Chemical looping combustion of petroleum coke with Co-based oxygen carrier

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Outline

- Introduction
- Reaction kinetics and thermodynamics
- Fluidized bed experiment of O₂ sorption and desorption
- Chemical looping combustion of petroleum coke
- Conclusions
Chemical looping combustion (CLC) is one of the promising techniques to obtain pure CO₂.

**Fuel reactor:**
\[(2n + m)\text{MeO} + C_{n\text{H}_{2m}} \rightarrow (2n + m)\text{Me} + m\text{H}_2\text{O} + n\text{CO}_2\]

**Air reactor:**
\[
\text{Me} + \frac{1}{2}\text{O}_2 \rightarrow \text{MeO}
\]

After removing water by condensing, pure CO₂ stream can be obtained easily.

Gas fuel is suitable for CLC, such as natural gas or syngas.
Chemical-looping with oxygen uncoupling (CLOU)

- 2005, Lyngfelt and Mattisson proposed CLOU
- Solid fuel (coal, petroleum coke, etc)
- In the temperature range of 800~1200°C, the reaction between O₂ and oxygen carrier is required to be reversible
- Oxygen carrier: CuO/Cu₂O, Mn₂O₃/Mn₃O₄, Co₃O₄/CoO
- Char is burnt directly by O₂ released from oxygen carrier, combustion rate is fast

<table>
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<tr>
<th>Metal</th>
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<th>Metal Oxide</th>
<th>Cost</th>
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<td>Co</td>
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Solid fuel (coal, petroleum coke, etc)
Chemical-looping with oxygen uncoupling (CLOU)

\[ 2\text{Co}_3\text{O}_4 + \text{C} \leftrightarrow 6\text{CoO} + \text{CO}_2 \]
\[ \Delta H_{950} = 4.96 \text{kJ/mol Co}_3\text{O}_4 \]

<table>
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<tr>
<th>Author</th>
<th>Oxygen carrier</th>
<th>Fuel</th>
<th>Apparatus</th>
<th>Temperature</th>
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Objective

Focus on two reactions:

\[ 2\text{Co}_3\text{O}_4 \leftrightarrow 6\text{CoO} + \text{O}_2(\text{g}) \]

The characteristic of oxygen sorption and desorption on Co-based oxygen carrier – TGA
Experiment and Modeling of \( \text{O}_2-\text{CO}_2 \) Production with Co-based Oxygen Carrier - Fluidized bed

\[ 2\text{Co}_3\text{O}_4 + \text{C} \leftrightarrow 6\text{CoO} + \text{CO}_2 \]

Chemical looping combustion of petroleum coke – Fluidized bed

Oxygen carrier particle:

\( \text{Co}_3\text{O}_4/\text{Al}_2\text{CoO}_4 \) (60/40 wt %), 100~200um
Reaction kinetics and thermodynamics

**Dupont 951 TGA (TA Instrument 1200)**

Co-based oxygen carrier: <15 mg.

Particle size: 100-200um.

Temperature raising rate: 10 °C /min.
Reaction kinetics and thermodynamics

Co-based oxygen carrier

After using CO₂ to release O₂

Before using CO₂ to release O₂

A: CoO  B: Co₃O₄

higher oxygen capacity
and higher reaction rate

XRD results indicated it does not
react with CO₂ at high temperature

6CoO + O₂ ⇔ 2Co₃O₄ theoretical oxygen capacity is 7.11wt%.
Reaction kinetics and thermodynamics

The reaction of CoO with O₂ in the range of 500-850°C is very fast. When the reaction temperature is increased to 880°C, the reaction rate begins to decrease.
Oxygen desorption on $\text{Co}_3\text{O}_4$ at different temperature and oxygen partial pressures with $\text{CO}_2$ as the purge gas.

The desorption reaction rate depends strongly on temperature and oxygen partial pressure. $\text{O}_2$ equilibrium pressure increase with higher temperature, resulting in a faster desorption rate. As the oxygen partial pressure increases, the desorption rate will decrease.
Reaction kinetics and thermodynamics

This figure shows the O$_2$ sorption in air and O$_2$ desorption in CO$_2$ atmosphere quantified as mass variation. Extended testing of the Co-based oxygen carrier over 20 cycles at 840 °C was carried out. It can be seen that the sorption capacity did not decrease with increasing of cycle number.
After many cycles, no obvious sinter phenomenon were found in micro structure.
Reaction kinetics and thermodynamics

Equilibrium P and T

Decomposition temperature increases with O\textsubscript{2} partial pressure

Temperature vs O\textsubscript{2} partial pressure

The fitted equation can be used to determine the appropriate oxygen sorption and desorption temperature at different O\textsubscript{2} partial pressure.

