H$_2$
Oxidative coupling of methane is economically viable, if:

- added value is high
- methane is not wasted
- energy demand is appropriate
- capital expenditure is reasonable
M. Hinsen, M. Baerns, Chem. Z. 1983, 107, 223
A.C. Jones, J.J. Leonardo et al., US patent 4 443644, 1984

Milestone 1: The Lunsford Mechanism of OCM

- Optimal loading for initial activity: 0.5 wt% Li/MgO
- No stable Li/MgO-catalyst
- Still active after Li-Loss
- No selectivity

Milestone 2: The first kinetic model

![Reaction scheme diagram]

\[ r_2 = \frac{k_{0,2}e^{-E_{a,2}/RT}(K_{0,0}e^{-\Delta H_{ad,O_2}/RT}p_{O_2})^{n_2}p_{Cl}}{[1 + (K_{0,0}e^{-\Delta H_{ad,O_2}/RT}p_{O_2})^{n_2} + K_{j,CO_2}e^{-\Delta H_{ad,O_2}}]} \]

\[ r_7 = k_{0,7}e^{-E_{a,7}/RT}p_{C_2H_6} \]

\[ r_8 = k_{0,8}e^{-E_{a,8}/RT}p_{C_2H_4}^{m_8}p_{H_2O}^{n_8} \]

\[ r_9 = k_{0,9}e^{-E_{a,9}/RT}p_{CO}^{m_9}p_{H_2O}^{n_9} \]

\[ r_{10} = k_{0,10}e^{-E_{a,10}/RT}p_{CO_2}^{m_{10}}p_{H_2}^{n_{10}} \]

LaO\textsubscript{2}O\textsubscript{3} (27at\%)/CaO

**Figure 8.** Reaction scheme.

Milestone 3: Mn-doped Na$_2$WO$_4$/SiO$_2$


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<tr>
<th></th>
<th>X CH4</th>
<th>S C2</th>
<th>Y C2</th>
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<tr>
<td>Na$_2$WO$_4$/SiO$_2$</td>
<td>0.11</td>
<td>0.75</td>
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<tr>
<td>MnO$_x$/SiO$_2$</td>
<td>0.16</td>
<td>0.34</td>
<td>0.07</td>
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<tr>
<td>Na$_2$WO$_4$/Mn/SiO$_2$</td>
<td>0.37</td>
<td>0.65</td>
<td>0.24</td>
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</table>


200 g batches with spray drying technology

Milestone 4: OCM at La$_2$O$_3$

CH$_4$ $\xrightarrow{[1]}$ CO$_x$ $\xrightarrow{[1]}$ O$_2$ $\xrightarrow{[1]}$ CH$_4$ $\xrightarrow{[4,7]}$ CH$_3^-$ $\xrightarrow{[4,5]}$ CH$_4$ $\xrightarrow{[7]}$ O$_2^-$

EA = 39 kcal/mol

10 kcal/mol

$\xrightarrow{[2,3]}$ CO$_2$

increase selectivity!

La$_2$O$_2$CO$_3$

La$_x$Fe$_y$O$_3$

La$_x$Ce$_y$O$_z$

Milestone 5: unconventional approaches

Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen
Xiaoguang Guo et al.
Science 344, 616 (2014);
DOI: 10.1126/science.1253150

Sulfur as a selective ‘soft’ oxidant for catalytic methane conversion probed by experiment and theory
Qingjun Zhu¹, Staci L. Wegener¹, Chao Xie¹, Obioma Uche², Matthew Neurock²* and Tobin J. Marks¹*
Who is who in OCM

<table>
<thead>
<tr>
<th>Author</th>
<th>Publications*</th>
<th>Citations*</th>
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<td>J.H. Lunsford</td>
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<td>V.R. Chaudhary</td>
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<td>J.R.H. Ross</td>
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<td>K. Fujimoto</td>
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<td>J.B. Moffat</td>
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<td>C. Mirodatos</td>
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<td>A.G. Anshitz</td>
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<td>261</td>
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* Web of Science, 25.7.2014
The UNICAT concept

Multi scale approach for atomic to plant level
Model studies for understanding complexity
Feasibility studies in mini-plant

