TECHNISCHE UNIVERSITÄT
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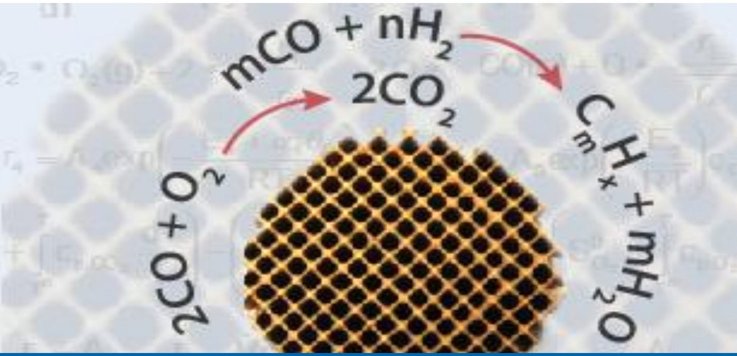
Soot oxidation on manganese oxide catalysts in gasoline exhaust gas



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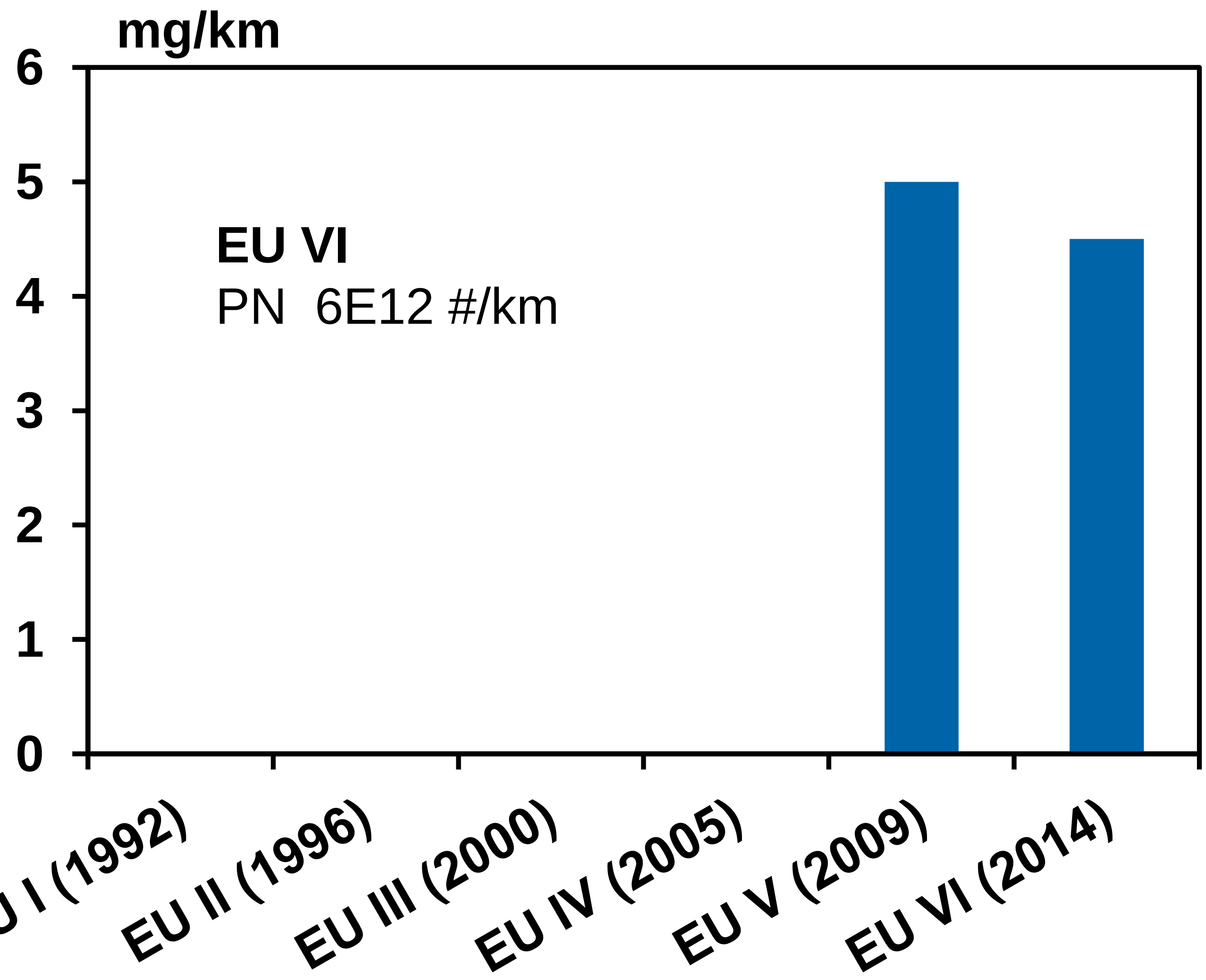
Development of particulate emission limits of EU for gasoline cars

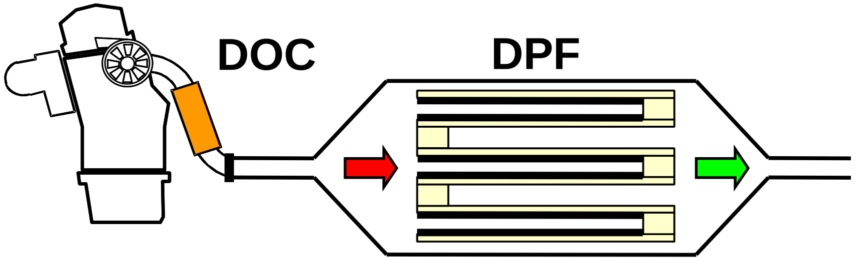


Strategies of particulate filter regeneration

- Passive regeneration (T=200…450°C)

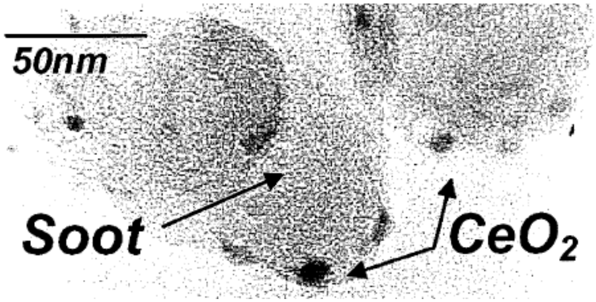
  $2\ NO + O_2 \rightarrow 2\ NO_2$

  $2\ NO_2 + \text{“C”} \rightarrow CO_2 + 2\ NO$



- Fuel Borne Catalyst: metal-organic compounds

  $\text{“C”} + O_2 \rightarrow CO_2$ T > 300°C



K. Ohno, Ph.D. thesis 2005

- Active regeneration (fuel post-injection)

  $\text{“C”} + O_2 \rightarrow CO_2$ T > 600°C

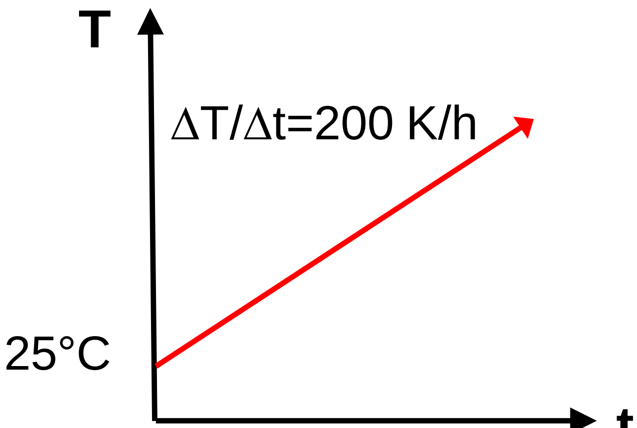
- Catalytic GPF (CGPF): CeO_2 and Fe_2O_3 based catalysts

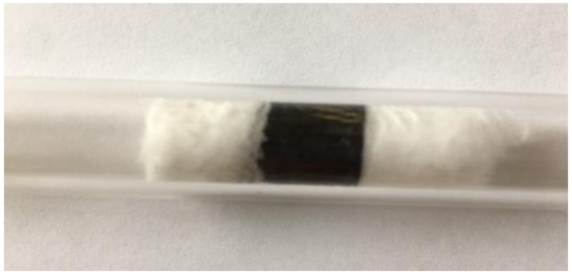
  $\text{“C”} + O_2 \rightarrow CO_2$ T > 500°C

