Unravelling of the kinetics of the Oxygen Carriers for Chemical Looping Combustion

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Emissions of greenhouse gases (GHG) to the atmosphere are expected to cause significant global climate change.

**CCS**: Important strategy for reducing CO₂ emissions from fossil based power plants.

**Chemical Looping** is one of the most promising technologies of CCS as it presents the **lowest energy penalty**.
**Fluidized Bed Reactors (FBR)**

- Two Interconnected FBR
  - Fuel reactor
  - Air reactor
- Redox chemistry (metal)
- High level of CO$_2$ capture
- Low energy carbon capture penalty

**Packed Bed Reactors (PBR)**

- Oxygen carrier (OC) stationary
  - Reduced
  - Oxidized
- Fuel or Air stream
- Separation intrinsic
- Periodic operation
- High level of CO$_2$ capture
- Low energy carbon capture penalty
**OC**: Crucial step for CLC

**OC**: Determines the overall process efficiency

**PBR**: Conversion 0-100% every cycle

**Important to predict the real final conversion**

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**Motivation**

CuO/Al₂O₃ conversion profiles as a function of time on stream (with 50% H₂ in N₂)
Gas-phase Diffusion

Experiment | Surface Area (m²/g)
--- | ---
Fresh CuO/Al₂O₃ | 227.07
10 redox cycles CuO/Al₂O₃ | 63.08
25 redox cycles CuO/Al₂O₃ | 33.66
50 redox cycles CuO/Al₂O₃ | 33.15

M.A. San Pio, I. Roghair, F. Gallucci, M. van Sint Annaland, Investigation on the decrease in the reduction rate of oxygen carriers for chemical looping combustion, Powder Technol. 301 (2016) 429–439
**CONCLUSIONS**

- **Gas phase-diffusion limitations do not play** a role in the redox kinetics

- **The morphology changes in terms of porosity but doesn’t influence** the redox kinetics

- **Spinel kinetics (CuO*Al$_2$O$_3$)** can play a role in the CuO reduction
**Spinel studies**

**Reduction reaction:**

\[
2CuO \rightarrow 2Cu_2O + \frac{1}{2}O_2
\]

\[
Cu_2O + H_2 \rightarrow 2Cu + H_2O
\]

\[
CuAl_2O_4 + H_2 \rightarrow Cu + Al_2O_3 + H_2O
\]

\[
CuAl_2O_4 + H_2 \rightarrow CuAlO_2 + Al_2O_3 + H_2O
\]

**Oxidation reaction:**

\[
2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O
\]

\[
Cu_2O + \frac{1}{2}O_2 \rightarrow 2CuO
\]

\[
CuO + Al_2O_3 \rightarrow CuAl_2O_4
\]

\[
CuAlO_2 + \frac{1}{2}Al_2O_3 + \frac{1}{2}O_2 \rightarrow CuAl_2O_4
\]

**Spinel oxidation**

**Spinel reduction**

**M.A. San Pio**, I. Roghair, F. Gallucci, M. van Sint Annaland, Temperature study on the redox kinetics of Cu-based oxygen carriers to explain the drop in reaction rate, Powder Technol. In Press
**Oxidation reaction:**

2\(Cu + \frac{1}{2} O_2 \rightarrow Cu_2O\left( + \frac{1}{2} O_2 \right) \rightarrow 2CuO\)

\(CuO + Al_2O_3 \rightarrow CuAl_2O_4\)

\(CuAlO_2 + \frac{1}{2} Al_2O_3 + \frac{1}{2} O_2 \rightarrow CuAl_2O_4\)
Reduction reaction:

\[
CuO + H_2 \rightarrow Cu_2O (+H_2) \rightarrow Cu
\]

\[
CuAl_2O_4 + H_2 \rightarrow Cu + Al_2O_3 + H_2O \quad 1,4 \quad 3,6
\]

\[
CuAl_2O_4 + H_2 \rightarrow CuAlO_2 + Al_2O_3 + H_2O \quad 2,5
\]
Reduction conversions of CuO/SiO$_2$

$CuO + H_2 \rightarrow Cu_2O(+H_2) \rightarrow Cu$

- Conversion [%]
  - Reduction at 870 °C
  - Reduction at 700 °C
  - Reduction at 600 °C

- Time [s]

Cu
SiO$_2$
M.A. San Pio, I. Roghair, F. Gallucci, M. van Sint Annaland, Temperature study on the redox kinetics of Cu-based oxygen carriers to explain the drop in reaction rate, Powder Technol. In Press

CONCLUSIONS

- The oxidation reaction is not limiting the redox kinetics.
- The reduction reaction is limiting the redox kinetics, being the drop and final conversion different at different temperatures.
- Spinel is the cause of the drop in reaction rate as well as the slow-down in conversion.
Gas-phase diffusion does not play a role on the redox kinetics

Spinel causes the drop in the reduction kinetics

Pressure does not play a role on the redox kinetics if the flows are high enough

Spinel kinetics have to be included in the model to better predict the CLC process

Integration of the particle model in the reactor model
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