UNIVERSITY OF PATRAS
DEPARTMENT OF CHEMICAL ENGINEERING
LABORATORY OF HETEROGENEOUS CATALYSIS

Chemical Reaction Engineering & Catalysis in Future Distributed Power Generation Systems

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New Frontiers in Chemical & Biochemical Engineering

In Honor of Professors Anastasios Karabelas and Stavros Nychas

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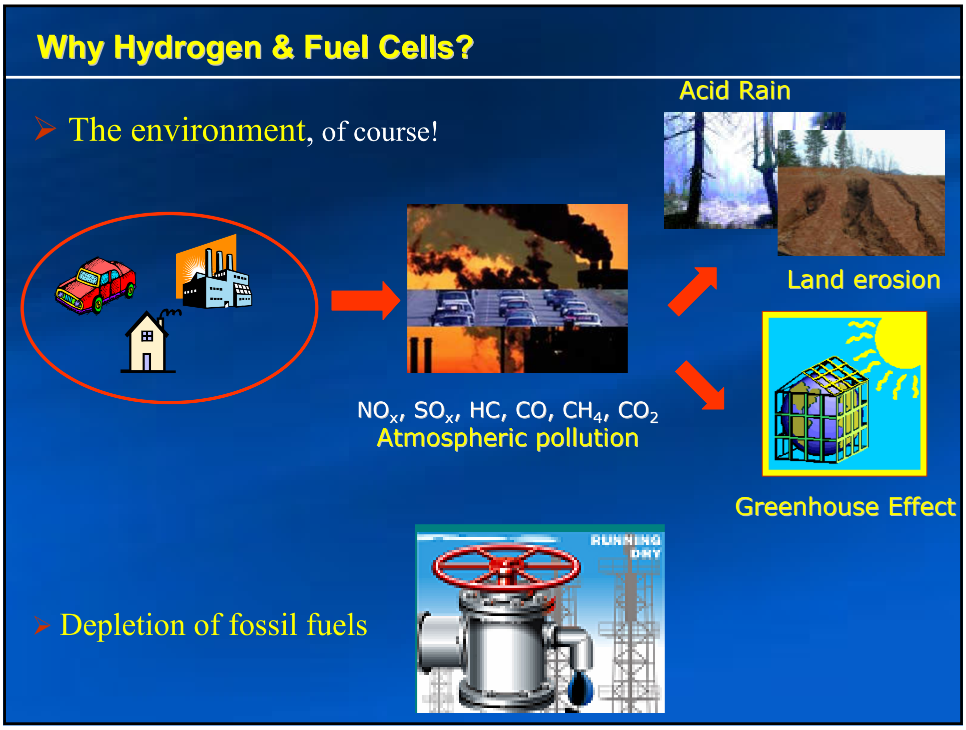
Why Distributed Power Generation?

Currently: Centralized power generation (coal or gas power plants, nuclear power plants, hydropower plants)

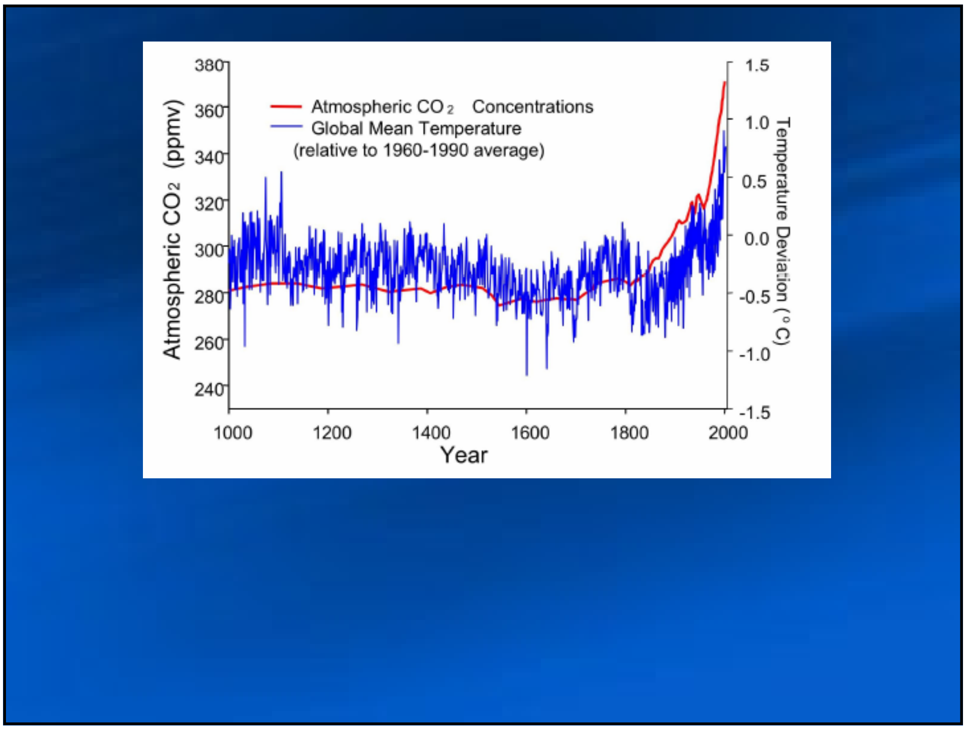
Advantages: Economy of scale
Disadvantages: Long distance transmission of electricity (cost, loss of power)
Health and safety issues
Environmental problems

Future: Distributed power generation – Power production on site and on demand

Advantages: District heating – high efficiency
Lower maintenance costs
Less capital intensive
Reduced pollution – **Early adaptation of fuel cells & hydrogen**

