STRUCTURED CATALYSTS FOR BIO-HYDROGEN PRODUCTION

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The energetic problem

- Growing world energy demand
- Depletion of fossil fuels

Alternative energy sources are needed

- Solar
- Eolic
- Nuclear
- Biomass
- Hydrogen
Hydrogen = Energetic vector

Water electrolysis
Hydrocarbons reforming

Green Energy

METHANE
STEAM REFORMING

\[ CH_4 + H_2O \rightleftharpoons 3H_2 + CO \]
\[ \Delta H_{298K}^0 = +206 \text{ kJ/mol} \]

Highly diffused process
High hydrogen yield

High fixed and operative costs
Fossil fuel sources

Hydrogen = Energetic vector
Biomass

- Sugarcane
- Corn
- Solid waste
- Potatoes
- Lignocellulose
- Switchgrass

Energy from biomass

- Fermentation
- Gasification
- Combustion
- Pyrolysis

Bio-Ethanol

Biogas

Bio-methane
Bio-ethanol production

Lignocellulosic biomass
+ URBAN AND INDUSTRIAL WASTE

PRE-TREATMENT

CONSOLIDATED BIOPROCESS

CONCENTRATION

HYDROLYSIS

FERMENTATION

DISTILLATION

MICROBIOLOGY

GENETIC / MOLECULAR BIOLOGY

DESMOCOCUS

CELLULASES

HEMIEELLULASES

PENTOSE (C5)

GLUCOSE (C6)

ETHANOL + CHEMICAL INTERMEDIATES

BIOFUELS
+ CHEMICALS, FRAGRANCES, FLAVORS, RUBBER...

Typical composition:

$\text{C}_2\text{H}_5\text{OH} : 3\text{-6\%}$

$\text{H}_2\text{O} : 94\text{-97\%}$

Impurities: < 1\%
Biogas production

Typical composition:

\[ CH_4: 50-75\% \]
\[ CO_2: 25-45\% \]
Bio-fuels to energy

Energy

Bio-Ethanol

Bio-Hydrogen

Combustion

Reforming

Co-generation

But... CO2 Emission

Is this really green energy?

Biogas

Green Energy
**Main Advantages**

- Employment of a mature technology
- Exploiting of **green raw materials**
- Reducing **green-house emissions**
Main difficulties

- Old technologies in the plants
- Heat management in the reforming volume
- Different reactions involved
- Thermal stability of biogas and bio-ethanol
- Catalyst lifetime
- Side products

Process intensification

High thermal conductivity structured catalysts
Ni loading investigation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Ni-CeO2</td>
<td>5 %wt</td>
</tr>
<tr>
<td>10Ni-CeO2</td>
<td>10 %wt</td>
</tr>
<tr>
<td>20Ni-CeO2</td>
<td>20 %wt</td>
</tr>
</tbody>
</table>

GHHSV = 20,000 h⁻¹
S/C = 3
800 to 500°C @ 2°C/min

Low nickel content resulted in a better dispersion, thus in a smaller crystallite size.

Better performances
Cheaper catalyst
Support investigation

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<tr>
<td>5Ni-CeO2</td>
<td>5 %wt</td>
</tr>
<tr>
<td>5Ni-CeO2-ZrO2</td>
<td>5 %wt</td>
</tr>
</tbody>
</table>

Ceria based catalyst more active at higher temperature

GHSV = 20,000 h⁻¹
S/C = 3
800 to 500°C @ 2°C/min
### Support investigation

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<td>5Ni-CeO2-ZrO2</td>
<td>5 % wt</td>
</tr>
</tbody>
</table>

**Ceria-Zirconia based catalyst more active towards WGS reaction**

**GHSV = 20,000 h⁻¹**

**S/C = 3**

800 to 500°C @ 2°C/min

**Hydrogen Yield**

**Carbon Dioxide Yield**
BIOGAS DRY REFORMING

\[ CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \]

\[ \Delta H^\circ = +247 \text{ kJ/mol} \]

Highly endothermic reaction
Increasing moles number
\( CH_4 > CO_2 \) (biogas)

Coke deposition minimization required
Oxygen co-feeding
OXIDATIVE DRY REFORMING

Thermodynamic
High Temperature
Low pressure
COKE
Support investigation

Support investigation

\[ T = 750^\circ C \quad \text{GHSV} = 60 \text{ NL} \quad \text{gC}_\text{cat}^{-1} \quad \text{h}^{-1} \]

\[ \text{CH}_4/\text{CO}_2 = 1.5 \quad \text{O}_2 / \text{Biogas} = 0.1 \]

Sample | Ni loading
--- | ---
10Ni/Al$_2$O$_3$ | 10 %wt
10Ni/MgO-Al$_2$O$_3$ | 10 %wt
10Ni-CeO$_2$ | 10 %wt

Alumina support enhanced catalytic activity: Better nickel dispersion?

