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# Low Temperature Catalytic Partial Oxidation (LTCPO) of methane to syngas for Gas-To-Liquids applications

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## INTRODUCTION

***Low Temperature Catalytic Partial Oxidation of methane (LTCPO)***

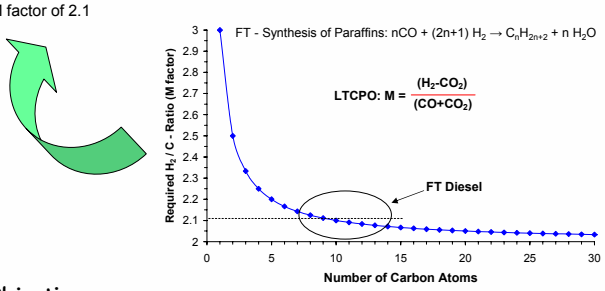
- Proposed Technology Autothermal Reforming (ATR) operates at high temperatures ⇒ stable (and expensive) materials are needed
- LTCPO operates at low temperatures and higher steam-to-carbon ratios ⇒ a $CO_2$-rich syngas is produced
- Advanced Fischer Tropsch (AFT) Technology is currently developed ($CO_2$ active catalysts, dewatering membranes)
- ***LTCPO-AFT could be a low cost alternative to ATR-FT technology***

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


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


***Key Parameters for an efficient LTCPO – GTL Process***

- High methane conversions (> 95 % are needed))
- M factor of 2.1




### Objectives

-To find suitable catalysts for the LTCPO of methane (noble metal catalysts)

- Optimization of reaction conditions

- To study the methane activation on noble metal catalysts

## EXPERIMENTAL

**Catalyst Preparation**

- Rhodium and ruthenium catalysts were prepared by impregnation of the support material with aqueous noble metal nitrate solutions. Platinum catalysts were prepared from a $Pt^{II}(NH_3)_4(OH)_2$ solution
- Calcination in air at 550 °C for 3 h

**LTCPO, Dry CPO and Steam Reforming Experiments**

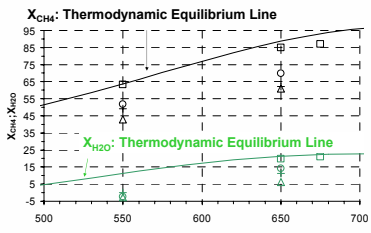
- Continuous flow fixed-bed microreactor (glass lined stainless steel tube, 4 mm inner diameter) using air as oxidant
- Catalyst particle size: 125-250 µm, dilutor: sea sand
- Products were analyzed by on-line gas chromatography

**TG-FTIR Experiments**

- A Netzsch STA 409 thermogravimetric analyser coupled with a Bruker FTIR spectrometer was used
- Pre-reduced catalyst (50 mg, 10 % $H_2$ in Ar, 650 °C, 1h)
- After cooling to RT in an argon flow, the sample was heated up to 800 °C (10 °C / min) in a methane / argon flow (20 % $CH_4$). The weight change was recorded
- After cooling in an argon flow, temperature programmed oxidation (TPO) was performed (20 % $O_2$ in Ar). Carbon dioxide was monitored by FTIR spectroscopy

## RESULTS AND DISCUSSION

### I) CATALYSTS FOR THE LTCPO OF METHANE



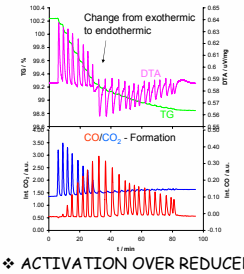

p = 3 bar, O/C = 0.85; S/C = 2.9; WHSV = 96 $g_{Feed}/g_{cat}/h$

- ***Pt catalysts: lower catalytic activity towards the LTCPO of methane (thermodynamic equilbrium was not achieved). M factors are too low for an efficient LTCPO-GTL process.***
- ***5%Ru/γ-$Al_2O_3$ Catalyst: Activity close to the thermodynamic equilibrium***
- ***M factor is suitable for LTCPO-GTL.***
- ***A 1%Rh/5%Ce-$ZrO_2$ catalyst revealed similar performance.***
- ***Maximum conversion of 91 % was observed for the Ru catalyst at a pressure of 2 bars and an S/C ratio of 4-5.***

