

# **Kinetic modelling of the catalytic soot oxidation on $\text{Fe}_2\text{O}_3$**

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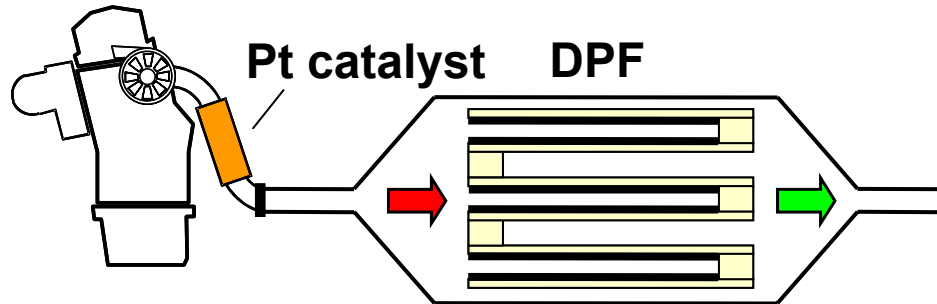
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- **Introduction**
- **Experimental studies**
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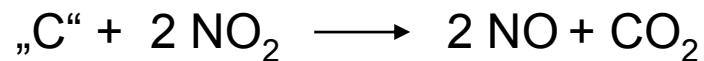
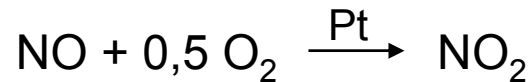
# Removal of soot from diesel exhaust

- Separation of soot by Diesel Particulate Filters (DPF)



- DPF regeneration

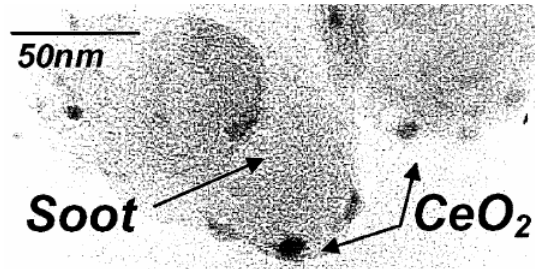
- Continuously Regeneration Trap (CRT)



- Catalytic DPF (C-DPF)



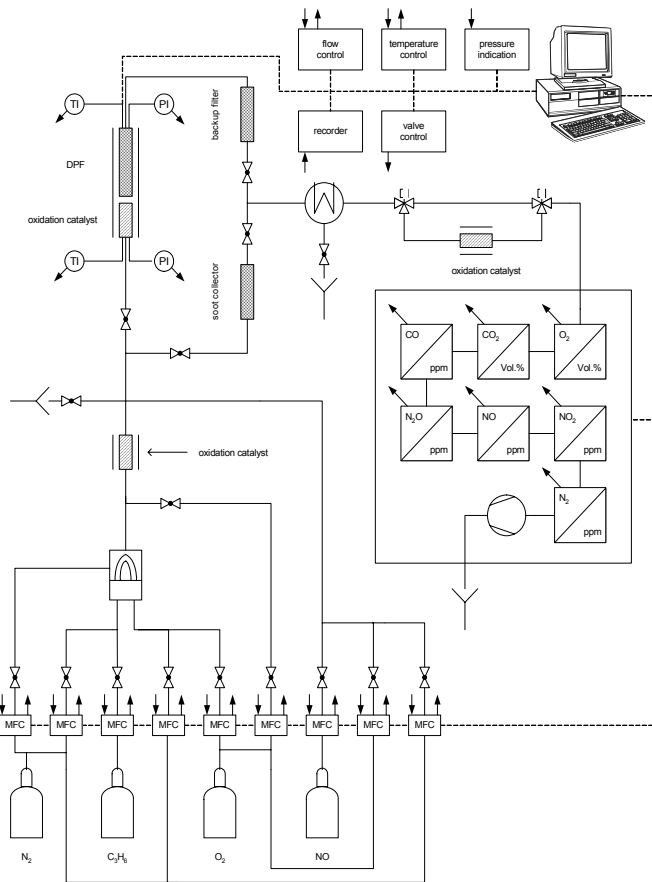
- $\text{CeO}_2$  and  $\text{Fe}_2\text{O}_3$  originated from Fuel Borne Catalysts (FBC) enhance oxidation of deposited soot



