Advanced CO$_2$/H$_2$ Separation Materials
Incorporating Active Functional Agents

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Outline

1. Membrane Challenge for Cost Reduction in CCS
2. CO₂ Molecular Gate Function for CO₂ Separation Membrane
3. Dendrimers for Promising Molecular Gate Materials
4. Dendrimer Hybrid Membranes
5. Next Generation of CO₂ Molecular Gate in GCEP Research
6. Concluding Remarks
CO₂ Capture Methods for CCS

1. CO₂ Sources

- Fossil Fuel
- Bio-Mass

Power plant (Combustion)

Blast-furnace

Gasification

2. CO₂ Capture (Chemical Research Group in RITE)

Absorption

- CO₂ < 2%
- CO₂ > 99%

Absorber

Regenerator

Absorbent

Novel process

Waste heat utilization

Membrane

- CO₂ > 95%

CO₂ < 2%

Polymer

Zeolite

Carbon

Nono composite material

Adsorption

- CO₂ < 2%

CO₂ > 97%

Zeolite,

Mesoporous silica

Plant analysis for the decreasing energy and cost

3. Storage (CO₂ Storage Group in RITE)

- Geological
- Utilization
- Ocean
Present Cost of CCS (coal fired power plant)

- Recovery amount: 1 Mt-CO$_2$/yr, distance: 20 km, pressure: 7 MPa
- Injection method: ERD, injection amount: 0.1 Mt-CO$_2$/yr/well

Power loss for extraction steam from low pressure turbine: 0.05 kWh/MJ

- New plant
  - Coal fired plant to aquifer

- Existing plant
  - Existing coal fired plant to aquifer
  - Upgrading desulfurization facilities & Auxiliary coal fired boiler

Avoided cost JPY/t-CO$_2$

NET storage = 670/1000

Capture cost 4,200 JPY/t-CO$_2$

CCS total cost 7,300 JPY/t-CO$_2$
Membrane Performance and CO₂ Capture Cost

**IGCC with WGS (CO₂ conc. 40%)**:
- CO₂ Permeance: $7.5 \times 10^{-10}$ m³/(m² s Pa)
- CO₂/H₂ Selectivity: 30
- Cost: 1,500 JPY/t-CO₂
- Cost: 1,000 JPY/t-CO₂

Ref: MDEA: 2,500-3,000 JPY/t-CO₂

**Natural Gas (CO₂ conc. 50%)**:
- CO₂ Permeance: $7.5 \times 10^{-10}$ m³/(m² s Pa)
- CO₂/CH₄ Selectivity: 40
- Cost: <1,000 JPY/t-CO₂
- 1/5 of MDEA method

Basic Membrane Performance:
- Permeance & Selectivity
What ideal membrane?

A wet towel balloon may hint an ideal gas separation membrane.
Basic Concept of CO₂ Molecular Gate for CO₂/H₂ Separation

CO₂ : 0.33 nm
H₂ : 0.29 nm

Feed
High Pressure Difference
Low Permeate

Membrane Material

Excellent CO₂ selectivity

Polyamidoamine (PAMAM) dendrimer (0-OH-PAMAM dendrimer)
**H₂ Blockage by CO₂ in Dendrimer**

- **H₂ Permeability**
  - Pure gas > Mixed-gas
  - (CO₂: 5 %)

- **CO₂ blocks H₂ permeation**

- **Graph**
  - RH [%] in Feed Gas vs. H₂ Permeability [Nm³ m⁻² s⁻¹ Pa⁻¹]
  - Pure H₂
  - Mixed-gas (H₂/CO₂=95%/5%)

- **4-OH PAMAM dendrimer**
Possible Model of H₂ Permeation Blockage

Carbamate Formation
Pseudo-cross-linkage
H₂ permeation blockage

Concentration of Carbamate & Bi-carbonate in 4-OH Dendrimer at 80 RH%

<table>
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<tr>
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<th>(mol/mol-dendrimer)</th>
<th>2.6</th>
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<tr>
<td>Carbamate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi-carbonate</td>
<td></td>
<td>0.36</td>
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</table>

CO₂
H₂
Dendrimer Hybrid Membrane for CO$_2$ Capture from Pressurized Gas Stream

```
H$_2$N-\(\text{NH}_2\)
\text{H}_2\text{N-\(\text{O}\)O-\(\text{NH}\)NH}_2\)
\text{H}_2\text{N-\(\text{O}\)O-\(\text{NH}\)NH}_2\)
O-OH-PAMAM dendrimer
+ PEGDMA
+ TMPTMA
```

UV Curing
CO₂/H₂ Separation Properties of Dendrimer Hybrid Membrane at Elevated Pressure