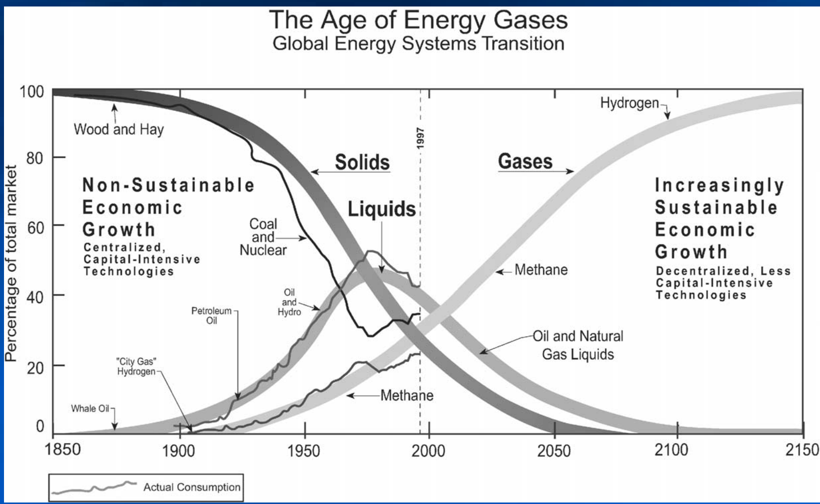


Why Hydrogen & Fuel Cells?
The environment, of course!
Acid Rain
Land erosion
NOx, SOx, HC, CO, CH4, CO2
Atmospheric pollution
Greenhouse Effect
Depletion of fossil fuels
RUNNING DRY



Atmospheric CO2 Concentrations
Global Mean Temperature
(relative to 1960-1990 average)
Atmospheric CO2 (ppmv)
380
360
340
320
300
280
260
240
Temperature Deviation (°C)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
1000
1200
1400
1600
1800
2000
Year

Global Fuel Mix



Where does hydrogen fuel come from?

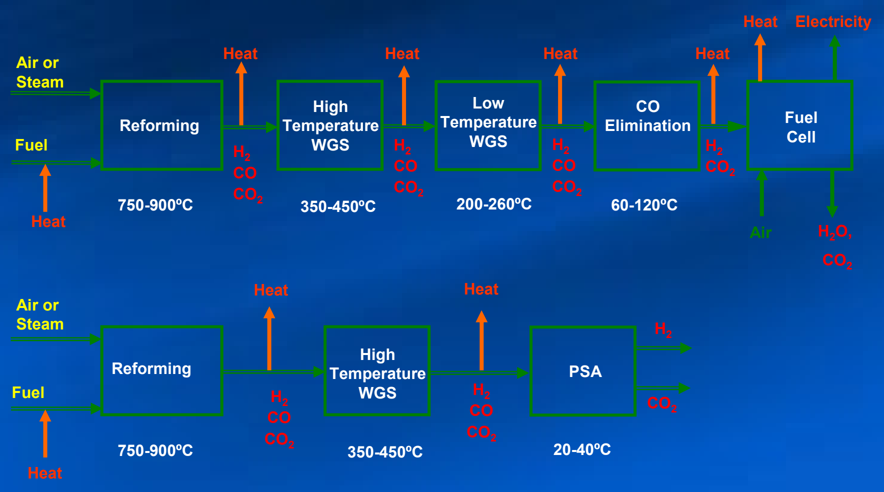
- Renewable electricity (photovoltaic, wind) via electrolysis
- No GHG emissions

- Biomass – derived fuels (bioethanol, biogas, etc.)
- Very low GHG emissions
- > high capital cost
- > technically challenging integration

- Fossil fuels - Natural gas
- GHG emissions reduction by 50%

NEED FOR FUEL REFORMATION & PROCESSING

HYDROGEN PRODUCTION VIA FUEL PROCESSING



Catalytic Reactions Taking Place

<u>Steam Reforming:</u> $CH_4 + H_2O = CO + 3H_2$
$C_mH_n + mH_2O = mCO + (m+1/2\ n\ H_2$
$CH_3OH + H_2O = CO_2 + 3H_2$

Partial Oxidation: $CH_4+O_2= CO+2H_2$
$C_mH_n+1/2mO_2=mCO+1/2nH_2$
$CH_3OH + ½\ O_2=CO_2+2H_2$

<u>Autothermal Reforming:</u> $CH_4 + ½\ H_2O + 1/2\ O_2 = CO + 5/2\ H_2$
$C_mH_n + ½\ m\ H_2O + 1/4\ m\ O_2 = mCO + (½\ m + ½\ n)\ H_2$
$CH_3OH + ½\ H_2O + ¼\ O_2 = CO_2 + 2.5\ H_2$

<u>Carbon Formation</u>: $CH_4 = C + 2H_2$
$C_mH_n = xC + C_{m-x}H_{n-2x} + xH_2$
$2CO = C + CO_2$
$CO + H_2 = C + H_2O$

<u>Water - gas shift</u>: $CO + H_2O = CO_2 + H_2$

<u>CO oxidation</u>: $CO+O_2 =CO_2$
$H_2 + ½\ O_2 = H_2O$

OR

<u>CO methanation</u> : $CO + 3\ H_2 = CH_4 + H_2O$
$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$