Evaluation of MnO_x catalysts

Evaluation of soot oxidation activity

Temperature Programmed Oxidation (TPO)

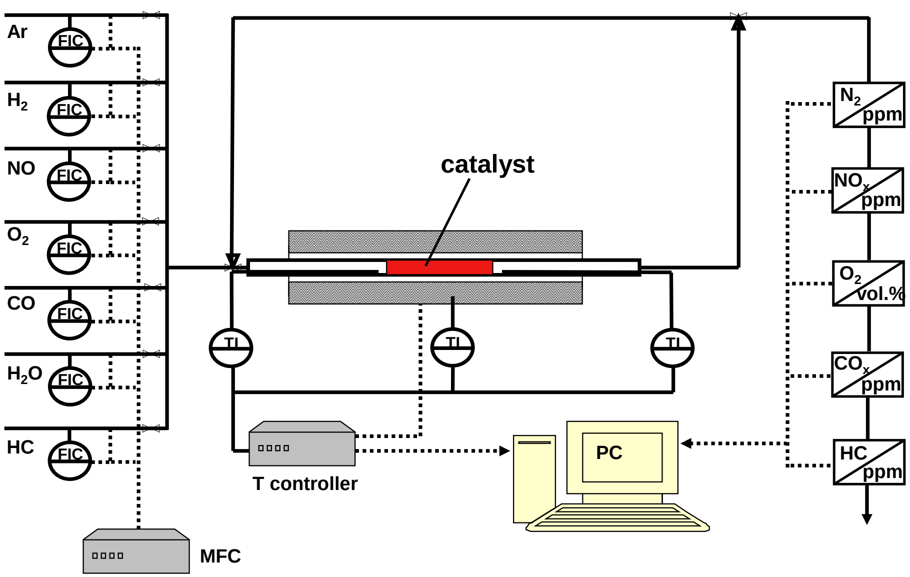




Plug flow reactor with packed bed

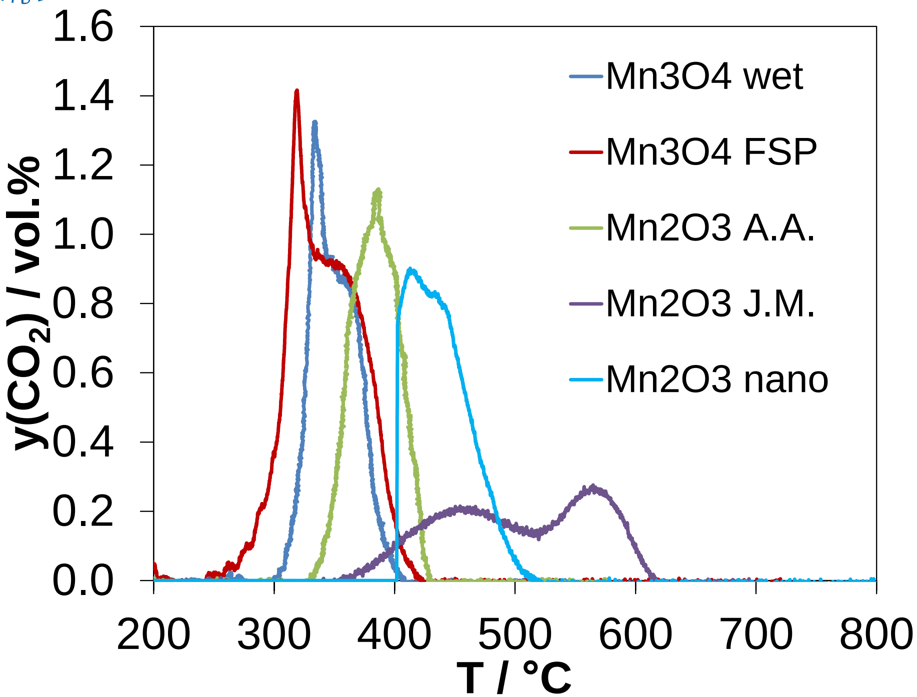
TPO conditions

- $y(O_2)=1\%$, $y(H_2O)=2\%$, $y(N_2)=97\%$
- F=500 ml/min (STP)
- tight contact, loose contact
- m=0.9 g ($n_{cat}/n_{soot}=2$)
- Model soot Printex U