□: 5%Ru/γ-$Al_2O_3$ △: 0.3%Pt / γ-$Al_2O_3$ +: 1%Pt / γ-$Al_2O_3$ ○: 0.6% Pt / $SnO_2$

### II) ACTIVATION OF METHANE OVER Ru AND Rh CATALYSTS

❖ PULSE TGA EXPERIMENTS OVER PRE-OXIDIZED RUTHENIUM CATALYSTS



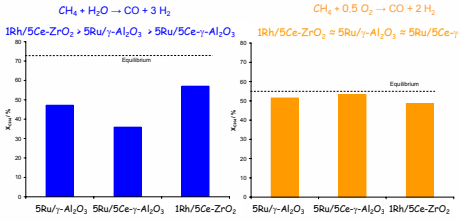

*Reaction Conditions*
- CH4: 0.5 ml/Pulse
- T=550 °C
- Pre-oxidized Ru Catalyst

- ***Fully oxidized ruthenium surface ($RuO_2$): Total Oxidation ($CH_4$ + n $RuO_2$ → $CO_2$ + 2 $H_2O$ + 2 Ru ), Exothermic***
- ***Partially reduced ruthenium surface: CO formation ($RuO_{(2-x)}$ + (2-x) $CH_4$ → (2-x) CO + 2 (2-x) $H_2$, Endothermic***
- ***From TG-DTA: $RuO_{0.27}$ is most efficient for CO formation***

❖ ACTIVATION OVER REDUCED Ru- AND Rh-CATALYSTS: TG-FTIR EXPERIMENTS

STEAM REFORMING (SR) $CH_4 + H_2O \rightarrow CO + 3\,H_2$

DRY CATALYTIC PARTIAL OXIDATION (CPO) $CH_4 + 0.5\,O_2 \rightarrow CO + 2\,H_2$

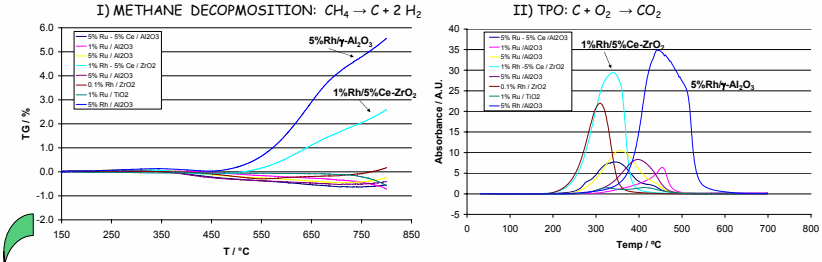



- ***Dry CPO: similar results were for Rh and Ru catalysts***
- ***SR: The 1%Rh/5%Ce-$ZrO_2$ Catalyst is more active.***
- ***The presence of cerium seems to inhibit the SR activity of the ruthenium based catalysts***

SR: WHSV = 77 $h^{-1}$, 650 °C, $p_{tot}$ = 3.1 bar, S / C = 2.9 CPO: WHSV = 57 $h^{-1}$, 650 °C, $p_{tot}$ = 3.1 bar, O / C = 0.85

I) METHANE DECOMPOSITION: $CH_4 \rightarrow C + 2\,H_2$

II) TPO: $C + O_2 \rightarrow CO_2$




- ***Activation / decomposition of methane to carbon (CH4 → C + 2 H2 ) occurs on reduced rhodium catalysts at much lower temperatures as on reduced ruthenium materials (450 °C compared to 675 °C)***
- ***Steam reforming activity seems to be strongly affected by the methane decomposition on reduced catalytic sites***
- ***In contrast, no correlation between dry CPO activity and methane activation is observed. The presence of oxygen therefore seems to influence the methane activation pathway***
- ***Temperature Programmed Oxidation (TPO) studies of the carbon deposits on the different catalysts revealed that the oxidation of the deposited carbon is enhanced on ceria/zirconia supports***