

NATO/CCMS Pilot Study Meeting on Clean Products and Processes
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Hydrogen economy and fuel cells: Energy for the future

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*Spanish
Council for
Scientific
Research*



*Group of
Structure and
Activity of
Catalysts*



Group of Structure and Activity of Catalysts

Personal resources:

5 Staff researchers

7 Postdoctoral Researchers

10 PhD Students

Research Topics:

- **Energy:**

*Catalytic Combustion, Fuel Cells electrocatalysts,
Fuel Cell reformers, Hydrogen production.*

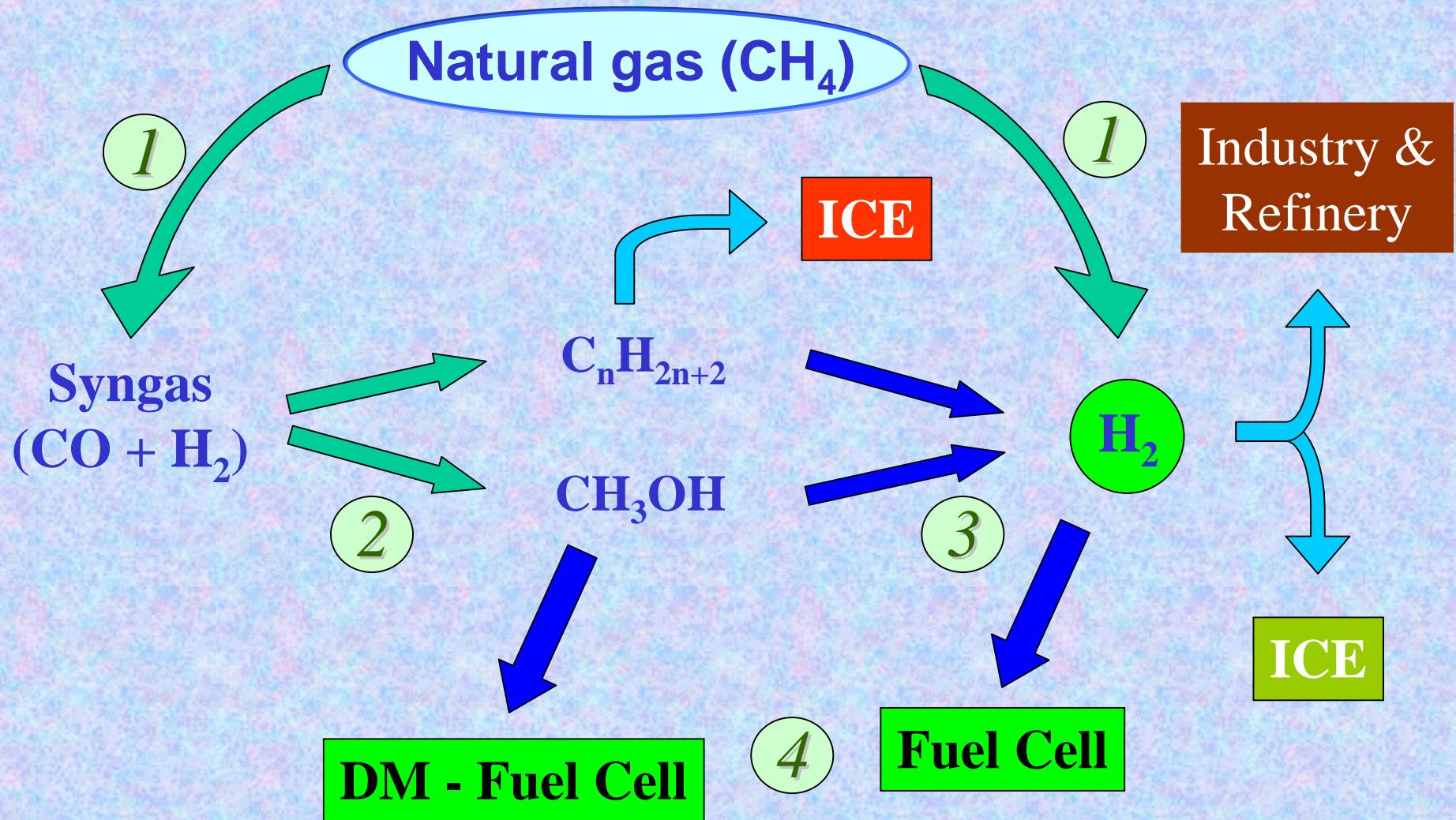
- **Environmental:**

DeNOx catalytic processes, VOCs removal, Hydrotreatments

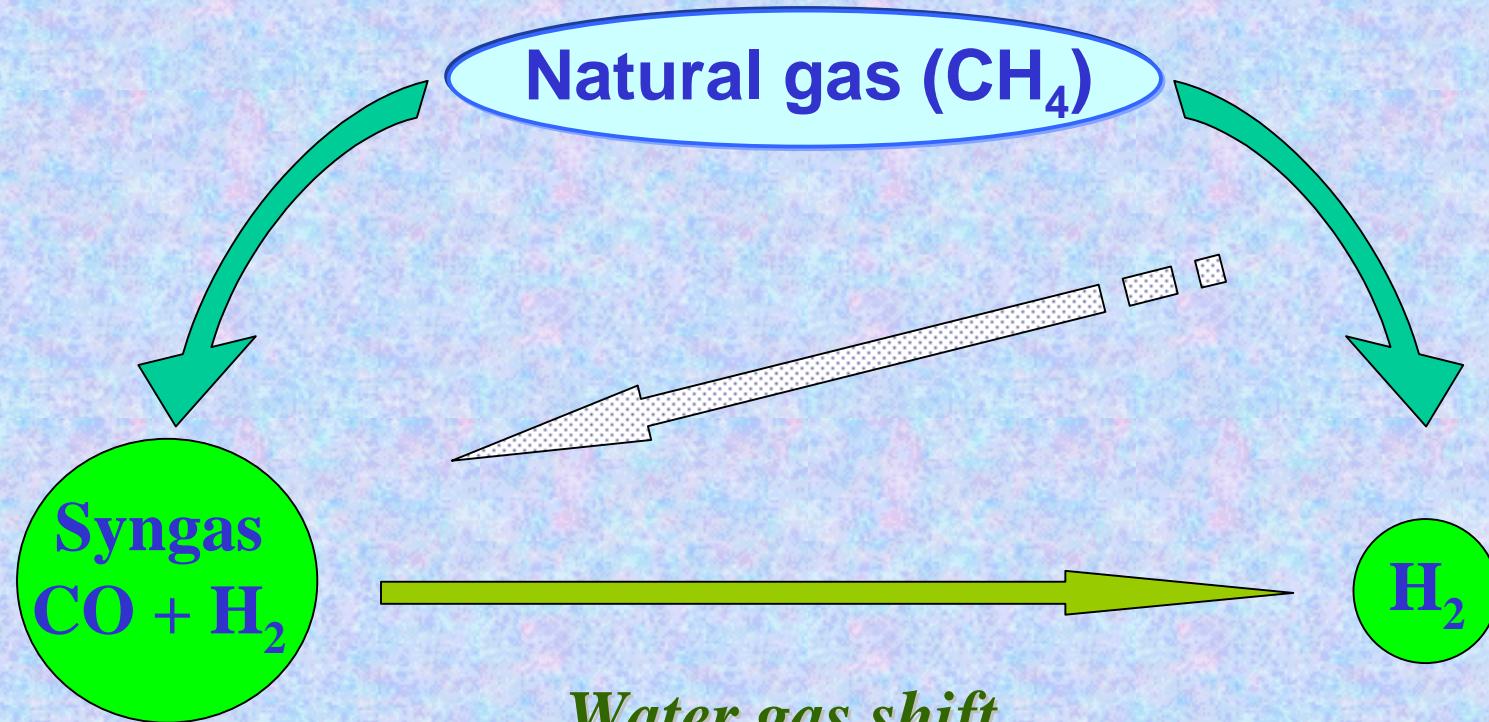
- **Petrochemistry:**

*Selective oxidation of hydrocarbons, Fischer Tropsch,
Natural gas conversion (hydrogen, oxygenates)*

A new energy framework: The hydrogen economy



1. Syngas production from natural gas



Water gas shift

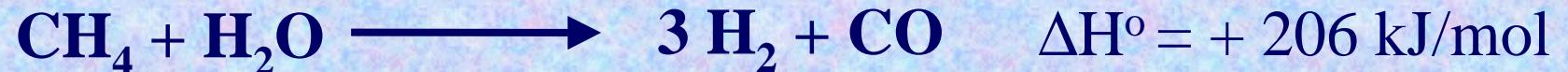


$\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3 - \text{Cu/ZnO}$
400-200°C

CO₂ removal

1. Syngas production from natural gas

Steam Reforming (SR)



- ↳ Highly Endothermic
- ↳ Relatively slow
- ↳ Overheating water at 800°C
- ↳ Ratio H₂/CO= 3 (2 for Methanol, Fischer-Tropsch)

Catalytic Partial Oxidation (CPO)



➡ At 700°C 90% Conversion / 90% Selectivity

1. Syngas production from natural gas

Process Reactions

		ΔH°
Steam Reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3 \text{ H}_2 + \text{CO}$	Endo
Partial Oxidation	$\text{CH}_4 + 1/2 \text{ O}_2 \rightleftharpoons 2 \text{ H}_2 + \text{CO}$	Exo
Combustion	$\text{CH}_4 + 2 \text{ O}_2 \rightleftharpoons 2 \text{ H}_2\text{O} + 2 \text{ CO}_2$	Exo
Water Gas Shift	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$	Exo
Dry Reforming	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2 \text{ H}_2 + 2 \text{ CO}$	Endo
Boudouart Eq.	$2 \text{ CO} \rightleftharpoons \text{C} + \text{CO}_2$	Exo
Decomposition	$\text{CH}_4 \rightleftharpoons \text{C} + 2 \text{ H}_2$	Endo

