Heterogeneous Catalysts for the Thermal Conversion of Methane to Products

Workshop on Advances in Conversion of Methane to Fuels and Chemical
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Source Materials

The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production
Implications for Catalysis
A Workshop Report

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Methane conversion into different hydrocarbons or oxygenates: current status and future perspectives in catalyst development and reactor operation†

Evgenii V. Kondratenko,* Tim Peppel, Dominik Seeburg, Vita A. Kondratenko, Narayana Kalevaru, Andreas Martin and Sebastian Wohlrab*

This Perspective highlights recent developments in methane conversion into different hydrocarbons and oxygenates (methanol, its derivatives, and formaldehyde) with the purpose to address the global demand for efficient and environmentally friendly production of these bulk chemicals. Our analysis identified possible directions for further research to bring the above approaches to a commercial level. As no progress in the development of catalysts for the oxidative coupling of methane could be identified, improvements are expected through reactor operation, cost- and energy-efficient methods for product separation and for providing pure oxygen. With respect to methane oxidation to methanol, further progress can also be achieved by proper catalyst design on the basis of fundamental knowledge especially gained from homogeneous and enzymatic catalysts as well as from theoretical calculations.

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Outline

• Background and motivation
• Oxidative coupling of methane—catalysts and processes
• Methane pyrolysis
• Direct oxidation of methane to methanol
• Direct oxidation of methane to formaldehyde
• Outlook and Perspective for future research
The rapid growth in shale gas production in the US has made methane and attractive and relatively inexpensive source of carbon for fuels and chemicals.
The price of NG in the US has fallen since 2005 from ~ $9/MM BTU to ~ $2.5 MM BTU in 2015.

Over the same period the price of NG in Europe and Asia has risen significantly relative to the US.

Likewise the cost oil on a BTU basis has risen.
• During the past 12 years, the US has moved from having the highest production costs for chemicals to being one of the lowest.
The shale gas boom has led to rapid increases in capital investments, number of jobs, economic output, and new tax revenue.
Components of Natural Gas

Natural Gas: $\text{CH}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_8$

Chemical Feedstocks: $\text{CO}/\text{H}_2$, $\text{CH}_2=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CH}_2$, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_6$

• All of the components of natural gas can be converted to fuels and chemicals
Options for Using Shale Gas

- In principle, shale gas can be used to produce all chemical intermediates needed for the chemical industry.

What else can be made from CH$_4$ in addition to CO/H$_2$?
Options for Converting Methane to Chemicals

Conversion of Methane

Pyrolysis: \[ \text{CH}_4(g) \overset{\text{C}}{\rightleftharpoons} \frac{1}{6} \text{C}_6\text{H}_6(g) + 1.5 \text{H}_2(g) \]

\[ \text{CH}_4(g) \overset{\text{C}}{\rightleftharpoons} \frac{1}{2} \text{C}_2\text{H}_4(g) + \text{H}_2(g) \]

Steam Reforming: \[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \overset{\text{C}}{\rightleftharpoons} \text{CO}(g) + 3 \text{H}_2(g) \]

Dry Reforming: \[ \text{CH}_4(g) + \text{CO}_2(g) \overset{\text{C}}{\rightleftharpoons} 2 \text{CO}(g) + 2 \text{H}_2(g) \]

Oxidative Coupling: \[ \text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \overset{\text{C}}{\rightleftharpoons} \frac{1}{2} \text{C}_2\text{H}_4(g) + 2 \text{H}_2\text{O}(g) \]

Partial Oxidation: \[ \text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \overset{\text{C}}{\rightleftharpoons} \text{CH}_3\text{OH}(g) \]

\[ \text{CH}_4(g) + \text{O}_2(g) \overset{\text{C}}{\rightleftharpoons} \text{H}_2\text{C}=\text{O}(g) + \text{H}_2\text{O}(g) \]

We will look at each of the options with an eye towards determining what is new and perspective
# Options for Converting Methane to Chemicals

