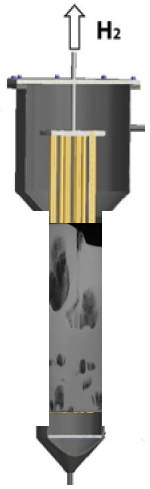
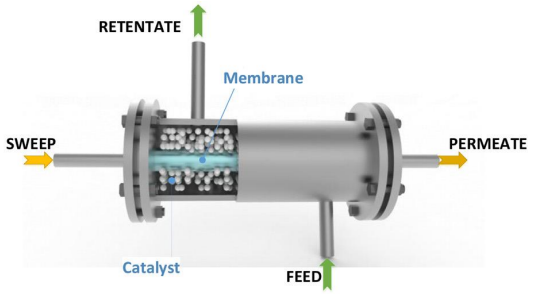
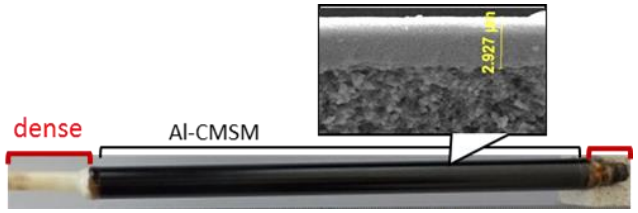
Membranes for hydrogen separation and membrane reactors



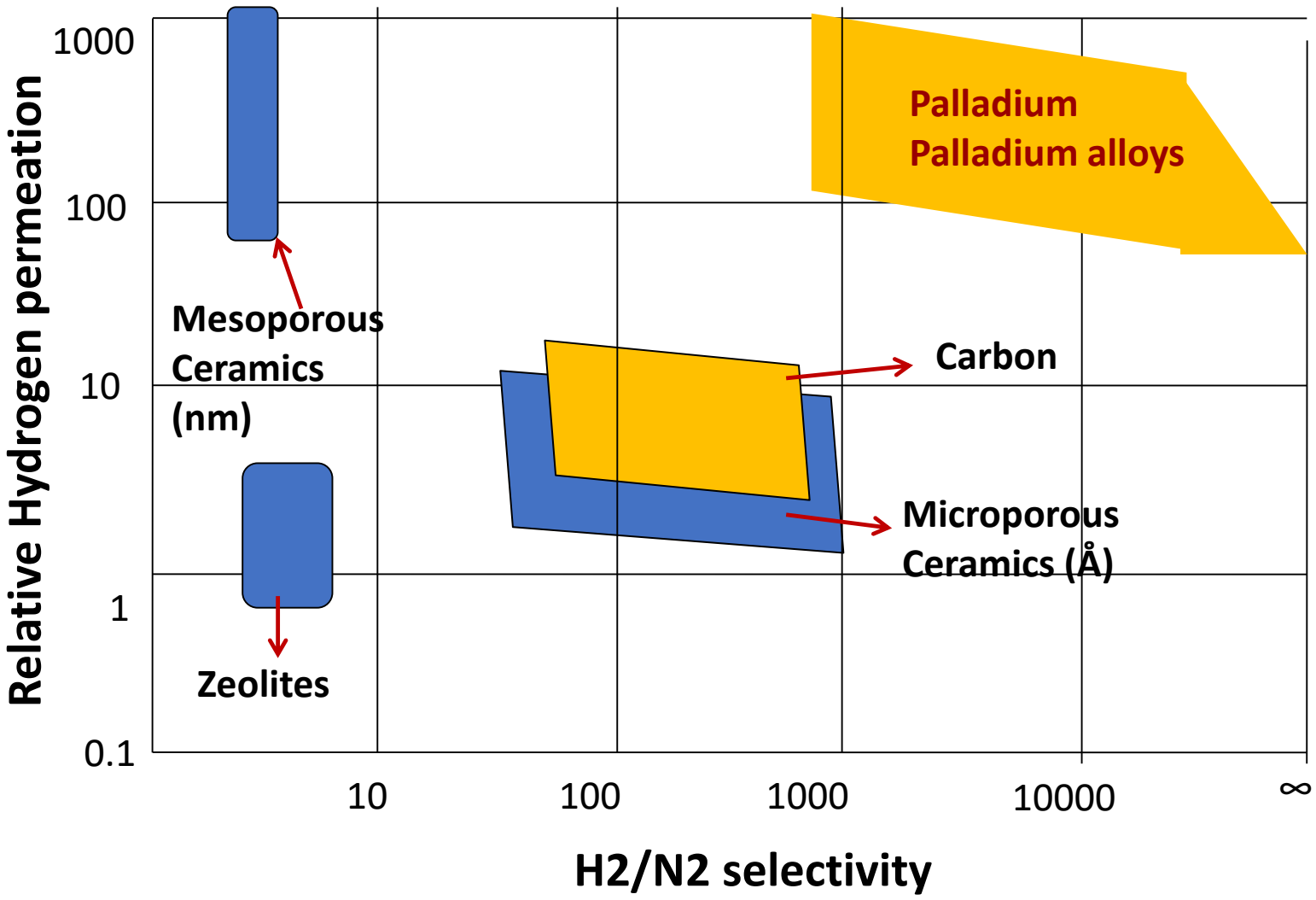




tecnalia Inspiring Business

David Alfredo Pacheco Tanaka
alfredo.pacheco@tecnalia.com

Membranes for hydrogen separation



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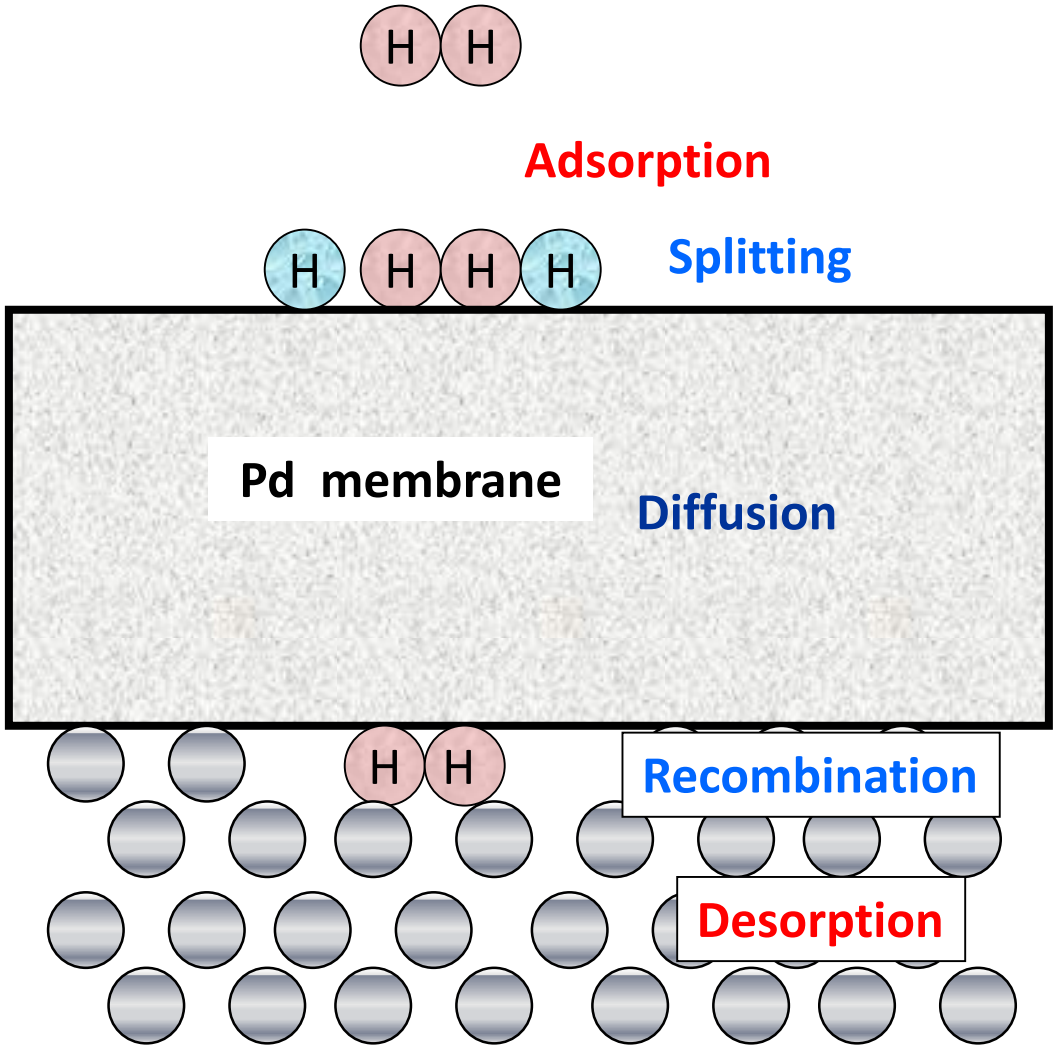
H2 permeation in Pd membranes