1. Syngas production from natural gas

Spanish Companies in Natural Gas Market

ENAGAS - GAS NATURAL → Supplier
REPSOL Petróleo → Refining

Industrial Application of the Partial Oxidation of Methane:

High Pressure ⇒ Monoliths
High Space Velocity

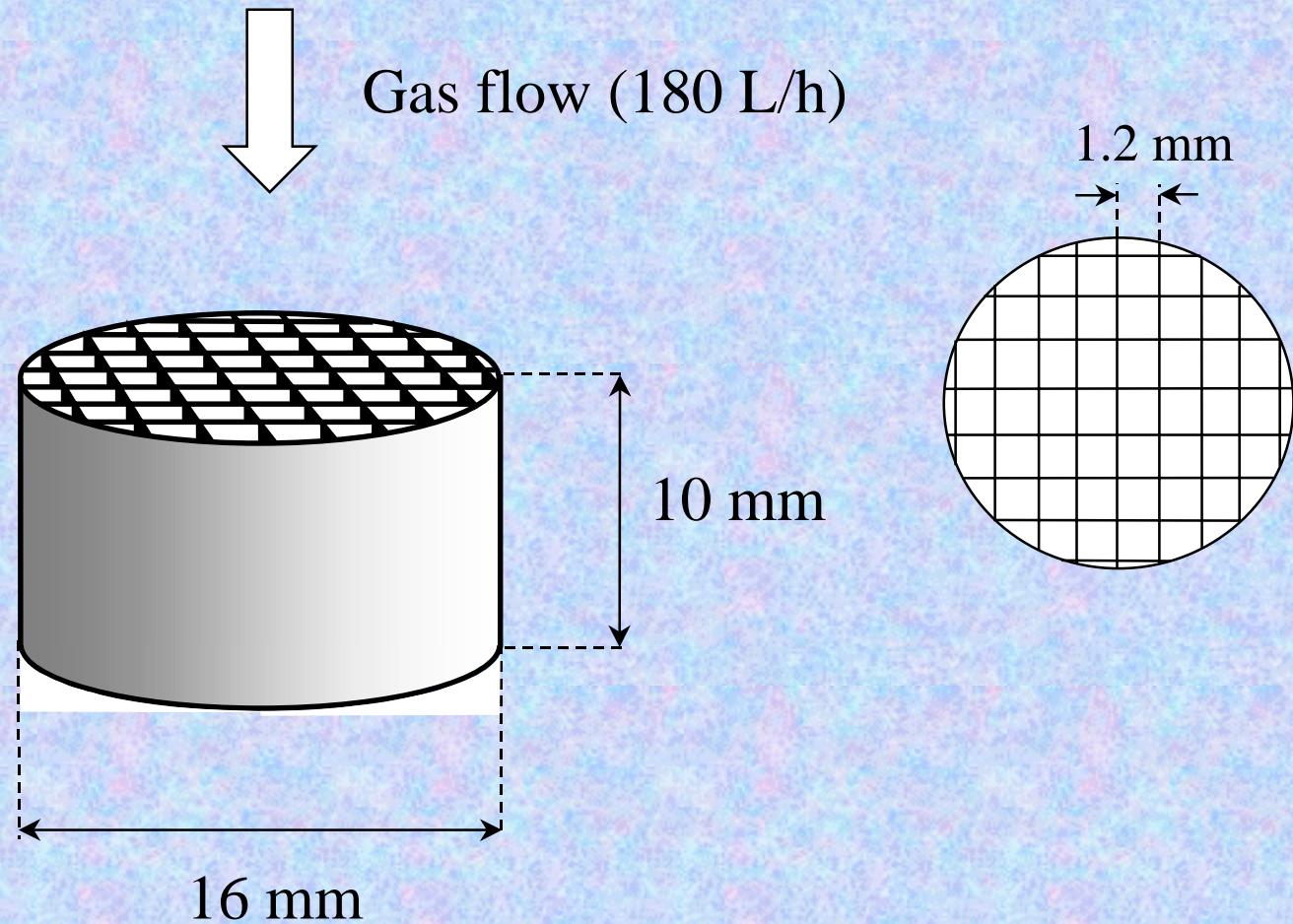
- Preparation of honeycombs:
 - ⇒ Starting from solid powders
 - ⇒ Different method and supports for incorporation of Ni
- Catalysts characterisation:
 - ⇒ TPR. Reducibility of nickel
 - ⇒ XPS. Surface analysis
- Catalytic activity:
 - $\text{CH}_4/\text{O}_2/\text{N}_2 = 2/1/3$
 - $F_T = 180 \text{ L (STP)}/\text{h}$
 - $T = 700 - 850^\circ\text{C}$
 - $P = 20 \text{ atm}$

1. Syngas production from natural gas

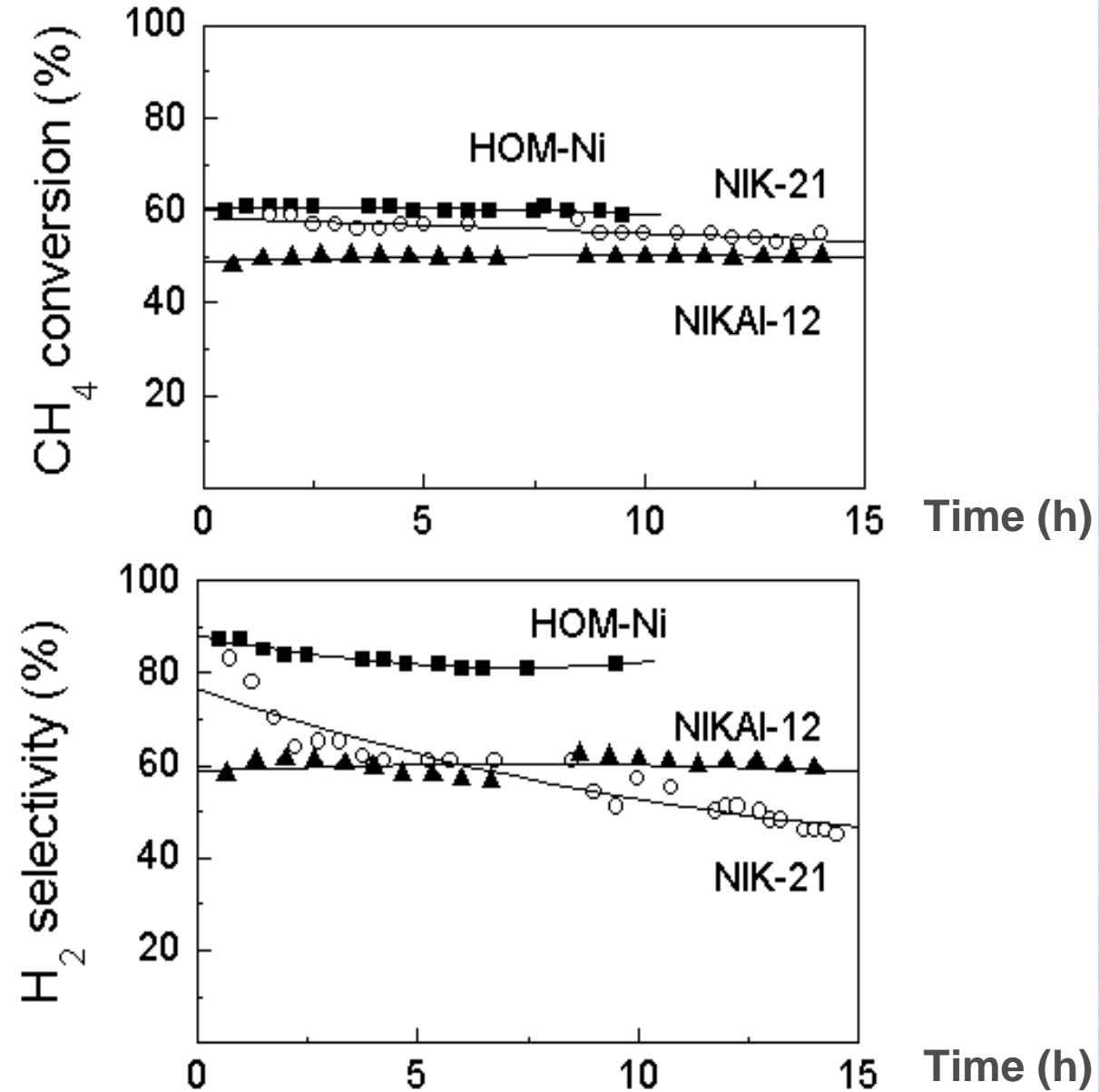
GENERAL CHARACTERISTICS OF HONEYCOMB CATALYSTS

Catalyst	Support	Precalcination	Preparation	% Metal
NIK-21	$\gamma\text{-Al}_2\text{O}_3 + 5\%$ clay	-----	Kneading	9.4 % Ni
NIKAI-12	$\gamma\text{-Al}_2\text{O}_3 + 12\%$ clay	523 K, 8 h	Impregnation	16.0 % Ni
NIKAI-30	$\gamma\text{-Al}_2\text{O}_3 + 12\%$ clay	1273 K, 8 h	Impregnation	11.5 % Ni
HOM-Ni	Silica	-----	Impregnation	8.9 % Ni
RH-1	Cordierite	-----	Impregnation	0.9 % Rh

