CARENA WP3: Valorization of CO$_2$ to MeOH and DMC

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Introduction

AkzoNobel incentive for CARENA:

- Interest in new affordable processes for green Methanol and green Di Methyl Carbonate (DMC)
- Open innovation driver
- Catalytic membrane reactors identified as high risk high reward option

EU FP7 programme:

- Working with excellent EU expertise on catalysts, membranes and process design
- Substantial technical and financial leverage realized
- Expected low Probability of Success acceptable
WP3 - Participants

AkzoNobel

Sintef

Johnson Matthey

ECN

University Twente

PDC

CNRS-IRCE
Valorization of CO$_2$: 

- Methanol synthesis:
  \[ \text{CO}_2(g) + 3\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \]

- DMC synthesis:
  \[ \text{CO}_2(g) + 2\text{MeOH} \rightleftharpoons \text{DMC} + \text{H}_2\text{O} \]

- Selective removal of H$_2$O/products through a membrane reactor
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- Selective removal of H$_2$O/products through a membrane reactor

Commonalities:

- Equilibrium reactions → need for high pressure
- Need for catalysts
- Water produced as co-product
- Reaction T: 120 – 300 °C
Challenges for Methanol process
Methanol synthesis: non-membrane process

- Total electricity usage: 700 kWh/t MeOH
- Total steam consumption: 2 - 3 t steam/t MeOH
Methanol synthesis: non-membrane process

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CARENA - Workshop - PETTEN, 29 April 2015
Potential economic gain of membrane process

- Reduction in investment costs due to removal of recycle loop: one compressor and one heat exchanger
- Reduction in energy consumption of compressor(s)

Incompatibility of reaction conditions (250 °C, 50 bar) and membrane limitations will require need for recycle
⇒ Reduces cost advantage
• **Methanol:** Mismatch between operating window of membrane and reaction
Challenges for DMC process
DMC synthesis

- Non-membrane process for DMC synthesis not feasible due to large recycles
- Membrane process requires a membrane with a large selectivity of $H_2O$ over methanol: >50
Processing options for DMC production

Options:
• R&S in same unit
• R&S in same unit and cat on membrane (most likely)

T = 110 - 180 °C

Membrane reactor

\[ \text{CO}_2(g) \rightarrow \text{CH}_3\text{OH} \] (g)

\[ \text{H}_2(g) \rightarrow \text{H}_2\text{O} \] (g)
Required operating window for DMC production

Issue:
• DMC equilibrium conversion is only around 1%!
Workpackage 3

Objectives

• Catalyst for hydrogenation of CO\textsubscript{2} to MeOH

• More active DMC catalyst

• Hydrothermally stable membranes for selective removal of water/ products and retention of gases

• Labscale demo unit MeOH/DMC membrane process

• First economic evaluation
Model

Catalytic membrane reactor
(CMR)

Inert membrane reactor
(IMR)

Theory

Model

- Reaction

\[ 2A + B \rightleftharpoons E + H_2O \]

- Bulk membrane reactor: CSTR

- Mass transport: Maxwell Stefan

\[ \Delta x_i = \sum_{i \neq j} \left( \frac{x_j N_i - x_i N_j}{k_{bl} c} \right) \]

- Only \( H_2O \) permeates through the membrane

- Only mass transfer limitations in boundary layer and membrane

Results

Conclusions

• Process and material parameters have a strong influence on results

• Selection membrane reactor depends on equilibrium
  • Low $K_{eq}$ CMR
  • Intermediate $K_{eq}$ CMR
  • High $K_{eq}$ IMR

• Exact position of maximum depends on
  • $k_{bl}$
  • $k_f$
  • $P_{H_2O}$
  • $\tau$
  • $A/V$
Membranes

Clean Membrane

Coated Membrane

State of the art test setup at the UT

Pictures courtesy of Johnson Matthey, 2015

Picture courtesy of the UT
IPR + PhD’s

• 3 patent applications

• 8 publications

• PhD. Cécile Daniel, CNRS-IRCE Lyon

• PhD. Harro Mengers, University of Twente

• PhD. Michiel Raaijmakers, UT → AkzoNobel

• PhD. Nanyi Wang, Leibnitz University Hannover
Highlight summary

- New catalysts produced and tested for hydrogenation of CO$_2$ to MeOH
- New DMC catalyst developed and tested
- Development of hydrothermally stable membranes for selective removal of water/products and retention of gases at high temperature made good progress
- Two new state of art testing facilities for membranes realized and in operation
- Economic evaluation almost finalized
Many thanks for your attention!