Operational behavior and reforming kinetics over Ni/YSZ of a planar type pre-reformer for SOFC systems

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Outline

- Introduction
- Global reaction kinetics
- Experimental setup
- Results
- Modeling
- Conclusions
Basic layout of the SOFC system

**Reaction in the Cathode:**
\[ O_2 + 4 \text{ e}^- \leftrightarrow 2 \text{ O}^{2-} \]

**Reactions in the Anode:**
\[ \text{H}_2 + \text{O}^{2-} \leftrightarrow \text{H}_2\text{O} + 2 \text{ e}^- \]
\[ \text{CO} + \text{O}^{2-} \leftrightarrow \text{CO}_2 + 2 \text{ e}^- \]

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# Steam reforming reactions of methane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Equation</th>
<th>$\Delta H$ (25 °C) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2$</td>
<td>-206</td>
</tr>
<tr>
<td>R2</td>
<td>$\text{CH}_4 + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4 \text{H}_2$</td>
<td>-165</td>
</tr>
<tr>
<td>R3</td>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{CO} + 2 \text{H}_2$</td>
<td>-247</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$</td>
<td>41</td>
</tr>
<tr>
<td>R5</td>
<td>$\text{CH}_4 \leftrightarrow \text{C} + 2 \text{H}_2$</td>
<td>-75</td>
</tr>
<tr>
<td>R6</td>
<td>$2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2$</td>
<td>172</td>
</tr>
<tr>
<td>R7</td>
<td>$\text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O}$</td>
<td>131</td>
</tr>
</tbody>
</table>
Models for global reaction kinetics

1) Arrhenius type

\[ r_{r, \text{Arr}} = F \cdot p_{\text{CH}_4}^\alpha \cdot p_{\text{H}_2\text{O}}^\beta \cdot \exp \left( -\frac{E_a}{R \cdot T} \right) \]

2) Langmuir-Hinshlewood type

\[ r_{r, \text{Lang}} = k \frac{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}} \cdot K_{\text{CH}_4} \cdot K_{\text{H}_2\text{O}}}{\left( 1 + p_{\text{CH}_4} K_{\text{CH}_4} + p_{\text{H}_2\text{O}} \cdot K_{\text{H}_2\text{O}} \right)^2} \]

3) Equilibrium approach

\[ r_{r, \text{eq}} = k \cdot p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}} \cdot \left( 1 - \frac{p_{\text{CO}} \cdot p_{\text{H}_2}^3}{K_{e,\text{STR}} \cdot p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}} \right) \]

4) Water shift reaction approach

\[ r_s = k_s \cdot p_{\text{CO}} \cdot \left( 1 - \frac{p_{\text{CO}_2} \cdot p_{\text{H}_2}}{K_{e,s} \cdot p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}} \right) \]
Global reaction kinetics (Arrhenius type)

$$r_{r,\text{Arr}} = k \cdot p_{\text{CH}_4}^\alpha \cdot p_{\text{H}_2\text{O}}^\beta$$

where

$$k = A \cdot \exp \left( -\frac{E_a}{R \cdot T} \right)$$

**Literature data review:** inconsistent results of kinetics *

$\alpha$: 0.85 – 1.4 ($\alpha=1$ was used very often)

$\beta$: negative and positive values

$E_a$: 42 - 208 kJ/mol

**Motivation:**

- Find the ”real” global kinetics of steam reforming reactions
- Optimization of pre-reformer for SOFC-system

* Andersson M, Yuan J, Sunden B, Applied Energy 2010; 87:1461
Design of a 5-layer pre-reformer using air heater

Catalyst: Ni/YSZ (Ni + 8 mol% Y$_2$O$_3$-stabilized ZrO$_2$)
Flow scheme of the experimental setup

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Results

The comparison between the compositions for equilibrium and measurement as function of temperature and space-time

Analytical methods

- dew-point-measurement
- gas-chromatographic method

\[ \tau = \frac{V}{v_o} \]  
reactor volume  
volumetric feed rate
Graphs of concentration versus space time

The experimental data fit not first order kinetics for methane concentration.

At 610°C, the concentration of methane can be described by the following equations:

- \( y = e^{-1.861x} \)
- \( y = e^{-2.25x} \)
- \( y = e^{-3.09x} \)

- For S/C=2, \( k = 46 \)
- 70% AOGGR, \( k = 155 \)
- 80% AOGGR, \( k = 372 \)

\( \tau = \frac{V}{v_o} = \frac{\text{reactor volume}}{\text{volumetric feed rate}} \)
Modeling (Arrhenius type)

\[
\begin{align*}
\tau &= \frac{V}{v_o} = \text{reactor volume} \\
&= \frac{\text{volumetric feed rate}}{
\end{align*}
\]

Integrated reaction rates from exp. data of the both reformers

\[
- \int_0^\tau \frac{dx_{CH_4}}{x_{CH_4}^2 \cdot x_{H_2O}} = k \cdot \tau
\]

\[
\int_0^\tau \frac{d(\xi)}{\left(x_{0,CH_4} - \xi\right)^2 \cdot \left(x_{0,H_2O} - \xi\right)} = k \cdot \tau
\]

\(\xi\): Progress variable of reforming reaction

\[
\begin{align*}
k &= 106 \\
k &= 66 \\
k &= 35 \\
k &= 14 \\
k &= 6.3
\end{align*}
\]
Temperature dependency of reaction rate

\[ \ln(k) = -6,314 \times \left( \frac{1000}{T} \right) + 10,87 \]

Temperature: 350°C – 620°C
\[ E_a = 53 \text{ kJ/mol}^* \]

Temperature: 460°C – 740°C
\[ E_a = 54 \text{ kJ/mol} \]


\[ \ln(k) = -6,524 \times \left( \frac{1000}{T} \right) + 11,316 \]

Ea = 50 kJ/mol**

*** Liu, K., Song, C., Subramani, V. (Eds.) Wiley & Sons Publication; 2010.
Effect of anode off-gas recycling (AOGR)

\[ \int_0^\tau \frac{dx_{\text{CH}_4}}{x_{\text{CH}_4}^2 \cdot x_{\text{H}_2\text{O}}} = k \cdot \tau \]

\[ \int_0^\tau \frac{d\xi}{(x_{0,\text{CH}_4} - \xi)^2 \cdot (x_{0,\text{H}_2\text{O}} - \xi)} = k \cdot \tau \]

\( \xi \): Progress variable of reforming reaction

**AOGGR at 70% fuel utilization**

Example at 610°C:

Without AOGR, \( k = 46 \)

70% AOGR, \( k = 155 \)

80% AOGR, \( k = 372 \)

\( \text{Ea} = 117 \text{ kJ/mol} \)
Conclusions

- Two different planar pre-reformers containing Ni/YSZ catalyst were tested for operational behavior and kinetics of methane steam reforming reactions in a temperature-range of 350°C - 740°C.

- Experimental results for the two reformers are close to each other.

- The developed kinetic expression of Arrhenius type (second order with respect to mole fraction of methane and first order with respect to mole fraction of water) gives a good agreement with the experimental results.

- This kinetic expression ($\alpha = 2; \beta = 1$) is universally applicable for different steam to carbon ratios and also for the case of anode off-gas recycling (AOGR).

- In the case of anode off-gas recycling the reaction rate constant is larger than that without AOGR.

- Understanding of the methane steam reforming reactions is expected to be of significant importance for the further development of SOFC systems.
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Thank you for your attention!