1. Syngas production from natural gas



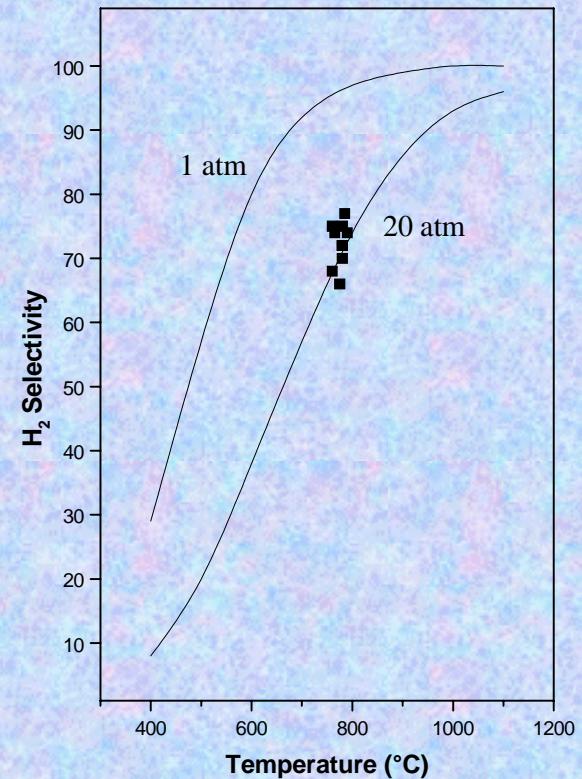
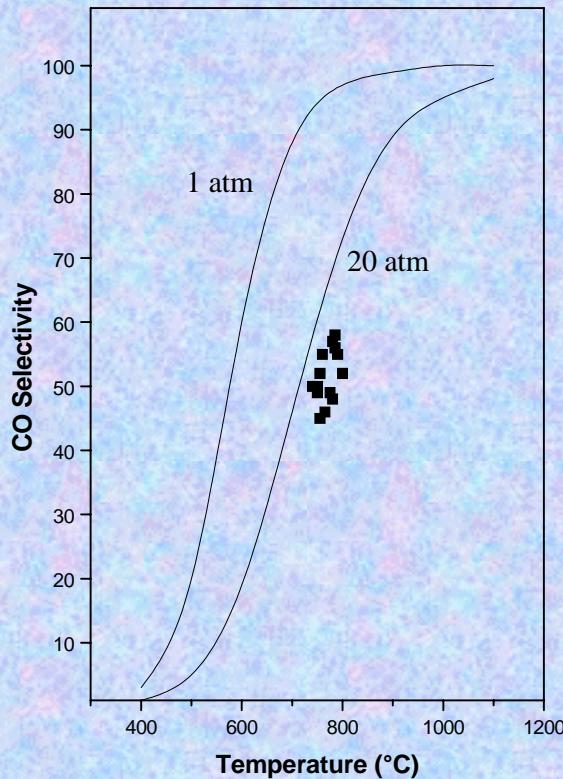
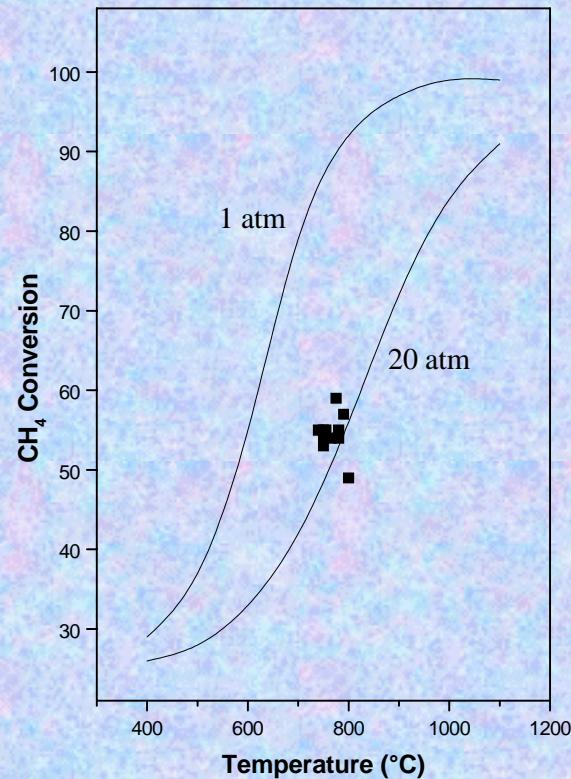
1. Syngas production from natural gas



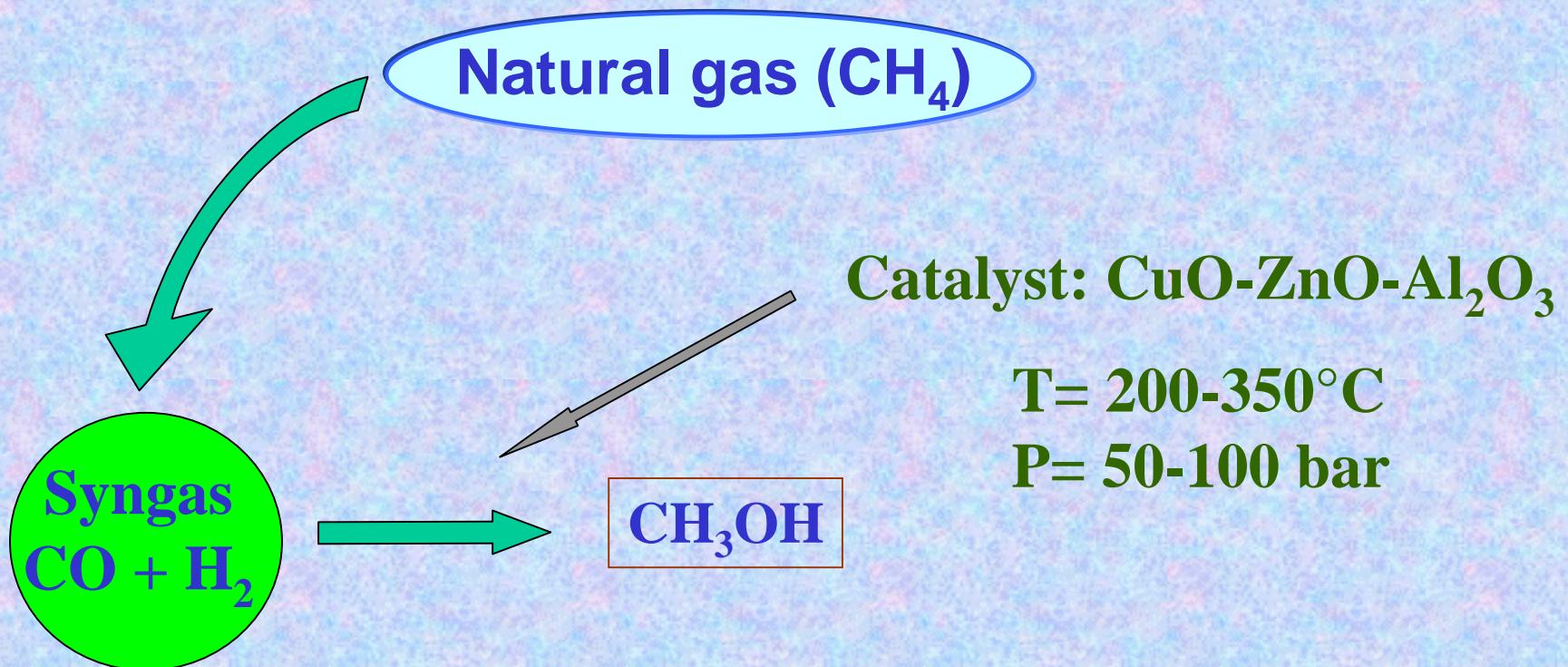
1. Syngas production from natural gas

COMPARATION WITH THE EQUILIBRIUM VALUES

P= 20 atm. Ratio CH₄/O₂/N₂ = 2/1/3



2. Synthesis of Methanol from Syngas



↳ High equilibrium limitation

2. Synthesis of Methanol from Syngas

↳ Alternative process: *CO₂ hydrogenation*



Difficulties:

- ↳ *CO₂ more stable than CO*
- ↳ *Water production can deactivate catalyst surface*
- ↳ *CO₂ can oxidize active phase of catalyst (Cu^o)*