<table>
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<tr>
<th>Catalyst</th>
<th>( T/K )</th>
<th>( p(\text{CH}_4)/\text{kPa} )</th>
<th>( p(\text{O}_2)/\text{kPa} )</th>
<th>( P_{\text{total}}/\text{kPa} )</th>
<th>( X(\text{CH}_4)/% )</th>
<th>( S(\text{C}_2)^a/% )</th>
<th>( Y(\text{C}_2)^b/% )</th>
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<tbody>
<tr>
<td>Li/MgO</td>
<td>1013</td>
<td>10</td>
<td>5</td>
<td>100</td>
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<td>50.3</td>
<td>19</td>
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<tr>
<td>30% BaO/Ga(_2)O(_3)</td>
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<td>16.8</td>
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<td>32</td>
<td>54</td>
<td>17.3</td>
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<tr>
<td>95 \text{mol% BaF}_2/Y(_2)O(_3)</td>
<td>1023</td>
<td>16.8</td>
<td>6.8</td>
<td>100</td>
<td>36.1</td>
<td>62.1</td>
<td>22.4</td>
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<td>La/MgO</td>
<td>1073</td>
<td>80</td>
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<td>100</td>
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<td>58.8</td>
<td>17.2</td>
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<td>Rb(_2)WO(_4)/SiO(_2)</td>
<td>1123</td>
<td>82</td>
<td>18</td>
<td>100</td>
<td>32</td>
<td>78</td>
<td>25</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Y(</em>{0.3})Sm(_{0.2})O(_3-\delta)</td>
<td>1223</td>
<td>33.3</td>
<td>16.6</td>
<td>100</td>
<td>43.5</td>
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<tr>
<td>La(_2)O(_3-)CeO(_2)</td>
<td>1048</td>
<td>83.6</td>
<td>16.4</td>
<td>100</td>
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<td>66</td>
<td>14.7</td>
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<td>Na(_2)WO(_4)/SiO(_2)</td>
<td>1123</td>
<td>82</td>
<td>18</td>
<td>100</td>
<td>44</td>
<td>52</td>
<td>22.9</td>
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<tr>
<td>Sm(_2)O(_3)</td>
<td>1053</td>
<td>87.4</td>
<td>12.6</td>
<td>100</td>
<td>20</td>
<td>65.4</td>
<td>13.1</td>
</tr>
</tbody>
</table>

\( ^a S(\text{C}_2) = \) selectivity towards \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \).

\( ^b Y(\text{C}_2) = \) yield of \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \).

* table adopted from E. V. Kondratenko, M. Baerns
Handbook of Heterogeneous Catalysis, Vol. 6, Ch. 13.17, 2008
Multi-scale approach to OCM

Mechanism of Oxidative Coupling of Methane

2 \( \text{CH}_4 \) + \( \text{O}_2 \) \( \rightarrow \) \( \text{C}_2\text{H}_4 \) + 2 \( \text{H}_2\text{O} \) (+ \( \text{CO}_2 \))

**Origin of low selectivity**

- OCM is initiated by oxygen activation (**AFM, DFT, Model catalysts**)
- Selective and **inselective** oxygen species at all catalysts (**TAP, TPSR**)
- Electron donors (dopants, defects) cause oxygen dissociation (**AFM, Model catalyst**)
- Formation of methyl radicals at selective oxygen species (**Kinetics, KIE, Model cat.**)
- Combustion of methane at inselective species (**Kinetics, KIE**)
- Parallel **gas phase combustion** at increased oxygen partial pressure (**Profile R.**)

The Puzzle of Information

How to get started?

Searching for more pieces?

Joining central pieces?
A simple example
A simple example
Experiments in a TAP reactor

- Time-resolved technique (10^{-3} s)
- Reaction intermediates
- Sequence in a multistep reaction
- Complex kinetic phenomena
- Number of active sites

Pump experiments
- Size ~ 10^{13}-10^{17} molec.
- Width ~ 100 \mu s
- Pulse rate ~ 0.1-50 s^{-1}
- Increasing delay of CH$_4$ leads to decrease of CO$_2$ and C$_2$H$_6$ stays constant

- weakly adsorbed oxygen leads to total oxidation
  \[ * + O_2 \rightarrow *O_2 \]

- strongly adsorbed oxygen is responsible for methyl radical formation
  \[ * + O \rightarrow *O \]

- smaller ratio between weakly and strongly adsorbed oxygen at Mn/Na$_2$WO$_4$/SiO$_2$
Dynamic experiment

750 °C, 30 nml/min, 1g catalyst
S(C2) = 0.89

- C2 Selectivity unexpected high in dynamic experiments at constant temperature
- less oxygen species on the catalyst surface than in steady state exp.
Characteristics of MgO prior to reaction

