
In-situ atmosphere monitoring of the debinding of PM steel components with large amounts of organic additions



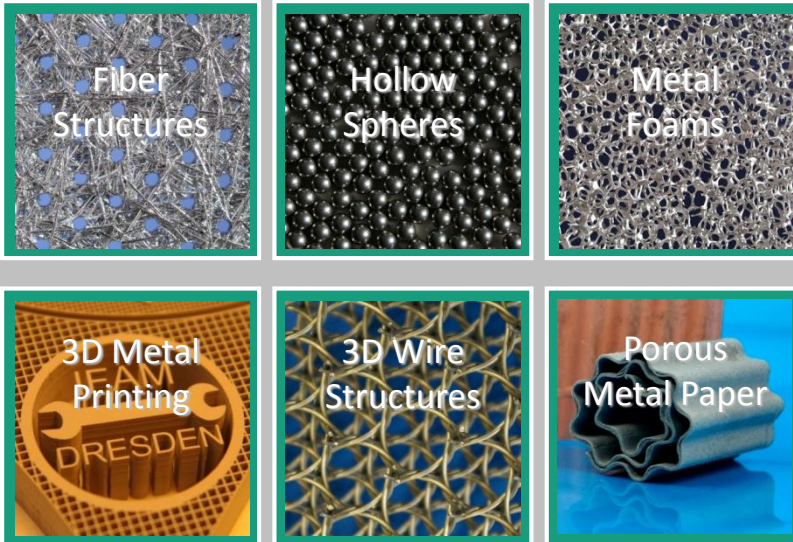
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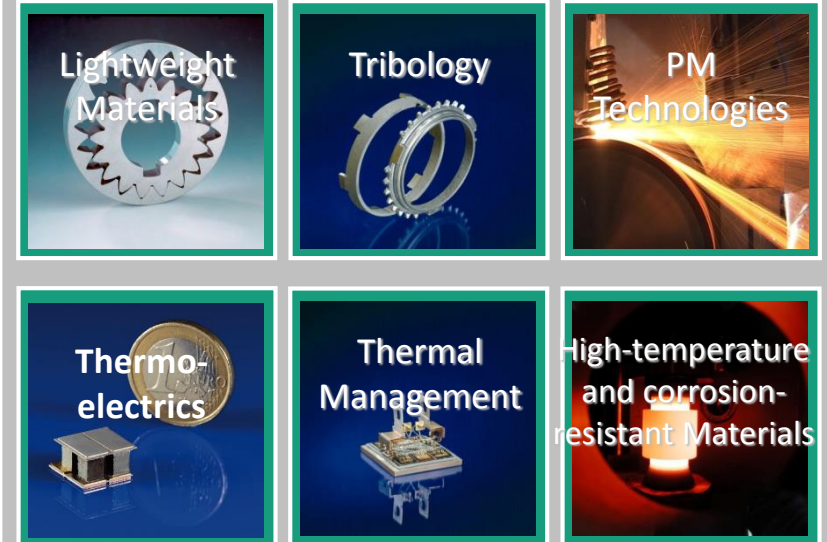
Fraunhofer IFAM Dresden

Fields of Competence

Cellular Metallic Materials



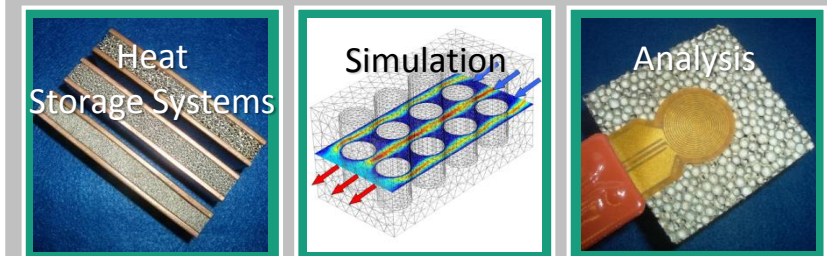
Sintered and Composite Materials



Hydrogen Technology



Energy und Thermal Management



Introduction

PM technologies with high organic contents

Metal Injection Moulding



Cellular Metals



Porous Implants



Micro MIM



Catalytic Converter Carrier

Introduction

PM Technologies With High Organic Contents

Debinding of organic additives

- Degradation and transportation of large amounts of gasified organic materials
- Amount is dependent on process parameters and component properties
- High risk of carbon residuals with high organic contents

