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Advanced Multi-Fuel Reformer for Fuel CELL CHP Systems

ReforCELL

new catalytic materials for reforming

Workshop 11 december - CEA Grenoble
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Industrial reforming

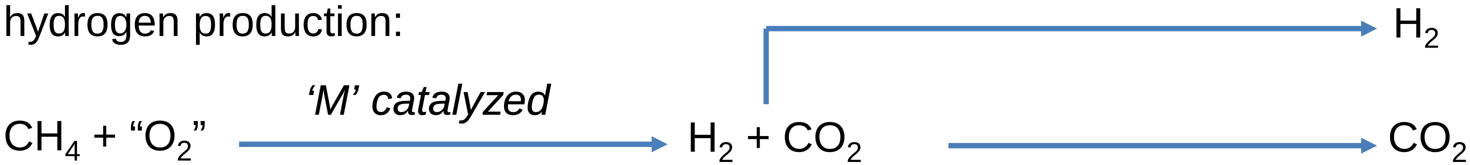
Auto-thermal reforming (ATR)

dry reforming	$2\ CH_4 + O_2 + CO_2$	$\rightleftharpoons$	$3\ H_2 + 3\ CO + H_2O$
Steam methane reforming (SMR)	$4\ CH_4 + O_2 + 2\ H_2O$	$\rightleftharpoons$	$10\ H_2 + 4\ CO$

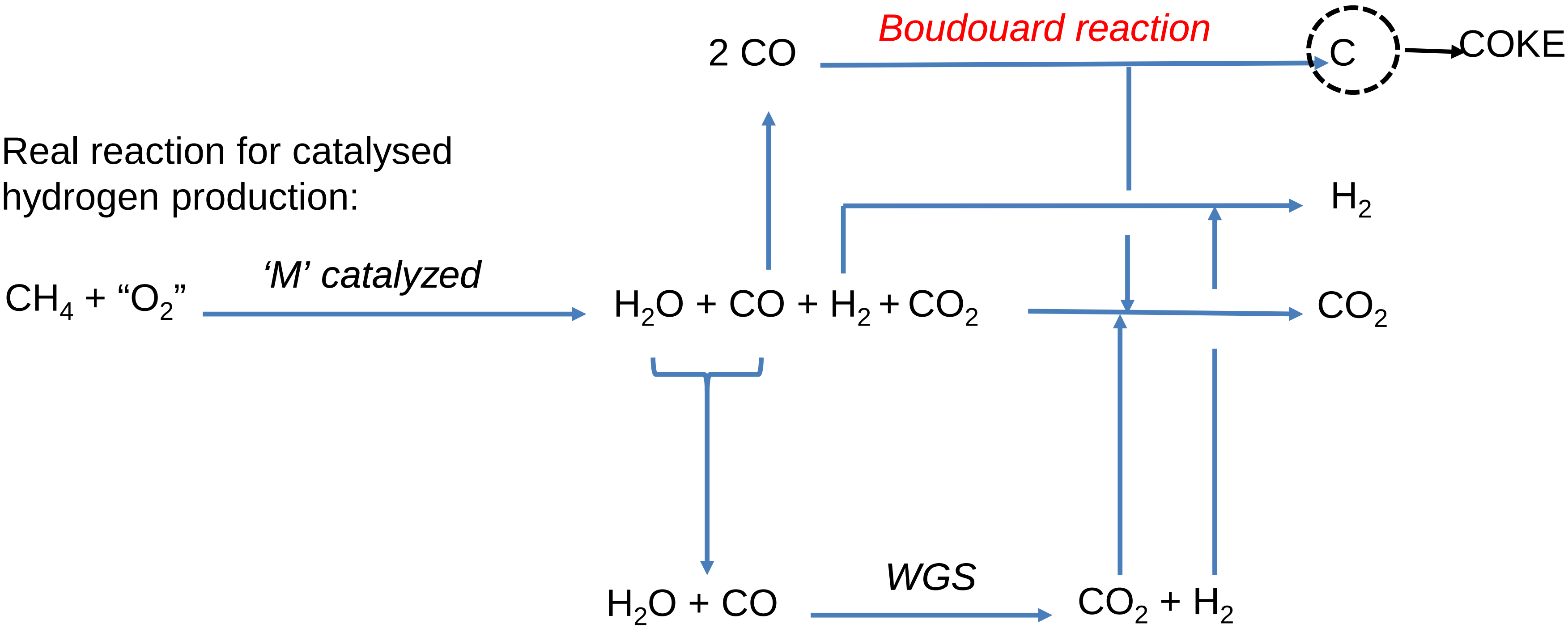
- Industrially reactions are performed over nickel based catalysts
- Typical loading in the range of 20-50 wt % depending on the type of catalyst (e.g. SMR, ATR)
- High reaction temperature (800 – 1100 ^{o}C) is maintained to prevent coking of the catalyst