S-MgO

Ultra pure commercial MgO

Sol-gel synthesis

C-MgO

Mg oxidation

SG-MgO

Hydrothermal post treatment

MW-MgO

Hydrothermal post treatment in microwave autoclave

Rate of methane consumption decreases with decreasing number of monoatomic steps observed with CO as probe molecule by IR
Structure sensitivity of MgO during reaction

Eley-Rideal mechanism

<table>
<thead>
<tr>
<th></th>
<th>rate $[\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{cat}}^{-1}]$</th>
<th>rate $[\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}_{\text{cat}}^{-2}]$</th>
<th>$X(\text{CH}_4) [%]$</th>
<th>$S(\text{C}_2) [%]$</th>
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<tbody>
<tr>
<td>initial state</td>
<td>214.4</td>
<td>5.56</td>
<td>25.04</td>
<td>29.84</td>
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<tr>
<td>final state</td>
<td>8.57</td>
<td>1.26</td>
<td>4.70</td>
<td>13.85</td>
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</table>

- CH$_4$ adsorbes and is activated
- O$_2$ leads to methyl radical formation
- Superoxide identified by EPR

Mechanism of OCM at MgO

- $\text{CH}_3^-/\text{H}^+$
- $\text{O}_2$ ads
- $\text{TS}$
- $\text{Int-1a}$
- $\text{Int-1b}$
- $\text{O}_2^-$
- $\text{Int-2}$

Energy, Gibbs free energy (kJ/mol)

- $d(\text{O-O})/d(\text{Mg-O})$
- $1013 \text{ K, 0.1 MPa}$

$\text{CH}_3^-/\text{H}^+$ + $\text{O}_2$ → $\text{TS}$ → $\text{Int-1a}$ → $\text{Int-1b}$ → $\text{Int-2}$


Baldowski, Sauer, unpublished
**Mechanism:**
- Mo-donors in CaO transfer charges into O$_2$ molecules bound to surface
- Formation of pre-dissociated O$_2^-$ species
- Final dissociation via electron tunneling from STM tip

**Experimental evidence:**
- Work function increase after O$_2$ dosage only in the case of doped films
- no O$_2$ adsorption at 300 K for pristine CaO

Mo-doped CaO films on Mo(001)

As dosed $O_2$: Molecular species
(scanning below 2.5 V sample bias)

After dissociation with STM tip
(electron injection with 3.0 eV energy)

Doping of MgO with Fe

Figure 1. a) HRTEM image showing the stepped surface of Au-Fe-MgO. b) HAADF STEM image with characteristic bright contrast at steps and edges due to decoration with heavy atoms. c) Columns of heavy atoms can also be seen in thin regions in HRTEM.
OCM on MgO

O₂ → O₂⁻ [Mg²⁺, HO⁻] → HO₂⁻ [Mg²⁺, HO⁻] → COₓ

CH₄ → CH₃⁻ [Mg²⁺, HO⁻] → OH⁻ [Mg²⁺, HO⁻] → H₂O

Fe doping [2] or N₂O as oxidant [3] increase selectivity

EA 0K [kJ/mol]
Gibbs Free Energy, 1013 K, 0.1 MPa

Bi-metallic Na₂WO₄/Mn/SiO₂ catalysts for OCM

- Provides/stores lattice oxygen
- Works without gas phase oxygen
- Deep oxidation catalyst for methane

How does it work?

- Selective OCM catalysts
- Needs oxygen source to form methyl radicals

OCM in transient experiments

Electronegativity (Pauling Scale) Oxides

- V₂O₅
- Mn₂O₃
- Na₂WO₄
- MgO
Support variation for $\text{Mn}_x\text{O}_y/\text{Na}_2\text{WO}_4/\text{SiO}_2$

silica support

commercial

nanostructured (SBA-15)

pre-catalyst

Impregnation

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$

Mn(ac)$_2\cdot 4\text{H}_2\text{O}$

catalyst

Calcination

750°C

Up-scaling of catalyst synthesis

Support variation for $\text{Mn}_x\text{O}_y/\text{Na}_2\text{WO}_4/\text{SiO}_2$

Distribution of Mn-Na$_2$WO$_4$ on commercial

Green - W
Red - Mn

nanostructured (SBA-15)
silica supports

M. Yildiz, U. Simon, T. Otremba, K. Kailasam, Y. Aksu, A. Thomas, R. Schomäcker, S. Arndt *Catalysis Today* 2014, 228, 5-14
Support variation for $\text{Mn}_x\text{O}_y/\text{Na}_2\text{WO}_4/\text{SiO}_2$

