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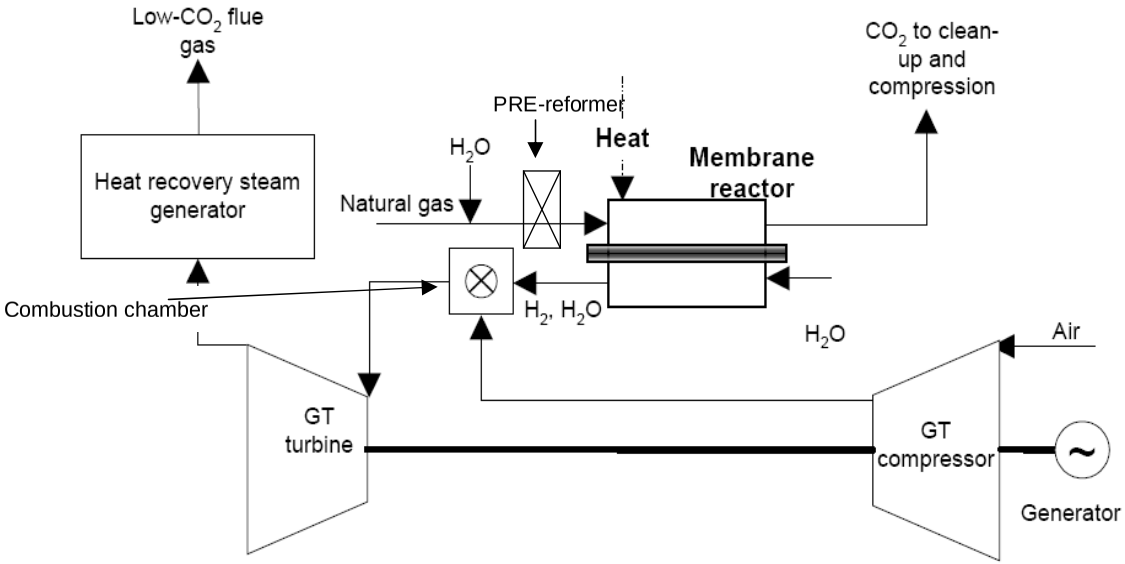
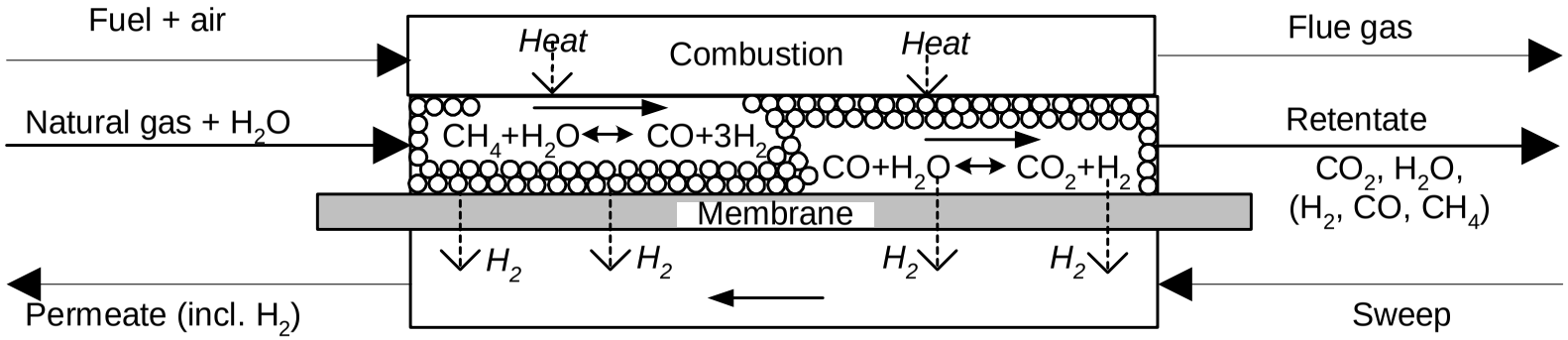
Hydrogen Membrane reactors for pre-combustion CO_2 capture

- **Develop, and evaluate the potential of Pd H_2 membrane reactors for CO_2 capture in natural gas combined cycle power plant**



Integrated membrane reformer combined cycle

Membrane principle



Steam reforming: $CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ (ΔH = 206 kJ/mol)

Water-gas shift: $CO + H_2O \rightleftharpoons H_2 + CO_2$ (ΔH = - 41 kJ/mol)

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

- Parallel reaction and H_2 removal shift equilibrium towards high conversions
- Favorable heat integration:
  - No low temperature WGS and separation sections needed
  - Reforming at decreased temperature

Process conditions in the membrane reformer

Feed pressure 45 bar: available from the grid

Permeate pressure 5-10 bar: driving force for permeation

Sweep for lowering the membrane surface area

Steam to carbon ratio ≤ 3

Use sufficient Temperature for favorable kinetics :

Trade off:

1) High T to boost permeance and limit costly membrane surface area and to obtain high catalyst activity

2) Too high T increases design costs and limited thermal stability of membrane materials