Ultra-thin membranes

-Surface interference
- H_2 splitting

resistance of support



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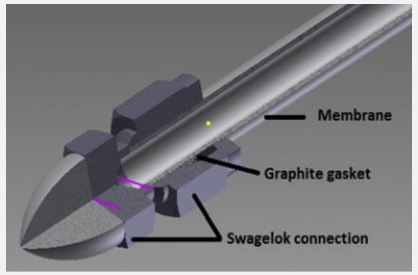
Thin supported Pd Membranes < 5 µm

Ceramic support

Leak zone

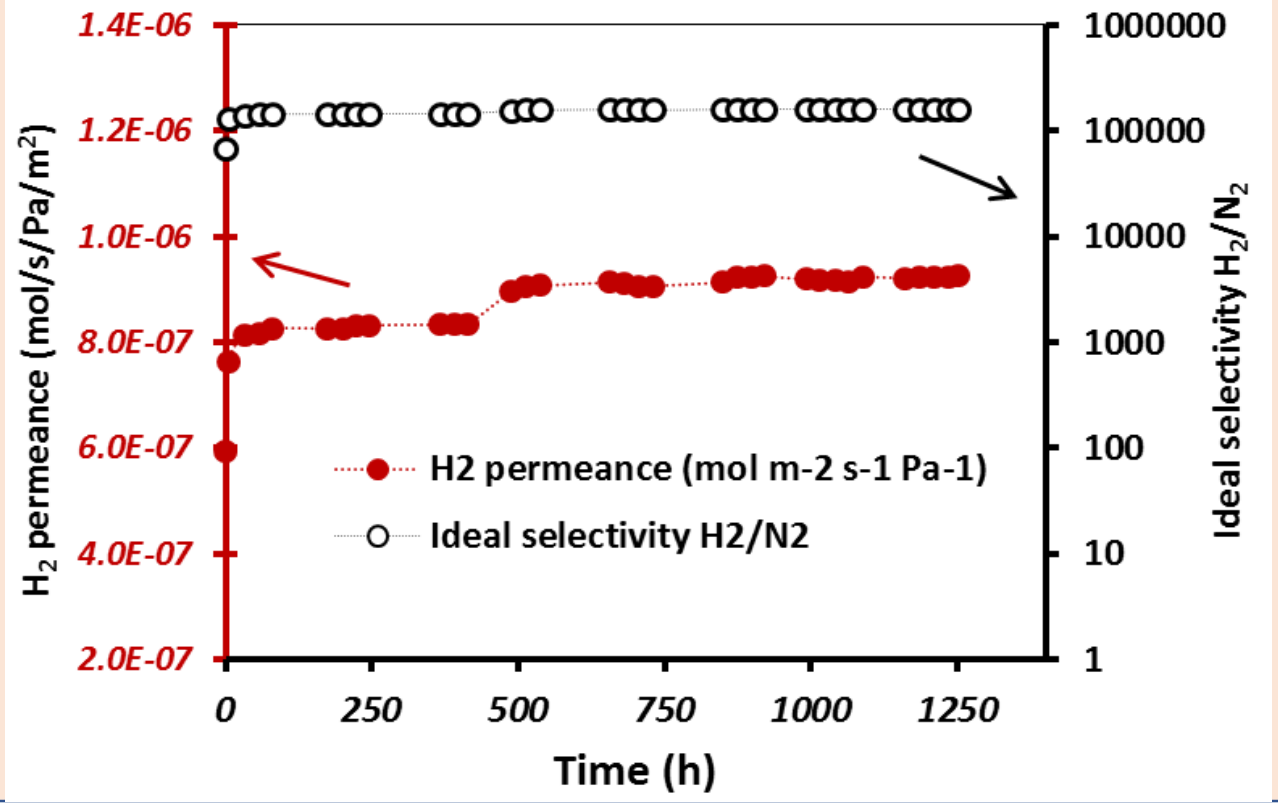


Metallic support

No Leak

No Leak

Long term permeation test at 400 °C



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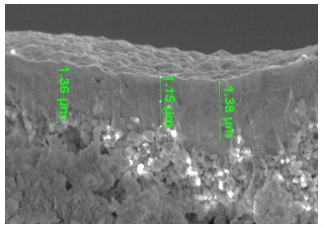
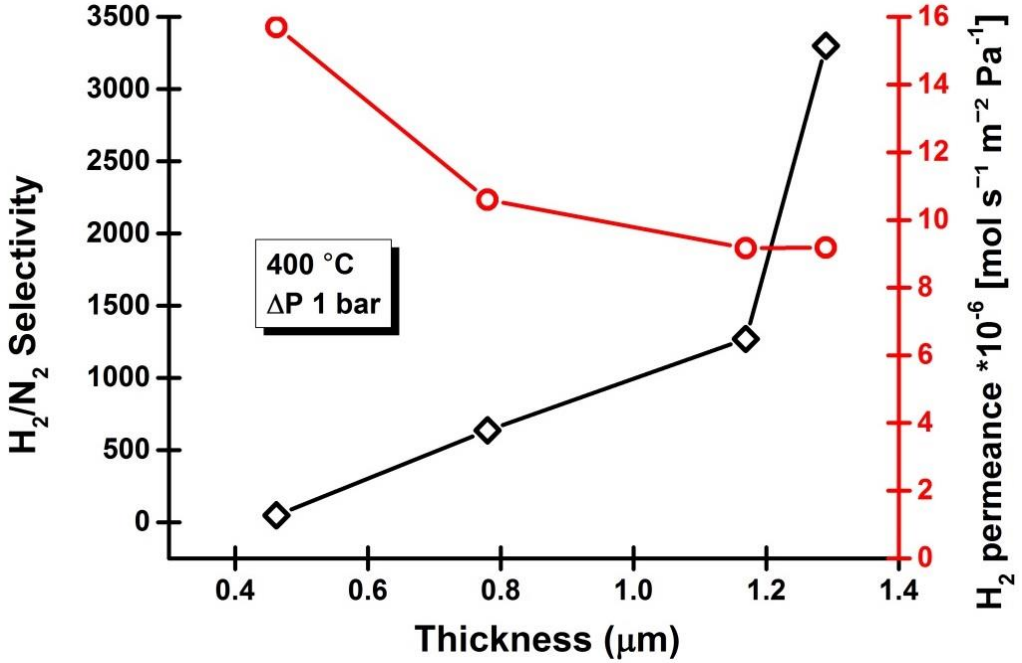
Ultra-thin PdAg membranes

