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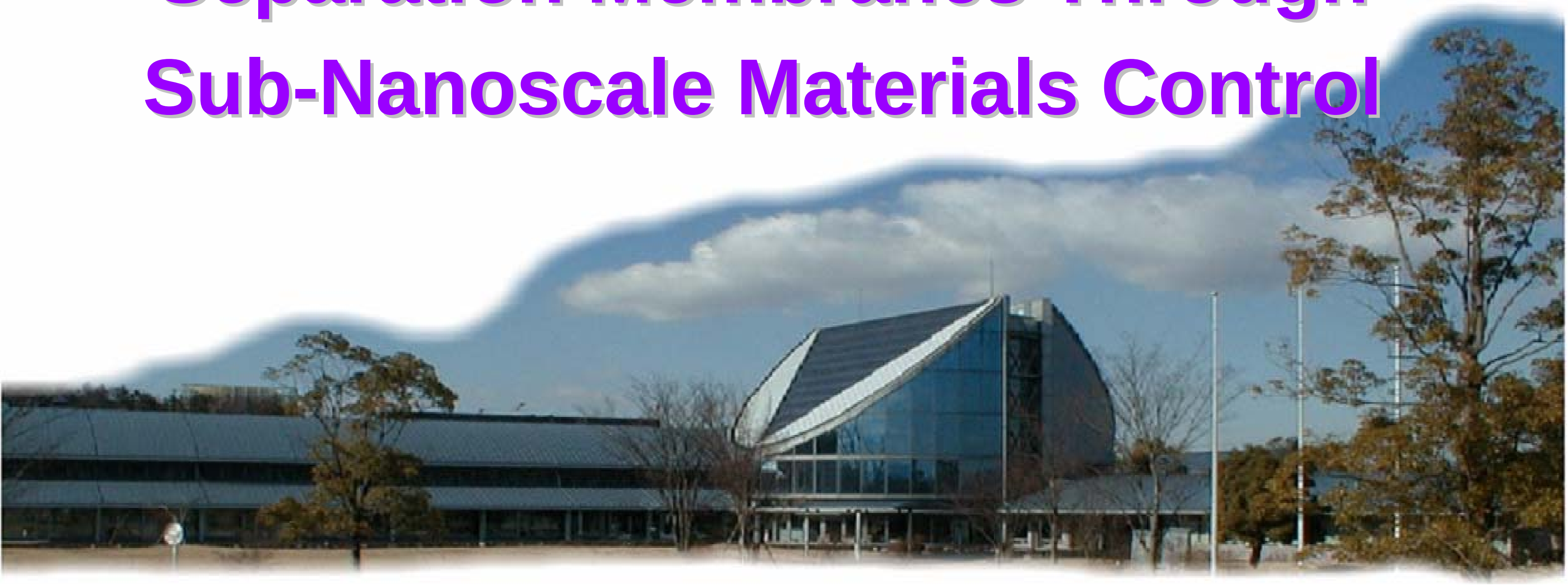
Development of Innovative Gas Separation Membranes Through Sub-Nanoscale Materials Control



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2. Development of carbon membrane
   a. Defect of membrane and performance
   b. Pore size orientation
3. Development of Functionalized mesoporous oxide membrane
4. Development of zeolite membrane
   a. Crystal face orientation method
   b. Rubbing method

Technological Options for 550 ppmv Stabilization

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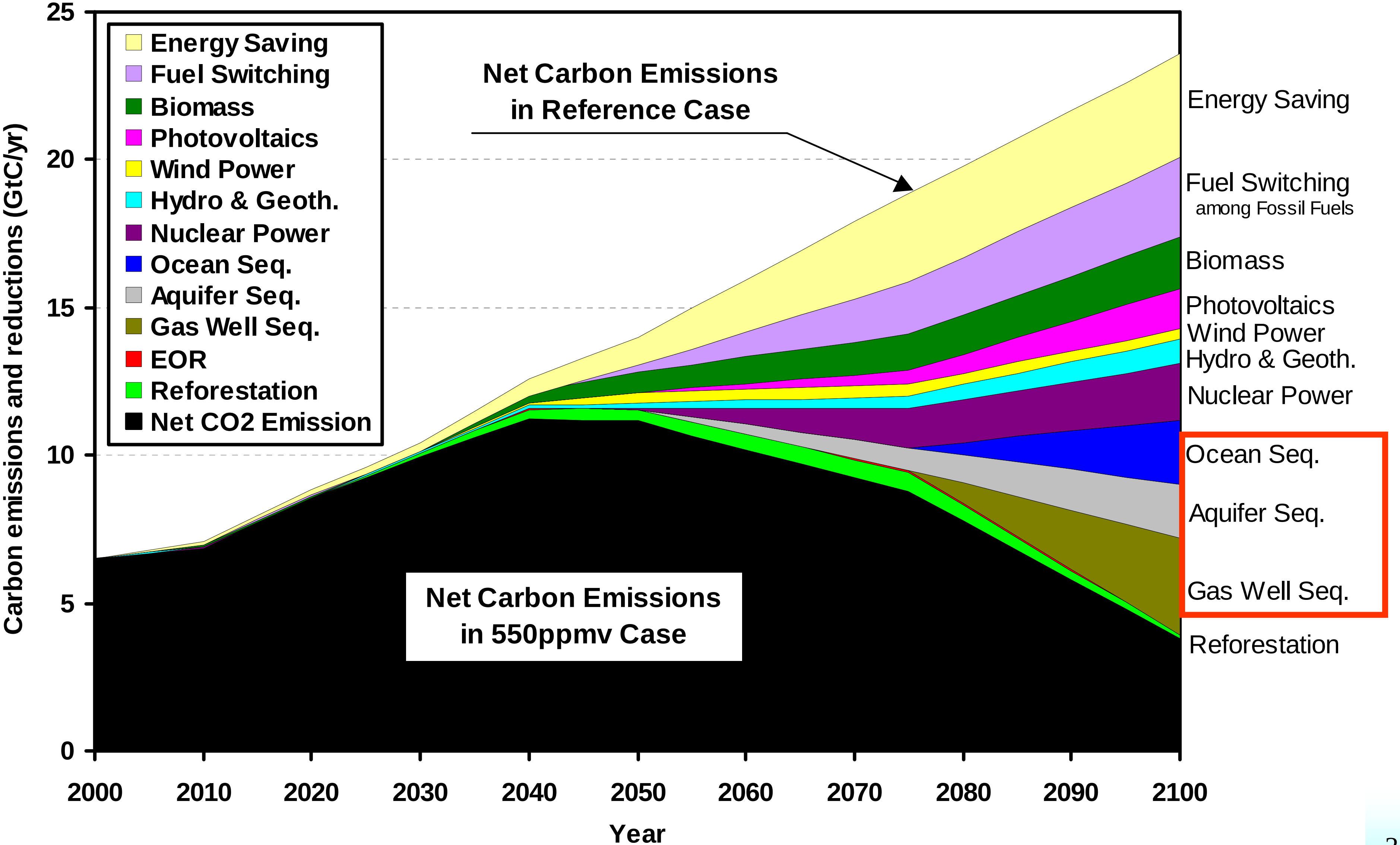

CO_2 chemical absorption efficiency (Coal fired power plant)

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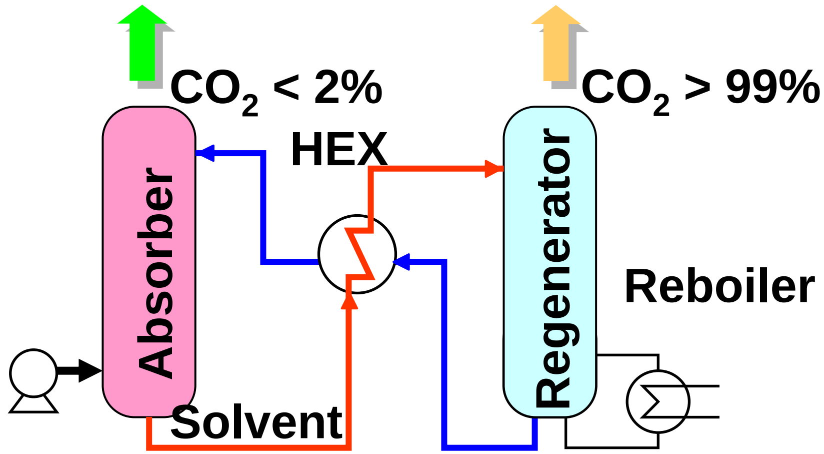
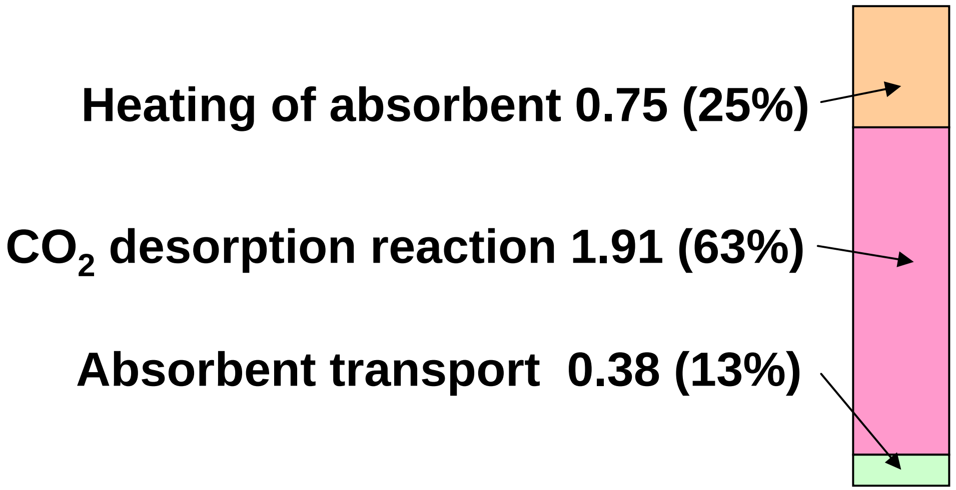
1. Separation Energy of Chemical absorption = 3.0 GJ/t-CO_2



Chemical absorption



2. Efficiencies

Coal = 13.3 GJ/t- CO_2

$$\left(\frac{3.0}{13.3}\right) \Rightarrow 26\%$$

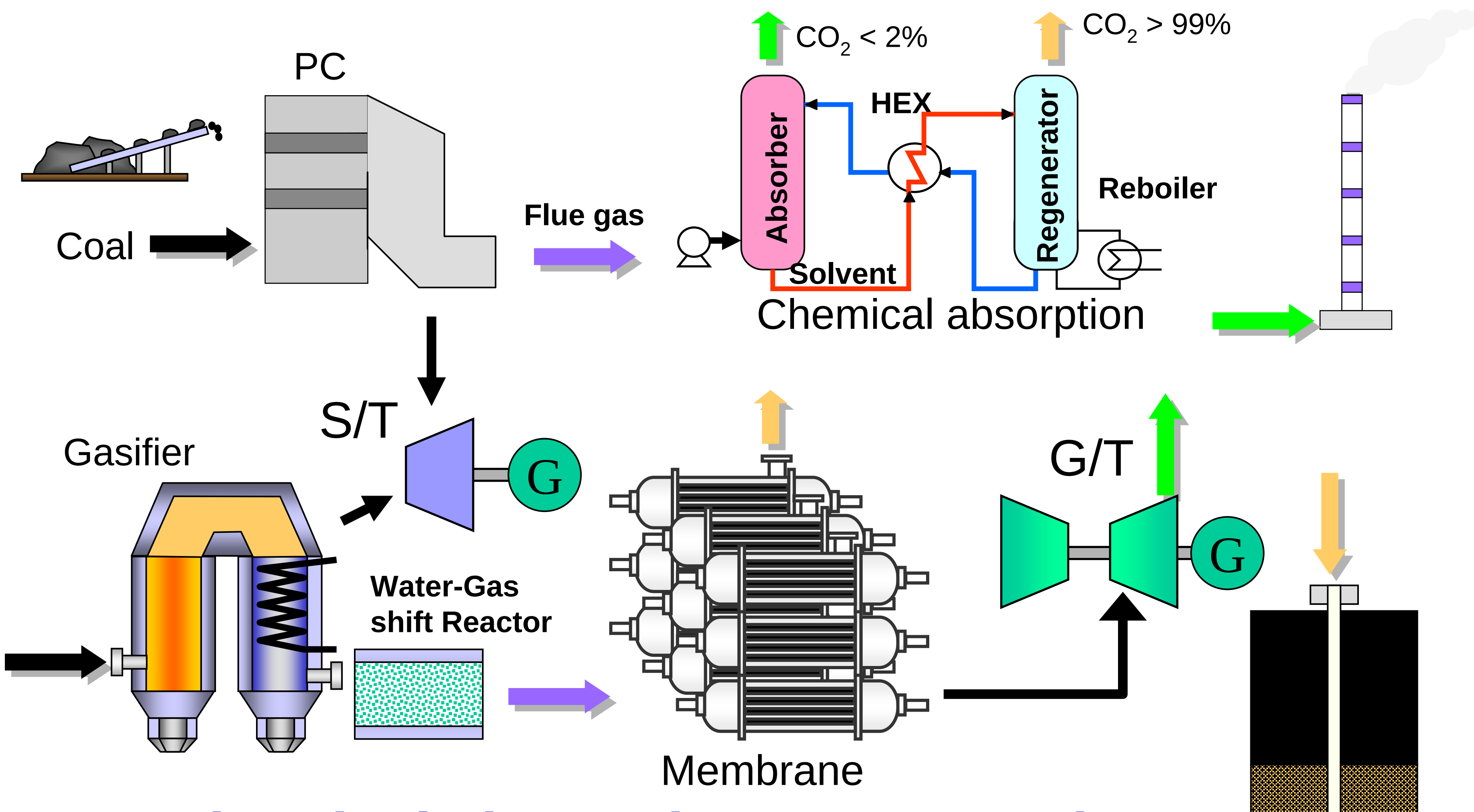
- **Theoretical separation energy (10%, 50 degree-C) = 0.18 GJ/t- CO_2**