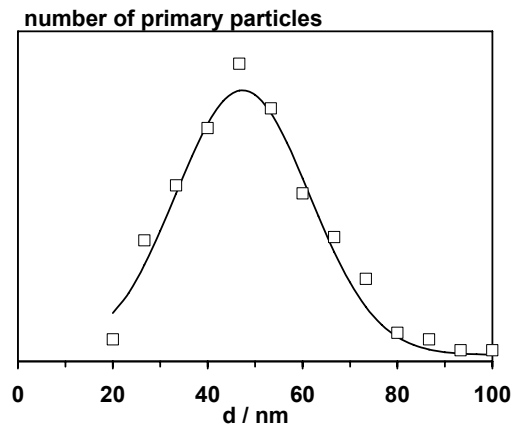
K. Ohno, Ph.D. thesis, 2006

**➔  $\text{Fe}_2\text{O}_3$  reveals practical relevance for catalytic soot oxidation**

- In our mechanistic studies:  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and a C<sub>3</sub>H<sub>6</sub> soot are used
- Model soot prepared by diffusion burner (C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> flame)



- 2.6 wt.% adsorbed species
- 98.8 wt.% C  
0.7 wt.% O  
0.5 wt.% H  
0 wt.% N
- $S_{\text{BET}} = 91 \text{ m}^2/\text{g}$
- $d = 45 \text{ nm}$  (most frequent diameter)

