Development and application of high temperature CO$_2$ sorbents

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Outline

► Background and principles
► Our approach:
  ▪ Continuous lab scale reactor testing
    • Recent results using natural Ca-based sorbents
  ▪ Search for new sorbents
    • Search based on thermo-dynamic properties
► Conclusions and further prospects.

http://www.epa.gov/climatechange/effects/
Background

Separation of CO$_2$ from gas mixtures using solid sorbents at high temperature (500-900 °C) represents an alternative to processes at ambient or sub-ambient temperatures. Two important examples:

- The carbonate looping process (CL) [1]
- Sorption enhanced -steam methane reforming/-water-gas shift reactions (SE-SMR) [2].

Application principles

► The sorbents are typically a metal oxide that reacts with CO$_2$ and form a carbonate.

► A subsequent regeneration decomposes the carbonate and thus releases CO$_2$ as a gas. The newly reformed metal oxide is then ready for use again.

\[
\text{MO} + \text{CO}_2 \quad \overset{500-700 \, \text{C}}{\leftrightarrow} \quad \text{MCO}_3 \\
\overset{700-900 \, \text{C}}{\longrightarrow} 
\]
Carbonate looping

Flue gas – CO₂ → MCO₃ → MO → CO₂

Fuel burning in this reactor provides heat for regeneration of sorbent

Flue gas 500-700 C
Gas/coal/biomass + O₂

Sorption-enhanced methane steam reforming

Hydrogen production from natural gas with simultaneous capture and separation of CO₂.

One possible concept:
Sorption enhanced methane steam reforming, SE-SMR [1].

SE-SMR has been proposed to be an economical competitive alternative to conventional steam methane reforming with CO₂ capture [2].

Lab-scale testing of SE-SMR

Reforming: \( \text{CH}_4(g) + 2\text{H}_2\text{O}(g) + \text{MO}(s) \rightleftharpoons \text{MCO}_3(s) + 4\text{H}_2(g) \)

Feed gases: \( \text{CH}_4 + \text{steam} + \text{N}_2 \)

Near thermoneutral

Regeneration: \( \text{MCO}_3(s) \rightleftharpoons \text{MO}(s) + \text{CO}_2(g) \)

Endothermic

Feed gases: \( \text{CH}_4 + \text{steam} + \text{N}_2 \)

Near thermoneutral

Reforming: \( \text{CH}_4(g) + 2\text{H}_2\text{O}(g) + \text{MO}(s) \rightleftharpoons \text{MCO}_3(s) + 4\text{H}_2(g) \)

Fluidization

Riser for transport

Loop seal 2

Loop seal 1

Cyclone

H$_2$

CO$_2$
SE-SMR (feed reformer: 50 ml/min CH₄, 200 ml/min H₂O, 1860 ml/min N₂ diluent)

- Effect of catalyst/sorbent ratio:

Catalyst/sorbent= 20/80

Catalyst/sorbent= 50/50
SE-SMR (feed reformer: 50 ml/min CH₄, 200 ml/min H₂O, 1860 ml/min N₂ diluent, initial catalyst/sorbent= 20/80, used and regenerated powder mixture)

- Effect of catalyst addition during experiment:

H₂ measured and calculated from conversion of methane and total Cs from R1 and R2 - exp 27- 580°C

[Graph showing methane conversion and flows over time]
SE-SMR (feed reformer: 50 ml/min CH₄, 200 ml/min H₂O, 1860 ml/min N₂ diluent, initial catalyst/sorbent= 20/80, used and regenerated powder mixture)

- Effect of reformer temperature:

Reformer outlet, [ml/min] 530°C

Reformer outlet, [ml/min] 630°C
The objectives of this WP is to develop solid sorbents for CO$_2$ capture processes at elevated temperatures (500-900 °C) and pressures (20-30 bar) suitable for industrial use.

Our long term goal is to identify a production method for new sorbent material, for a large demonstration unit, based on cheap raw materials.

States of the art (2009) high temperature CO$_2$ sorbents are usually based on Ca-oxides or Li/Na-silicates/zirconates.

**Li-based:**
- $\text{Li}_2\text{ZrO}_3$
- $\text{Li}_4\text{SiO}_4$

**Ca-based:**
- $\text{CaO}$ (lime)
- $\text{Mg}_{0.5}\text{Ca}_{0.5}\text{O}$ (from dolomite)
- $\text{CaO}/\text{support}$ (“synthetic”)

\[
\text{MO} + \text{CO}_2 \overset{500-700 \ \text{C}}{\leftrightarrow} \text{MCO}_3 \overset{700-900 \ \text{C}}{\leftrightarrow}
\]
Thermodynamic search for potential novel solid sorbents:

► using FactSage 6.1

► Use thermodynamic calculations to evaluate various oxides, both simple and mixed oxides for carbonate formation at realistic process conditions (SE-SMR: 44% H₂O, 35% H₂, 11% CH₄, 7% CO₂, 2% CO, 5 bar tot).

► Sulphur tolerance has been studied:
  ▪ Do sulphide species (as H₂S) react with the sorbent and if, does it form sulphides (S²⁻) or sulphates (SO₄²⁻)?
  ▪ How do such species influence CO₂ capacities and how must these sorbents be regenerated?
The CaO example:
Thermodynamic evaluation, example of data:

Gibbs free energy of carbonate formation at 873 K for selected hydroxides and oxides
Gibbs free energy of sulphide formation at 873 K for selected hydroxides and oxides
Summary thermodynamics

For single component sorbents based on alkali and alkaline earth oxides/hydroxides the main trends are:

- Most of the selected oxides/hydroxides have so high CO₂ affinity that thermal regeneration is challenging, and the incorporation of elements with less CO₂ affinity in the sorbent material may be necessary to facilitate a higher CO₂ equilibrium pressure.
- The alkaline earth metals have a stronger tendency to form both carbonates and sulphides than the alkali metals. The alkali metals are more selective towards carbonate formation.
- The regeneration should be performed in low O₂ concentration and at a rather high temperature to avoid sulphate formation.

- Rb, seem to have interesting properties with high CO₂ affinity and very low tendency for sulphide and sulphate formation.
- The modified alkaline earth metals are better suited as CO₂ sorbents in a sweet (H₂S free) feed gas.
- Bulk CaO have good thermodynamic properties for cyclic temperature swing sorption-desorption without modification/incorporation of new elements in the sorbent material.
CO₂ adsorption capacities
650°C, pCO₂=0.15 bar, pH₂O=0.29 bar, 1 gram, 30 ml/min total flow

![CO₂ adsorption capacity graph](image)
Summary

► Finally, a lab scale CFB reactor system is working well for SE-SMR using calcined dolomite as sorbent and NiO/NiAl$_2$O$_4$ as catalyst
  ▪ which can be used to evaluate novel sorbents (and catalysts) at a relatively small scale (approx 200 ml powder)

► Identification of novel sorbent compositions by the use of thermodynamic calculations using relevant process conditions are in progress.
  ▪ CaO has good thermodynamic properties (no surprise!)
  ▪ Some new leads will be tested.
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Thank you for your kind attention