Ceria showed more stable performances: coke formation 40 times lower
Active species effect

\[ T = 800{\degree}C \quad \text{GHSV} = 60 \text{ NL g}_{\text{cat}}^{-1} \text{ h}^{-1} \]
\[ \text{O}_2 / \text{Biogas} = 0.1 \quad \text{H}_2\text{O} / \text{Biogas} = 0.4 \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh loading</th>
<th>Ni loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Ni/Al(_2)O(_3)</td>
<td>0 % (\text{wt})</td>
<td>5 % (\text{wt})</td>
</tr>
<tr>
<td>0.5Rh/Al(_2)O(_3)</td>
<td>0.5 % (\text{wt})</td>
<td>0 % (\text{wt})</td>
</tr>
<tr>
<td>0.5Rh-5Ni/Al(_2)O(_3)</td>
<td>0.5 % (\text{wt})</td>
<td>5 % (\text{wt})</td>
</tr>
</tbody>
</table>

Noble metal enhanced catalytic performances

... but promotes coke formation! Nickel resulted in coke gasification.
Active species effect

\[ T = 300^\circ C \quad \text{GHSV} = 15000 \text{ h}^{-1} \]

\[ \text{H}_2\text{O} / \text{C}_2\text{H}_5\text{OH} = 3 \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Pt loading</th>
<th>M loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/M / CeO(_2)</td>
<td>Impregnation</td>
<td>3 %(_{wt})</td>
<td>10 %(_{wt})</td>
</tr>
<tr>
<td>M/Pt / CeO(_2)</td>
<td>Impregnation</td>
<td>3 %(_{wt})</td>
<td>10 %(_{wt})</td>
</tr>
<tr>
<td>M-Pt / CeO(_2)</td>
<td>Coprecipitation</td>
<td>3 %(_{wt})</td>
<td>10 %(_{wt})</td>
</tr>
</tbody>
</table>

(M=Ni or Co)

Ni showed better activity than Co

Pt availability at gas-solid interface improved catalytic performances
Support Investigation

\[ T = 300-600 ^\circ C \quad \text{GHSV} = 100000 \text{ h}^{-1} \]

\[ \text{H}_2\text{O} / \text{C}_2\text{H}_5\text{OH} = 3 \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt loading</th>
<th>M loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Ni / CeO\textsubscript{2}</td>
<td>3 %\textsubscript{wt}</td>
<td>10 %\textsubscript{wt}</td>
</tr>
<tr>
<td>Pt/Ni / CeO\textsubscript{2}-ZrO\textsubscript{2}</td>
<td>3 %\textsubscript{wt}</td>
<td>10 %\textsubscript{wt}</td>
</tr>
</tbody>
</table>

- **Higher activity** of Ce-Zr samples
- **Total EtOH conversion** at \( T > 500 ^\circ C \)
- **WGS promotion** at low \( T \)
- **SR promotion** at high \( T \)
- **Improved heat transfer** rates compared to random catalysts packaging

- **Flatter axial thermal profile** along the catalytic bed (higher average T)

- More **uniform thermal radial profile** (*reduced hot spot* phenomena)

- **High surface-to-volume ratio** and **low pressure drops**

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**But...**

- Choice of a **proper structured carrier** (material and geometry)

- **Washcoat optimization** for **good adhesion achievement**
Carrier selection

\[ T_{\text{in}} = 300^\circ C \]
\[ T_w = 800^\circ C \]

Temperature [°C]

Thermal Conductivity \([W \cdot m^{-1} \cdot K^{-1}]\)

