SYNTHESIS AND UPSCALING OF PEROVSKITE MN-BASED OXYGEN CARRIER BY INDUSTRIAL SPRAY DRYING ROUTE

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Key properties:
- High reactivity and selectivity
  - High and accessible surface area
- Structural integrity (lifetime)
  - Attrition resistance (strength)
  - Agglomeration resistance
- Sensitivity to poisoning (lifetime)
- Cost, including environmental, health and safety

Oxygen carrier compositions
- Active metal/metal oxides: Ni, Fe, Cu, Mn
- Support and binder metal oxides: alumina, zirconia, magnesia, ...
- Both natural ores and synthetic particles are evaluated
DEVELOPMENT OF MN-BASED OXYGEN CARRIER

Why Mn?
Cheap material
No toxic properties
CLOU effect: chemical looping with oxygen uncoupling

Developed in PF7 project INNOCUOUS
C28 with perovskite structure
Showed good mechanical and chemical properties
Based on pure materials

FP7 project SUCCESS
Use of raw materials which are widely available and cheaper
Up-scaling of C28 material to tonne scale by using large scale infrastructure
PRODUCTION OF OXYGEN CARRIERS BY SPRAY DRYING

- Raw materials
- Suspension preparation
- Spray drying
- Classification
- Calcination
- (Reactive) sintering

Spray-drying installation

Picture Niro
CaMn\textsubscript{1-x-y}Ti\textsubscript{x}Mg\textsubscript{y}O\textsubscript{3-δ} oxygen carriers based on different Mn ores and oxides were successfully spray dried.
## CHARACTERISTICS MN-BASED OXYGEN CARRIERS

<table>
<thead>
<tr>
<th>OC batch</th>
<th>Used material</th>
<th>d10 (µm)</th>
<th>d50 (µm)</th>
<th>d90 (µm)</th>
<th>CS (N)</th>
<th>StDev of CS (N)</th>
<th>Bulk density (g/cm³)</th>
<th>Attrition index (wt%/h)</th>
<th>CH₄ conversion @950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn₃O₄ source 1</td>
<td>103,3</td>
<td>151,5</td>
<td>215,3</td>
<td>1,59</td>
<td>0,72</td>
<td>1,63</td>
<td>0,83</td>
<td>0,93</td>
</tr>
<tr>
<td>2</td>
<td>Mn₃O₄ source 2</td>
<td>95,1</td>
<td>136,6</td>
<td>191,6</td>
<td>2,79</td>
<td>0,53</td>
<td>1,80</td>
<td>0,58</td>
<td>0,94</td>
</tr>
<tr>
<td>3</td>
<td>MnO</td>
<td>112,6</td>
<td>155,2</td>
<td>217,4</td>
<td>2,53</td>
<td>0,74</td>
<td>1,75</td>
<td>0,94</td>
<td>0,94</td>
</tr>
<tr>
<td>4</td>
<td>MnO₂ source 1</td>
<td>103,7</td>
<td>143,3</td>
<td>196,2</td>
<td>1,92</td>
<td>0,62</td>
<td>1,66</td>
<td>0,96</td>
<td>0,87</td>
</tr>
<tr>
<td>5</td>
<td>MnO₂ source 2</td>
<td>118,8</td>
<td>168,4</td>
<td>250,8</td>
<td>0,48</td>
<td>0,17</td>
<td>1,02</td>
<td>16,28</td>
<td>0,87</td>
</tr>
</tbody>
</table>

![Graph](image)

- **Crushing strength [N]**

![Graph](image)

- **Attrition index**

![Graph](image)

- **Bulk density [g/cm³]**
CHARACTERISTICS C28 WITH BEST PERFORMING MN AND TI OXIDE

