Investigating the performance of multifunctional materials in methane sorption enhanced reforming

Christina Martavaltzi, Sofia Aggeli, Angeliki Lemonidou

Department of Chemical Engineering
Aristotle University of Thessaloniki
Thessaloniki, Greece

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Hydrogen production

- Worldwide demand for hydrogen (2011) > 100,000 Nm³/h
- Hydrogen production contributes significantly to CO₂ emissions (High energy demand, byproduct)
Industrial process

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 + 206 \text{ kJ/mol} \quad \text{steam reforming} \]

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 - 41\text{kJ/mol} \quad \text{water gas shift} \]
**Industrial process**

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad +206 \text{ kJ/mol} \quad \text{Steam reforming}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad -41\text{ kJ/mol} \quad \text{water gas shift}
\]

- T>800°C
- Necessity for external heating
- Heat losses
- High energy demand for compression

High CO\textsubscript{2} emissions
Sorption enhanced reforming

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \rightarrow 206 \text{ kJ/mol}$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \rightarrow -41\text{ kJ/mol}$$

$$\text{CO}_2 + \text{CaO} \rightarrow \text{CaCO}_3 \rightarrow -178 \text{ kJ/mol}$$

Natural gas  steam

reformer

HT-WGS

LT-WGS

CH4, H2
CO, CO2

PSA

H2
Sorption enhanced reforming, SER

Loading the reformer tubes with a mixture of catalyst + sorbent

- In-situ CO₂ capture $\rightarrow$ separation train much simpler
- High hydrogen yield
- Lower temperature in the reformer
- Direct heat transfer in the reformer via carbonation reaction $\rightarrow$ reduction in heat losses

Carbon Footprint of hydrogen production much lower
Thermodynamics of SER product profiles vs temperature

- Window of operation: 500 – 650 °C

Martavaltzi et al., Energy Fuels 2010, 24, 2589
Sorption enhanced reforming over CaO-Ca$_{12}$Al$_{14}$O$_{33}$ (85/15 wt)

- Effective CO$_2$ capture
- > 93% hydrogen concentration

Commercial Ni-based reforming catalyst
CaO-Ca_{12}Al_{14}O_{33} stability-reforming conditions

- Satisfactory stability
  ~ 15% loss in sorption capacity after 60h testing

Martavaltzi et al, IECR (2010)
Challenge: Combine in one single pellet the functions of catalysis + sorption

- Metallic Ni
- Dissociative adsorption of CH$_4$
- Carrier with high thermal and mechanical strength Ca$_{12}$Al$_{14}$O$_{33}$
- Alkaline earth oxides (CaO) for coke prevention

NiO-CaO-Ca$_{12}$Al$_{14}$O$_{33}$
Synthesis & composition of materials

Aqueous solution
Al(NO₃)₃, Ni(NO₃)₂

Aqueous suspension CaO

Stirring

- Drying 110°C for 18h
- Calcination at 500°C for 3h
- Water addition
- Calcination 900°C for 1hr

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal composition, wt%</th>
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<tbody>
<tr>
<td></td>
<td>Ca:Al:Ni</td>
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<tr>
<td>CANi8</td>
<td>57:5:8</td>
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<tr>
<td>CANi11</td>
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<td>53:3:16</td>
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<tr>
<td>CANi20</td>
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Characterization

A: $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  B: $\text{CaO}$, C: $\text{NiO}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area, m²/g</th>
<th>Crystallite size NiO, nm</th>
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<tbody>
<tr>
<td>CANi8</td>
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<td>CANi20</td>
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</tbody>
</table>
NiO crystallite size around 30nm
Weak interaction of NiO and CaO – inhomogeneous distribution of NiO
Evaluation of sorption capacity
multiple cycles in TGA

- High stability in multiple cycles
- Optimum performance CANi16
  31% sorption capacity
  no deactivation

NiO-CaO-Ca_{12}Al_{14}O_{33}

Sorption: 690°C, 15% CO_2, 30 min
Desorption: 850°C, 100% N_2, 10 min
45 cycles, TGA

Sorption Enhanced Reforming Conditions

- Fixed Bed Reactor (OD:18mm)
- NiO-CaO-Ca_{12}Al_{14}O_{33}: 5gr
- Reduction Conditions (1hr, 30% H_{2}, 850°C)
- H_{2}O/CH_{4} = 3.4
- Reforming-Sorption Temperature: 650°C
- Desorption Temperature: 850°C
SER over 16%Ni -CaO-Ca$_{12}$Al$_{14}$O$_{33}$

Results

- 80% methane conversion
- 90% H$_2$, 2.8% CO$_2$, 2% CO

Satisfactory capturing capacity (33%)

Medium reforming activity compared to commercial Ni catalysts
Sorption enhanced reforming of methane

- Reforming activity increasing with Ni loading up to 16%
- Higher Ni loadings (20%)
  → low dispersion of active phase
  →→ low conversion
Gradual loss in the reforming activity was observed in consecutive cycles of reforming-sorption and regeneration-desorption

Possible reasons for this

1. Gradual saturation of CaO
2. Coke formation
3. Oxidation of metallic Ni
4. Sintering
Conclusions

Multifunctional materials with CO$_2$ capturing function (70% CaO) and reforming activity (Ni 8-25%) were synthesized and tested.

CaO-Ca$_{12}$Al$_{14}$O$_{33}$ serves as effective support for metallic Ni reforming active sites and as a CO$_2$ sorbent with high sorption capacity.

Satisfactory sorption capacity around 30% (based on total sorbent mass) is attained at 690°C in a stream of 15% CO$_2$. Minor losses in sorption capacity in 45 cycles of sorption-desorption.

Testing under methane reforming conditions demonstrated that hybrid materials effectively capture CO$_2$ formed on the active catalytic sites. Optimum catalytic performance attained with the 16%Ni sample.

Gradual loss of the reforming activity was observed in consecutive cycles of testing.
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