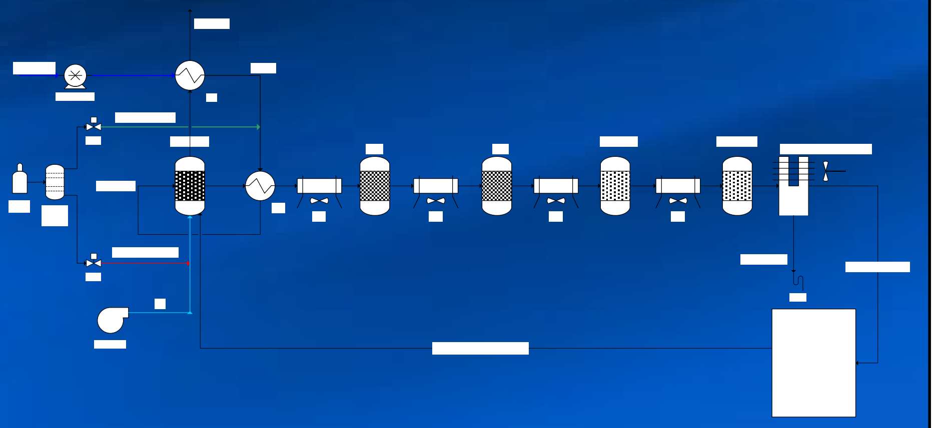
Catalytic Steam Reforming vs Autothermal Reforming

Advantages of Steam Reforming	Disdvantages of Steam Reforming
➢ *higher hydrogen yield*	➢ *need for heat exchanging surfaces*
➢ *higher hydrogen concentration*	⇒ *complicated reformers*
⇒ *higher F.C. efficiency*	➢ *slower start-up*
➢ *lower volumes*	➢ *carbon deposition issues*
➢ *less hazardous*	

ENERGY PRODUCTION VIA H_2 AND FUEL CELL

5 $KW_{(ELECTRIC)}$ NET POWER PRODUCTION

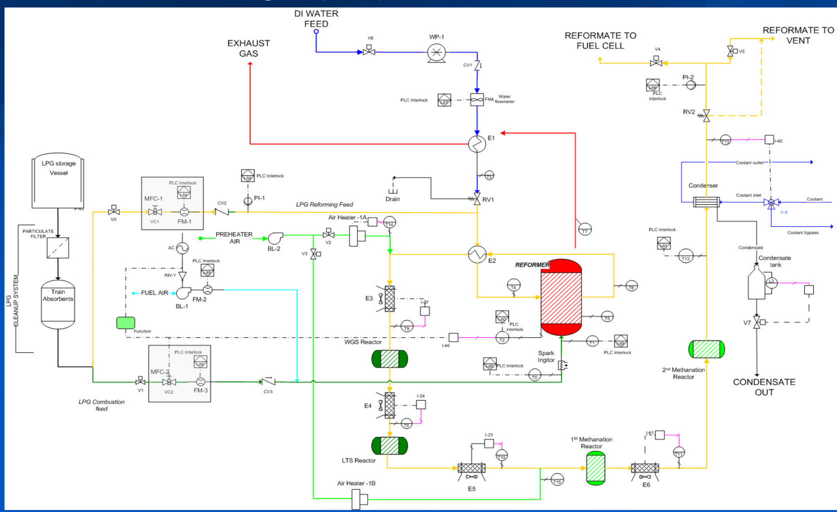
Process flow diagram and mass and energy balances draw-up



ENERGY PRODUCTION VIA H_2 AND FUEL CELL

5 KW$_{(ELECTRIC)}$ NET POWER PRODUCTION

Pipe and Instrumentation Diagram (P&ID)



Fuel processors for distributed power generation

DESIRABLE CHARACTERISTICS

- **Highly compact**
- **High efficiency**
- **Produce no atmospheric pollutants**
- **Produce hydrogen suitable to be fed to FCs**
- **Integrated with FCs in process and in control**
- **Short start –up time**

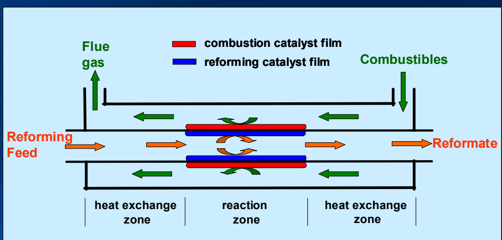
Main Issues / Problems in Fuel Processing

Steam reforming : Rapid heat transport to the reformation zone
(Heat-exchanger type reactors)
Heat transfer within catalyst pellets

Water – gas shift reaction: Very active catalyst so as to approach equilibrium rapidly

Methanation reaction: Selective catalyst for methanation of CO and **NOT** of CO2

Advanced Reactors for Steam Reforming- HIWAR

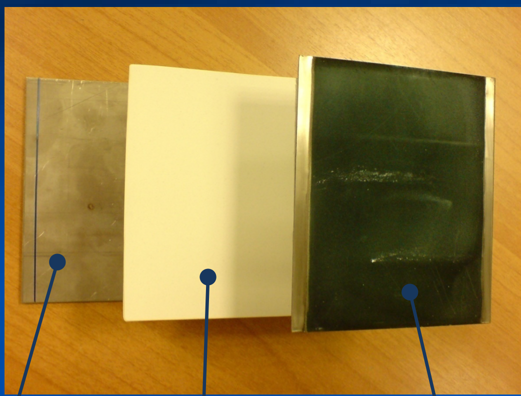


Heat-Integrated Wall Reactor (HIWAR)

> Heat Exchanger type reactor reduces dead volumes and heat transfer resistances
> Heat is produced very close to area of demand
>Very rapid heat transfer through the metallic tube wall (low resistance)
> Required amount of reforming catalyst is significant lower than in a typical fixed bed operation