	Pressed PM Parts	Cellular Metals	MIM
Organic material	wax, stearic acid, ...	PVA, Tylose, EPS, PUR,...	PP, PE, POM
Organic content	~ 2 m.-%	~ 15 m.-%	~ 15 m.-%
Component size	$10^2 - 10^1$ mm	$10^2 - 10^1$ mm	$10^1 - 10^0$ mm



Introduction

Early Stages of Heat Treatment

Debinding Mechanisms

- Thermal decomposition of organic materials in multiple steps
- Decomposition temperatures dependent on chemical composition

process	temperature	mechanisms
drying	100 – 200 °C	evaporation of water
carbonizing	200 – 500 °C	<ul style="list-style-type: none"> ■ side group scission of higher molecular weight substances ■ decomposition of backbones into liquid and gaseous forms
gas formation	500 – 1200 °C	solid carbon reduction and decarburization: H ₂ , CO, CO ₂ , CH ₄ , etc.

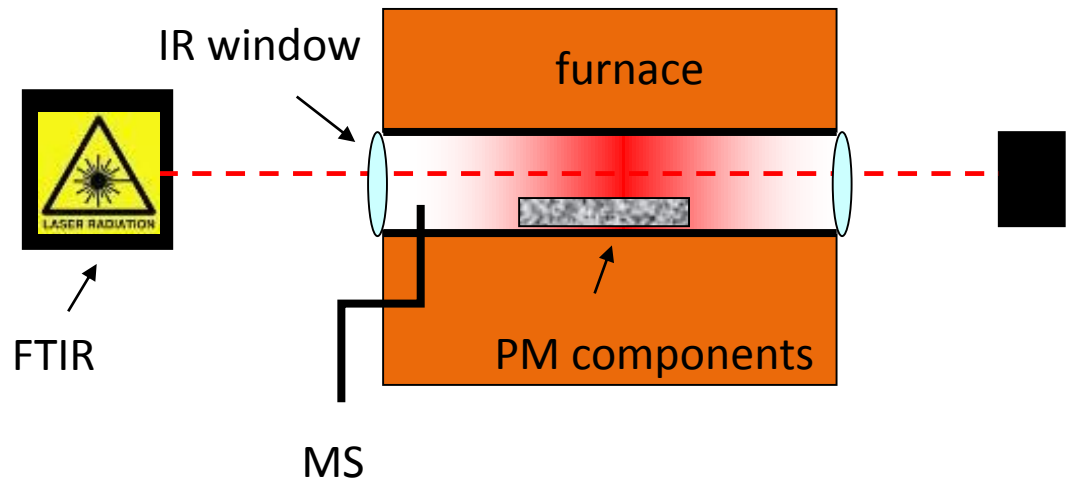
Experimental Setup

In Situ Atmosphere Monitoring via FTIR and MS



Method

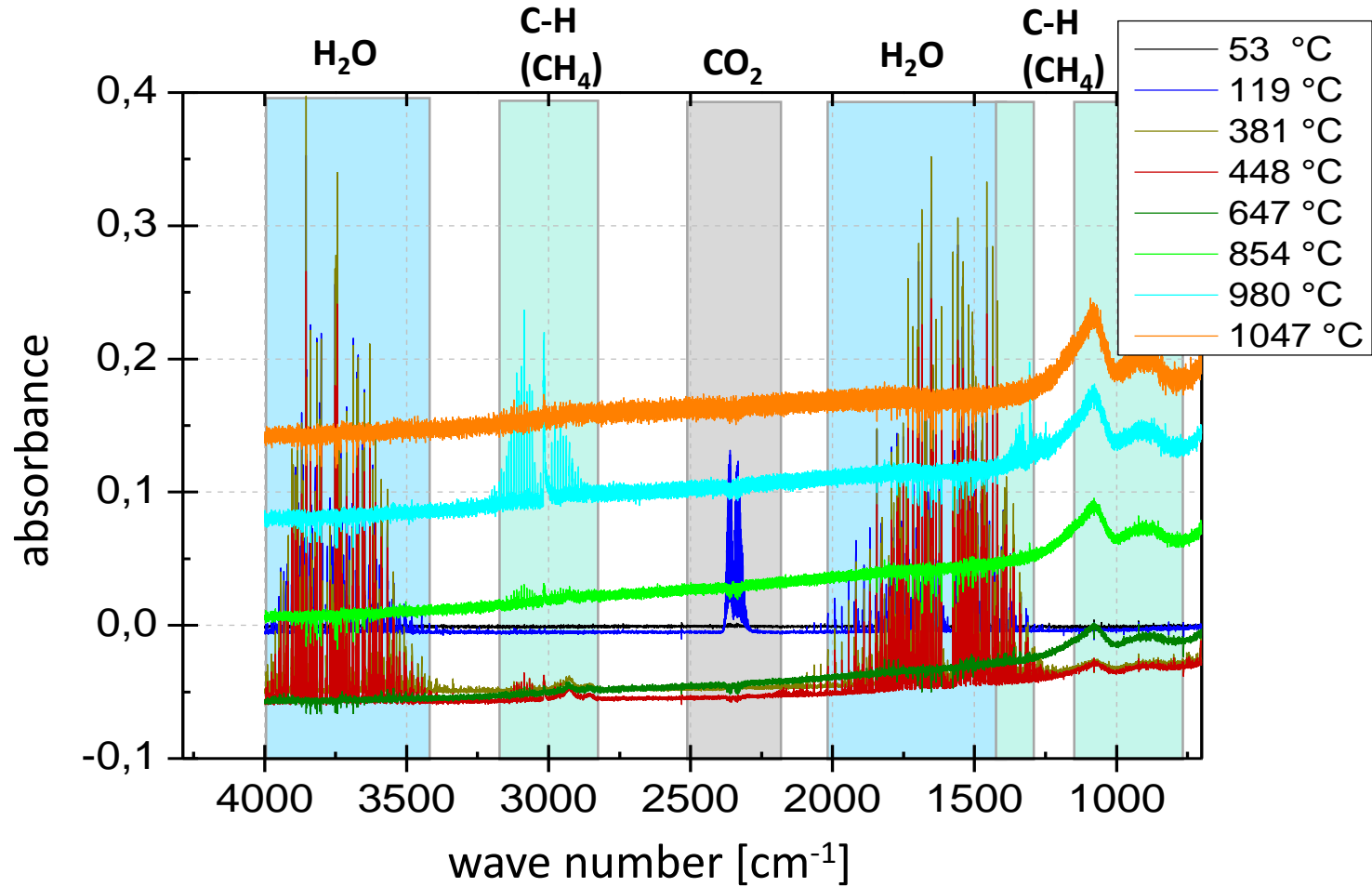
Optical in-situ analysis of
gas phase composition



- In-situ-measurement gives direct correlation between gas phase composition and process parameters (e.g. temperature, gas flow,...)
- Measurement in tube furnace and continuous belt furnace possible

