TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG

Effect of physical-chemical soot properties on the kinetics of catalytic soot oxidation

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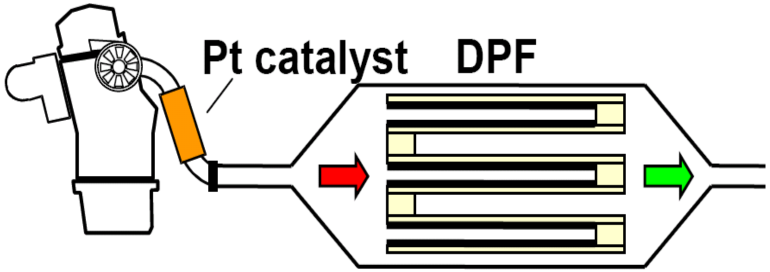
Strategies of DPF regeneration



- Continuously Regenerated Trap (CRT)

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

  $2\ NO_2 + \text{"C"} \rightarrow CO_2 + 2\ NO$ $T = 200\ldots450°C$

- Non-catalytic soot oxidation (induced by fuel post-injection)

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

- Fuel Borne Catalyst (FBC): metal-organic compounds

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

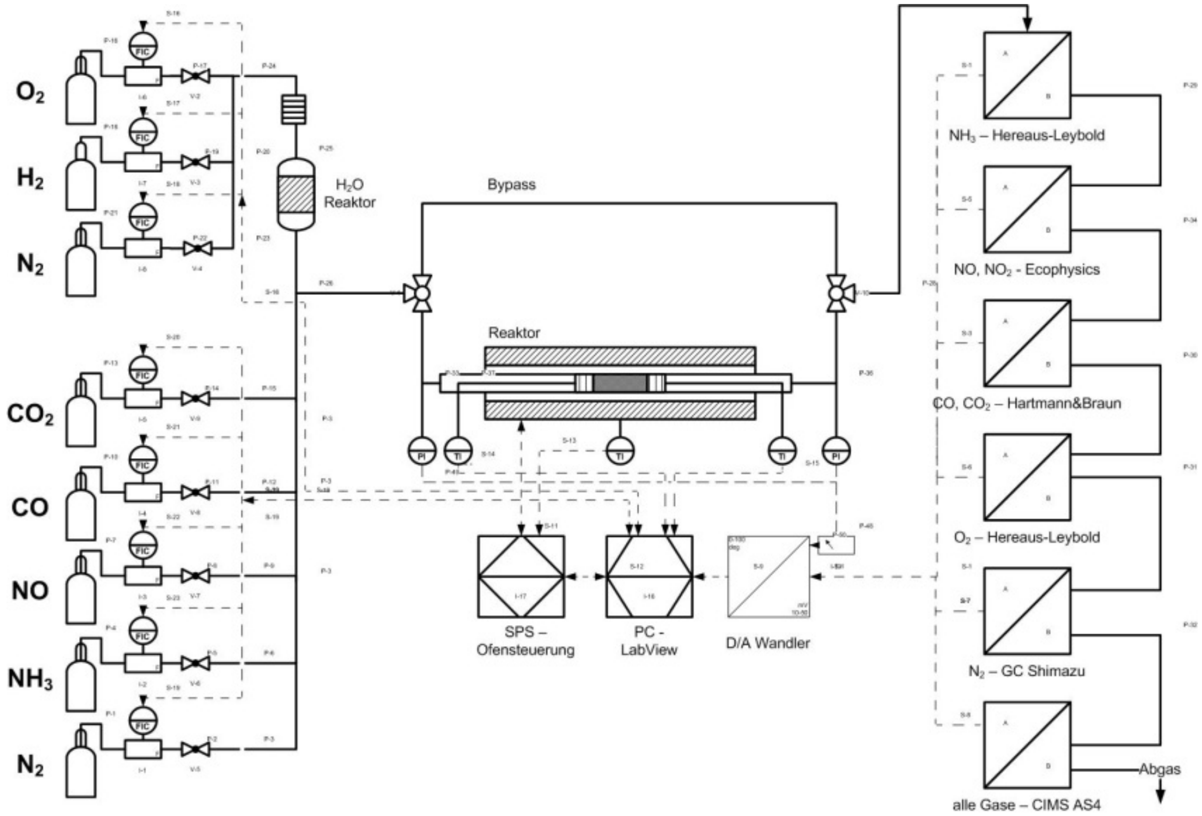
- Catalytic DPF (CDPF): CeO_2 and Fe_2O_3 based catalysts

