Ni-CaO Combined Sorbent Catalyst Materials usage for Sorption Enhanced Steam Methane Reforming

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1. SE-SMR

**SORPTION ENHANCED – STEAM METHANE REFORMING (SE-SMR)**

\[(T = 650 \, ^\circ \text{C} \; ; \; P = 1 \, \text{atm})\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Δ(H^0_{298 , K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Methane Reforming (SMR)</td>
<td>(\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2)</td>
<td>+206.2 \text{kJ/mol}</td>
</tr>
<tr>
<td>Water Gas Shift (WGS)</td>
<td>(\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2)</td>
<td>-41.2 \text{kJ/mol}</td>
</tr>
<tr>
<td>Carbonation</td>
<td>(\text{CaO}_{(s)} + \text{CO}_2 \rightarrow \text{CaCO}<em>3</em>{(s)})</td>
<td>-178.2 \text{kJ/mol}</td>
</tr>
</tbody>
</table>

**Calcium Looping**

- **Regenerated solid**
- **Solid saturated by CO\(_2\)**

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<td>Calcination</td>
<td>(\text{CaCO}<em>3</em>{(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_2)</td>
<td>+178.2 \text{kJ/mol}</td>
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</tbody>
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**Regeneration**

\[(T = 800 - 900 \, ^\circ \text{C} \; ; \; P = 1 \, \text{atm})\]

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2. CSCM

\[ \text{CO}_2 \text{ SORBENT} + \text{SMR CATALYST} = \text{COMBINED SORBENT-CATALYST MATERIAL (CSCM)} \]

- Support
- CaO - binder

3. CSCM synthesis methods

1) WET MIXING\textsuperscript{[4,5]}

**MAYENITE OR CAO-MAYENITE**

- Calcination of Ca(CH$_3$COO)$_2$ to CaO (4h ; 750 °C)

- CaO + Al(NO$_3$)$_3$·9H$_2$O
  - Stirring in distilled water (70 °C ; 1h)

- Drying (12h ; 120 °C)

- Calcination 1 (4h ; 750 °C)

- Hydratation + Drying (12h ; 120 °C)

- Calcination 2 (1.5h ; 900 °C)

2) WET IMPREGNATION\textsuperscript{[6,7]}

**NI-MAYENITE OR NI-CAO-MAYENITE**

- Mayenite or CaO-Mayenite + Ni(CH$_3$COO)$_2$·4H$_2$O or Ni(NO$_3$)$_2$·6H$_2$O
  - Stirring in distilled water (70 °C ; 1h)

- Drying (12h ; 120 °C)

- Calcination (4h ; 900 °C)

\textsuperscript{[4]} Z. Li et al, Energy & Fuels 19, 2005, 1447-1452
\textsuperscript{[5]} I. Zamboni et al. PREPA11, 33 (2014) 10–11
\textsuperscript{[6]} A. D’Orazio et al, Int. J. Hydr. En. 2013, 38, 13282–13292
\textsuperscript{[7]} I. Zamboni, Ph.D. thesis, ICPEES 2013
4. CSCM Characterization

- **XRD** (X-Ray Diffraction):
  - Crystalline phases detection

- **TPR** (Temperature Programmed Reduction):
  - Reducibility by $H_2$

- **BET** method:
  - Specific surface

- **TGA** (Thermo-Gravimetric Analysis):
  - Multiple $CO_2$-Sorption/Desorption cycles

- **SEM** (Scanning Electron Microscope):
  - Morphology
XRD: Effect of Wet Impregnation

Wet Impregnation with both Ni-Acetate and Ni-Nitrate succeed in adding Nickel
TPR: Effect of CaO fraction (1)

CaO0Ni(Ac)3 and CaO15Ni(Ac)3 have main reduction peaks beyond 800 °C (2);
CaO30Ni(Ac)3 and CaO45Ni(Ac)3 have their main peak at around 550 °C (1)
TPR: Effect of CaO fraction (2)

CaO0Ni(N)3 and CaO15Ni(N)3 have main reduction peaks beyond 800 °C (2);
CaO30Ni(N)3 and CaO45Ni(N)3 have their main peak at around 550 °C (1)
TPR: Effect of CaO fraction (3)

CaO0Ni(N)10 has a large main reduction peak at 880 °C (2); CaO30Ni(N)10 and CaO54Ni(N)10 have their peaks between 400 - 700 °C (1)
XRD: Effect of TPR (1)
For Impregnated mayenite the only modification after TPR in crystalline phases is NiO reduction to Ni
XRD: Effect of TPR (2)

For impregnated supported sorbents, the only modification after TPR in crystalline phases is NiO reduction to Ni.
BET method: Effect of Wet Impregnation

Wet impregnation improves specific surface of CSCM for CaO fraction in the originating sorbent < 15 %\(_w\), and makes the opposite for CaO fraction > 30 %\(_w\).
TGA: CO₂ sorption/desorption cycles (1)

Both supported sorbents and dolomite have a decrease in CO₂ sorption capacity, but after the 15th cycle they have a stabilization.
TGA: CO$_2$ sorption/desorption cycles (2)

