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 but today, the technology is mature enough to be considered an alternative to coal.
- Proposed Technology Autothermal Reforming (ATR) operates at high temperatures which make the investment required more expensive.
- LT-CPO (Low Temperature CPO): operates at lower temperatures (< 800 °C) costs reduction!

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

\[ \text{CH}_4 + \text{H}_2 \text{O} \rightarrow \text{CO} + 3 \text{H}_2 \] (Reforming)

\[ \text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3 \text{OH} \] (FTS)

Objectives
- To investigate the properties of noble metal catalysts for the CPO of methane
- To study the methane activation on noble metal catalysts below 800 °C

RESULTS AND DISCUSSION

I) CPO and Steam Reforming over Rhodium and Ruthenium Catalysts

EXPERIMENTAL
- To investigate the properties of noble metal catalysts for the CPO of methane
- To study the methane activation on noble metal catalysts below 800 °C
- 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 Pd(NH_2OH)_2Cl_2 solution.
  - Calcination in air at 550 °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% Rh in Al, 650 °C, 1 h).
- 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 argon flow, temperature programmed oxidation (TPO) was performed (20% O_3 in Ar).
- Carbon dioxide was monitored by FTIR spectroscopy.

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 Rh_2O_3 + 3 CH_4 → 8 Rh + 3 CO + 6 H_2, exothermic
- Partially reduced rhodium surface: CO formation
  - RhO_2(3+)+ (1.5-x) CH_4 → Rh + (1.5-x) CO + 2 (1.5-x) H_2, endothermic

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

- Activation / decomposition of methane to carbon (CH_4 → C + 2 H_2) occurs on treated rhodium catalysts at much lower temperatures as on reduced ruthenium materials (450 °C compared to 675 °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.