Experimental Setup

Typical Spectra Taken at Different Temperatures



Experimental Setup

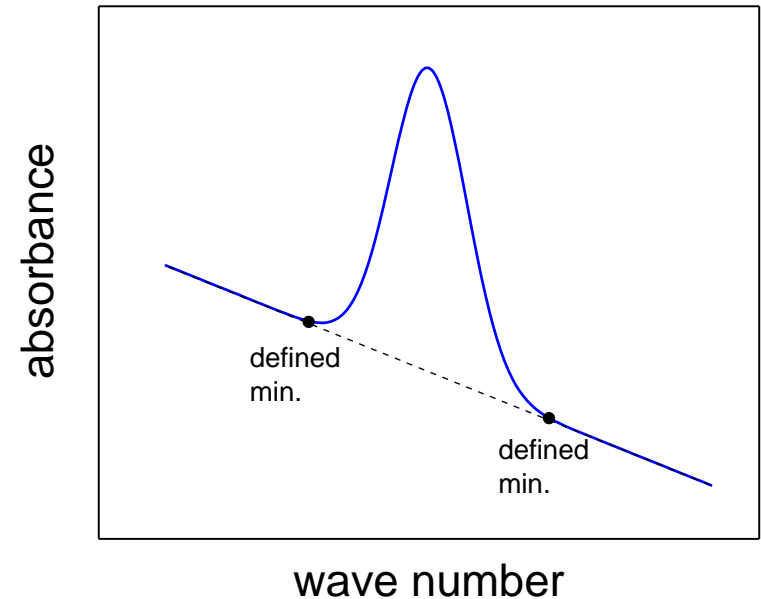
In-situ Atmosphere Monitoring

Identification of single species

- Reference spectra (CO, CO₂, CH₄)
- Spectra taken in temperature steps of 5 K

Calculation of relative concentration

- Baseline between defined fixed points
- Integrating area between the baseline and measured absorbance



	H ₂ O	CH ₄	CO ₂	CO	C ₂ H ₂
min [cm ⁻¹]	3890.59	3085.33	2331.32	2118.0	948.81
max [cm ⁻¹]	3892.49	3086.18	2332.82	2120.35	960.26

Experimental Setup

Materials

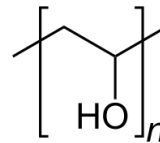
Metal powder: stainless steel 430L

Fe	C	Si	Ni	Cr	Mn
bal.	0.03	<1.0	<0.75	16.0 - 18.0	<1.0

Organic ingredients

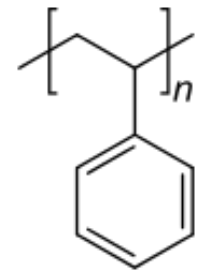
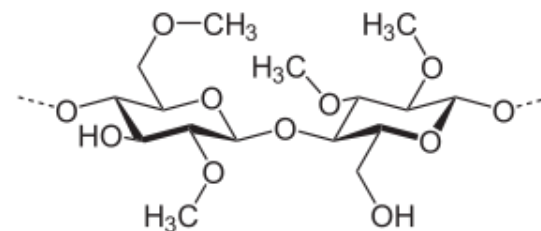
■ binder

