Catalytic soot oxidation in gasoline engine exhaust

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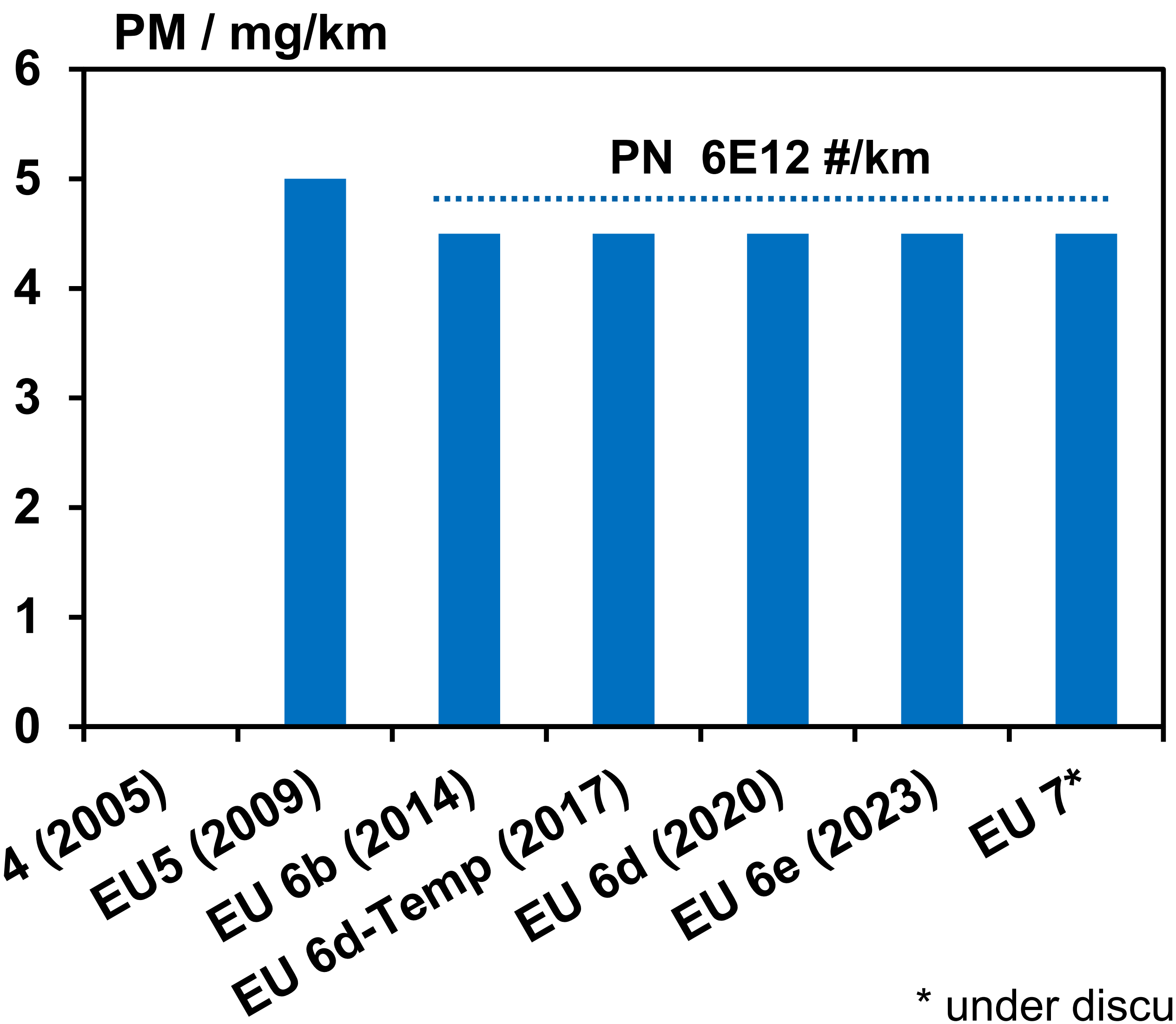
Particulate emission limits of the EU for GDI passenger cars