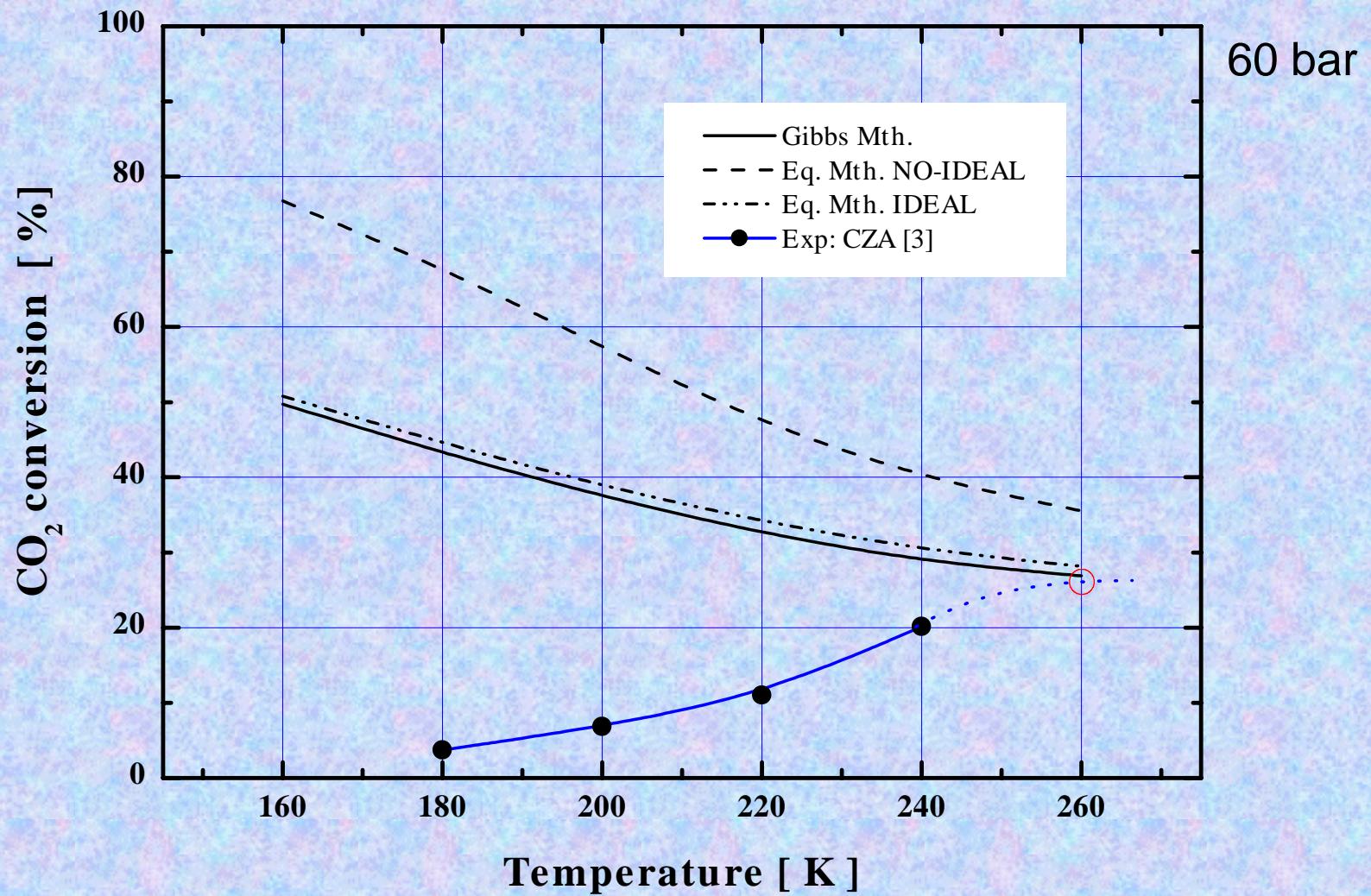
➤ *No commercial catalysts with enough efficiency*

