Performance of CaO/CuO Based Composite in Combined Calcium and Copper Chemical Looping

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Outline

1. Integration of CaL-CLC

2. Experimental section

3. Strategies for performance enhancement

4. Discussion and conclusions
1.1. Calcium looping process (CaL)

**Advantages:**
- System: 1. lower cost (~30% reduction with respect to oxy-fired system); 2. FBCs used as reactors.
- Sorbent: 1. CaO is cheap and abundant; 2. high theoretical CO$_2$ uptake capacity.

**Disadvantages:**
- System: high energy requirements in calciner cause expensive ASU.
- Sorbent: 1. solid attrition; 2. sorbent deactivation.
1.2. Chemical looping combustion (CLC)

- **Advantages:**
  - System: 1. Inherent separation of $CO_2$; 2. Minimize NOx formation; 3. Potential low energy penalty.

- **Disadvantages:**
  - Can not be applied in post-combustion for traditional fossil fuel fired power plants.
1.3. Integration of CaL and CLC

Gas without CO₂

Carbonation
CaO+CO₂=CaCO₃

Gas with CO₂

Calcination
CaCO₃=CaO+CO₂

Sorbet, Make-Up
Energy

Spent Sorbent

Oxidation
Cu+O₂=CuO

Air

Reduction
CH₄+CuO→Cu+CO₂+H₂O

CH₄

CO₂, H₂O

CuO, CaO

Air (less O₂)

Flue gas

Carbonator

N₂

CaCO₃, CuO

Regenerator

CO₂, H₂O

CaO, Cu

Air

Oxidator
1.4. Accelerated loss-in-capacity

- Left: (a) Carbonation curves in the 1st cycle, and (b) cyclic carbonation conversions of samples. Samples were pre-calcined at 900 °C for 1.5 h. Right: Carbonation conversions of CaO-MgO and CaO-CuO-MgO, which were both pre-calcined at various temperatures.

- Samples were tested in: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both at 650 °C for 10 min.

- This phenomenon of accelerated loss-in-capacity has been submitted to Industrial & Engineering Chemistry Research as “Behavior of CaO/CuO Based Composite in a Combined Calcium and Copper Chemical Looping process”.

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This text is formatted with bullet points and lists for clarity. The diagram includes graphs showing carbonation conversion over time and cycle for various samples. The text is clear and concise, providing a detailed explanation of the experimental setup and results. The phenomenon of accelerated loss-in-capacity is highlighted, and its submission to a reputable journal is mentioned.
1.5. Objectives

- Test the effectiveness of potential strategies to enhance the reactivity of CaO/CuO based sorbent in the Ca-Cu chemical looping:
  
  a. Sorbent synthesis with sintering-resistant precursors
  
  b. Enhancement of performance by steam addition
  
  c. Thermal Pre-treatment of CuO

- Identify the possible reason for the accelerated loss-in-capacity after addition of Cu/CuO.
2. Experimental section

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Abbreviation</th>
<th>Purity</th>
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<tr>
<td>Calcium Precursor</td>
<td>Calcium acetate hydrate</td>
<td>CA 99~100.5%</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Calcium hydroxide</td>
<td>CH</td>
<td>96%</td>
<td>Ajax Finechem</td>
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<tr>
<td>Calcium L-lactate hydrate</td>
<td>CL</td>
<td>98%</td>
<td>Aldrich</td>
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<td>20 nm calcium oxide</td>
<td>NC</td>
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<td>NanoScale</td>
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<td>Copper Precursor</td>
<td>Copper (II) acetate</td>
<td>UA 98~102%</td>
<td>Ajax Finechem</td>
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<tr>
<td>Copper (II) oxide</td>
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<td>Copper (II) formate</td>
<td>UF</td>
<td>97%</td>
<td>Aldrich</td>
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<tr>
<td>Calcium aluminate cement</td>
<td>CE</td>
<td></td>
<td>Kerneos</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>AO</td>
<td></td>
<td>Sigma</td>
</tr>
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</table>
Oxidation and carbonation conversions of various synthetic sorbents. Testing condition: calcination/reduction in 15% CH₄, oxidation in air and carbonation in 15% CO₂, all at 750 °C for 10 min.
3.1. Performance of Synthetic Sorbents (2/2)