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

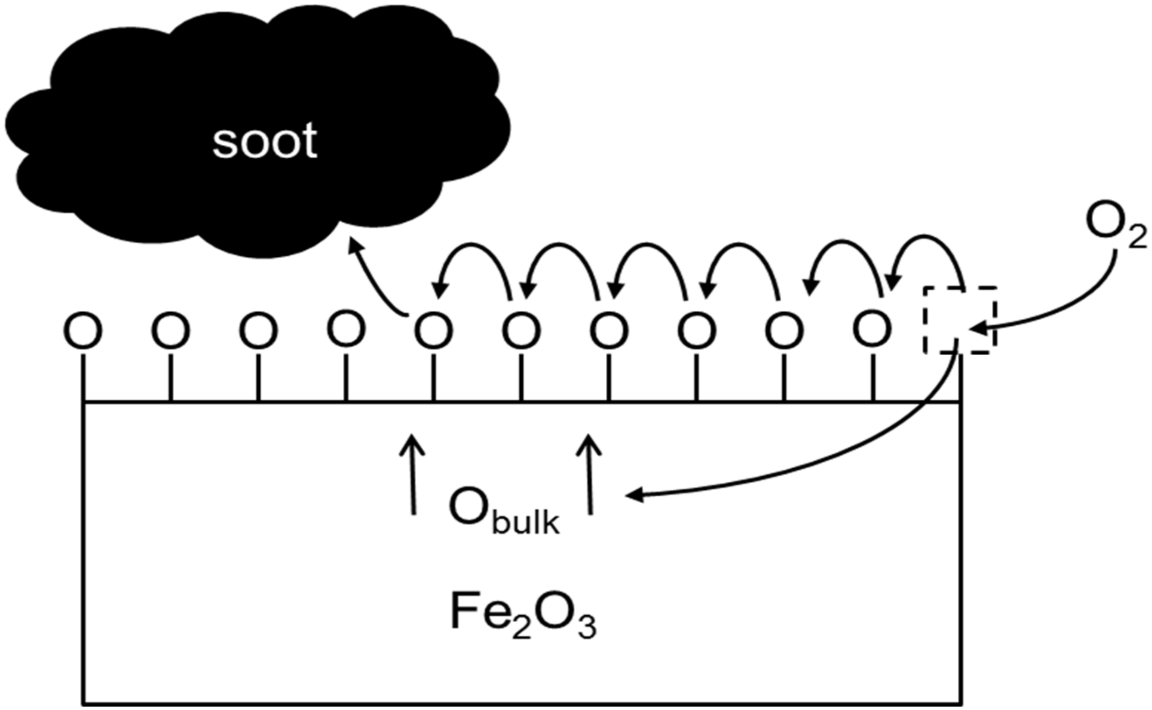
Evaluation of soot oxidation kinetics on Fe_2O_3 catalyst

- Temperature Programmed Oxidation (TPO)
  - n_{cat}/n_{soot} = 10 mmol /5 mmol
  - F = 500 mL/min, 10% O_2 , 90% N_2
  - Linear heating rate: 3.3 K/min
  - Mixing catalyst and soot by ball milling

Plug flow reactor with packed bed



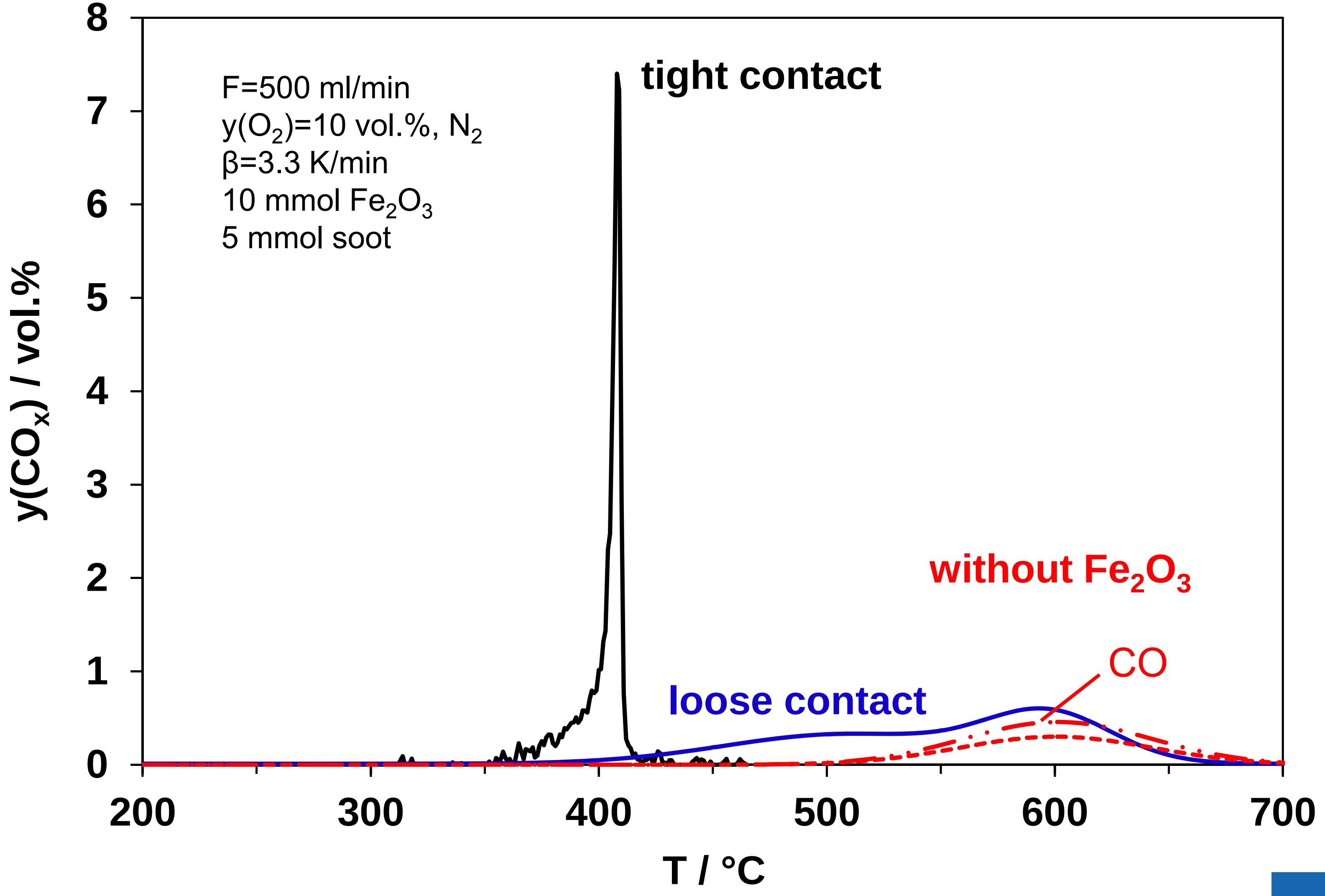
Mechanistic scheme of soot oxidation on Fe_2O_3