➤ *Research approach, Noble metals as additives:*

- ★ *Reduced state of metal by spillover*

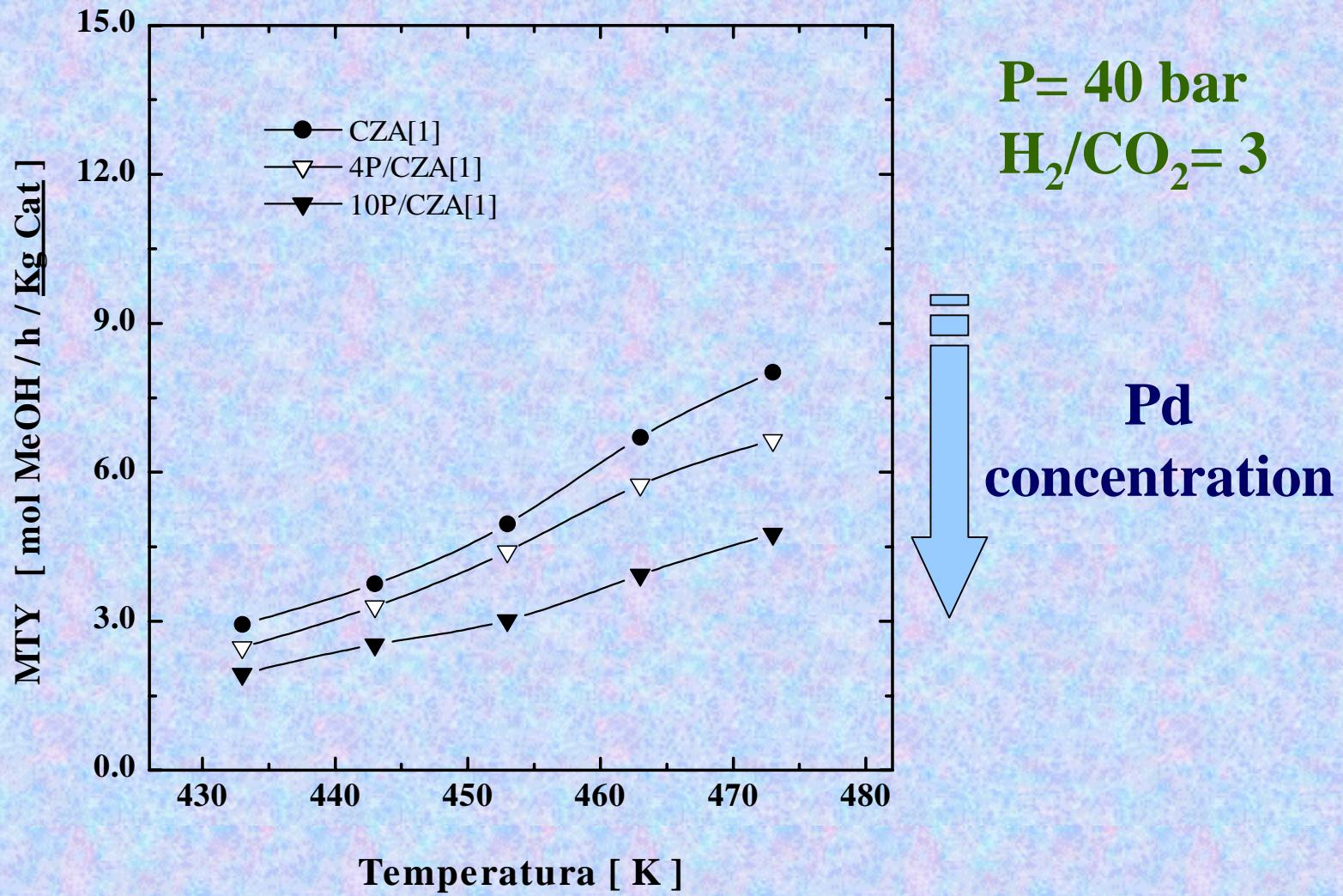
2. Synthesis of Methanol from Syngas

CO_2 hydrogenation. Equilibrium and experimental



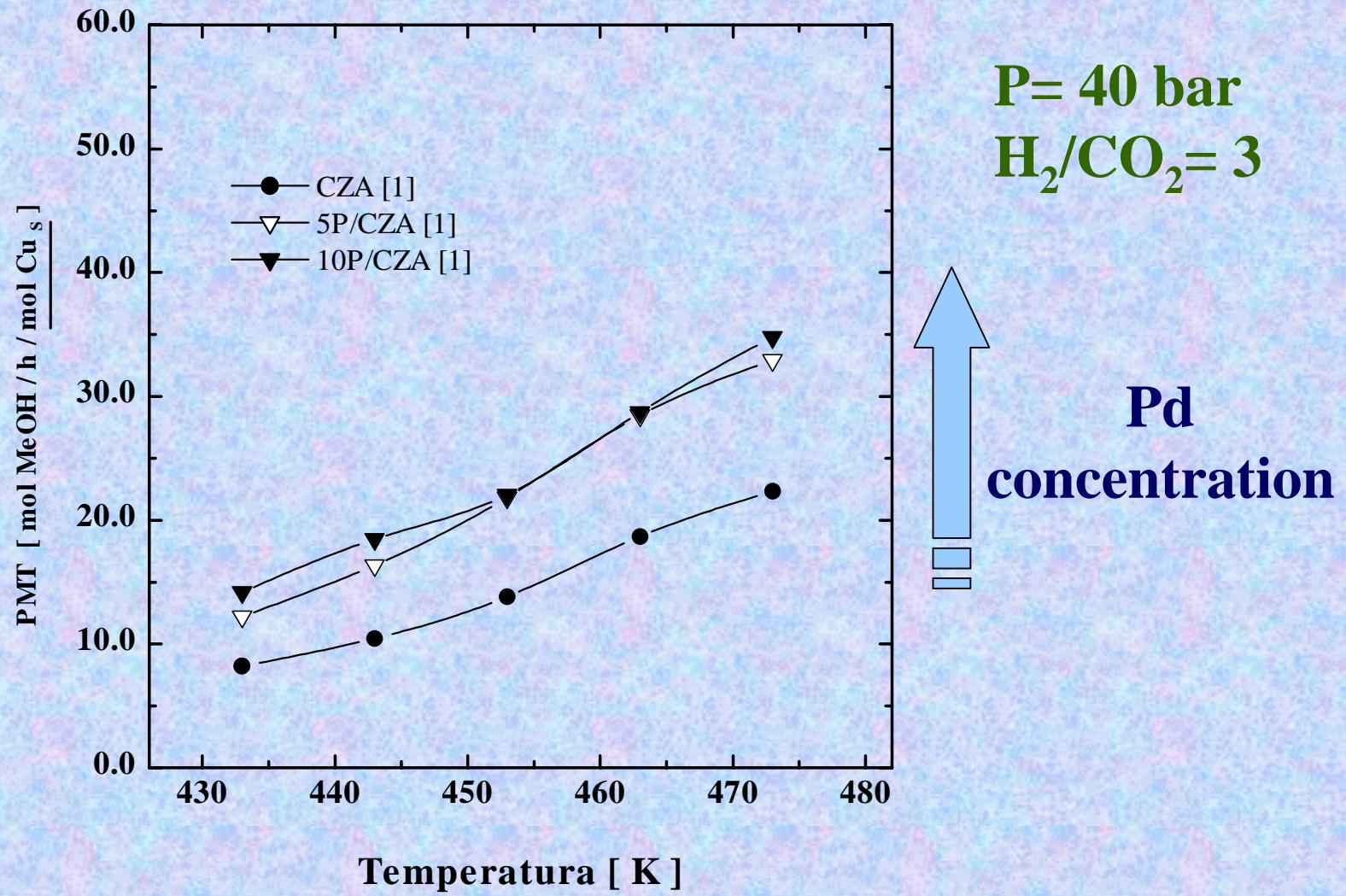
2. Synthesis of Methanol from Syngas

CO₂ hydrogenation. Pd/CuZnAl Catalysts

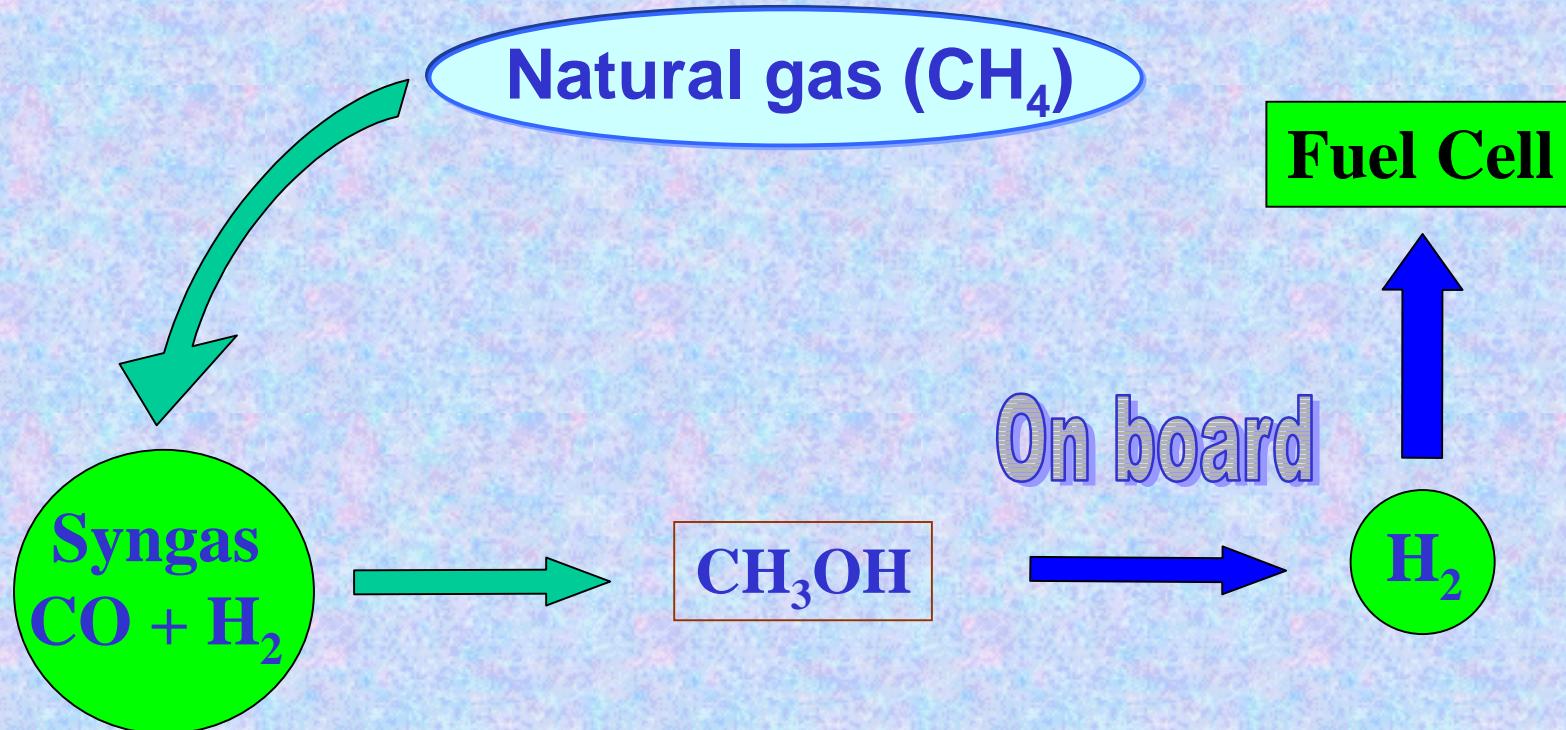


2. Synthesis of Methanol from Syngas

CO₂ hydrogenation. Pd/CuZnAl Catalysts



3. Hydrogen production by Methanol Oxidation



Requirements:

- ↳ Efficient Process: CO₂ production “well-to-wheels”
- ↳ Selective process: CO lower than 50 ppm

3. Hydrogen production by Methanol Oxidation

Steam Reforming



- ↳ Endothermic
- ↳ Relatively slow

Decomposition



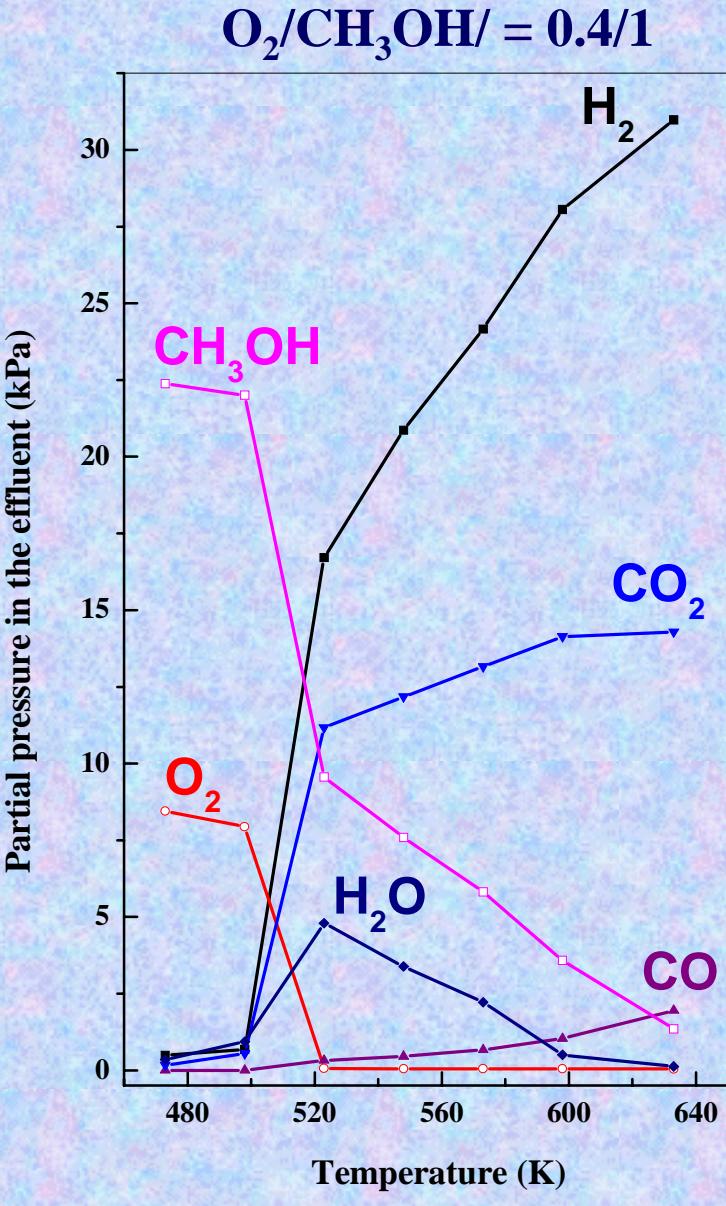
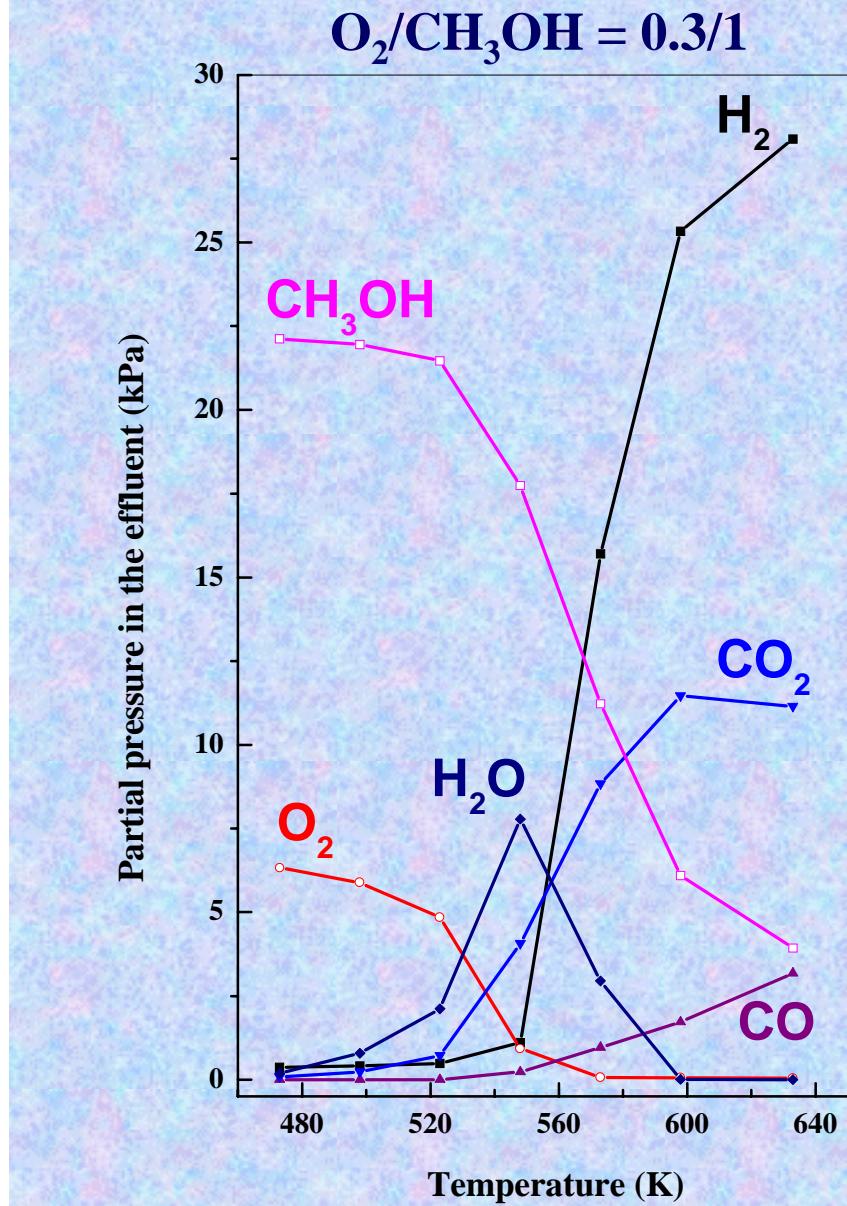
- ↳ CO production