- polyvinyl alcohol
- methyl cellulose



■ template

- expanded polystyrene

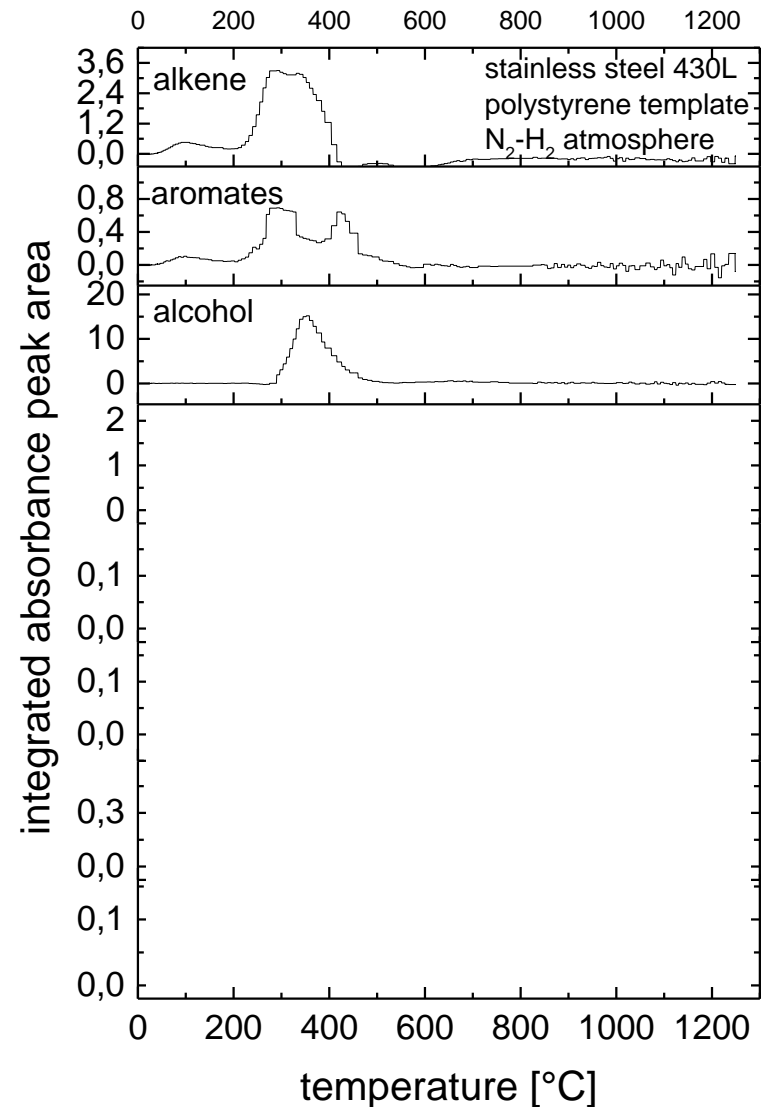


Results

Heat Treatment in N_2-H_2

Initial heat treatment

- Decomposition of polymeric backbone
- Styrene hydrogenates in further steps into ethylbenzene, toluol and ethene
- Species identified as aromatic hydrocarbons and alkene
- Side group scission of polyvinyl alcohol: formation of alcohol
- Decomposition process is completed at $\sim 500\text{ }^\circ\text{C}$