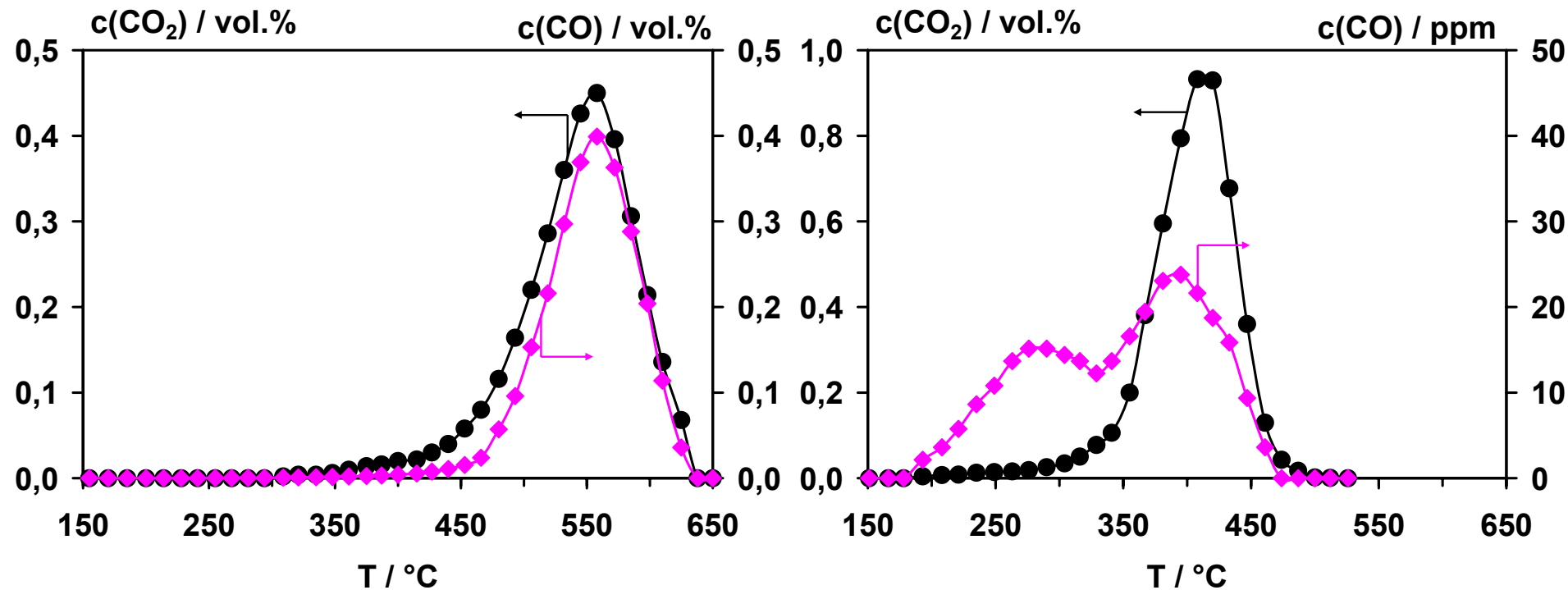


P. Balle, H. Bockhorn, B. Geiger, N. Jan, S. Kureti, D. Reichert, T. Schröder, *Chem. Eng. Process.* 45 (2006) 1065

# Effect of the $\text{Fe}_2\text{O}_3$ catalyst in Temperature Programmed Oxidation (TPO) of the soot

without catalyst

with  $\text{Fe}_2\text{O}_3$  catalyst

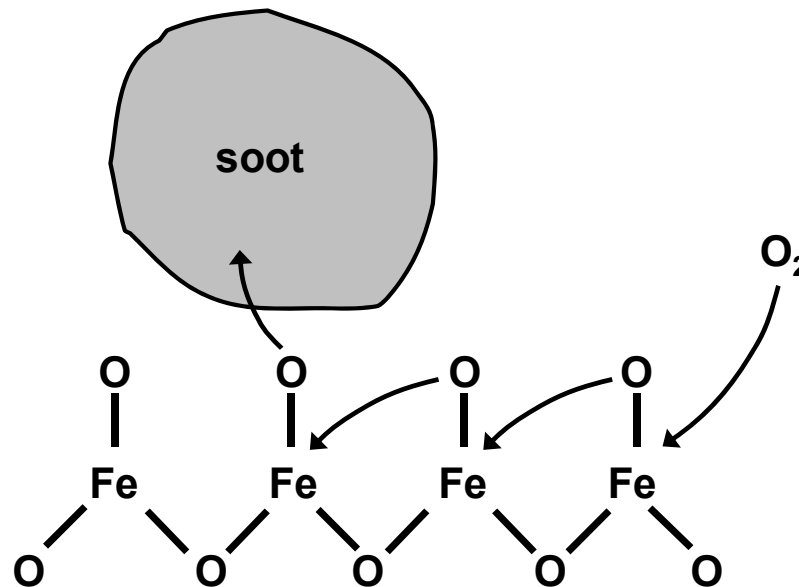


Conditions:  $c(\text{O}_2)=6.0 \text{ vol.}\%$  Flow: 500 ml/min (STP)  $\Delta T/\Delta t=90 \text{ K/h}$   
 $c(\text{N}_2)=94 \text{ vol.}\%$   $n(\text{Fe}_2\text{O}_3)=20 \text{ mmol}$   $n(\text{C})=10 \text{ mmol}$



# Role of the $\text{Fe}_2\text{O}_3$ catalyst in soot oxidation

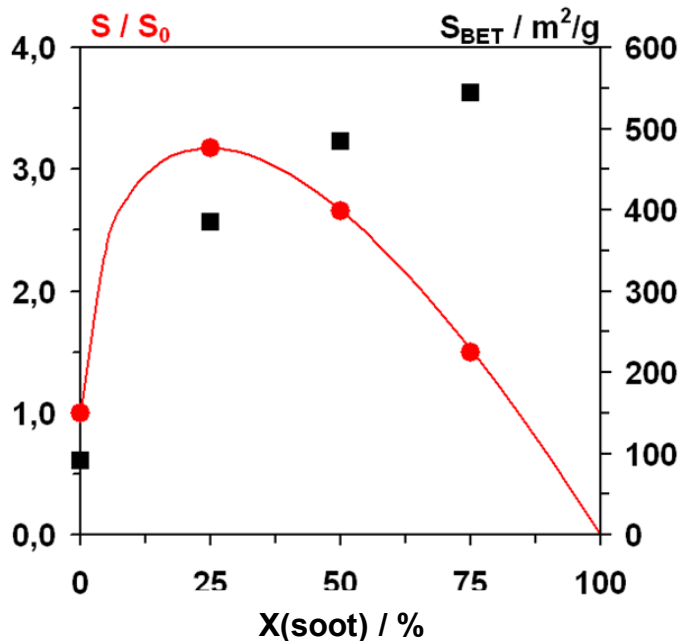
- $\text{Fe}_2\text{O}_3$  surface acts as „oxygen pump“
- transfer of O from the contact points of  $\text{Fe}_2\text{O}_3$  and soot
- contact maintains up to high conversion levels of the soot
- $\text{Fe}_2\text{O}_3$  is not directly involved in soot/ $\text{O}_2$  reaction



D. Reichert, H. Bockhorn, S. Kureti, *Appl. Catal. B* 80 (2008) 248

# Global kinetic modelling of the soot oxidation

- Potential law:  $r(\text{CO}_x) = k_{\text{CO}_x} \cdot n(\text{C}_f) \cdot c(\text{O}_2)^n$       $k_{\text{CO}_x} = A_{\text{CO}_x} \cdot e^{\left(\frac{E_{\text{A,CO}_x}}{RT}\right)}$
- Determination of  $n(\text{C}_f)$  :



From N<sub>2</sub> physisorption (BET):

$$\rightarrow S(X) = S_0 \cdot m_0 \cdot (1-X) \cdot (1+300 \cdot X)^{1/3}$$

From TPD with X(C) = 0, 25, 50, 75%:

$$\rightarrow \frac{n(\text{CO}_x)_{\text{des}}}{S(X)} = 8.7 \frac{\mu\text{mol}}{\text{m}^2} = \lambda$$