Partial Oxidation



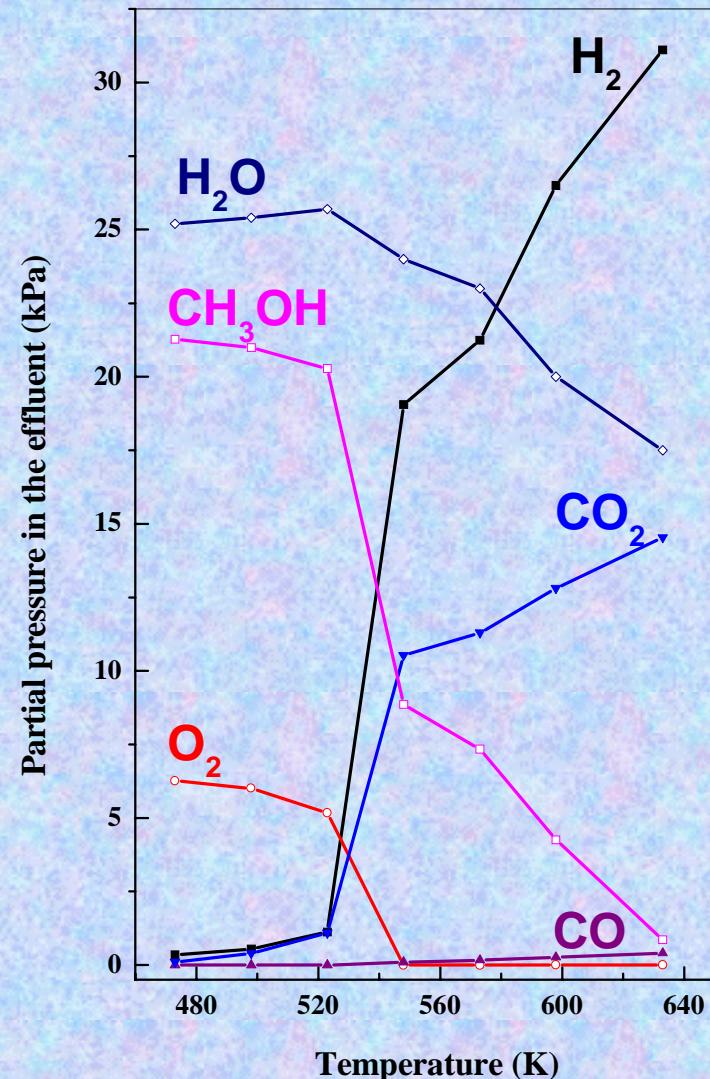
➡ At 300°C 90% Conversion / 85% Selectivity

3. Hydrogen production by Methanol Oxidation

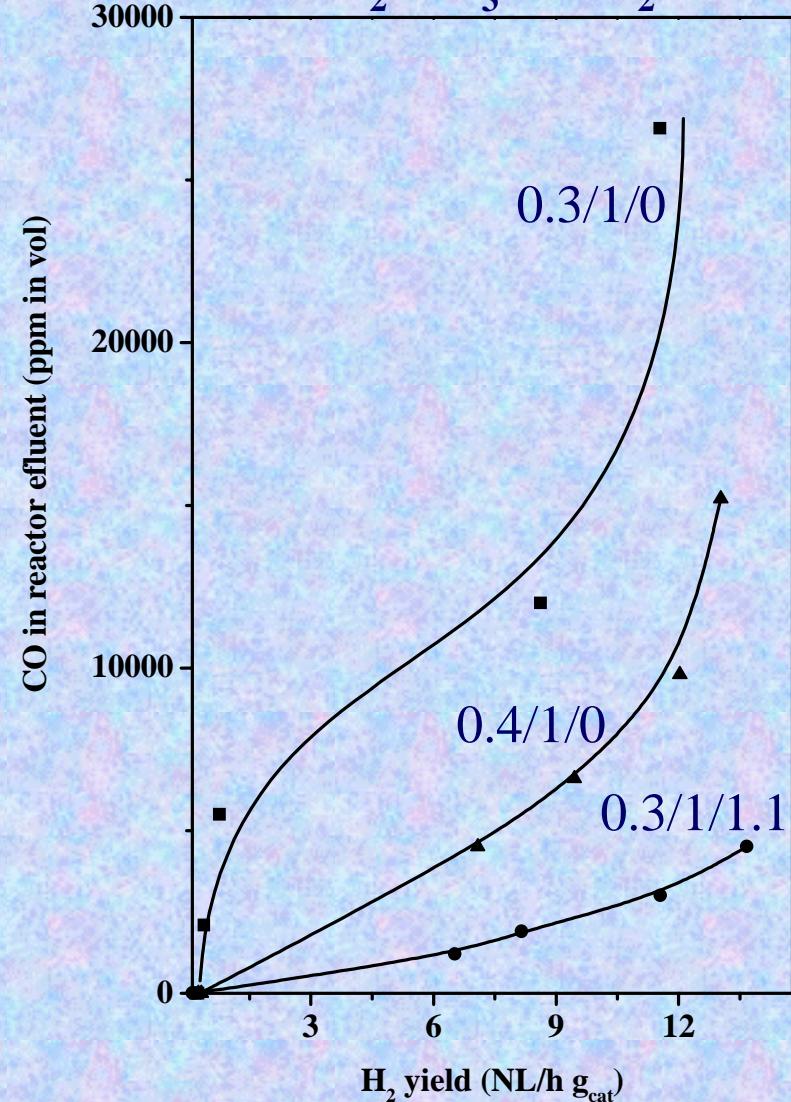


3. Hydrogen production by Methanol Oxidation

$$\text{O}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O} = 0.3/1/1.1$$



$$\text{O}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O}$$



3. Hydrogen production by Methanol Oxidation

CO as co-product

Reverse Water Gas Shift



CO removal

- Adsorption (large volume)
- Pd membranes (expensive, high pressure and temperature)
- Methanation (Non selective in presence of CO₂, loss of H₂)



