The reverse water-gas shift reaction over Pd membranes

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Hui received an award at ICCMR10: "Younger scientist Best presentation" and is now a member of the European Membrane Society.

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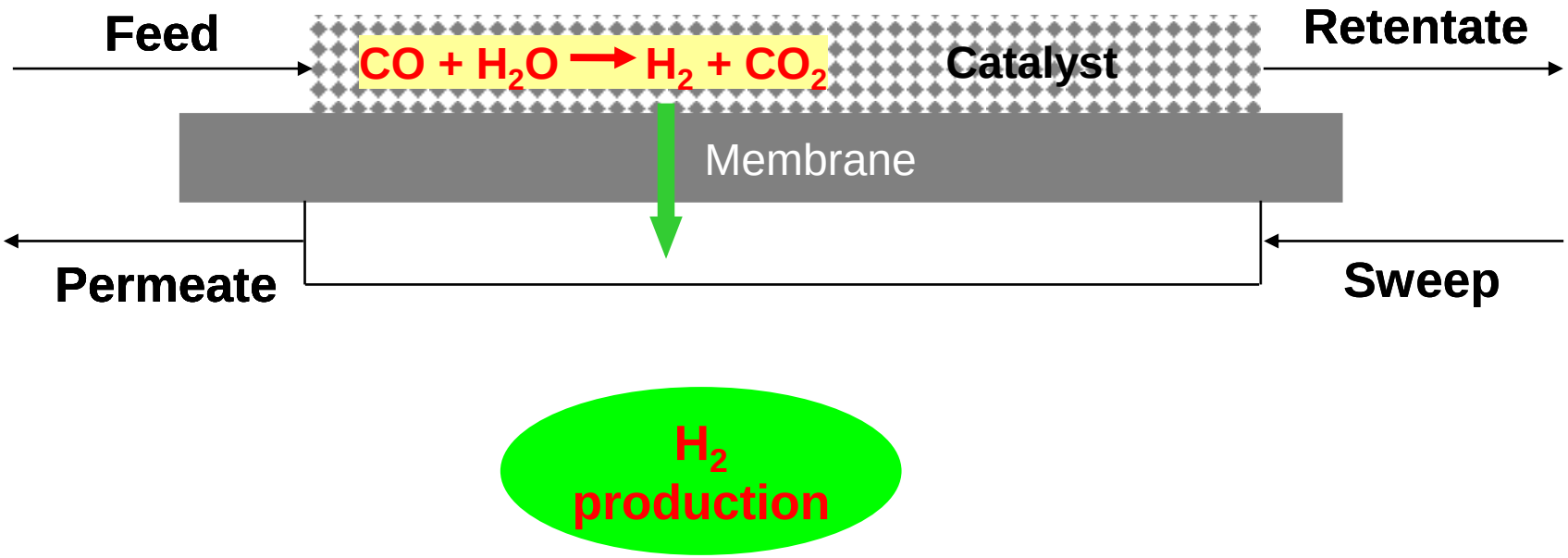
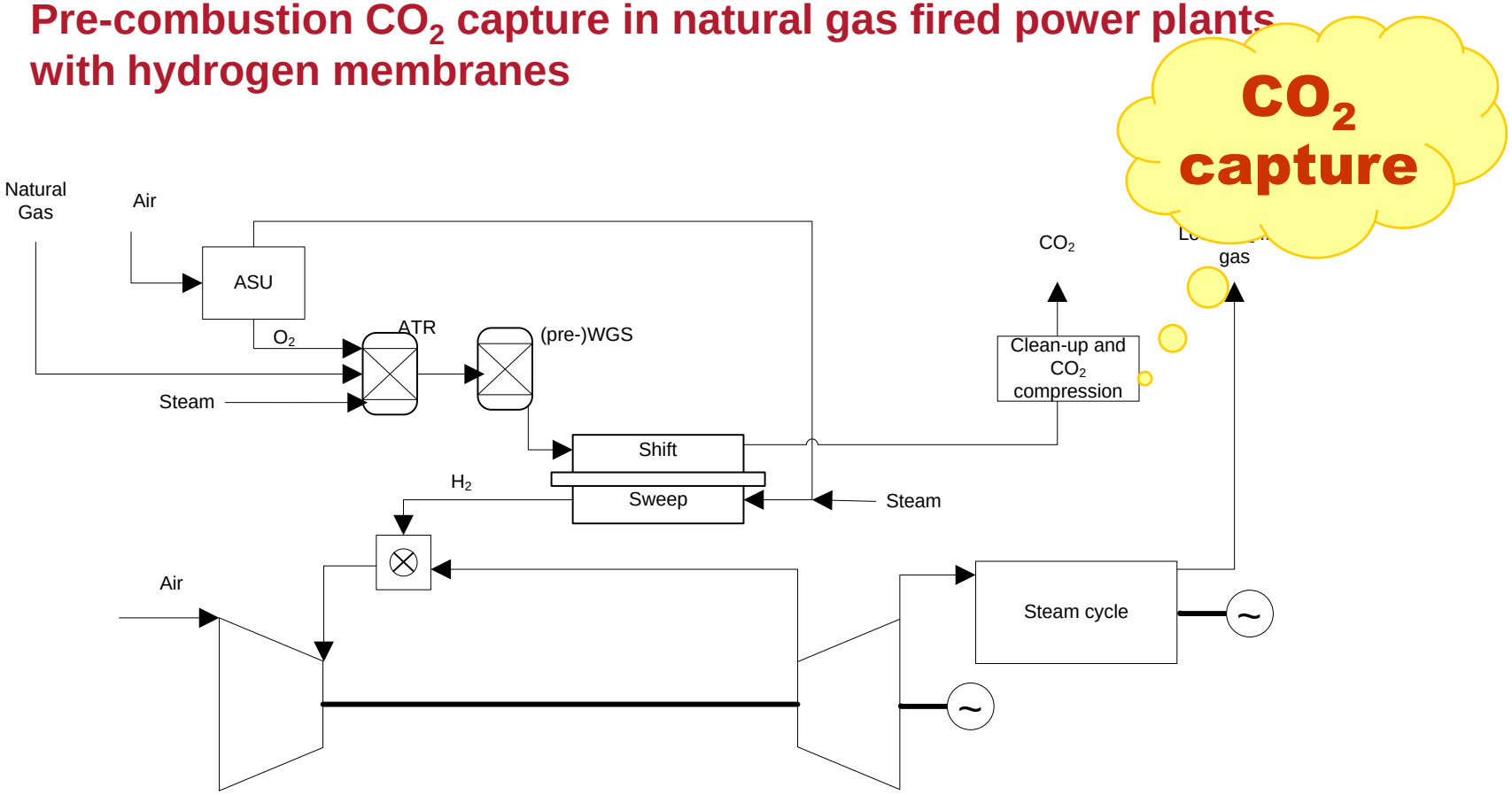
Outline

- *Why Pd membranes*
- Lab-scale observations
- Bench-scale observations
- Conclusion


Feed
CO + H2O → H2 + CO2
Catalyst
Retentate
Membrane
Permeate
Sweep
H2 production

Pre-combustion CO_2 capture in natural gas fired power plants with hydrogen membranes



*General layout of a power plant with a **membrane water gas shift reactor** (M-WGS)*

Chemical stability

Objective

- Investigate the influence of CO, CO_2 and CH_4 on the H_2 permeation of Pd membranes. *Lab-scale* investigation on Single component can provide background information for the influence of WGS mixtures.
- Investigate the influence of WGS mixtures ($CO/CO_2/H_2O/CH_4$) in a *bench-scale* membrane setup under near practical conditions.