Silicon Carbide

797°C

63.6
63.4
63.2
63.0
62.8
62.6
62.4
62.2

Cordierite

667°C

1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.31
# Washcoat optimization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active Metal</th>
<th>Support 1</th>
<th>Support 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Ni-CeO₂</td>
<td>5 %ₘₜ</td>
<td>-</td>
<td>100 %ₘₜ</td>
</tr>
<tr>
<td>5Ni-5W-CeO₂</td>
<td>5 %ₘₜ</td>
<td>5 %ₘₜ</td>
<td>95 %ₘₜ</td>
</tr>
<tr>
<td>5Ni-10W-CeO₂</td>
<td>5 %ₘₜ</td>
<td>10 %ₘₜ</td>
<td>90 %ₘₜ</td>
</tr>
<tr>
<td>5Ni-25W-CeO₂</td>
<td>5 %ₘₜ</td>
<td>25 %ₘₜ</td>
<td>75 %ₘₜ</td>
</tr>
<tr>
<td>5Ni-Al₂O₃</td>
<td>5 %ₘₜ</td>
<td>100 %ₘₜ</td>
<td>-</td>
</tr>
</tbody>
</table>

**MSR Catalyst Optimization**

- **GHHSV** = 100,000 h⁻¹
- **S/C** = 3
- **850 to 500°C @ 2°C/min**

**Highest activity for alumina content between 5 and 10 %**

**Notes:**
- Highest conversion at 5Ni-CeO₂ with 5% Al₂O₃ and 90% CeO₂.
- The graph shows conversion rates for different compositions at various temperatures.
**Materials**

- **Cordierite**
- **SiC-Flow Through**
  - **SiC-FT**
- **SiC-Wall Flow**
  - **SiC-WF**
- **Commercial**
  - **Ni-Comm**

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**Washcoat Amount: 1.6 g**

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m$^2$/g)</th>
<th>Mean pores d (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bare Cordierite</strong></td>
<td>1.0</td>
<td>0.31</td>
</tr>
<tr>
<td><strong>Bare SiC</strong></td>
<td>1.4</td>
<td>17.00</td>
</tr>
<tr>
<td><strong>Cordierite</strong></td>
<td>12.8</td>
<td>1.81</td>
</tr>
<tr>
<td><strong>SiC-FT / SiC WF</strong></td>
<td>12.4</td>
<td>6.13</td>
</tr>
<tr>
<td><strong>5Ni-5W-CeO2 (powder)</strong></td>
<td>30.6</td>
<td>-</td>
</tr>
</tbody>
</table>
Structured catalyst improved powder performances

SiC Supported catalysts very close to thermodynamic equilibrium
Washcoat optimization

3\%_{wt} Pt / 10\%_{wt} Ni/CeO_2 – ZrO_2

\[ \text{GHSV} = 60,000 \text{ h}^{-1} \]
\[ \text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 6 \]
Bioethanol (1 mol% impurities) 450°C

Boehmite-containing foam: lowest coke selectivity

Similar carbon formation over powder and silca-containing foam
Carrier effect

3%\textsubscript{wt} Pt / 10%\textsubscript{wt} Ni/CeO\textsubscript{2}–ZrO\textsubscript{2}

Relevant effect of thermal management on catalyst performances

 Foams and powder in the annular reactor: similar H\textsubscript{2} yield at T>400\degree C

\textbf{GHHSV = 100,000 h\textsuperscript{-1}}
\textbf{H\textsubscript{2}O/C\textsubscript{2}H\textsubscript{5}OH = 3}
\textbf{600 to 300\degree C @ 3\degree C/min}
Carrier effect

3%wt Pt / 10%wt Ni/CeO₂ - ZrO₂

GHSV = 100,000 - 400,000 h⁻¹
H₂O/C₂H₅OH = 3
450 °C

High Thermal conductivity

Lower T for heating medium
Carrier effect

\[ \Delta V, T \]

\[ x_{SR} \quad \Delta H_{SR}^{\text{reaz}} \quad x_{SR} + \Delta x_{SR} \]

\[ x_{WGS} \quad \Delta H_{WGS}^{\text{reaz}} \quad x_{WGS} + \Delta x_{WGS} \]

\[ Q_{\text{conv}} \]

\[ IN - OUT + GEN = 0 \]

\[ Q_{\text{conv}} = U \cdot \Delta A \cdot (T_{\text{oven}} - T_{\text{gass}}) \]

\[ GEN = \Delta x_{SR} \cdot \Delta H_{SR}^{\text{reaz}} + \Delta x_{WGS} \cdot \Delta H_{WGS}^{\text{reaz}} \]

\[
\begin{array}{c|c|c}
\text{Campione} & U [\text{W/m}^2\text{K}] & k [\text{m}^2\text{K/ W}] \\
\hline
\text{Ni-COMM} & 21.4 & 0.047 \\
\text{FT} & 85.6 & 0.012 \\
\text{WF} & 121.8 & 0.008 \\
\end{array}
\]
Carrier effect