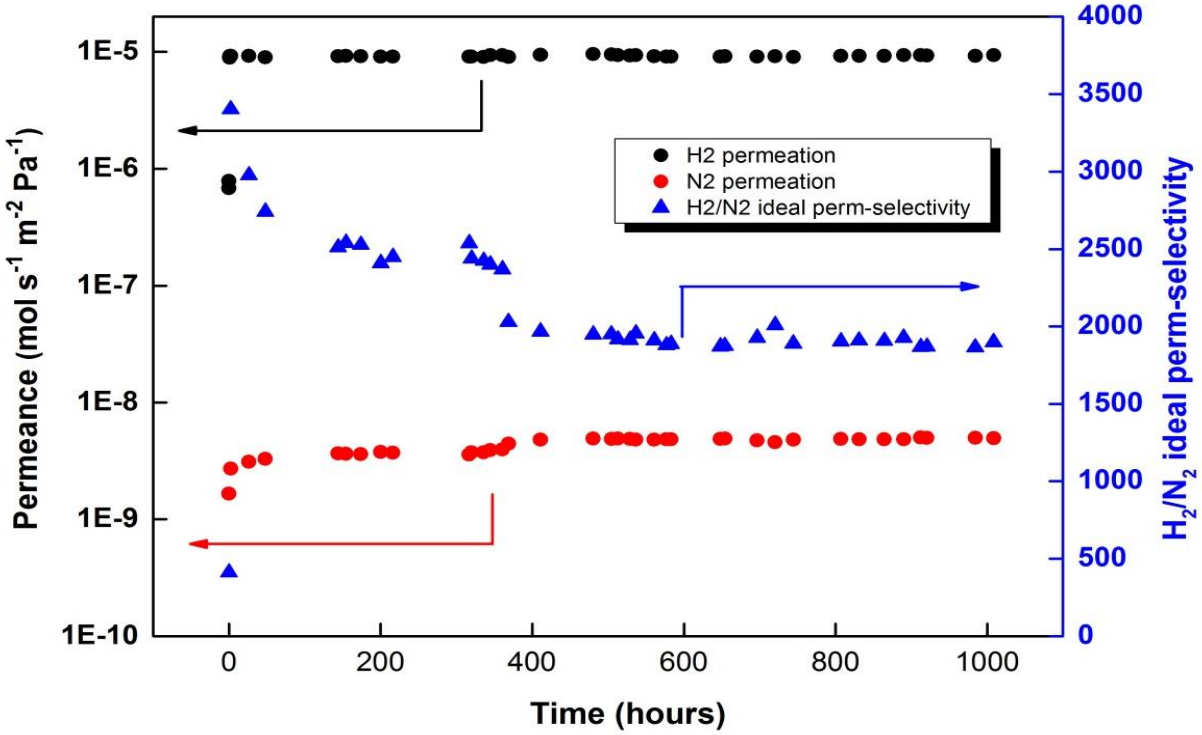
Tubular alumina Support 10/7



1.3 µm PdAg at 400 °C 1 bar

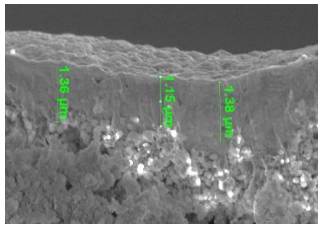
H_2 permeance and H_2/N_2 selectivity





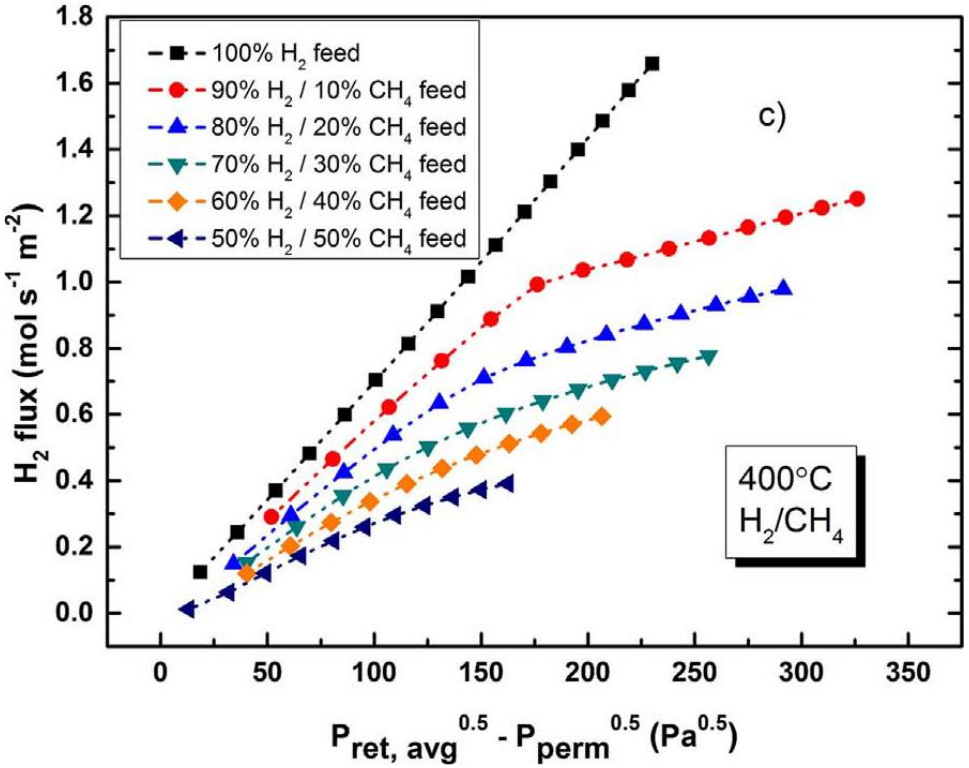
J. Melendez… J. Membr. Sci 528 (2017) 12-23

Effect of the concentration of H_2

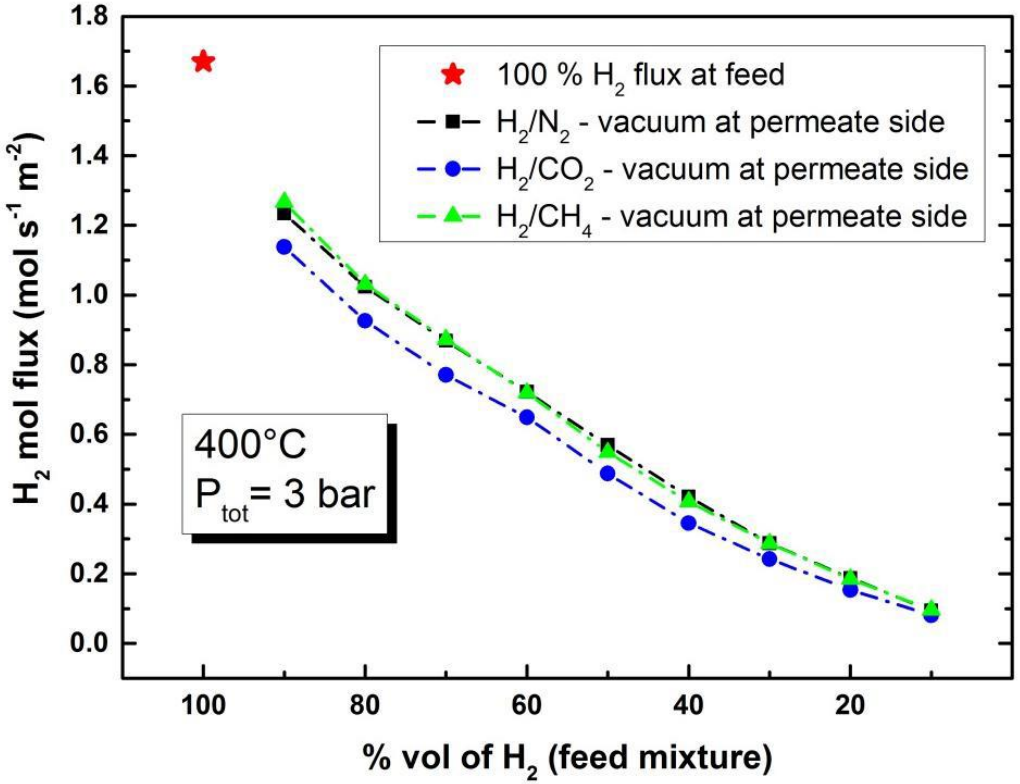


1.3 µm PdAg at 400 °C

H_2/CH_4 and H_2 partial pressure



% of H_2 (total pressure 3 bar)