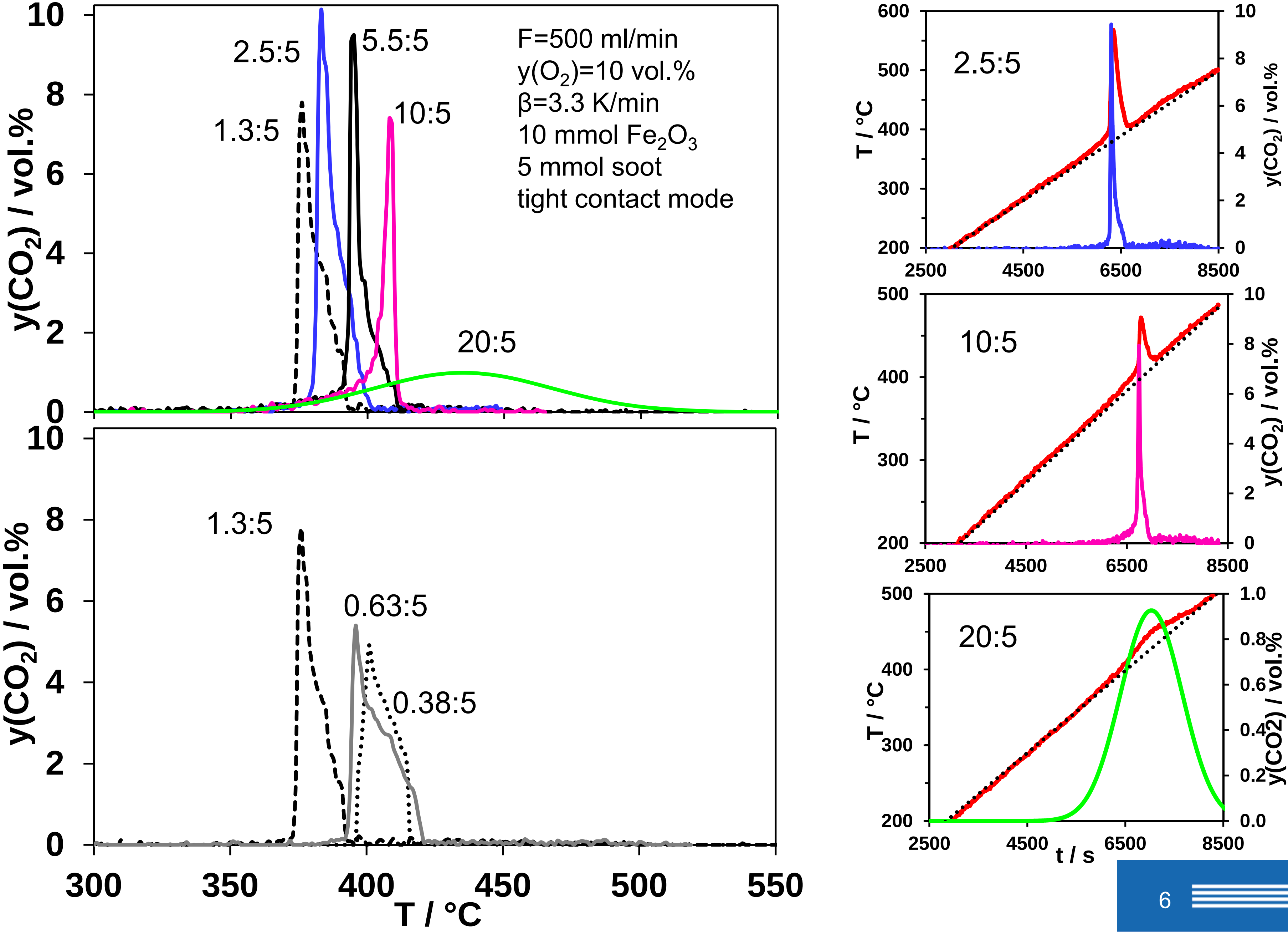
S. Wagloehner, S.Kureti, Appl. Catal. B 125 (2012) 185

