

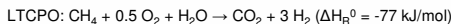
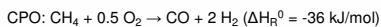
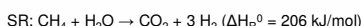
Reforming of Methane to Synthesis Gas over a Ruthenium Catalyst: an in-situ X-Ray Absorption Spectroscopic Study

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INTRODUCTION

Catalytic Partial Oxidation of methane (CPO)

Methane is an important feedstock for producing liquid hydrocarbons (via Fischer-Tropsch synthesis) or chemicals (via methanol). The first step is always the reforming of methane to synthesis gas (CO and H₂). Several reforming methods have been applied. Steam reforming (SR) and autothermal reforming (ATR) are used on an industrial scale. An alternative reforming process is provided by the "wet" catalytic partial oxidation at low temperatures (LTCPO), which generates a CO₂ rich synthesis gas. The corresponding reaction equations are shown below.



Ruthenium catalysts have been used successfully for this reforming reaction. In this contribution we report new results on the catalytic reforming of methane over a ruthenium catalyst highlighting the role of the oxidation state, using in-situ and ex-situ techniques.

CONCLUSIONS

➤ Oxidation State of catalyst influences strongly the product formation: Oxidized ruthenium sites formed CO₂, reduced sites yielded CO

➤ Temperature influences the oxidation state of the catalyst: at temperatures below the ignition point of the CPO the catalyst is oxidized, above it is reduced

➤ Ru⁰ plays an important role in all reforming reactions. Steam reforming is inhibited if the catalyst is oxidized.

➤ Further studies are needed to understand the role of the oxygen in the reaction mechanism

EXPERIMENTAL

Catalyst Preparation

- A Ru^γ-Al₂O₃ catalyst (5% Ru) was prepared by impregnation
- Calcination in air at 550 °C for 3 h

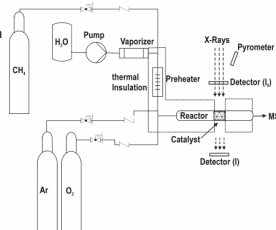
TG-FTIR Experiments (Transient Experiments)

- A Netzsch thermogravimetric analyser (STA 449) coupled with a Bruker FTIR spectrometer was used
- Pulses (0.5 ml) of CH₄/Ar (33.3 % CH₄) and CH₄/O₂ were applied
- The bulk oxidation state of ruthenium (RuO_x) was calculated from the observed weight loss (WL_{obs}) and the maximum weight loss (WL_{max}) which represents the total reduction to ruthenium metal:

$$\text{RuO}_x = 4 \cdot (1 - \text{WL}_{\text{obs}} / \text{WL}_{\text{max}})$$

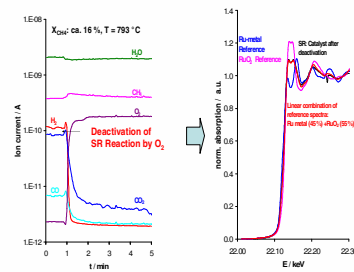
In-Situ X-ray absorption:

- Quartz glass reactor (ID: 1 mm, OD: 1.2 mm, L: 20 cm)
- Optical Pyrometer for T-Measurement
- Feed was preheated to 250 °C
- Catalyst weight: 8 mg
- Online MS-Analysis
- Experiments were performed at SNBL located at the ESRF/Grenoble



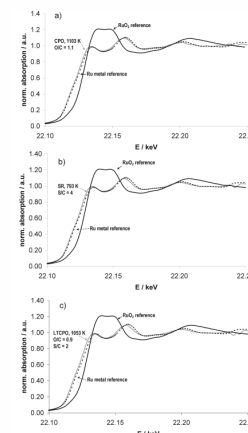
RESULTS AND DISCUSSION

I) In-Situ X-Ray Absorption Spectroscopy

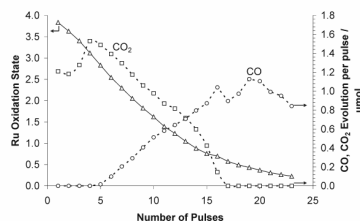


Normalized XAS spectra recorded at different reaction conditions (SR, CPO, LTCPO) revealed that Ru⁰ is the dominant ruthenium species

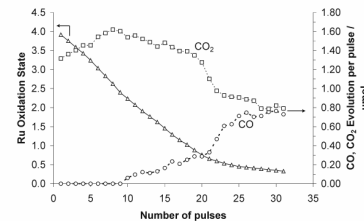
Oxygen addition to methane steam reforming at 768 K: Deactivation of the catalyst by oxidation.



II) Transient Experiments



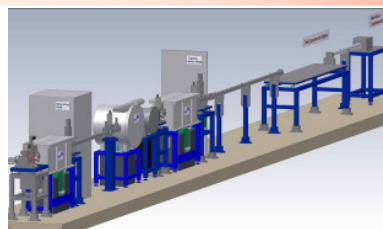
CH₄/Ar pulses (0.5 ml, 13.6 μmol CH₄), 823 K. X_{CH₄}: ca. 12% per pulse



CH₄/O₂ pulses (0.5 ml, 13.6 μmol CH₄), 823 K. X_{CH₄}: ca. 17% per pulse

- ⇒ Exclusive formation of CO over reduced sites is observed
- ⇒ CO₂ is mainly generated at oxidized sites

Outlook: The „Super-XAS“ Beamline at the Swiss Light Source (SLS)



Technical Specifications

- Energy range: 5-35 keV
- High energy resolution: 2x10⁻⁴
- Spot size: 10x10 μm to 1 x 1mm
- Flux on the sample: 10¹¹-10¹² photons/sec

- ❖ Uniqueness for Catalysis Research
- ❖ Quick scanning monochromator
 - XANES: 12.5 ms
 - EXAFS: 0.1 s
- ❖ Gas infrastructure
- ❖ Well equipped Lab
- ❖ Flexible sample environment

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<http://sls.web.psi.ch/view.php/beamlines/superoxas/index.html>

References

Rabe S, Nachtegaal M, Vogel F
PHYSICAL CHEMISTRY CHEMICAL PHYSICS 9 (12): 1461-1468 2007