* under discussion

Future development of GDI technology

- Global GDI market is expected to increase from 10.6 bn US$ (2023) to 25.8 US$ (2033)

  https://www.futuremarketinsights.com/reports/gasoline-direct-injection-gdi-market

  → Soot emissions of GDI cars may come increasingly under pressure

  → Gasoline particulate filters (GPF) might be introduced widely

- Sustainable gasoline such as methanol, ethanol and synthetic MtG fuel may support the market growth of GDI technologies

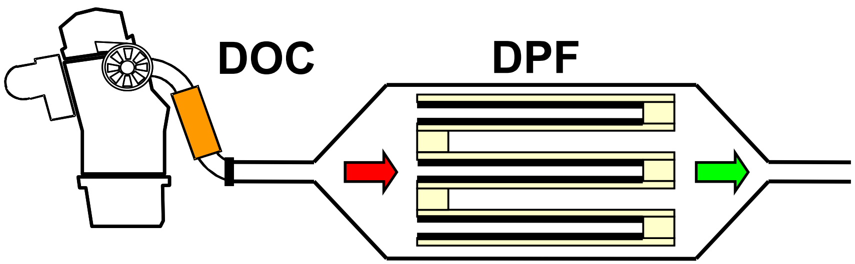
MtG demonstration plant of TU Freiberg (STF technology of CAC)

Strategies of particulate filter regeneration

- Passive regeneration (T=200…450°C)

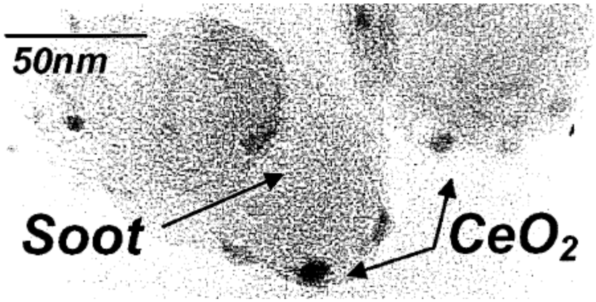
  $2\ NO + O_2 \rightarrow 2\ NO_2$

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



- 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

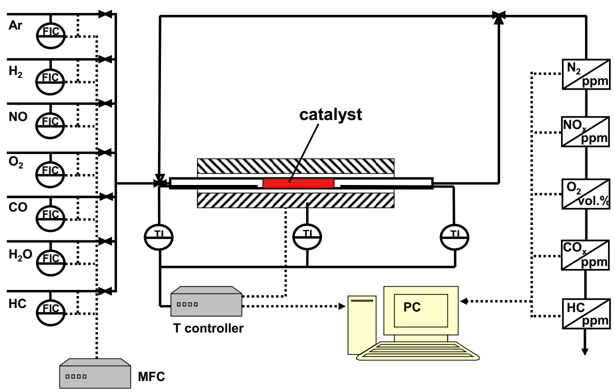
Mn_2O_3 catalyst and test conditions

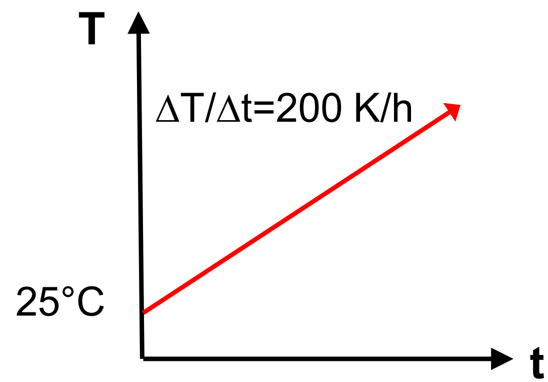
- Mn_2O_3 catalyst has been developed for soot oxidation in diesel exhaust
  → transfer to gasoline exhaust conditions

  Chem. Eng. J. 259 (2015) 492
  Appl. Catal. B 272 (2020) 118961

- Preparation by flame spray pyrolysis followed by treatment at 550°C in air
- Catalytic tests made in laboratory using TPO with tight catalyst/soot mixtures