- **Separation efficiency**

$$\left(\frac{0.18}{3.0}\right) \Rightarrow 6\%$$

Future CO_2 Separation and Capture

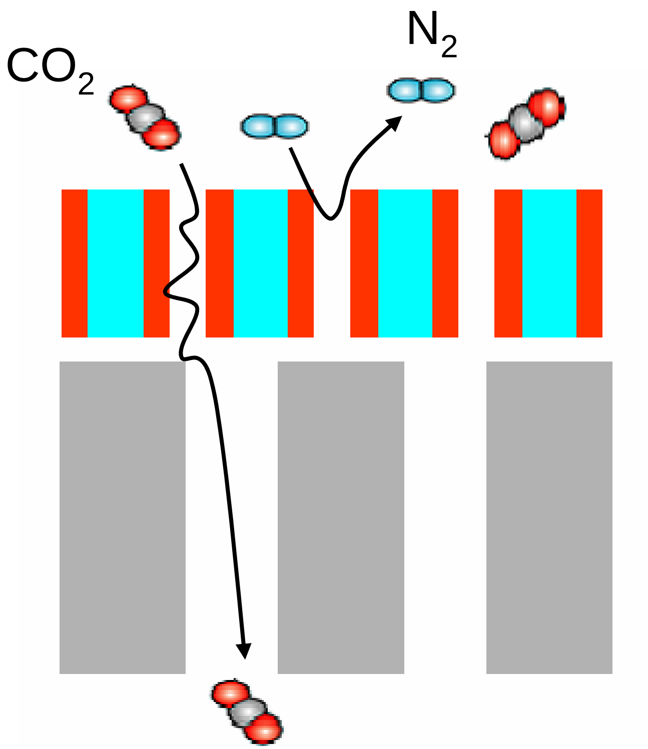
PC → Gasifier



Chemical absorption → Membrane

CO_2 Separation Membranes Through Sub-Nanoscale Materials Control

Membrane concept

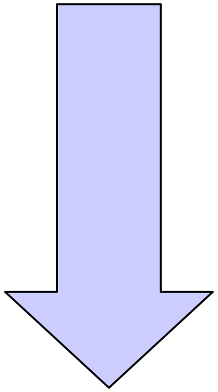


Selective Layer

Porous Substrate

Sub-Nanoscale Materials Control

- CO_2 affinity
- Pore diameter
- No structural defect



High CO_2 selectivity and permeability

2. Development of carbon membrane
   a. Defect of membrane and performance
   b. Pore size orientation by carbonization

Definition of Permeance & Selectivity

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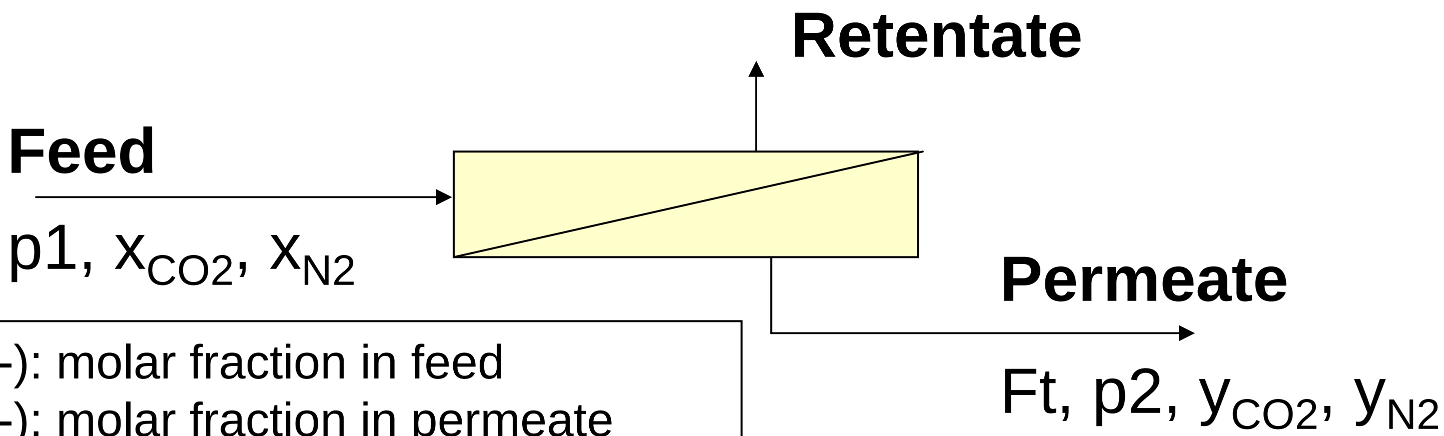


x (-): molar fraction in feed
y (-): molar fraction in permeate
p1 (Pa): total pressure in feed
p2 (Pa): total pressure in permeate
Ft ($m^3\ s^{-1}$): total gas flux of permeate
A (m^2): membrane area

CO_2 permeance ($m^3\ m^{-2}\ s^{-1}\ Pa^{-1}$) :

$$Q_{CO2} = Ft \cdot y_{CO2} / (p1 \cdot x_{CO2} - p2 \cdot y_{CO2}) / A$$

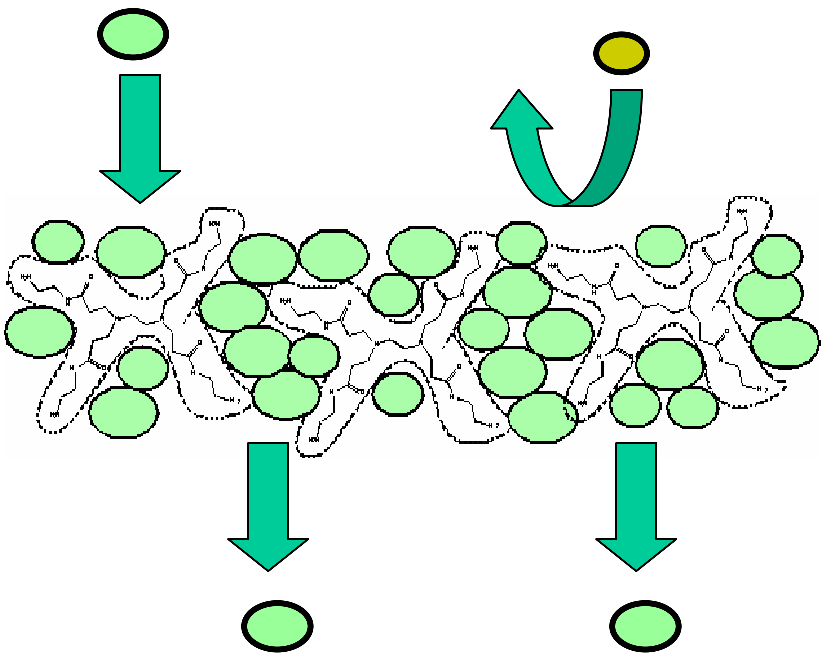
N_2 permeance : $$Q_{N2} = Ft \cdot y_{N2} / (p1 \cdot x_{N2} - p2 \cdot y_{N2}) / A$$

CO_2/N_2 selectivity : $$\alpha_{CO2/N2} = Q_{CO2}/Q_{N2}$$

Concept for High CO2 Selectivity

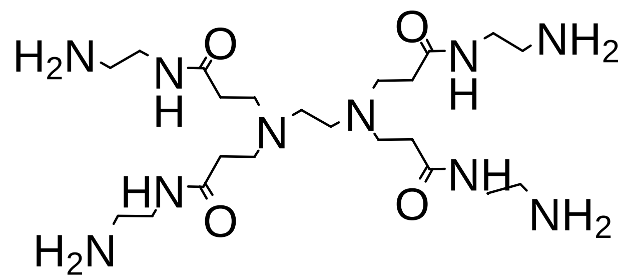
CO_2
0.32nm

N_2, H_2etc.
0.26, 0.22 nm

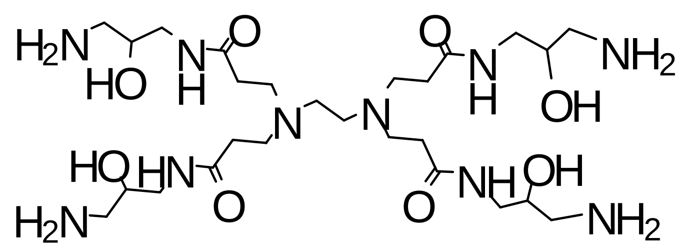


CO_2 Molecular Gate

Candidate materials
Polyamidoamine(PAMAM) dendrimers



CO_2/N_2 separation:
A. S. Kovvali, H. Chen, and K. K. Sirkar
J. Am. Chem. Soc. 2000, 122, 7594-7595



CO_2/H_2 separation:
S. Kazama et al., 8th Intl. Conf. on Greenhouse Gas Control Technologies(GHGT-8), Trondheim, Norway (2006)

Dendrimer Composite Membrane Modules

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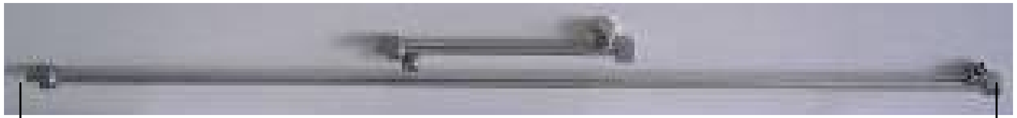
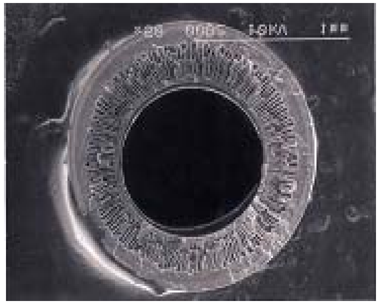
#1, 2



200, 800 mm, 3/8 inch

#3

1100 mm in length, 1 inch in diameter



1 mm

Cross section of membrane

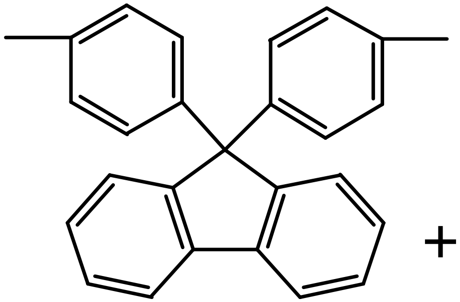
Module #	Membrane Area cm^2	CO_2/N_2 Selectivity $\alpha_{CO2/N2}$
1	17	290
2	180	150
3	4000	150

Dendrimer: conventional PAMAM dendrimer

Temperature: 25 °C

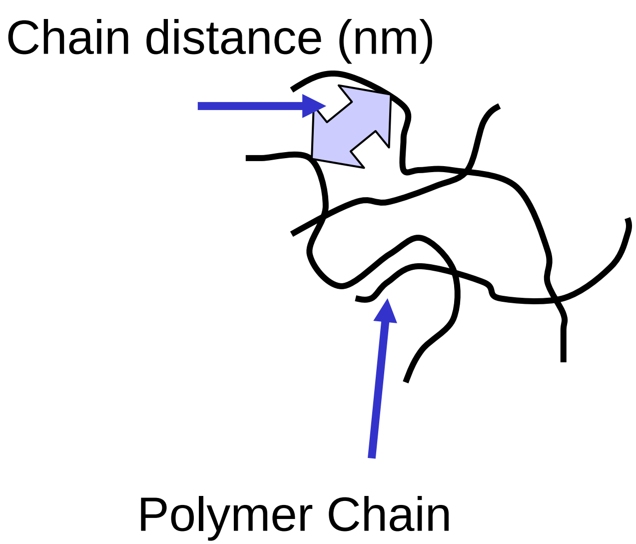
Design of Precursor (1)

Selection of functional group, polymer unit and polymer



Cardo moiety: Low volatility & Large chain distance

\+ Unit X1 + Unit X2 + UnitX3 + UnitY1+UnitY2



High volatility pore-size controller

CO_2 affinity enhancer

Design of Precursor (2)

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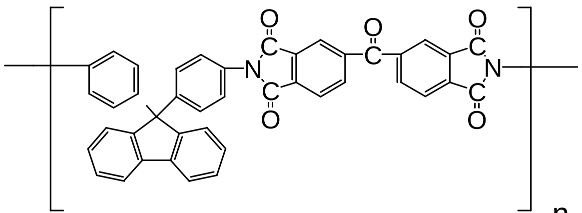
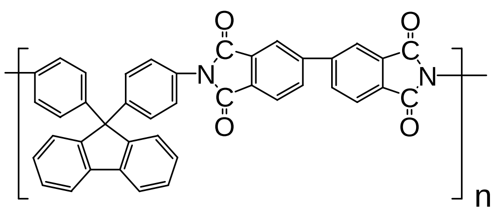
Chain distance control in sub-nano size