Laboratory test bench

Screening of MnO_x catalysts

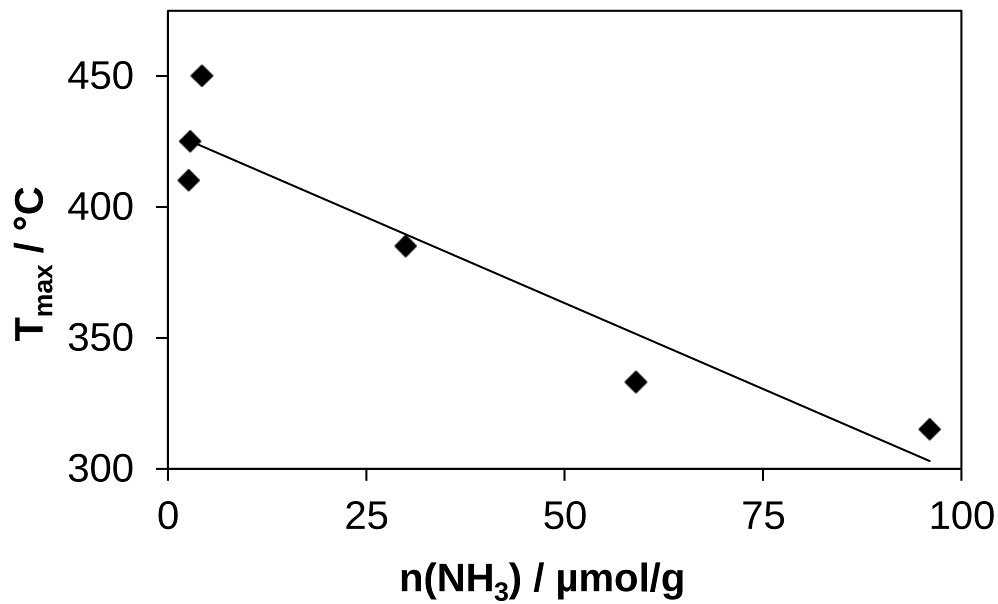


→ FSP-MnO_x best catalyst

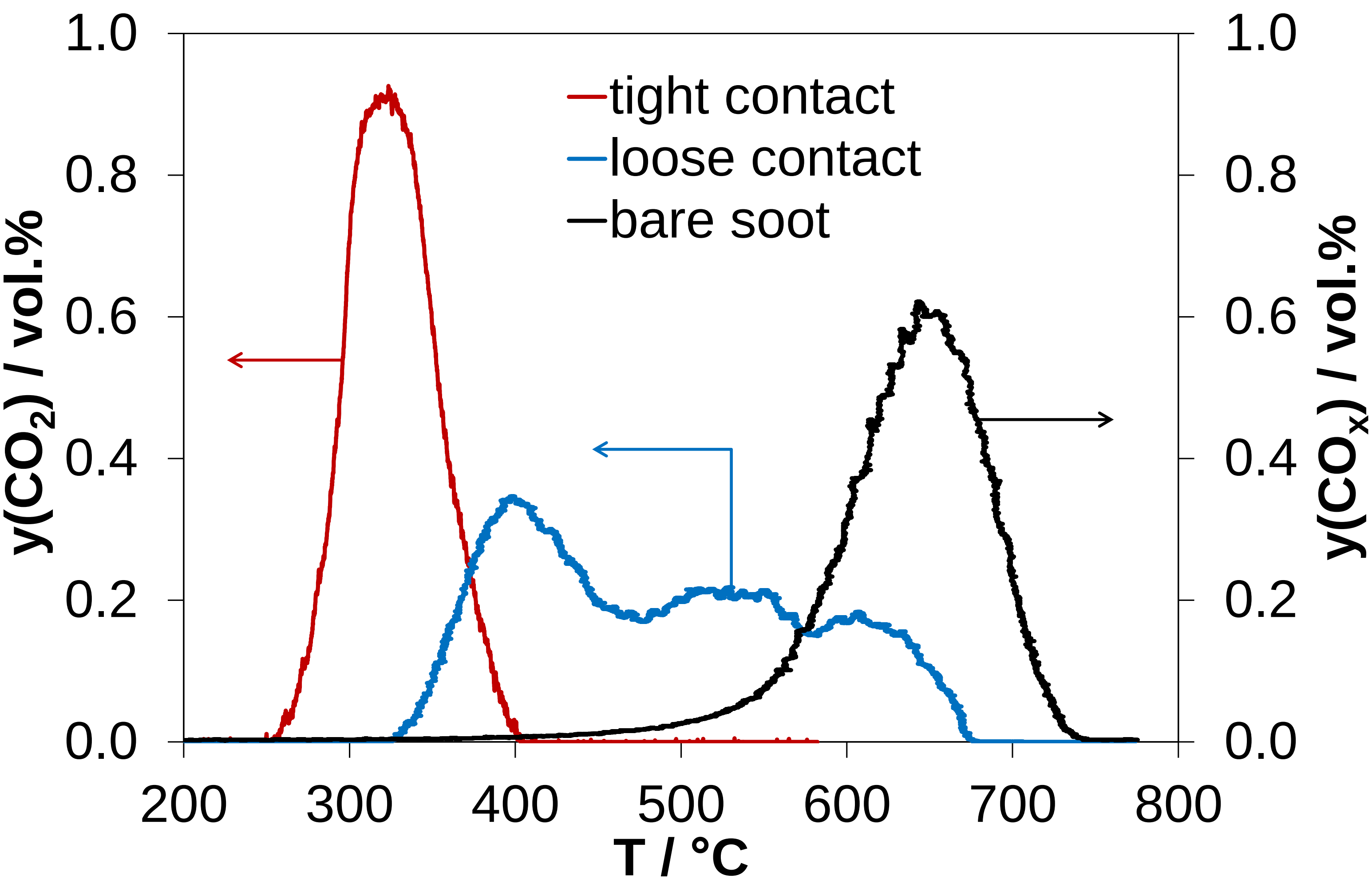
Physical-chemical characterisation

- XRD
- N_2-physisorption (BET, BJH)
- SEM
- NH_3-TPD

Structure-activity correlation



Effect of contact: tight vs. loose



→ FSP-Mn_2O_3 requires contact to soot particles

Tight and loose contact mode

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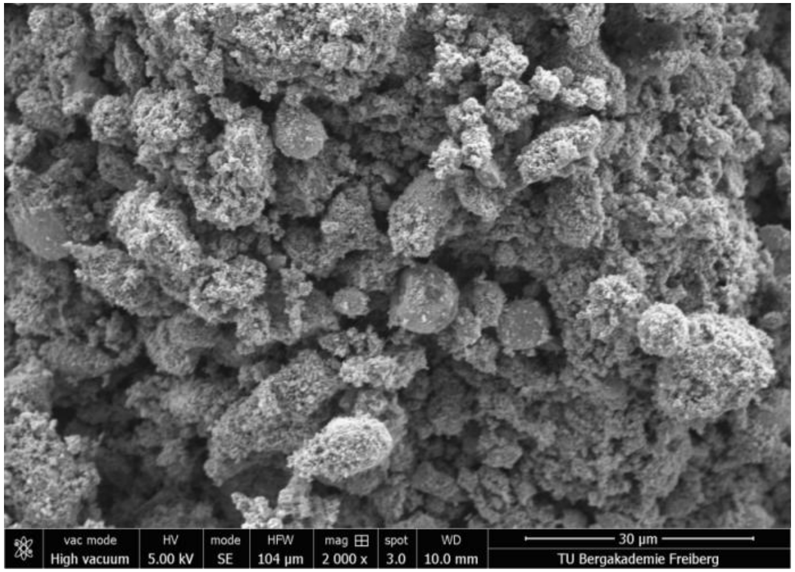
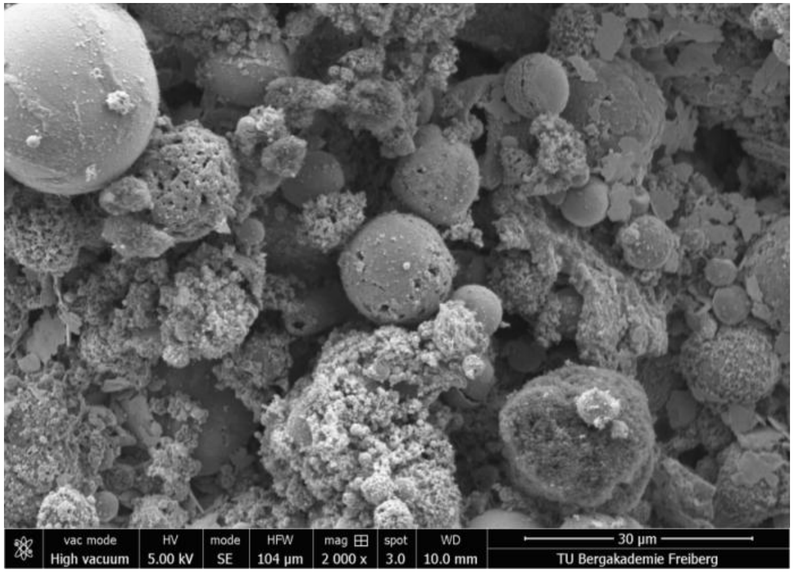
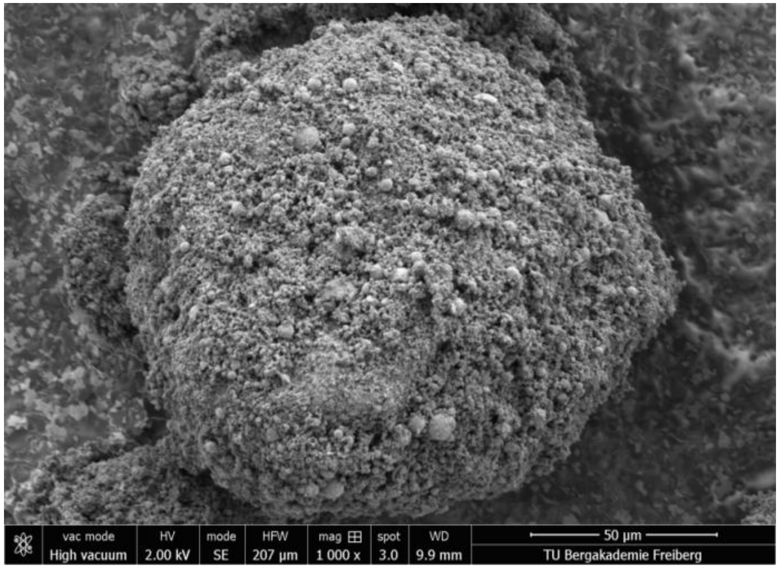
Tight contact