Hydrogen production by reforming

Ideal reaction for catalysed hydrogen production:



Real reaction for catalysed hydrogen production:



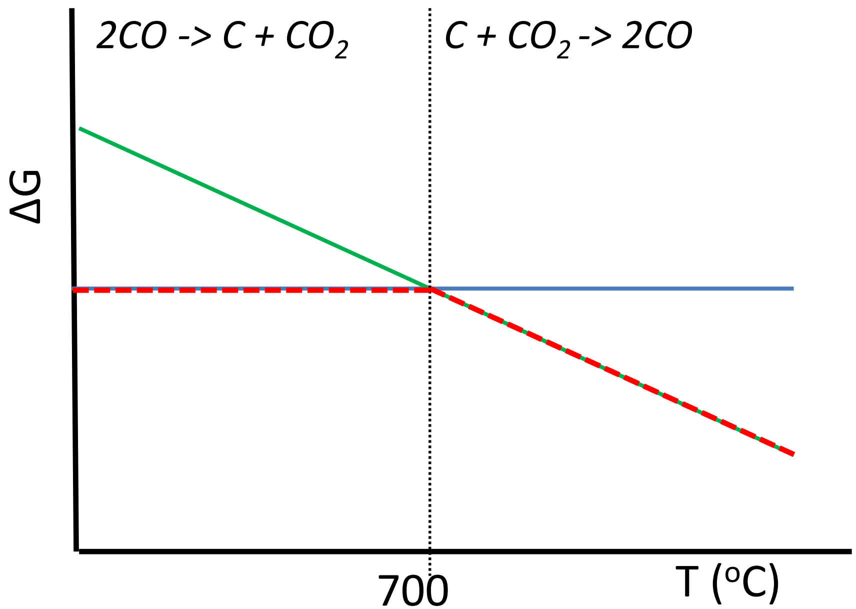
Thermodynamics of coke formation

Boudouard reaction:

$$2\,CO \rightleftharpoons C + CO_2$$

- T < 700°C formation of CO_2 and C dominant
- T > 700°C formation of CO dominant
- T = 700°C reaction equilibrium

Ellingham diagram for boudouard:

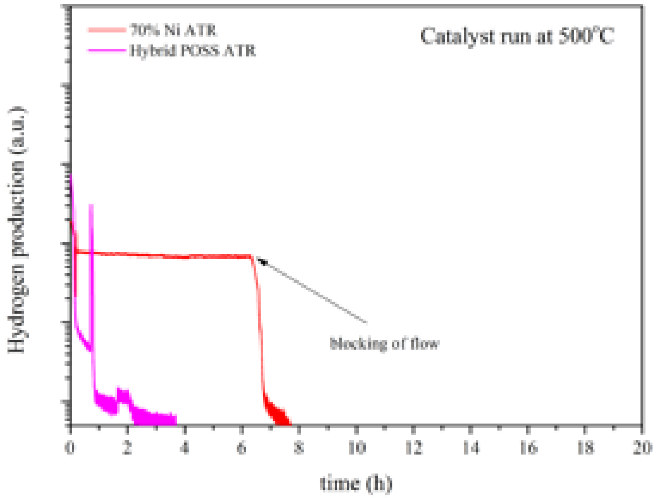


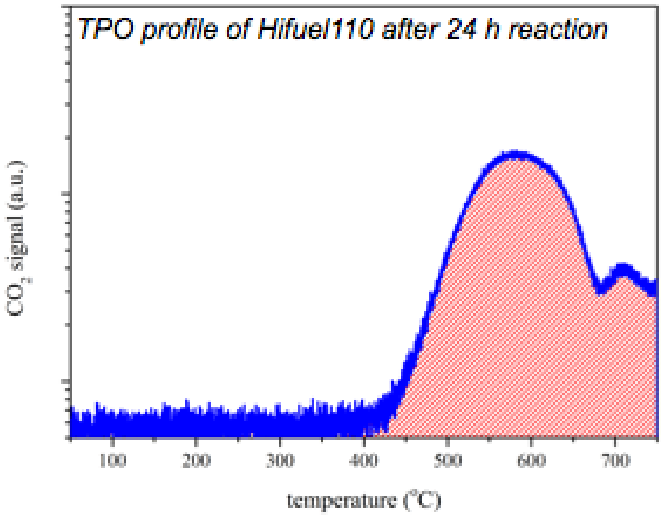
Oxidation of methane over Ni catalysts below 700°C will indefinitely lead to coke formation
All commercial catalysts for ATR and SMR are Ni based -> high T necessary

- *Membrane should be stable at 700°C or higher*
- *CO concentration in the reaction mixture should be minimalised*

Ni based catalyst

- Nickel catalysts show activity at 500ºC however they deactivate due to severe coke formation
- Regeneration can be achieved by calcination at high temperature





Catalyst	gcoke/gcat
commercial SMR	0.14
commercial ATR	0.19
20% Ni Hybrid catalysis	0.06

Low temperature catalyst

- Platinum group metals catalyze reforming reactions at lower temperature with less formation of coke
- Rhodium, Ruthenium and Platinum show reasonable to good activity
- Ceria zirconia support increases the catalyst effectivity

Ru:
- Good activity
- Less expensive
- Sensitive to high T

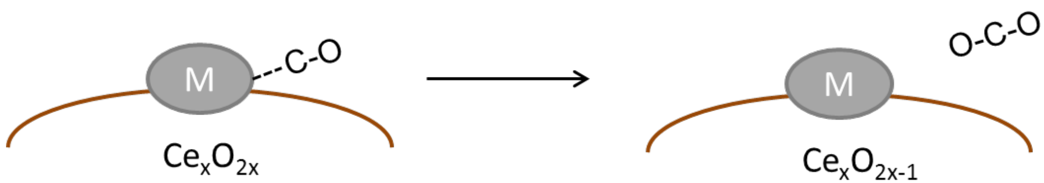
Rh:
- Good activity
- €€€
- Tested at TU/e

Ru	Rh	Pd
Os	*Ir*	*Pt*

Os:
- Extremely toxic
- Volatile

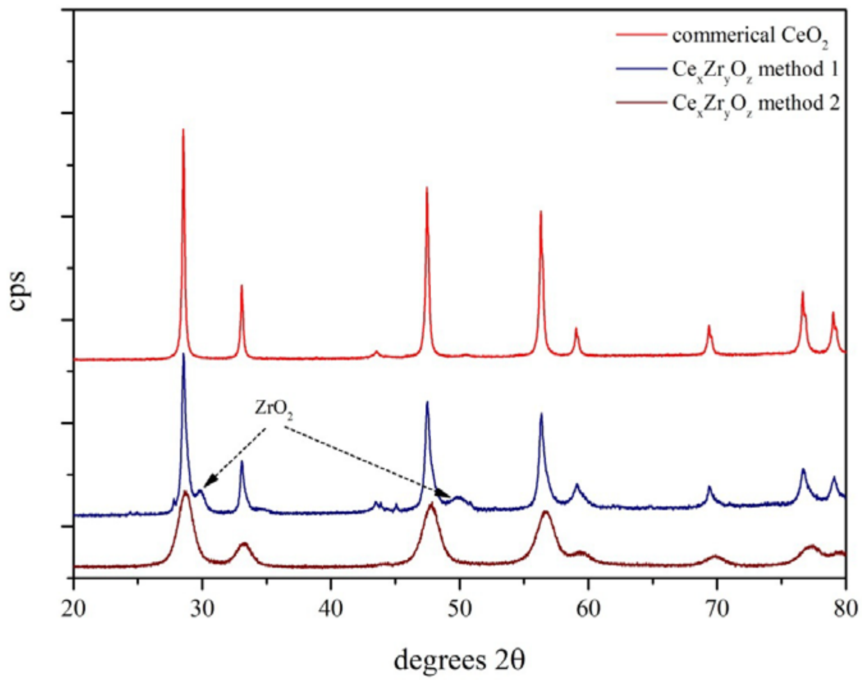
Ir:
- Less active

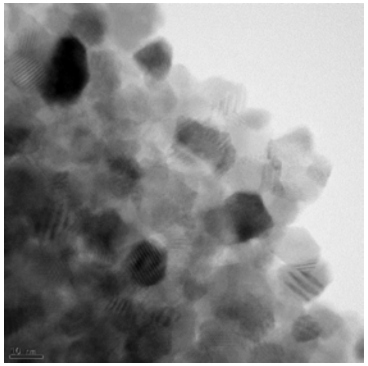
Pd, Pt:
- Active
- Expected to have good coke resistance