H. Li et al., J. Phys. Chem. B, 112 (2008) 12182

H. Li, et al., J. Membr. Sci., 324 (2008) 95

H. Li et al., J. Membr. Sci., 299 (2007) 130

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Lab-scale

Test:

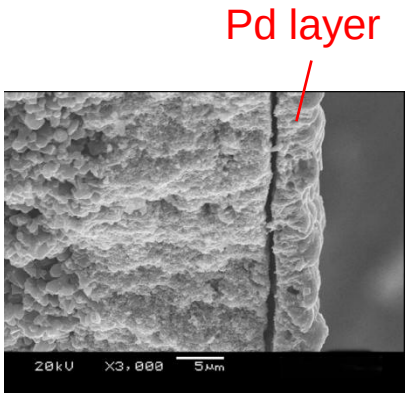
- Separation of H_2 from CO_2/H_2 mixtures

Equipment:

- A ***lab-scale*** membrane setup

Membranes:

- Pd membrane tubes (electroless plating) supported on Al_2O_3 substrate (glazed support)
- 5 cm long, 2 µm thick Pd layer, sel. >2000



Test program (CO_2/H_2 separation)

Conditions:

- ✓ Temp: 250-500 ℃
- ✓ ***10%*** CO_2/H_2, ***20%*** CO_2/H_2, ***40%*** CO_2/H_2
- ✓ P_{feed}: 2-***5*** bar, P_{perm}: 1 bar
- ✓ Feed: 0.1 Nl/min-2.5 Nl/min, no sweep

Objective

- Examine the surface reaction on the catalytically active Pd membrane surface during the separation of CO_2/H_2 mixtures.
  - Measure the retentate gas composition by ***GC***
  - Investigate the ***H_2 permeation flux*** of CO_2/H_2 mixtures as a function of time.
- Investigate the influence of operation parameters.

Feed flow rate

Feed pressure

Temperature

CO_2 concentration

Main observations:

- Possible reactions existing on membrane surface

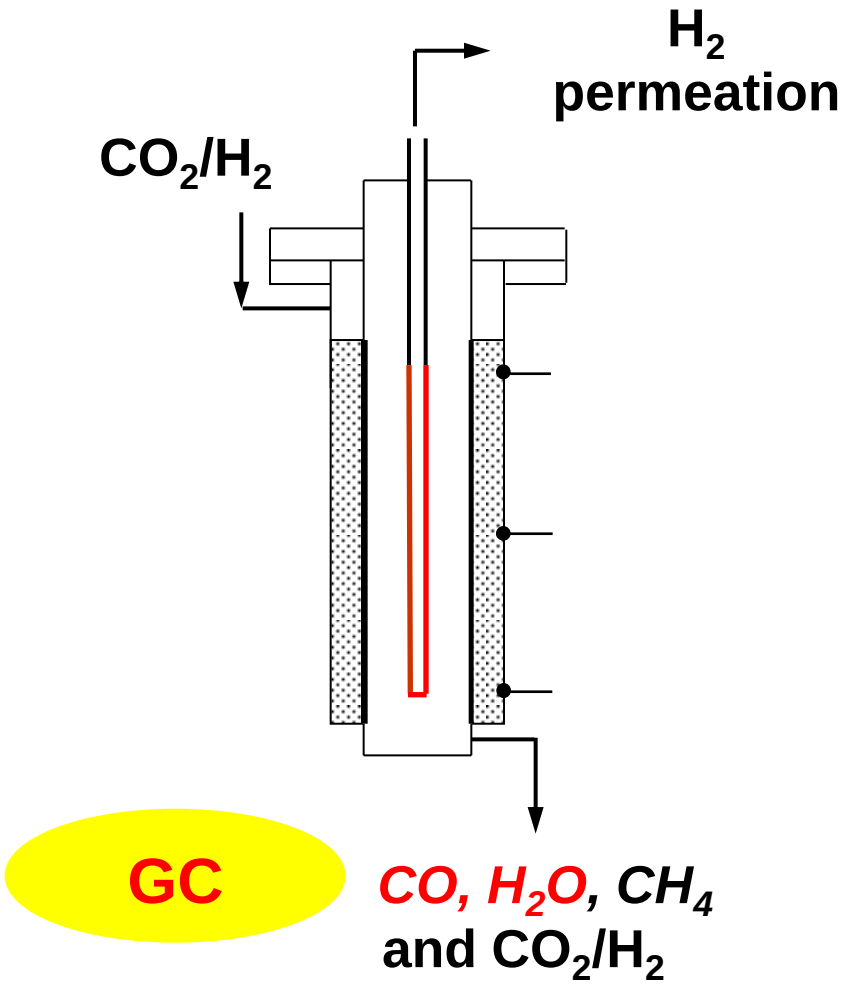
$CO_2 + H_2 \rightarrow CO + H_2O$

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

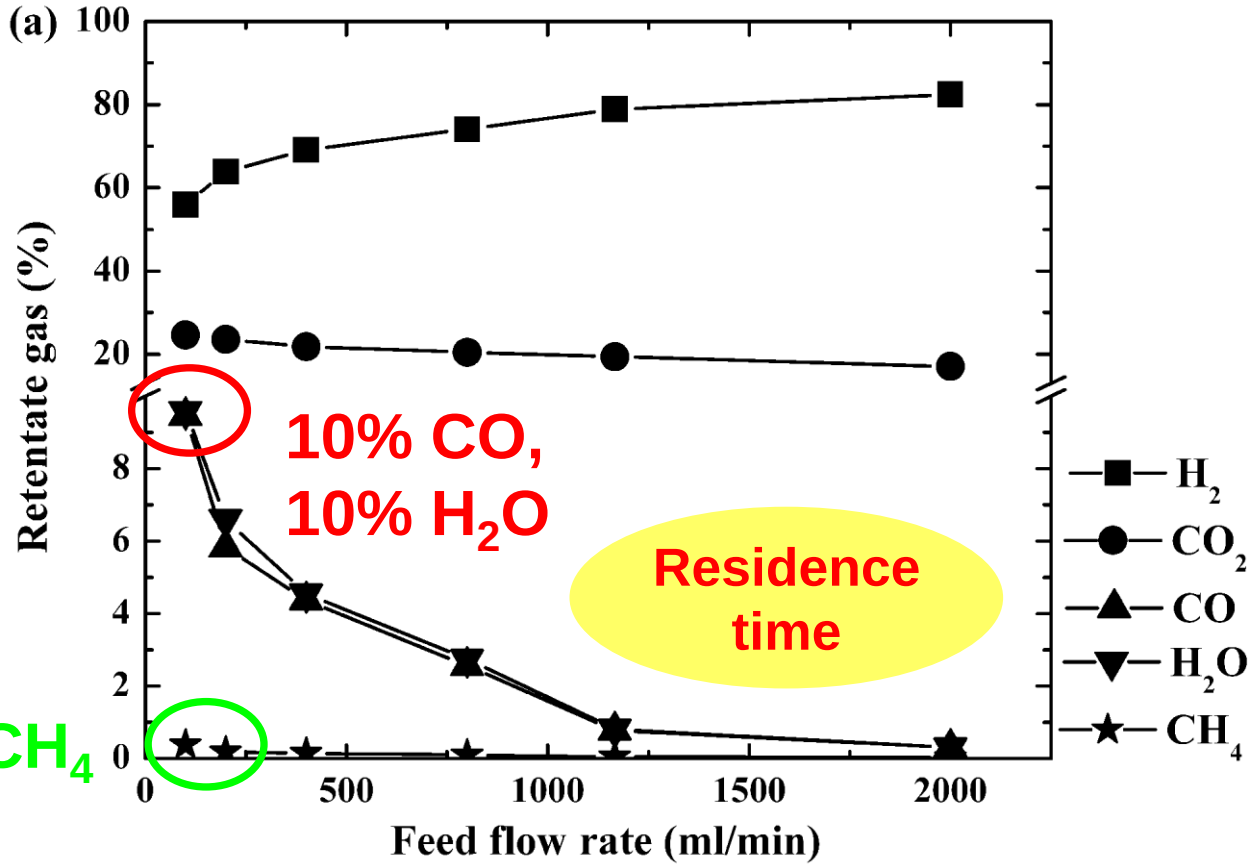
$CO_2 + 2H_2 \rightarrow C + H_2O$

$2CO \rightarrow CO_2 + C$

$CH_4 \rightarrow C + 2H_2$

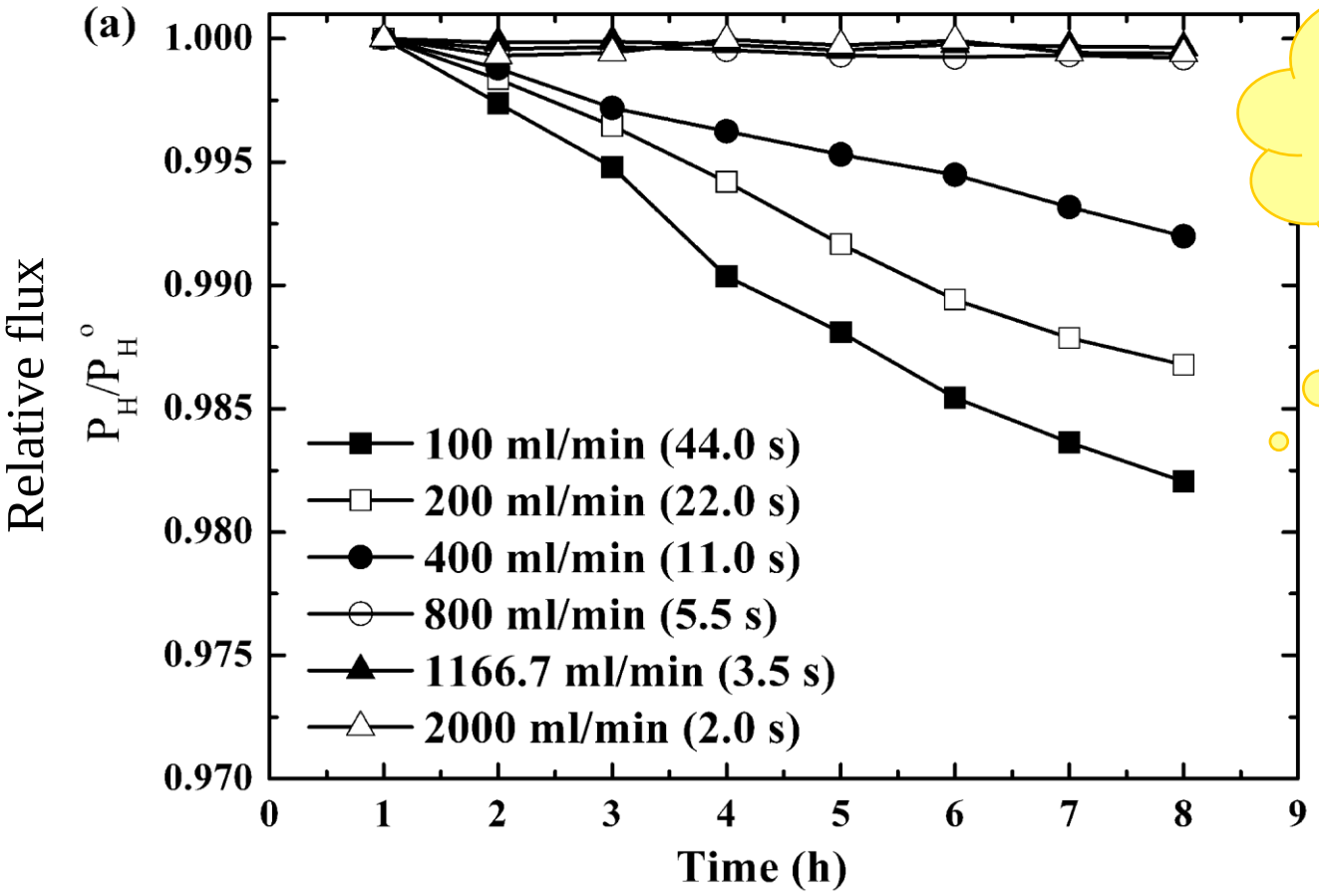


Influence of feed flow rate



10% CO_2/H_2 mixtures at 450 ^oC and 2 bar(a)