Unit X1

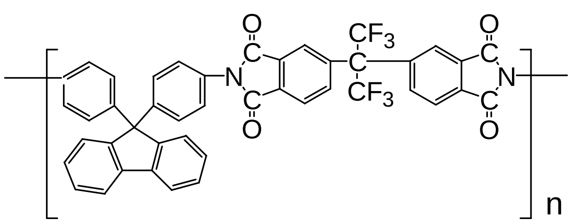
A



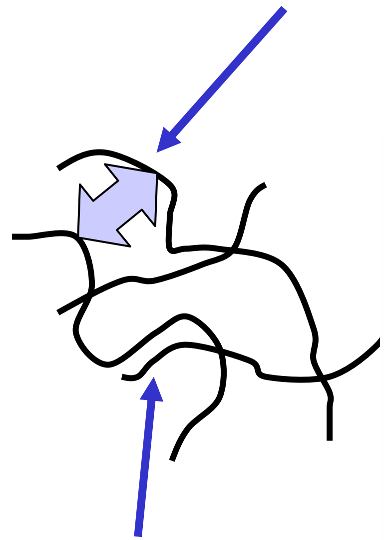
B



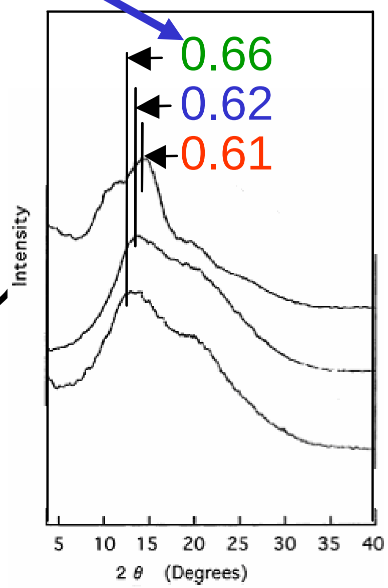
C



Chain distance (nm)



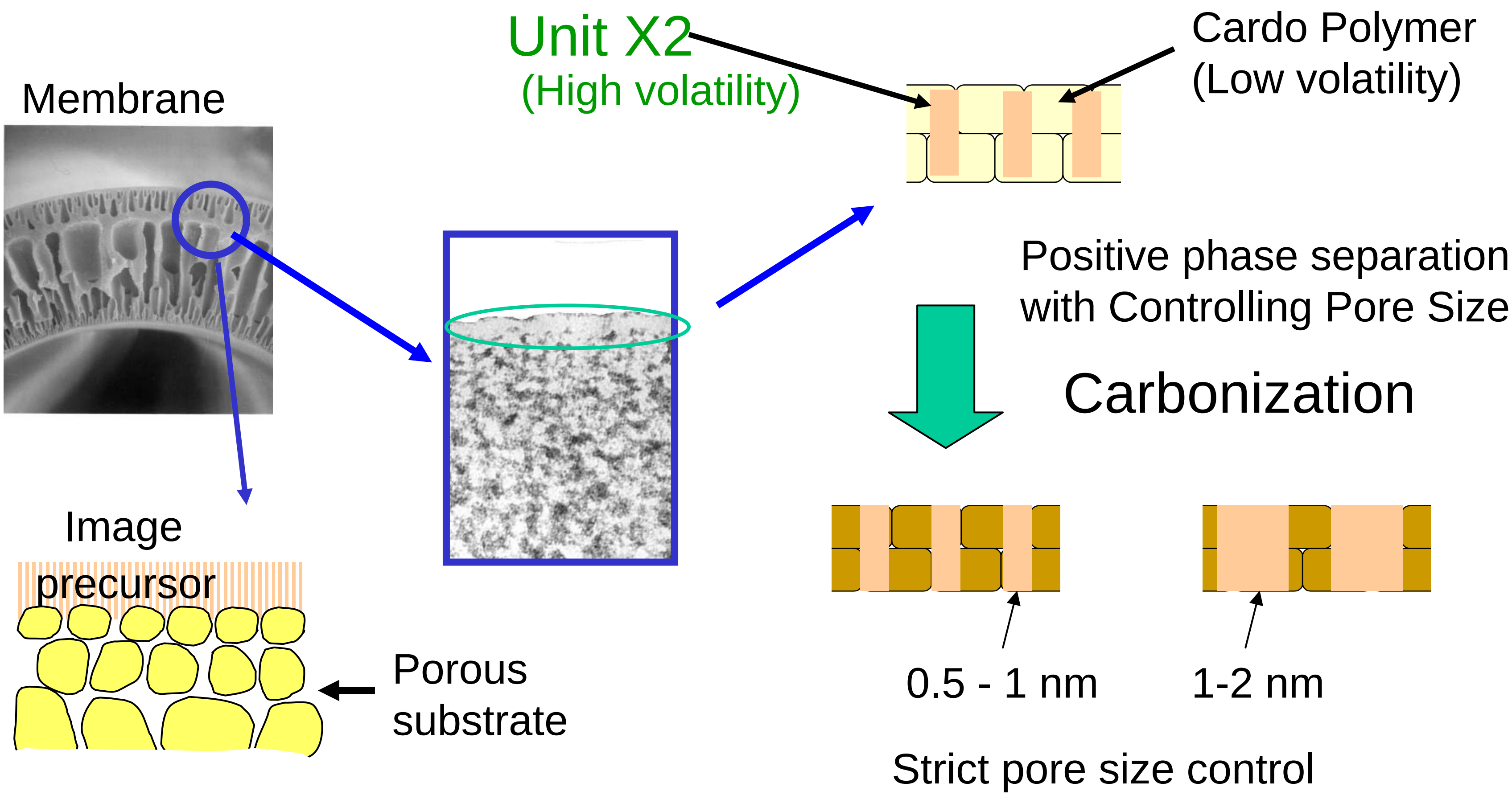
Polymer Chain



X-ray diffraction

Carbonization

Manufacturing larger pore size of carbon membrane through carbonization process (temperature, pressure, atmosphere)



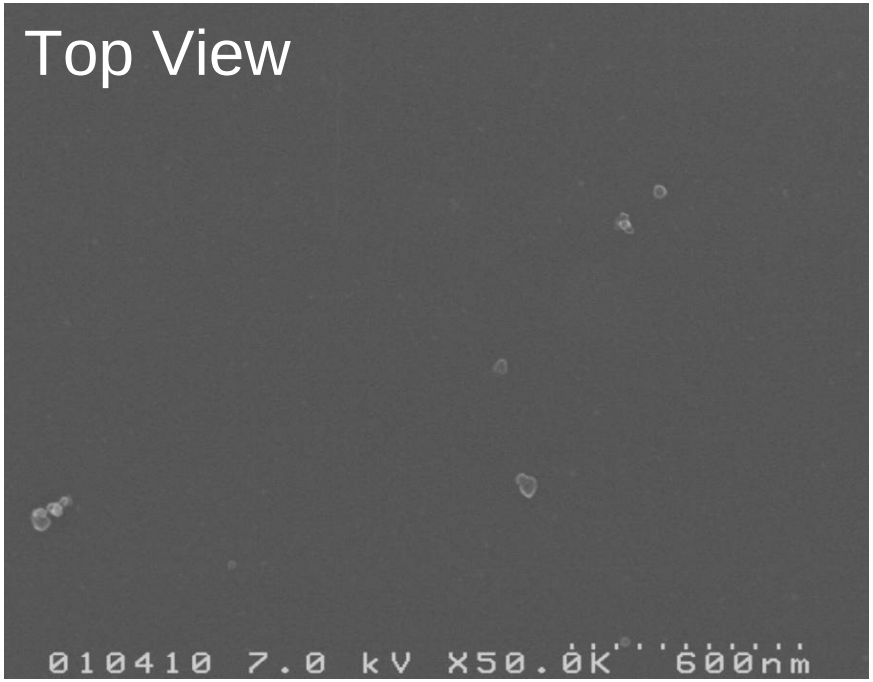
Pre- & post Carbonization Membrane

Precursor-coated membrane

Carbon membrane

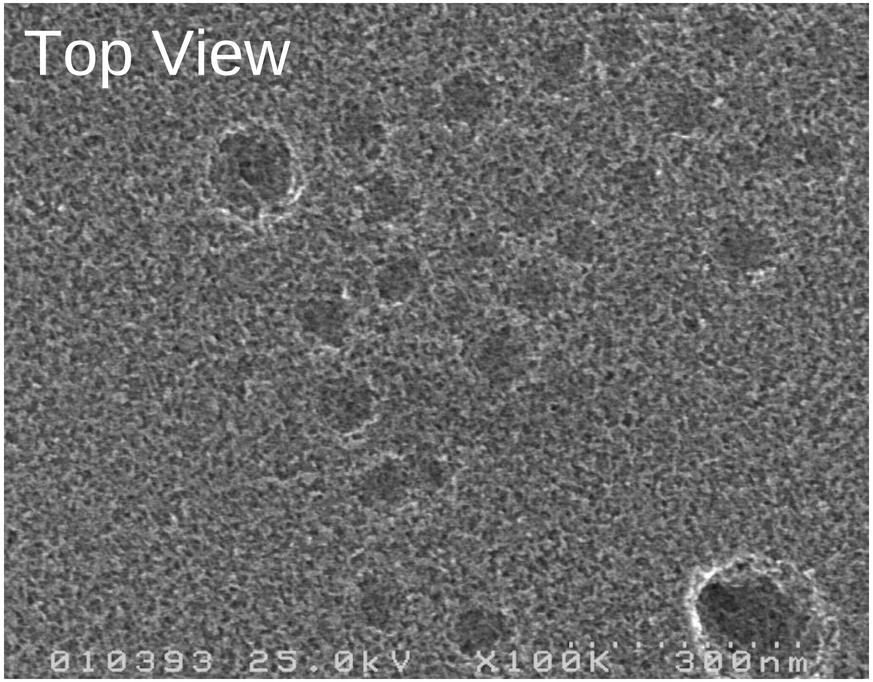
Substrate: porous alumina

Porous Carbon Membrane (PCM)



300nm

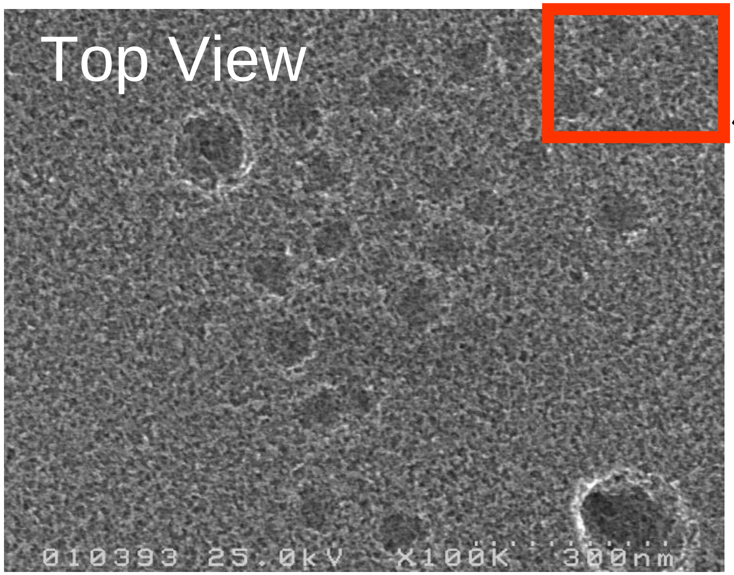
Carbon membrane prepared from Cardo polyimide



300nm

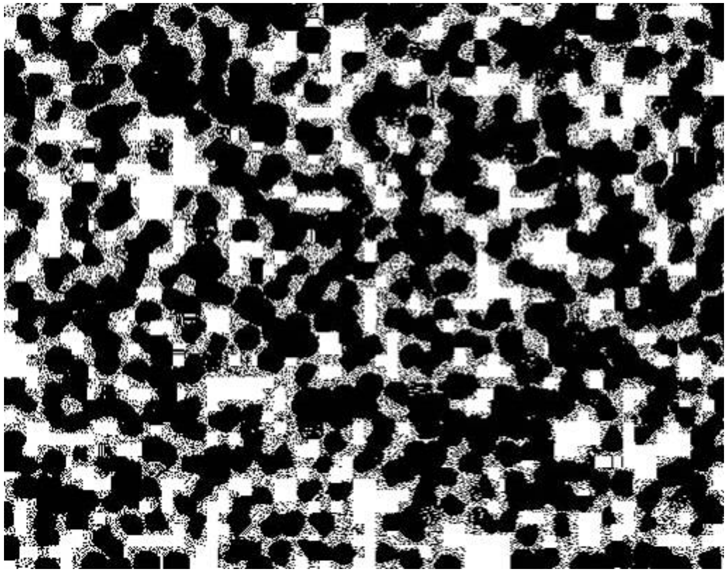
Carbon membrane prepared from Cardo polyimide and Poly(ethylene glycol)(PEG)
Pore size : ca. 10 nm