<table>
<thead>
<tr>
<th></th>
<th>C28 batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap density</td>
<td>1.8 g/cm³</td>
</tr>
<tr>
<td>PSD</td>
<td>d&lt;sub&gt;50&lt;/sub&gt; 143 µm</td>
</tr>
<tr>
<td>Feret ratio</td>
<td>0.87</td>
</tr>
<tr>
<td>Crushing strength</td>
<td>2.3 ± 0.8 N</td>
</tr>
<tr>
<td>Methane conversion @ 950°C</td>
<td>0.93</td>
</tr>
</tbody>
</table>
UPSCALING OF SPRAY DRYING PROCESS TO TONNE SCALE
Switch to large scale infrastructure for production of oxygen carriers is needed to provide sufficient quantities that accommodate for large scale chemical looping plants.

- Every step in the production process must be evaluated at large scale, to study differences with lab-scale.
- Same process steps are needed as on lab-scale + extra rework step to reduce amount of generated waste.
SPRAY DRYING EQUIPMENT

Lab-scale: 2 fluid nozzle
- Droplets are formed by the compressed air that is micronizing slurry that is fed under low pressure (0 to 0,5 bar) into a fine spray
- Viscosity of the slurry, pressure and air to product ratio mainly determine the particle size of the formed spheres

Large-scale: high pressure fountain nozzle
- Narrower droplet distribution, thus also particle size distribution → increase yield
- Amount of material that can be dried per hour is significantly higher → saving energy
- Assumes a minimum size for the spray dryer
- Fluid dynamics of the slurry inside the swirl chamber in combination with the selected nozzle and the applied pressure are responsible for the spray formation
- Pressure from 20 to 220 bar
SUSPENSION

- Due to the different spraying mechanism of the nozzles suspension developed at lab-scale not successful at large scale as the requirements for the viscosity of the slurries are different
- Suspension must be stable during days to weeks at large scale

→ Composition of suspension was adapted in order to achieve low viscosity, high solids content and long stability
  - Use of Ca-carbonate instead of Ca-hydroxide
  - Change of dispersant and binder system

Non-optimized suspension

Optimized suspension
THERMAL TREATMENT

- Large-scale: initial thermal treatments resulted in dense spheres of $>2.2 \text{ g/cm}^3$, high crushing strength, low attrition rate, but nearly no oxygen release during reactor tests
  - Due to interaction with saggar
  - New calcination tests at other temperatures and with non-reacting saggars were needed
  - Possible to achieve the desired density, but differences in physical characteristics were measured depending on position in saggar
### CHARACTERISTICS OF O-CARRIERS PRODUCED AT TONNE SCALE

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tapped density</td>
<td>1,7-1,8 g/ml</td>
</tr>
<tr>
<td>Phase composition</td>
<td>&gt;95% perovskite</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>d10: 90-130 µm</td>
</tr>
<tr>
<td></td>
<td>d50: 140-180 µm</td>
</tr>
<tr>
<td></td>
<td>d90: 190-230 µm</td>
</tr>
<tr>
<td>Methane conversion @ 950°C</td>
<td>0.94</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Switch to raw materials

- Mn-based O-carriers have been successfully spray dried at VITO with different Mn ores and oxides
  - Properties of Mn source have a strong influence on characteristics oxygen carriers
  - Highest crushing strength of 2.8 N obtained with a Mn$_3$O$_4$ as Mn source
  - Most particles show attrition index below 1 wt%/h

- Methane conversion
  - Highest methane conversion for the more pure Mn sources (around 0.94 at 950 °C)
  - Mn ores with high amount of impurities: conversion of about 0.87 at 950 °C

Switch to large infrastructure of Euro Support

- Change of nozzle system and thus change of suspension rheology was needed to successfully spray dry O-carriers up to tonne scale
- Best particles showed up to 0.94 methane conversion at 950°C
- Batch inhomogeneity should be further reduced in the future

→ Strong Mn-based oxygen carriers with an optimized lifetime and good reactivity can be produced up to tonne scale by spray drying using raw Mn and Ti oxide sources
Thank you for your attention!

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