$\lambda$ : Surface concentration of C<sub>f</sub> ( $\lambda \neq \lambda(X)$ )

$$\rightarrow n(\text{C}_f) = \lambda \cdot S(X)$$

- $r(\text{CO}_x) = A_{\text{CO}_x} \cdot e^{(-E_{\text{CO}_x}/RT)} \cdot S_0 \cdot m_0 \cdot (1-X) \cdot (1+300 \cdot X)^{1/3} \cdot c(\text{O}_2)^n$

D. Reichert, T. Finke, N. Atanassova, H. Bockhorn, S. Kureti, *Appl. Catal. B* in press



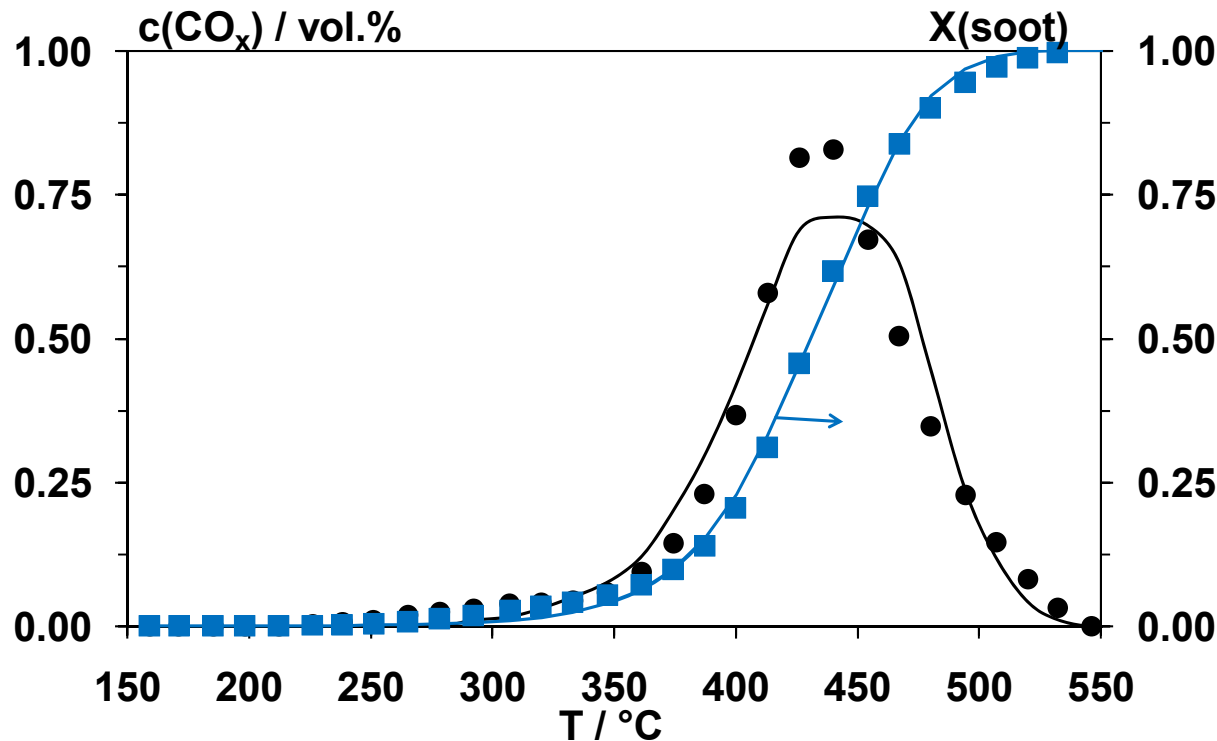


# Modelling of the soot oxidation on $\text{Fe}_2\text{O}_3$ catalyst

$$E_{A, \text{CO}_x} = 85 \text{ kJ/mol (fitted)}$$

$$A_{\text{CO}_x} = 1.8 \cdot 10^6 \text{ m}^3/(\text{mol} \cdot \text{s}) \text{ (fitted)}$$

$$n_{\text{O}_2} = 1 \quad \text{J.P.A. Neeft et al., } \textit{Fuel} \text{ 76 (1997) 1129}$$