CSCM deriving from CaO30 have a decrease in sorption capacity in comparison to their parent sorbent. Wet impregnation with Ni-acetate gives the biggest decrease.
TGA: CO\textsubscript{2} sorption/desorption cycles (3)
CSCM deriving from CaO54 have a decrease in sorption capacity in comparison to their parent sorbent.
XRD: Effect of TGA

Materials are extracted after last CO₂ capture: CaCO₃ is detected, together with residual CaO
SEM: Morphology

All materials from CaO54 show a granular structure, with grains in an order of magnitude within the range 100 nm – 1 µm. This morphology doesn’t change after impregnation or after TGA cycles. The same happens for CaO50.
5. SMR andr SE-SMR Tests

**Pre-reduction:**
- 10 °C/min until 900 °C
- 900 °C for 1 h
- 10.2 Nml/min Ar
- 2 Nml/min N₂
- 2.8 Nml/min H₂

**Reforming:**
- 650 °C (constant)
- 10 Nml/min Ar
- 2 Nml/min N₂
- 2 Nml/min CH₄
- Steam/C molar = 3

**Fixed bed**
- 200 mg or 500 mg
- d_p = 100 – 125 μm ; P = 1 atm
SMR tests (Ni-mayenite catalysts) (1):

Ni-mayenite produced by Wet Impregnation with Ni-nitrate performed SMR tests. For each material, the same sample performed SMR 1 and then SMR 2, just separated by cooling at room temperature under inert stream.

SMR 1: reforming starts at 850 °C; after one hour temperature is decreased to 750 °C; after another hour temperature is decreased to 650 °C

SMR 2: reforming starts directly at 650 °C
SMR tests (Ni-mayenite catalysts) (2):

CH$_4$ conversions ($\chi_{CH4}$) are influenced by the quantity on Ni available for the same rate of CH$_4$ fed, and by temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>WHSV</th>
<th>Ni</th>
<th>$\chi_{CH4}$, SMR1</th>
<th>$\chi_{CH4}$, SMR2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N$_I$CH$_4$ h$^{-1}$ g$^{-1}$ cat</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>CaO0Ni(N)10</td>
<td>0.245</td>
<td>10</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>CaO0Ni(N)6</td>
<td>0.240</td>
<td>6</td>
<td>100.0</td>
<td>99.6</td>
</tr>
<tr>
<td>CaO0Ni(N)4.5</td>
<td>0.239</td>
<td>4.5</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>CaO0Ni(N)3</td>
<td>0.239</td>
<td>3</td>
<td>100.0</td>
<td>99.5</td>
</tr>
<tr>
<td>CaO0Ni(N)3</td>
<td>0.545</td>
<td>3</td>
<td>100.0</td>
<td>99.0</td>
</tr>
</tbody>
</table>
SE-SMR tests (CSCM) (1):

CaO-sorbent with 54 \%_w of free CaO was impregnated with Ni-nitrate. Resulting CSCM with 3 \%_w of Ni cannot stably catalyze reforming, while 10 \%_w of Ni made possible to observe SE-SMR and SMR after sorbent saturation.
SE-SMR tests (CSCM) (2):
CaO-sorbent with 30 %w of free CaO was impregnated with Ni-nitrate. Resulting CSCM with 3 %w of Ni cannot stably catalyze reforming, while 10 %w of Ni made possible to observe SE-SMR and SMR after sorbent saturation.
SE-SMR tests (CSCM) (3):
CaO-sorbent with 15 %\textsubscript{w} of free CaO was impregnated with Ni-nitrate. Resulting CSCM with 3 %\textsubscript{w} of Ni made possible to observe SE-SMR and SMR after sorbent saturation, having a trend similar to CaO30Ni(N)10.
### SMR tests (CSCM) (4):  
In CSCM from sorbents with 30 %\(_w\) of free CaO or more, \(\chi_{CH4}\) and catalysis stability are influenced by available Ni, for the same rate of CH\(_4\) fed. Decreasing free CaO to 15 %\(_w\) makes possible to catalyze SE-SMR with 3 %\(_w\) of Ni.
6. Conclusions

- XRD shows that **Wet mixing and Wet impregnation are effective** in producing CaO-mayenite sorbents, Ni-mayenite catalysts and Ni-CaO-mayenite CSCM.

- TPR and XRD reveal that the **only crystalline phase modification (in reducing atmosphere)** is NiO reduction to Ni and that **this reaction is influenced by CaO fraction**.

- BET method shows that **Wet impregnation improves specific surface of CSCM for CaO fraction in the originating sorbent < 15 %_w and makes the opposite for CaO fraction > 30 %_w**.

- Multicycle Ca-looping performed in TGA show a **decrease in CO₂ sorption capacity of CaO-mayenite and Ni-CaO-mayenite in first 15 cycles; after that stabilization at acceptable values occurs**.

- Reactivity tests on microreactor scale show that:
  - Ni-mayenite with different loads of Ni (from 10 %_w to 3 %_w) can catalyze successfully SMR.
  - Ni-CaO-mayenite CSCM can perform SE-SMR.
  - **For Ni-impregnated sorbents with 30 %_w of free CaO of more, a 3 %_w Ni load is not sufficient to catalyze SE-SMR and SMR, while a 10 %w Ni load is**.
  - For Ni-impregnated sobent with 15 %_w of free CaO, a 3 %_w Ni load is sufficient to catalyze SE-SMR and SMR.
Thanks for your attention