Effect of contact on soot oxidation kinetics

- Performance in tight and loose contact vs. bare soot



Effect of catalyst/soot ratio on soot oxidation kinetics



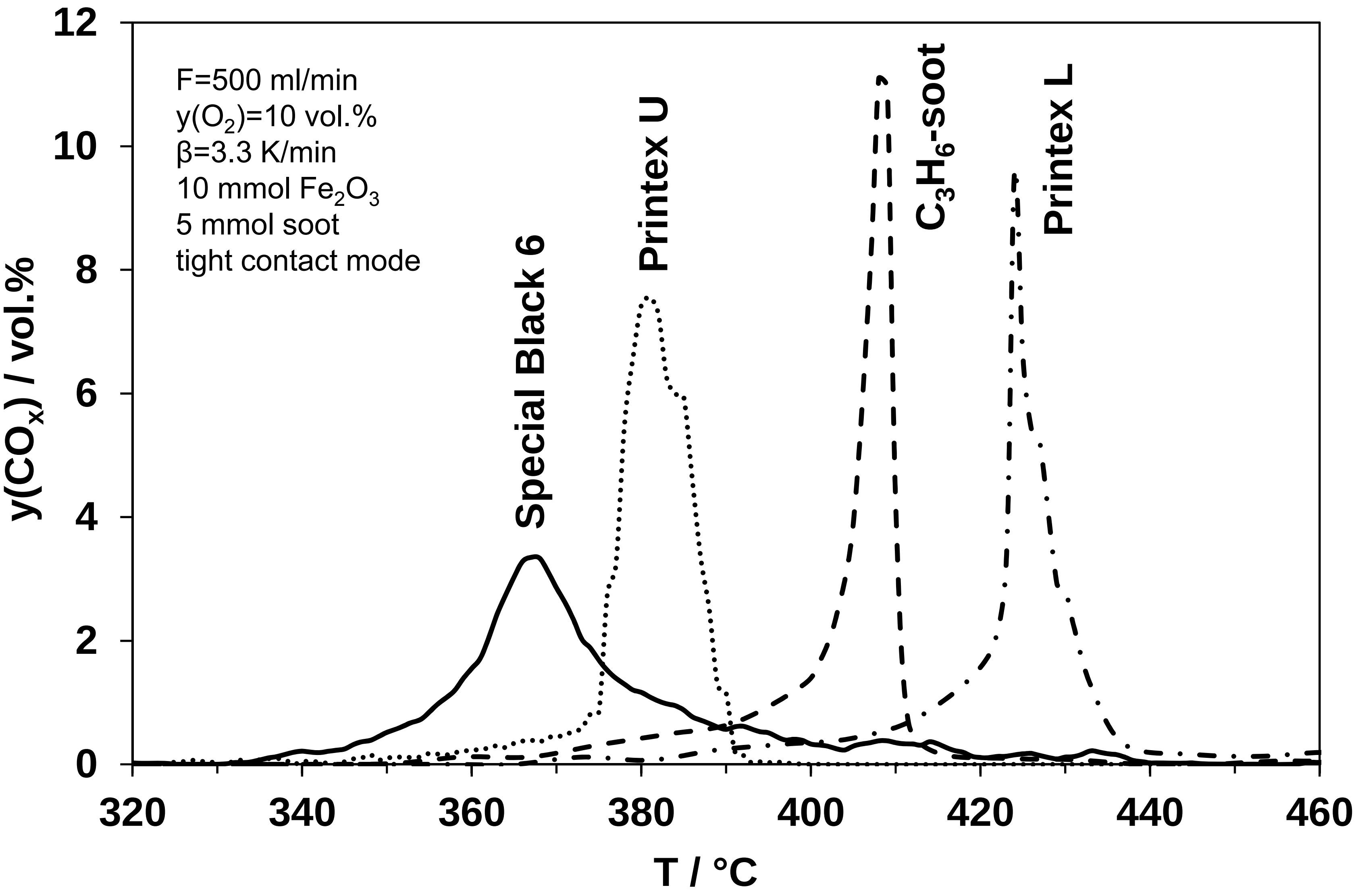
Effect of type of soot on catalytic oxidation kinetics

- 4 different types of model soot
  - C_3H_6-soot (home-made) — soot formed at full load
  - Printex U — soot formed at full load
  - Special Black 6 — soot formed at partial load
  - Printex L — mature soot