⇒ **focus on 500 – 600℃**

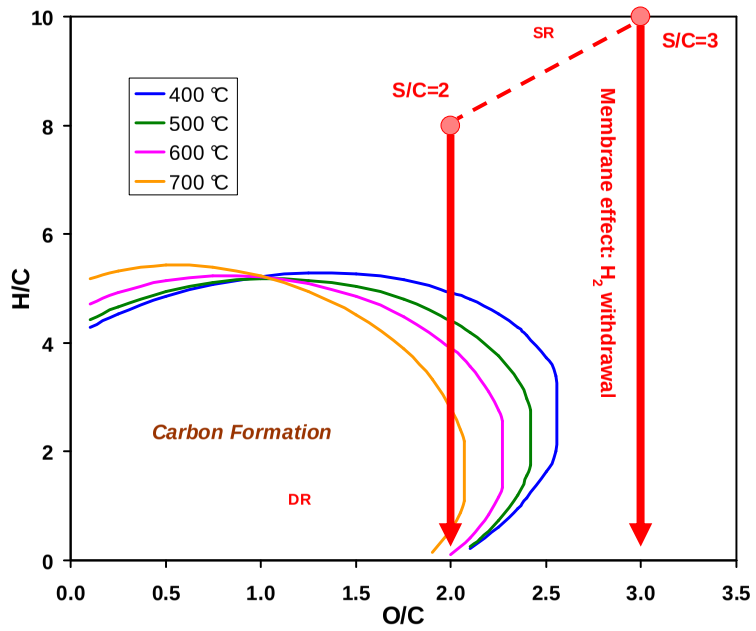
⇒ **What about the catalyst activity and stability?**

Objective

Can we use Ni catalysts in the hydrogen-lean membrane reforming conditions or should we rather look at Precious Metal catalysts ?

Is Ni active and stable enough?

- **Ni-based catalysts**
  - Used in industrial reforming at 800 – 1000 ℃
  - Prone to e.g. carbon formation
- **Precious-metal based catalysts**
  - Mainly Rhodium
  - Used/developed for low-temperature/pressure reforming and heavy feeds
  - High costs



➢**Problem: membrane operations, lower H/C, increased risk carbon formation**

Experimental approach

1) Activity: Ni versus Rh catalysts

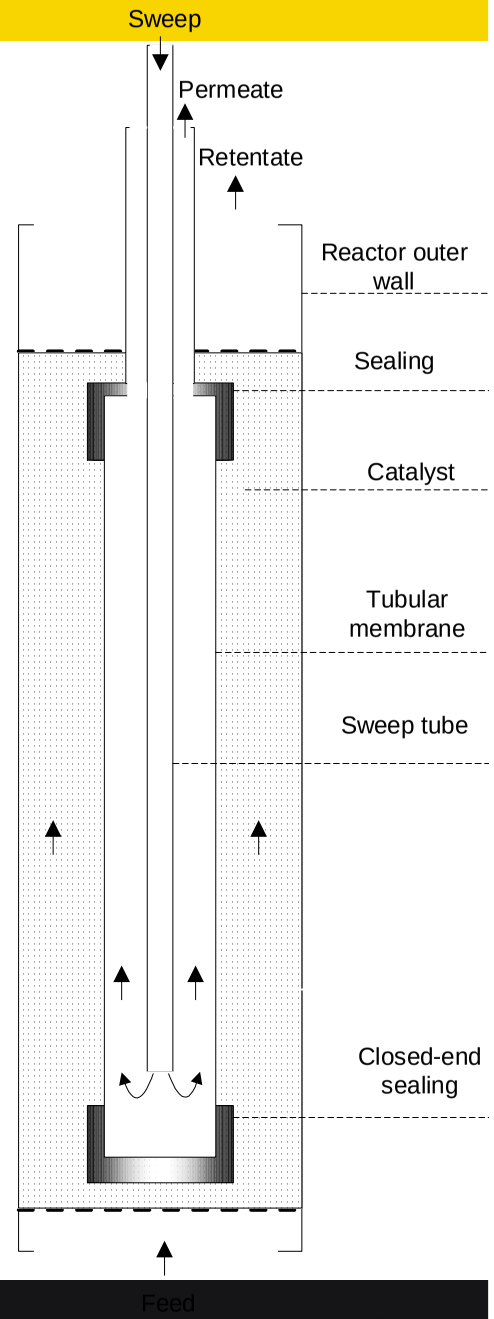
- **Determine whether hydrogen production rate is sufficient to match the hydrogen flux of the membrane**

➢ **1D model: use high pressure reaction kinetics of Ni and Rh catalysts and state-of-the-art permeance of Pd based membranes**

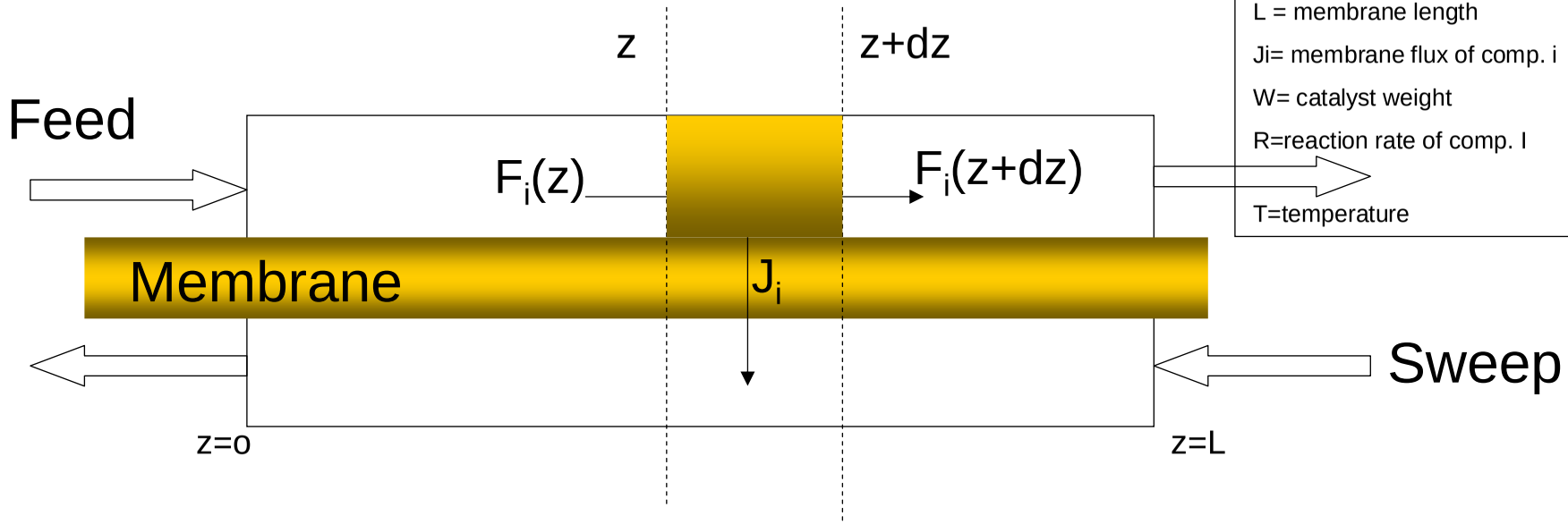
2) Stability testing of Ni and Rh catalysts under simulated (low H/C) membrane conditions