Test bench

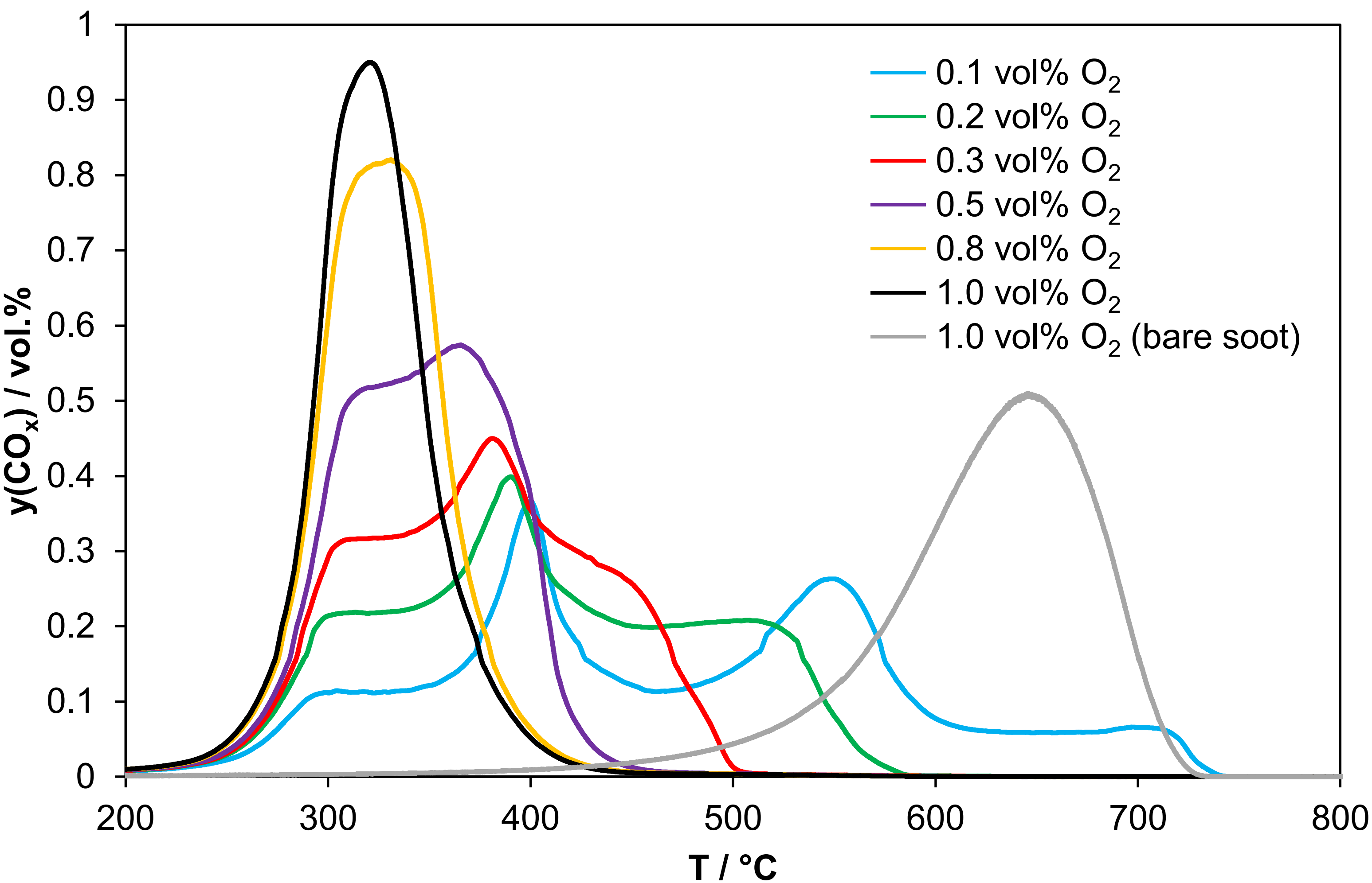




- TPO conditions
  - $y(O_2)=0.1\text{-}1.0\%$, $y(H_2O)=2\%$, N_2 balance
  - F=500 ml/min (STP)
  - $m = 960$ mg ($n_{cat}/n_{soot}=2$)
  - Model soot Printex U