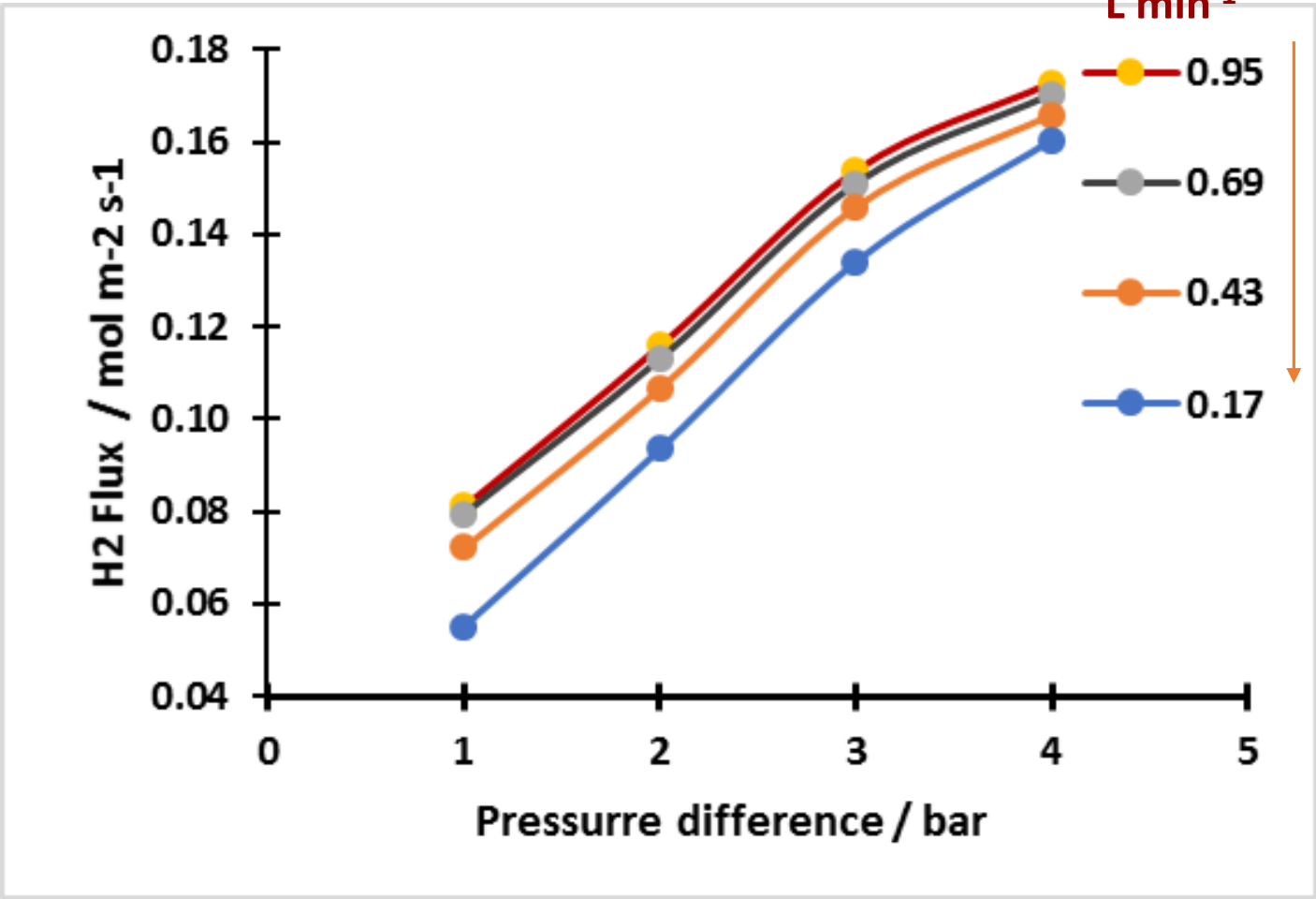


J. Melendez… J. Membr. Sci 528 (2017) 12-23

Inlet gas: 50% H_2- 50% CH_4
Total flow rate:2 l/min
Sweep gas permeate side

Effect of the sweep gas flow in the H2 flux at 400°C

14/7 Finger type



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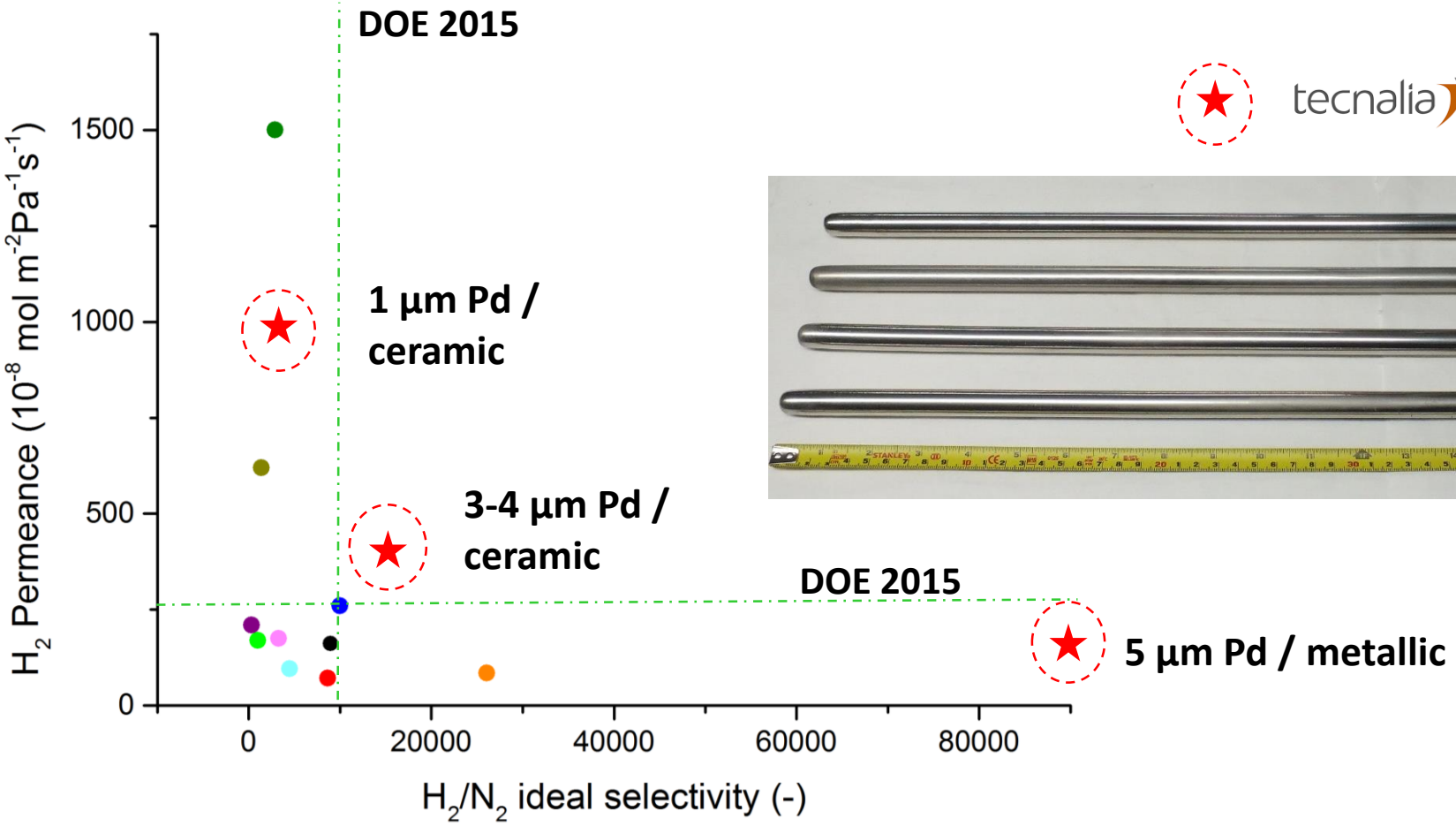
Comparison between other R&D and TECNALIA membranes

DOE 2015 target : Purity > 99.99% >100 $Nm^3/m^2.h$ (6.9 bar ΔP)



Gallucci et al., Chem. Eng. Sci 92 (2013) 40–66

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EU projects on membrane reactors for H_2 production

Water gas shift reaction (WGS)

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Steam reforming of methane (SMR)

$$CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2$$

Ethanol steam reforming

$$C_2H_5OH + 3\,H_2O \rightleftharpoons 2\,CO_2 + 6\,H_2$$

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H_2 production

Steam Methane Reforming / Water Gas Shift

		$\Delta H_{600\,C}$ Kj/mol	Favored Temp	Favored Pressure
Steam Methane Reforming				
$CH_4 + H_2O \rightleftharpoons CO_2 + 3\,H_2$		223.5	High	Low
Water gas shift				
$CO + H_2O \rightleftharpoons CO_2 + H_2$		- 36.1	Low	Independient

