CaO–based sorbent development for carbon capture and the study of critical thickness of CaCO$_3$ layer

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Background

U.S. National Climate Assessment (2014)
The application of different types of adsorbents at different temperature

$X_N$: the molar conversion in each cycle
$X_K$: the molar conversion in fast reaction stage
$X_D$: the molar conversion in diffusion-controlled stage

No direct measurement or observation of the critical thickness of product layer

CaO/KIT-6 materials development

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>Ave. Size</th>
<th>CaSiO₃</th>
<th>Ave. Size</th>
<th>Ca₂SiO₄</th>
<th>Ave. Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaK-0.5</td>
<td>0%</td>
<td>n.a.</td>
<td>100%</td>
<td>45 nm</td>
<td>0%</td>
<td>n.a.</td>
</tr>
<tr>
<td>CaK-1</td>
<td>4%</td>
<td>40 nm</td>
<td>66%</td>
<td>35 nm</td>
<td>30%</td>
<td>18 nm</td>
</tr>
<tr>
<td>CaK-2</td>
<td>15%</td>
<td>40 nm</td>
<td>0%</td>
<td>n.a.</td>
<td>85%</td>
<td>30 nm</td>
</tr>
<tr>
<td>CaK-4</td>
<td>54%</td>
<td>87 nm</td>
<td>0%</td>
<td>n.a.</td>
<td>46%</td>
<td>37 nm</td>
</tr>
<tr>
<td>CaO</td>
<td>100%</td>
<td>120 nm</td>
<td>0%</td>
<td>n.a.</td>
<td>0%</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Phase composition and average crystallite size of CaO-based adsorbents

Textural properties derived from different CaO-based adsorbents

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_BET/</th>
<th>S_micro/</th>
<th>S_meso/</th>
<th>V_total/</th>
<th>V_micro/</th>
<th>V_meso/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m²/g)</td>
<td>(m²/g)</td>
<td>(m³/g)</td>
<td>(cm³/g)</td>
<td>(cm³/g)</td>
<td>(cm³/g)</td>
</tr>
<tr>
<td>KIT-6</td>
<td>545</td>
<td>265</td>
<td>280</td>
<td>0.40</td>
<td>0.11</td>
<td>0.29</td>
</tr>
<tr>
<td>CaK-0.5</td>
<td>16.2</td>
<td>8.6</td>
<td>7.8</td>
<td>0.08</td>
<td>0.005</td>
<td>0.075</td>
</tr>
<tr>
<td>CaK-1</td>
<td>11.1</td>
<td>7.0</td>
<td>4.1</td>
<td>0.04</td>
<td>0.003</td>
<td>0.035</td>
</tr>
<tr>
<td>CaK-2</td>
<td>2.9</td>
<td>1.0</td>
<td>1.9</td>
<td>0.007</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>CaK-4</td>
<td>2.7</td>
<td>1.0</td>
<td>1.7</td>
<td>0.005</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>
$N_2$ adsorption-desorption isotherms (a: KIT-6; c: CaO-based adsorbents) and pore size distribution calculated from the BJH adsorption branch (b: KIT-6; d: CaO-based adsorbents)
SEM images of (a) parent KIT-6, (b) CaK-0.5, (c) CaK-1, (d) CaK-2 and (e) CaK-4, with (f) representative EDX spectra for CaK-2
TEM images of parent KIT-6 and CaK-x adsorbents
XRD analysis of CaO-based adsorbents
Schematic diagram of the atmospheric carbonation/calcination reactor system (fixed bed)
Fixed bed CO₂ capture performance of different adsorbents (a: adsorption of CaK-2; b: desorption of CaK-2; c: adsorption of CaK-4; d: desorption of CaK-4)
Cyclic capture capacity and conversion of different adsorbents per gram of CaO at 650 °C
Carbon capture using two CaO materials

Characterisations of two CaO adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{meso}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{meso}}$ (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20.96</td>
<td>17.26</td>
<td>0.0314</td>
<td>0.0331</td>
</tr>
<tr>
<td>sol-gel CaO</td>
<td>38.51</td>
<td>30.01</td>
<td>0.1527</td>
<td>0.1511</td>
</tr>
</tbody>
</table>
Carbon capture test of two CaO adsorbents

a) CaO, b) sol-gel CaO, carried out in a fixed-bed reactor

<table>
<thead>
<tr>
<th>CO₂ uptake (mmol)</th>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO 400 °C</td>
<td>2.92</td>
<td>0.30</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO 600 °C</td>
<td>3.63</td>
<td>3.51</td>
<td>2.03</td>
</tr>
<tr>
<td>sol-gel CaO</td>
<td>4.25</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>sol-gel CaO 600 °C</td>
<td>3.08</td>
<td>2.56</td>
<td>2.10</td>
</tr>
</tbody>
</table>

CO₂ uptake of a commercial CaO and a sol-gel CaO at different temperatures for 3 cycles
(1) T<515 °C, pore surface:
\[ \text{CO}_2 (g) \rightleftharpoons (\text{CO}_2)_{\text{ads}} \]
\[ (\text{CO}_2)_{\text{ads}} + \text{O}^- \rightarrow \text{CO}_3^{2-} \]

\[ \text{CaO} \quad \text{g} \quad \text{ads} \]

88.9 kJ/mol

(2) T>515 °C, CaO-CaCO\textsubscript{3} interface:
\[ \text{CO}_3^{2-} + \text{CaO} \rightarrow \text{CaCO}_3 + \text{O}^- \]

\[ \text{g} \quad \text{ads} \]

179.2 kJ/mol

Ex-situ XRD analysis
SEM analysis of carbonated samples
FIB-SEM images coupled with EDX mapping of the cross-section product layer

a) FB-400, b) FB-600, c) sol-gel FB-400, d) sol-gel FB-600, e) Ca element mapping, f) O element mapping, g) C element mapping
FIB-SEM images and carbon element content

a) and b) FB-400

c) and d) FB-600

e) and f) sol-gel FB-600
In-situ XRD analysis

CaO

(a): CaO 400°C; b): CaO 500°C; c): CaO 600°C; d): sol-gel CaO 400°C; e): sol-gel CaO 500°C; f): sol-gel CaO 600°C
FIB-TEM sample preparation

CaO 400°C

CaO 600°C

Sol-gel CaO 600°C
FIB-TEM images and selected-area electron diffraction pattern of the cross-section product layer

CaO 400 °C →

CaO 600 °C →

~90 nm

Sol-gel CaO 600 °C →
**a**

Fresh sorbent particles → mesopores 2-10 nm → CaO grains ~1.5 μm → unreacted CaO → intra-grain mesopores filled up with CaCO₃ → 400 °C → 600 °C → CaCO₃ product layer formed → Spent sorbent particles

**b**

Fresh sorbent particles → mesopores 2-100 nm → sol-gel CaO grains ~150 nm → unreacted CaO → intra-grain mesopores filled up with CaCO₃ → 400 °C → 600 °C → Lack of useful porosity → Spent sorbent particles
Conclusions

• Pore structure of CaO is an important parameter for carbon capture
• A layer around 90 nm of CaCO$_3$ seems to be crucial for commercial CaO to capture CO$_2$
• Develop nano-scale CaO material with sufficient local space is suggested
Acknowledgement

• Miss Hongman Sun (University of Hull)
• Prof Paul Williams (University of Leeds)
• Prof Boxiong Shen, Mr Jianqiao Wang (Hebei University of Technology)
• Dr Chris Palette (Aston University)
• Prof Ben Anthony (Cranfield University)
Thank you for your attention!