Testing in lab scale reactor at 750 °C ($C_2$-Yield= 12 %)
In mini-plant membrane reactor at 810 °C ($C_2$-Yield= 23 %)

Dynamic Experiments

- At reaction temperature the catalyst is **oxidized by air**

- Reactor is **purged with Helium** to remove oxygen in gas phase and weakly adsorbed one

- Defined amount of **methane is dosed** into the reactor

- Reaction mixture is analysed by mass spectroscopy

- Catalyst activity can be analyzed without gas phase oxidation reactions
Repetitive dynamic experiments

- Repetitive methane pulses allow to study the available amount of oxygen

<table>
<thead>
<tr>
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<th>Na\textsubscript{2}WO\textsubscript{4} (5%) / Mn (2%)@Quartz</th>
<th>Na\textsubscript{2}WO\textsubscript{4} (5%) / Mn (2%)@SBA15</th>
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<tbody>
<tr>
<td>O ((\mu\text{mol/g}_{\text{cat}}))</td>
<td>20.5</td>
<td>68.9</td>
</tr>
</tbody>
</table>
OCM at Na$_2$WO$_4$/Mn/SiO$_2$

- Infeasibility of various spectroscopic techniques
- Mechanism proposed by analogy to other systems

\[ \text{CH}_4 \xrightarrow{[1]} \text{CO} \xrightarrow{[1]} \text{CH}_4 \]

\[ \text{H}_2\text{O} \xrightarrow{\text{CUS}} \text{CH}_3\cdot \]

\[ \text{O}_2 \xrightarrow{\text{O}_2,\text{ads}} \]

\[ \text{CH}_4 \xrightarrow{\text{O}^-} \text{H}_2\text{O} \]

\[ \text{Mn doping [2] increases activity and selectivity} \]

Network of surface reactions at $\text{Mn}_x\text{O}_y/\text{Na}_2\text{WO}_4/\text{SiO}_2$.

**Activity**
- Catalyst oxidation
- Methane activation

**Selectivity**
- $\text{C}_2\text{H}_6^{+} + \text{M} \rightarrow \text{C}_2\text{H}_5^{+} + \text{M}^+$
- $\text{C}_2\text{H}_5^{+} + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$

**Support Material**
- SiO$_2$ - support material ($\alpha$ - cristobalite)
- Na$_2$WO$_4$/Mn$_2$O$_3$ - amorphous/glass phase

**Notes**
- Na$^+$ ions induce support material phase transition
- M: collision partner
OCM in a mini-plant reactor

**Fluidized Bed Reactor**

- Isothermal reaction
- Sensitive to free gas volume

**Reactor performance**

2% Mn-2.2% Na₂WO₄/SiO₂ catalyst, particle size 250-450 μm
Bed height: 10 cm, CH₄:O₂ = 1.7 to 10,
Feed Flow rate: 0.1 l/min – 40 l/min, 45 g catalyst
OCM membrane reactor set-up
Performance indicators of the membrane reactor

2%Mn-5%Na$_2$WO$_4$/SiO$_2$ catalyst (4 g), average particle size 250-450 μm

Contours were made by using 40 experimental data
Reactor concept: Chemical looping

**Operation steps:**

1. $O_2$ is dosed to oxidize the catalyst
2. Reactor is purged with inert gas to remove gas phase oxygen
3. $CH_4$ dosage to perform OCM
4. Purge with He to remove unconverted methane
Continuous operation

Early pulses

Late pulses

Early pulses

Late pulses

Looping

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<td>$X_{\text{CH}_4}$</td>
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<tr>
<td>$S_{\text{C}_2}$</td>
<td>0.78</td>
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<tr>
<td>$Y$</td>
<td>0.22</td>
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<td>STY $\mu\text{mol}(\text{C}_2)/\text{g}^{*}\text{h}$</td>
<td>83 with diluent</td>
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Steady State

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<tbody>
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<td>$X_{\text{CH}_4}$</td>
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<tr>
<td>$S_{\text{C}_2}$</td>
<td>0.63</td>
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<tr>
<td>$Y$</td>
<td>0.18</td>
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<tr>
<td>STY $\mu\text{mol}(\text{C}_2)/\text{g}^{*}\text{h}$</td>
<td>529</td>
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</table>

2 g catalyst, 1 ml CH$_4$ pulse, 1 ml O$_2$ pulse, 775 °C, 30 nml/min
Continuous operation