$$CH_4 + H_2O \longrightarrow CO_2 + H_2$$

Pd membrane

$$H_2$$

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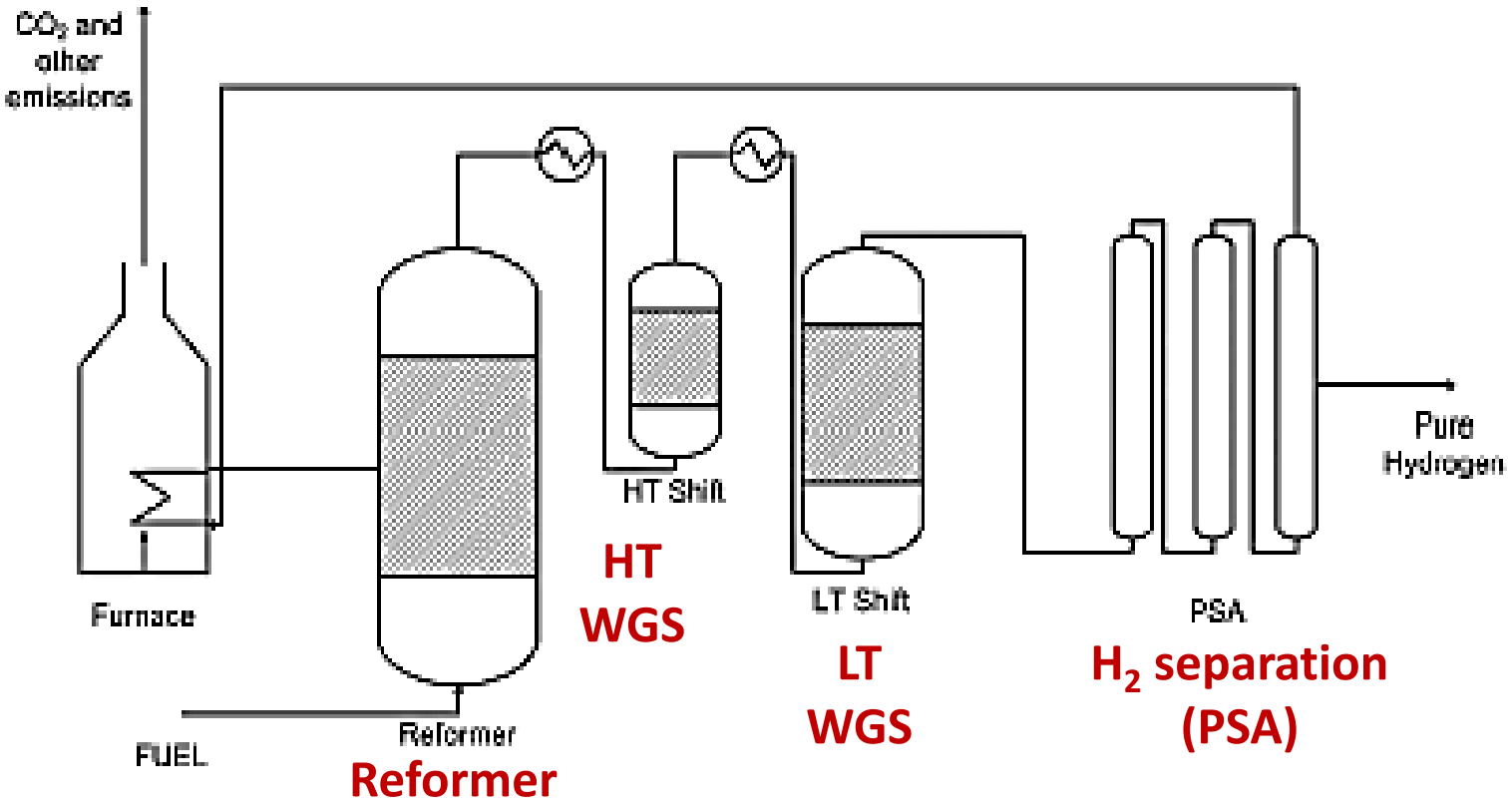
H_2 production: Conventional Steam Methane Reforming



F. Galucci ….. Chemical Engineering Science 92 (2013) 40–66

Steam reforming at 850 – 900 ° C

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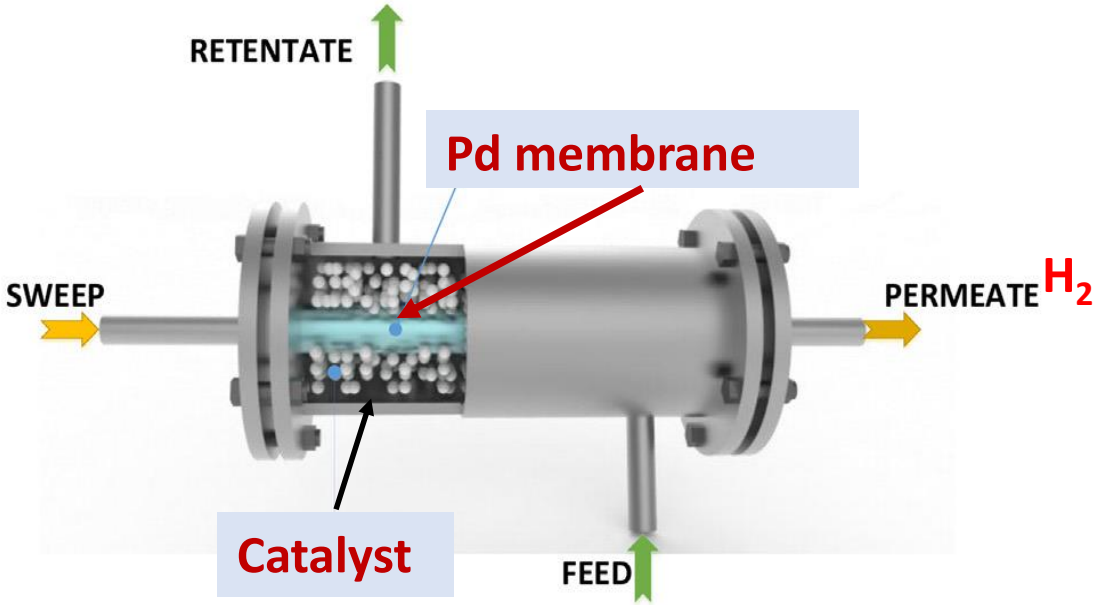
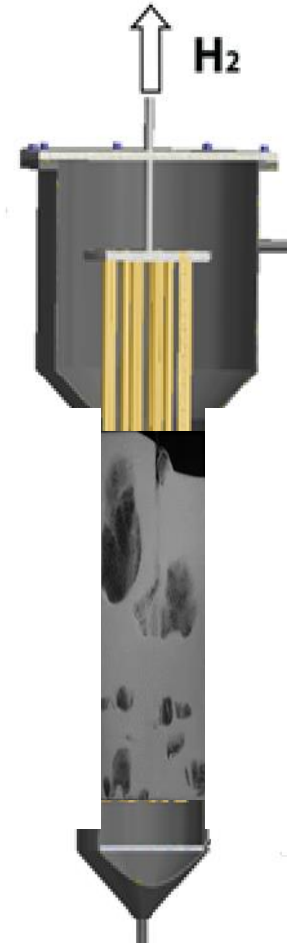
H_2 production: Membrane reactor

Packed bed



Fluidized bed



- Bed to membrane mass transfer limitations (concentration polarization)
- Pressure drop along the reactor
- Possible intra-particle mass transfer limitation
- Hot spots in highly exothermic reactions

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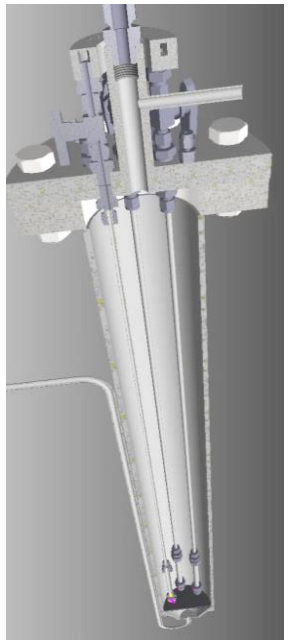
Water Gas Shift membrane reactor (II) Fluidized bed



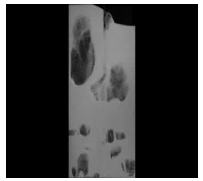
Temperature 400 °C

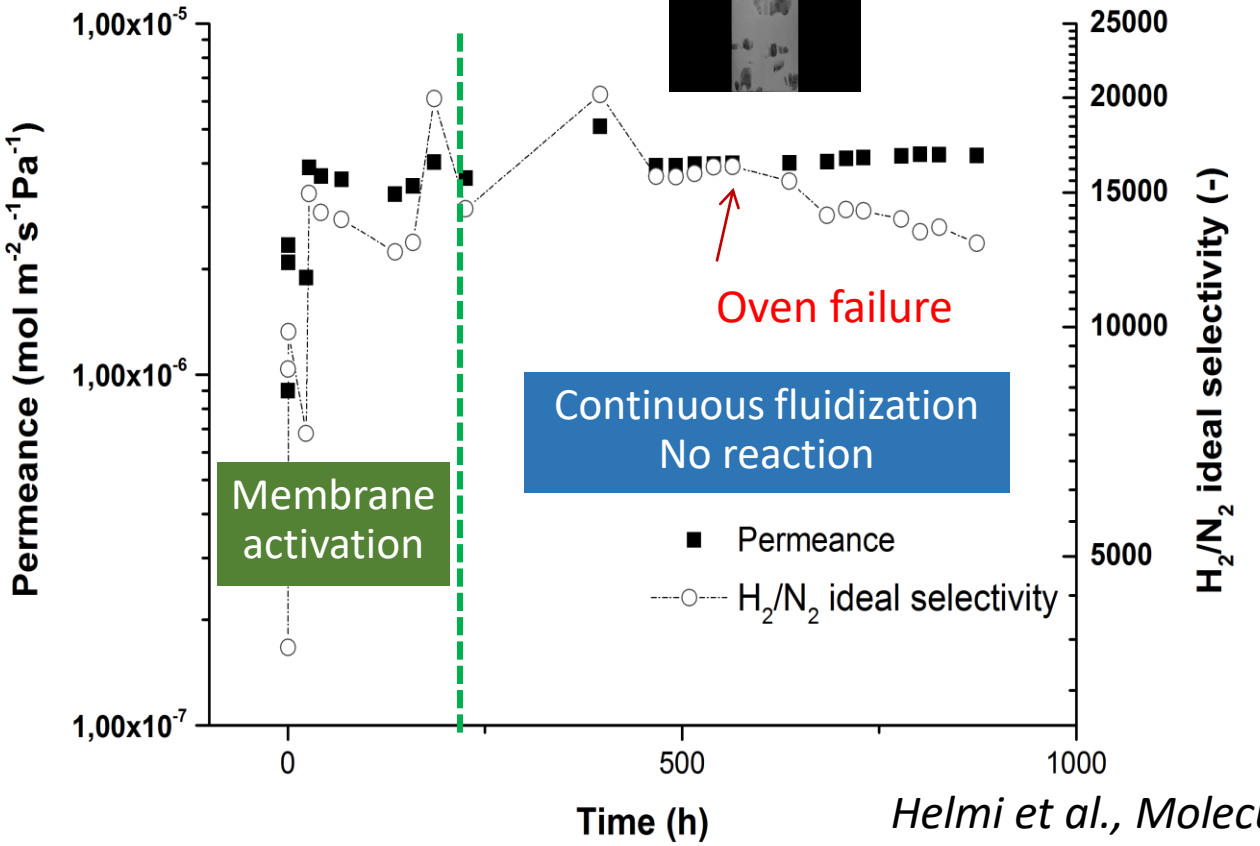
$P_{permeate}$ 1bar, $P_{retentate}$ 2 bar