Plate type HIWAR

Reformer plate preparation



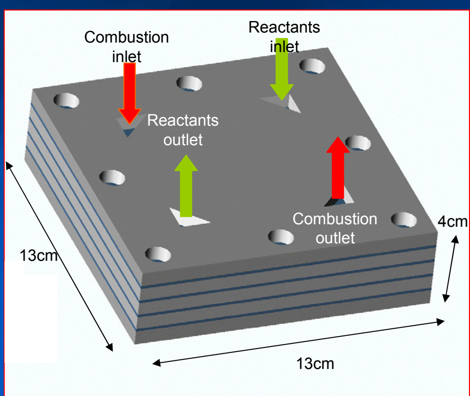
Raw Plate

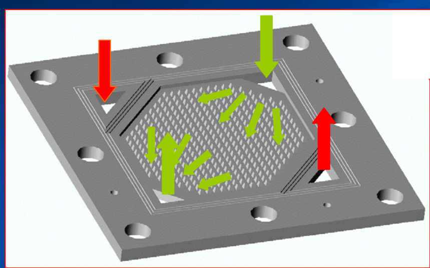
Plate coated w/ Alumina by plasma spraying

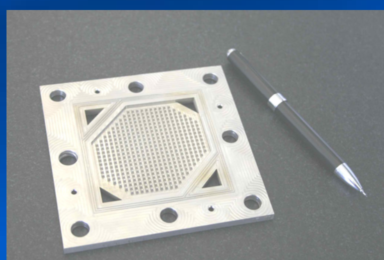
Plate coated w/catalyst

Plate reactor for steam reforming

Plate reformer 450W

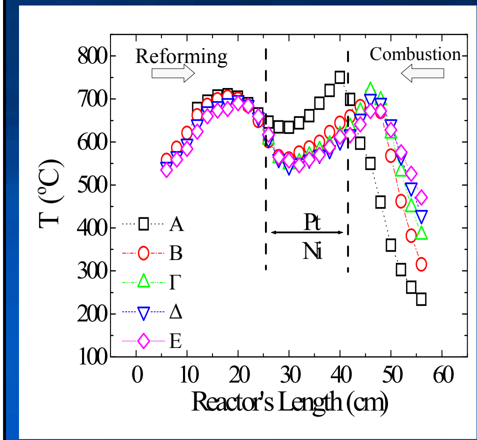


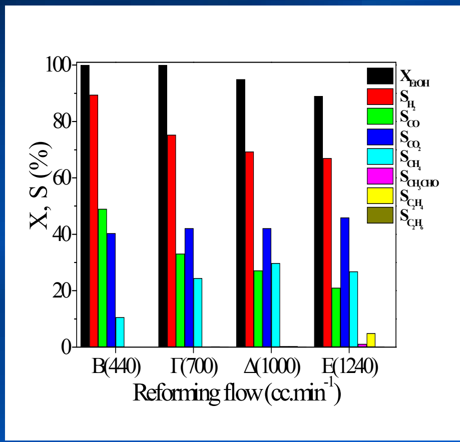




Advanced Reactors for Steam Reforming

Effect of reforming flow

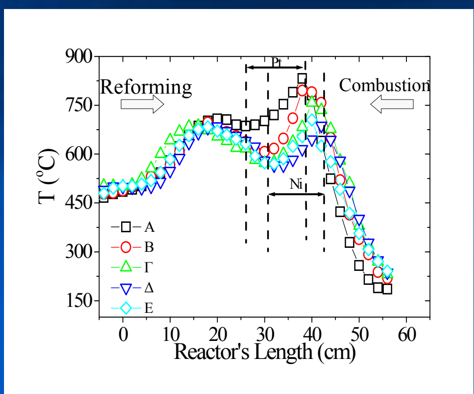


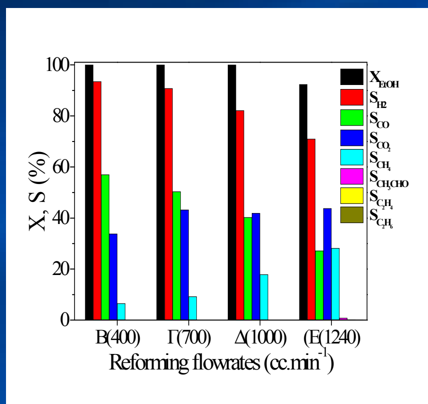


***Combustion feed*: 5.5 % EtOH, 7.5 % H_2O, 87% Air, F_T=2300 cc.min^{-1}**
***Reforming feed*: (A) 300 cc.min^{-1} He, (B-E) EtOH/H_2O = 1/3**

Advanced Reactors for Steam Reforming

Change of the catalysts position





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***Reforming feed*: (A) 300 cc.min^{-1} He, (B-E) EtOH/H_2O = 1/3**

Water-gas Shift reaction

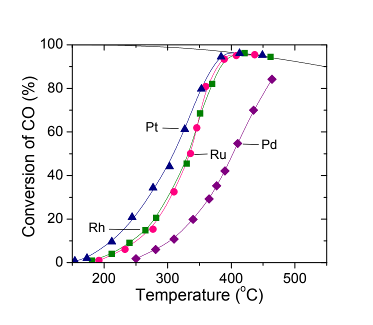
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

ΔH= - 41.1 kJ/mol

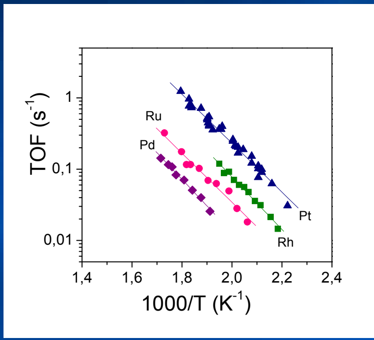
Effect of the nature of the dispersed metallic phase

$3\%CO, 10\%H_2O$

$0.5\%M/TiO_2$



Effect of reaction temperature on the conversion of CO over Pt, Rh, Ru and Pd catalysts supported on TiO_2.