2 g catalyst, 1 ml CH₄ pulse, 1 ml O₂ pulse, 30 nml/min
Simulations with Aspen Plus & Aspen Process Economic Analyzer v8.8

Production capacity is one million tonnes per year
Ethylene price 947 Euro/tone

1. Case I (OCM Reaction Unit + CO$_2$ separation Unit + Demethanizer Unit + C$_2$-Splitter Unit)

2. Case II (OCM Reaction Unit + CO$_2$ separation Unit + Demethanizer Unit + C$_2$-Splitter Unit + Ethane Dehydrogenation Unit)

3. Case III (OCM Reaction Unit + C$_2$H$_4$ adsorption/Desorption Unit + C$_2$-Splitter Unit + Ethane Dehydrogenation Unit)
OCM to Ethylene (Case I)

Amine scrubbing (30% wt MEA)
Energy needed: 8 GJ/t-CO₂
Energy cost associated: 14.3 €/t-CO₂

OCM reactor: Mn-Na₂WO₄/SiO₂ catalyst
Membrane reactor (40% conv. & 62% sel.)
<5% N₂, dense membrane, air separation

Methane-cryogenic media cycle
Energy needed: 4.8 GJ/t-CO₂
Energy cost associated: 104.4 €/t-C₂H₄

Propylene-cryogenic media cycle
Energy needed: 4.7 GJ/t-CO₂
Cost associated: 8.8 €/t-C₂H₄
99.8 % Ethylene purity
OCM to Ethylene (Case II)

Amine scrubbing (30%wt MEA)
Energy needed: 5.8 GJ/t-CO₂
Energy cost associated: 12.8 €/t-CO₂

EDH reactor (60% conv. & 65% sel.)
Conventional performance

Methane-cryogenic media cycle
Energy needed: 6.5 GJ/t-C₂H₄
Cost associated: 120.5 €/t-C₂H₄

Compression
Energy needed: 0.4 GJ/t-C₂H₄
Electricity cost: 8.6 €/t-C₂H₄

Propylene-cryogenic media cycle
Energy needed: 3.8 GJ/t-C₂H₄
Cost associated: 7.3 €/t-C₂H₄
99.9 % Ethylene purity
OCM to Ethylene (Case III)

OCM reactor:
Mn-Na$_2$WO$_4$/SiO$_2$ cat.
40% conv. 62% sel.
air separation

Amine scrubbing (30%wt MEA)+Membrane (Hybrid)
Energy needed: 10.93 GJ/t-CO$_2$
Energy cost associated: 22 €/t-CO$_2$

EDH reactor (58% conv. & 63% sel.)
Conventional performance

Propylene-cryogenic media cycle
Energy needed: 3.38 GJ/t-C$_2$H$_4$
Cost associated: 10.42 €/t-C$_2$H$_4$
99.9% Ethylene purity
## Results of Economic Analysis

<table>
<thead>
<tr>
<th>Economic Parameter</th>
<th>Case I (Millions € per year)</th>
<th>Case II (Millions € per year)</th>
<th>Case III (Millions € per year)</th>
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<tbody>
<tr>
<td>Project Capital Cost</td>
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<td>334</td>
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<td>Operating Cost</td>
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<td>907</td>
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<td>Raw Material Cost</td>
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<td>Utilities Cost</td>
<td>418</td>
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<tr>
<td>Product (C₂H₄) Sales</td>
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<td>1136</td>
<td>1208</td>
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<tr>
<td>Desired Rate of Return</td>
<td>15%</td>
<td>15%</td>
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<tr>
<td>Pay Out Period (years)</td>
<td>7</td>
<td>5</td>
<td>4</td>
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</table>
OCM integrated with dry reforming of methane

Further Modifications: Autothermal Reactor

Further Options: OCM with methanol
OCM with styrene
OCM with Ethylene oxide
OCM with oligomerization
- The puzzling informations about OCM are essembled in a complete picture

- Oxygen activation is the key step in OCM mechanism

- Selectivity is controlled by different oxygen species

- Implications for new catalyst materials and their synthesis
  - single phase, highly conductive, non-reducible, e-donor/acceptor

- New options with chemical looping technology

- Techno-economic analysis shows potential for further optimization
The authors acknowledge the support from the Cluster of Excellence „Unifying Concepts in Catalysis“ coordinated by the Berlin Institute of Technology - Technische Universität Berlin and funded by the German research foundation - Deutsche Forschungsgesellschaft – DFG.

Thank you for the attention!