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High Temperature Solid Looping Cycles, Milano 1-2 September 2015
Outline

- SER process: description and objective
- Materials synthesis and characterisation
- Experimental set-up and routines
- Reforming Experiments
- Sorption Enhanced Reforming Experiments
- Conclusions
Sorption-Enhanced Reforming (SER)

**Objective:** To obtain mayenite supported materials with Ni loads ranging from 5 to 18 wt.% with catalytic activity for the SER process

**Principle and basic concept**

H₂-production with integrated CO₂-capture in one single step

**Combined Sorbent-Catalyst Material (CSCM):**

- Ceramic Substrate (Mayenite) - CaO - Catalyst

Ni-Mayenite

CaO-Mayenite

Agglomeration 1-particle System
Materials Synthesis and Characterisation

Selection of inert support presenting suitable textural properties

Modified hydrothermal method leading to a mayenite support \((\text{Ca}_{12}\text{Al}_{14}\text{O}_{33})\)

Characterization Techniques
- He picnometry (density \(\rho\))
- BET (Surface Area \(S_{\text{BET}}\))
- Pore Size Distribution
- Hg porosimetry (total porosity \(\varepsilon\))

<table>
<thead>
<tr>
<th></th>
<th>(\rho) (g/cm(^3))</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(\varepsilon) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gk017j</td>
<td>2.888</td>
<td>50.15</td>
<td>69.11</td>
</tr>
<tr>
<td>Gk017i</td>
<td>2.882</td>
<td>42.71</td>
<td>69.64</td>
</tr>
<tr>
<td>Gk017m</td>
<td>2.902</td>
<td>38.48</td>
<td>69.67</td>
</tr>
<tr>
<td>Gk017k</td>
<td>2.833</td>
<td>34.55</td>
<td>69.61</td>
</tr>
<tr>
<td><strong>Gk017h</strong></td>
<td><strong>2.871</strong></td>
<td><strong>27.88</strong></td>
<td><strong>70.73</strong></td>
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**Gk017h**: Highest calcination time and Temperature; conservative case

![Pore diameter distribution](image)

![SEM image](image)
Materials Synthesis and Characterisation

Catalyst synthesis via impregnation methods (wet and incipient)

- Addition (while stirring) of a volume of a Ni(NO₃)₂ solution in excess (wet)/equal (incipient) to the solid sample pore vol.
- The Ni load in the material is controlled by the molar concentration of the Ni solution.

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<th>Support material</th>
<th>Ni load (% wt.)</th>
<th>Impregnation method</th>
<th>Calcination T (ºC) in N₂</th>
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<td>18, 10, 7.5, 5</td>
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<td>700, 800</td>
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XRD indicated no new phases in the crystalline structure
Materials Synthesis and Characterisation

Catalyst synthesis via impregnation methods (wet and incipient)

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TPR

- Materials present three different reduction peaks indicating different interaction Ni-support
- The materials with lower Ni content present strongest interaction with the support shifting the reduction peaks to higher temperatures
- Temperatures below 700 ºC allow to reduce the majority of the Ni present in the catalyst

Influence on material morphology
Materials Synthesis and Characterisation

Catalyst synthesis via impregnation methods (wet and incipient)

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SEM

5 % Ni wt.

7.5 % Ni wt.

10 % Ni wt.

• The wet impregnated materials showed a worst Ni dispersion on the material
• The wet impregnation process was not ‘straight forward’ as lumps were formed during the stirring process

Used 3 cycles without reduction after regeneration
Materials Synthesis and Characterisation

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Incipient

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15 reaction cycles reforming and regeneration
Reforming tests

<table>
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<tr>
<th>Material</th>
<th>Reforming T (°C)</th>
<th>S/C ratio</th>
<th>Spatial velocity (mol CH₄/(hr gr Ni))</th>
<th>Cycles routine</th>
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<tr>
<td>18% wt-Ni- Gk017h-inc</td>
<td>685</td>
<td>5</td>
<td>0.35</td>
<td></td>
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<tr>
<td>10% wt-Ni- Gk017h-inc</td>
<td>585-735</td>
<td>3.3-6.6</td>
<td>0.65</td>
<td>• Wet regeneration plus Reduction</td>
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<td></td>
<td>• Wet regeneration</td>
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<td>7.5% wt-Ni- Gk017h-inc</td>
<td>585-735</td>
<td>2-4</td>
<td>1-1.71</td>
<td>Wet regeneration</td>
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1- gas cylinders
2- gas mass flow controllers
3-4 vessel and water mass flow controller
5- evaporator
6- pressure gauge
7- micro-fixed bed reactor
8- gas chromatograph
9- control system
Reforming tests

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| Test Cyclic Routine       | Wet Regeneration plus Reduction | Wet Regeneration |

Both Regeneration routes gave similar results in terms of materials characterisation and reforming results.
Reforming tests

Effect of Reforming T @ S/C=3

- The materials are able to achieve equilibrium composition at 735 °C
- @ 685 °C the 10 % wt Ni achieves equilibrium
- @ 630 °C and below none of the materials achieve equilibrium

Effect of S/C ratio, @ 685 °C

- The S/C ratio did not have important effect
Reforming tests: Cyclic stability

• The materials present high stability over reforming/regeneration cycles
• It is necessary to assess the combined performance together with a CO₂ sorbent to determine the lowest limit for the combined Ni-material
Sorption Enhanced Reforming tests

Sorbent + Catalyst aming for a total Ni amount in the bed from 3 to 5% wt.

<table>
<thead>
<tr>
<th>% wt. Ni content in bed</th>
<th>Catalyst material</th>
<th>S/C ratio</th>
<th>T (° C)</th>
<th>Spatial velocity (mol CH₄/(hr gr Ni))</th>
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<tr>
<td>3%</td>
<td>7.5%wt-Ni-Gk017h-inc</td>
<td>3</td>
<td>685, 710</td>
<td>0.38</td>
</tr>
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<td>5%</td>
<td>7.5%wt-Ni-Gk017h-inc</td>
<td>3</td>
<td>710, 685, 660, 630</td>
<td>0.1-0.38</td>
</tr>
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Sorbent: 30% wt. CaO on to mayenite, Sorption capacity: 0.23 grs. CO₂/gr. calcined sorbent

5% wt. Ni in bed,
Cat: 7.5%wt.-Ni-Gk017h-inc,
@ 710 ° C and 0.1 1mol CH₄/hr gr Ni)
Sorption Enhanced Reforming tests

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<td>0.11-0.17</td>
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H₂ % in product gas stream of SER tests compared with theoretical equilibrium

- **3 % Ni in bed (0.38 mol CH₄/hr gr. Ni)**
- **5 % Ni in bed (0.17 mol CH₄/hr gr. Ni)**

- Temperatures ≥ 685 ºC allow 3% wt. Ni in bed to reach equilibrium composition
- Reforming activity of the bed depends on the total Ni in bed regardless the catalyst Ni content
- Temperatures ≤ 630 ºC result in poor catalytic activity
Conclusions

• Stable Ni-based materials with reforming catalytic activity have been synthesised on to mayenite inert support (Ni wt. 5-18 %)

• Catalyst activity is highly affected by reforming T and Ni content

• The presence of CO₂ sorbent allows lowering the Ni content of the ‘combined material’

• Promising results from the joint performance sorbent-catalyst... still work to do to determine the operation limits for the material

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