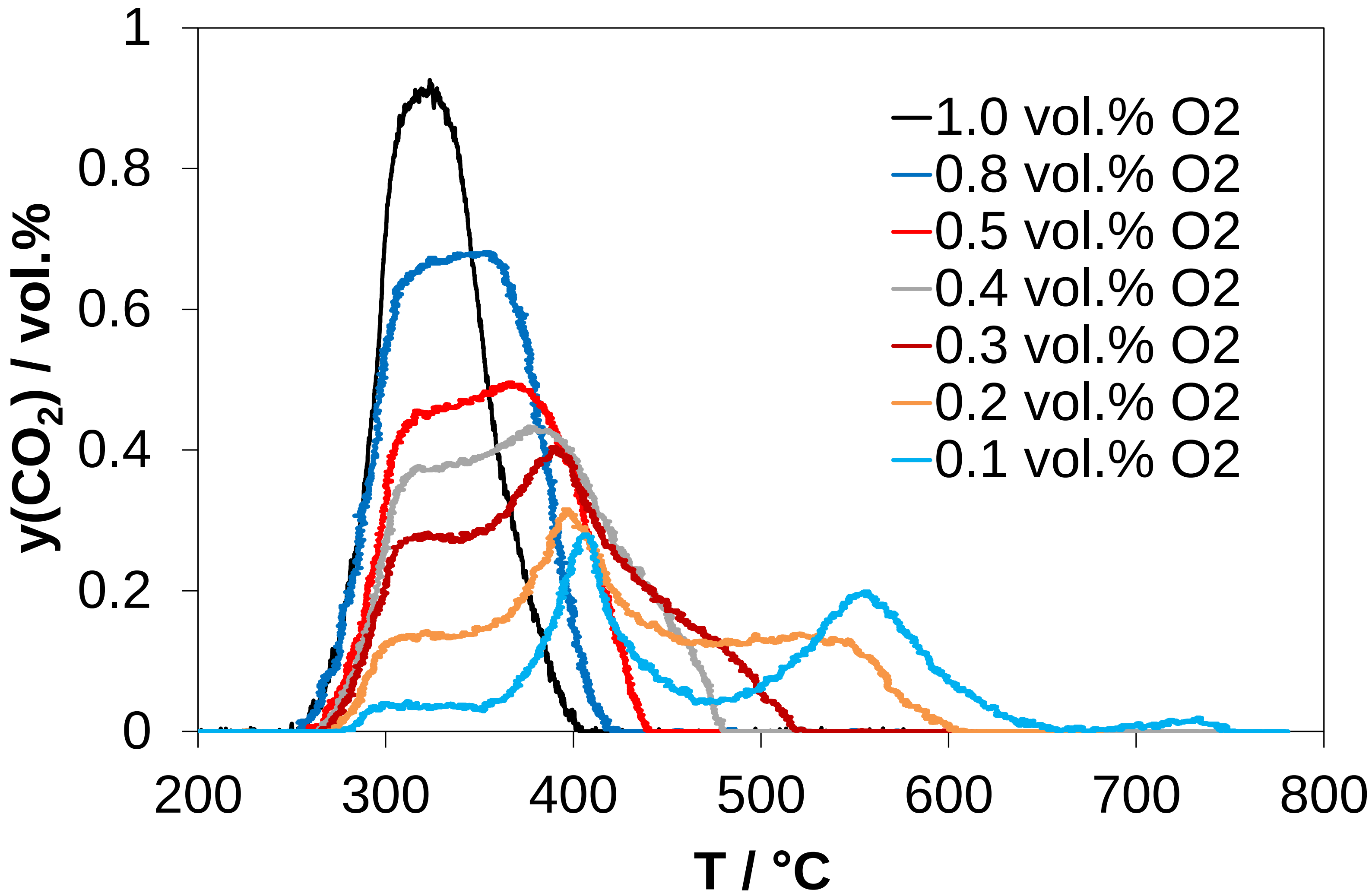


Loose contact



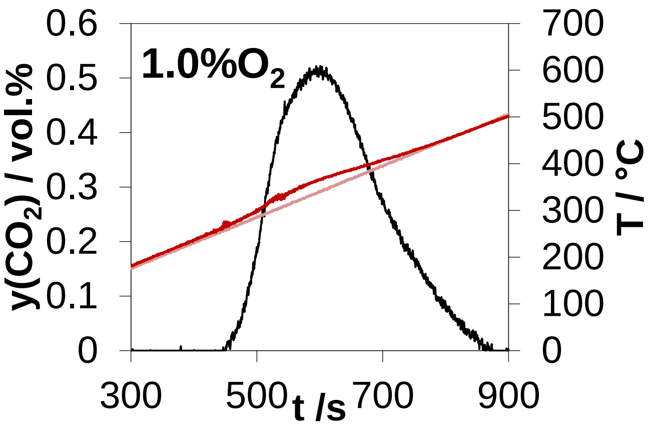


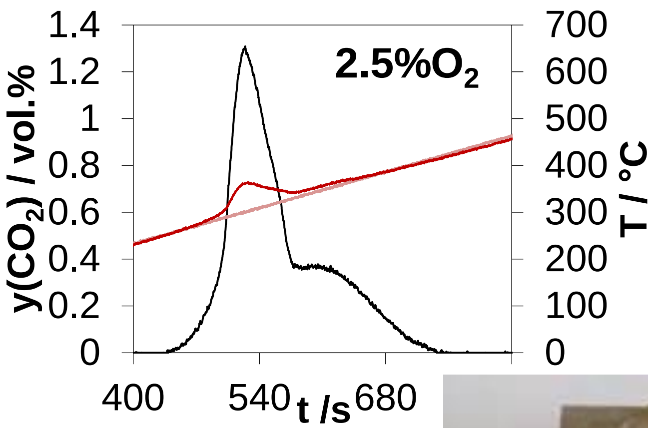
Effect of O_2 on activity of FSP-Mn_2O_3



