



Catalytic Partial Oxidation (CPO) of Methane to Synthesis Gas over Noble Metal Catalysts

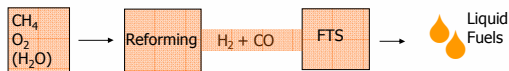
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INTRODUCTION

Catalytic Partial Oxidation of methane (CPO) and the Gas-To-Liquids process

- The conversion of natural gas into liquid hydrocarbons (Gas-To-Liquids, GTL) by combining synthesis gas production and Fischer-Tropsch Synthesis (FTS) is gaining more and more interest.
- The costs of syngas production (reforming) influence strongly the costs of a GTL plant
- Proposed Technology Autothermal Reforming (ATR) operates at high temperatures \Rightarrow stable (and expensive) materials are needed
- LTCPD (Low Temperature CPO): operates at lower temperatures ($< 800 \text{ }^\circ\text{C}$) \Rightarrow cost reduction !

Gas-To-Liquids: Reforming and Fischer-Tropsch Synthesis (FTS)



Objectives

- To investigate the properties of noble metal catalysts for the CPO of methane
- Optimization of reaction conditions
- To study the methane activation on noble metal catalysts below $800 \text{ }^\circ\text{C}$

CONCLUSIONS

- CPO: Similar activity for Rh and Ru catalysts**
- Steam Reforming (SR): Higher Activity for Rh catalyst observed**
- Activation / decomposition of methane to carbon ($\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$) occurs on reduced rhodium catalysts at much lower temperatures as on reduced ruthenium materials ($450 \text{ }^\circ\text{C}$ compared to $675 \text{ }^\circ\text{C}$)**
- 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**

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 $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ solution
- Calcination in air at $550 \text{ }^\circ\text{C}$ for 3 h

CPO and Steam Reforming Experiments

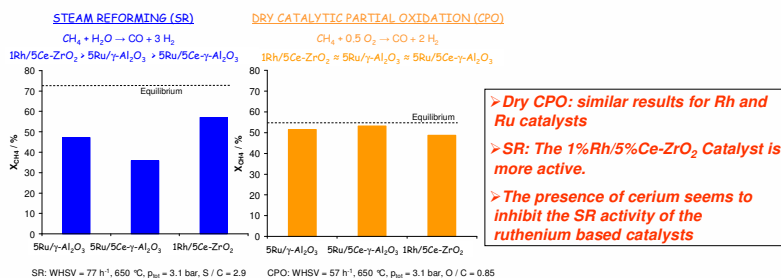
- Continuous flow fixed-bed microreactor (glass lined stainless steel tube, 4 mm inner diameter) using air as oxidant
- Catalyst particle size: 125-250 μm , diluent: sea sand
- Products were analyzed by on-line gas chromatography

TG-FTIR Experiments

- A Netzsch thermogravimetric analyser (STA 449) coupled with a Bruker FTIR spectrometer was used
- Pre-reduced catalyst (50 mg, 10 % H_2 in Ar, $650 \text{ }^\circ\text{C}$, 1h)
- After cooling to RT in an argon flow, the sample was heated up to $800 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C} / \text{min}$) 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

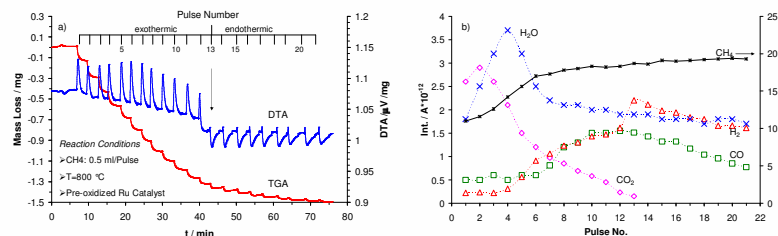
RESULTS AND DISCUSSION

I) CPO and Steam Reforming over Rhodium and Ruthenium Catalysts



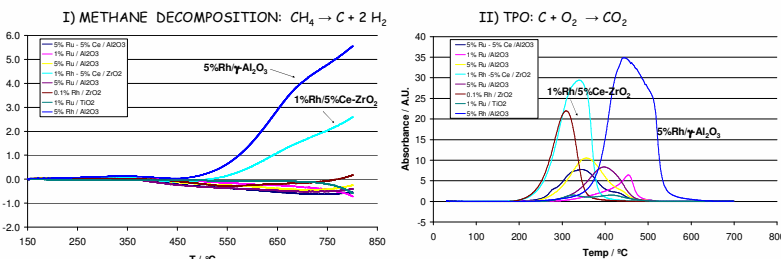
II) ACTIVATION OF METHANE OVER Ru AND Rh CATALYSTS

❖ PULSE TGA EXPERIMENTS OVER A PRE-OXIDIZED RHODIUM CATALYST



- Fully oxidized rhodium surface (Rh_2O_3): Total Oxidation**
 $4 \text{Rh}_2\text{O}_3 + 3 \text{CH}_4 \rightarrow 8 \text{Rh} + 3 \text{CO}_2 + 6 \text{H}_2\text{O}$, exothermic
- Partially reduced rhodium surface: CO formation**
 $\text{RhO}_{(1.5-x)} + (1.5-x) \text{CH}_4 \rightarrow \text{Rh} + (1.5-x) \text{CO} + 2(1.5-x) \text{H}_2$, endothermic

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



- Activation / decomposition of methane to carbon ($\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$) occurs on reduced rhodium catalysts at much lower temperatures as on reduced ruthenium materials ($450 \text{ }^\circ\text{C}$ compared to $675 \text{ }^\circ\text{C}$)**
- 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**