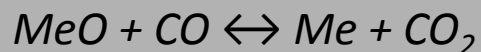


Results

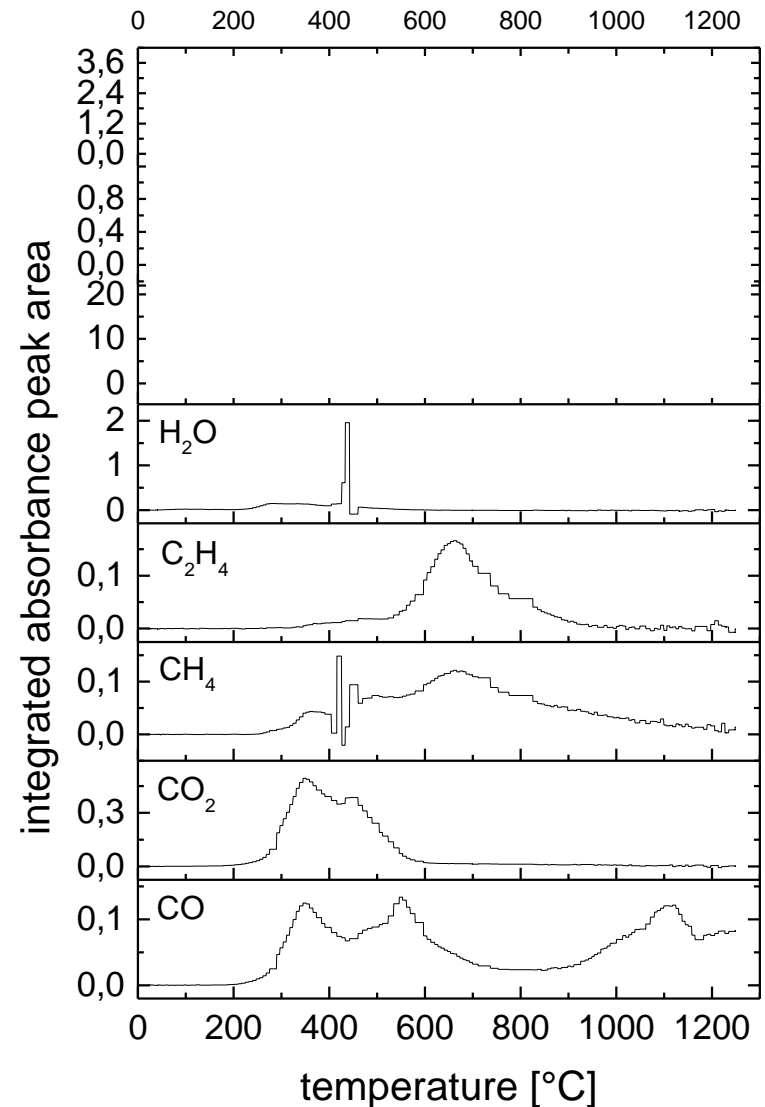
Heat Treatment in N₂-H₂

Reduction of steels:

- Formation of sinter necks needs reduction of surface oxides
- Cr alloyed steels: no surface oxide reduction below 800 °C
- Reduction reactions via