Reactor with Mn_2O_3/soot blend

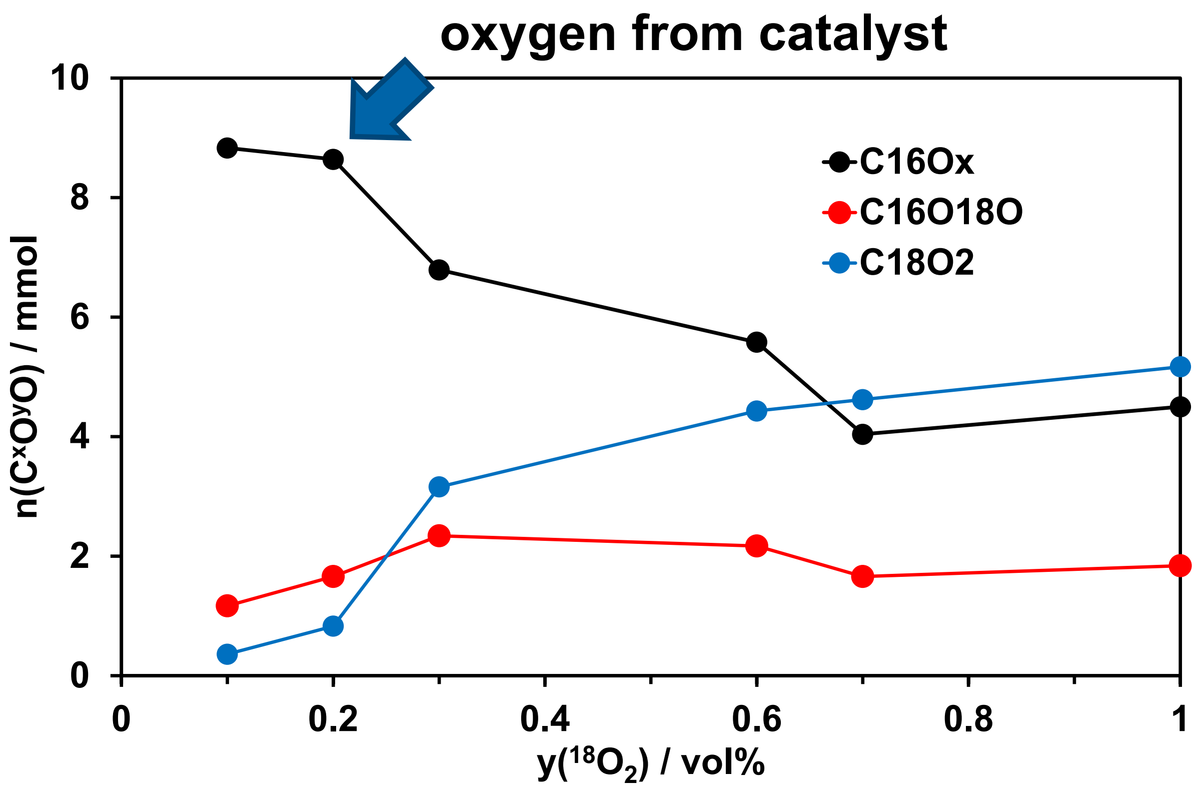
Effect of O_2 on soot oxidation activity of Mn_2O_3



→ Increasing O_2 fraction enhances soot oxidation and suppresses temporal reduction of the catalyst