Surface morphology of PCM



300nm

Porous Carbon Membrane

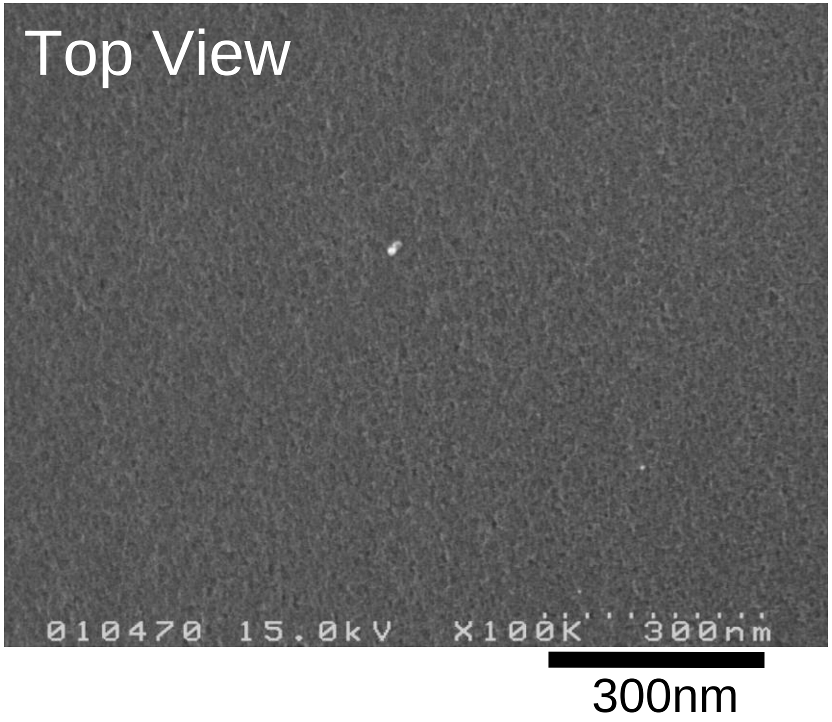


100nm

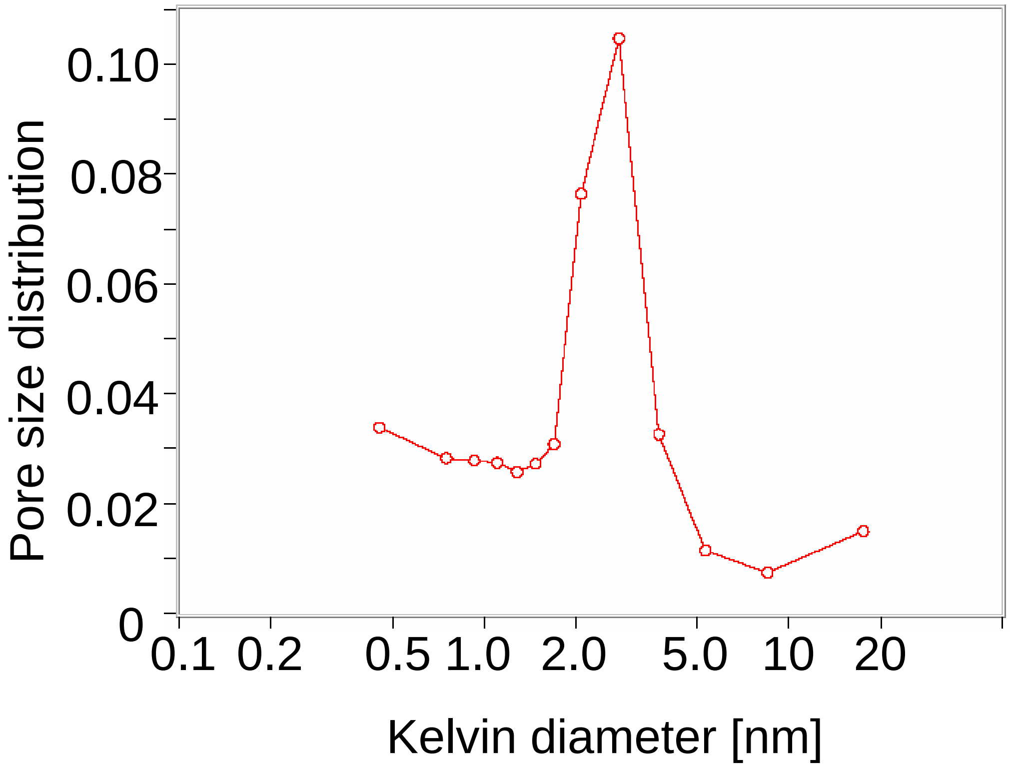
Schematic image

Original photo was contrasted with black and white

SEM images and pore diameter distribution



Surface of carbon layer



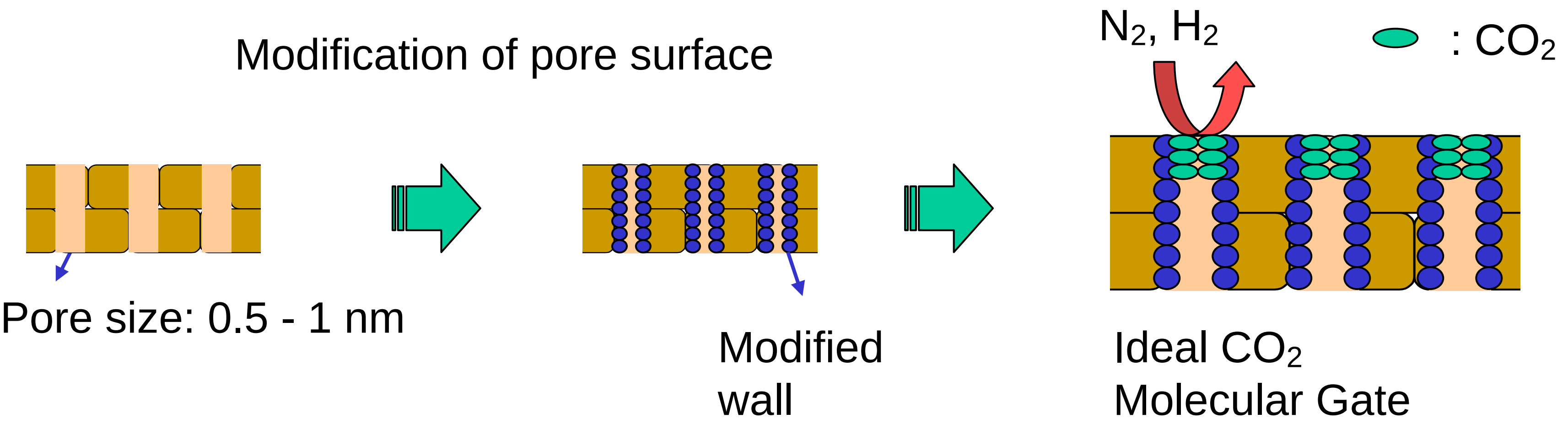
Pore size distribution using Nano-permporometer

SEM photograph and pore size distribution of carbon membrane prepared from polyimide/poly(ethylene glycol) precursor.

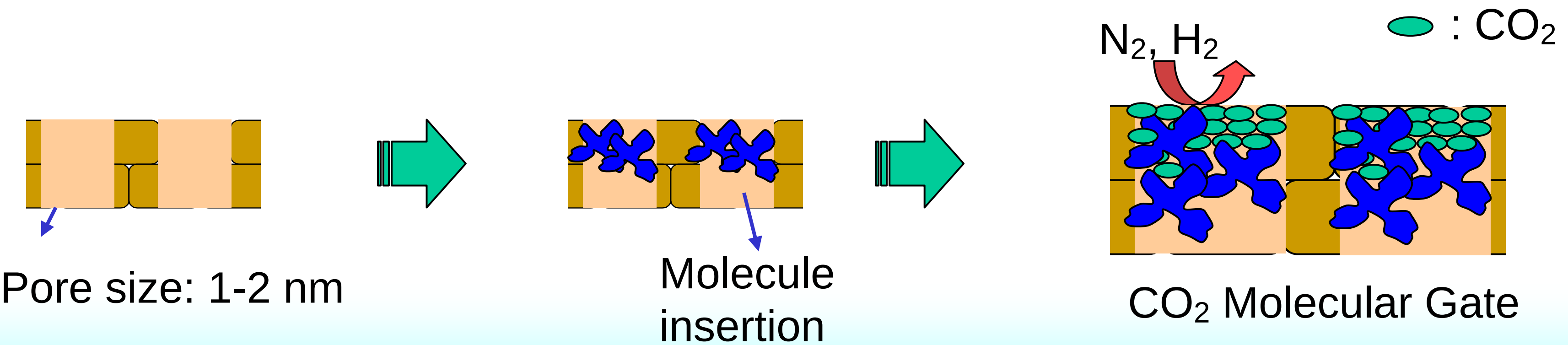
Future work: Enhancement of CO_2 Affinity

Modification of pore property for high CO_2 affinity

Modification of pore surface



-Insertion of molecule having CO_2 molecular gate function



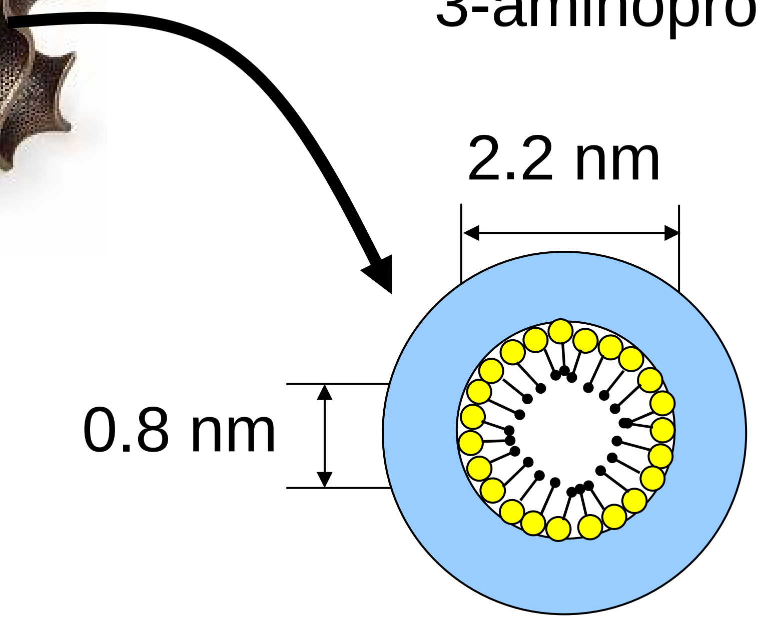
3. Development of Functionalized mesoporous oxide membrane

Amine-modified MCM-48

CO_2=0.33nm
APS=0.7nm ➡ MCM-48(2nm pore) is promising

APS:H_2**N**⁄\⁄ $Si(OCH_2CH_3)_3$
3-aminopropyltrietoxysilane

MCM-48



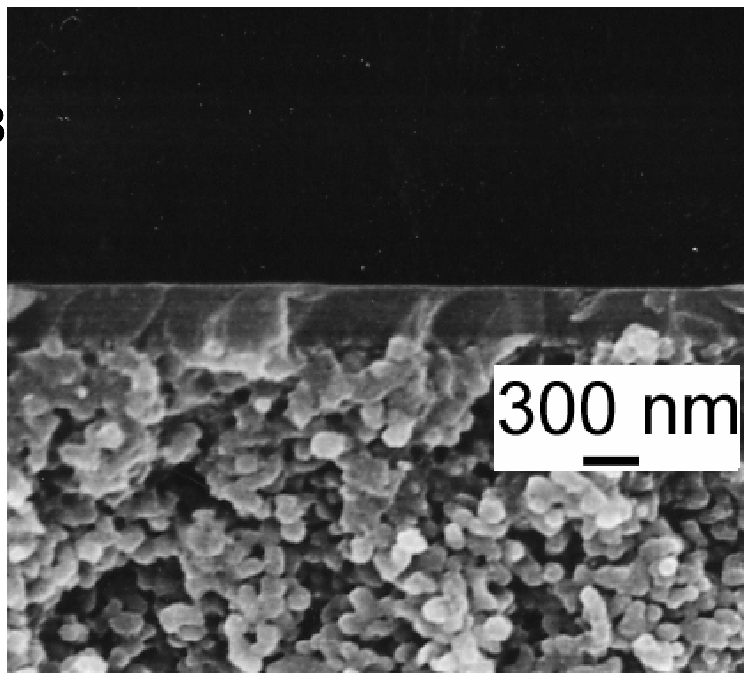
APS/MCM-48

MCM-48 Membrane

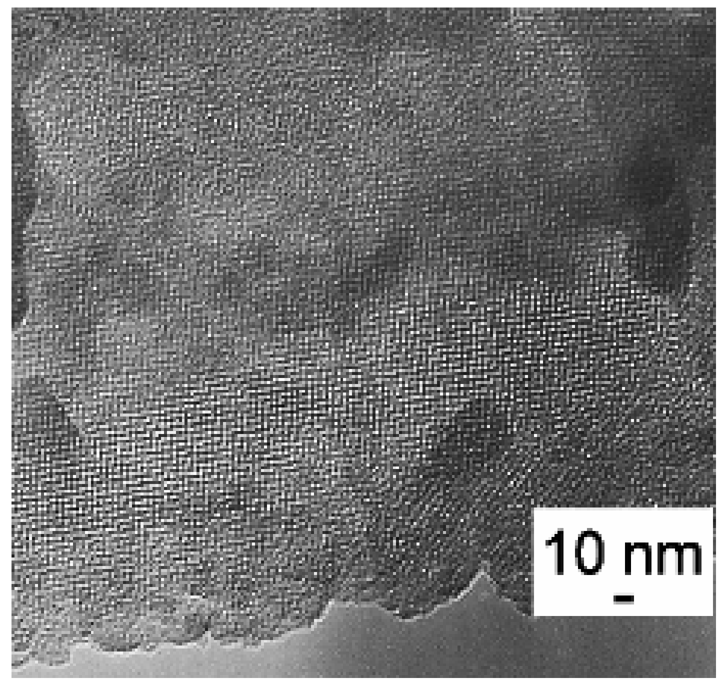
MCM-48 membrane synthesized by spin coating.