Feed 10NL/min pure H_2

Catalyst: 2% Pt/Al_2O_3 180 µm 88g

Al_2O_3 filler 160 µm 866 g





Helmi et al., Molecules 2016, 21, 376

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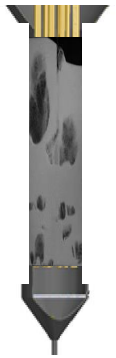
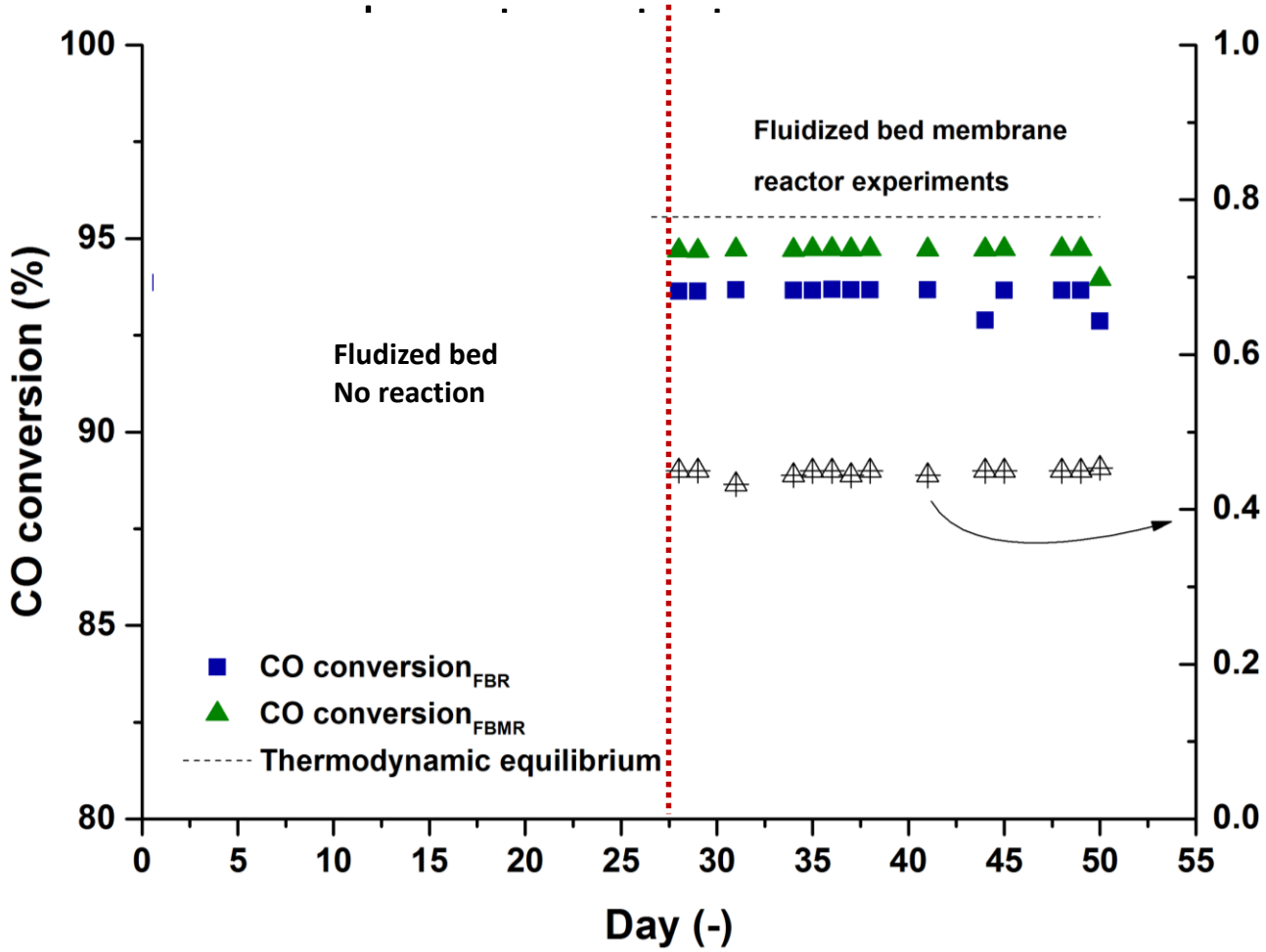
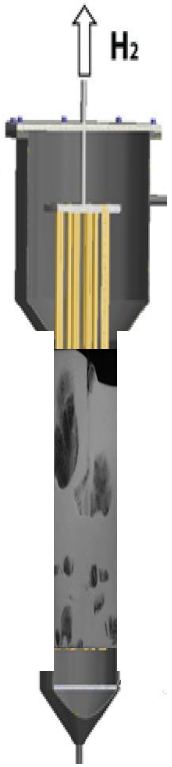
Water Gas Shift membrane reactor (III) Fluidized bed Reactor

Fluidized bed membrane reactor (FBMR) vs Fluidized bed reactor (FBR)



FBR





FBMR

Helmi et al., Molecules 2016, 21, 376

DEMCAMER
Catalytic Membrane Reactors

SEVENTH FRAMEWORK PROGRAMME

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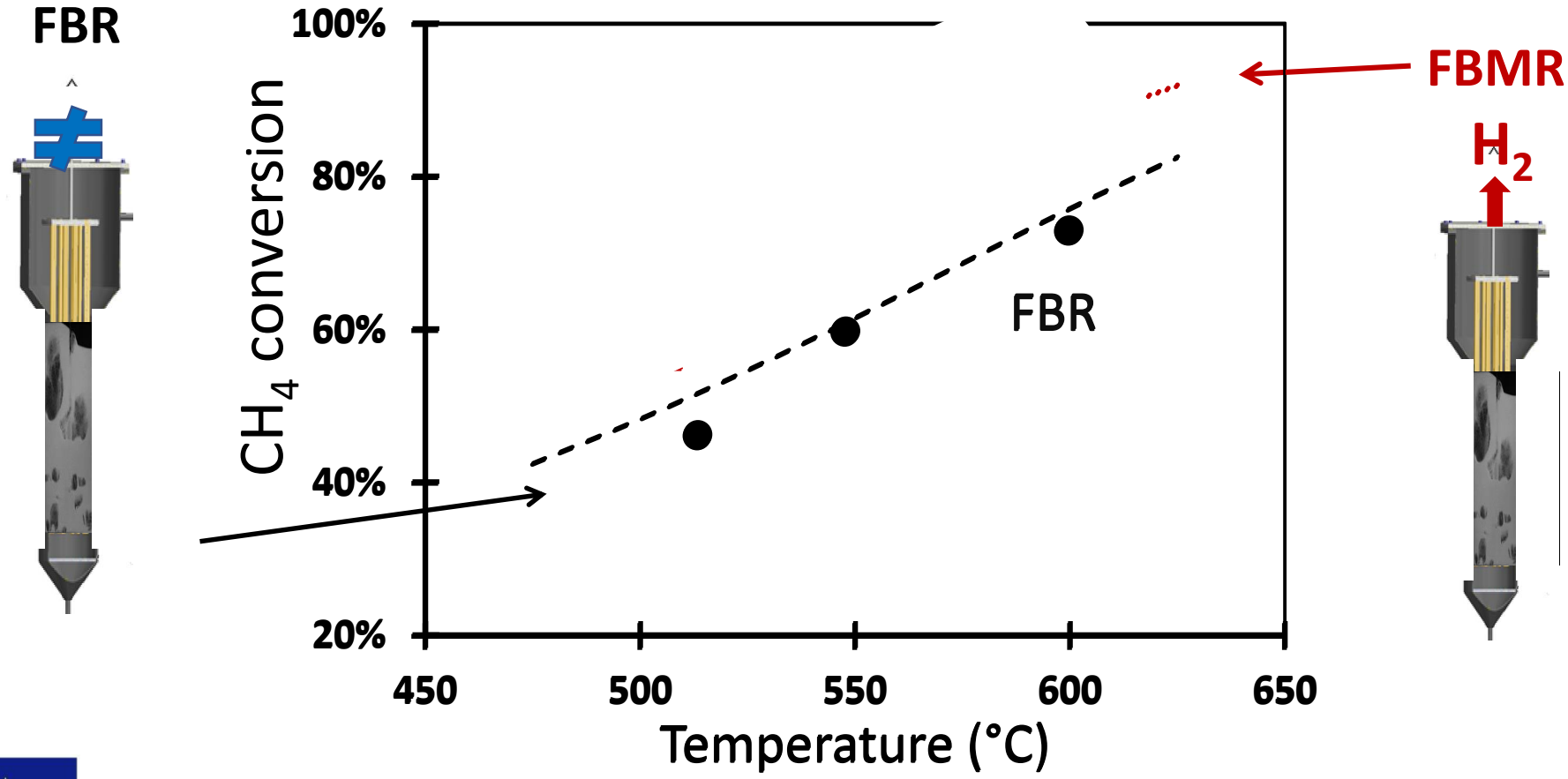
Autothermal Methane Reforming membrane reactor