Temperature evolution in catalyst bed

Temperature inside catalyst bed



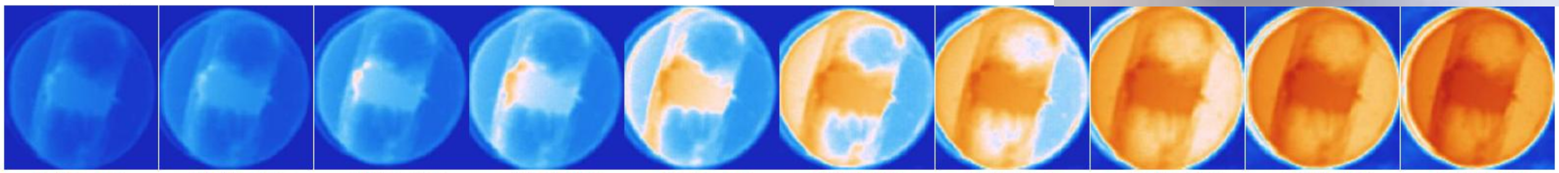


1.0% O_2: ΔT_{max}=25 K

2.5% O_2: ΔT_{max}=70 K

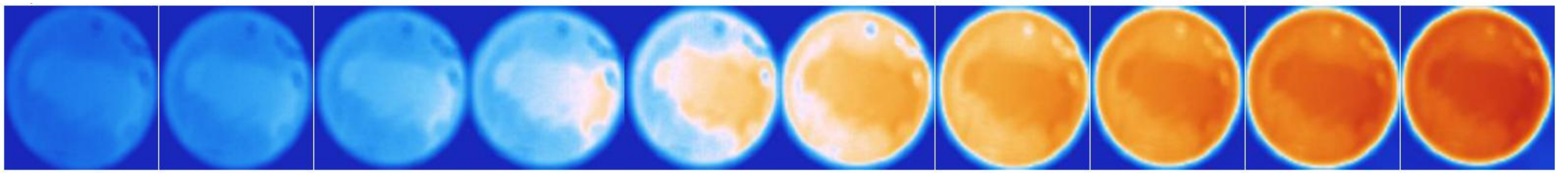
Temperature on catalyst surface

1.0%O_2

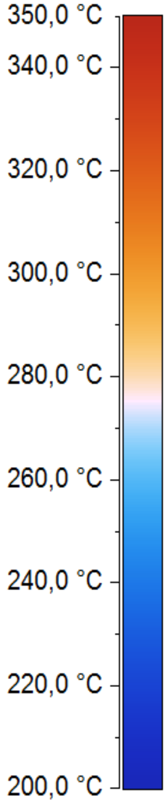


240 °C 250 °C 260 °C 270 °C 280 °C 290 °C 300 °C 310 °C 320 °C 330 °C

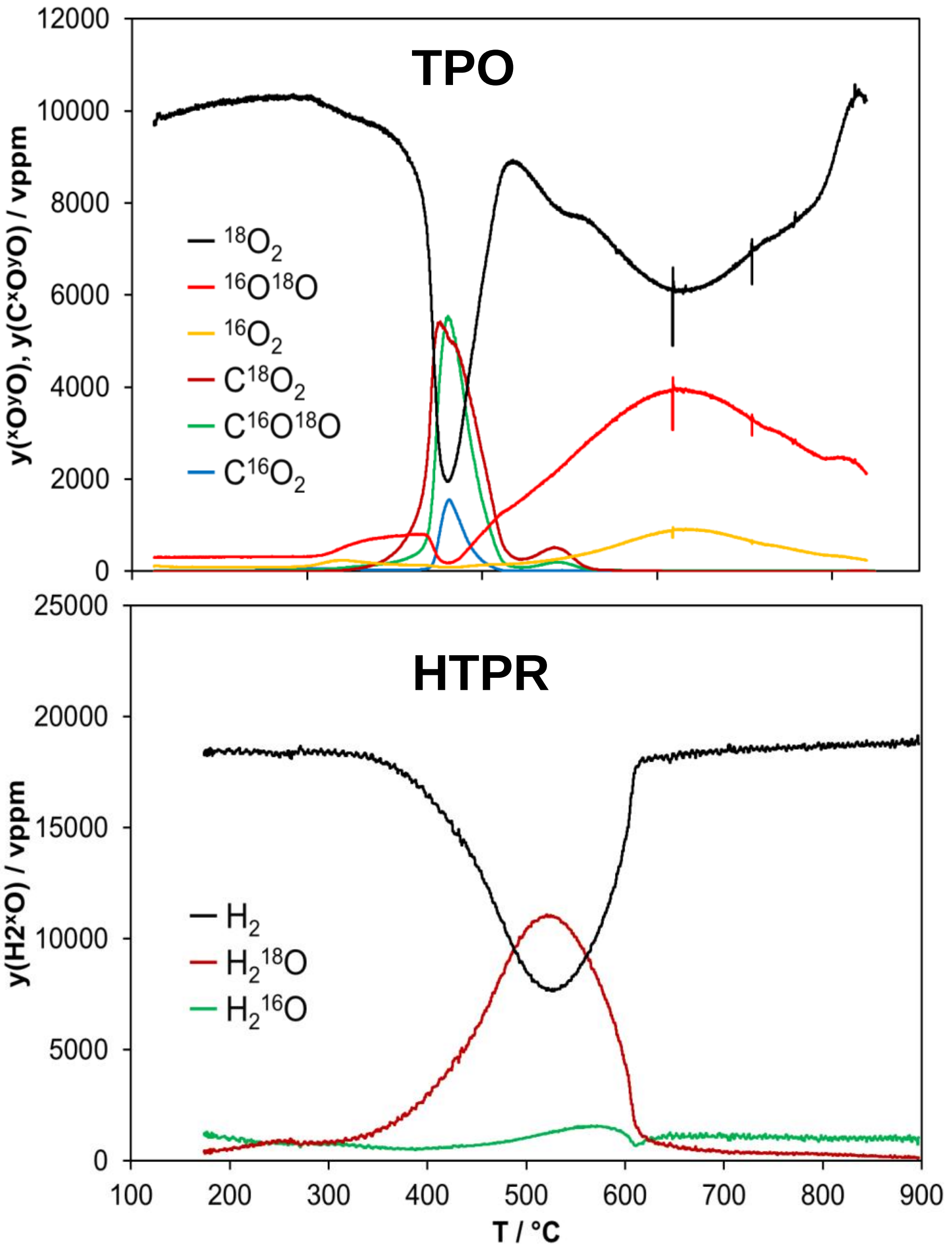
2.5%O_2



240 °C 250 °C 260 °C 270 °C 280 °C 290 °C 300 °C 310 °C 320 °C 330 °C

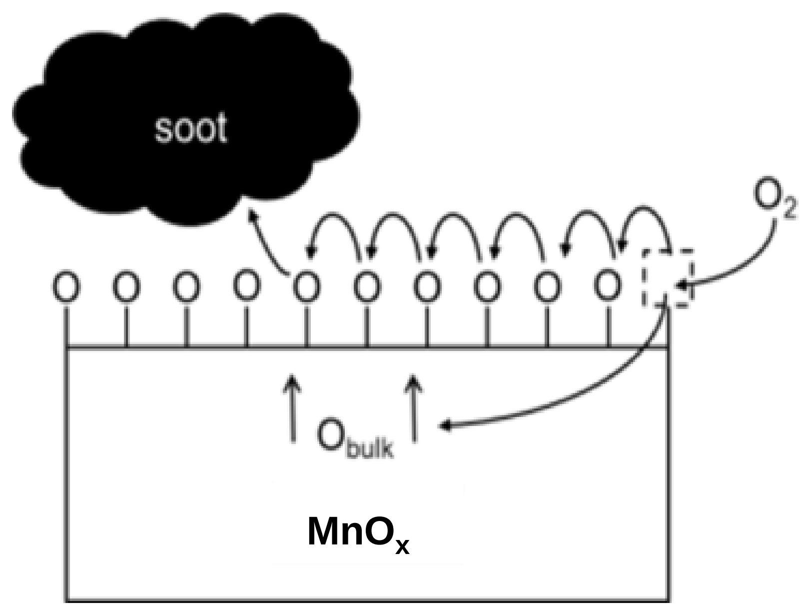


Isotopic TPO with $^{18}O_2$



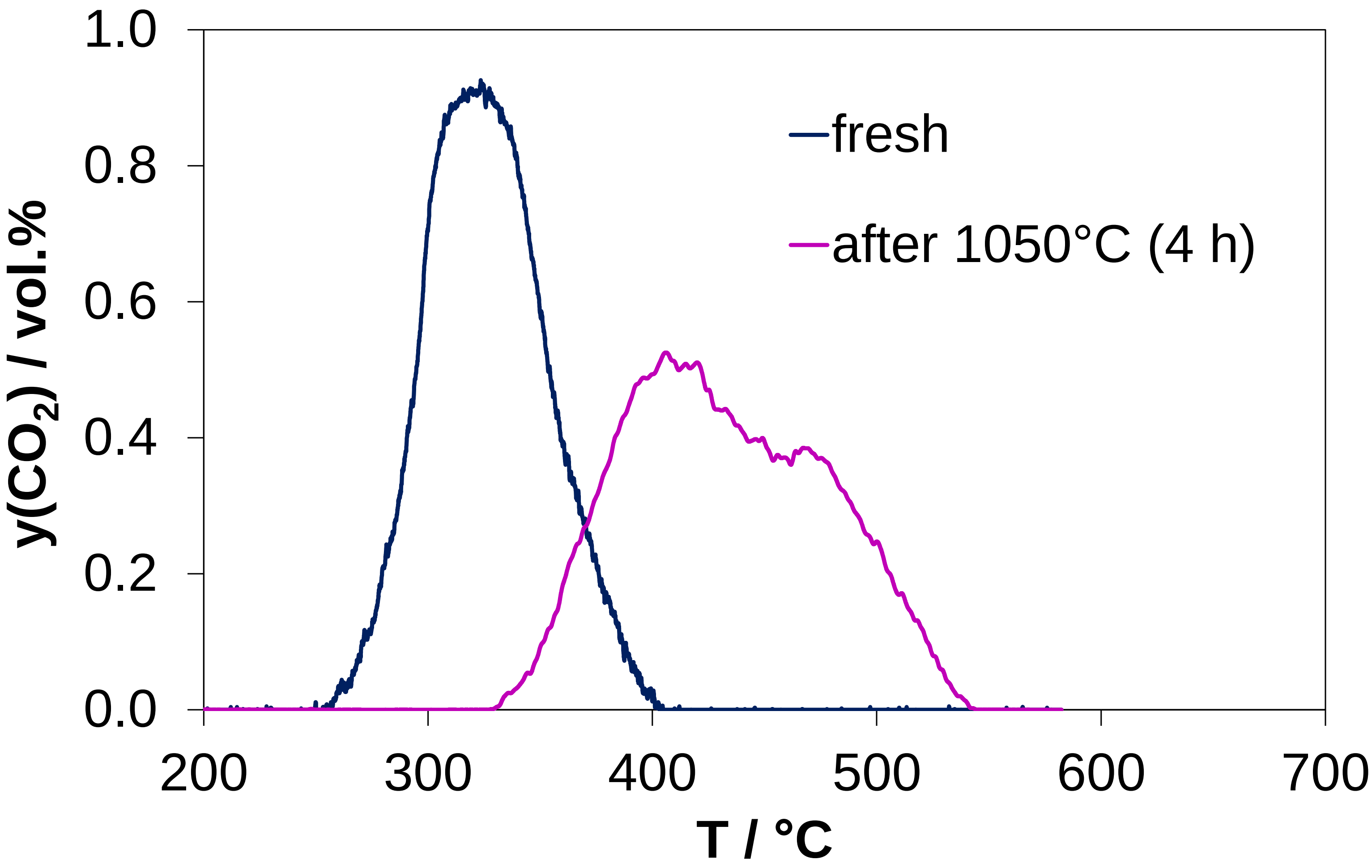
→ transfer of ca. 17% of catalyst oxygen

→ importance of bulk oxygen



Thermal stability of FSP-Mn_2O_3

Activity after exposure for 4 h at 1050°C (static air)