SEM image
Cross view

MCM-48
(300nm)

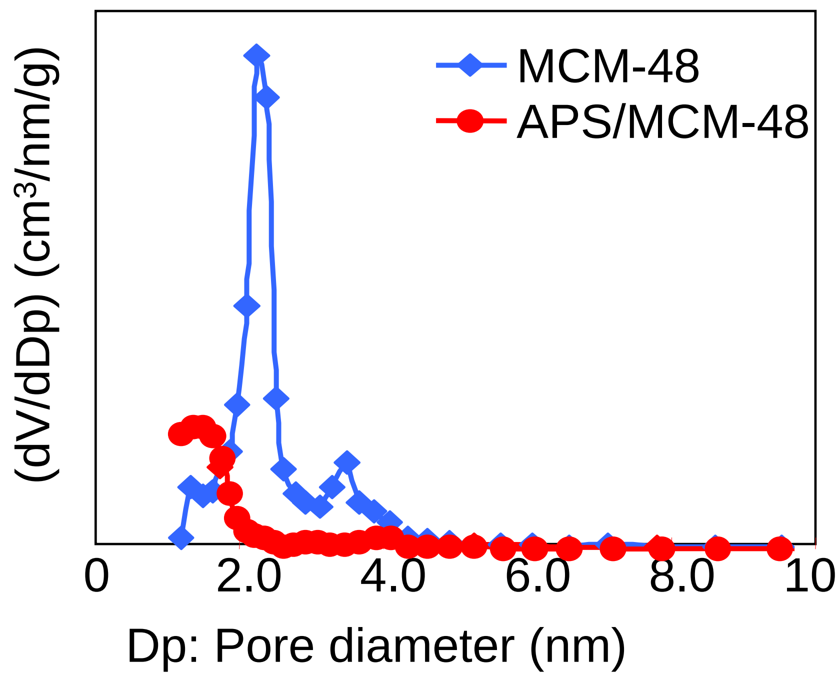


TEM image
Top view



Pore diameter : 2 nm

Pore size distributions of mesoporous silica



	Surface area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})
MCM-48	1083	1.0
APS/ MCM-48	324	0.2

(measured at powder)

APS: H_2N–(CH₂)₃–$Si(OCH_2CH_3)_3$

3-aminopropyltrietoxysilane

Ammonium carbamate formation

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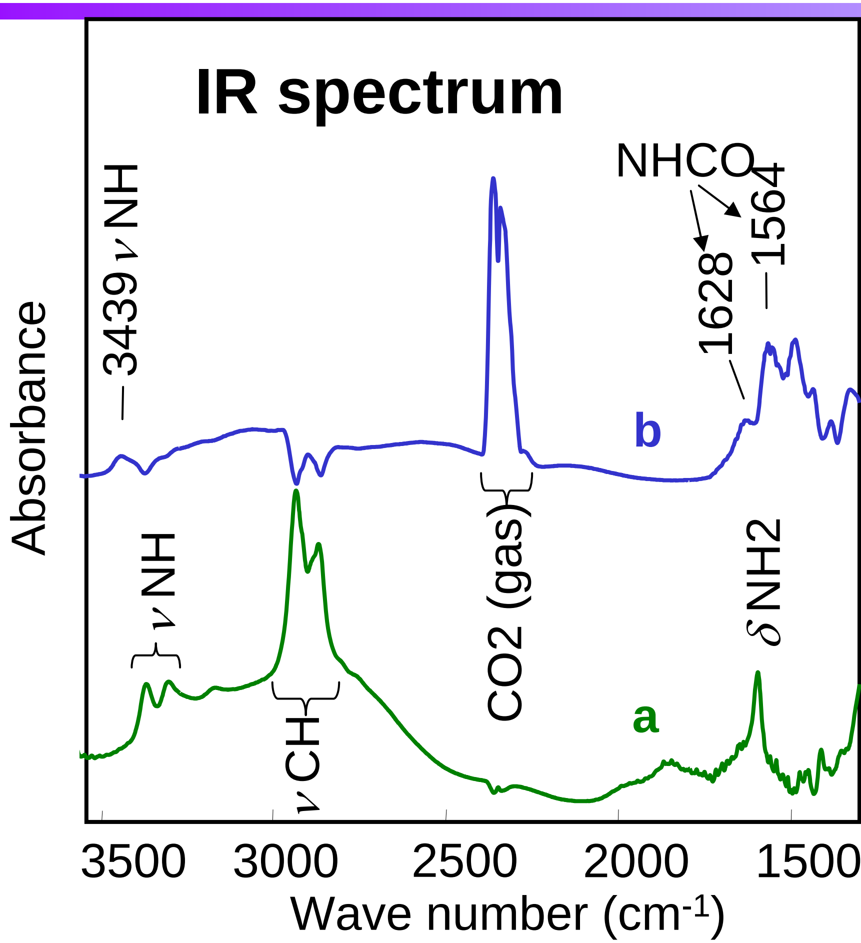
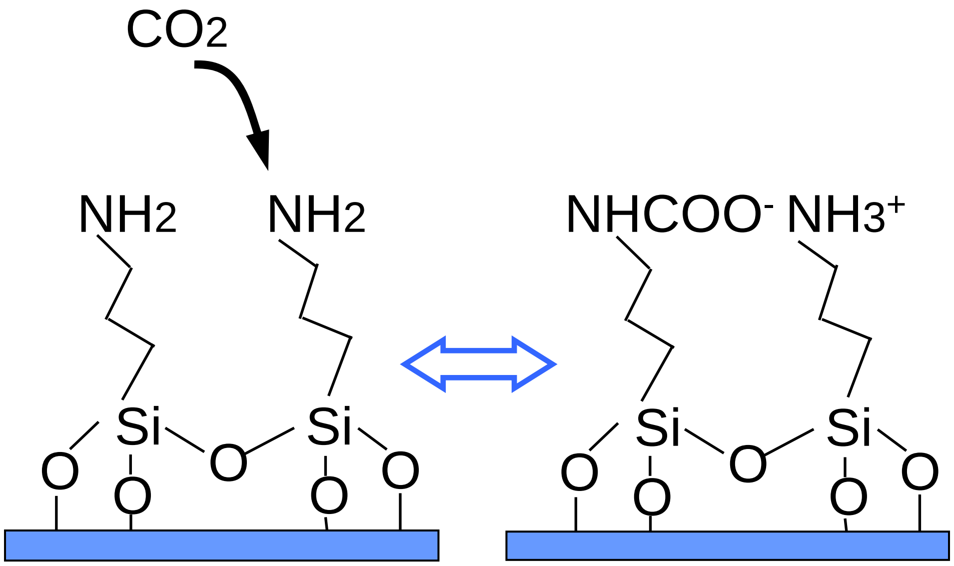


a: Dried APS/MCM-48

b: After CO_2 adsorption

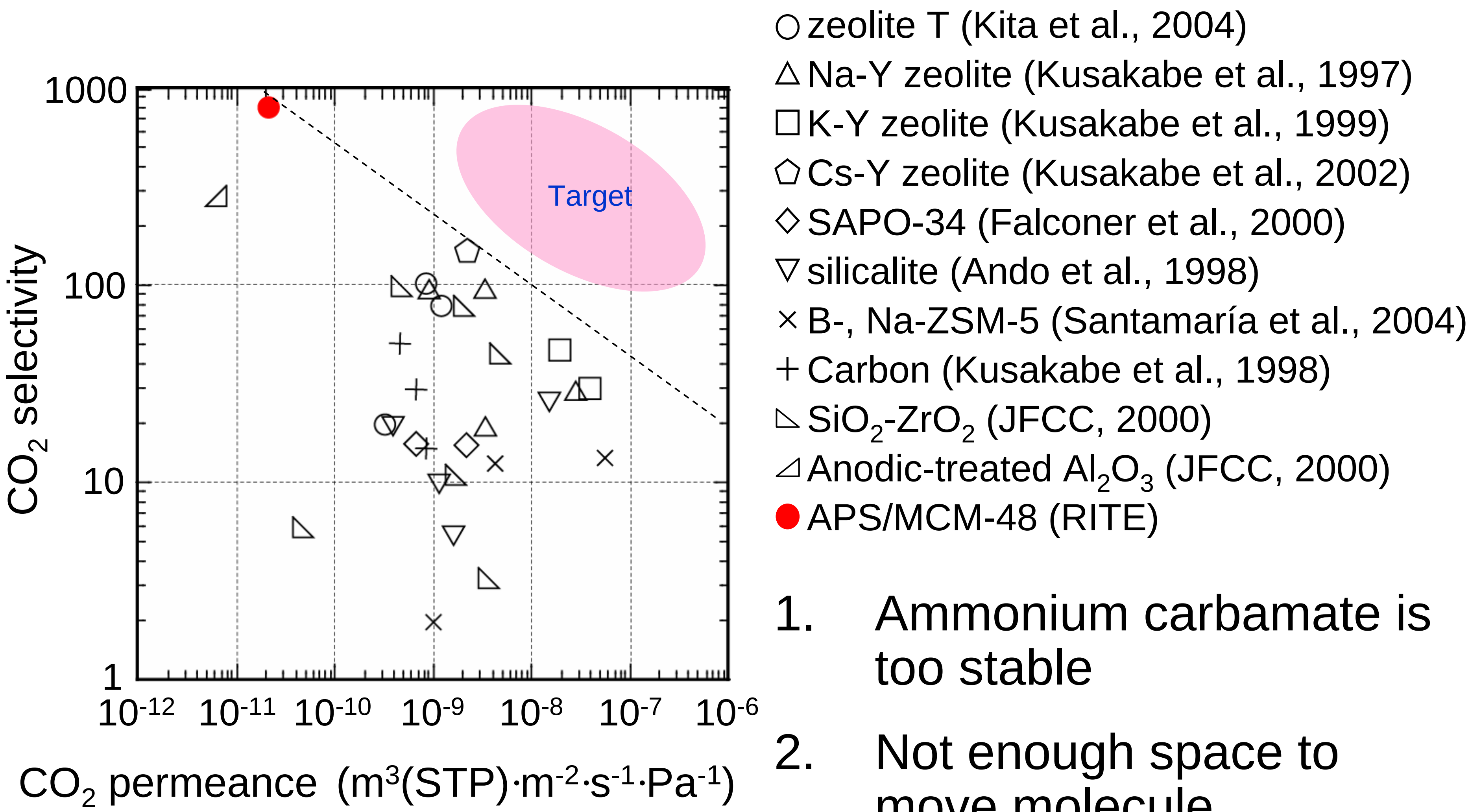


CO_2 adsorption:

Ammonium carbamate formation on the pair site of amino-group

Amino group on pore surface is effective for CO_2 adsorption

Comparison of CO_2 separation performances



1. Ammonium carbamate is too stable
2. Not enough space to move molecule
3. Membrane defect

Future work:
Functionalized mesoporous oxide membrane

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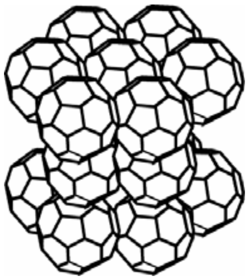
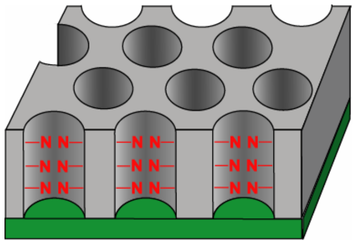
Selection of optimum porous structure



- pore size/structure
- chemical composition

Membrane preparation & Functionalization



Organic hybrid

Preparation of ultra thin separation layer:

- Dip coating
- Hydrothermal synthesis

Affinity control：

- selection of functional group
  carbamate formation
  N-atom density

Target

High permeability

- Permeance
  1000 times

High selectivity

- $\alpha_{CO2/N2}$=1000

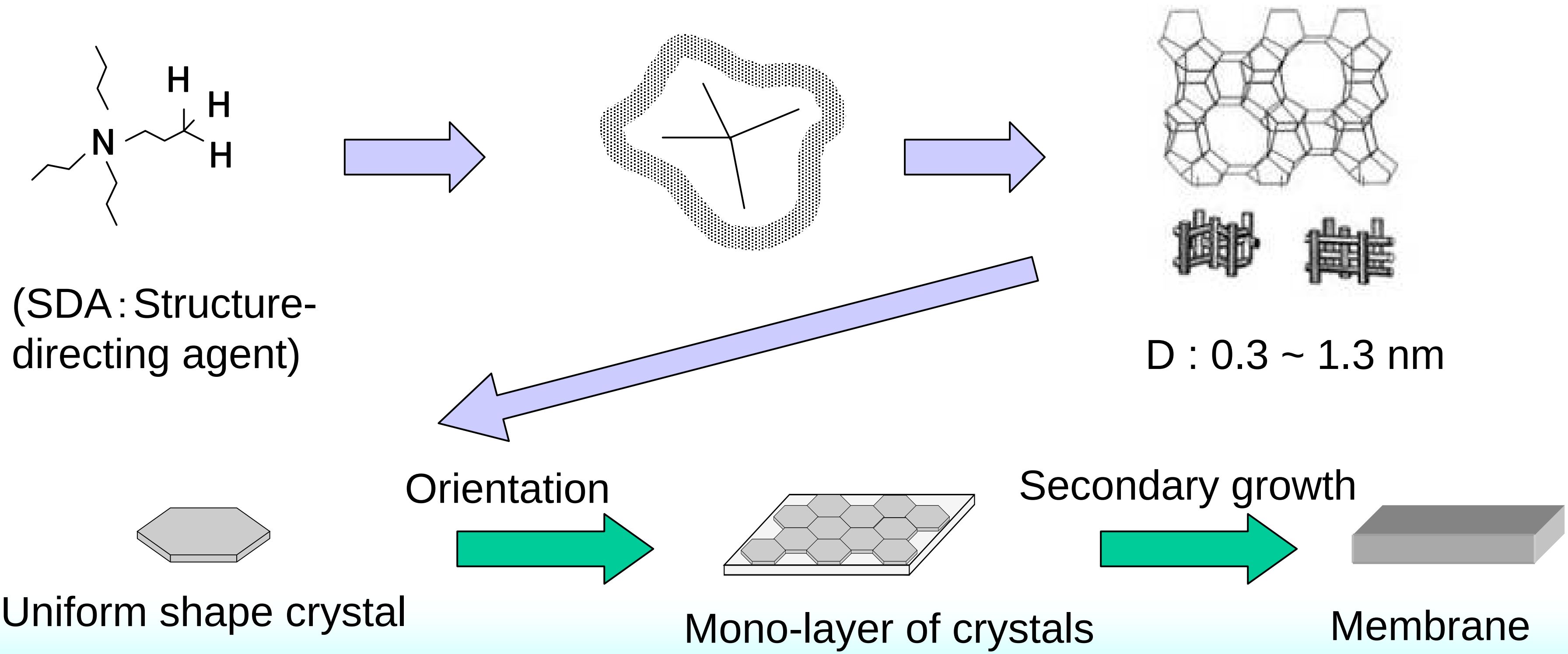
4. Development of zeolite membrane
    a. Crystal face orientation method
    b. Rubbing method