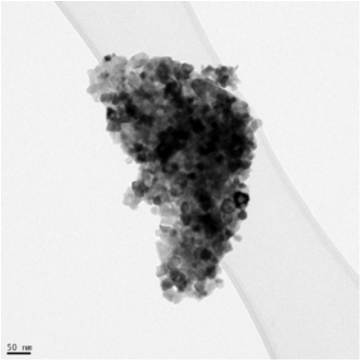


Support preparation

1. Co-precipitation of $Ce(NO_3)_3$ + $ZrOCl_2$ solution
2. pH controlled precipitation of $(NH_4)_2Ce(NO_3)_6$ and $ZrO(NO_3)_2$ using urea





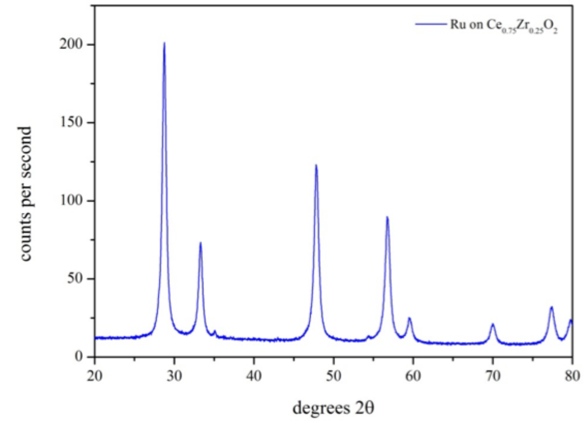


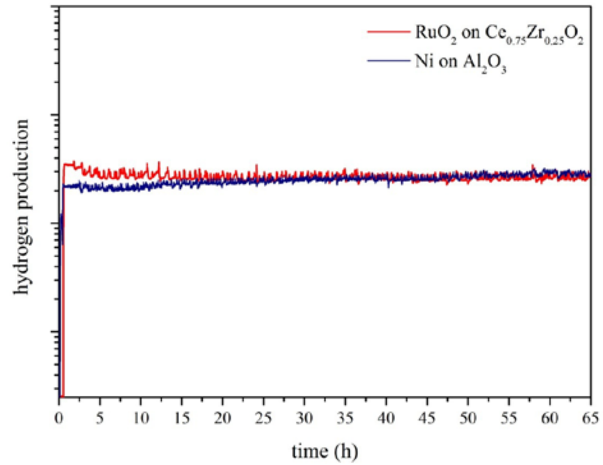
Support consist of crystallites in the 10 – 20 nm range BET surface area ~ 90 m^2/g

Ruthenium Loading

Ruthenium loading:

- incipient wetness impregnation of a ruthenium acetylacetonate precursor
- impregnation using aqueous ruthenium chloride
- controlled depositions precipitation of ruthenium from solution