Arrhenius plot of TOFs obtained over Pt, Rh, Ru and Pd dispersed on TiO_2

Catalytic activity depends on the nature of the dispersed metallic phase, following the order:

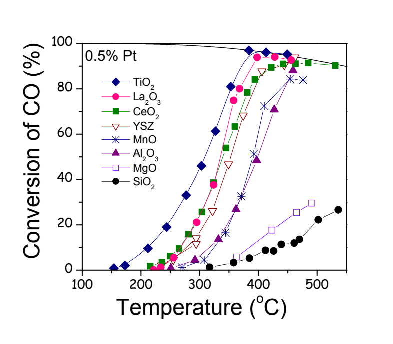
Pt > Rh > Ru > Pd

with Pt being about 20 times more active than Pd.

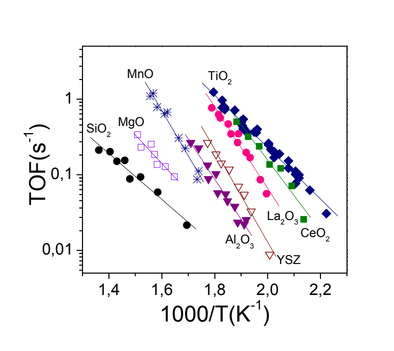
Effect of the nature of the support - Pt catalysts

3%CO, 10%H_2O

0.5%Pt/MO_x



Catalytic performance of Pt supported on commercial oxides



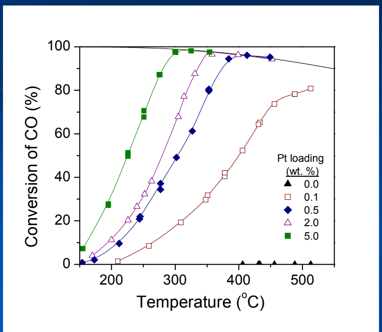
Arrhenius plot of turnover frequencies (TOF) of Pt catalysts dispersed on the indicated metal oxides

The turnover frequency (TOF) is 1-2 orders of magnitude higher when Pt is supported on "reducible" (e.g. TiO_2, CeO_2 etc.) rather than on "irreducible" (e.g. Al_2O_3, MgO, SiO_2) metal oxides.

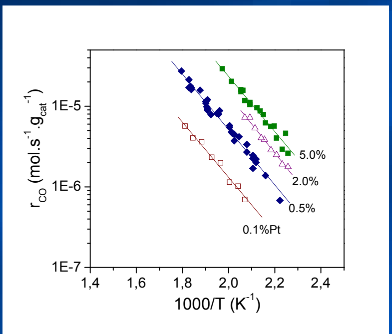
Effect of metal loading and crystallite size – Pt/TiO_2

3%CO, 10%H_2O

x%Pt/TiO_2



Effect of metal loading on the catalytic performance of Pt/TiO_2 catalysts.



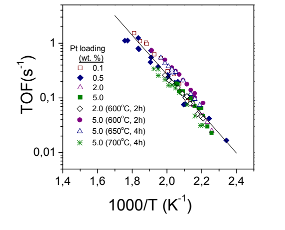
Arrhenius plots of rate of CO conversion obtained over x%Pt/TiO_2 catalysts.

- **Conversion of CO at a given temperature increases significantly with increasing Pt loading in the range of 0.1 – 5.0%.**
- **The activation energy of the reaction does not practically change.**

Effect of metal loading and crystallite size

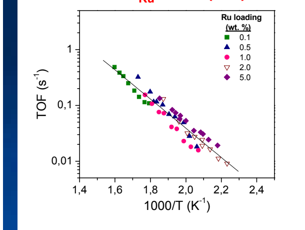
x%Pt/TiO_2

1.2 < d_{Pt} < 16.2 (nm)



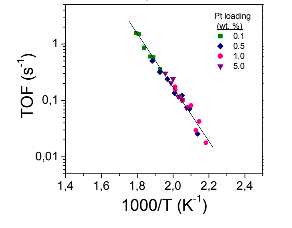
x%Ru/TiO_2

1.0 < d_{Ru} < 4.5 (nm)



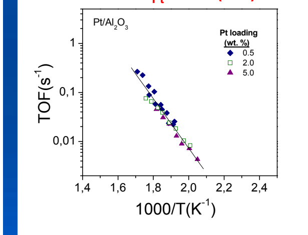
x%Pt/CeO_2

2.0 < d_{Pt} < 9.1 (nm)



x%Pt/Al_2O_3

0.9 < d_{Pt} < 1.7 (nm)

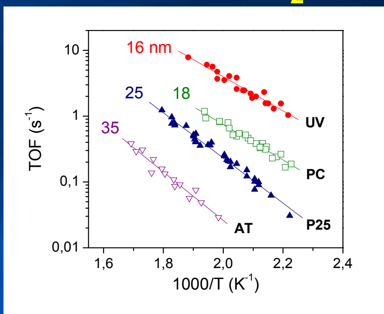


TOF does not depend on metal loading, dispersion and mean crystallite size but only on the amount of exposed surface metal atoms.

