Novel Catalytic Membrane Micro-Reactors for CO₂ Capture via Pre-combustion Decarbonisation

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Funded under EPSRC UK-China Research Projects in CCS

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14 July 2011
Content

- **Research background & overview**
  - Why membrane technology (hollow fibres)
  - How it works
  - What are the challenges & how to deal with them

- **Progress** – Pd/Al\(_2\)O\(_3\) composite hollow fibre membranes
  - Fabrication & characterization of asymmetric Al\(_2\)O\(_3\) hollow fibre substrates
  - Electroless plating of Pd & Ag membranes
  - Effects of substrate resistance on H\(_2\) permeation

- **Conclusions**
SMR + WGS

Molar fraction

Temperature [°C]

SMR + WGS

Membrane process

CH

CO

H₂O

H₂

CO₂

CH₄

Conversion

Temperature [°C]

SMR + WGS

Membrane process

CH

CO

H₂O

H₂

CO₂

CH₄

Conversion
Catalytic membrane reactor: loading and membrane separation area

Under realistic reaction conditions:
- Typical methane space velocity: ~2-3000 h\(^{-1}\)
- Methane conversion: >90%
- \(\text{H}_2\) permeation flux: 0.75 m\(^3\)/m\(^2\)-h
- \(\text{H}_2\) selectivity: 100%

Trans-membrane pressure: 0.1 bar
Catalytic Membrane Micro-Reactor

Asymmetric ceramic hollow fibre substrate

Catalyst in "micro-channels"

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2 \]

Pd-based H\(_2\) separation layer

- "Shifting" reaction towards product side
- Higher conversion/yield at lower temperatures by
  - Removing pure hydrogen from the reaction zone

Membrane reactor

- High surface area/volume ratio
- Less material
- Improved efficiency

Hollow fibre membrane

- Improved mass and heat transfer
- Higher operation efficiency
Challenges

Fabrication
• Single-step fabrication of asymmetric ceramic HF
• Smooth surface for high quality membrane coating
• Uniform coating free of defects and cracks
• Thin gas-tight coating for high \( H_2 \) permeation
• Improved adhesion with the ceramic support
• Mechanical stability

Catalyst
• Optimized catalyst loading
• Uniform dispersion for efficient catalytic reaction
• Long-term activity/stability (deactivation)

Process
• Matching conversion and \( H_2 \) separation rates
• Heat transfer and temperature profile
• Methane & \( H_2 \) slip
• Overall system performance
Fabrication and characterization of asymmetric Al$_2$O$_3$ hollow fibre substrates

Asymmetric alumina hollow fibres prepared by combined phase inversion and sintering process
Fabrication and characterization of asymmetric Al₂O₃ hollow fibre substrates

Asymmetric pore structure:
- Uniform finger-like macro-voids (for catalyst deposition)
- Uniform thin sponge-like layer (for Pd membrane coating)

Mechanical property:
- Increase with elevated temperatures before being over-sintered
- A small percentage of smaller particles improves mechanical strength, without significantly reducing pore size
Electroless plating of Pd & Ag

Effects of
- Activation
- Plating solution composition
- Temperature
- Bubbling rate
- Ultrasonic

... on membrane plating

Control over the electroless plating of Pd and Ag on Al₂O₃ hollow fibre substrate
Electroless plating of Pd & Ag
Hydrogen permeation through Pd/Al$_2$O$_3$ composite HF

Composite Pd/alumina hollow fibre membrane
Effects of substrate pore structures on $\text{H}_2$ permeation

- **Sub-80F**
- **Sub-50F**
- **Sub-30F**

![Substrate images](image)

**Graphs**

- **N$_2$ permeance (µmol m$^{-2}$ s$^{-1}$ Pa$^{-1}$)**
- **Pressure difference across the substrate (kPa)**

- **Sub-80F**
- **Sub-50F**
- **Sub-30F**

- **Fibre80F**
- **Fibre50F**
- **Fibre30F**

- $\epsilon_s = 0.2427$
- $\epsilon_s = 0.2378$
- $\epsilon_s = 0.3179$

- At various temperatures (450°C, 400°C, 350°C, 300°C)

$\text{H}_2$ permeation flux (mol m$^{-2}$ s$^{-1}$)

$\text{Pressure difference across the membrane, kPa}$
Effects of substrate pore structures on $\text{H}_2$ permeation

A 10 micron Pd membrane coated onto a substrate with the effective porosity of 1000 m$^{-1}$, the effect of the substrate on hydrogen permeation is lower than 5%
Effects of substrate pore structures on $\text{H}_2$ permeation

- $\text{H}_2$ permeation increases with bigger mean pore size
- Optimum standard deviation for the substrate is around 1.2
- Uniform mean pore size is desired for high quality Pd coating

At elevated temperatures, the role of the permeation in Pd membrane is less dominated

Permeation in Pd membrane start to play an important role

Controlled by permeation in the substrate
Conclusions

- Alumina hollow fibre substrates with certain asymmetric structures have been fabricated (Task 1).
- The inner finger-like voids (micro-channels) can be used for catalyst deposition.
- The outer sponge-like layer is smooth enough for a direct coating of \( \text{H}_2 \) separation layer.
- Electroless plating of Pd and Ag on such substrates has been investigated to control membrane thickness and composition.
- Effects of substrate resistance to \( \text{H}_2 \) permeation has been studied, which can be used for further optimization of substrate structures.
Many Thanks !
Example: Steam Methane Reforming & membrane process

The diagram shows the molar fractions of CH₄ and H₂O, H₂, and CO as a function of temperature. The membrane process region is highlighted, showing the conversion of CH₄ to H₂ and CO as the temperature increases.
Activation of asymmetric Al$_2$O$_3$ hollow fibre surface

Effects of activation loops on Pd seeding
Effects of surface activation on Pd plating

![Graph showing Pd deposition over time and number of activation loops.](Image)

- **Pd deposition (mg/cm²)**
- **Time (min)**
- **Number of activation loops**

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**Figure 1:**
- **Pd layer**
- **Pd deposit intrusion**

**Figure 2:**
- **Graph comparing Pd deposit over different activation loops.**

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**Legend:**
- L_2
- L_4
- L_6
- L_8
- L_10