Zeolite Membrane

Zeolite

- Highly ordered structure with same pore diameter
- High thermal stability

Zeolite membrane



Silicalite synthesized by conventional method

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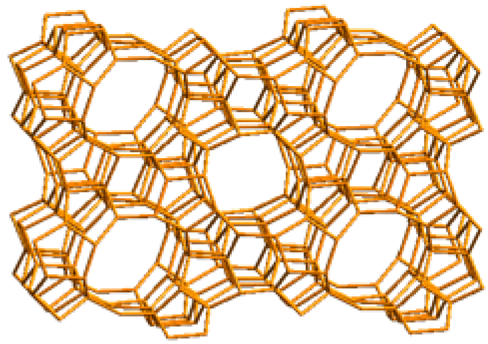
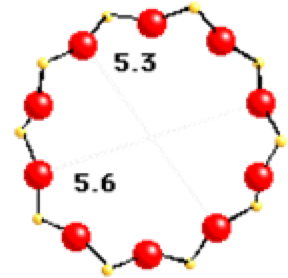
Silicalite (MFI)

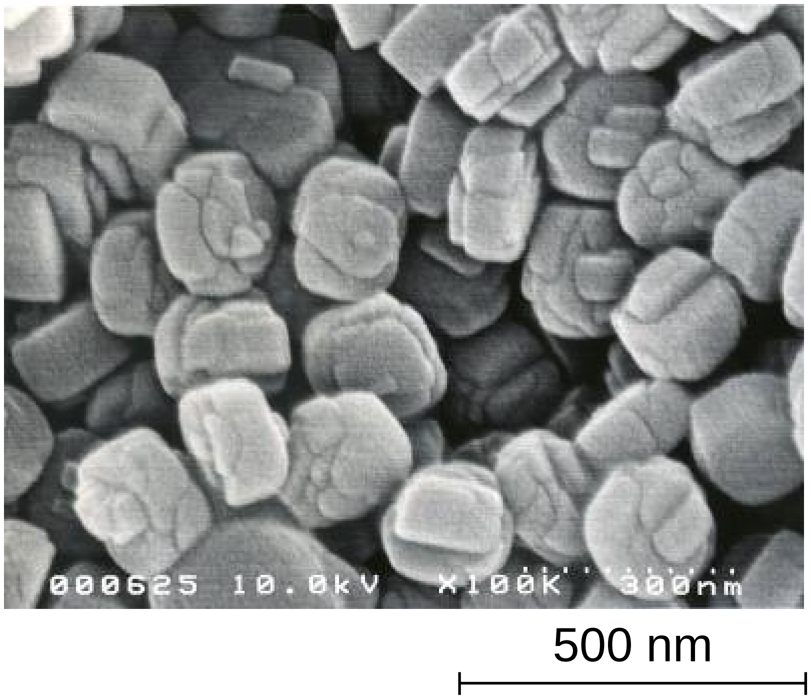
Former Crystal

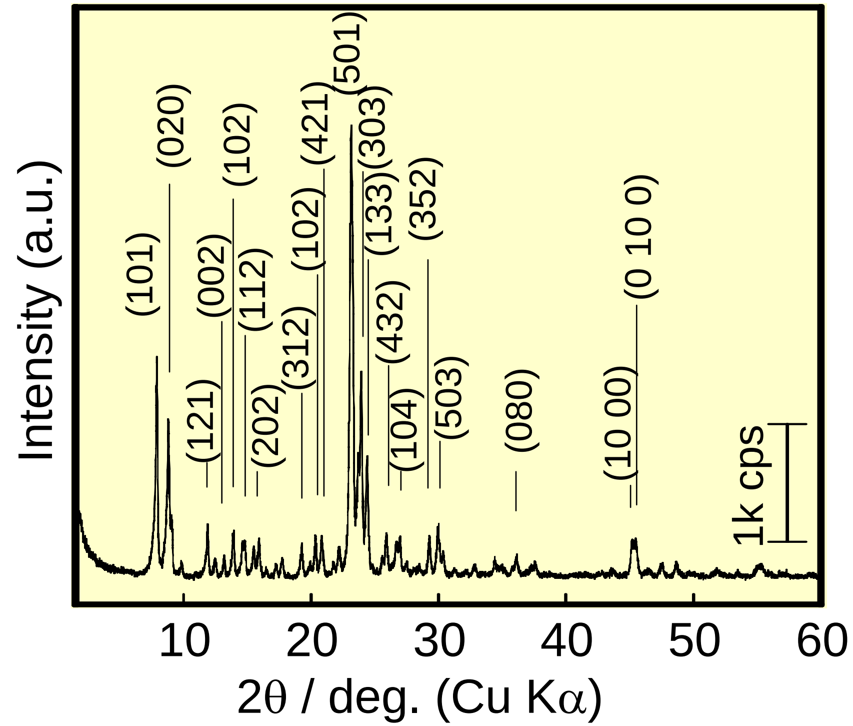


view (010)



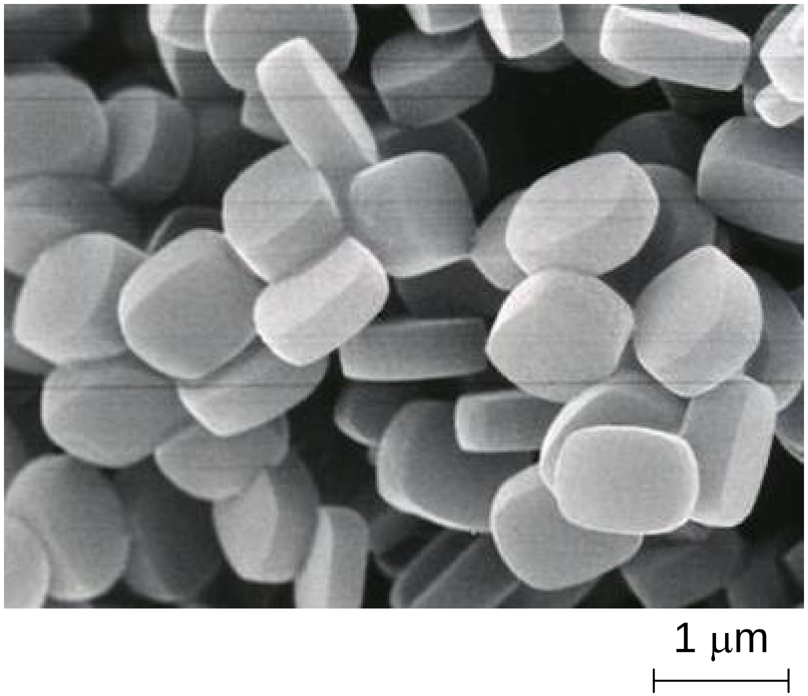
pore size :
0.56 × 0.53 nm

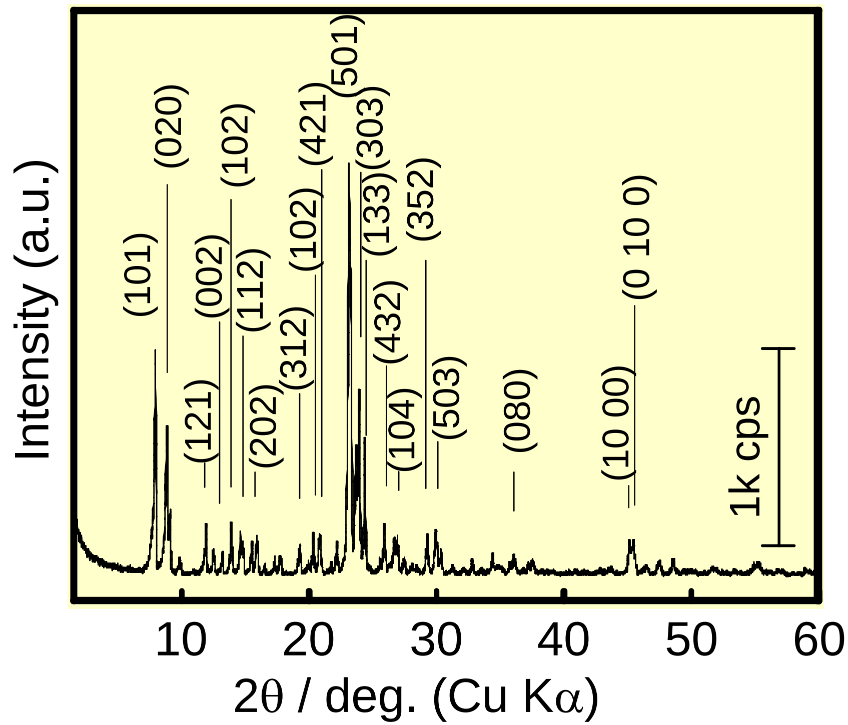




- **twin crystal**
- **crystal size (0.2×0.15×0.1 μm)**

Synthesis of Uniform crystal





Crystal size (1.0×0.7×0.3 μm)

Random Crystal face

Morphology controlled crystallization (rate of nucleation / crystal growth)

Control addition rate of SDA

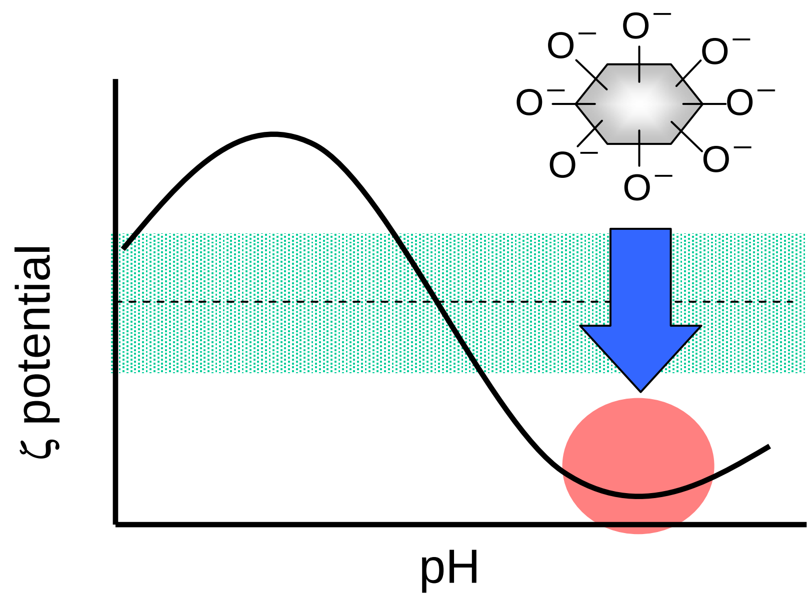
Crystalline orientation

pH control

ζ potential is dependent on pH

Surface (minus) charge of crystal is dependent on the ζ potential

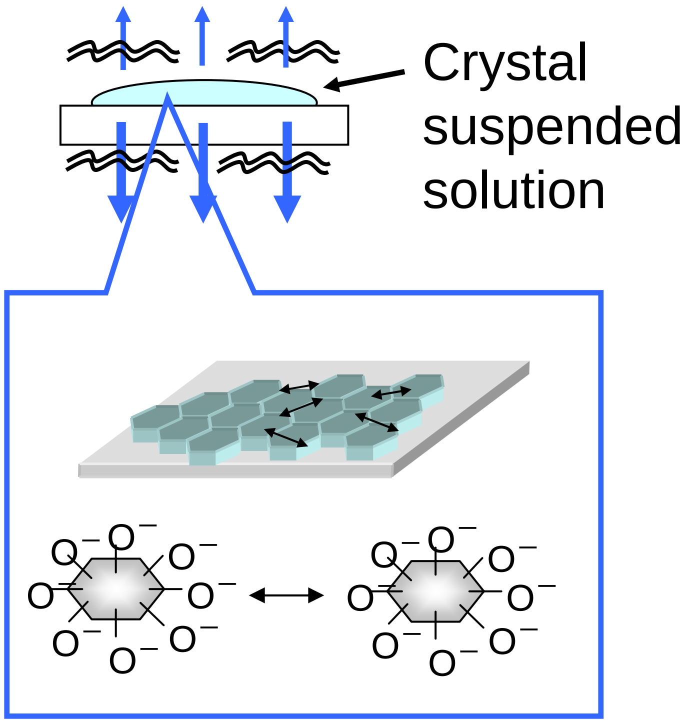
Force of repulsion between crystals is dependent on the surface charge



