Flame-Made Ca-Based Nanosorbents with High CO$_2$ Uptake Efficiency

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Separation CO₂, why Calcium-Based Sorbents

• Possible technologies for CO₂ separation:
  – Absorption (amine, carbonates, IL)
  – Adsorption: AC, zeolites, alumina, metal oxides
  – Membrane separation
  – Cryogenic distillation

• Calcium-based sorbents:
  ❑ Operation at elevated temperatures (550 - 950 °C)
  ❑ May be used in post- and pre-combustion systems, in-situ capture systems, and industrial process stream capture systems.
  ❑ Major obstacle: performance decay
  ❑ Challenges for new sorbents:
    ➢ High Capacity and Selectivity, Durability, Fast Kinetics,

(Flue Gas CO₂ Recovery Unit (Using KS-1 )
Synthesis of CaO by Flame Spray Pyrolysis (FSP)

- An O₂-assisted dispersion spray
- Seven supporting CH₄/O₂ flames
- The precursors were dispersed by oxygen
- Formed nanoparticles collected at a filter above the flame

0.5 M Ca-naphthenate in Xylene

I. Calcium-Based CO$_2$ Sorbents Made by Flame Spray Pyrolysis
XRD Patterns of FSP-Made Sorbents

Intensity (a.u.)

* Calcium carbonate
# Calcium oxide

2 Theta (degree)

F1

F2

F3
Percent Weight Change during Pretreatment of FSP-Made Sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>d(nm)</th>
<th>CaO%</th>
<th>CaCO₃%</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>48</td>
<td>36(37)</td>
<td>56(55)</td>
</tr>
<tr>
<td>F2</td>
<td>41</td>
<td>43(43)</td>
<td>48(48)</td>
</tr>
<tr>
<td>F3</td>
<td>34</td>
<td>22(22)</td>
<td>73(73)</td>
</tr>
</tbody>
</table>
Adsorption of CO₂ over FSP-Made Sorbents

Molar Conversion/%

T = 700 °C

70% conversion means 1 kg sorbent captured 550 g CO₂

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>BET SSA (m²/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>41</td>
</tr>
<tr>
<td>F2</td>
<td>47</td>
</tr>
<tr>
<td>F3</td>
<td>59</td>
</tr>
</tbody>
</table>
TEM Images of FSP-CaO (Top) and CaCO$_3$-CaO (Bottom)

\[ d_{\text{BET}} = 39 \text{ nm} \]
Extended Operation Cycles with CaO by FSP

CaO + CO₂ ⇌ CaCO₃

T = 700 °C

Molar conversion (%)

Carbonation/decarbonation cycles

60 min Car/30 min Decar
5 min Car/5 min Decar

T = 700 °C

50th Cycle
II. Durable Doped-CaO Nanosorbents for CO$_2$ Capture
XRD Patterns of FSP-Made M/Ca Sorbents

Intensity (a.u.)

2 theta (degree)

Zr/Ca=1:10
Ce/Ca=1:10
Ti/Ca=1:10
Si/Ca=1:10
Cr/Ca=1:10
Co/Ca=1:10

CaCO₃, PDF number: 00047-1743
Capture of CO$_2$ over FSP-Made Dopant-Incorporated Sorbents

![Graph showing molar conversion (CaO%) vs. time (min) at T=700 °C for different dopants.]

- CaO
- Co/Ca=1:10
- Ti/Ca=1:10
- Zr/Ca=1:10
- Cr/Ca=1:10
- Ce/Ca=1:10
- Si/Ca=1:10

Carbonation and Decarbonation stages are indicated on the graph.
Extended Operation Cycles of FSP-Made Dopant-Incorporated Sorbents

![Graph showing carbonation and decarbonation cycles with different dopants.]