SO_2 stability of FSP-Mn_2O_3

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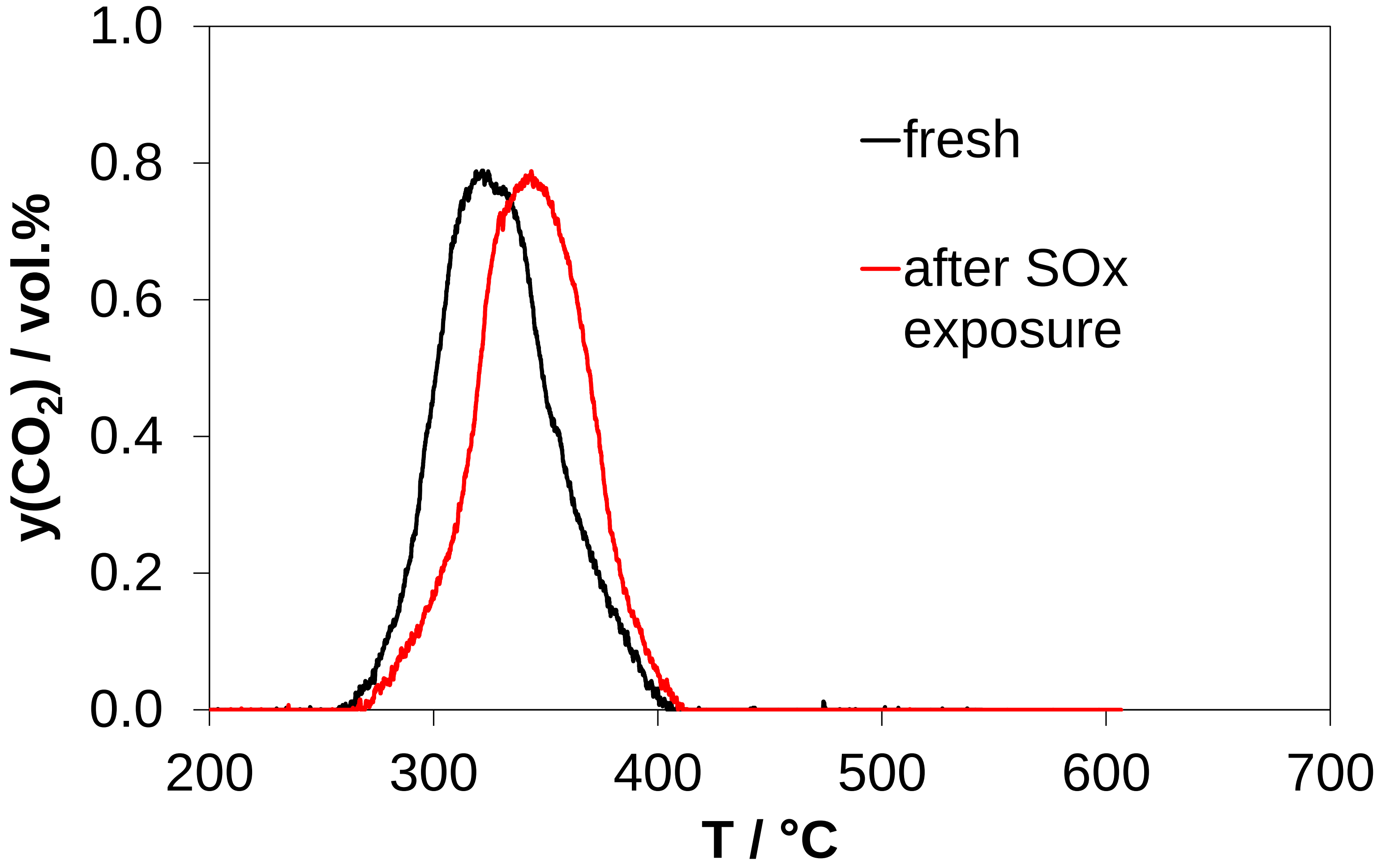
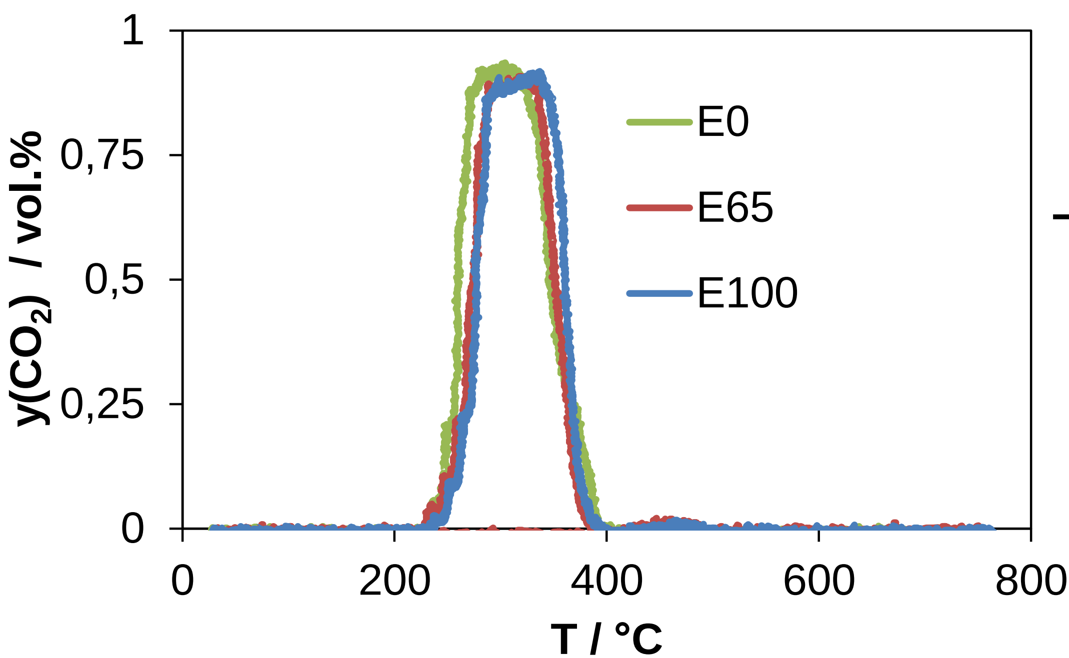
Activity after SO_2 exposure for 16 h at 250°C
(20 ppm SO_2, 5% O_2, 8% H_2O, N_2 balance)



Oxidation of ethanol-based soot on FSP-Mn_2O_3

- Soot obtained from combustion of iso-octane/ethanol (Prof. Trimis, KIT)
- Soot characteristics and catalytic oxidation

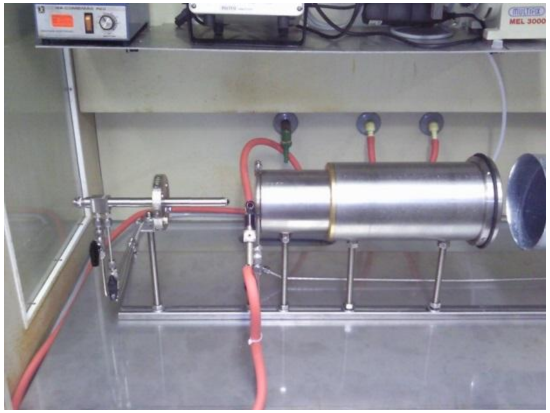
Soot	d / nm	S(BET) / m^2/g
PrintexU	25	91
E0	12	425
E65	10	211
E100	6	96