Force of repulsion makes crystal face orientation

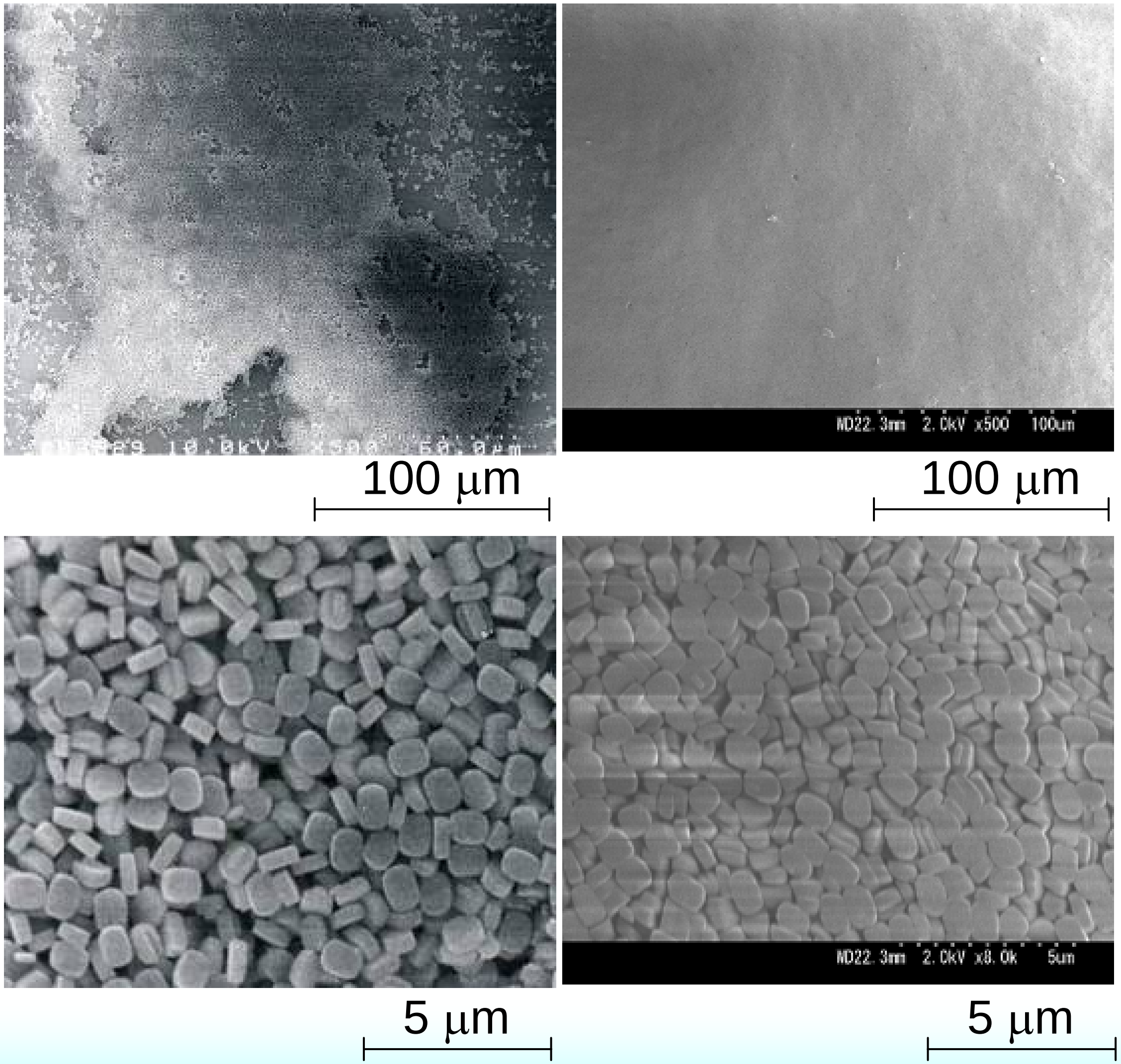
Orientation by ultrasonic oscillation

Water evaporation under ultrasonic oscillation

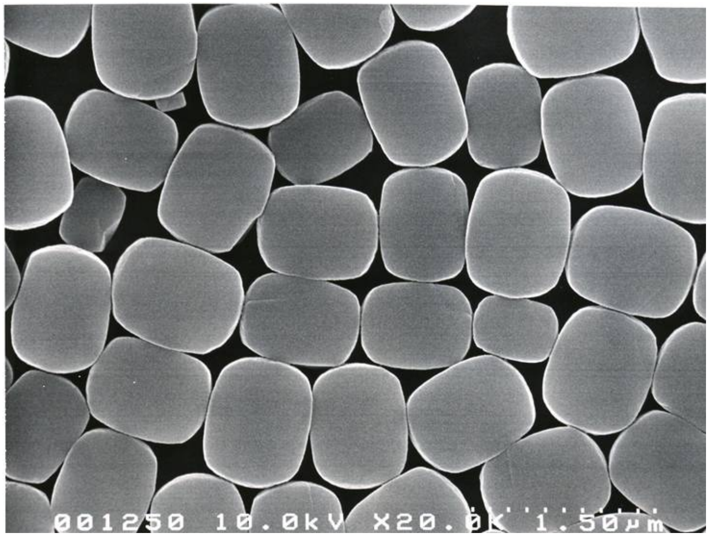


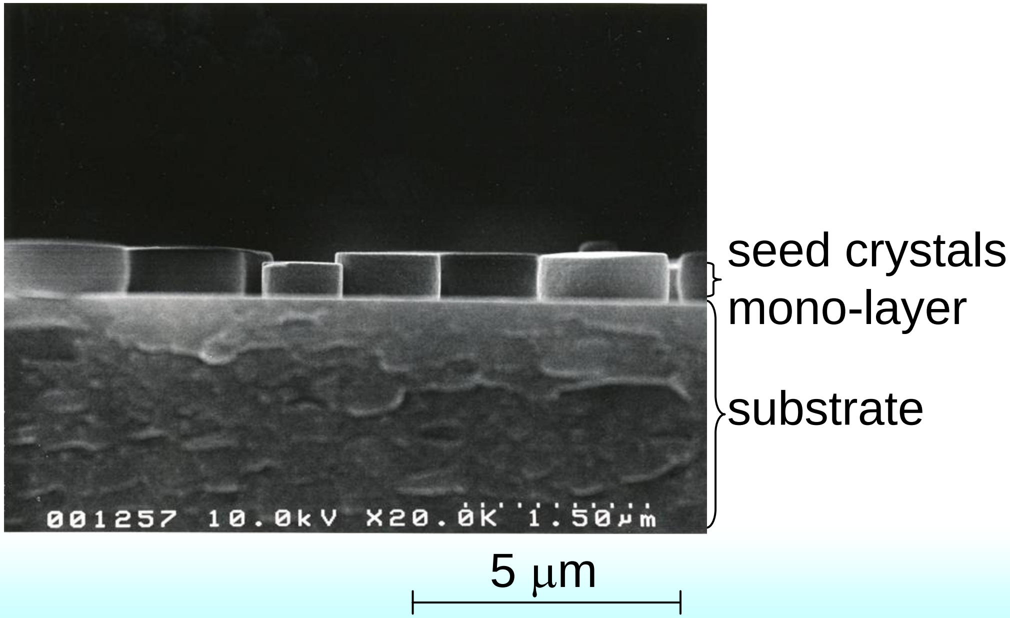
Crystals is oriented monolayer by ultrasonic oscillation

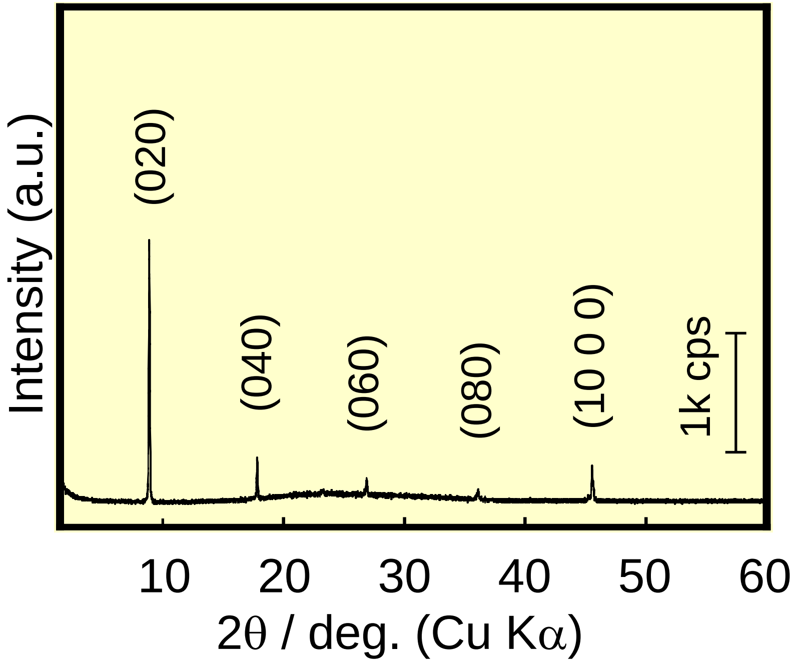
pH = 11	pH =12.5
$I_{(020)}/I_{(002)}$=6.8	$I_{(020)}/I_{(002)}$=119



Orientation of silicalite seed crystals







Uniform Crystal face

Zeolite membranes after secondary growth

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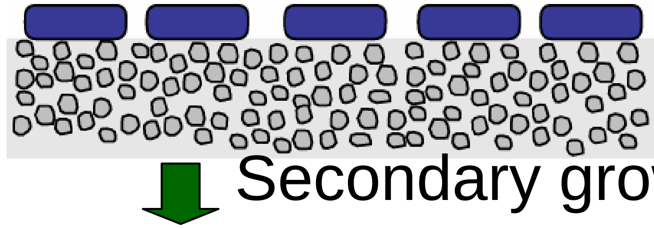
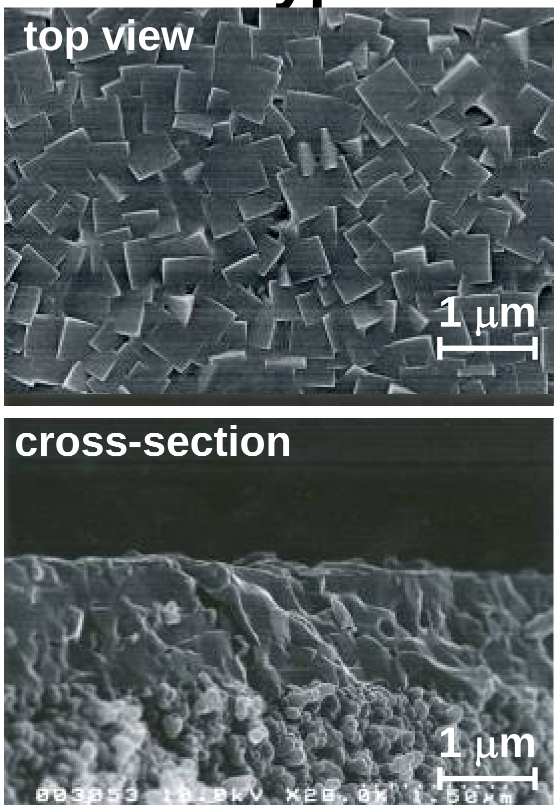
Monolayer of seed crystals