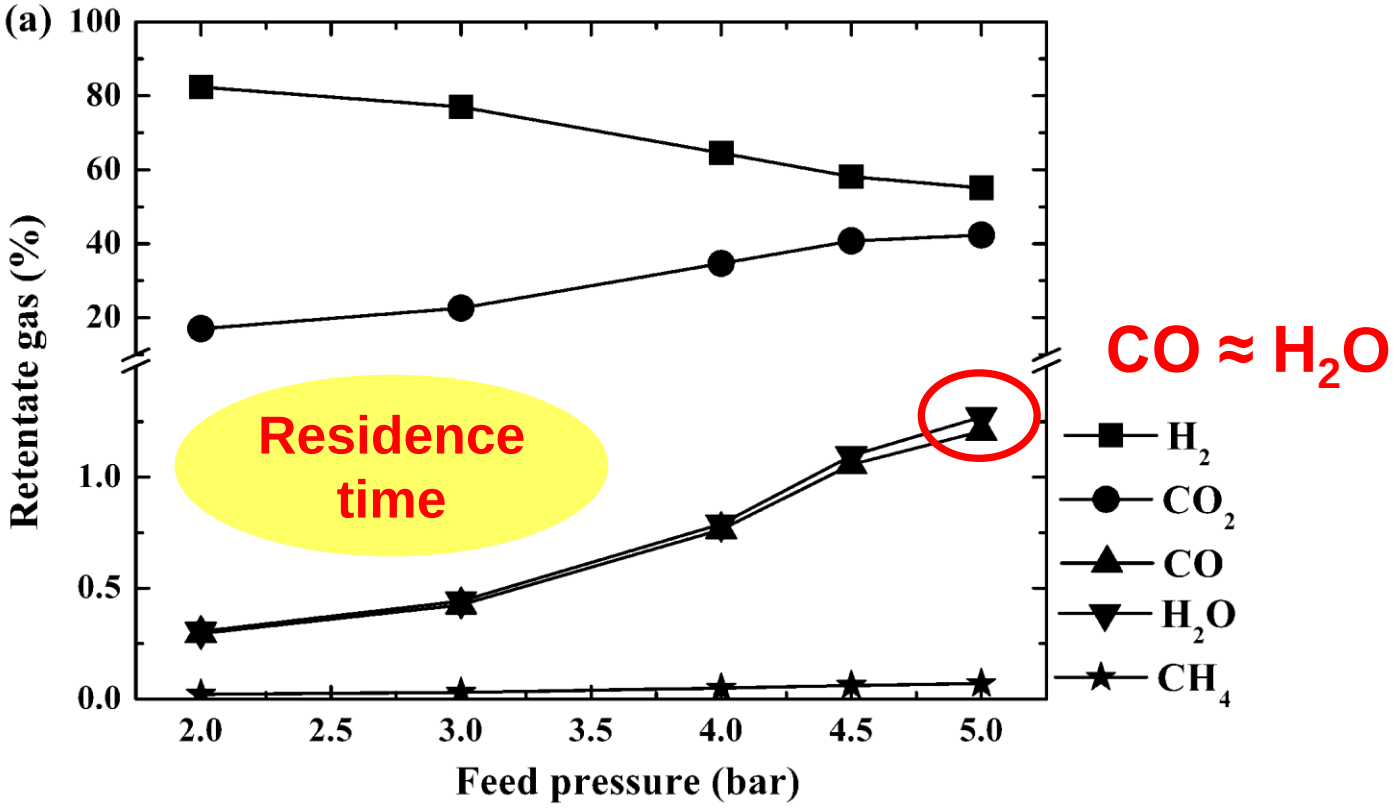
Influence of feed flow rate



Carbon deposition

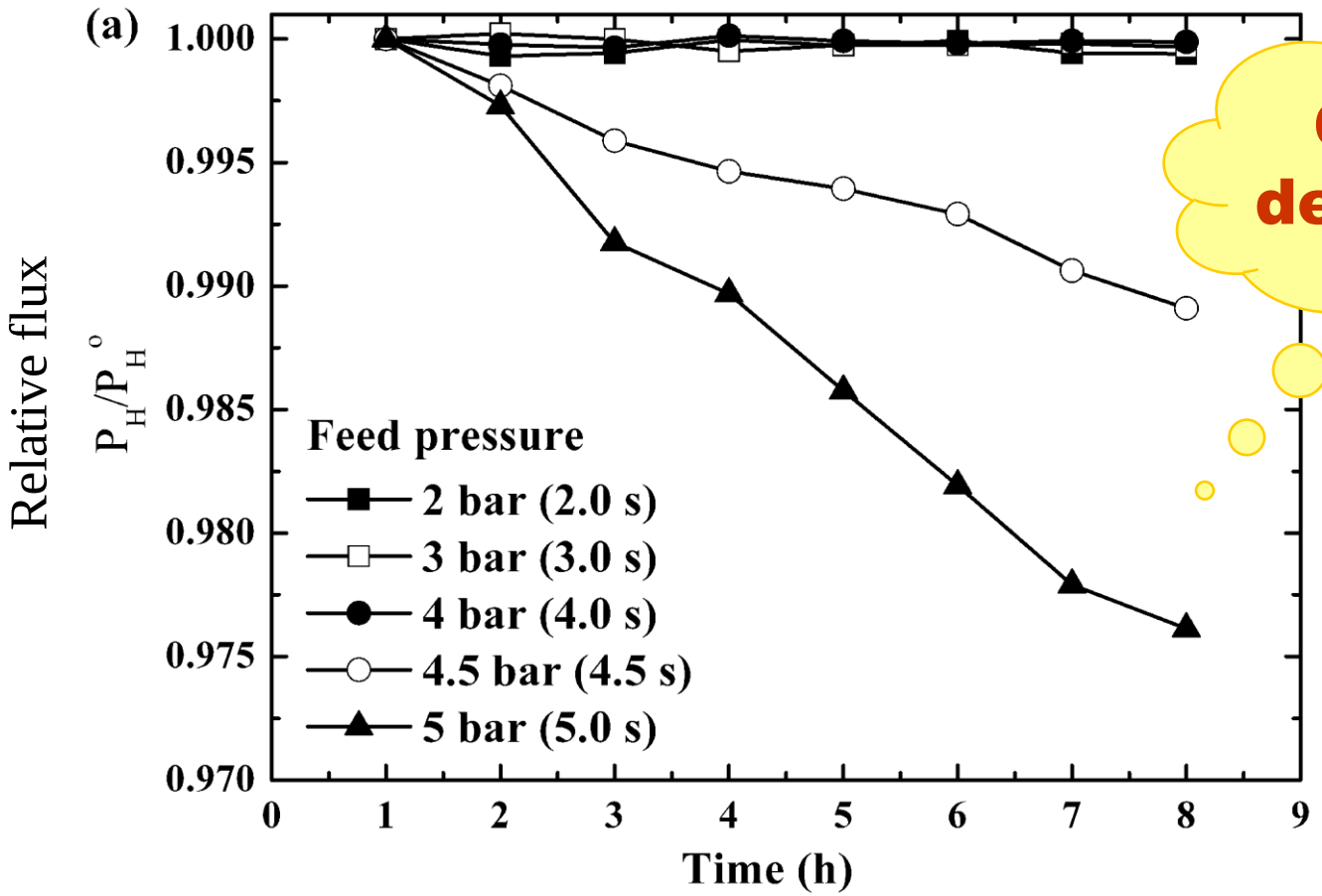
10% CO_2/H_2 mixtures at 450 ^oC and 2 bar(a)