- Carbothermic reduction requires sufficient carbon content

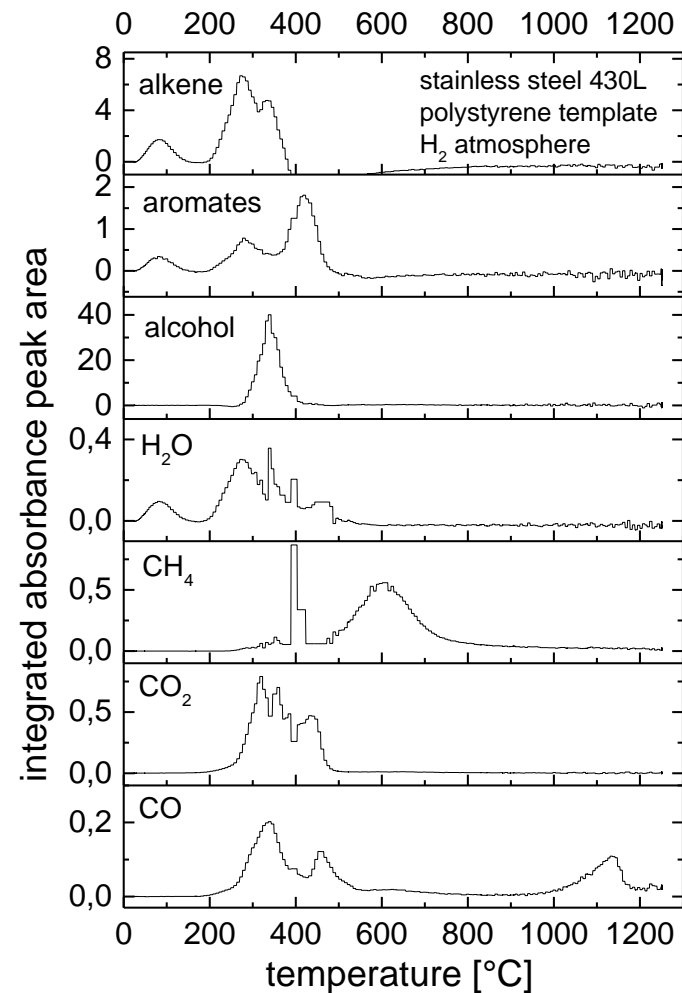


Results

Pure Hydrogen Atmosphere

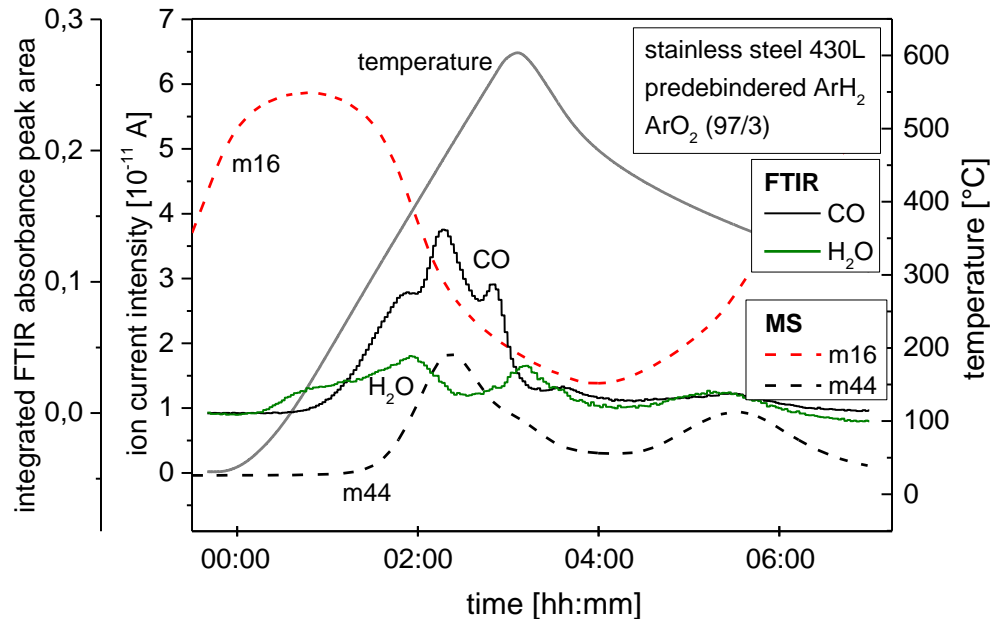
Effect of pure hydrogen

- Gas formation resembles the formation under N₂-H₂ atmosphere
- Peaks of gas formation are more pronounced
- Main difference: much stronger formation of methane with a maximum at 600 °C



Results

Preoxidation Treatment



Oxidative Treatment

- Samples pre-debindered in ArH₂