## Conversion of Methane

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis:</td>
<td>[ \text{CH}_4 (g) \rightleftharpoons \frac{1}{6} \text{C}_6\text{H}_6 (g) + 1.5 \text{H}_2 (g) ]</td>
</tr>
<tr>
<td></td>
<td>[ \text{CH}_4 (g) \rightleftharpoons \frac{1}{2} \text{C}_2\text{H}_4 (g) + \text{H}_2 (g) ]</td>
</tr>
<tr>
<td>Steam Reforming:</td>
<td>[ \text{CH}_4 (g) + \text{H}_2\text{O} (g) \rightleftharpoons \text{CO} (g) + 3 \text{H}_2 (g) ]</td>
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<td>[ \text{CH}_4 (g) + \text{CO}_2 (g) \rightleftharpoons 2 \text{CO} (g) + 2 \text{H}_2 (g) ]</td>
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<tr>
<td>Partial Oxidation:</td>
<td>[ \text{CH}_4 (g) + \frac{1}{2} \text{O}_2 (g) \rightleftharpoons \text{CH}_3\text{OH} (g) ]</td>
</tr>
<tr>
<td></td>
<td>[ \text{CH}_4 (g) + \text{O}_2 (g) \rightleftharpoons \text{H}_2\text{C}=\text{O} (g) + \text{H}_2\text{O} (g) ]</td>
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</tbody>
</table>

We will look at each of the options with an eye towards determining what is new and perspective.
Syngas generation – 45% of CAPEX
Fischer-Tropsch synthesis – 15% of CAPEX
Product separation and upgrading – 20% of CAPEX

$83,000/bbl oil equivalent
Economic of NG Conversion to Liquid Fuels

• Today’s NG costs ~ $2.50/MMBTU and crude oil costs ~ $50/bbl, which make the economics for GTL prohibitive
Options for Converting Methane to Chemicals

Conversion of Methane

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We will look at each of the options with an eye towards determining what is new and perspective
Most of the publication on OCM catalysts were reported between 1985 and 2005.

Since 2005 there has been a renewed level of interest in OCM.

Catalysts tested since 2010 do not differ significantly from those tested earlier.
Only four catalysts lie above the 30% yield line.
No significant breakthroughs in OCM catalyst performance have been achieved by using single-pass reactors with O$_2$ since 2010.

Catalyst Engineering – $\text{Mn}_x\text{O}_y\cdot\text{Na}_2\text{WO}_4/\text{SiO}_2$

### Table 1
The codes of $\text{Mn}_x\text{O}_y\cdot\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts, the origin of support materials and surface areas of the applied silica support materials and catalysts

<table>
<thead>
<tr>
<th>Silica support material</th>
<th>Surface area of the catalyst (m² g⁻¹)</th>
<th>Surface area of the catalyst (m² g⁻¹)</th>
<th>Before reaction</th>
<th>After reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst code</td>
<td>Origin</td>
<td>Comment</td>
<td>Surface area</td>
<td>Before reaction</td>
</tr>
<tr>
<td>Cat-1</td>
<td>Synthesized</td>
<td>SBA-15</td>
<td>616.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Cat-2</td>
<td>BASF</td>
<td>D 11-10</td>
<td>105.4</td>
<td>6.7</td>
</tr>
<tr>
<td>Cat-3</td>
<td>Sigma</td>
<td>Silica gel, grade 923</td>
<td>492.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

- Use of SBA-15 as a support results in a highly active catalyst
- Cat-1 provides $Y_{C2} = 8.5\%$ at $X_{\text{CH}_4} = 13\%$

Y\textsubscript{C2} and X\textsubscript{CH4} depend on reactor choice

Highest Y\textsubscript{C2} is obtained with a membrane reactor

A significant fraction of the byproducts are CO and CO\textsubscript{2}


Using a membrane reactor it is possible to achieve $Y_{C_2} = 40\%$ at $X_{CH_4} = 80\%$

By combining OCM and FTS it is possible to achieve $Y_{C2} = 38\%$ at $X_{CH4} = 64\%$

**Combined OCM and Dry Reforming of Methane (DRM)**

- Coupling of OCM and DRM enables good heat integration
- C₂ yields of 36% at X_{CH₄} = 60% can be achieved

The double membrane OCM/DRM is projected to produce a C2 yield of 20% for $X_{CH4} = 63\%$
• 90% of the CO$_2$ produced by OCM is converted to a H$_2$/CO = 1.0 mixture

