Catalytic Membrane Reactors for Small Molecule Processing

Lecture IV

The ‘Ultimate’ Green Reactor

“Catalytic Membrane Reactors Allow for Innovative and Highly Effective Solutions for Major Challenges in Green Chemistry“

Underlying Concepts

- Dalmon*: Function of the membrane
  - Membrane I: transfer control only
    - Catalyst AND membrane compatible:
      - Extract and generate at comparable rates
  - Membrane II: transfer control & catalysis
    - Porous => enough residence time?
    - Dense (e.g. Pd) => reactive enough?

CMR Classification: Extractor

- CMR Classification: Distributor
  - Controlled reactant feed
    - High total reactant concentration
    - Low local concentration
    - Selectivity increase:
      - Oxidations => can operate in explosive zone

**CMR Classification: Contactor**

- Facilitate contact between reactants and catalyst:
  - Membrane also acts as catalyst or catalyst support
  - Interfacial mode
    - Reactants meet in cat. zone
    - Gas-liquid reactions
      - Gaseous mass transfer not rate limiting
    - Organic/aqueous systems
      - Excellent mass transfer

**Hypothesis**

- Catalytic Membrane Reactors Can Provide Highly Effective Solutions For:
  - Alkane Hydro-Isomerisation
  - Hydrogen Storage
  - Direct Oxidation of Benzene to Phenol
  - Gas to Liquids Technology

**Component Properties in a C₆-feed**

<table>
<thead>
<tr>
<th>Component</th>
<th>Kinetic diameter (Å)</th>
<th>Research octane number (RON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane (n-C₆)</td>
<td>4.8</td>
<td>24.8</td>
</tr>
<tr>
<td>2-methylpentane (2-MP)</td>
<td>5.0</td>
<td>73.4</td>
</tr>
<tr>
<td>3-methylpentane (3-MP)</td>
<td>5.0</td>
<td>74.5</td>
</tr>
<tr>
<td>2,2-dimethylbutane (2,2-DMB)</td>
<td>6.2</td>
<td>91.8</td>
</tr>
<tr>
<td>2,3-dimethylbutane (2,3-DMB)</td>
<td>5.6</td>
<td>105.0</td>
</tr>
</tbody>
</table>

1.3 Å difference!!

**Total Isomerisation Process**

- Boasting Gasoline RON
- Replacement of or reduction in:
  - Lead Alkyl Additives
  - Oxygen containing components, e.g. (MTBE, ETBE)
  - Olefins and Aromatics

**Pressure-Swing Adsorption**

Large gas volumes pumped continuously
Current Process, TIP

Process Intensification

Integration of separation and reaction via a membrane reactor

Membrane Configuration

Iso-hexane (RON 80+)

Linear/branched feed:
- Remove linears selectively
  => Concentrate feed
- Then isomerise
  => Prevents cracking

n- and iso-hexane (RON 40)

Membrane/Reactor Materials

- Silicalite-1:
  - Pore diameter: 0.56*0.53 nm²
    - Diffusion: competitive adsorption
  - Hydrophobic
  - High-temperature stability

- Catalyst:
  - AT-2G Pt (Pt-oxide/chlorinated alumina)
  - Allows low temperature operation

Supported (TRUMEM™) Silicalite-1 Membranes

Membrane on Support
Permeation Fluxes and Selectivity vs. Temp.

- **2-MP**
- **n-C6**
- He sweep flow rate 50 ml/min
- Δp=0, p=atm
- Feed 80/15/5 mixture n-C6/2-MP/2,2-DMB

### Permeation Fluxes

- **Temperature [K]**
- **Flux [mmol/m²s]**
-\[\text{Flux: 2-MP}\]
-\[\text{Flux: n-C6}\]

### Selectivity

\[\text{Selectivity: } n-C6/(2-MP+2,2-DMB)\]

### Distribution [molar]

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>WHSV [gHC/gcat h]</th>
<th>H2/HC [molar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.13</td>
<td>14.96</td>
</tr>
<tr>
<td>100</td>
<td>0.18</td>
<td>11.12</td>
</tr>
<tr>
<td>120</td>
<td>0.21</td>
<td>9.76</td>
</tr>
<tr>
<td>140</td>
<td>0.21</td>
<td>9.96</td>
</tr>
</tbody>
</table>

### Isomerised Hexane Product Distribution

- **n-C6**
- **3-MP**
- **2-MP**
- **2,3-DMB**
- **2,2-DMB**

### Optimised System

- **Distribution [%]**
- **n-C6**
- **3-MP**
- **2-MP**
- **2,3-DMB**
- **2,2-DMB**

### RON Values

- **Feed** 40
- **Permeate** 31
- **Reaction product** 76
- **Reaction product + Retentate** 80-93

### Reactor Combination

- **n/iso-hexane**

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Th. Maschmeyer, School of Chemistry, Lab. of Advanced Catalysis for Sustainability
**Reactors Combination: Product Distribution**

![Graph showing product distribution](image)

**Technical Feasibility?**

**Convention (Van de Graaf):**
- Space Time Yield (STY), reactor:
  - 1 – 10 mol m\(^{-3}\) s\(^{-1}\)
- Area Time Yield (ATY), membrane:
  - 2 – 50 mmol m\(^{-2}\) s\(^{-1}\)
- STY/ATY = 20 – 5000 m\(^{-1}\)

=> Optimised membrane: 877 m\(^{-1}\)

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**De-hydrogenation of Cyclohexane**

- Aim to recover H\(_2\) from a convenient carrier:
  - Cyclohexane
  - 7.1 wt% recoverable H\(_2\)
  - < 3 wt% in metal hydrides