→ very similar oxidation kinetics of different soot samples

Test of catalytic particulate filters

Catalytic coating of lab-GPF

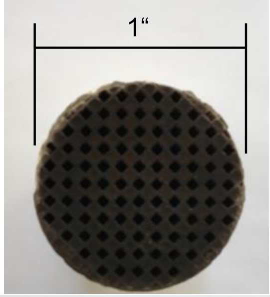


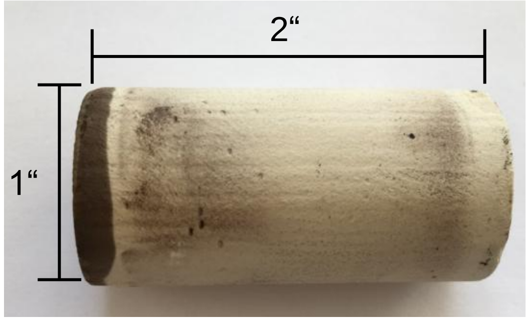
FSP bench

Lab-GPF

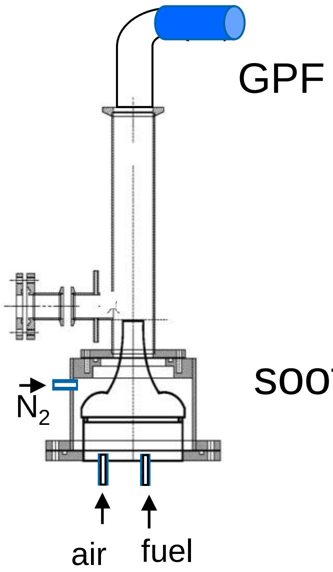
300 cpsi

60% porosity





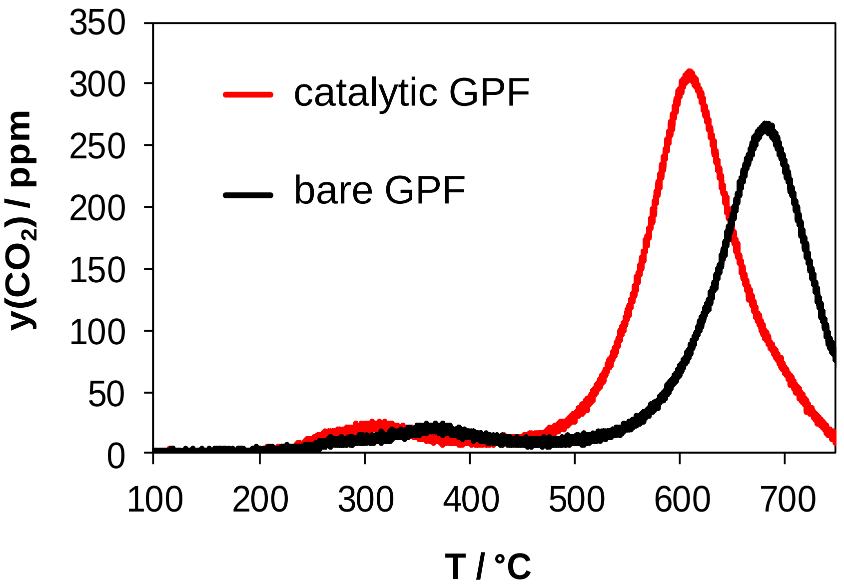
Soot deposition on catalytic GPF



TPO conditions

- Catalyst loading: 22 g/L
- Soot loading: ca. 1.5 g/L
- $y(O_2)$=1%, $y(H_2O)$=2%, N_2 balance
- F=6500 mL/min (S.V.≈20’000/h)

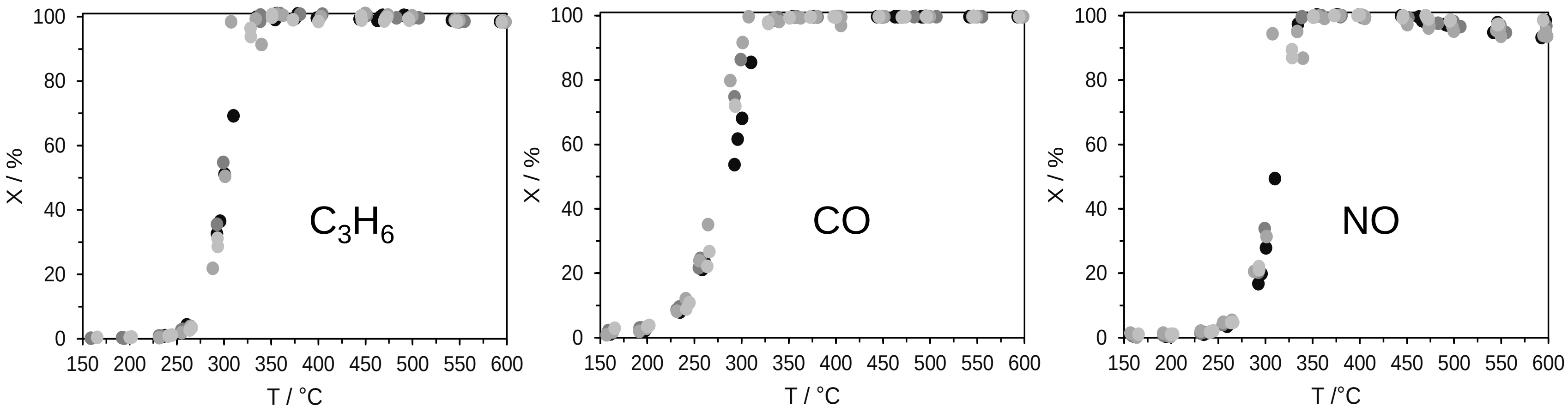
Activity of GPF coated with FSP catalyst



→ Effect of catalytic coating

→ Presence of loose and tight contact mode

Implementation into Three Way Catalysts



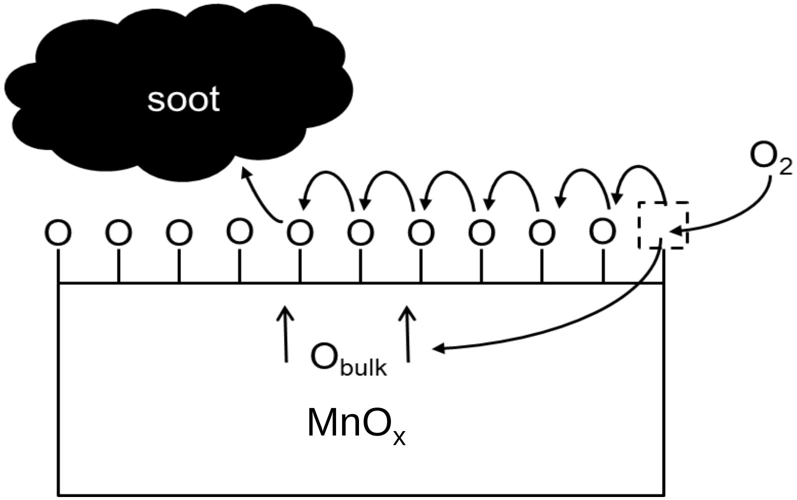
Summary

- Manganese oxides are effective in soot oxidation and show high resistance towards thermal and SO_x exposure

- Manganese oxide catalyst requires intimate contact to soot

- FSP-Mn_2O_3 strongly supplies bulk oxygen to soot

- Beneficial effect of FSP catalyst also occurs onto particulate filters



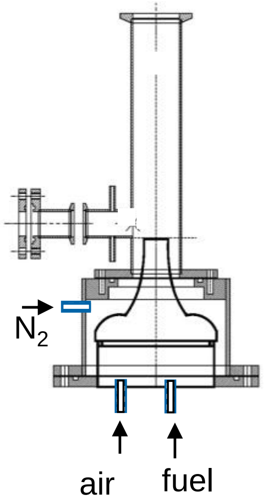
Financial support from German Agency of Renewable Resources (project BiOtto) is thankfully acknowledged

Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz

FACHAGENTUR NACHWACHSENDE ROHSTOFFE e.V.

Preparation and characterisation of the soot

- C_3H_6/O_2 diffusion flame



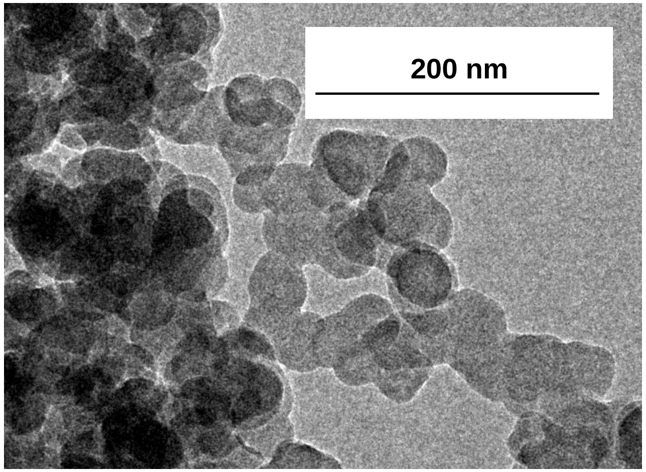
- Adsorbed species: 2.5 wt.%
- Chemical composition

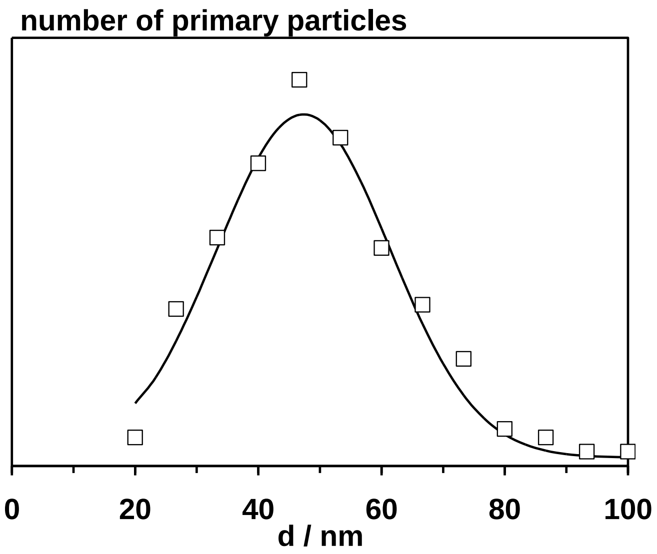
  98.8 wt.% C

  0.7 wt.% O

  0.5 wt.% H

  <0.1 wt.% N
- S_{BET} = 65 m^2/g
- d = 45 nm (most frequent diameter)