**Carbonation time:** 30 min

**Melting and Tammann temperatures** for various compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature (°C)</th>
<th>Tammann temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>2572</td>
<td>1150</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>1339</td>
<td>533</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1722</td>
<td>725</td>
</tr>
<tr>
<td>CoO</td>
<td>1830</td>
<td>779</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1843</td>
<td>785</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2329</td>
<td>1028</td>
</tr>
<tr>
<td>CeO₂</td>
<td>2400</td>
<td>1064</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2709</td>
<td>1218</td>
</tr>
</tbody>
</table>
XRD Patterns of FSP-Made Zr/Ca Sorbents

Zr/Ca=1:5
Zr/Ca=3:10
Zr/Ca=1:10
Zr/Ca=1:20
Zr/Ca=1:50

+: CaZrO$_3$, PDF number: 00-035-0790;
#: CaCO$_3$, PDF number: 00047-1743)
Evolution of CO₂ Capture Capacity of FSP-Made Zr/Ca Sorbents with Cycles

Performance of the Zr/Ca (3:10) does not decrease during extended operation.

<table>
<thead>
<tr>
<th>Zr/Ca ratio</th>
<th>1st X₀CaO</th>
<th>100th X₀CaO</th>
<th>Cycle X₀CaO started to decrease</th>
<th>Ratios of X₀CaO 100th to 1st</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>14%</td>
<td>16%</td>
<td>N.O.</td>
<td>114%</td>
</tr>
<tr>
<td>3:10</td>
<td>64%</td>
<td>64%</td>
<td>N.O.</td>
<td>100%</td>
</tr>
<tr>
<td>1:5</td>
<td>72%</td>
<td>68%</td>
<td>~80</td>
<td>92%</td>
</tr>
<tr>
<td>1:10</td>
<td>83%</td>
<td>44%</td>
<td>~30</td>
<td>53%</td>
</tr>
<tr>
<td>1:20</td>
<td>88%</td>
<td>34%</td>
<td>~16</td>
<td>39%</td>
</tr>
<tr>
<td>1:50</td>
<td>92%</td>
<td>32%</td>
<td>~13</td>
<td>35%</td>
</tr>
</tbody>
</table>
# The BET SSA & Pore Volume of Various Sorbents by FSP & Wet Chemical Routes

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP Si/Ca(1:10)</td>
<td>78</td>
<td>0.34</td>
</tr>
<tr>
<td>FSP Ti/Ca(1:10)</td>
<td>61</td>
<td>0.38</td>
</tr>
<tr>
<td>FSP Cr/Ca(1:10)</td>
<td>74</td>
<td>0.39</td>
</tr>
<tr>
<td>FSP Co/Ca(1:10)</td>
<td>80</td>
<td>0.42</td>
</tr>
<tr>
<td>FSP Ce/Ca(1:10)</td>
<td>89</td>
<td>0.42</td>
</tr>
<tr>
<td>FSP Zr/Ca(1:10)</td>
<td>74</td>
<td>0.23</td>
</tr>
<tr>
<td>FSP Zr/Ca (1:5)</td>
<td>67</td>
<td>0.23</td>
</tr>
<tr>
<td>FSP Zr/Ca (3:10)</td>
<td>71</td>
<td>0.24</td>
</tr>
<tr>
<td>Wet Zr/Ca (3:10)</td>
<td>6.8</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Typical BET surface areas of CaO sorbents are 0.5-20 m²/g (Jose Corella et al., Ind. Eng. Chem. Res. 45 (2006), 6137-6146)
Extended Operation Cycles with FSP-Made Zr/Ca (3:10) with Vapor

Operation with the presence of water vapor at 700 °C.
Extended Operation Cycles with Zr/Ca(3:10) by FSP (T=550 °C)

$T_{\text{car}}=550 \, ^{\circ}\text{C}$
Carbonation time: 30 min

$T_{\text{dec}}=700 \, ^{\circ}\text{C}$
Decarbonation time: 30 min

Sample TGA Plots
Summary

- CaO sorbents made by flame spray pyrolysis demonstrated high capacity for CO$_2$ uptake due to their nanosize and high surface area.

- Nanosized CaO sorbents doped with refractory oxides (Zr/Ca=3:10) could exhibit high reversibility during cyclic operation. High and stable activity (above 60% conversion after 100 continuous carbonation/decarbonation cycles) was observed.
Acknowledgements

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