Origin of oxygen involved in soot oxidation

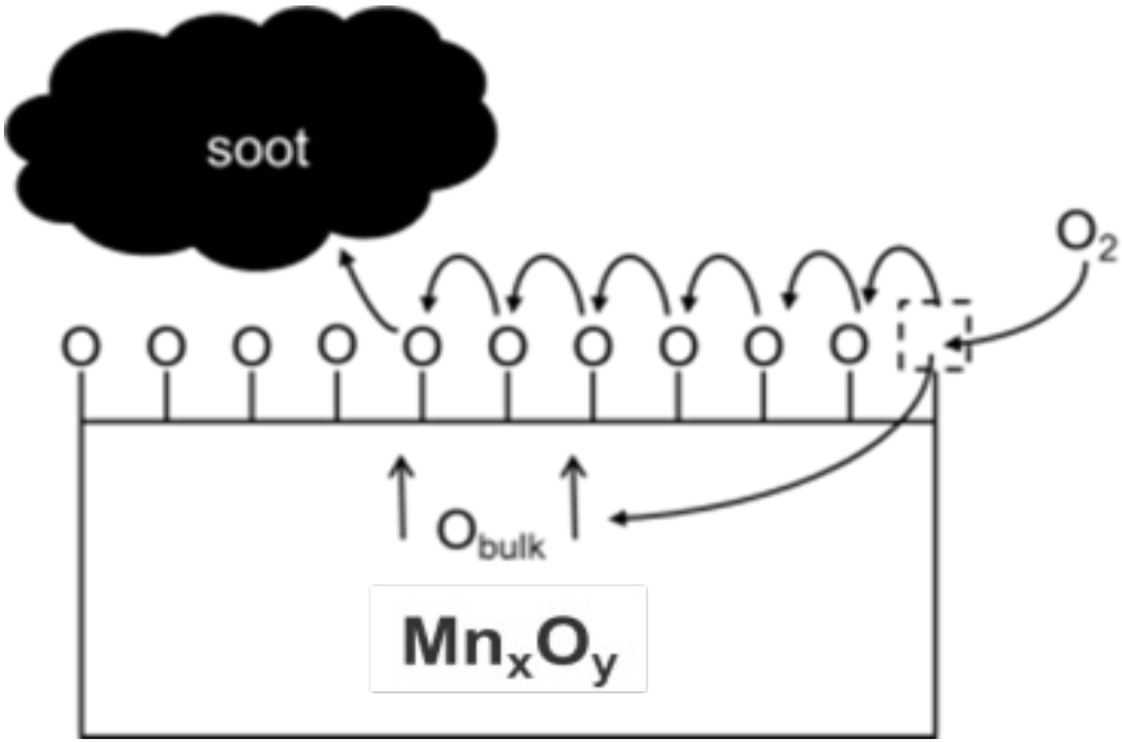
- Isotopic TPO studies with tight contact Mn_2O_3/soot mixtures using $^{18}O_2$ fractions from 0.1 -1.0 vol.% followed by HTPR



TPO conditions
$y(^{18}O_2)$=0.1-1.0%, N_2 balance
F=500 ml/min (STP)
m = 960 mg (n_{cat}/n_{soot}=2)
Model soot Printex U

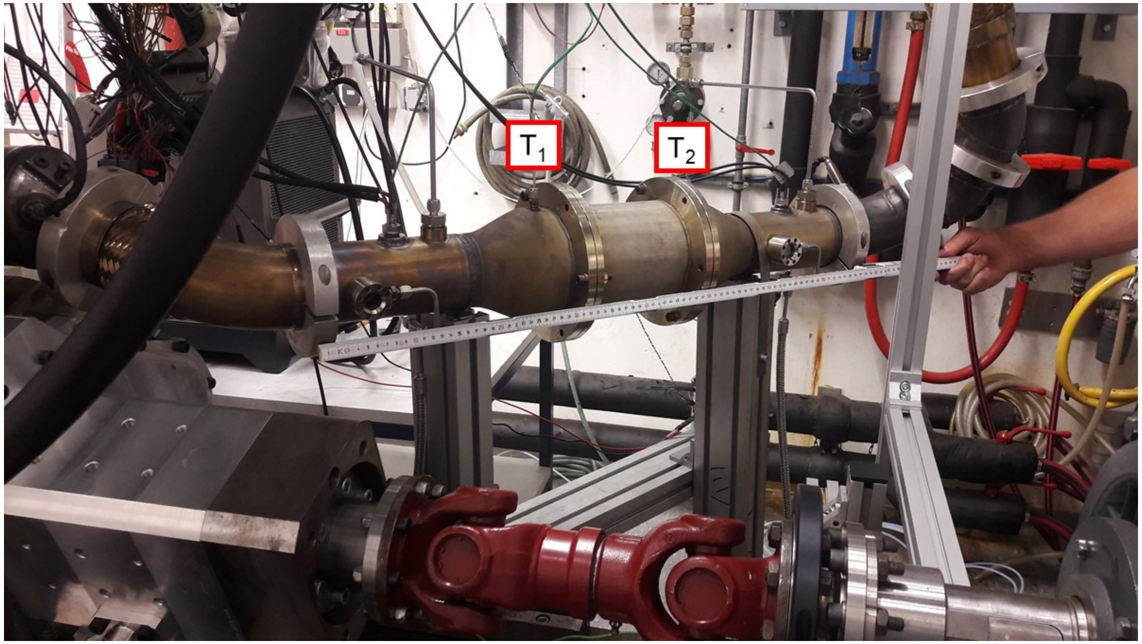
→ Surface and particular bulk oxygen is increasingly transferred from the catalyst to the soot with decreasing O_2 content in the gas phase