➢ **Microflow testrig, 600℃, 1 atm, H/C=10 (7.5%CH_4, 22.5%H_2O) periodically changed to H/C=2.5 (1.3%CH_4,0.14%CO,11.6%CO_2, 16%H_2O)**

3) Membrane reformer testing at high pressure with membrane and catalyst



Structure of 1-d model



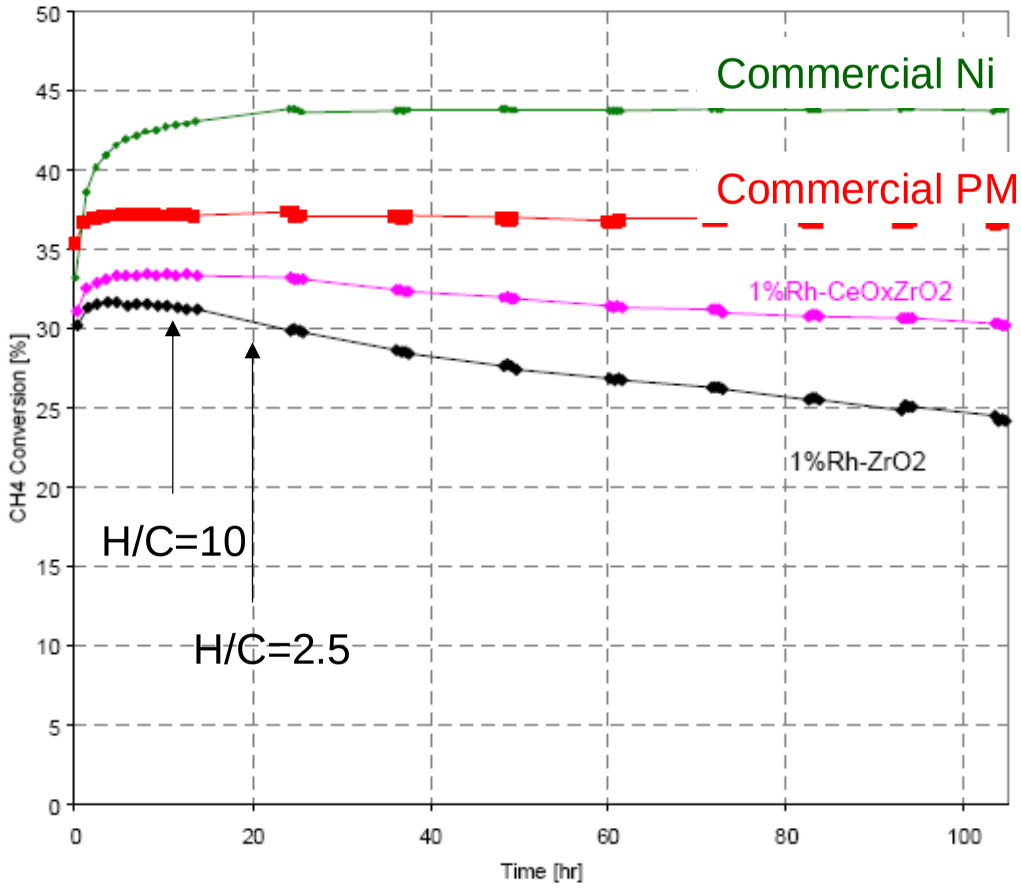
F_i=feed side flux of component i
z=length coordiate
Amem = membrane surface area
L = membrane length
Ji= membrane flux of comp. i
W= catalyst weight
R=reaction rate of comp. I
T=temperature

Out = In – Permeance + reaction

$$F_i(z+dz) = F_i(z) - \left[\frac{A_{mem}}{L}\right] dz \cdot J_i(z,T) + \left[\frac{W}{L}\right] dz \cdot \sum_{reactions} R_i(z,T)$$

