Methanation of CO$_2$

the power to gas approach

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The Power to Gas approach

1. Surplus from renewable energies
2. \( \text{H}_2 \) (Electrolysis of Water)
3. \( \text{CO}_2 \) (flue gas, Oxyfuel, Biogas)
4. Methanation: \( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \)
5. Storage
6. Gas to Power/Gas to ?
The Sabatier Reaction

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H^0 = -167 \text{ kJ/mol}, \text{exothermic at } 25^\circ \text{C} \]

Conversion \( X \propto \exp \left( -\frac{E_{\text{Activation}}}{RT} \right) \)

For a NiO/SiO\(_2\) catalyst, an activation energy of 56.0 kJ/mol is extracted.

For a RuO\(_2\)/Al\(_2\)O\(_3\) catalyst, an activation energy of 70.4 kJ/mol is calculated.
Reaction of CO$_2$, even with H$_2$ is slow at low temperatures: We need an enhancement of the reaction rate: We need a catalyst!

Catalysts:
- enhancement of reaction rate
- without structural/chemical changes
- without change of thermodynamic equilibrium

- Enables lower energy effort for reactions
- Reactions in industrial scale (for example Haber-Bosch-method)
- selective production without byproducts
- the „workhorse“ of chemical industry
- very important for CO$_2$ - utilisation

Ref: Hans Niemantsverdriet, University of Technology, Eindhoven
Experimental setup schematic

Reaction Line 1:
- MFC-2a: 20-200 sccm min\(^{-1}\) N\(_2\)
- MFC-2b: 10-100 sccm min\(^{-1}\) N\(_2\)
- MFC-2c: 0-10 sccm min\(^{-1}\) N\(_2\)

Reaction Line 2:
- MFC-1a: 156 – 2800 sccm min\(^{-1}\) H\(_2\)
- MFC-1b: 14 – 700 sccm min\(^{-1}\) CO\(_2\)
- MFC-1c: 100 sccm min\(^{-1}\) N\(_2\)

Financial Support: BMBF: GeoEN

~2 kg /d
Catalysts for Methanation of $\text{CO}_2$

**RuO/Al$_2$O$_3$**

**NiO/SiO$_2$**

**Conversion**

\[
X_{\text{CO}_2} = \frac{\dot{n}_{\text{CO}_2,\text{in}} - \dot{n}_{\text{CO}_2,\text{out}}}{\dot{n}_{\text{CO}_2,\text{in}}}
\]

**Yield**

\[
Y_{\text{CH}_4} = \frac{\dot{n}_{\text{CH}_4,\text{out}}}{\dot{n}_{\text{CO}_2,\text{in}}}
\]

**Selectivity**

\[
S_{\text{CH}_4} = \frac{\dot{n}_{\text{CH}_4,\text{out}}}{\dot{n}_{\text{CO}_2,\text{in}} - \dot{n}_{\text{CO}_2,\text{out}}}
\]
Stability

RuO/Al₂O₃ Catalyst

NiO/SiO₂ Catalyst

Temperatur 350°C

Übersicht über die Stabilität der beiden Katalysatoren RuO/Al₂O₃ und NiO/SiO₂ unter der Bedingung einer Reaktortemperatur von 350°C. Die Grafiken zeigen die Veränderung der Umsatzrate, Ausbeute an Methan und Selektivität über die Zeit.
Technical Oxyfuel CO₂

NiO/SiO₂ catalyst

Composition of Oxyfuel CO₂

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>&gt;99.7%</td>
</tr>
<tr>
<td>N₂, Ar, O₂</td>
<td>&lt;0.3%</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>&lt; 2.5 ppm</td>
</tr>
<tr>
<td>SO₃</td>
<td>&lt; 0.5 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>&lt; 5.0 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>&lt; 15 ppm</td>
</tr>
</tbody>
</table>

Reference: Vattenfall Europe, Pilot Plant Schwarze Pumpe

In technical oxyfuel CO₂ (from pilot plant Schwarze Pumpe, Vattenfall) the conversion remains stable and is not influenced by contamination,

Synthetic mixtures with more SO₂ (12.5ppm) and NO₂ (25ppm) show also no differences in performance.
The direct CO₂ methanation of flue gas from conventional power plants

typical compositions

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>N₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>H₂S</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas</td>
<td>14%</td>
<td>75%</td>
<td>5%</td>
<td>4%</td>
<td>&lt;90ppm</td>
<td>&lt;120ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxyfuel</td>
<td>&gt;99%</td>
<td>&lt;0,3%</td>
<td>&gt;0,3%</td>
<td>&lt;50ppm</td>
<td>&lt;2,5ppm</td>
<td>&lt;15ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biogas</td>
<td>25-50%</td>
<td>0-10%</td>
<td>0-1%</td>
<td>0-6%</td>
<td>-</td>
<td>-</td>
<td>0-3%</td>
<td>50-75%</td>
</tr>
</tbody>
</table>

A mixture of five parts N₂ and one part CO₂ reflects a synthetic flue gas composition. Four parts H₂ are necessary as additive for the methanation:

**Synthetic gas mixture N₂: CO₂ :H₂ = 5:1:4**

but without oxygen and minor SO₂ and NO₂ contaminations.

Financial Support BMWi/03ET7002A
Methanation in **synthetic flue gas**

Reference gas mixture with $N_2:CO_2:H_2 = 5:1:4$

NiO/SiO$_2$ catalyst

- A **highly selective** conversion of CO$_2$ with a CH$_4$ yield $> 80\%$ was measured also for flue gas.
- The **catalyst performance is stable** investigated time frame of 2 days.
- Influence of oxygen is due to oxygen hydrogen reaction.
Demonstration plant

- Upscaling to 1.) 20g Catalyst 2) 5-10kg Catalyst
- Demonstration plant for **estimation of energy balance and costs for industrial application**

Technical data

- Catalyst:
  Nickel on Silica/Alumina wt% 66
- Reactor volume:
  30 dm$^3$
- Amount of catalyst:
  up to 2 kg
- Temperature:
  350°C
- Pressure:
  10 bar
- maximal gas flow:
  1200 Nm$^3$/Day  ->  500 kg CO$_2$/Day
- CH$_4$ Yield:
  200 Nm$^3$/Day

Financial support: EFRE/80149806)
Demonstrator – Setup of reactor

- UHV Vacuum chamber
- Quadrupole mass-spectrometer
- Cooling trap
- Tube reactor
- Preheater
- Mass Flow Controller
- Thermoelements for temperature control inside reactor

Financial support: EFRE/80149806)
Laboratory scale vs Demonstrator

Laboratory scale
- Conversion > 85%
- Yield > 85%
- Selectivity = 100%

Demonstrator
- Conversion > 80%
- Yield > 80%
- Selectivity = 90 – 100%

Financial support: EFRE/80149806)
Possible Cooperations

• Catalyst Development for Mass Production

• Reactor design for the Sabatier reaction in technical scale

• Production of Methanol from CO$_2$: Catalyst development, Scale up into technical value