The rate is proportional to the metal surface area

Effect of the morphology of the support – TiO_2

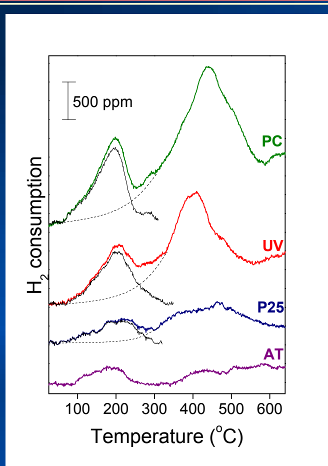
0.5%Pt/TiO_2



Effect of the nature of TiO_2 support on the catalytic activity of Pt.

The catalytic activity of Pt is improved significantly when supported on TiO_2 with low primary crystallite size (high surface area).

The WGS activity of Pt/TiO_2 catalysts is enhanced with increasing the "reducibility" of the support.



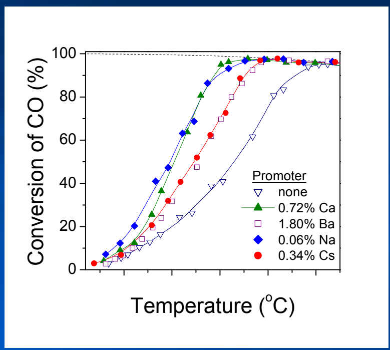
Consumption of H_2 obtained during TPR of preoxidized Pt/TiO_2 catalysts with 0.5%H_2/He

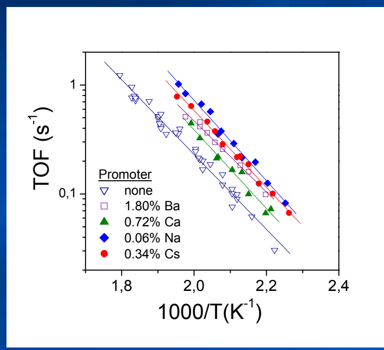
The "reducibility" of the support increases with decreasing the primary crystallite size (d_{TiO2}).

Effect of the addition of alkali/alkaline earth promoters

3%CO, 10%H_2O

0.5%Pt/(TiO_2-alkali/alkaline earth)



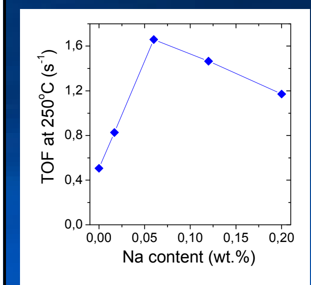


Effect of the addition of alkali/alkaline earth on the catalytic performance and reaction rate of 0.5%/TiO_2 catalysts

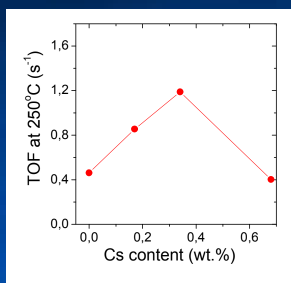
Addition of small amounts of alkalis/alkaline earths results in a significant improvement of catalytic activity

Effect of the addition of alkali/alkaline earth - TOF

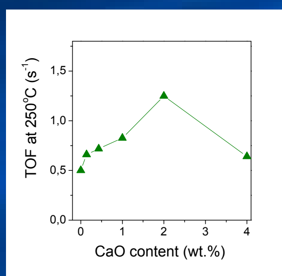
x% Na



x% Cs



x% CaO

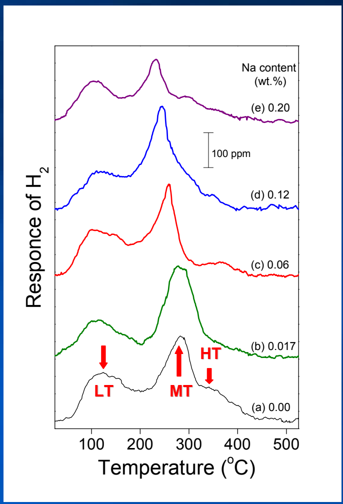


Effect of alkali/alkaline earth-promotion on TOFs at 250°C of Pt/TiO_2 catalysts

The specific reaction rate goes through a maximum for alkali:Pt =1 and Ca:Pt=14

Effect of the addition of alkali/alkaline earth - H_2-TPD

x% Na



Temperature programmed desorption of H_2 obtained from Na doped Pt/TiO_2 catalysts

LT: **Hydrogen chemisorbed on the surface of dispersed metal crystallites.**

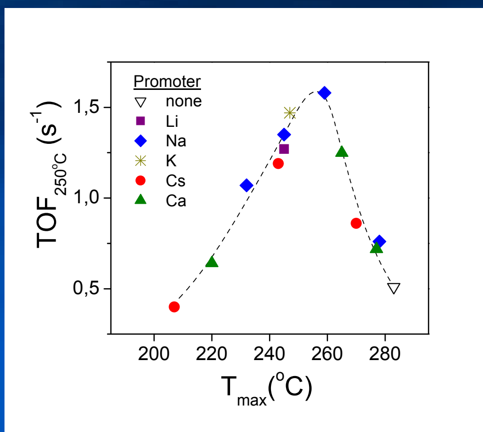
HT: **Spillover hydrogen associated with the support.**

MT: **Hydrogen adsorbed at sites located at the metal/support interface.**

Addition of alkali/alkaline earth results in weakening of hydrogen adsorption on sites located at the metal/support interface, which is reflected to a significant shift of the corresponding TPD peak toward lower temperatures.