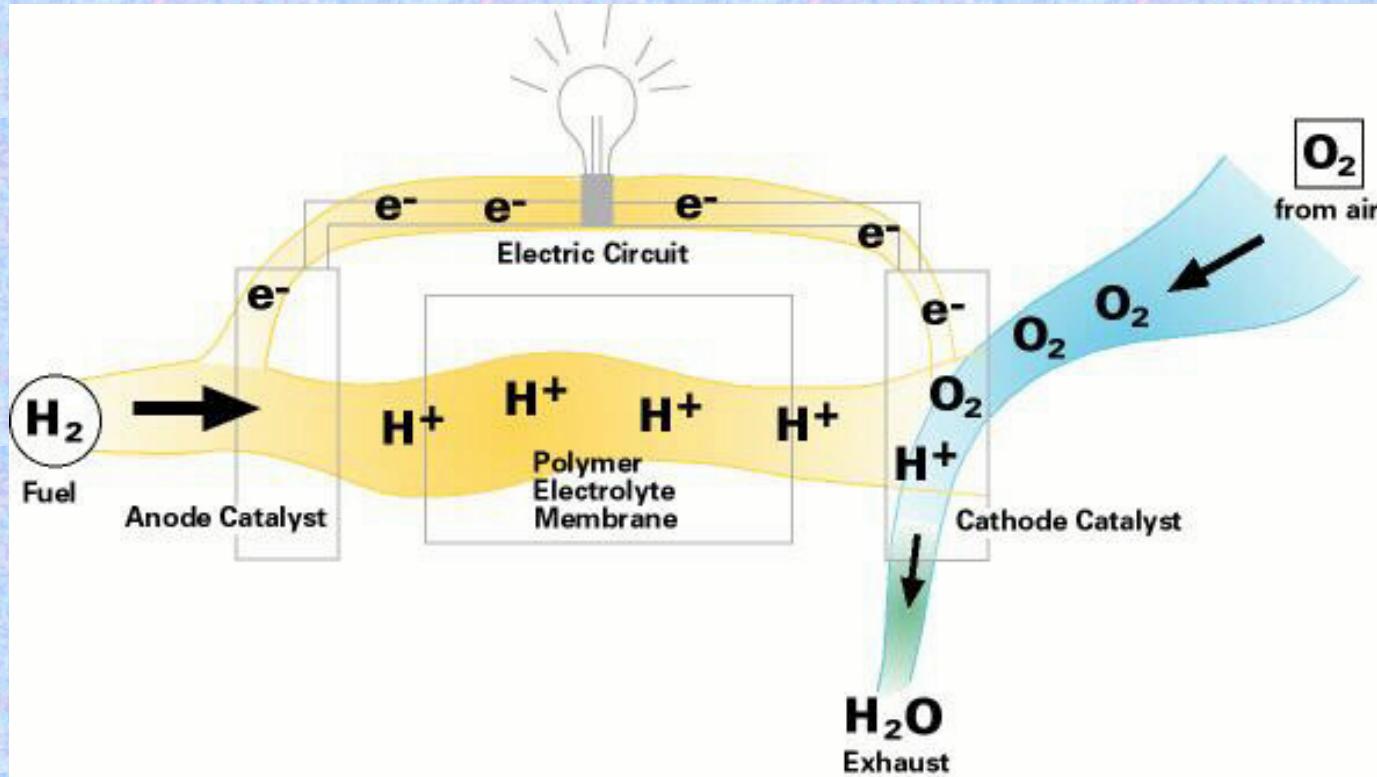
- Preferential oxidation (Pt, Ru, Rh/Al₂O₃, Au/MnO_x)



Competitive with hydrogen oxidation

- Low temperature (>175°C) reforming (Cu/Al₂O₃-Zn)

4. Fuel Cell Technology



- *Clean energy ($H_2 + 1/2 O_2 \longrightarrow H_2O$)*
 - ↳ Depending on fuel processing
- *High yield, compared with combustion engines.*

Alkaline (AFC)

Electrolyte: KOH / H₂O

Charge carrier: OH⁻

Electrocatalyst: Ni

Temperature: 90 - 100 °C

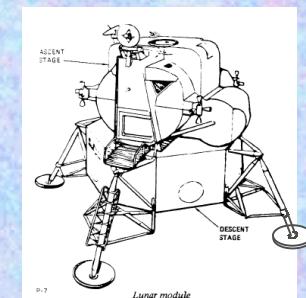
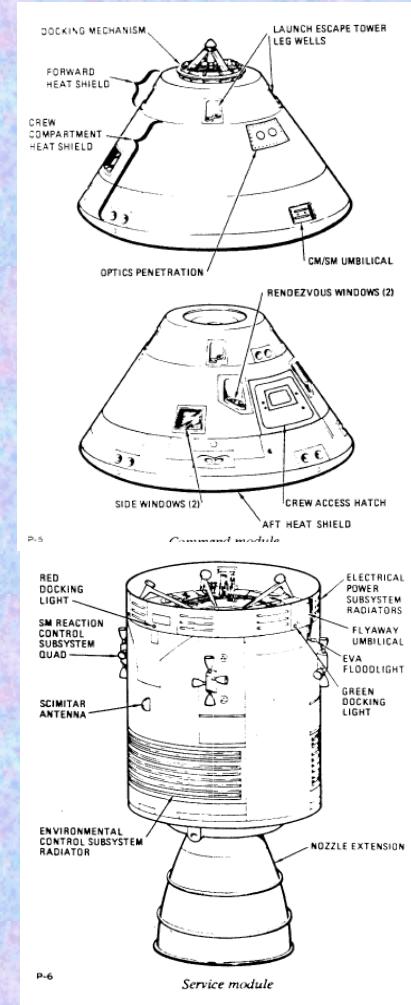
Yield: 70 %

Fuel: H₂

Carbonation by CO and CO₂
(also in oxidant)

Units: Space missions

- Reliability
- High current density
- High price of the integrated system



Phosphoric Acid (PAFC)

Electrolyte : Molten H₃PO₄

Charge carrier: H⁺

Electrocatalyst: Pt

Temperature: 175 - 200 °C

Yield: 40 - 50 %

Yield: Reformed CH₄, max. 2 % CO.

Units: Only Fuel Cell of comitital application
50 - 500 kW (some prototypes of 11 MW),
most usual 200 kW. Used for 40,000 h

- Cogeneration electricity + heat
 - Cost: 3,500 €/ kW (three times competitive price)
 - Unique uses:
 - Police station Central Park (N.Y.)
 - Technical center F.N.B. Omaha

Molten Carbonates (MCFC)

Electrolyte: Molten Li_2CO_3 / K_2CO_3

Charge carrier: CO_3^{2-}

Electrocatalyst: Ni

Temperature: 600 - 1000°C

Yield: > 60 %

Fuel: CH_4 or Reformed CH_4 (no CO problems)

Units: 200 kW - 2 MW Prototypes.

- Cogeneration electricity + heat
- Short working time, yield not reached

Solid Oxides (SOFC)

Electrolyte: Ceramic Oxide: Y-ZrO₂, Ga-CeO₂

Charge carrier: O²⁻

Electrocatalyst: TiCaO₃ (perovskites)

Temperature: 800-1000°C

Yield: > 60 %

Fuel: CH₄ or Reformed CH₄ (no CO problems)

Units: Prototypes up to 100 kW

- Cogeneration electricity + heat
- Short working time, yield not reached

Proton Exchange Membrane (PEMFC)

Electrolyte: Proton conducting membrane (Nafion)