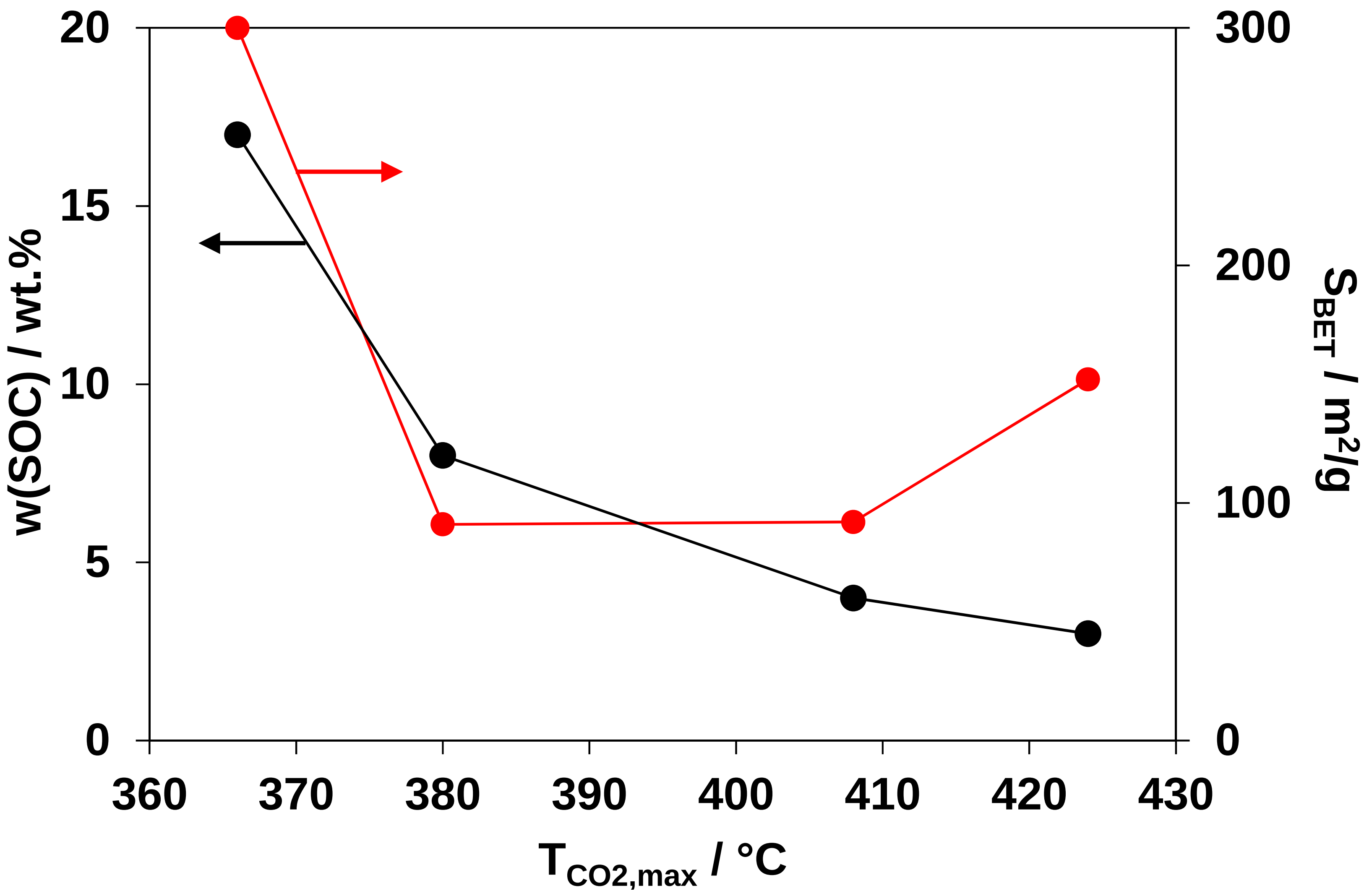
- Detailed physical-chemical analysis of the model soot samples (ashless)

	Ultimate analysis				Proximate analysis					
	C	H	N	O	HHV	S_{BET}	w_{H2O}	VM	w_{CO}	w_{CO2}
	[wt.%]				[MJ/kg]	[m^2/g]	[wt.%]			
Special Black 6	89.5	0.4	0.6	9.0	29.86	300	5	17	8.0	15.2
Printex U	96.7	0.7	0.3	2.0	33.37	91	2	8	3.1	5.6
C_3H_6-Soot	97.5	0.6	0.2	1.5	33.35	92	0	4	2.8	4.1
Printex L	99.2	0.1	0.3	0	33.47	152	1	3	0.5	2.5