XRD patterns of samples after 1.5 h calcination at different temperatures. (a) CL-UO-CE calcined at 600 °C; (b) CL-UO-CE calcined at 750 °C; (c) CL-UO-CE calcined at 900 °C; (d) CA-UA-AO calcined at 600 °C; (e) CA-UA-AO calcined at 750 °C; (f) CA-UA-AO calcined at 900 °C.
3.2.1. Steam Addition in Different Stages

(a) oxidation and (b) carbonation conversion of sorbent tested with steam addition in different reaction stages. The concentration of $CH_4$ and $CO_2$ was maintained to be 15% during calcination and carbonation respectively.
3.2.2. Effect of Steam Concentration on Reactivity

(a) oxidation and (b) carbonation conversion of sorbent tested in different steam concentration. The concentration of \( \text{CH}_4 \) and \( \text{CO}_2 \) was maintained to be 15% during calcination and carbonation respectively.
(a) Oxidation and (b) carbonation conversion of different sorbents when 27.2% steam was added during cyclic reactions.
3.2.3. Steam Hydration for Different Samples (2/2)

Scanning electron microscope (SEM) images of CA-UA-MA (a) after 1st calcination, (b) after 11th calcination, (c) after 11th calcination (27.2% steam added in all stages); and CH-UO-MA (d) after 1st calcination, (e) after 11th calcination, (f) after 11th calcination (27.2% steam added in all stages).
3.3. Thermal pre-treatment of CuO

- (a) oxidation and (b) carbonation conversions of sorbents after they were pre-treated. Test condition: calcination/reduction in 15% CH₄, oxidation in air and carbonation in 15% CO₂, all at 750 °C for 10 min.
4.1. Discussion: Possible mechanism (1/2)

X-ray diffraction patterns of CaO-CuO-MgO after 1.5 h pre-calcination at the temperature of 400-900 °C.

No chemical interactions between CaO and CuO or MgO, because only crystals of CaO, CuO, MgO and CaCO₃ or Cu₂O were found from XRD patterns of the composites after calcined at different temperatures.

The prolonged carbonation of CaO-CuO-MgO, which was pre-calcined at 900°C for 1.5 h in advance before the following test: calcination/reduction in 15% CH₄ at 800°C for 10 min (20 h at the 3th carbonation), oxidation in air and carbonation in 15% CO₂, both at 650°C for 10 min.
4.1. Discussion: Possible mechanism (2/2)

(a) 1. CaO precursor  
2. CuO precursor  
3. MgO precursor

Mixing → Drying → Cyclic reactions

(b) 1. CaO precursor  
2. Agglomerated CuO  
3. MgO precursor

Mixing → Drying → Cyclic reactions

CO₂ needs to diffuse through the layer firstly

CO₂ is easy to contact with CaO

CaO  MgO  CuO  Agglomerated CuO
4.2. Conclusions

- The addition of Cu/CuO could accelerate the loss-in-capacity of CaO, and this is possibly caused by the agglomeration of Cu/CuO under high temperature;

- The reactivity and recyclability of CaO/CuO based sorbents were affected by the precursors; MgO is good inert support, cement and Al₂O₃ could react with active material and reduce its content;

- Steam addition during the reactions could be an effective approach to maintain the recyclability of the CaO/CuO based sorbents, though the effectiveness is affected by the steam concentration and the types of sorbent;

- Thermal pre-treatment of CuO could reduce the negative effect caused by the agglomeration on the active CaO, then good for resistance to the loss-in-capacity.
Related work in our group

- Development of HotPSA system (use the heat from carbonation to support the decompostion of CaCO₃ in calciner);

- Modelling and testing of coal gasification with in-situ CO₂ capture for hydrogen production;

- Reactivation of CaO-based sorbents by steam/water hydration;

- Particle manufacture and the effect of steam on its mechanical strength;

- The effect of SOₓ on the CaO-based sorbents (mainly in the oxy-combustion atmosphere).