Influence of feed pressure



10% CO_2/H_2 mixtures at 450 ^oC and a feed flow rate of 2 Nl/min

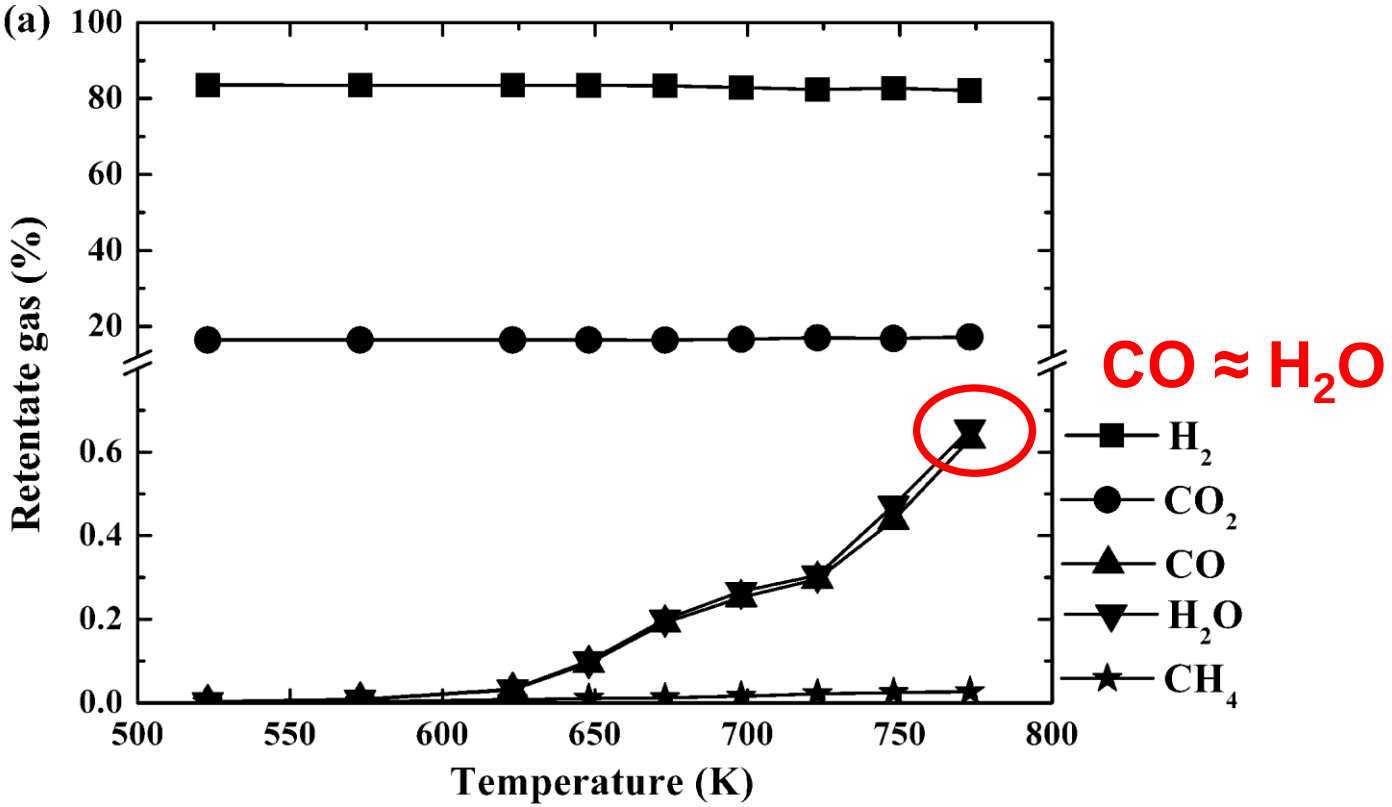
Influence of feed pressure



Carbon deposition

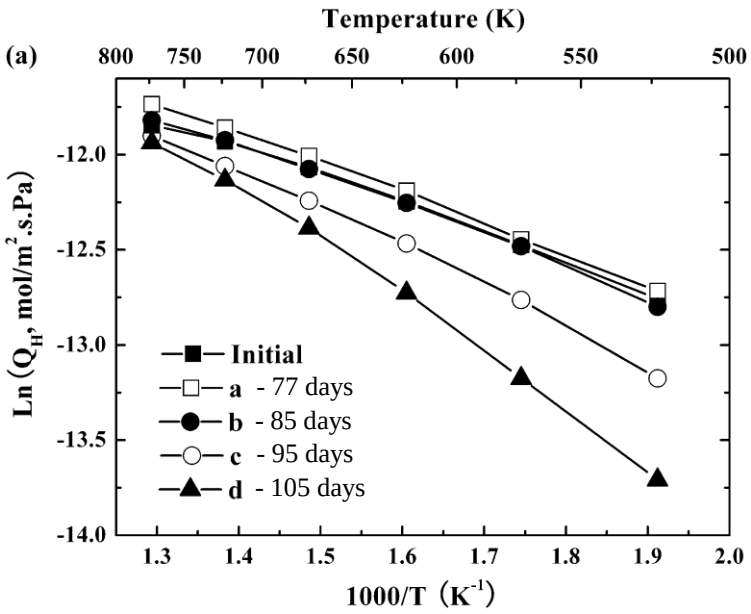
10% CO_2/H_2 mixtures at 450 ^oC and a feed flow rate of 2 Nl/min

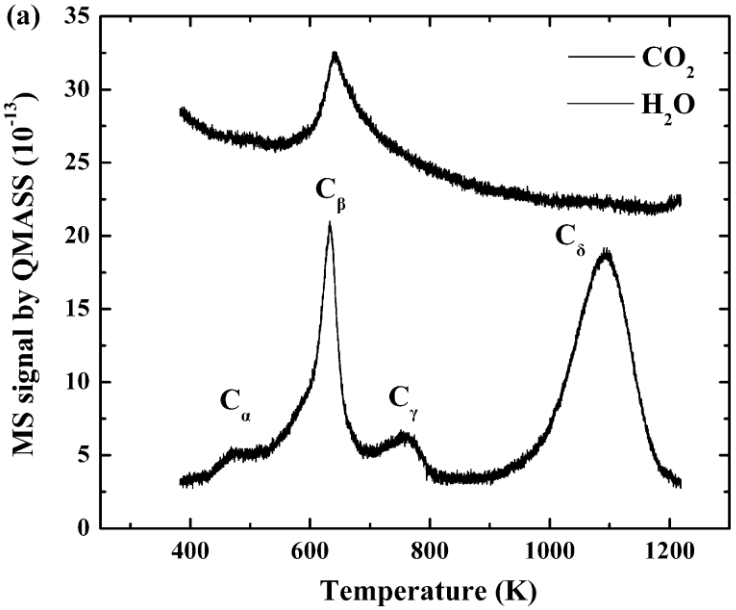
Influence of temperature



10% CO_2/H_2 mixtures at 2 bar(a) and a feed flow rate of 2 Nl/min

Evidence of carbon deposition





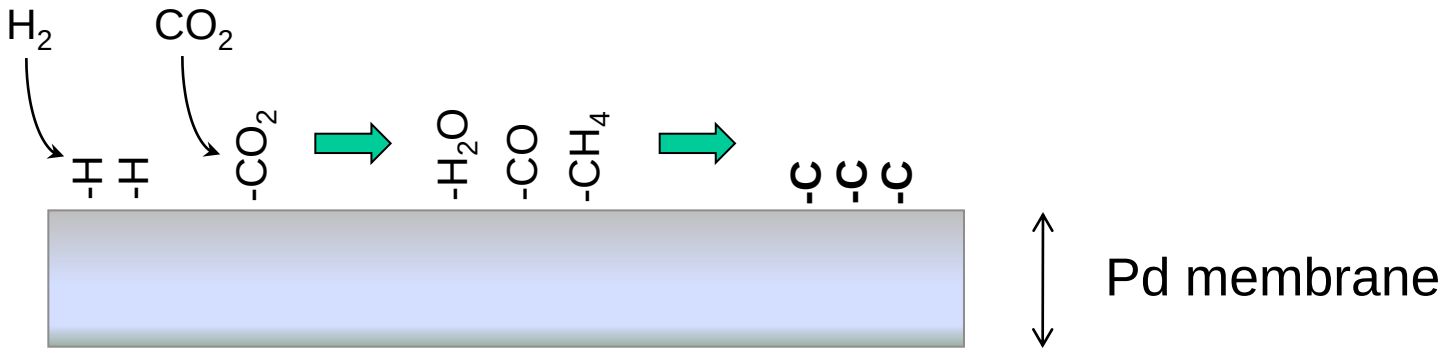
Pure H_2 permeance

TPO

(Temperature programmed oxidation)

Summary:

- Significant ***RWGS*** reaction and minor methane formation was observed on the Pd membrane surface during separation of CO_2/H_2 mixtures, which were enhanced with decreasing feed flow rate and increasing feed pressure, temperature and CO_2 concentration.
- Under certain conditions, also degradation of the membrane performance was observed, due to ***carbon deposition*** on the membrane surface.