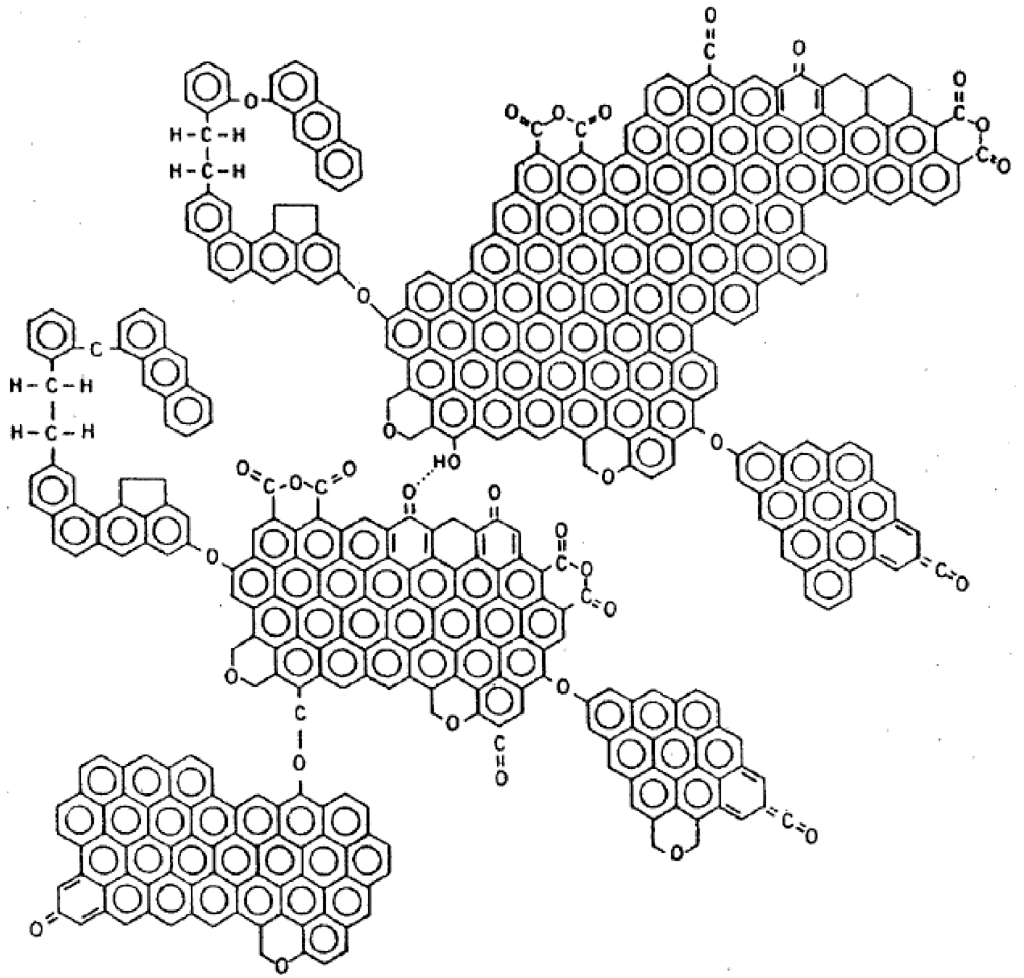
Effect of type of soot on catalytic oxidation kinetics



Correlation of catalytic oxidation kinetics with soot properties



Role of surface oxygen compounds (SOC) of soot



M.S. Akhter et al.,
Appl. Spetrosc. 39 (1985) 143

Reactions of SOC:

$CCC(O) + O_s \longrightarrow CC^* + CO_2$

$CCC(O) \longrightarrow CC^* + CO$

Subsequent reactions on soot:

$CC^* + O_s \longrightarrow CC(O)$

$CC^* + 2\ O_s \longrightarrow CC(OO)$

$CC(O) \longrightarrow C^* + CO$

$CC(OO) \longrightarrow C^* + CO_2$

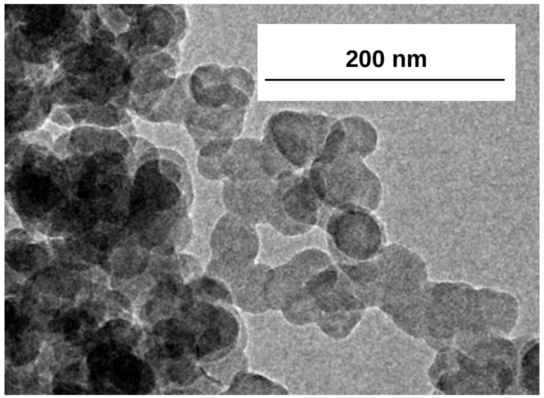
Summary

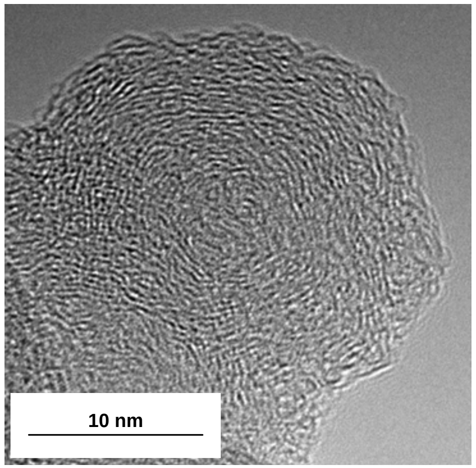
- Fe_2O_3 is an effective catalyst for soot oxidation
- Soot oxidation kinetics depend on type of contact, local heat evolution and type of soot
- SOC determine the kinetics of soot oxidation on Fe_2O_3 catalyst
- SOC are the initial precursors of carbon sites supplied by oxygen from the Fe_2O_3 catalyst

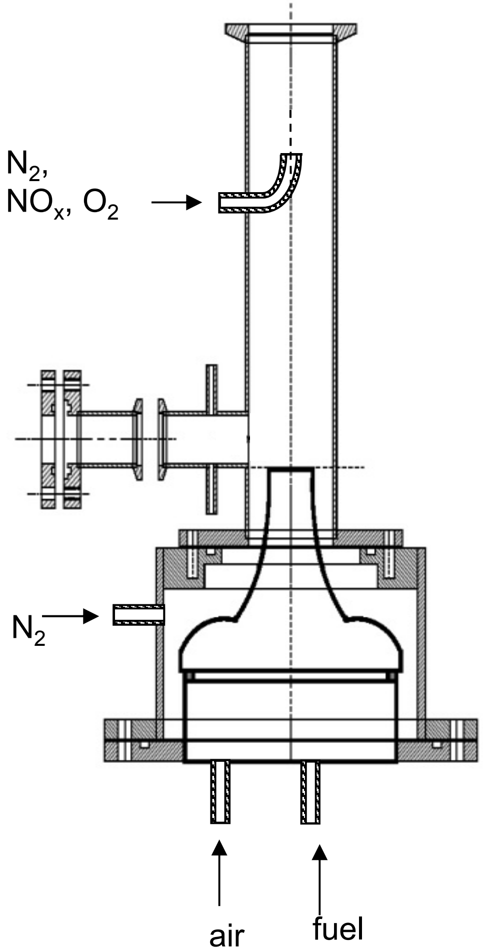
We thankfully acknowledge the financial support from Umicore.