- Dehydrogenation is equilibrium limited

**De-hydrogenation of Cyclohexane**

- Solution: Palladium membrane reactor

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Partial Oxidation: Phenol

- 8.3 Megatons in 2003:
  - 8,300,000,000 kg/y => 1.3 kg/y/per human being

- Cumene-based Process:

Traditional Process

- Benzene + propylene \(\rightarrow\) cumene
  - supported phosphoric acid catalyst, 200-250 deg. C, conv. 20%, almost 100% selectivity

- Cumene oxidation to cumene hydroperoxide
  - 25% yield
Traditional Process

- Decomposition of cumene hydroperoxide to phenol and acetone (sulfuric acid catalyst):
  - Phenol yield 93%

\[
\begin{align*}
  \text{Cumene Hydroperoxide} & \rightarrow \text{Phenol} + \text{Acetone} \\
  \text{H}_2\text{SO}_4 & \text{H}_2\text{SO}_4
\end{align*}
\]

- Combined:
  - 20% x 25% x 93% = 5% overall yield
    (based on initial benzene converted)

Direct Oxidation

- Usual yields of direct oxidation (i.e. hydroxylations of benzene with oxygen and hydrogen):
  - Mixing aromatic, oxygen, hydrogen, liquid phase
  - Low yields 0.0014 to 0.69% (based on aromatic used)

More Recent Processes: Panov

- Direct oxidation benzene to phenol using nitrous oxide

Where To Get The N\textsubscript{2}O?

- Need oxidation of ammonia produced from N\textsubscript{2} and H\textsubscript{2}
  => very expensive
A More General Solution?

Catalytic palladium membrane for reductive oxidation of benzene to phenol

\[
\text{C}_6\text{H}_6 + \text{O}_2 + \text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{O}
\]


Using a Palladium Membrane for Distributed Feed

A More General Solution?

Overall Performance

Conditions:
- Temp.: 200 °C.
- Flow rates:
  - shell (outside), 25 ml/min (H₂/He 5.6/20, volume ratio);
  - tube (inside), 25 ml/min (benzene/O₂/He 0.4/3.8/25, volume ratio).

Solid circles, squares, and open circles denote benzene conversions, phenol yields, and phenol selectivities, respectively.

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Solid Membranes: Gas-to-Liquids

- Partial Oxidation of Methane followed by Fischer –Tropsch

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2
\]
\[
n \text{CO} + 2n \text{H}_2 \rightarrow (\text{CH}_2)_n + n \text{H}_2\text{O}
\]

Solid Membranes: Gas-to-Liquids

- Cryogenic air separation major cost

Alternative Air Separation

- Oxygen perm-selective perovskite membranes
- High temp. operation (>700 °C) similar to POM processes
- Oxygen consumption increases driving force
- Combination => greater efficiency/reduced cost

Model of Working Membrane


Alternative Air Separation

- Avoids cryogenic separation
- Compact and modular => can be used in remote areas
- No external energy supply needed due to exothermicity of CPO
- Safer as pre-mixing of oxygen and natural gas is avoided: less chance of local hot spots (danger in co-feed reactors)
- Infinite selectivity towards oxygen, if no cracks

Materials

- Acceptor-doped perovskite oxides:
  - \( \text{La}_{1-x}A_x\text{Co}_{1-y}B_y\text{O}_{3-\delta} \)
  - \( (A = \text{Sr, Ba}; B = \text{Fe, Cr, Mn, Ga}) \)
- Partial substitution of metal cations with lower valency leads to the formation of oxygen vacancies
- Disordering of the oxygen vacancies at higher temperatures leads to ionic conductivity
**Oxygen Conduction**

Y. Mishin, Defect and Diffusion Forum, 143 - 147, 1357 (1997).

M. Calleja, Dept. Earth Sciences, Univ. Cambridge.

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**How Many Defects?**

- Increasing oxygen vacancies/defects can lead to structural re-arrangement with subsequent loss of conductivity.

- Usually a 5 – 8% oxygen vacancy rate gives the maximum performance and stability.

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**La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ Membrane**

*After: 3 days in 100% CH$_4$ at 830 °C.*

- At about 10 µm perovskite
- Basic oxides, some elemental Co and Fe
- Porous crust of SrCO$_3$

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**Stability Measurements**

<table>
<thead>
<tr>
<th>Membrane materials</th>
<th>$O_2$ flux (ml cm$^{-2}$ min$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFeCo$<em>{0.8}$O$</em>{3}$</td>
<td>2 – 4</td>
<td>850</td>
<td>1000</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-\delta}$</td>
<td>11.5</td>
<td>875</td>
<td>500</td>
</tr>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$Co$<em>{0.8}$Fe$</em>{0.2}$Cr$<em>{0.1}$O$</em>{3-\delta}$</td>
<td>14.5</td>
<td>900</td>
<td>340</td>
</tr>
<tr>
<td>BaCo$<em>{0.4}$Fe$</em>{0.4}$Zr$<em>{0.2}$O$</em>{3-\delta}$</td>
<td>5.6</td>
<td>850</td>
<td>2200</td>
</tr>
<tr>
<td>La$<em>{0.3}$Sr$</em>{1.7}$Ga$<em>{0.6}$Fe$</em>{1.4}$O$_{5+d}$</td>
<td>6 – 7</td>
<td>900</td>
<td>1000</td>
</tr>
</tbody>
</table>

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**Membrane Stability**

- CH$_4$ conversion
- $O_2$ flux
- CO selectivity
- $H_2CO$