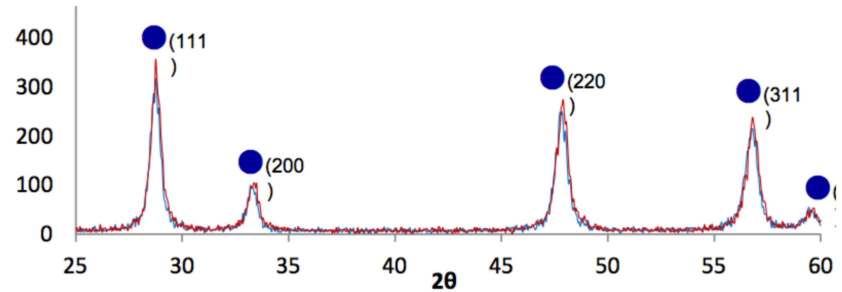


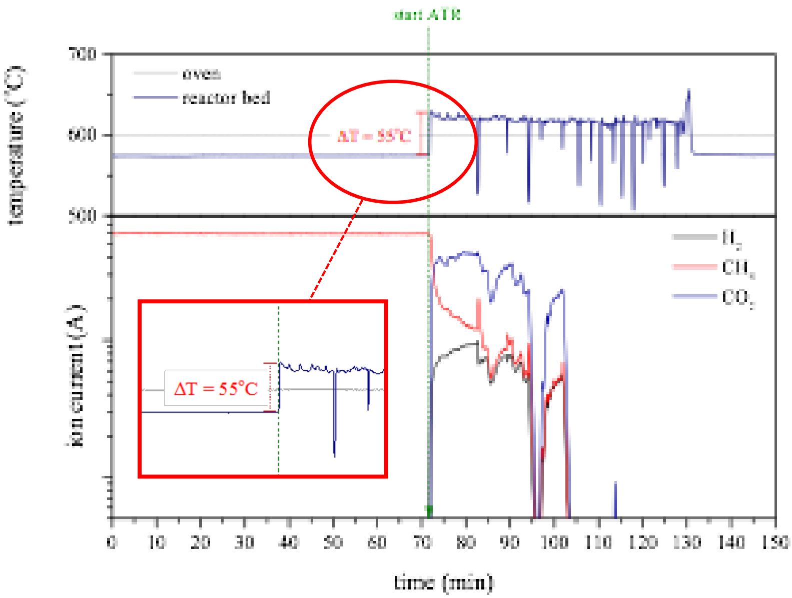


$Ar/CH_4/H_2O = 80:5:15$

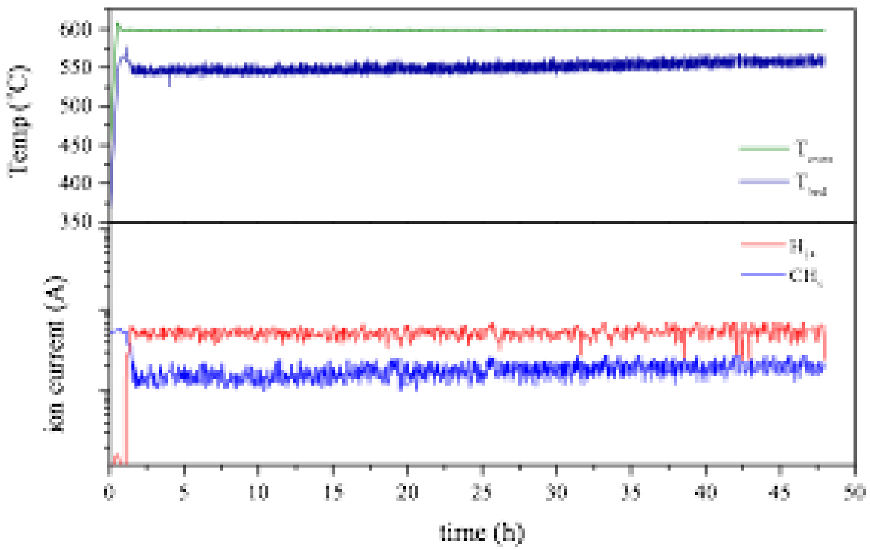
Catalyst testing and stability

- Support thermally stable up to 750ºC
- Strong temperature increase in fixed bed ATR during star up -> catalyst is damaged above 600ºC
- Stable operation in SMR