Production of realistic diesel model soot

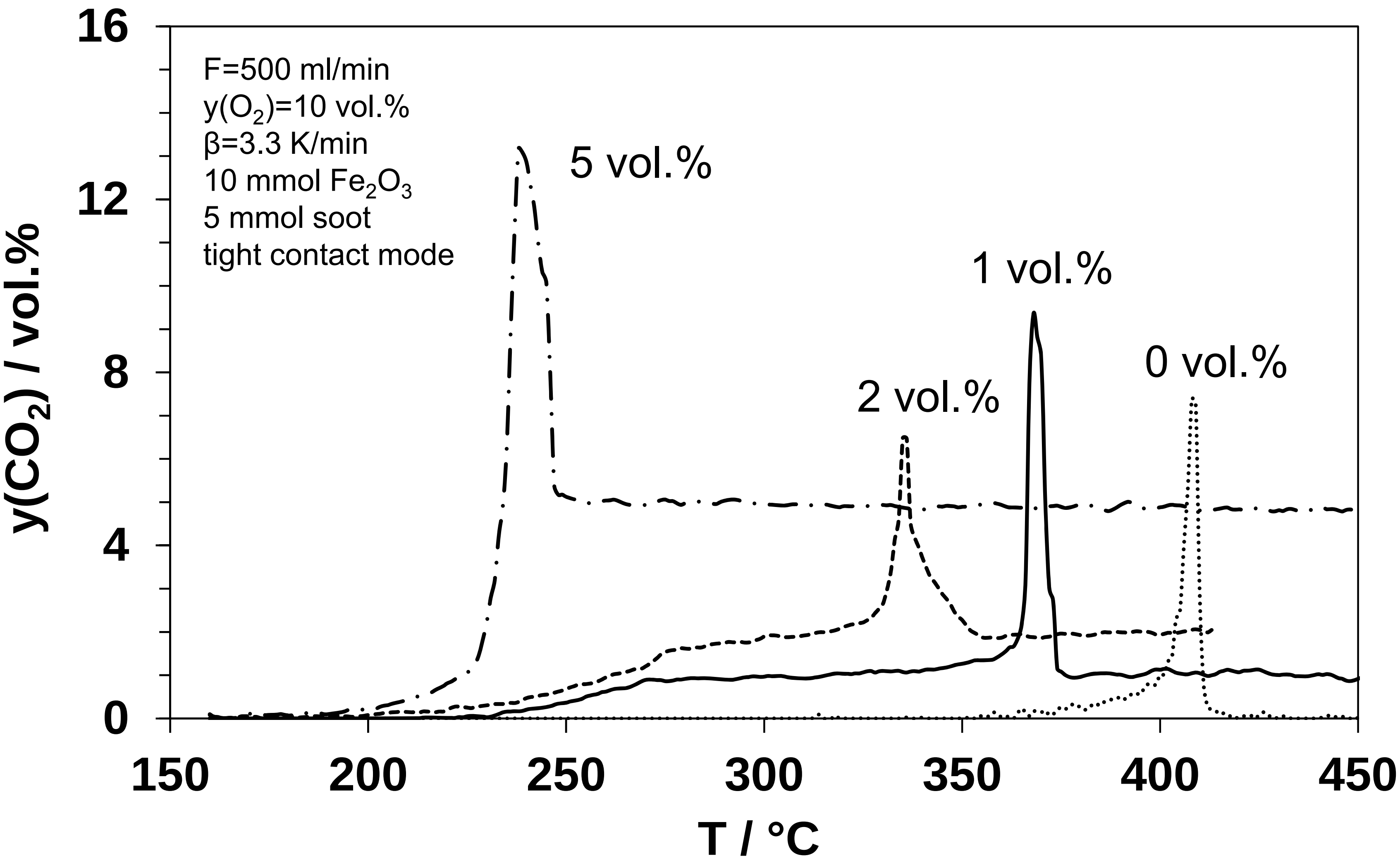
- Diffusion burner (C_3H_6/O_2 flame)
- Physical-chemical properties
  - 2.6 wt.% adsorbed
  - 98.8 wt.% C
    0.7 wt.% O
    0.5 wt.% H
  - Most frequent diameter: ca. 45 nm
  - S_{BET} = 90 m^2/g