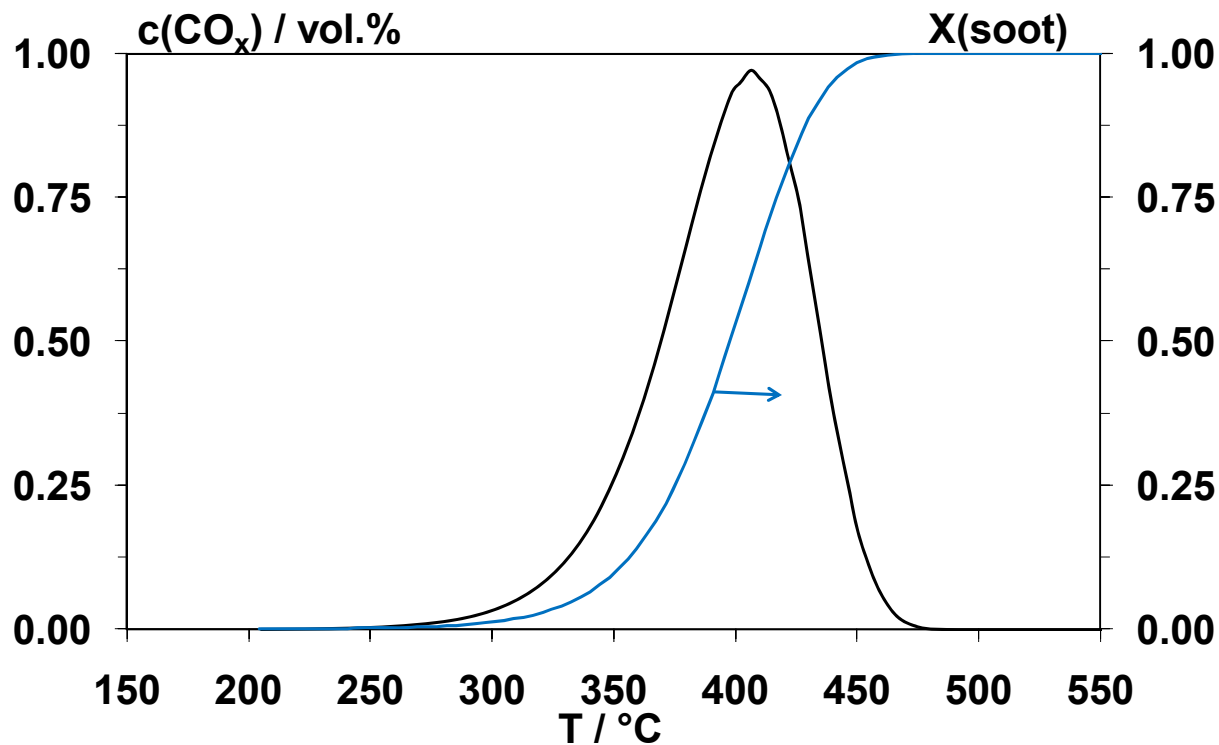
Conditions:  
 $c(\text{O}_2) = 6.0 \text{ vol.}\%$   
 $c(\text{N}_2) = 94 \text{ vol.}\%$   
 $F = 500 \text{ ml/min (STP)}$   
 $\Delta T / \Delta t = 90 \text{ K/h}$   
 $n(\text{Fe}_2\text{O}_3) = 20 \text{ mmol}$   
 $n(\text{C}) = 10 \text{ mmol}$

→ experimental data are well described by the calculation



## Model validation by simulating TPO profiles

- Variation of O<sub>2</sub> (10 vol.%) and soot (0.01g)



