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Low Temperature Catalytic Partial Oxidation of Hydrocarbons on Ru- and Rh-based Catalysts

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Introduction

- The catalytic partial oxidation (CPO) of methane to synthesis gas and the further conversion to clean liquid transportation fuels (Gas-To-Liquids; GTL) is gaining considerable interest. The conversion of higher hydrocarbons to hydrogen containing fuels for fuel cell applications is another important topic.
- ***Low Temperature Catalytic Partial Oxidation of methane (LTCPO)***
  A proposed technology for synthesis gas generation is autothermal reforming (ATR) which operates at high temperatures. The Low Temperature Partial Oxidation (LTCPO) of Methane produces a CO_2 rich synthesis gas. Thus, an advanced Fischer-Tropsch reaction system (AFT) is currently developed including novel CO2 active catalysts and a dewatering membrane. The LTCPO-AFT concept could be an alternative low cost route for synthesis gas production. The aim of our work was to find catalysts with suitable methane conversion at low temperatures.

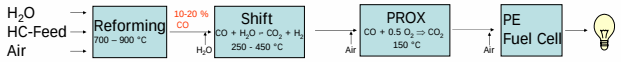
Autothermal Reforming (ATR) and Fischer-Tropsch (FT)

Low Temperature Catalytic Partial Oxidation (LTCPO) and Advanced Fischer-Tropsch (AFT)

- ***„Shift-less" Fuel processing for hydrogen production from gasoline***

Currently discussed concepts for gasoline reforming include a shift catalyst which reduces the amount of CO in a first step. The PSI „shift-less" concept operates at lower temperatures in the reformer. Thus, less CO is produced. This allows to omit the shift reactor. To demonstrate the „shift-less" concept a lab-scale fuel processor was linked-up to a PE fuel cell.

„Conventional " Process



„Shiftless" Fuel Processing

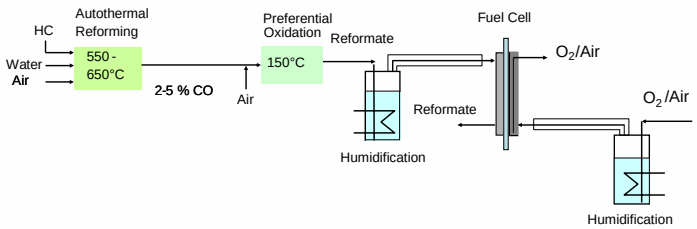
Experimental

LTCPO of Methane
Feed: CH_4/Air/H_2O; O/C=0.85; S/C=3-5
WHSV=30-100 $g_{Feed}/g_{cat}/h$
Reactor: Fixed-bed

Gasoline Reforming
Feed: Air, Water, and Gasoline (RON = 95, S < 1 ppm)
Reactor: Fixed-bed
Catalyst: 16 g 1%Rh/CeO_2/ZrO_2

PROX
Feed: Reformate, Air
Reactor: Annular fixed-bed
Catalyst: 6 g 5%Ru/CeO_2/ZrO_2

Lab-scale gasoline fuel processor

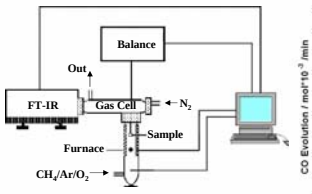


Schematic of the gasoline reformer-fuel cell system linkup.

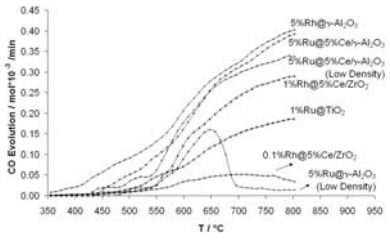
Results and Conclusions

LTCPO of Methane: Catalysts Screening by TG-FTIR Experiments

Catalyst screening experiments were performed with a DuPont thermogravimetric analyser 951 coupled with a BOMEM 100 FTIR spectrometer (TG-FTIR).
For FT and also for AFT synthesis a high CO content is desireable. Thus, in a first series of experiments different Ru- and Rh-containing catalysts were screened.

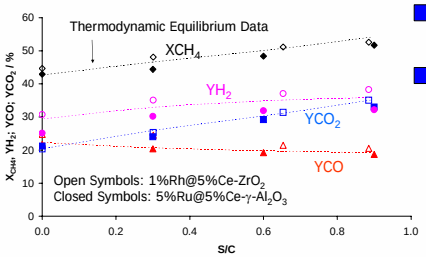


TG-FTIR Setup



CO Evolution of ruthenium and rhodium based catalysts
Feed: CH_4: 10 %; O_2: 5%; Ar: 85 %; p = 1 bar; GHSV = 227000 h^{-1}

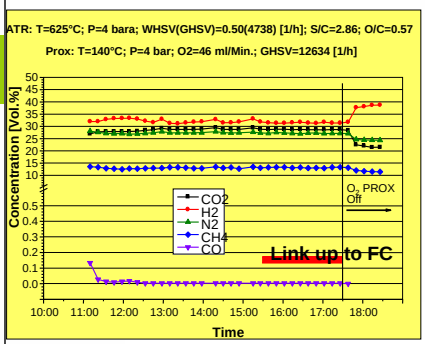
LTCPO of Methane: Microreactor Experiments



- *CO formation is influenced by support material and metal loading*
- *CPO on Ru- and Rh-catalysts is close to thermodynamic equilibrium*

Reaction conditions: T = 650 °C; p = 11 bar; O/C = 0.9; WHSV = 65 $g_{Feed}/g_{cat}/h$

„Shift-less" Gasoline Reformer linked-up to PE fuel cell



ATR conditions	
Reformer outlet temperature	610°C
S/C	2.86
O/C	0.57
WHSV	0.5 $g_{gasoline}/(g_{cat}.h)$
GHSV	4'738 h^{-1}

PROX conditions	
Inlet temperature	140°C
O_2/CO	1.24
GHSV	12'634 h^{-1}

Results (after PROX, dry)					
H_2	32 Vol. %	N_2	27 Vol. %	CO Conversion	> 99.93 %
CO_2	29 Vol. %	CO	< 36 ppmv	H_2 loss	27 %
CH_4	13 Vol. %	Carbon conversion (C_2+)	100 %	H_2 yield	7.5 mol H_2 / mol $C_{7.5}H_{12.6}$
				Reformate (dry)	47 L/h

- Reforming gasoline at lower temperatures (550 – 650 °C) over a proprietary catalyst resulted in lower CO concentrations (2 - 5 %) than conventional reformers.
- The CO content in the hydrogen-rich reformate could be reduced to < 36 ppmv in one annular fixed-bed PROX reactor.
- A PE fuel cell was operated with reformate gas. A cell voltage of 700 mV (with oxygen) at a current density of 500 mA/cm2 was observed which is only 40 mV less compared to pure hydrogen.