MSR structured catalysts

<table>
<thead>
<tr>
<th>Campione</th>
<th>U [W/m²K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>JM</td>
<td>21.4</td>
</tr>
<tr>
<td>FT</td>
<td>85.6</td>
</tr>
<tr>
<td>WF</td>
<td>121.5</td>
</tr>
</tbody>
</table>

T Furnace = 750°C

$X_{CH4} = 95\%$

Reactor Length

- JM: 61%
- FT: 68%
**SR: Process intensification**

- **Low temperature processes**
- **Alternative heat sources**
- **Innovative products purification**

**MEMBRANES**

- **Thermodynamic limitations overcoming**
- **Compatible with molten salts heating**
- **High hydrogen purity**
Comethy Project

FEED FLEXIBILITY
Bioethanol / Biogas

Reaction and separation integrated in one step
Comethy Project

Structured catalysts and membranes

Mass transfer
Flatter concentration profile improve membrane separation (membrane polarization)

Heat transfer
Improved heat management and reduced membrane embrittlement

Combined effect of structured catalysts and membrane

![Graph showing methane conversion vs. molten salts inlet temperature](image_url)
CO + H₂O ↔ CO₂ + H₂  \( \Delta H_{298K} = -41.09 \text{ kJ} \cdot \text{mol}^{-1} \)

**High Temperature shift**
- \( T = 350-450^\circ \text{C} \)
- CO conversion ≈ 90%
- Fe/Cr-based catalysts
- Thermodynamic limitations

**Low Temperature shift**
- \( T = 200-260^\circ \text{C} \)
- CO conversion ≈ 99%
- Cu/Zn-based catalysts
- Kinetic limitations

**Drawbacks...**
- High energy consumption (inter-cooling)
- Slow system kinetics
- High process activation time
- Not feasible in small scale applications
Possible actions

Catalyst formulation
- Development of **active catalysts** at low temperature (even 150°C)

Catalyst structure (more effective)
- Use of **structured catalysts** with high thermal conductivity and specific flow geometries, resulting in a decrease of the temperature in the outlet section, and an increase in the inlet section.
## Materials

<table>
<thead>
<tr>
<th></th>
<th>FeCr Alloy</th>
<th>Aluminum Foam</th>
<th>Ferritic Foam</th>
<th>Al92 Foams</th>
</tr>
</thead>
<tbody>
<tr>
<td>k foam</td>
<td>1.8 W/mK</td>
<td>60.1 W/mK</td>
<td>1.5 W/mK</td>
<td>12.7 W/mK</td>
</tr>
<tr>
<td>$T_{g,\text{out}}$</td>
<td>350 °C</td>
<td>360 °C</td>
<td>348 °C</td>
<td>325 °C</td>
</tr>
</tbody>
</table>

$Q_{\text{bat}} = 2.4 \text{ l/min}^{-1}$

**450 °C**
Aluminium foam catalyst modelling

POWDER Catalyst in WGS reaction

Surface: Temperature (K) Arrow Surface: Conductive heat flux

Conductive flux mainly due to the stainless steel reactor effect!
Aluminium foam catalyst modelling

Foam Catalyst in WGS reaction

Aluminum Foam effect: Redistribution of the Heat Flux

Heat redistribution due to the high conductive Aluminum carrier

Adiabatic reactor
Aluminium foam catalyst

Foam Catalyst in WGS reaction

\[ t_e = 214 \text{ ms} \]

200°C

WGS structured catalysts

\[
\begin{align*}
\text{Foam catalyst} & \quad T_{\text{in}} \text{ higher than powder} \\
& \quad T_{\text{out}} \text{ lower than powder}
\end{align*}
\]

Quasi-Isothermal conditions

Higher CO conversion

Graph:

- \( x_{\text{CO}} \) vs. \( T \) [°C]
  - Powder: blue line
  - Foam: red line
  - Equilibrium: black line
  - \( T_{\text{in}} \) by-pass: dashed black line

- Ranges:
  - \( x_{\text{CO}} \) from 0.00% to 100.00%
  - \( T \) from 200°C to 300°C
Conclusions

Structured catalysts for biohydrogen production

- Hydrogen from renewable sources via reforming technology
- Main challenges: catalysts and process
- Process intensification: high thermal conductivity structured catalysts
  Carrier selection and washcoat development

- Structured catalysts: high conversion and hydrogen yield
Thank you for your attention

FOR MORE INFORMATION:
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