Reforming: isothermal

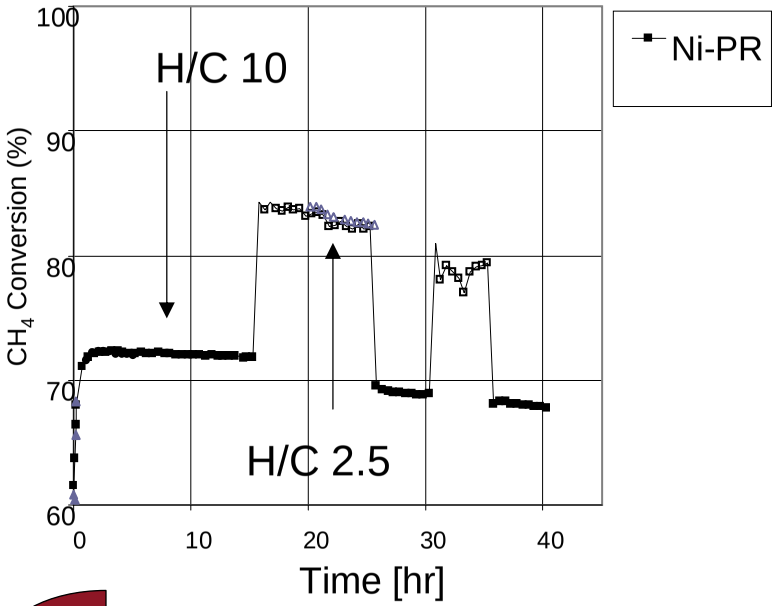
Results Stability



at 500 deg C, good stability, but…….

But, at 600 deg C:

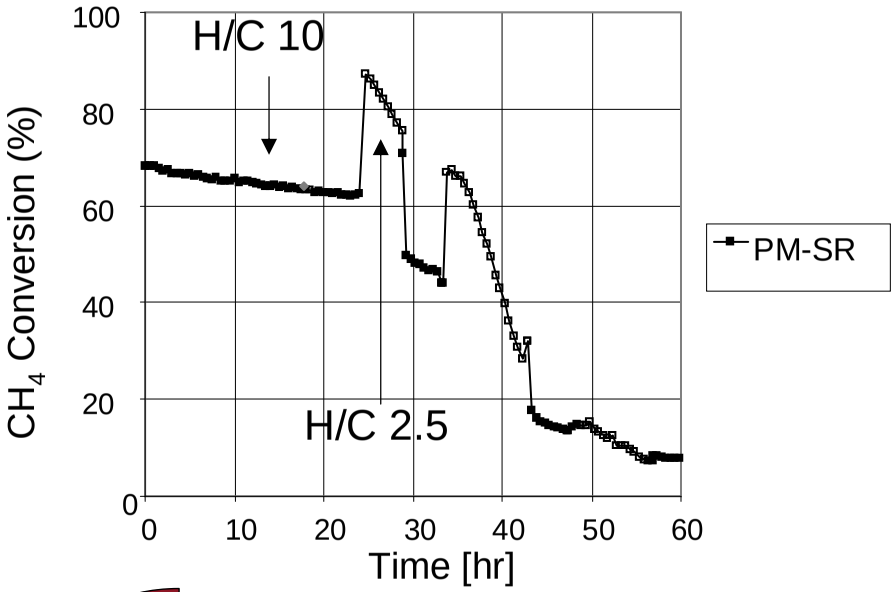
Commercial Ni



Modest stability loss

RAMAN: carbon

Commercial Precious Metal



Dramatic stability loss after exposure to H/C 2.5

RAMAN: little carbon

CO chem: sintering related

=> Further research devoted to the optimization of Ni catalyst

- Prepare series of Ni-$MgAl_2O_4$ catalysts ($MgAl_2O_4$: basic → prevents "C" formation, used in industry; dry impregnation)
- Prepare series of Ni+promotor-$MgAl_2O_4$ catalysts
  - Choice promotors: Lanthanides particularly **Lanthanum**
- Characterize the deactivation at 600℃
  - Focus on carbon

Possible role of Ln/Lanthanum in prevention coking

1.

Carbon formation

$$CH_4 + S \xleftrightarrow{K_1} S\text{–}CH_4 \quad \text{(equilibrium)}, \tag{4}$$

$$S\text{–}CH_4 \xrightarrow{k_2} S\text{–}C + 2H_2 \quad \text{(slow step)}, \tag{5}$$

$$CO_2 + La_2O_3 \xleftrightarrow{K_3} La_2O_2CO_3 \quad \text{(equilibrium)}, \tag{6}$$

Carbon gasification

$$La_2O_2CO_3 + C\text{–}S \xrightarrow{k_4} La_2O_3 + 2CO + S \quad \text{(slow step)}. \tag{7}$$

Verykios et al.,Munera et al.

2. Improved steam sorption, to aid the gasification of C with surface OH

3. Stabilization Particle size

4. Oxygen buffer - 'O' to gasify C precursors (Ceria)

Effect of Lanthanides

- 19 Wt% Ni (9nm particle), added **2**Wt% **La, Ce, Pr, Gd** and **8**Wt% **Pr, Ce** by sequential impregnation: **no significant effect of Ln addition on stability**
- **8** Wt% La (close to theoretical monolayer):