Effect of the addition of alkali/alkaline earth

0.5%Pt/(TiO_2-alkali/alkaline earth)

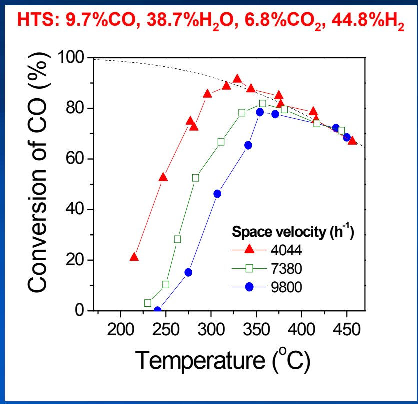


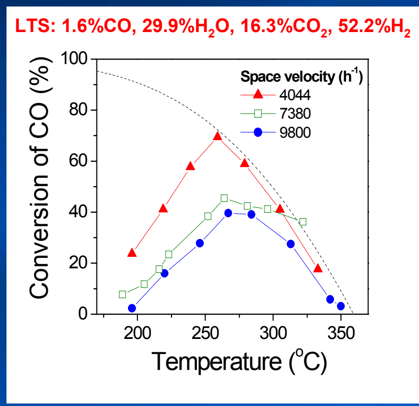
Volcano-type dependence of TOF at 250°C on the desorption temperature (T_{max}) of the medium temperature (MT) peak observed in H_2-TPD profiles of Pt/X-TiO_2 catalysts

The specific reaction rate is determined to a large extent by the chemisorptive properties of sites at the metal-support interface.

Effect of space velocity under realistic reaction conditions

0.5%Pt/(1%CaO-TiO_2)



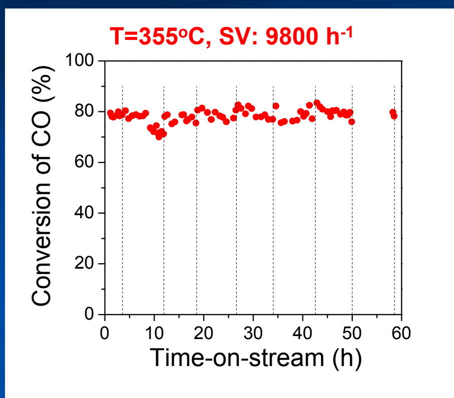


Effect of space velocity on the conversion of CO

The conversion of CO increases with decreasing space velocity.

Long-term stability test- 0.5%Pt/1%CaO-TiO_2

9.7%CO, 38.7%H_2O, 44.8%H_2, 6.8%CO_2



Long-term stability test of 0.5%Pt/1%CaO-TiO_2 catalyst:
Alterations of the conversion of CO with time on stream.

Selective methanation of CO

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

ΔH= - 206.2 kJ/mol

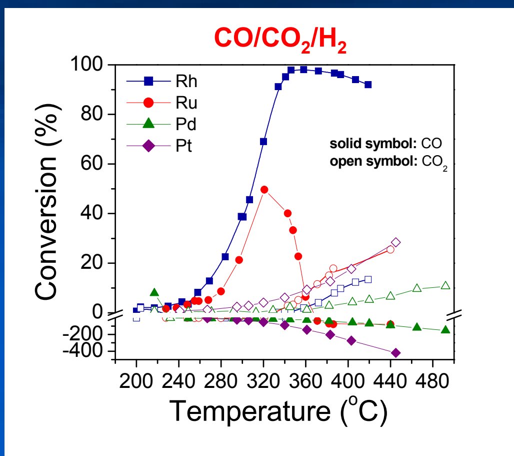
$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

ΔH= - 165.0 kJ/mol

Effect of the nature of the metallic phase – Al_2O_3

1%CO, 15%CO_2, 50%H_2

0.5%Ru/Al_2O_3



$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

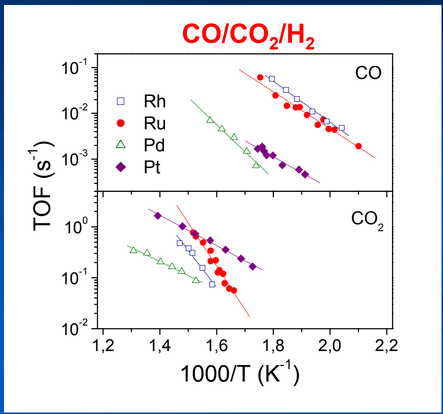
$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

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

Conversions of CO and CO_2 as functions of reaction temperature obtained over Ru, Rh, Pt and Pd supported on Al_2O_3.

Effect of the nature of the metallic phase – Al_2O_3

0.5%M/Al_2O_3



Arrhenius plots of turnover frequencies (TOF) of CO and CO_2 conversion obtained over M/Al_2O_3

CO conversion

The turnover frequency (TOF) of CO conversion follows the order:

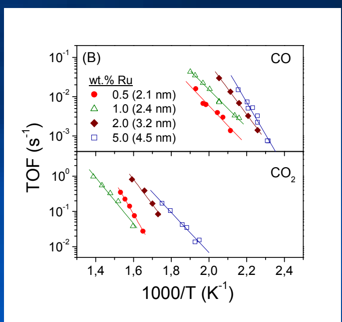
Rh > Ru >> Pt > Pd

with Rh and Ru catalysts being 1-2 orders of magnitude more active than Pt and Pd.