Siluria Pilot Plant for Converting Methane to Ethene

- May be an option for conversion of stranded gas to marketable products
Overall Conclusions for OCM

Conversion of Methane

Oxidative Coupling: \[ \text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \frac{1}{2} \text{C}_2\text{H}_4(g) + 2 \text{H}_2\text{O}(g) \]

Findings
- Limited catalysts with single-pass ethene yields above 30%
- Higher C2 yields can be obtained using a membrane reactor
- Coupling OCM with FTS, DRM, or ETL is an economically attractive option
- Capital and operating costs are high relative to ethane steam cracking

Conclusions
- Cost of ethene produced by OCM is 2-3x higher than by steam cracking
- OCM might be useful for converting stranded gas
Options for Converting Methane to Chemicals

Conversion of Methane

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\[ \text{CH}_4(g) \rightleftharpoons \frac{1}{6} \text{C}_6\text{H}_6(g) + 1.5 \text{H}_2(g) \]
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\]

\[
\text{CH}_4(g) \rightleftharpoons \frac{1}{2} \text{C}_2\text{H}_4(g) + \text{H}_2(g)
\]

- Catalyst is stable and does not form coke
- Principle products are ethene, benzene and naphthalene
- Process requires $> 1300$ K, resulting in high energy demand and CO$_2$ emissions

X. Bao and coworkers, Sci., 344, 616, 2014
Options for Converting Methane to Chemicals

Conversion of Methane

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Oxidation of Methane to Methanol

Solid black dots – heterogeneous catalysts reported between 1985-2010
Solid red dots – heterogeneous catalysts reported since 2010
Open black and red circles – homogeneous catalysts


• With one exception, none of the heterogeneous catalysts listed can achieve selectivities or productivities that are of industrial interest
Protocol for Preparing “Precipitated” Fe on SiO$_2$

• At 750°C, a methanol yield of 10 % can be achieved for $X_{\text{CH}_4} = 14\%$
A variety of Cu cations clusters exchanged into zeolites have been shown to be competent for carrying out the sequential oxidation of methane to methanol.
Sequential Oxidation of Methane to Methanol

Partial Oxidation: \( \text{CH}_4(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \)

Sequential Oxidation of Methane to Methanol

\[
\text{CH}_4 + [\text{Cu}_2(\mu-\text{O})_2]^{2+} \rightarrow [\text{Cu}_2(\text{CH}_3\text{O})(\text{OH})]^{2+} \\
[\text{Cu}_2(\text{CH}_3\text{O})(\text{OH})]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Cu}_2(\mu-\text{OH})_2]^{2+} + \text{CH}_3\text{OH} \\
[\text{Cu}_2(\mu-\text{OH})_2]^{2+} \rightarrow [\text{Cu}_2(\mu-\text{O})_2]^{2+} + \text{H}_2\text{O}
\]


S. Grunder et al., Nature Comm. DOI: 10.1038/ncomms8546

• Low yields
• Cyclical operation
Sequential Oxidation of Methane to Methanol

- Particularly high yields of CH$_3$OH can be achieved by O$_2$ pretreatment at 200°C followed CH$_4$ exposure at this temperature

Sequential Oxidation of Methane to Formaldehyde

Solid **black** dots – heterogeneous catalysts reported between 1985-2010
Solid **red** dots – heterogeneous catalysts reported since 2010

- No studies published since 2010 have reported $\text{H}_2\text{C}=\text{O}$ selectivity $> 50\%$ for $X_{\text{CH}_4} > 3\%$
- One of the issues is that $\text{H}_2\text{C}=\text{O}$ decomposes to CO and $\text{H}_2$ at elevated temperatures
Summary and Outlook

Summary and Outlook

- OCM coupled with DRM, FTS, or ETL may offer potential for the utilization of stranded NG to produce ethene.

- Partial oxidation of methane to methanol or formaldehyde appears to be far from achieving productivity levels required to become commercial.
The CO₂ footprint for producing ethene via OCM is comparable to that for producing it via SC of ethane.

Production of ethene via MTO has a higher CO₂ footprint than ethane SC.