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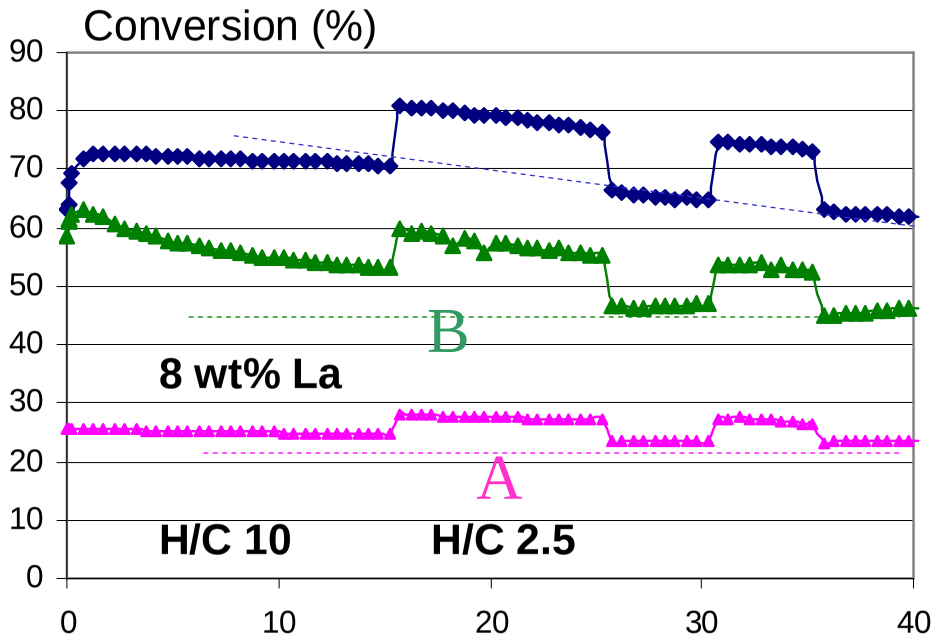
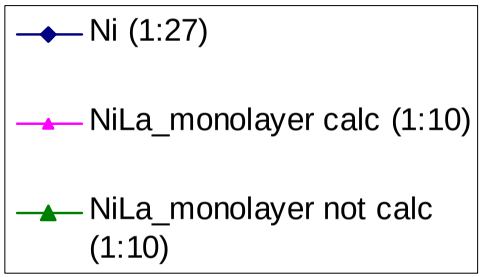
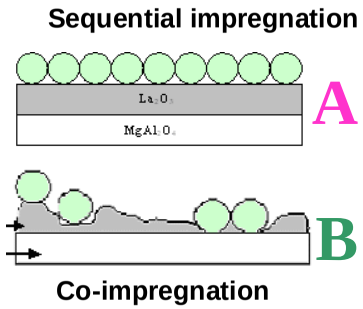


->Time on stream (h)

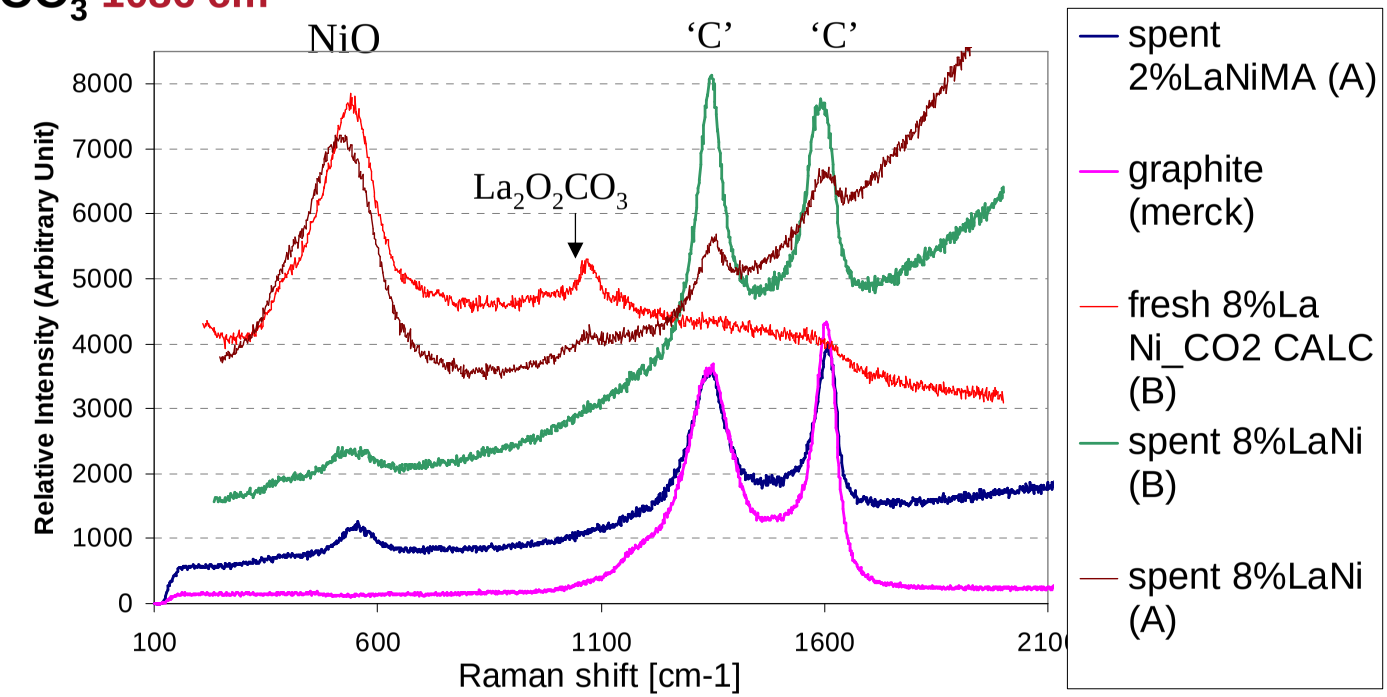




- La ↑ stability but ↓ conversion activity
- **No effect of electronegativity Ln => role in steam gasification not indicated**
- **Role of gasification of ''C'' by $La_2O_2CO_3$?**

Characterization: RAMAN

$La_2O_2CO_3$ 1086 cm^{-1}



- $Ni\text{-}MgAl_2O_4$ and $2\%LaNi\text{-}MgAl_2O_4$: carbon of high graphitic nature
- Spent Impregnated 8%La :, lower amount carbon (supported by TPO experiments), carbon with ''less graphitic nature''

  => SR used catalysts characterized show small amount $La_2O_2CO_3$ and low amount of C

