THE SORBENT AND THE PROCESS

CO₂ and H₂O Sorption Enhancement in Chemical Reactors

CHEMREACTOR-23, 5-9 November 2018, Ghent Belgium | Jurriaan Boon
Towards a CO₂-neutral INDUSTRY

GOALS 2050
ALL INDUSTRY HAS A ZERO NET CO₂ EMISSION
SUSTAINABLE SUPPLY AND (RE-)USE OF INDUSTRIAL HEAT
> 40% PROCESS EFFICIENCY IMPROVEMENT
COMPLETE ELECTRIFICATION
CO₂ CAPTURE CONVERSION AND STORAGE

LINE 1
HEAT

LINE 2
EFFICIENCY AND CIRCULARITY

LINE 3
ELECTRIFICATION

LINE 4
CCU, CCS
SORPTION-ENHANCED REACTIONS FOR CCS AND CCU

- Water-gas shift
  \[ CO + H_2O \rightleftharpoons H_2 + CO_2 \]

- Sorption-enhanced water-gas shift (SEWGS)
  \[ CO_2 + \ast \rightarrow CO_2 \ast \]
  \[ CO + H_2O \rightarrow H_2 \ ( + CO_2) \]

- Reverse water-gas shift
  \[ CO_2 + H_2 \rightleftharpoons CO + H_2O \]

- Sorption-enhanced reverse water-gas shift
  \[ H_2O + \ast \rightarrow H_2O \ast \]
  \[ CO_2 + H_2 \rightarrow CO \ ( + H_2O) \]

- Sorption-enhanced DME synthesis (SEDMES)
  \[ H_2O + \ast \rightarrow H_2O \ast \]
  \[ 2CO_2 + 6H_2 \rightarrow CH_3OCH_3 \ ( + 3H_2O) \]
SORPTION-ENHANCED REACTIONS

ADSORPTION AND REGENERATION

The Sorbent and the Process

Reaction

\[ A + B \rightleftharpoons C + D \]

Adsorption

\[ D + \ast \rightarrow D\ast \]

SEWGS: 400 °C, 25 bar

SEDMES: 275 °C, 30 bar

400 °C, 25 bar

---

400 °C, 3 bar

400 °C, 3 bar
PRECOMBUSTION CO$_2$ CAPTURE: SORPTION-ENHANCED WATER-GAS SHIFT – SEWGS
Hydrotalcite, a layered double hydroxide mineral

\[ \text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot4\text{H}_2\text{O} \]

(varying Mg:Al ratio)

Under reaction conditions: disordered mixed metal oxide

- Adsorbs and releases \( \text{CO}_2, \text{H}_2\text{O} \); catalytically active for WGS
- Capacities around 1 mol/kg, for \( \text{CO}_2 \text{ and } \text{H}_2\text{O} \)
- Stable under high temperatures, high \( p(\text{H}_2\text{O}) \)
SEWGS: ISOTHERM

SEWGS: ISOTHERM

400 °C

CO₂

H₂O

$q_i$ [mol kg⁻¹]

$p_i$ [bar]

$p_{H₂O} = 0$

$p_{H₂O} = 20$ bar

$p_{CO₂} = 0$

$p_{CO₂} = 5$ bar

$p_{CO₂} = 20$ bar

Adsorptive rinse
(high partial pressure steam)

→ enhanced efficiency

The Sorbent and the Process

**SEWGS: I\(\text{SO}\)THERM**

- **CO\(_2\)**
- **H\(_2\)O**

- **400 °C**
  - \(p_{\text{H}_2\text{O}} = 0\)
  - \(p_{\text{H}_2\text{O}} = 20 \text{ bar}\)

- **Multiple sites** including CO\(_2\)-\(H_2\)\(O\) exchange site

\[p_{\text{H}_2\text{O}} = 0, \quad p_{\text{CO}_2} = 0, \quad p_{\text{CO}_2} = 5 \text{ bar}, \quad p_{\text{CO}_2} = 20 \text{ bar}\]