H. Li et al., J. Phys. Chem. B, 112 (2008) 12182

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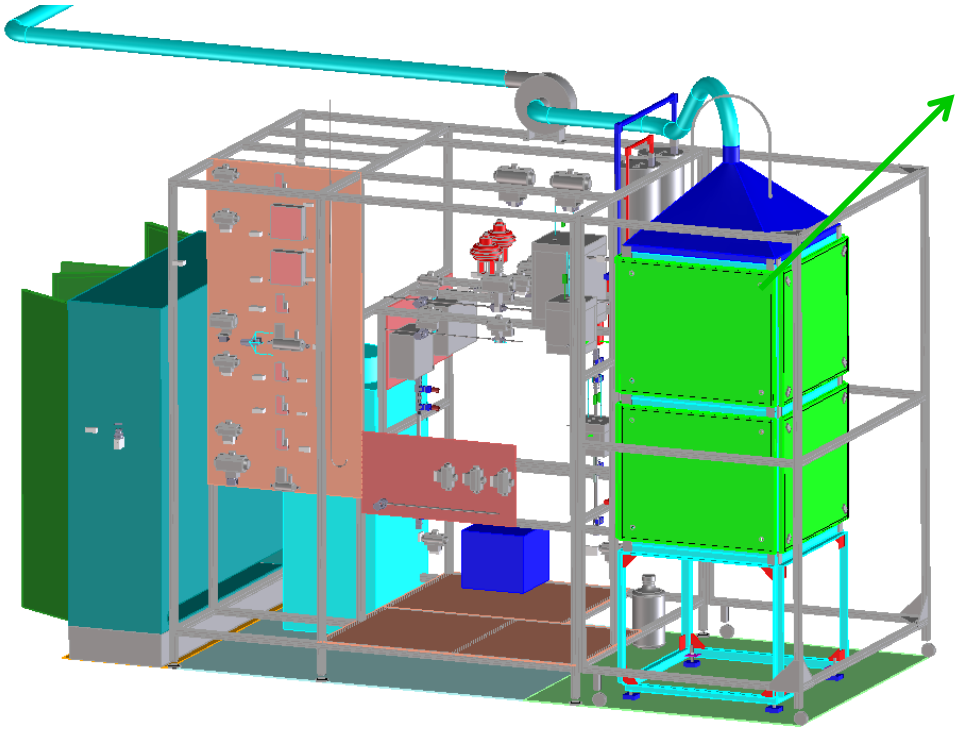
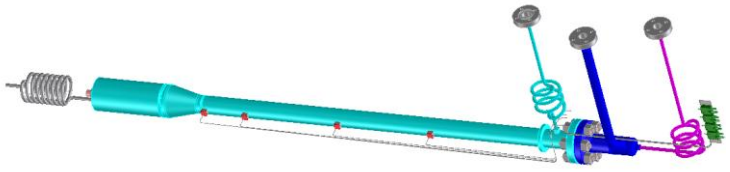
PDU overview

Test rig



Membrane reactor

8X 44 cm



1550 cm^2， 8.5 $Nm^3/hr\text{-}H_2$

Metal-graphite sealings

ECN

ECN

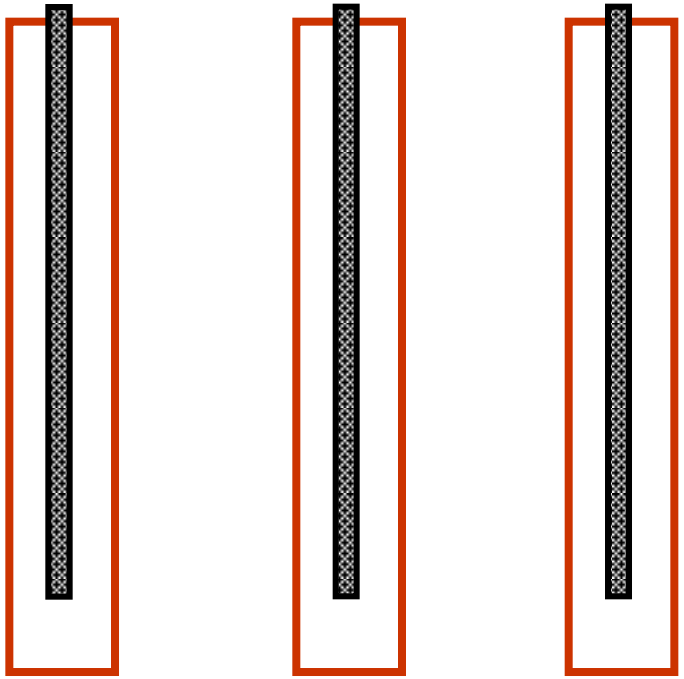
Electroless-plating (DICP)

Alumina tube

Membrane tube

WO 2005/065806 A1
WO01/63162A1, 2001

Separation only



3 Pd membranes

44 cm effective length, 5.6-6.2 µm Pd layer

H_2/N_2 sel. 4000

316Ti reactor tubes

no catalyst

Test program (separation of WGS mixtures)

Conditions:

- ✓ Temperature: 400 ^{o}C
- ✓ 4% CO, 19.2% CO_2, 15.4% H_2O, 1.2% CH_4 and 60.1% H_2
- ✓ P_{feed}: ***20-35*** bar(a), P_{perm}:***15*** bar(a)
- ✓ Feed: 30 l/min-90 l/min, sweep: 19.57 l/min

- **GRACE project (EU FP 6): upstream ATR@1000 ^{o}C + pre-wgs @350 ^{o}C**
- **Negative equilibrium conversion @400 ^{o}C**