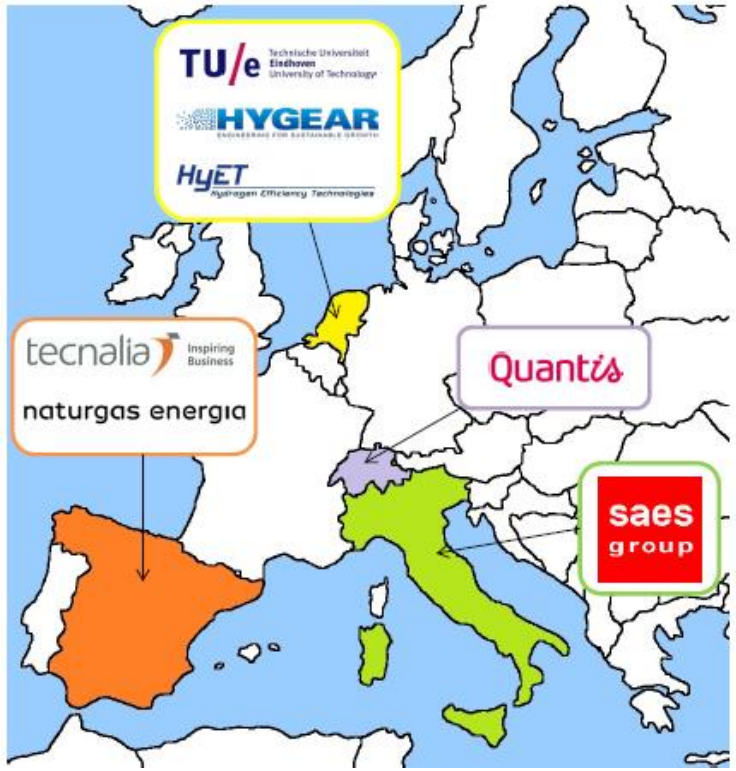
Fluidized bed membrane reactor (FBMR) vs Fluidized bed reactor (FBR):
CH_4 conversion as a function of the temperature



Ethanol steam reforming

$$C_2H_5OH + 3\,H_2O \longleftrightarrow 2\,CO_2 + 6\,H_2$$

Development of a hydrogen separation system capable of targeting low (2-10%) H_2 blends in natural gas grids



Membranes for hydrogen separation

Pd membranes

Carbon molecular sieves Membranes

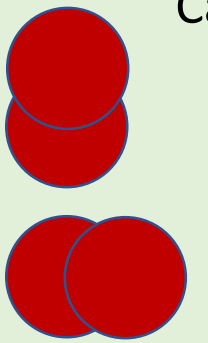
Molecular sieves membranes

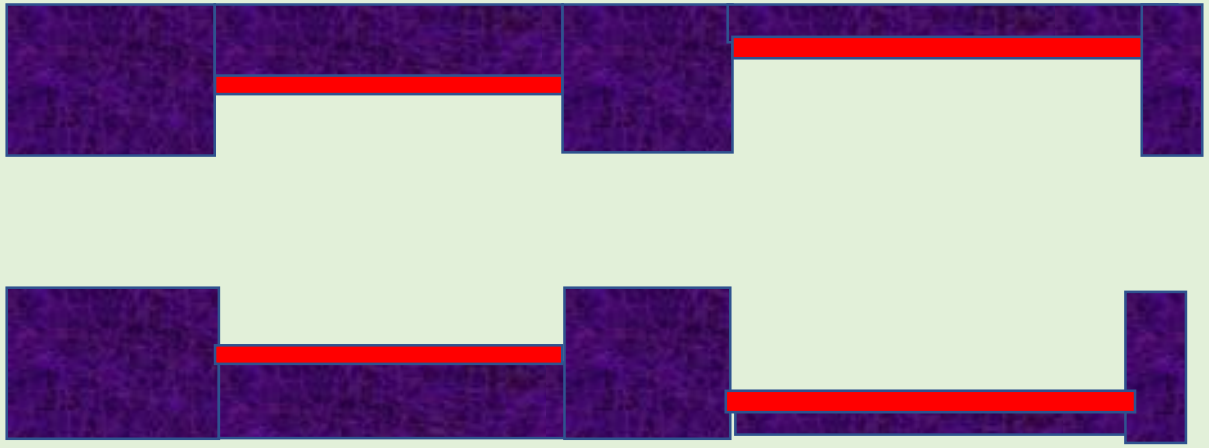
Zeolite membranes

- Difficult to obtain crack-free
- Intercrystallite voids affecting selectivity

Carbon Molecular sieves membranes

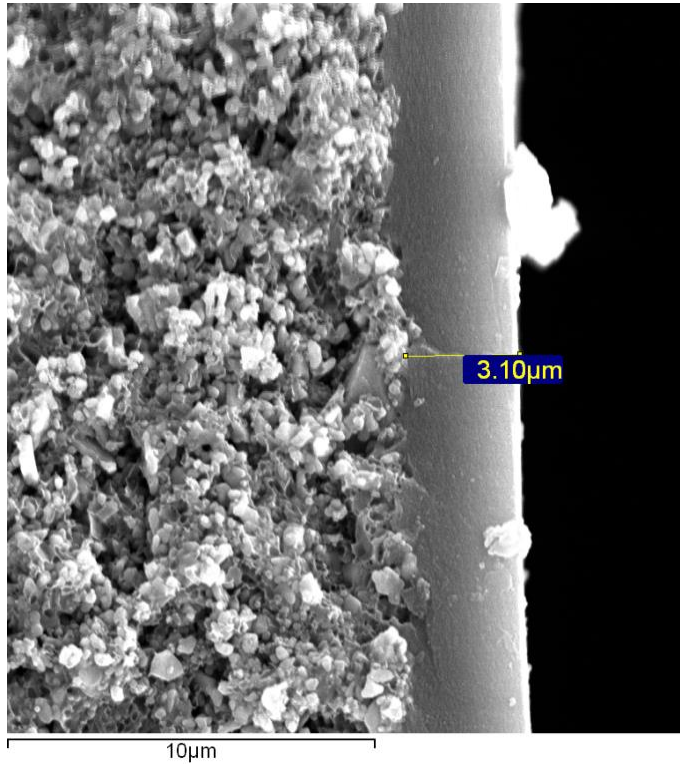
Carbonization of a polymer precursor under inert atmosphere or vacuum