Thermal stability of FSP-Mn_3O_4 catalyst

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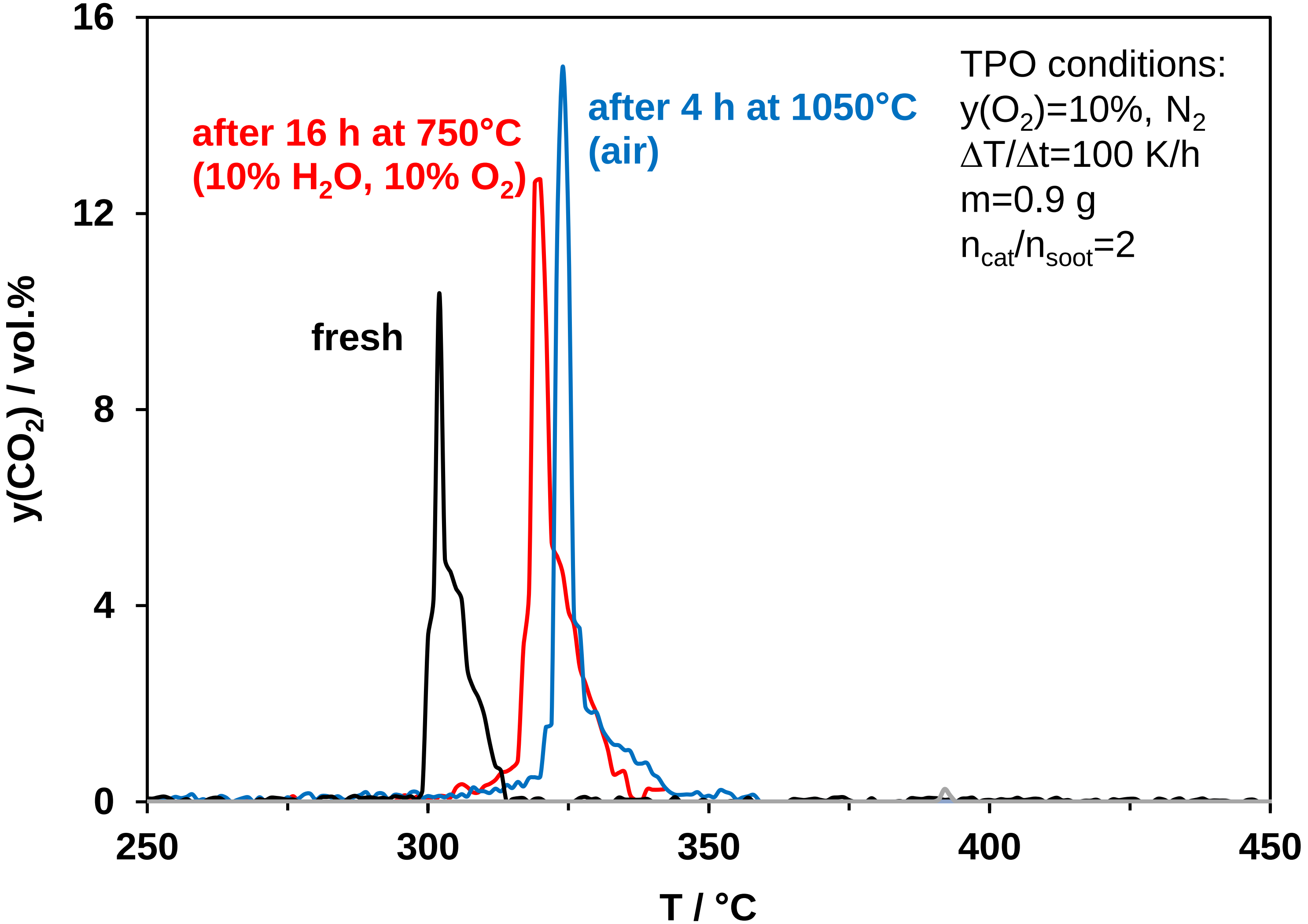
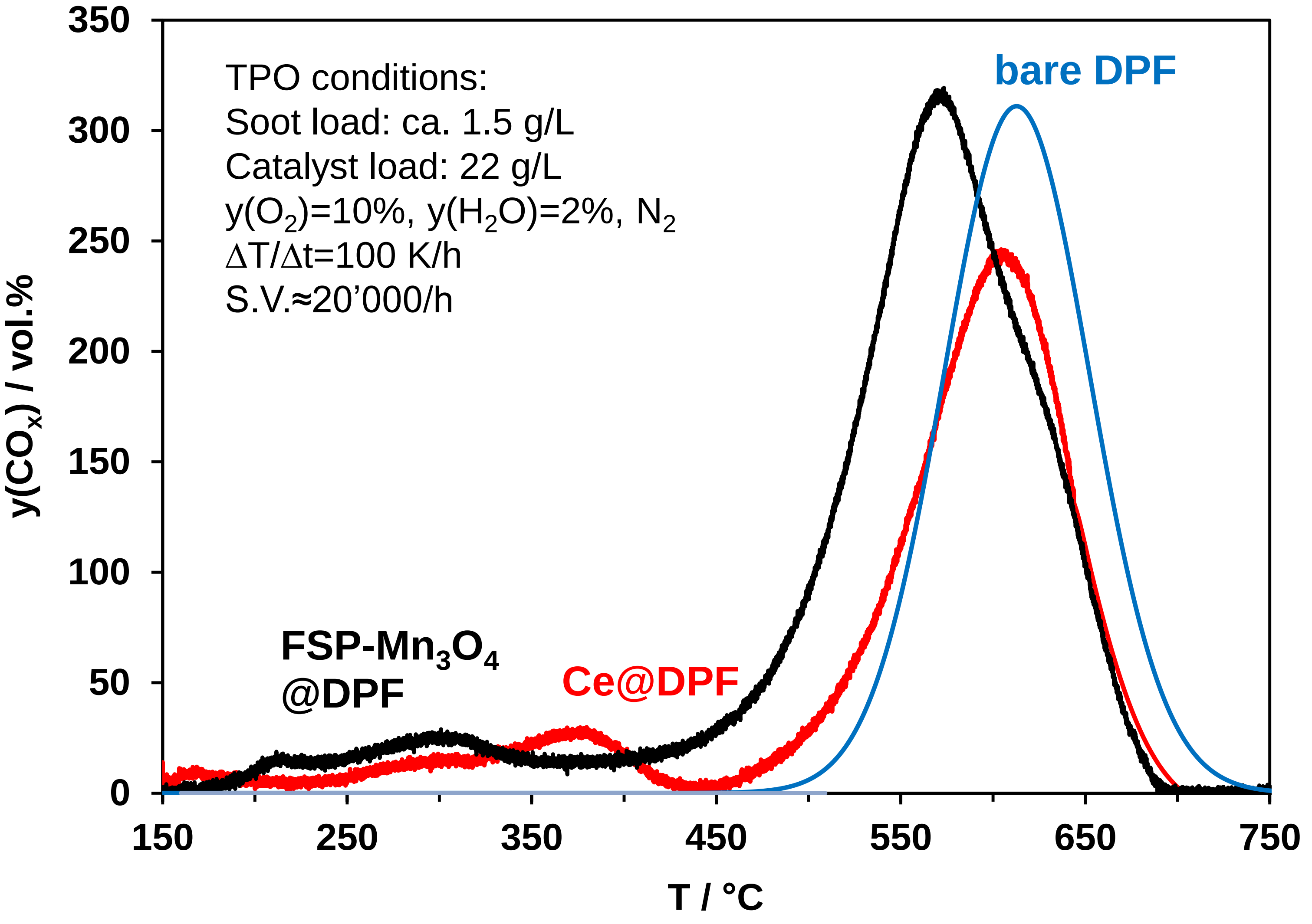


Performance of lab-DPF coated with FSP-Mn_3O_4 under diesel conditions



Performance of lab-DPF coated with FSP-Mn_3O_4 under diesel and lean gasoline conditions