RWGS on membrane surface

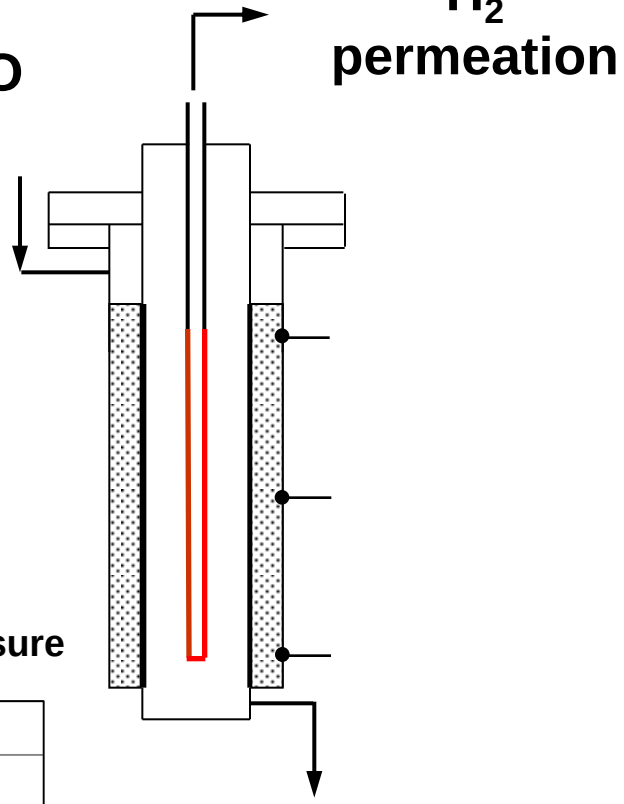
O_2/CO =4.8

Retentate side

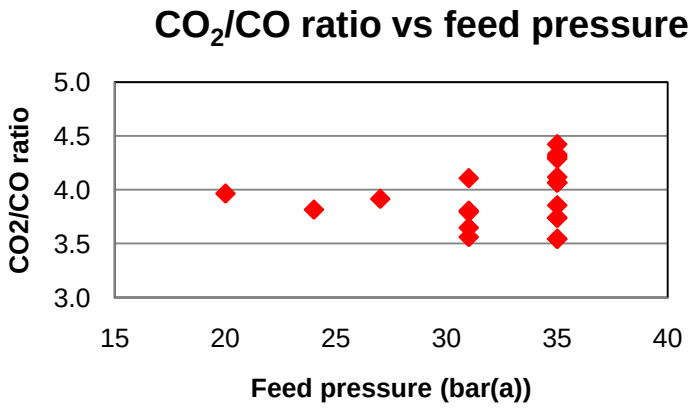
Equilibrium

3.7

3.4



CO_2/CO =3.7



H_2 permeance remained stable for 23 days

8×10^{-7} mol/m^2.s.Pa

Wet syngas feed mixture

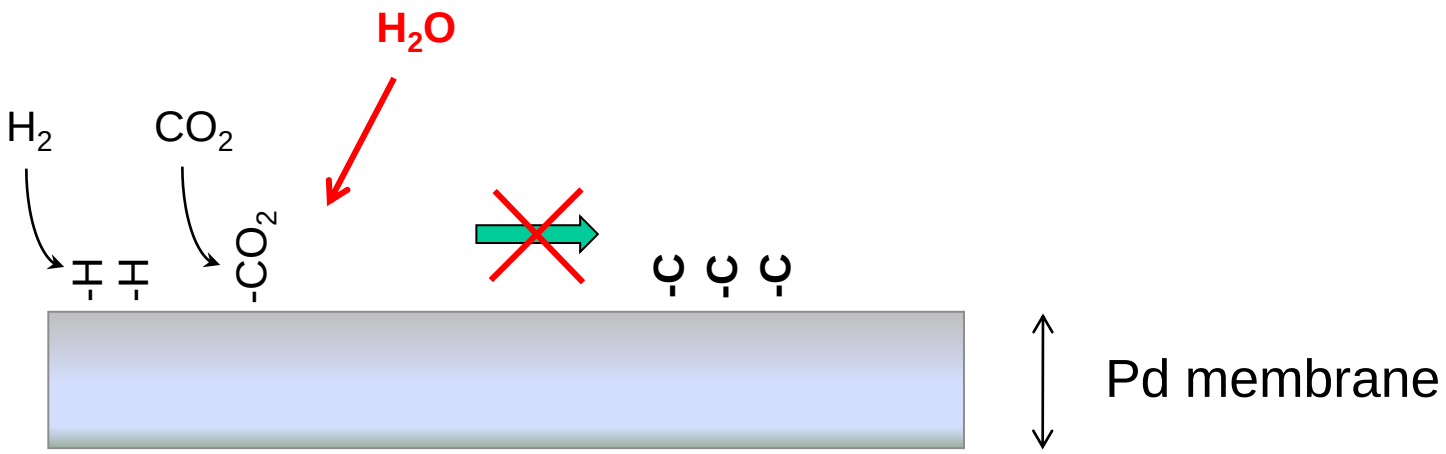
4% CO, 19.2% CO_2, 15.4% H_2O, 1.2% CH_4 and 60.1% H_2

Main conclusions:

- Significant *RWGS* reactions were observed during the separation of CO_2/H_2 mixtures and wet syngas mixtures respectively in a lab-scale and bench-scale setup.
- Under certain conditions, also degradation of the membrane performance was observed, due to *carbon deposition* on the membrane surface.

Main conclusions:

- In the presence of ***steam*** the membrane performance remained stable.



The Ministry of Science and Technology of China

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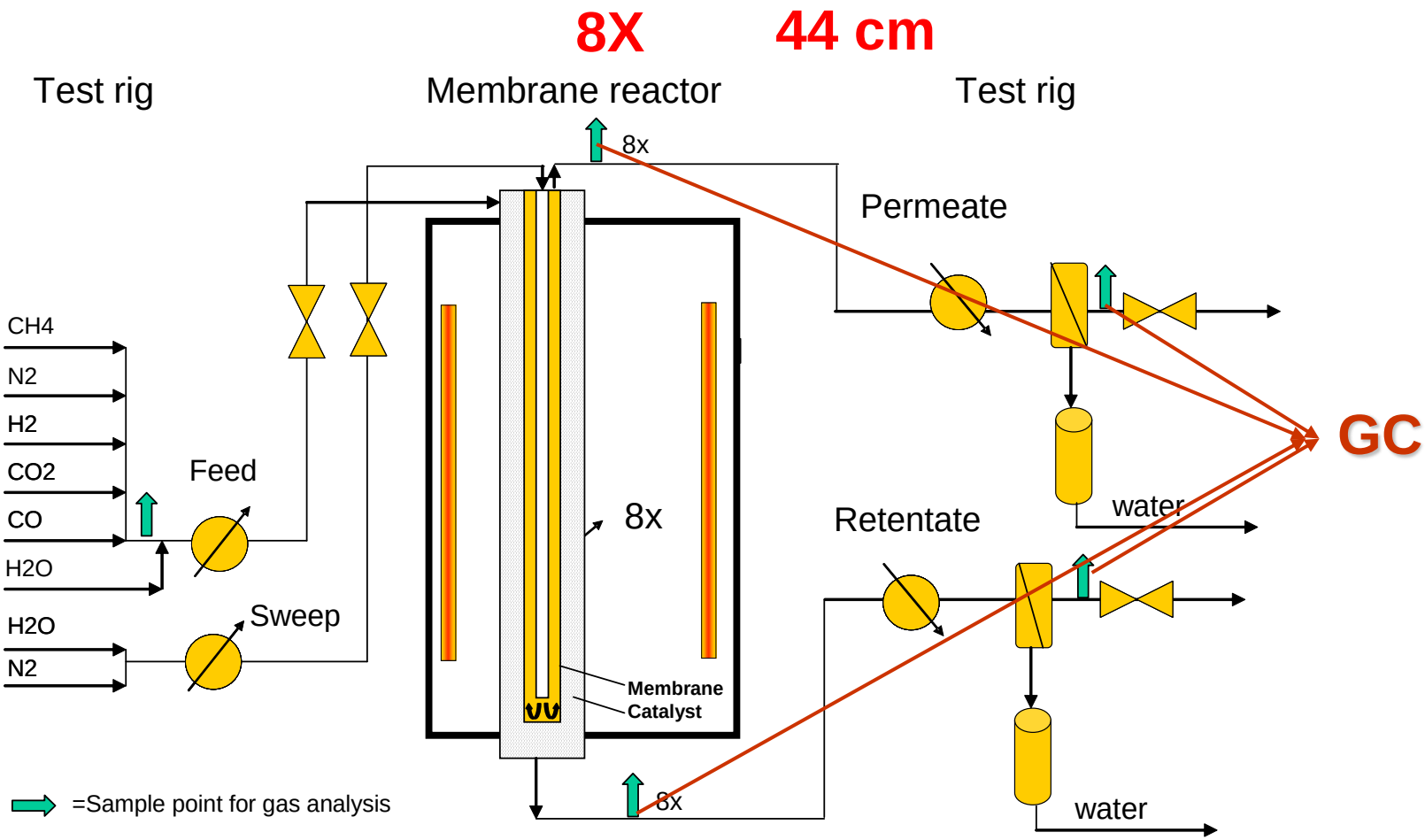
ECN