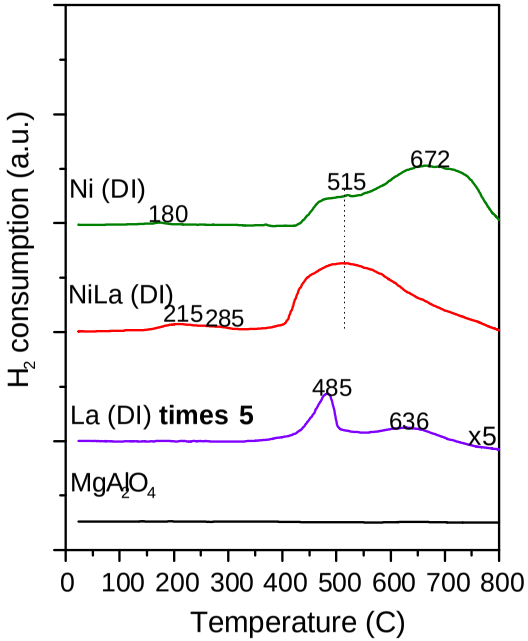
Characterization: TPR & XPS

TPR:

- La improves the reduction of Ni-species, weakens the interaction between Ni^{2+} ions and $MgAl_2O_4$;
- Smaller Ni particles ?

XPS:

- Indications of presence of Ni^{2+} in La-Ni phase (La_2NiO_4 or $LaNiO_3$)

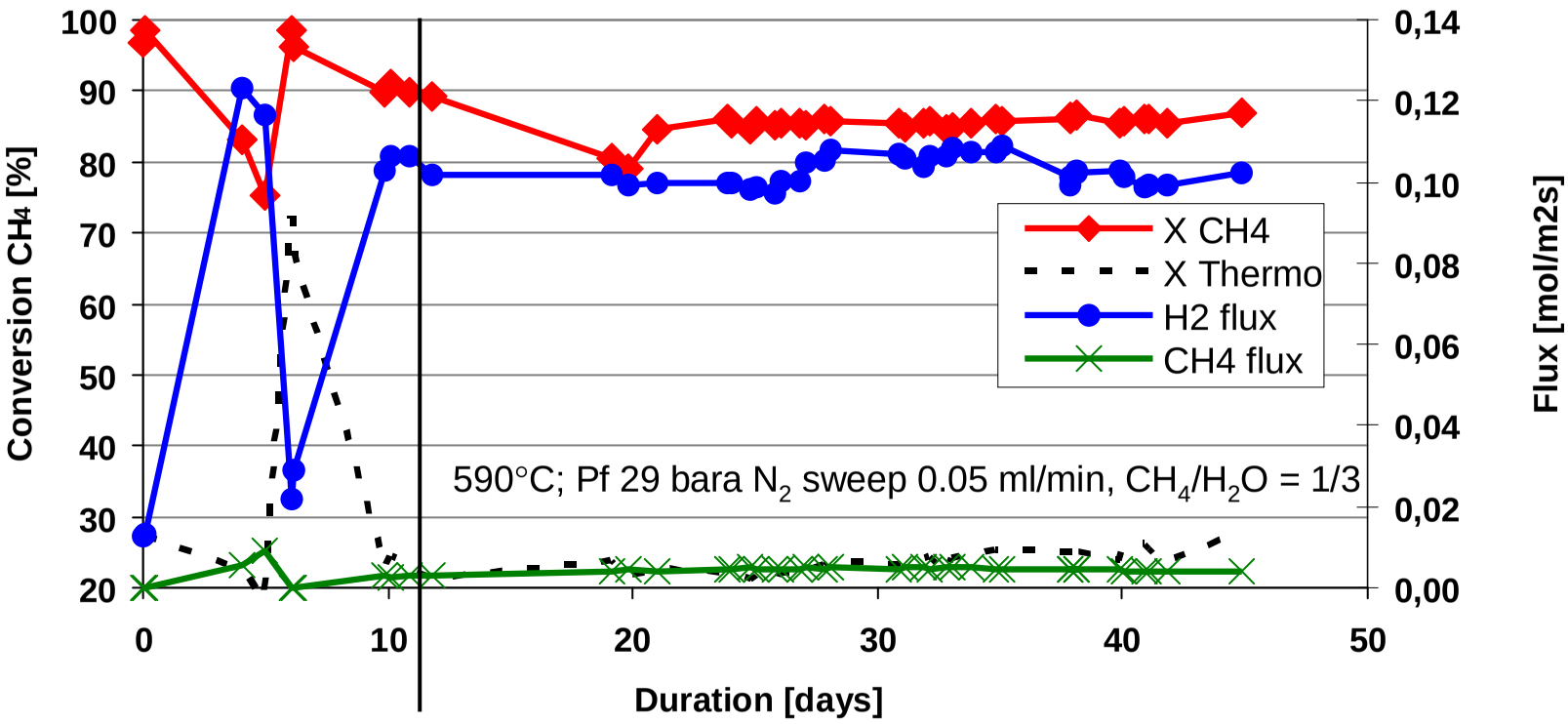


Catalyst	Total H_2 consumed (mmol x 10^2)
Ni (DI)	5.36
NiLa (DI)	6.20
La (DI)	0.28

➢ **Beneficial role of La on the stability of Ni catalyst is not yet solely assigned to gasification of ''C'' by $La_2O_2CO_3$**