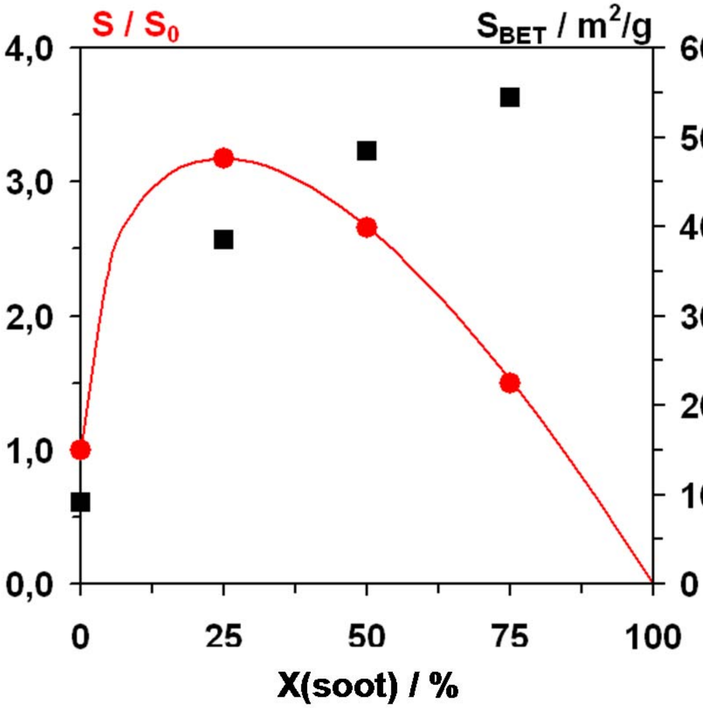


Effect of CO on soot oxidation kinetics on Fe_2O_3



Global kinetic model

$r(CO_x) = k_{CO_x} \cdot n(C_f) \cdot c(O_2)$ $k_{CO_x} = A_{COx} \exp(-E_{COx}/RT)$



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

$$\rightarrow \frac{n(CO_x)_{des}}{S(X)} = 8{,}7 \frac{\mu mol}{m^2} = \lambda$$

From evolution of S_{BET}:

$$\rightarrow S(X) = S_0 \cdot m_0 \cdot (1-X) \cdot (1+60 \cdot X)^{1/2}$$

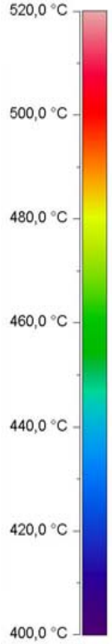
$$\rightarrow n(C_f) = \lambda \cdot S(X)$$

S.K. Bhatia, D.D. Perlmutter,
J. Am. Inst. Chem. Eng. 26 (1980) 379

$$\rightarrow r(COx) = A_{COx} \cdot \exp(-E_{COx}/RT) \cdot S_0 \cdot m_0 \cdot (1-X) \cdot (1+60 \cdot X)^{1/2} \cdot \lambda \cdot c(O_2)$$

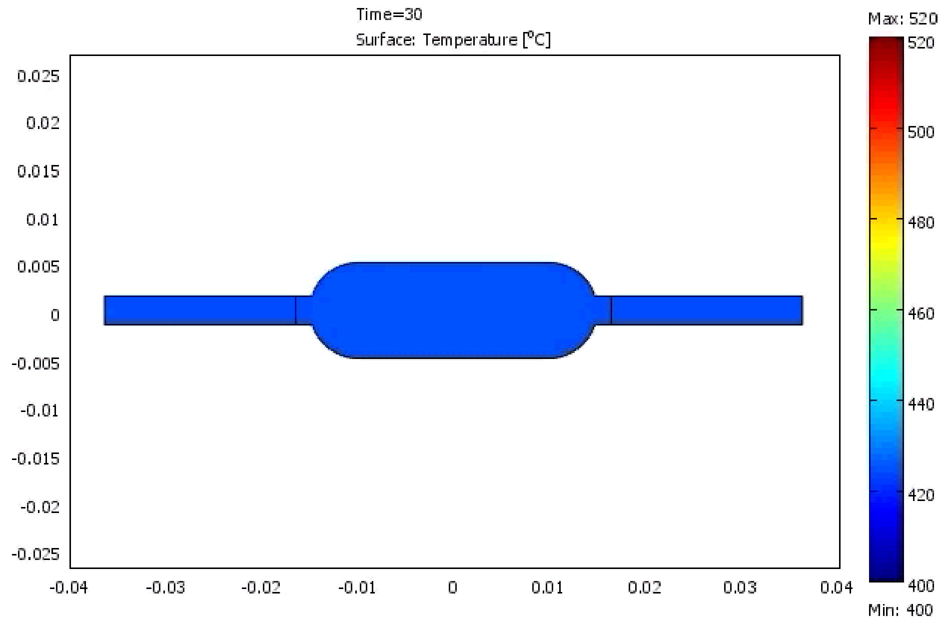
Experiment vs. Simulation

Experiment

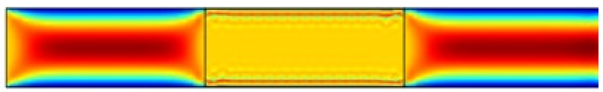


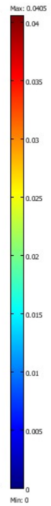
10 vol.% O_2 in N_2,1,5 K/min
10 mmol Fe_2O_3, 5 mmol Ruß

Simulation

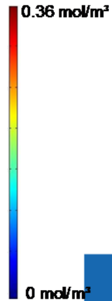


Simulation (T=420°C)





Flow velocity



CO_2 concentration