c(O<sub>2</sub>)=10 vol.%

c(N<sub>2</sub>)=90 vol.%

total flow: 500 ml/min

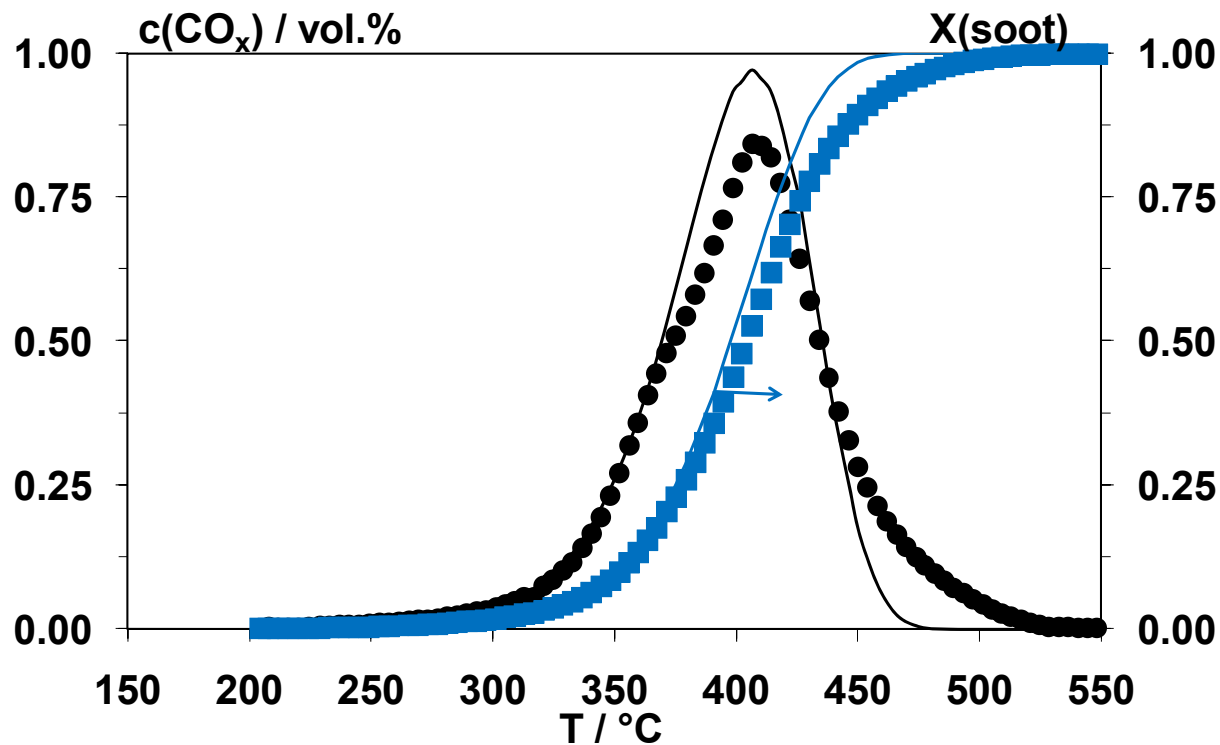
n(Fe<sub>2</sub>O<sub>3</sub>)=20 mmol

W/F=0.39 gs/ml

ΔT/Δt= 90 K/h

## Model validation by simulating TPO profiles

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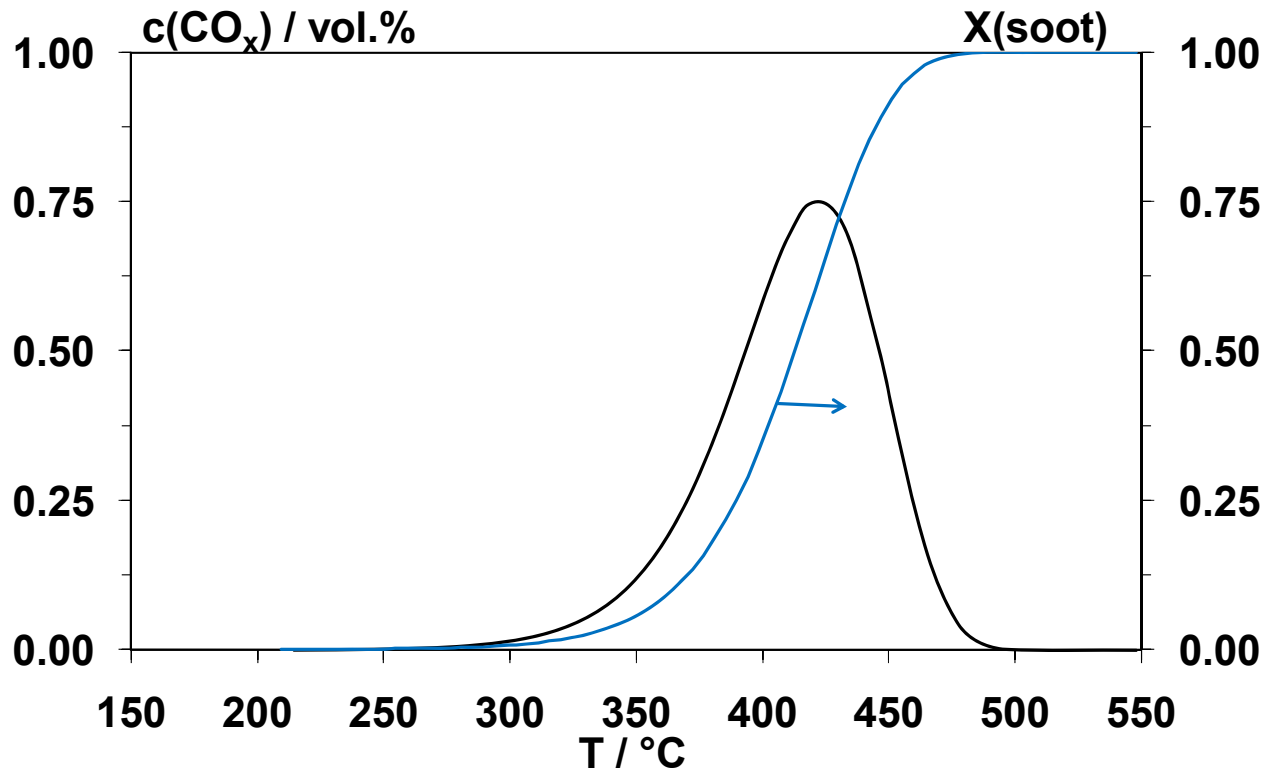
total flow: 500 ml/min