Catalyst in membrane reformer testing

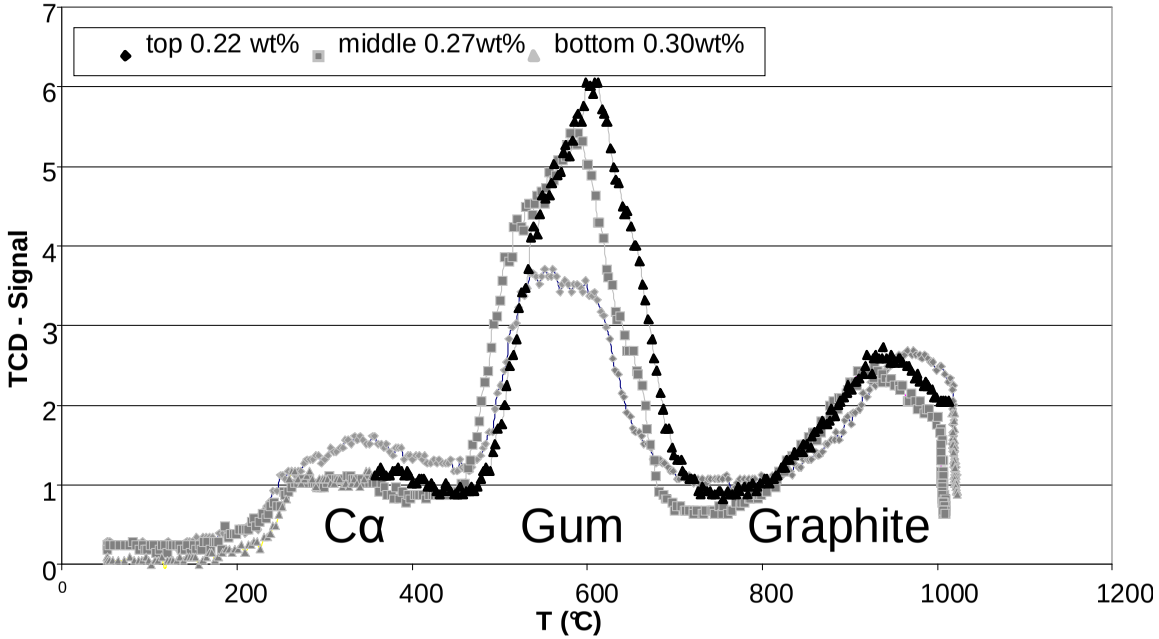
530-590°C; Pf 25-42 bara feed: CH_4/H_2O = 1/3 $NiLaMgAl_2O_4$; 3.8 µm $Pd/\alpha Al_2O_3$, 35 cm length, OD 1.4 cm, 155 cm^2, co-current



- 99% conversion possible (up to 70 % higher than equilibrium conversion)
- Stable membrane operation, stable conversion

Characterization carbon with TPR

Catalyst collected at 3 locations along the reactor: Top, Middle and Bottom



	Total carbon (CHNS) (wt% C)
Top	1.1
Middle	1.3
Bottom	1.2

Mc Carthy, 1982

•Carbon is formed with catalyst used in membrane reformer

•Role of depleted hydrogen concentration to carbon formation unclear (similar values %wt C along reactor coordinate)

•Different forms of carbon: not all carbon contributes equally to deactivation; higher steam use may be necessary to prevent plugging after extended periods of operation

Summary

- ''Conventional'' Ni-$MgAl_2O_4$ have sufficient activity for use in steam reforming in membrane reformers
- Promotion with Lanthanum improves stability of Ni-$MgAl_2O_4$ (albeit at the cost of activity)
- The role of La could be related to the formation of $La_2O_2CO_3$ during reaction and subsequent gasification of carbon precursors but may very well be more complex (more in situ characterization planned)
- Good performance Pd membranes and catalyst in membrane reactor testing (lower amount of catalyst necessary to study deactivation in more detail)

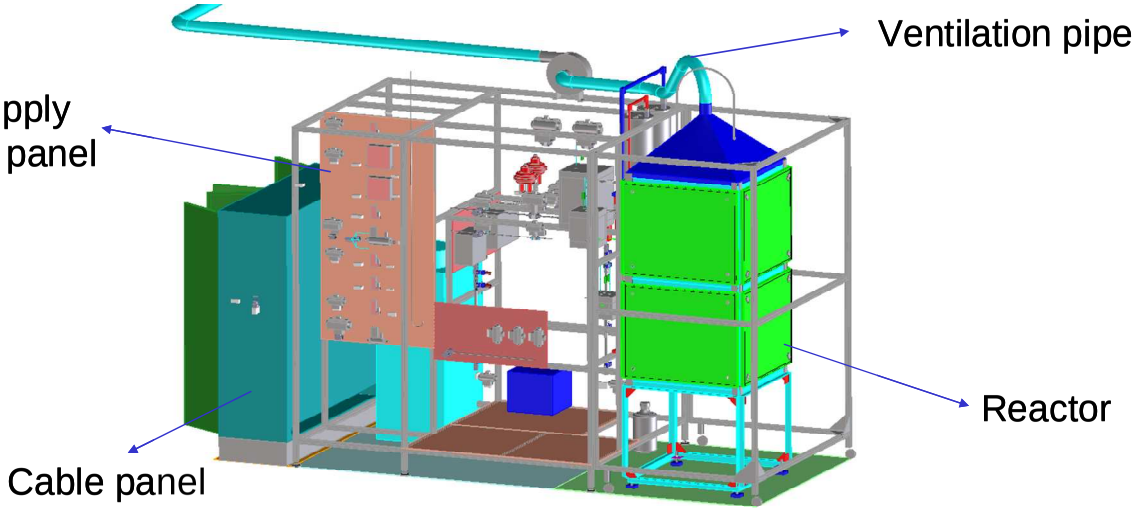
Outlook

- **Membrane reactor testing:**
  - better dimensioned catalyst-membrane surface area testing to study catalyst deactivation
  - characterization membrane after testing – interaction catalyst-membrane
- **2D** reactor model : heat, mass transfer, radial coking profiles
- Characterization of the synergy Ni-La, improve activity
- **8-tube membrane reactor testing to determine feasibility of larger scale hydrogen production**