Charge carrier: H⁺

Electrocatalyst: Pt

Temperature: 60 – 90°C

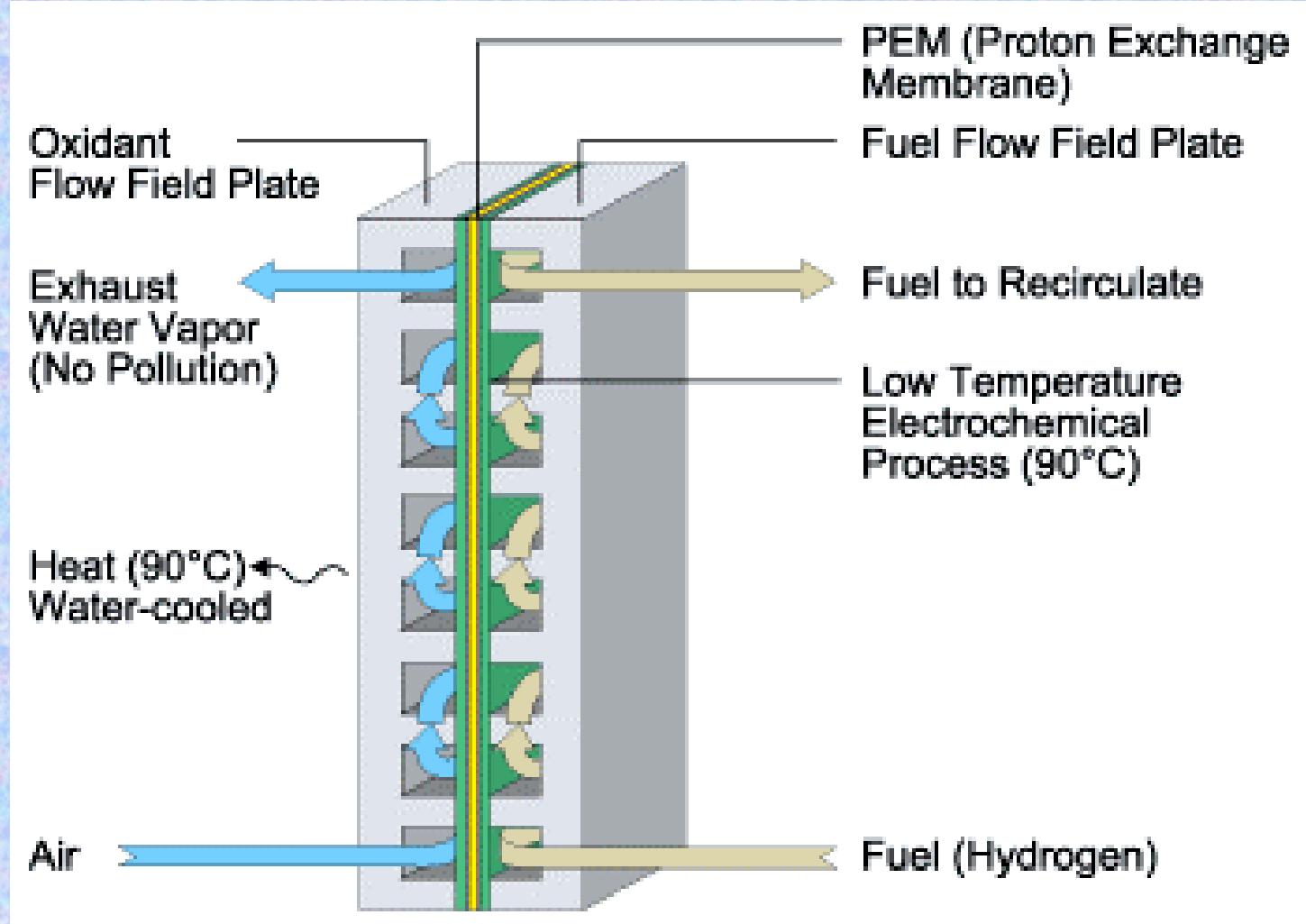
Yield: 40 - 50 %

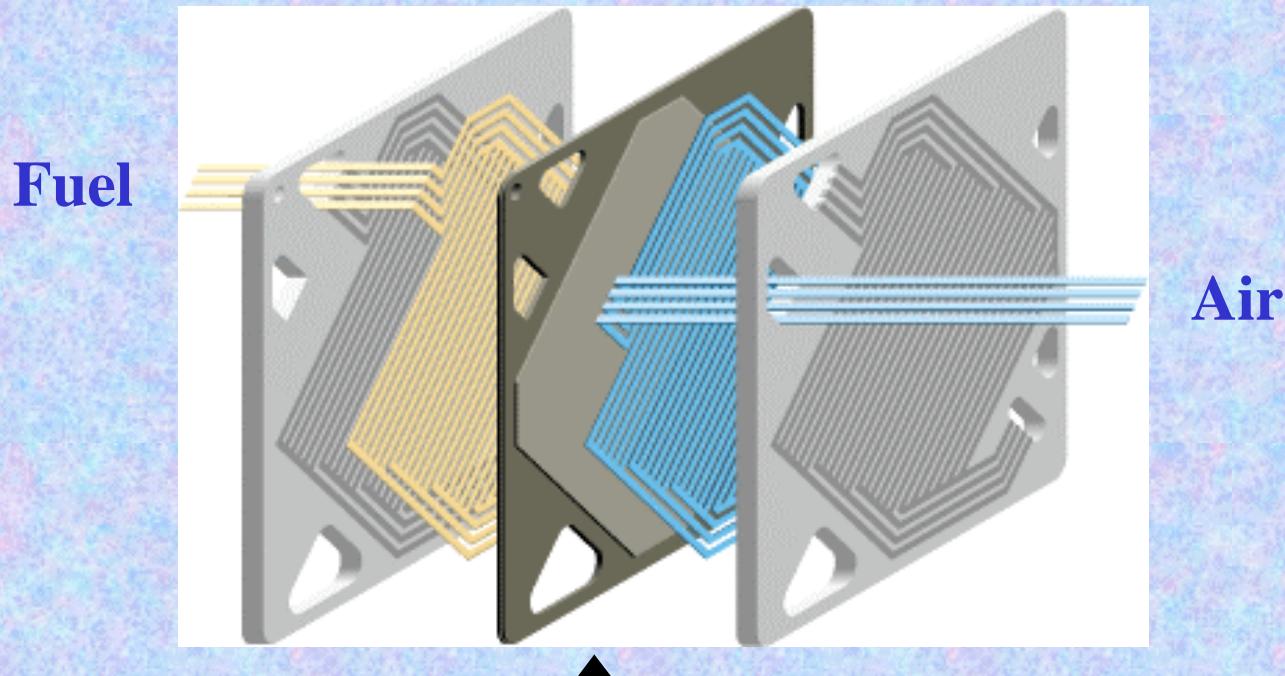
Fuel: H₂, CH₃OH (DMFC). CO < 50 ppm.

Units: "Commercial" up to 50 kW

- Hydrated polymer (T<100°C) → efficient catalysts

Proton Exchange Membrane Fuel Cell





Cooling water Humidification water

MEA: Membrane Electrode Assembly

Commercial PEMFC (Ballard)



1990

5 kW

(0.1 kW/L)

10 kW

28 kW

1996

50 kW

(1.2 kW/L)

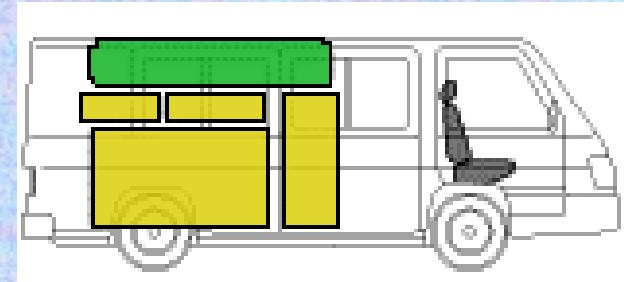
Fuel for Fuel Cells

	<u>Energy Density</u>	.
	<u>Mass (w·h/kg)</u>	<u>Volume (w·h/L)</u>
<u>Comp. Hydrogen</u>	20,000	1,000
<u>Liquid Hydrogen</u>	33,000	2,500
<u>Metallic Hydride</u>	370	3,300
<u>Methanol</u>	6,200	4,900
<u>Gas</u>	12,000	9,000
<u>H₂/C nanotubes</u>	16,000	32,000

Daimler-Chrysler

NECAR 1 (1994)

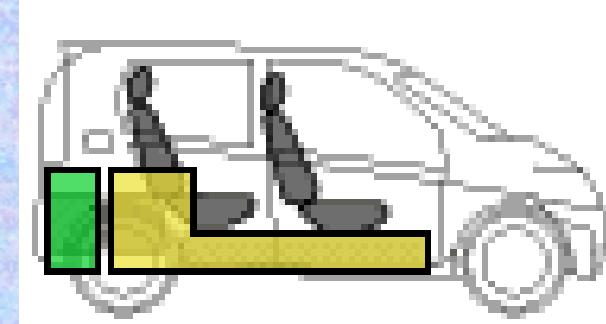
- Mercedes-Benz Van 190
- 50 kW
- 12 Stacks (167 W/L) 
- Fuel: Hydrogen 



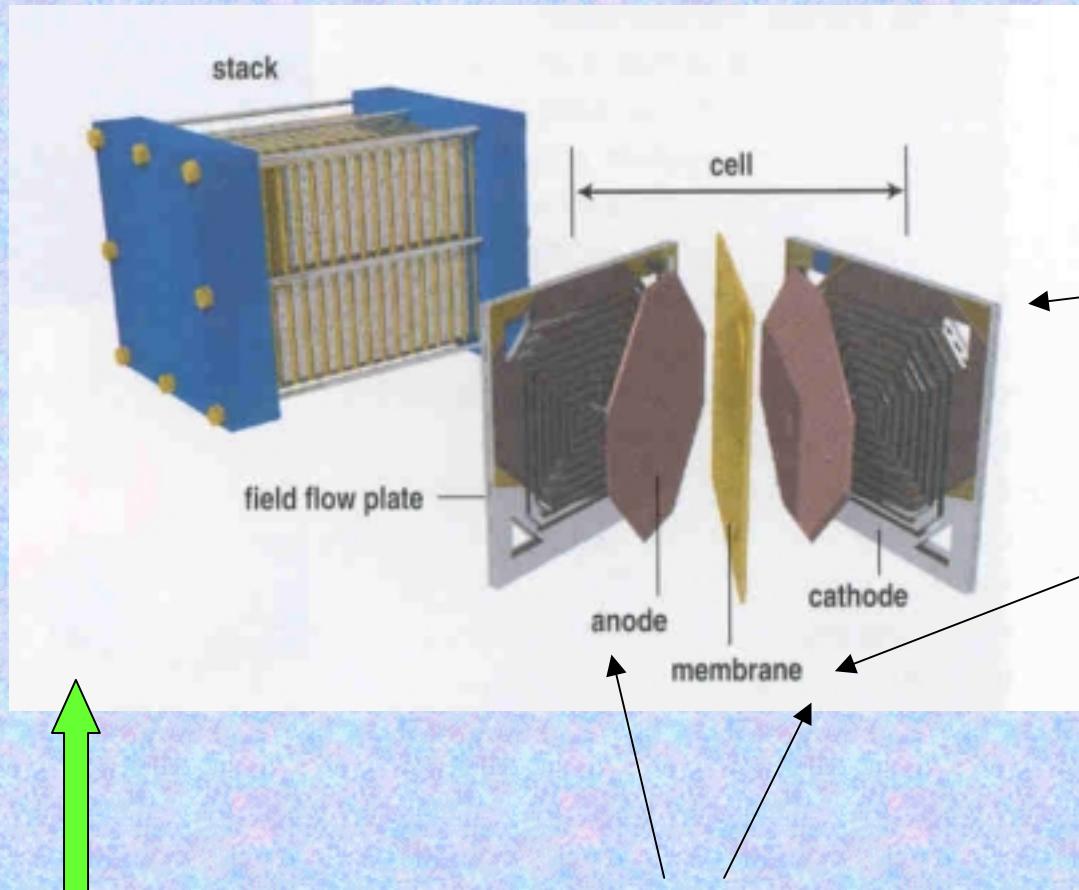
NECAR 4 (1999)

- Mercedes-Benz Class A
- 50 kW
- 2 Stacks (1.2 kW/L) 
- Fuel:

Methanol + Hydrogen 



FC Improvements



Reformer

- Flexible catalysts for several fuels
(Yield >33-37%)
- Free sulfur fuel

Bipolar plate

- Conducting polymers

Membrane

Nafion substitutes:

- Lower cost (90 €/kW)
- No crossover (DMFC)

Electrodes

- Lower Pt load (principally DMFC)
1986: 16 g/kW --> 0.5 g/kW (~6 €)
- Alternative electrodes (cathode)

FC Competitive cost: 50 €/kW

Acknowledges

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 Dr. M.L. Granados

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 Mrs. L. Blanco ()*
 Mrs. I. Cabrera ()*

Synthesis of Methanol: *Mr. I. Melián*

Hydrogen from Methanol: *Dr. R. Navarro*
 Dr. S. Murcia-Mascarós

Electrocatalysts for FC: *Dr. C. Larese*

A new energy framework: The hydrogen economy