n(Fe<sub>2</sub>O<sub>3</sub>)=20 mmol

W/F=0.39 gs/ml

ΔT/Δt= 90 K/h

- Variation of O<sub>2</sub> (14 vol.% O<sub>2</sub>)



$c(\text{O}_2) = 14 \text{ vol.}\%$

$c(\text{N}_2) = 86 \text{ vol.}\%$

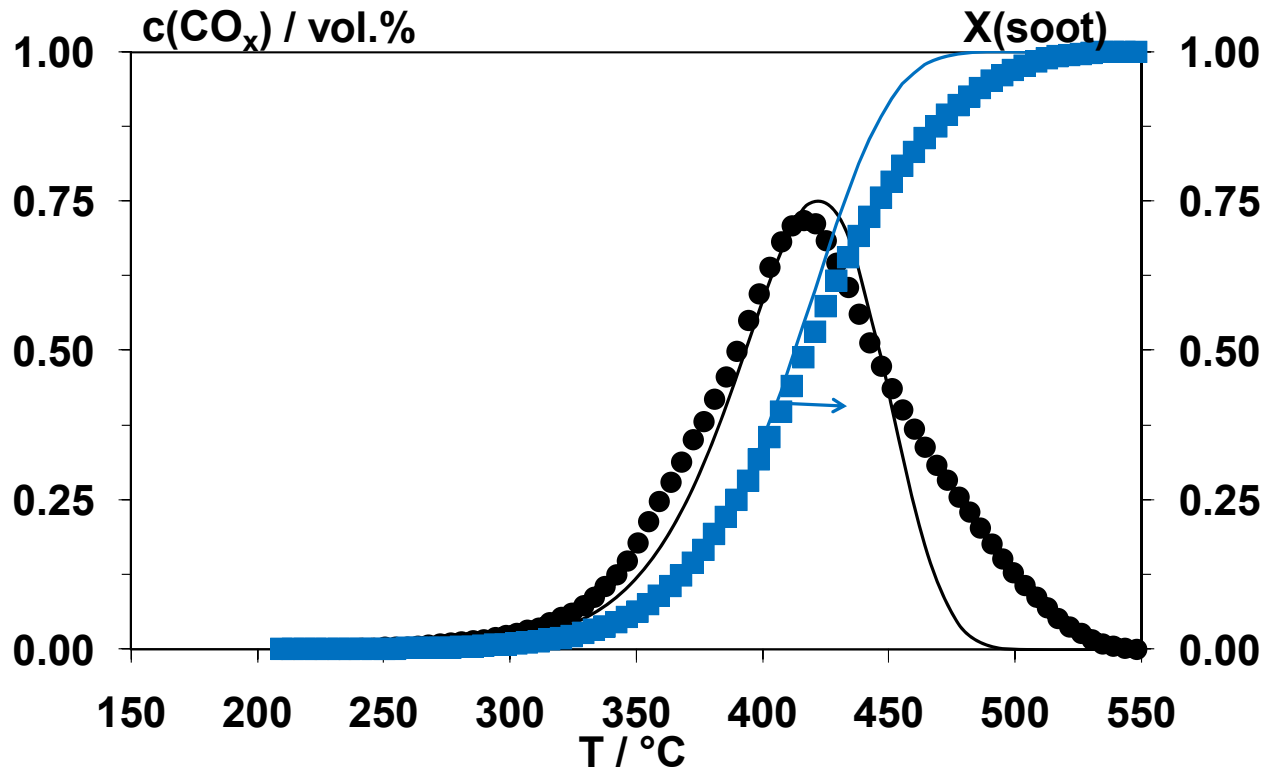
total flow: 500 ml/min

$n(\text{Fe}_2\text{O}_3) = 20 \text{ mmol}$

$W/F = 0.39 \text{ gs/ml}$

$\Delta T / \Delta t = 90 \text{ K/h}$

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$c(\text{O}_2) = 14 \text{ vol.}\%$

