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

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Chair of Reaction Engineering
Strategies of DPF regeneration

- **Continuously Regenerated Trap (CRT)**
  
  \[2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2\]
  
  \[2 \text{NO}_2 + \text{“C”} \rightarrow \text{CO}_2 + 2 \text{NO}\]  
  \[T = 200…450^\circ\text{C}\]

- **Non-catalytic soot oxidation (induced by fuel post-injection)**
  
  \[\text{“C”} + \text{O}_2 \rightarrow \text{CO}_2\]  
  \[T > 600^\circ\text{C}\]

- **Fuel Borne Catalyst (FBC): metal-organic compounds**
  
  \[\text{“C”} + \text{O}_2 \rightarrow \text{CO}_2\]  
  \[T > 300^\circ\text{C}\]

- **Catalytic DPF (CDPF): CeO_2 and Fe_2O_3 based catalysts**
  
  \[\text{“C”} + \text{O}_2 \rightarrow \text{CO}_2\]  
  \[T > 500^\circ\text{C}\]
Evaluation of soot oxidation kinetics on Fe$_2$O$_3$ catalyst

- Temperature Programmed Oxidation (TPO)
  - $n_{\text{cat}}/n_{\text{soot}} = 10 \text{ mmol} / 5 \text{ mmol}$
  - $F = 500 \text{ mL/min, 10\% O}_2 , 90\% \text{ N}_2$
  - Linear heating rate: 3.3 K/min
  - Mixing catalyst and soot by ball milling

![Plug flow reactor with packed bed](image)

![Diagram of reaction setup](image)
Mechanistic scheme of soot oxidation on Fe$_2$O$_3$

Effect of contact on soot oxidation kinetics

- Performance in tight and loose contact vs. bare soot

- Chart showing:
  - T / °C on the x-axis
  - $y(CO_x)$ / vol.% on the y-axis

- Conditions:
  - $F=500$ ml/min
  - $y(O_2)=10$ vol.%, $N_2$
  - $\beta=3.3$ K/min
  - $10$ mmol Fe$_2$O$_3$
  - $5$ mmol soot

- Curves for:
  - Tight contact
  - Loose contact
  - Without Fe$_2$O$_3$
Effect of catalyst/soot ratio on soot oxidation kinetics

F=500 ml/min
\(y(O_2)=10\) vol.\%
\(\beta=3.3\) K/min
10 mmol Fe\(_2\)O\(_3\)
5 mmol soot
tight contact mode
Effect of type of soot on catalytic oxidation kinetics

- 4 different types of model soot
  - $C_3H_6$-soot (home-made)
  - Printex U
  - Special Black 6
  - Printex L

- Soot formed at full load

- Soot formed at partial load

- Mature soot

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

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th>Proximate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>[wt.%]</td>
</tr>
<tr>
<td>Special Black 6</td>
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<tr>
<td>Printex L</td>
<td>99.2</td>
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</tbody>
</table>
Effect of type of soot on catalytic oxidation kinetics

- F=500 ml/min
- y(O$_2$)=10 vol.%
- $\beta=3.3$ K/min
- 10 mmol Fe$_2$O$_3$
- 5 mmol soot
- tight contact mode
Correlation of catalytic oxidation kinetics with soot properties

- $w_{\text{SOC}}$ / wt.%
- $T_{\text{CO}_2, \text{max}}$ / °C
- $S_{\text{BET}}$ / m$^2$/g
Role of surface oxygen compounds (SOC) of soot

Reactions of SOC:

\[ 
\text{CCC(O)} + \text{Os} \rightarrow \text{CC}^* + \text{CO}_2 
\]

\[ 
\text{CCC(O)} \rightarrow \text{CC}^* + \text{CO} 
\]

Subsequent reactions on soot:

\[ 
\text{CC}^* + \text{Os} \rightarrow \text{CC(O)} 
\]

\[ 
\text{CC}^* + 2\text{Os} \rightarrow \text{CC(OO)} 
\]

\[ 
\text{CC(O)} \rightarrow \text{C}^* + \text{CO} 
\]

\[ 
\text{CC(OO)} \rightarrow \text{C}^* + \text{CO}_2 
\]

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

- Fe$_2$O$_3$ 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$_2$O$_3$ catalyst
- SOC are the initial precursors of carbon sites supplied by oxygen from the Fe$_2$O$_3$ catalyst

We thankfully acknowledge the financial support from Umicore.
Production of realistic diesel model soot

- Diffusion burner (C$_3$H$_6$/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
  - $S_{\text{BET}} = 90$ m$^2$/g
Effect of CO on soot oxidation kinetics on Fe$_2$O$_3$

\[ y(CO_2) / \text{vol.\%} \]

- F = 500 ml/min
- \( y(O_2) \) = 10 vol.\%
- \( \beta \) = 3.3 K/min
- 10 mmol Fe$_2$O$_3$
- 5 mmol soot
- tight contact mode

Graph showing the effect of CO on soot oxidation kinetics with different CO concentrations: 5 vol.\%, 1 vol.\%, 2 vol.\%, and 0 vol.\%.
Global kinetic model

\[ r(CO_x) = k_{CO_x} \cdot n(C_f) \cdot c(O_2) \]

\[ k_{CO_x} = A_{CO_x} \exp(-E_{CO_x}/RT) \]

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

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

From evolution of \( S_{\text{BET}}: \)

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

\[ n(C_f) = \lambda \cdot S(X) \]

S.K. Bhatia, D.D. Perlmutter,

\[ r(CO_x) = A_{CO_x} \cdot \exp(-E_{CO_x}/RT) \cdot S_0 \cdot m_0 \cdot (1-X) \cdot (1+60 \cdot X)^{1/2} \cdot \lambda \cdot c(O_2) \]
Experiment vs. Simulation

**Experiment**

10 vol.% O₂ in N₂, 1.5 K/min
10 mmol Fe₂O₃, 5 mmol Ruß

**Simulation (T=420°C)**

Temperature distribution

Flow velocity

CO₂ concentration