Transfer of oxygen from catalyst to soot



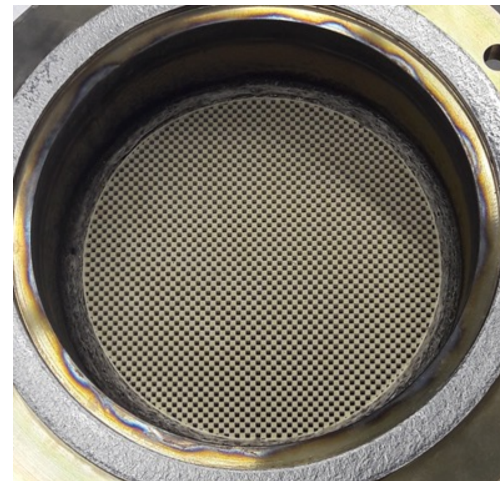
Evaluation of Mn_2O_3 catalyst in gasoline exhaust

1.4 l GDI engine with 4 cylinders and max. 45 kW



Coated GPF

Catalyst load: 20 g/l
D: 118.4 mm, L: 120 mm, 240 cpsi, 9.5 mil



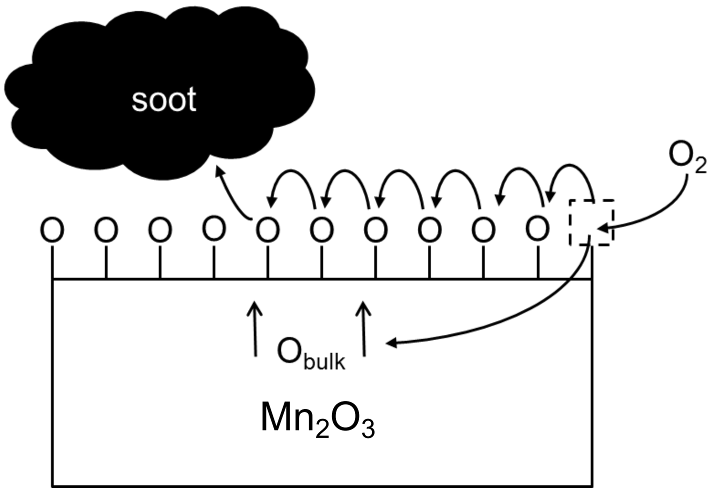
- Soot deposition at λ=0.77 (p_{mi}=10 bar, F=93 kg/h) for 45 min using a bare and catalytically coated GPF → soot load: approx. 1.1 g/l
- Regeneration by increasing temperature to 500°C using engine management (λ=1.1, p_{mi}=9 bar, F=87 kg/h)

→ Rate of soot oxidation: **3.5 g/h with catalyst vs. 1.0 g/h without catalyst**

Summary

- Mn_2O_3 prepared from flame spray pyrolysis is effective for soot oxidation in gasoline exhaust

- Mn_2O_3 catalyst requires intimate contact to soot



- Mn_2O_3 strongly supplies bulk oxygen to soot

- Beneficial effect of catalyst is confirmed on the real world level

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