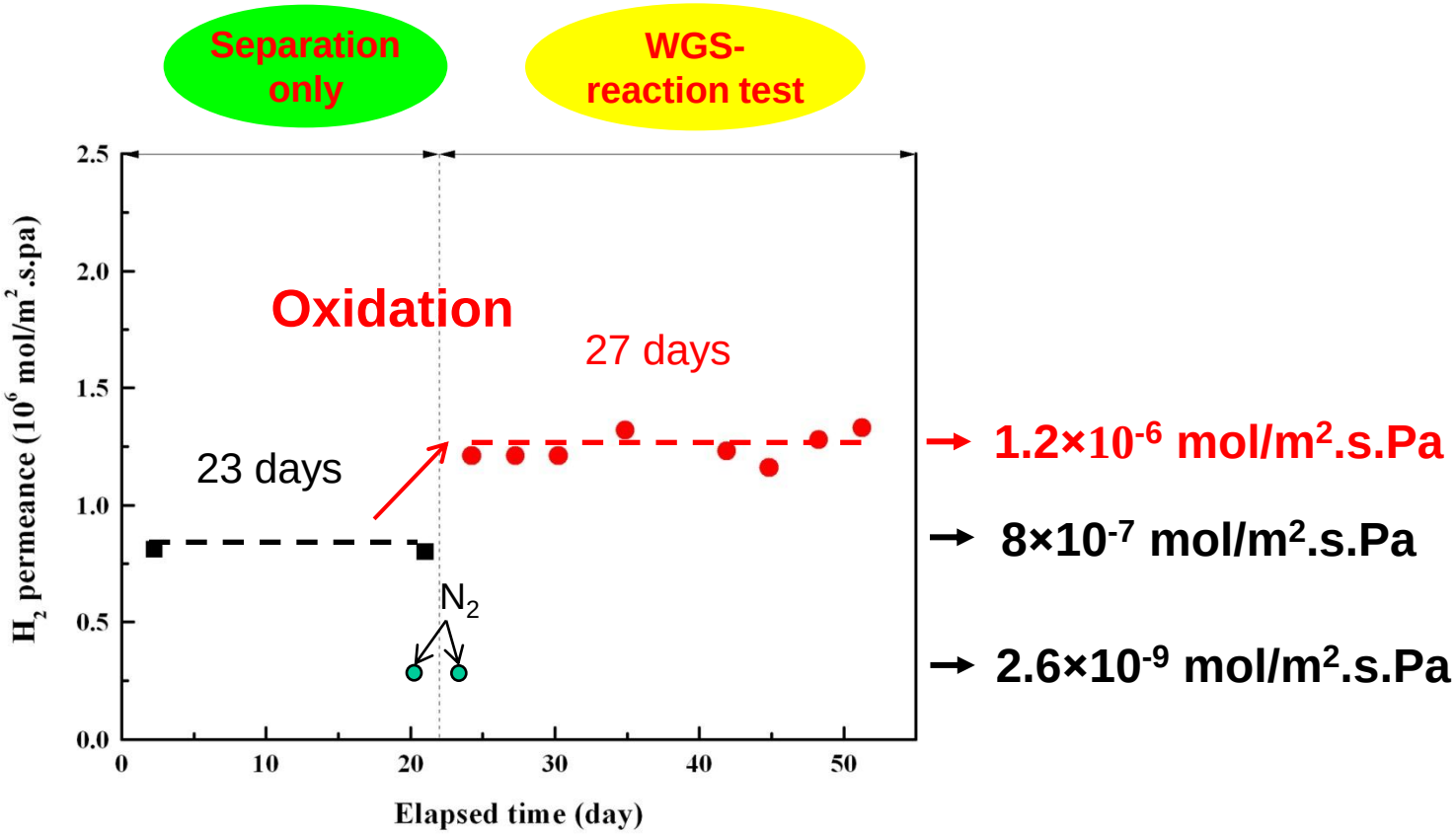
Energy research Centre of the Netherlands

Thank you for your attention



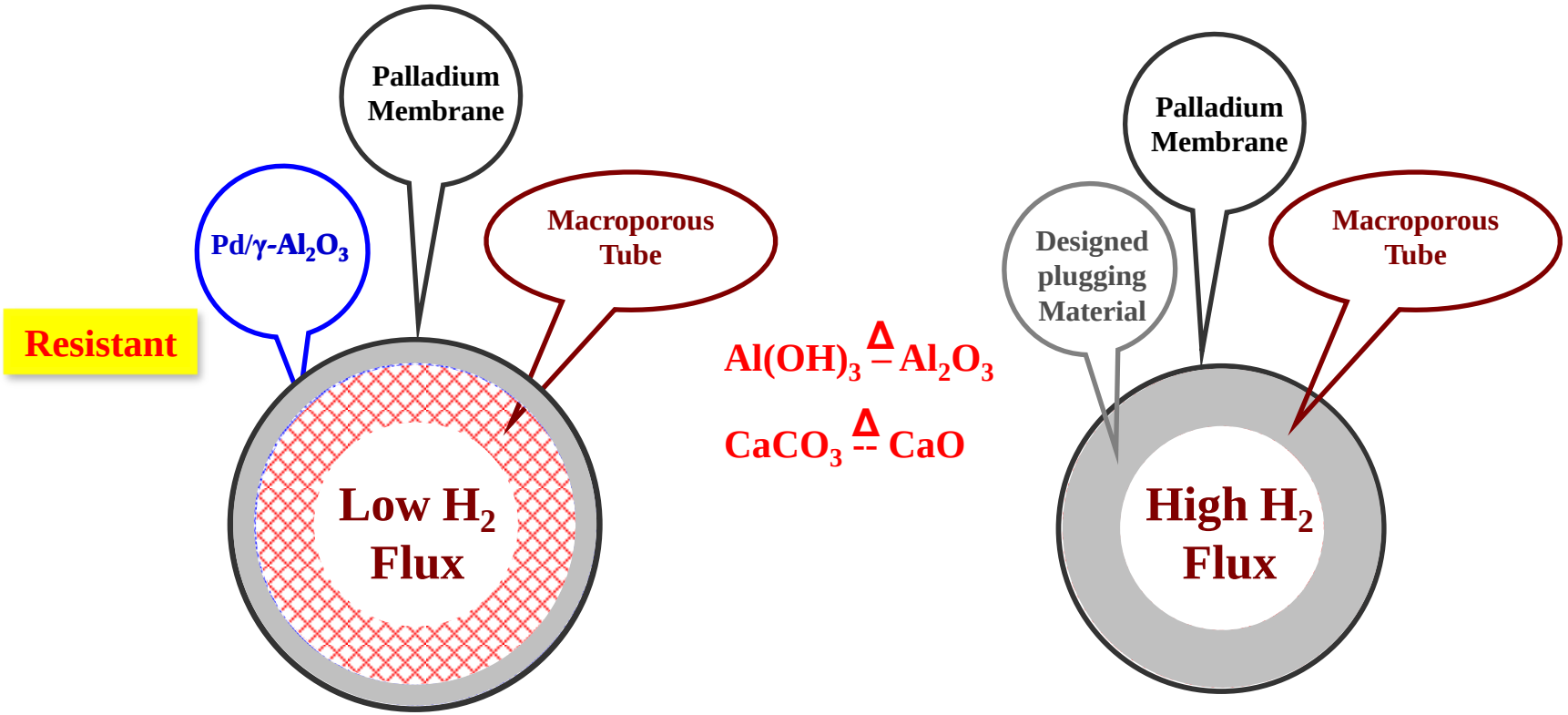
1550 cm^2， 8.5 Nm^3/hr-H_2

Pure H_2 permeance, *separation & shift* test



N_2 permeance remained unchanged after catalyst loading

DICP-proprietary method to prepare high flux Pd membranes



WO 2005/065806 A1