PAMAM/PEGDMA/TMPTMA = 50/37.5/12.5, Feed : 100 mL/min, Sweep: 20 ml/min, T = 313 K, R.H. = 80%
CO$_2$/H$_2$ Separation Properties of Various Dendrimer Hybrid Membranes

CO$_2$ Permeance $/ m^3$(STP)/(m$^2$ s Pa)

CO$_2$/H$_2$ Selectivity (-)

Film Thickness: 500 µm

Target value for 1,500 JPY/t-CO$_2$

CO$_2$ permeance: $7.5 \times 10^{-10} m^3/(m^2 s Pa)$

CO$_2$/H$_2$ Selectivity: 30

CO$_2$ partial press.: 6 bar

Temperature: 313 K

Now fabricating dendrimer membrane modules with membrane module makers under METI funding
CO₂/CH₄ Separation Properties of Dendrimer Hybrid Membrane

Gas permeance / Nm³/(m² s Pa)

CO₂

CH₄

CO₂ Partial Pressure / kPa

QCO₂ QCH₄

CO₂/CH₄ Selectivity: 58
GCEP Challenge in Molecular Gate Membrane

Present Situation:
High CO$_2$/H$_2$ selectivity
  at large CO$_2$ partial pressure
  at high water vapor content, e.g. 80 RH% or more
  - weak point for dry condition!

GCEP Challenge:
- Higher Permeance and Selectivity
- Well working at lower water vapor
CO₂ Transportation Model of Current Dendrimer Hybrid Membrane

Gas Feed

Hopping CO₂

2 R-NH₂
CO₂
H₂O R-NH₂
HCO₃⁻

Hopping CO₂

CO₂
HCO₃⁻

H₂O

Sorption

Diffusion

Desorption

Permeate

CO₂
H₂O
Sc-CO₂ Structure Directing Method for Next Generation Membrane

Basic Concept:

Pre-formed Solid Membrane

Inject Sc-CO₂

Remove Sc-CO₂

Amino moiety

CO₂

carbamate formation

CO₂ Hopping Channel
Diagram of Set-up for Sc-CO$_2$ Structure Directing Method

- Syringe pump
- Pre-formed membrane
- Sapphire window
- Camera
- High-pressure view cell
- Back-pressure regulator
- Membrane under Sc-CO$_2$
  - Pressure: 10 MPa
  - Temperature: 20-60°C
**Effect of Sc-CO$_2$ Treatment (1)**

**CO$_2$/H$_2$ separation performance**

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<th>Pre-:</th>
<th>Post-:</th>
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<tr>
<td>QCO$_2$ Permeance</td>
<td>$4.4 \times 10^{-12}$</td>
<td>$8.5 \times 10^{-12}$</td>
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<tr>
<td>CO$_2$/H$_2$ Selectivity</td>
<td>140</td>
<td>210</td>
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</table>

SC-CO$_2$ treatment condition: 10 MPa, 4 hr, 333 K
Effect of Sc-CO₂ Treatment (2)

\[ Q (m^3 \text{(STP)}/(m^2 \text{s Pa})) \]

**Poly ethylene imine (PEI)**

**sc-CO₂ treatment time (h)**

sc-CO₂ treatment: Temp. 50 °C, Press. 10 MPa

Gas Perm. Test(DPCO₂ = 100 kPa, 90%RH, 40°C)
Membrane application for CO$_2$ capture from a pressurized gas stream, e.g. IGCC, Natural gas, is promising way of reducing CO$_2$ capture cost and energy.
- Molecular Gate Membrane (MGM) is proposed for high CO$_2$ selectivity over H$_2$.
- Dendrimer membrane has good CO$_2$ separation performance over a wide range of CO$_2$ partial pressure and at highly water vapor condition.
- Next generation MGMs that work well in a wide range of humidity in a feed gas and have excellent selectivity and permeance are now under development in GCEP project.
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2. Venue        : Kyoto International Conference Center, Japan
3. Organizers : RITE & IEAGHG
   Themes are: Capture; Geo Storage; Other Storage; Industrial sources; Transport; Negative CO2; CO2 utilisation options;
   Demonstration; Tech Assess & Integration; Commercial Issues; Public Perception; Policies; Legal & Regulatory;
   Education, training, and capacity building
5. On-line Conference Registration
   Early Bird open: April 23rd, 2012      / Late on-line registration: July 24th – November 17th, 2012
6. Programme Overview
   ( Subject to change)
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   | Night        | Night       | Night        | Night        |
   | Night        | Night       | Night        | Night        |
7. Website http://www.ghgt.info/  !!! Sponsors are now being sought !!!
Thank you for your attention!

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