Thermodynamic calculations are compared with experimental results. The experimental data correspond to the starting point of Co\textsubscript{3}O\textsubscript{4} decomposition. Fitted equation agrees with the experimental results well. Thus, above equation can be used to determine the appropriate oxygen sorption and desorption temperature at different O\textsubscript{2} partial pressure.
Fluidized bed experiment of $O_2$ sorption and desorption

Multicycle tests of the $O_2$ sorption and desorption were carried out in a small fluidized bed reactor (30mm i.d.). The flow rates of $CO_2$, $N_2$ and air from high purity cylinders controlled by mass flow controllers. The temperatures in the reactor was measured by the thermocouple. The $O_2$ and $CO_2$ bulk fraction was determined by an on-line gas analyzer and recorded by a data acquisition system.
Fluidized bed experiment of O₂ sorption and desorption

The bubbling fluidized bed model (KL model) was adapted to describe the experimental phenomenon. Based on the KL model, the CO₂ axial concentration profile in the bubble $C_{b,CO₂}$ and that in the emulsion $C_{e,CO₂}$ with the bed height $z$ is

$$-u_b^* \frac{dC_{b,CO₂}}{dz} = K_{be}(C_{b,CO₂} - C_{e,CO₂}) + \gamma_b K_r (C_{b,CO₂} - C_{eq,CO₂})$$

and

$$-(1 - \delta)u_{mf} \frac{dC_{e,CO₂}}{dz} = (1 - \delta)(1 - \varepsilon_{mf})K_r (C_{e,CO₂} - C_{eq,CO₂}) - \delta K_{be}(C_{b,CO₂} - C_{e,CO₂})$$

Solid conversion rate,

$$\frac{dX_{sorp}}{dt} = k_{sorp} (1 - X)^{2/3} (C_{O₂} - C_{eq,O₂})$$

$$\frac{dX_{desorp}}{dt} = k_{desorp} (1 - X_{calci})^{2/3} (C_{eq,O₂} - C_{O₂})$$

The reaction rate, $K_r$ is

$$K_r = k_{sorp} f_a (1 - X)^{2/3} \text{ for O₂ sorption stage}$$

$$K_r = k_{desorp} f_a (1 - X_{calci})^{2/3} \text{ for O₂ desorption stage}$$
The evolutions O₂ concentration and reaction temperature with reaction time for the Co-based oxygen carrier during the O₂ sorption tests were shown. The outlet O₂ concentrations were not higher than 1% for a stable absorption period, and these experimental results show that O₂ in air can be absorbed effectively by Co-based oxygen carrier particle in the fluidized bed.
Fluidized bed experiment of O₂ sorption and desorption

The reactor temperature was gradually raised to 920 °C from 720 °C during desorption period, the decomposition rate of Co₃O₄ was accelerated, resulting into the O₂ fraction increasing gradually. With time increasing, the fraction of Co₃O₄ un-decomposition in reactor decreased and the O₂ fraction began to decrease with time. When all Co₃O₄ was decomposed, no O₂ was released.
Fluidized bed experiment of O$_2$ sorption and desorption

O$_2$ storage

Φ: 30mm
Sample: 83g
100~200 μm
Air(0.1m$^3$/h)

Experimental and simulated results of O$_2$ sorption on Co-based oxygen carrier at different temperature

O$_2$ can be absorbed effectively by Co-based oxygen carrier in the temperature range of 685°C~860°C. With temperature increasing, O$_2$ concentration increases due to the thermodynamic limit. The simulated O$_2$ profiles in the fluidized bed reactor agree reasonably with the experimental results.
Fluidized bed experiment of O$_2$ sorption and desorption

O$_2$ fraction in O$_2$-CO$_2$ stream increases with temperature increasing. When the temperature is increased to 900 °C, the O$_2$ fraction can approach 20%. An important feature of this process is that it can produce low-pressure oxygen at the concentration required for CLOU system.
The O₂ fraction in the gas mixture increases with increasing solid mass in bed. O₂ desorption step is governed by both thermodynamic and kinetic. If solid mass in bed is enough (such as >332g), thermodynamic limit and temperature is critical, and the O₂ fraction is determined mainly by reaction temperature. While the solid mass in bed is not enough, kinetic are also important.
Chemical looping combustion of petroleum coke

O₂ release and use @ 880°C

Sample: 100g
100~200 μm

Blend: 450~1000 μm

Petroleum coke: 0.5g

W: 0.76%; A: 0; V: 10.81%; C: 88.43%

0.5g petroleum coke was added into reactor, the CO₂ fraction is lower than the O₂ fraction. Petroleum coke mass (0.5g) is not enough to consume all O₂ released from Co-based oxygen carrier.
When petroleum coke added into reactor was increased to 1g, the CO₂ fraction increases, however, 1g petroleum coke is not enough to consume all O₂ released from Co-based oxygen carrier.
Chemical looping combustion of petroleum coke

With petroleum coke increasing further to 1.5g, the maximum CO₂ fraction (~25%) is higher than the maximum O₂ fraction (~7%). Most of O₂ released from Co-based oxygen carrier was used to burnt petroleum coke.
When 2g petroleum coke was added into reactor, O\textsubscript{2} released from Co-based oxygen carrier was not enough to burnt all petroleum coke. This can be concluded that CO\textsubscript{2} was released again when air was introduced into reactor after 50min.
Conclusions

- Co-based oxygen carrier has high oxygen capacity, reaction rate, cyclic reactivity stability.

- $O_2$ can be absorbed effectively by Co-based oxygen carrier in the temperature range of 685°C~860°C. With temperature increasing, $O_2$ concentration increases due to the thermodynamic limit.

- $O_2$ fraction in $O_2$-CO$_2$ stream increases with temperature increasing, $O_2$ desorption step is governed by both thermodynamic and kinetics.

- The bubbling fluidized bed model (KL model) can be used to describe the experimental phenomenon.

- Petroleum coke can be burned during the $O_2$ release process. $O_2$ concentration keeps low, indicates that petroleum coke can be burned completely and the reaction rate is limited by the $O_2$ release rate.
ACKNOWLEDGMENT

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