- Oxidation in 3% O₂ atmosphere
- Oxygen uptake at T > 200 °C
- Carbothermic CO formation with maximum at 456 °C

- ➔ Only low decarburization effects by oxidative treatment below 600 °C
- ➔ Main goal: oxygen supply to the system via metal oxide formation in order to enhance carbothermic reduction at higher temperatures

Results

Reduction in Pure H₂ After Preoxidative Treatment

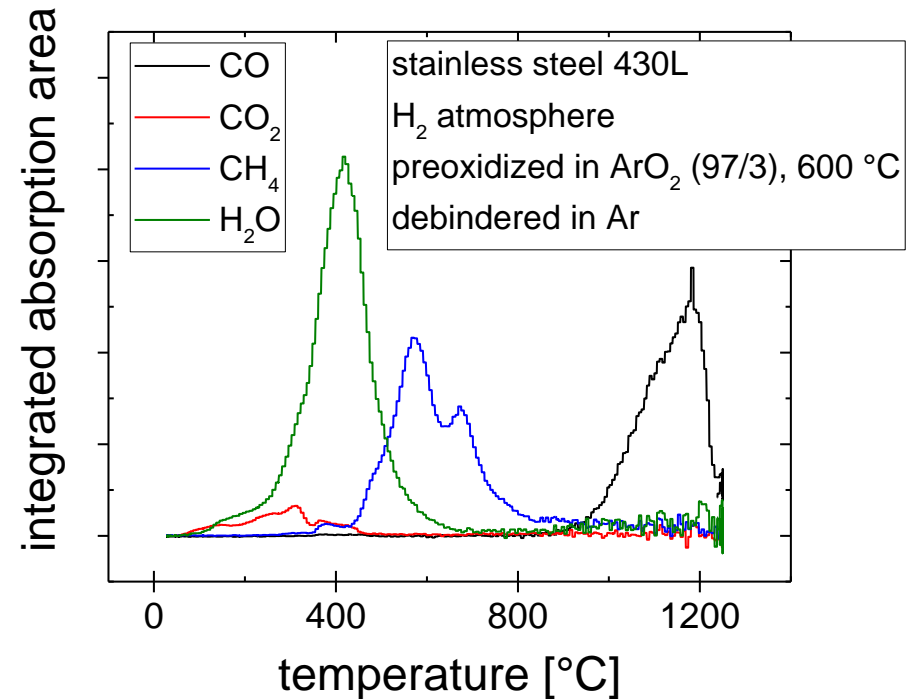
- Much more pronounced reduction processes via