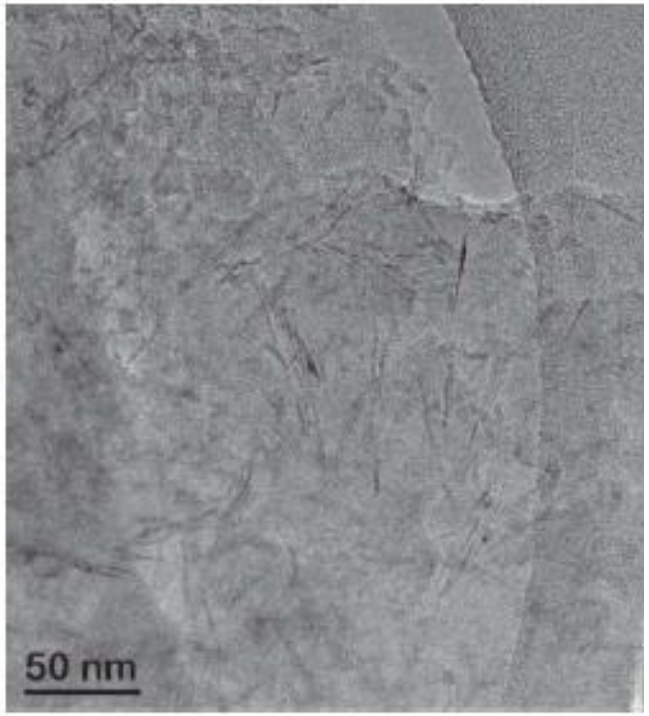




micropores (adsorption diffusion) 0.6- 2 nm
ultramicropores (molecular sieving) < 0.6 nm

SEM and TEM of the Al-CMSM





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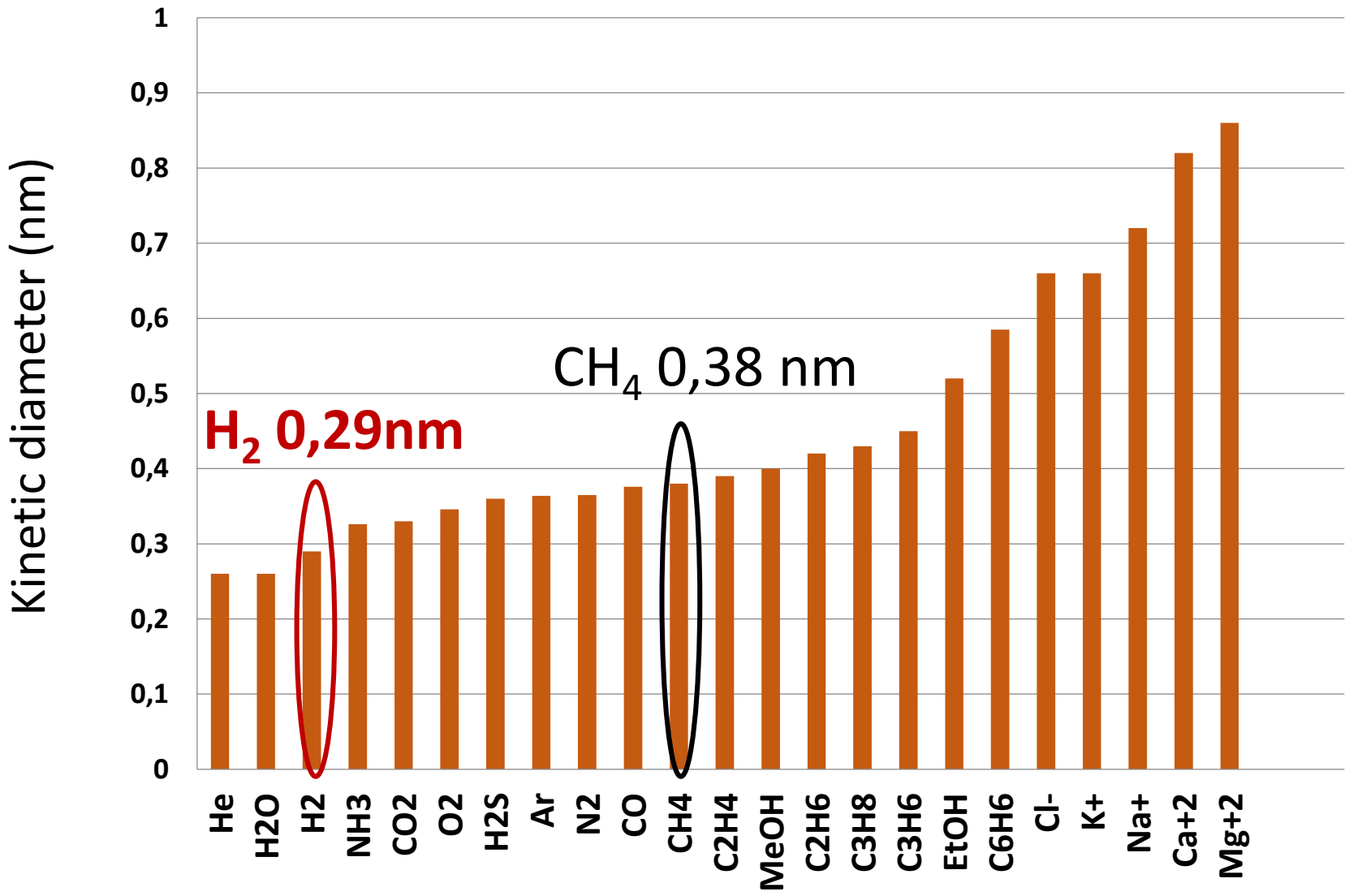
Kinetic diameter of various gases and ions



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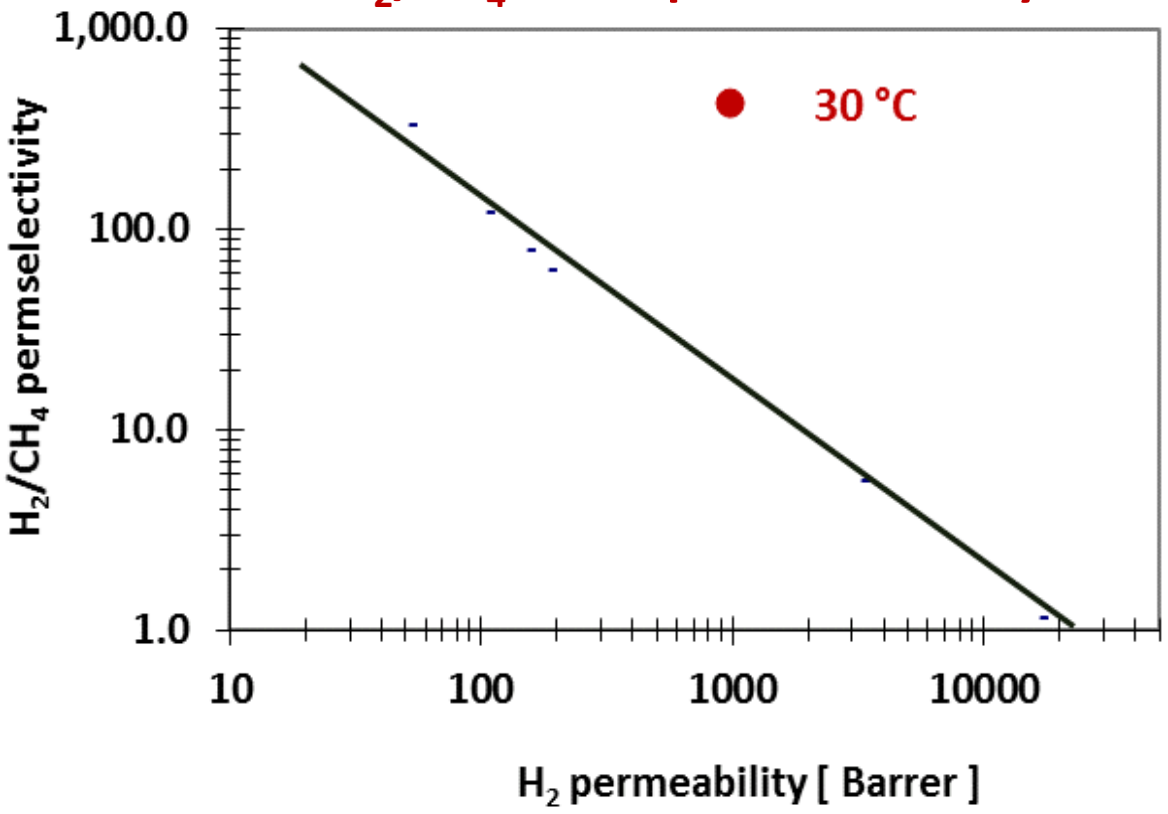
H_2 and CH_4 single gas permeation

Activated at 100 °C

Robeson plot

H_2/CH_4 Ideal permselectivity



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Many Thanks for your attention

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FCH

BIONICO

RE4CELL

Fluid CELL

FERRET

HyGrid

DEMCAMER
Catalytic Membrane Reactors

EUSKO JAURLARITZA
GOBIERNO VASCO

MALTA