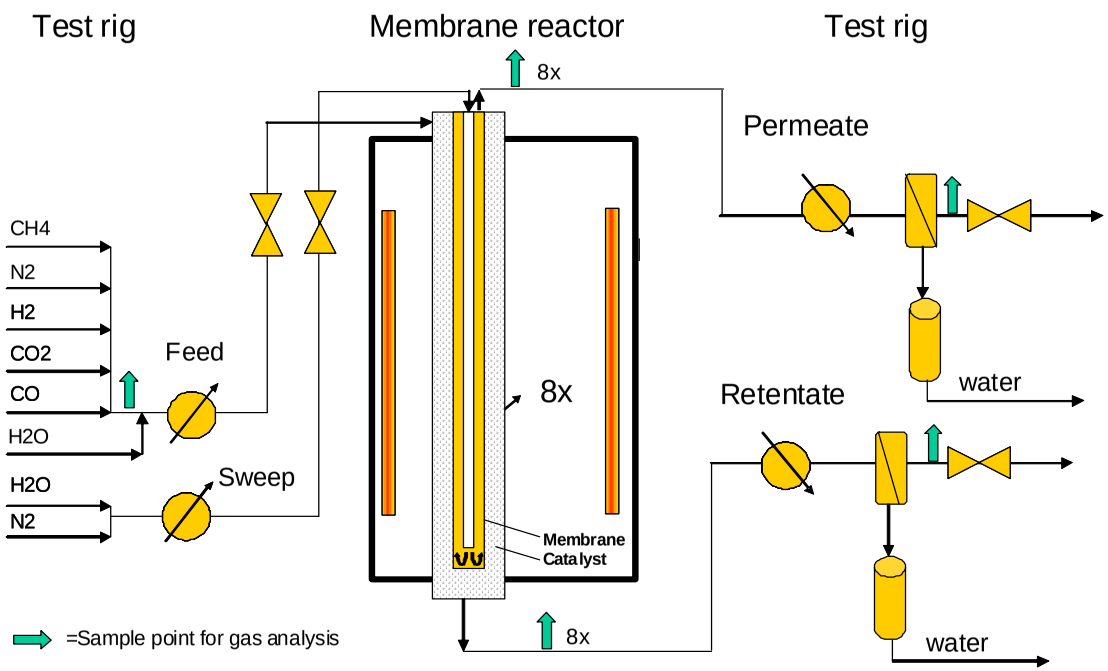
Process development Unit (PDU)

Demonstration of
membrane reactors at scale

- Multitube membrane reactor
- 8 tubes of 50 cm
- Membrane reforming and
- Membrane water gas shift
- Max 600℃, 40 bar



Process development Unit (PDU)



Gas mixing and pre-heating

Water removal and venting

Gas sampling on all tubes

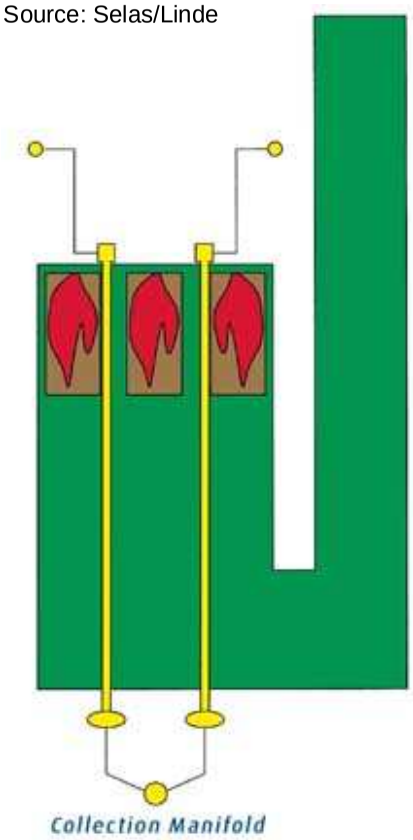
Reforming/shift:

150/400 l_n/min wet feed flowrate (2.5/6.7kWth product H_2)

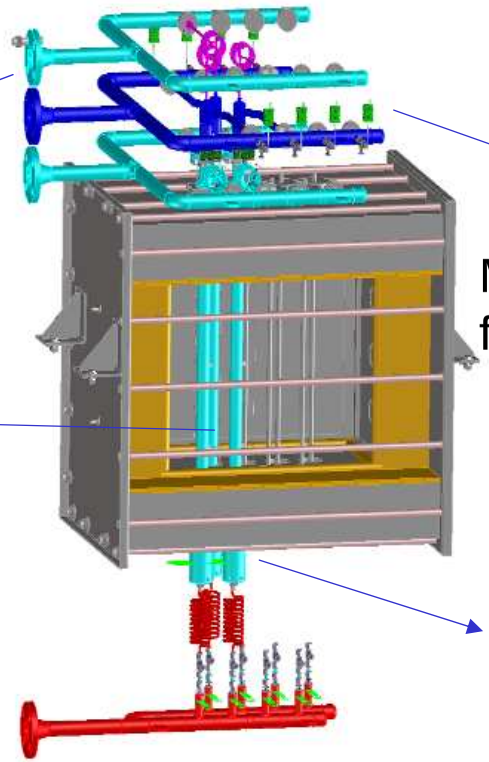
Operating window 25-400%

Reactor design

Source: Selas/Linde



Industrial SMR



PDU reactor design

The current design of the membrane reactor is derived from an envisaged full scale steam methane reformer type reactor with membranes inserted into the reactor tubes. Heating is done by radiating electrical elements, mimicking radiant burners.

PDU

Setup with membrane reactor

Reactor tubes

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