$$\text{MeO} + \text{H}_2 \leftrightarrow \text{Me} + \text{H}_2\text{O}$$

$$\text{MeO} + \text{C} \leftrightarrow \text{Me} + \text{CO}$$

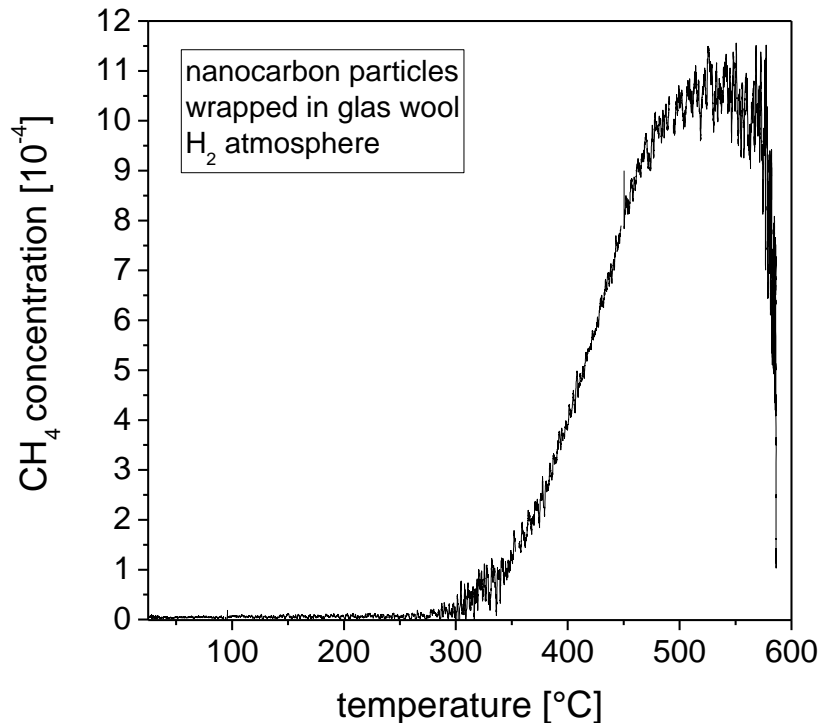
$$\text{MeO} + \text{CO} \leftrightarrow \text{Me} + \text{CO}_2$$

- Formation of a methane double peak at temperatures of 570 °C and 675 °C → direct methane formation and masked carbothermic reaction



Results

Direct Methane Formation – Control Experiment



Methane formation on graphite

- Nanographite wrapped in glas wool
- Heating in pure hydrogen
- Methane formation with maximum at 550 °C
- Direct formation via

$$C + 2 H_2 \rightarrow CH_4$$
- System is far away from equilibrium

Conclusions

Heat treatment of stainless steel 430L components with polystyrene templates and PVA binder:

- Decomposition of molecular backbone in N₂-H₂: high amounts of alcohol, aromatic compounds and alkene up to 500 °C
- Pure H₂ atmosphere: pronounced decarburization due to methane formation at 600 °C
- Industrial N₂-H₂ (95/5) atmosphere: methane formation can be almost completely neglected
- Reduction in H₂ after pre-treatment in Ar-O₂ (97/3) atmosphere:
 - two significant methane peaks at 570 and 675 °C
 - reactions attributed to direct methane formation and a masked carbothermic reduction

Fraunhofer-Gesellschaft

Partner for Innovation



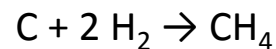
Results

Reduction after Preoxidative Treatment

Erratum!

Methane formation

- Lower peak:
direct methanization via



- Second peak only visible due to high oxygen content:
- ➔ masked carbothermic reduction
 $\text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$

➔ debinding atmospheres: Carbon content in H_2 ~0.4 % lower than in Ar