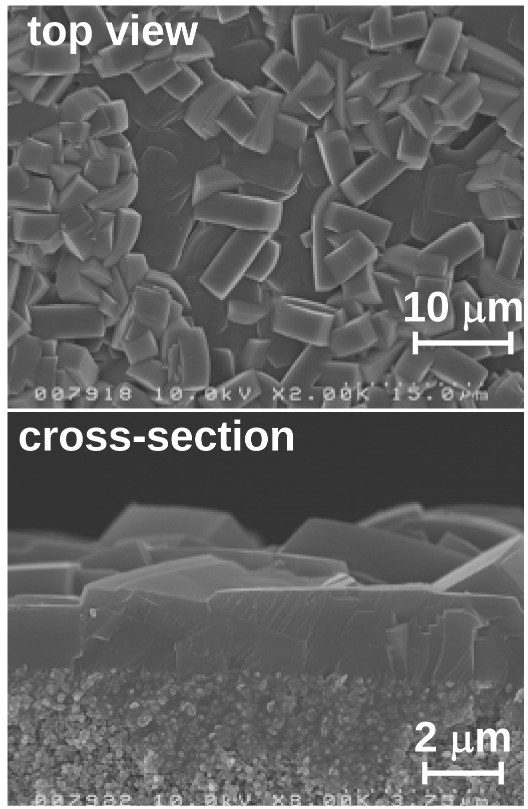
Secondary growth

A-type



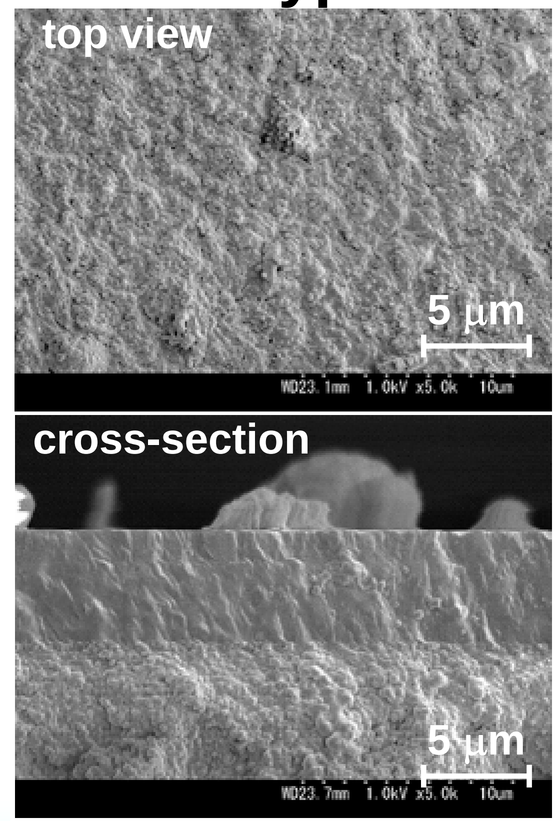
$\alpha_{CO2/N2} = 4.5$

Silicalite



$\alpha_{CO2/N2} = 2.5$

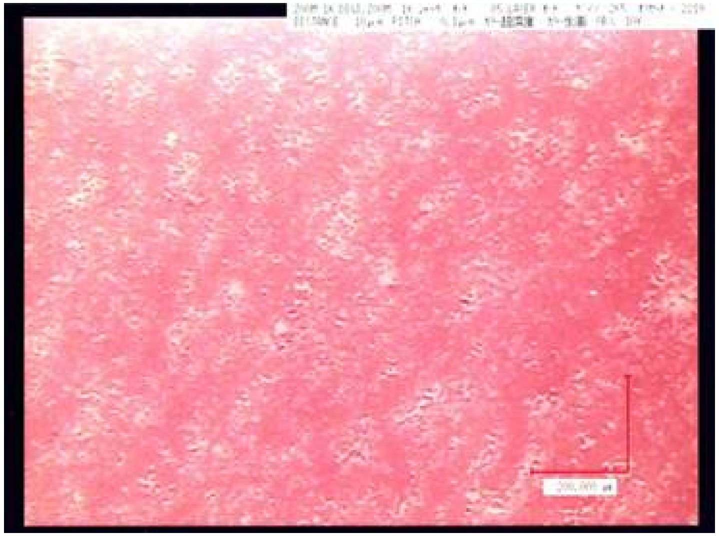
Y-type



$\alpha_{CO2/N2} = 2.4$

Defect in zeolite membrane

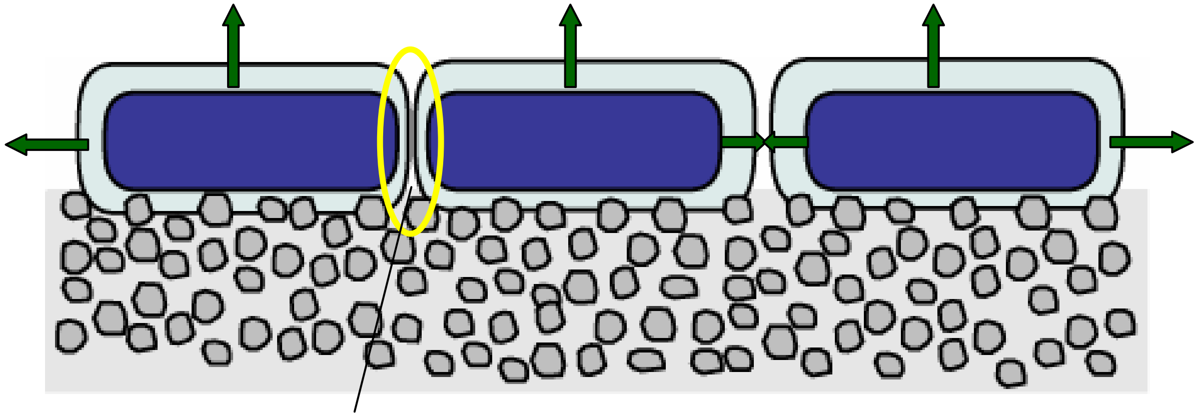
Rhodamine B staining of a silicalite membrane



CO_2 permeance : $2.76 \times 10^{-8}\ m^3 \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$

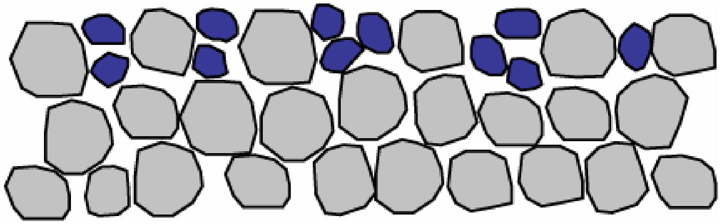
CO_2 selectivity : 1.33

A lot of defect larger than 2 nm
Silicalite pore size : 0.56 × 0.53 nm



Free space pace dose mot disappear after secondary growth
Movement & Slow diffusion of raw materials into the space

Membrane by rubbing method

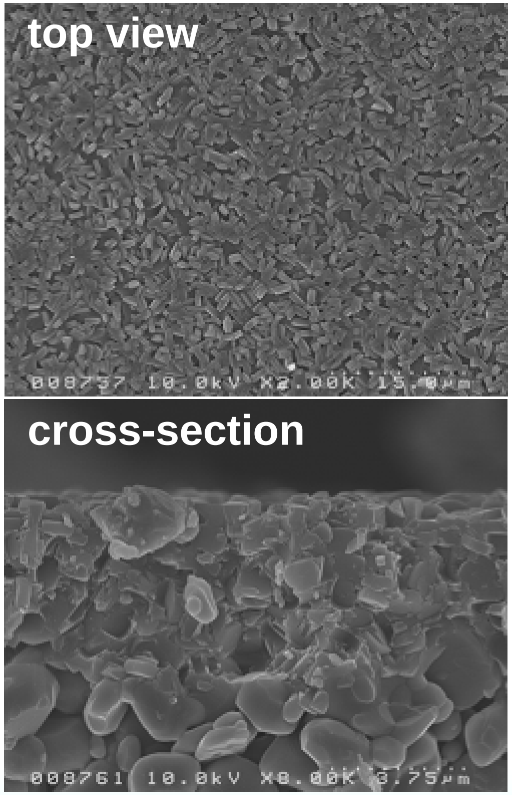


Fixation of seed crystal into the inside of substrate

(H. Kita et al., *Sep. Purif. Techol.*, **2001**, *25*, 261-268.)

secondary growth

Silicalite membrane

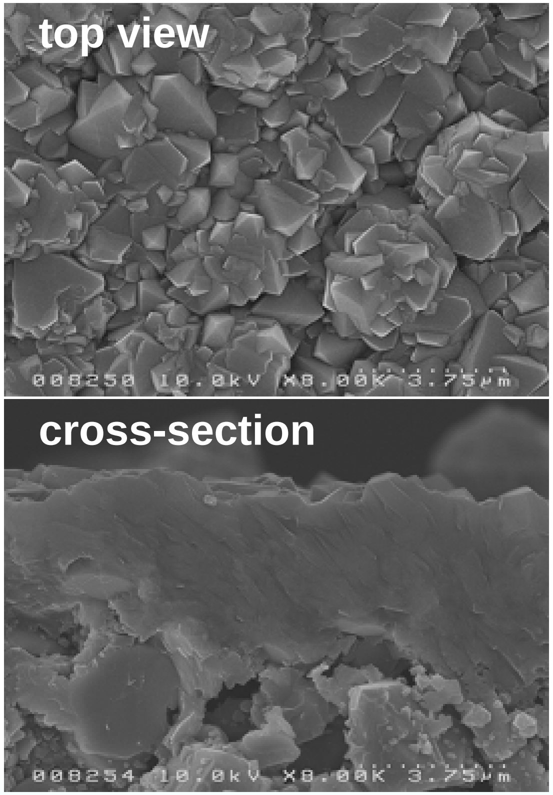


Silicalite

composite layer

substrate

Zeolite Y membrane



Zeolite Y

composite layer

substrate

Formation of mixed layer by growth of seed crystal inside of substrate

Performance of Membranes by rubbing method

RITE
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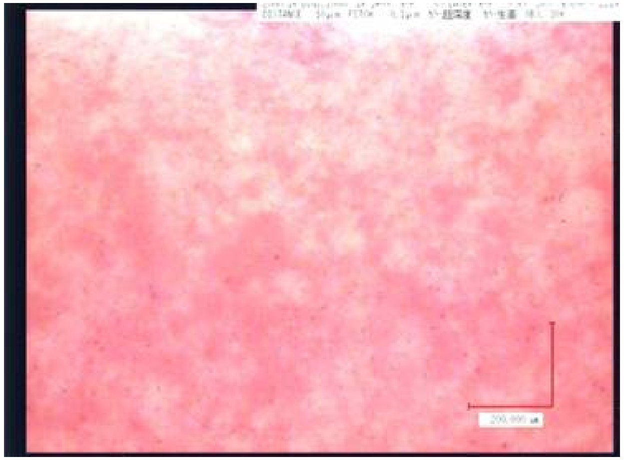
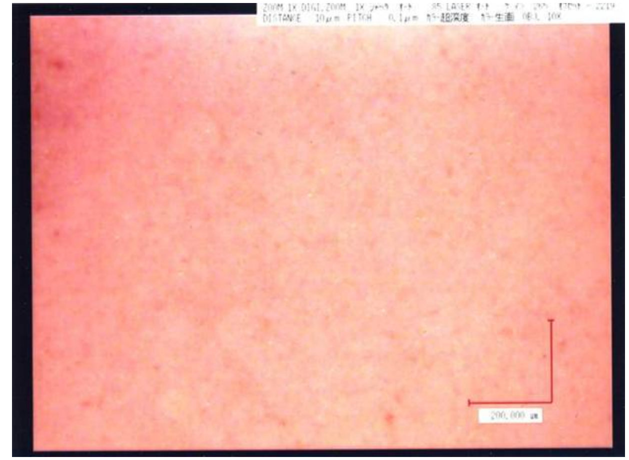
Silicalite membrane



CO_2 permeance ：1.08×10^{-8} $m^3 \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$

α_{CO_2/N_2} **= 3.24**

Zeolite Y membrane



CO_2 permeance ：6.79×10^{-9} $m^3 \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$

α_{CO_2/N_2} **= 69.3**

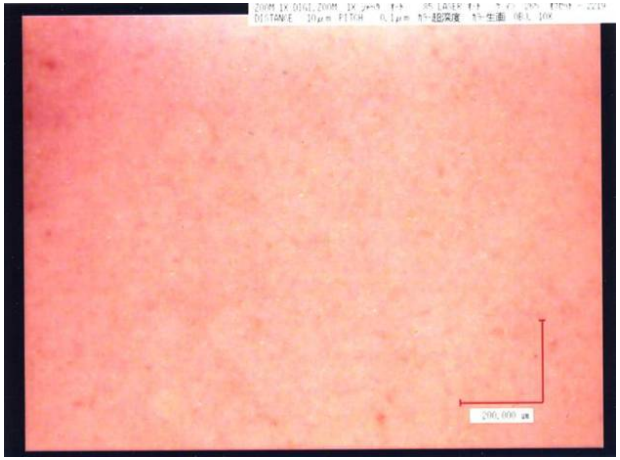
Evaluation method： soaking in 0.2 mmol/L Rhodamine B ethanol solution

Condition of permeation measurement： gas composition CO_2 20%（N_2 Balance）
feed gas pressure 0.05 MPa
temperature 298 K

CO_2 selectivity ： Crystal face orientation << Rubbing

Mechanism of Decreasing Defect

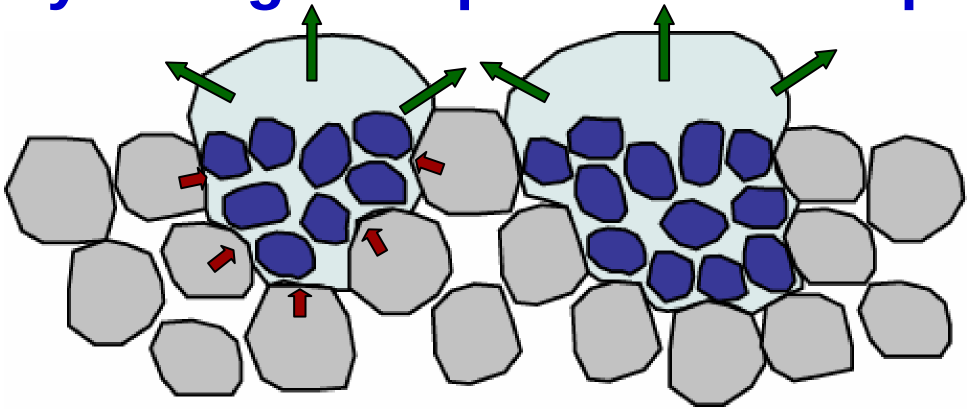
Zeolite Y membrane (0.7μm)



$\alpha_{(CO2/N2)}$=**69.3**

⇨ Few defects

Crystals grow up at a limited space



- Growing point is often broken or Direction of Crystal face is often moved by stress.
- New space where new solution can enter is generated.
- Generation and destruction around crystals decrease the defects during secondary growth.

Comparison of CO_2 separation performances

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