- **Activation with H\(_2\)O**
  - \(\text{C} \rightarrow \text{C}[\text{H}_2\text{O}]\)
  - \(\text{C}[\text{H}_2\text{O}] \rightarrow \text{C}[\text{OH}] + \text{CO}\)
  - \(\text{C}[\text{OH}] + \text{CO}_2 \rightarrow 2 \text{C}[\text{CO}] + \text{H}_2\text{O}\)

- **Activation with CO**
  - \(\text{C} \rightarrow \text{C}[\text{CO}]\)

\[A \quad \text{H}_2\text{O} + A[\bullet] \xrightleftharpoons{\gamma_{\text{H}_2\text{O}}} \xrightarrow{\gamma_{\text{A}}} A[\text{H}_2\text{O}]\]
\[B \quad \text{CO}_2 + B[\bullet] \xrightarrow{\gamma_{\text{CO}_2}} B[\text{CO}_2]\]
\[C \quad \text{C}[\bullet] + \text{CO}_2 \rightarrow \text{C}[\text{CO}_2]\]
\[D \quad \text{CO}_2 + D[\bullet] + A[\text{H}_2\text{O}] \xrightleftharpoons{\gamma_{\text{D}}} \xrightarrow{\gamma_{\text{A}}} D[\text{CO}_2] + A[\text{H}_2\text{O}]\]

Coenen et al. Chem Eng J 293 (2016) 9-23
Coenen et al. Chem Eng J 314 (2017) 554-569

\[\rightarrow \text{regeneration behaviour}\]
3.8 × 200 cm

3.8 × 600 cm

30 × 900 cm
TOWARDS CIRCULAR CARBON: SORPTION-ENHANCED DME SYNTHESIS – SEDMES
SEDMES: CATALYST AND ADSORBENT

Catalyst

\[ 2\text{CO}_2 + 6\text{H}_2 \rightarrow 2\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \]

CuZnAl
SEDMES: CATALYST AND ADSORBENT

Catalyst

\[ 2\text{CO}_2 + 6\text{H}_2 \rightarrow 2\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \]

CuZnAl \hspace{2cm} \gamma\text{-Al}
SEDMES: CATALYST AND ADSORBENT

- Catalyst
  - $2\text{CO}_2 + 6\text{H}_2 \rightarrow 2\text{CH}_3\text{OH} + 2\text{H}_2\text{O}$
  - CuZnAl

- Adsorbent
  - $\text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O}$
  - γ-Al
  - LTA
SEDMES: DME YIELD IMPROVEMENT

DME synthesis 275 °C & 40 bar(a)
SEDMES: DME YIELD IMPROVEMENT

Product C-distribution (mol%)

- CO
- CO2
- CH3OH
- DME

SEDMES 275 °C & 40 bar(a)
SEDMES: REGENERATION CONDITIONS

- TPSA regeneration (heating to 400 °C, depressurisation to 3 bar(a))
  - Improved water adsorption (lower water slip level)
  - Improved catalytic activity

- Separate tests water-induced deactivation of γ-alumina for methanol dehydration
SEDMES: REGENERATION CONDITIONS

- Separate tests water-induced deactivation of γ-alumina for methanol dehydration
SEDMES: REGENERATION CONDITIONS

- Separate tests water-induced deactivation of γ-alumina for methanol dehydration

- Reversible deactivation by γ-AlO(OH) formation

---

The Sorbent and the Process
SEDMES: PROCESS SCALE-UP

0.9 × 20 cm

3.8 × 200 cm

3.8 × 600 cm
THE SORBENT AND THE PROCESS
CO₂ and H₂O Sorption Enhancement

› Particle-scale phenomena for understanding sorption-enhanced processes

› SEWGS
  › Adsorptive rinse
  › CO₂-H₂O exchange site

› SEDMES
  › Adsorbent response to regeneration conditions
  › Catalyst response to regeneration conditions (reversible deactivation by H₂O)
ACKNOWLEDGEMENTS

› ECN part of TNO
   Biomass & Energy Efficiency
   Petten, The Netherlands

› Eindhoven University of Technology
   Department of Chemical Engineering and Chemistry
   Chemical Process Intensification
   Eindhoven, The Netherlands
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 640769.

http://www.stepwise.eu

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 727600.

http://www.fledged.eu
THANK YOU FOR YOUR ATTENTION

TNO.NL/ECNPARTOFTNO