Loading and metal crystallite size

$CO/CO_2/H_2$

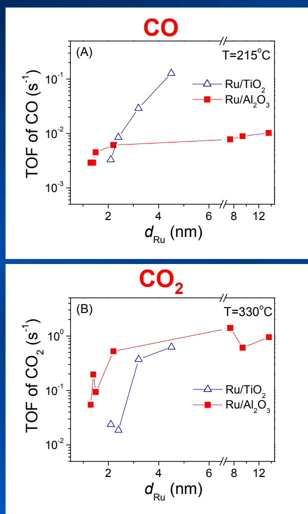
x%Ru/TiO_2



Arrhenius plots of turnover frequencies (TOF) of CO and CO_2 conversions obtained over x%Ru/TiO_2 catalysts.

The CO/CO_2 hydrogenation reactions are structure sensitive with respect to the metal.

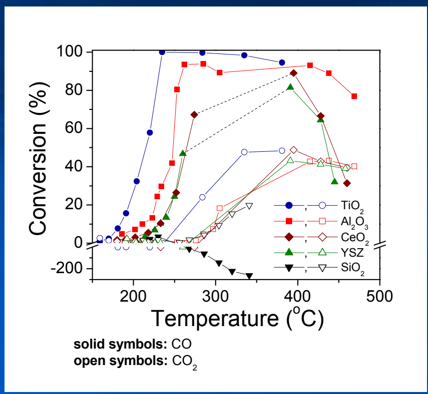
x%Ru/Al_2O_3, x%Ru/TiO_2



Effect of mean Ru crystallite size (d_{Ru}) of Al_2O_3- and TiO_2-supported catalysts on the turnover frequency (TOFs) of CO and CO_2

Influence of the nature of the support–Ru catalysts

$CO/CO_2/H_2$-5%Ru/MO_x



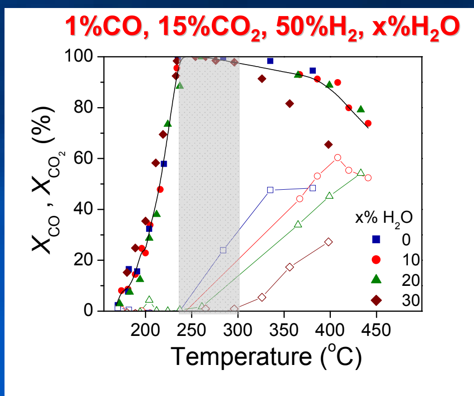
Catalytic performance of Ru (5 wt.%) supported on the indicated commercial oxide carriers.

Ru/TiO_2 catalyst exhibits a superior performance

it is able to completely and selectively hydrogenate CO at 230°C

Effects of water vapor in the gas mixture

5%Ru/TiO_2



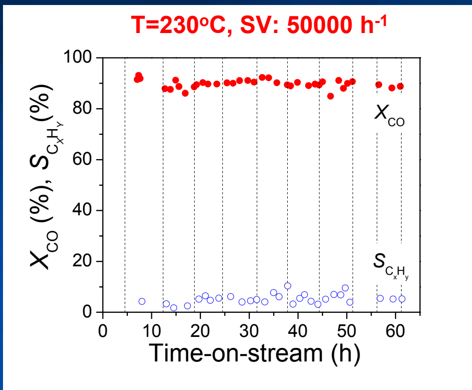
Effect of the addition of water vapor in the feed (0-30%) on the catalytic performance of 5%Ru/TiO_2 catalyst for the selective methanation of CO.

The conversion curve of CO remains practically unaffected by the presence of H_2O.

In contrast, the conversion curve of CO_2 is shifted toward higher temperatures with increasing water content from 0 to 30%.

Long-term stability test- 5%Ru/TiO_2

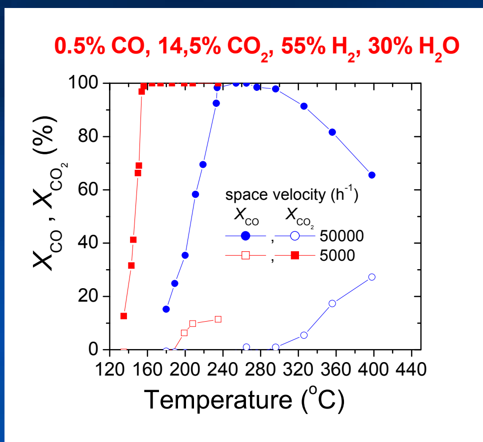
0.5%CO, 14%CO_2, 55.5%H_2, 30%H_2O



Long-term stability test of 5%Ru/TiO_2 catalyst: Alterations of the conversion of CO and selectivities toward higher hydrocarbons (C_xH_y) with time on stream.

Catalytic performance under realistic reaction conditions

5% Ru/TiO_2



Effect of space velocity on the conversion of CO and CO_2.

Conclusions

Fuel processing for hydrogen production for FC applications posses three significant requirements: rapid heat transport to the catalytic sites, active WGS catalysis and selective CO methanation catalysis.

- The HIWAR reactor in either the tubular or the plate form offers very rapid heat exchange which results in high efficiency and compact design of the reformer.
- Catalytic activity for the WGS reaction depends on both, the metallic phase and the support. The 0.5%Pt/TiO_2 catalyst is sufficiently active for the WGS reaction.
- The WGS reaction seems to be facile with respect to the metal and structure sensitive with respect to the support. Rate may be increased significantly by addition of suitable amounts of alkali or alkaline earth promoters.
- The catalytic performance of supported noble metal catalysts for the selective methanation of CO depends strongly on the metal-support combination employed. Increasing metal loading results in a significant shift of both CO and CO_2 conversion curves toward lower temperatures. The 5%Ru/TiO_2 catalyst is sufficiently active, selective and stable for practical applications.