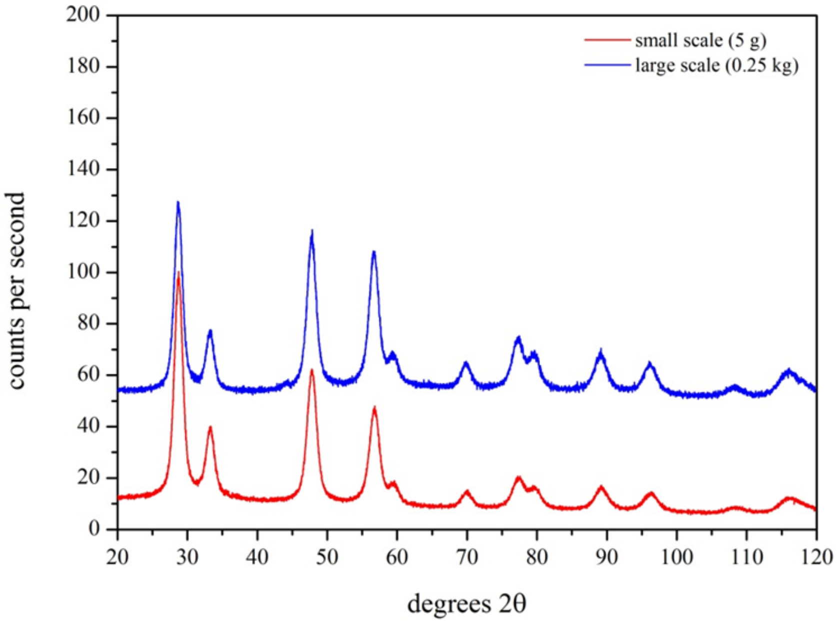
$CH_4/H_2O/O_2/Ar = 1/1.9/0.44/1.66$



$Ar/CH_4/H_2O = 80:5:15$

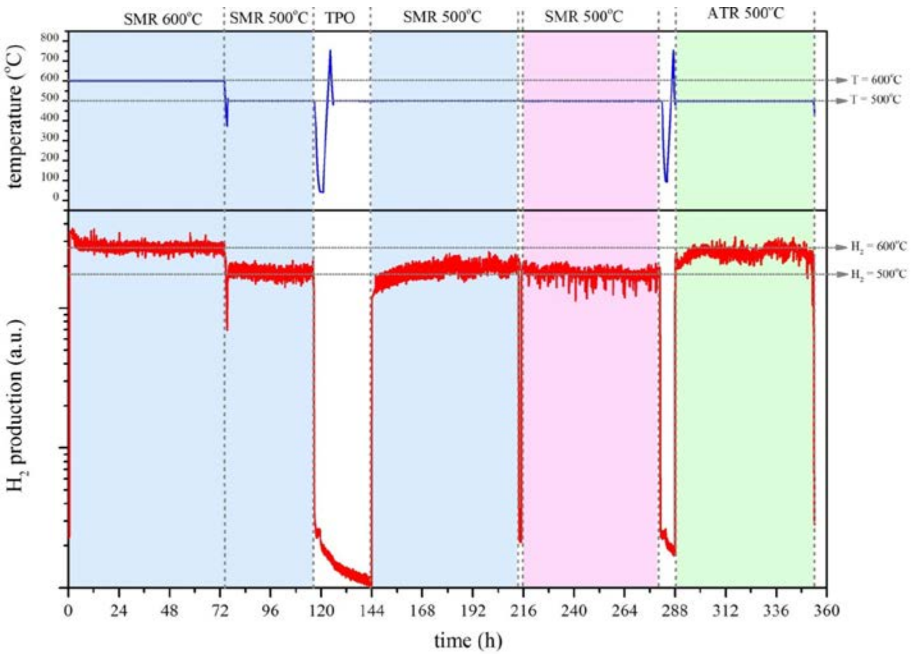
Bed: 200 mg cat / 800 mg inert
T_{oven} : 600; T_{bed} : 575

Upscaling of the catalyst preparation



- Support prepared in 10 L batch reactor on 0.5 kg scale XRD and TEM show no difference
- Ruthenium loaded on the support by controlled deposition
- Bed volume can be increased by addition of inert Zr based particles

Catalyst testing



- Catalyst tested in plug flow microreactor
- Stable operation at equilibrium conditions between 500°C and 600°C
- Catalyst runs under both SMR and "ATR" conditions

SMR conditions: 100 ml/min; 200 mg catalyst; Ar/CH_4/H_2O = 80:5:15;

SMR conditions: 100 ml/min; 200 mg catalyst; Ar/CH_4/H_2O/O_2 = 75:5:15:5;

'ATR' conditions: 100 ml/min; 200 mg catalyst; Ar/CH_4/H_2O/O_2 = 30:15:50:5

Conclusions

- Conventional reforming catalysts suffer from deactivation due to coking when applied at low temperature
- Platinum group metals dispersed onto a ceria based support show low temperature reforming activity
- The ruthenium based reforming catalyst as prepared on kg scale for the Reforcell project is both active and stable in the temperature range 500 - 600ºC