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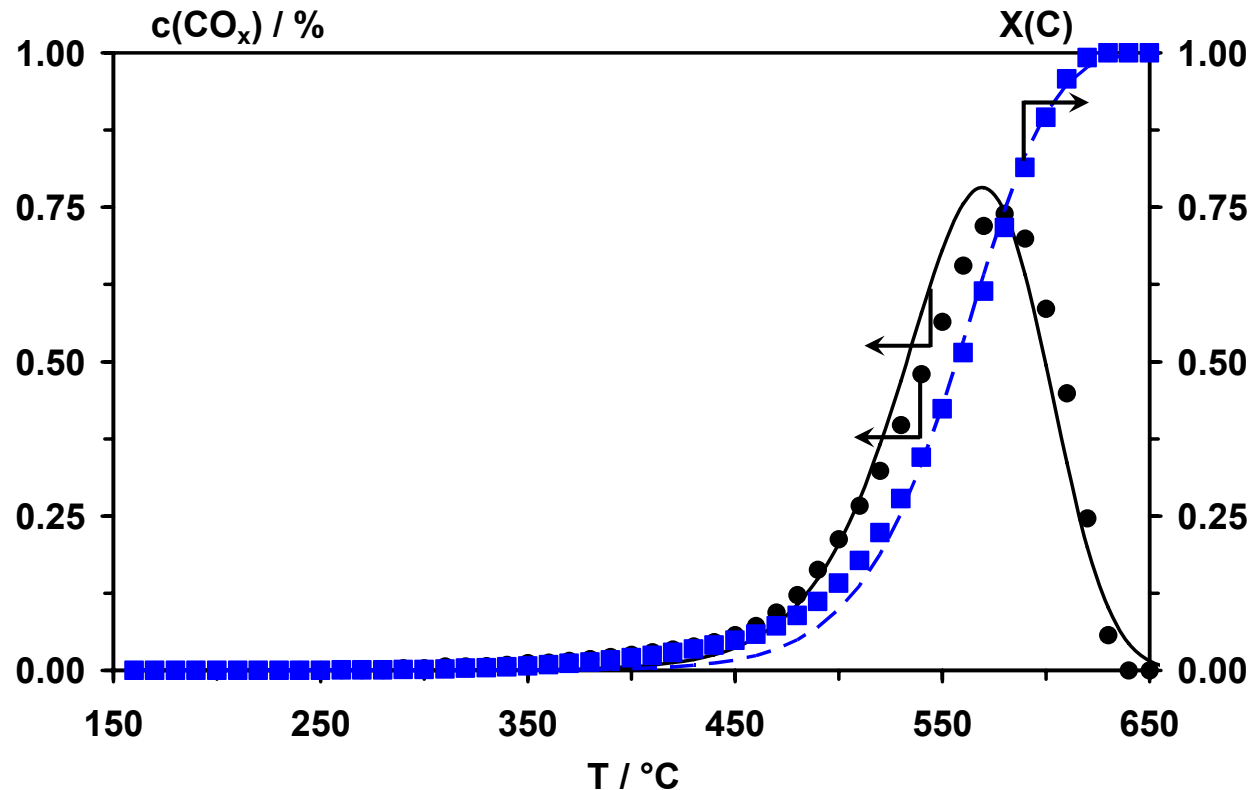
$\Delta T/\Delta t = 90 \text{ K/h}$

# Simulation of the soot oxidation without catalyst

$E_{A, CO_x} = 115 \text{ kJ/mol}$  (gradient free loop reactor)

$A_{CO_x} = 7 \cdot 10^6 \text{ m}^3/(\text{mol} \cdot \text{s})$  (transient experiments)

$n_{O_2} = 1$  J.P.A. Neeft et al., *Fuel* 76 (1997) 1129



Conditions:

$c(\text{O}_2) = 6.0 \text{ vol.}\%$

$c(\text{N}_2) = 94 \text{ vol.}\%$

$F = 500 \text{ ml/min (STP)}$

$\Delta T / \Delta t = 90 \text{ K/h}$

$n(\text{C}) = 10 \text{ mmol}$



## Summary

- $\text{Fe}_2\text{O}_3$  catalyst enhances the soot oxidation
- $\text{Fe}_2\text{O}_3$  catalyst transfers the oxygen from the gas-phase to the soot (“oxygen pump”)
- Using the catalytic mechanism a global kinetic model is constructed which is based on the number of  $\text{C}_f$  sites and  $c(\text{O}_2)$
- The global kinetic model is validated
- Further refinement of the model will be performed (towards an elementary approach)

