Title: Multifunctional Reactors for Diesel Nanoparticle Emission Control

Abstract: (min. 300 - max 500 words)

Monolithic reactors such as wall-flow Diesel Particulate Filters (DPFs) continue to be important components of diesel emission control systems, and are increasingly incorporating different functionalities such as gas species oxidation (such as CO, hydrocarbons and NO) storage phenomena (such as NOx and NH3 storage) in addition to soot nanoparticle filtration and oxidation. In the current work, novel catalytic coatings with a variety of methods based on conventional and novel synthesis routes are developed based on mixed oxides of base metals. The developed catalytic composition exhibits significant direct soot oxidation as evaluated by reacting mixtures of diesel soot and catalyst powders. The catalyst compositions were further deposited on porous filter structures that were evaluated on an engine bench with respect to their filtration efficiency, pressure drop behavior and direct soot oxidation activity under realistic conditions. Special emphasis was placed on investigating the effect of the catalyst amount on the filtration efficiency. Indirect soot oxidation through NO2 induced oxidation was optimized by noble metal addition to the base metal catalyst formulation via different techniques. In depth understanding of the coupled transport – reaction phenomena occurring inside the microstructure of the coated walls of DPFs is highly aided by employing computational approaches based on realistic representations of all “actors” involved: nano and microstructured porous substrates/filters, catalyst coatings and dispersions and soot nanoparticle aggregates.

Short CV: Athanasios G. Konstandopoulos, Descartes Laureate (2006) and SAE fellow has a hybrid background in Mechanical [Dipl. ME - Aristotle University of Thessaloniki, MScME - Michigan Tech)] and Chemical Engineering [MScChE, MPhil, PhD - Yale University]. He is Director of CPERI/CERTH where he founded and heads the Aerosol & Particle Technology Laboratory (APTL) since 1996 and a member of the faculty of Chemical Engineering at the Aristotle University of Thessaloniki, since 2007. He has many years of research and engineering consulting experience in combustion generated aerosols and particulate processes, and he is the author of numerous scientific and technical papers in the field.
Multifunctional Reactors for Diesel Nanoparticle Emission Control

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Characteristics of Structured Reactors

- Large surface/volume ratio (compactness)
- Low pressure drop compared to alternatives
- Can be easily be functionalized (e.g. coated)
- Can combine more than one function (e.g. separation/reaction)
Applications pursued at APT Lab

- **Diesel Emission Control** (Soot nanoparticles, CO/HC/NOx)
- Solar Thermochemical Reactors for H₂/solar fuels production
- Bio-diagnostics & Bio-reactors for high value products
Our Approach

- Materials synthesis with novel routes
- Functionalization (deposition/coating) technologies
- Experimental setups with small and full scale samples
- Coupled transport/separation/reaction phenomena framework
- Multi-scale simulations
# Trends in OEM DPF Functionalities

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td><strong>Uncoated DPF</strong>. Soot oxidation assisted by ceria/iron based fuel borne catalyst.</td>
</tr>
<tr>
<td>2003</td>
<td>Introduction of <strong>catalyst coated DPF</strong>. PGM-based catalysts aiming at NO/CO/HC oxidation and NO$_2^-$- assisted oxidation of soot (<strong>indirect action of catalyst</strong>).</td>
</tr>
<tr>
<td>2010</td>
<td><strong>Direct soot oxidation</strong> by oxygen transfer from base metal oxide catalysts. Reduction/elimination of PGM. Higher porosity substrates to accommodate larger (multi-functional) catalyst loads and provide better soot-catalyst contact.</td>
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<tr>
<td>&gt;2010</td>
<td><strong>Integration</strong> of additional functionalities (NOx treatment, nanoparticle number emissions compliance), reduction of emission control system size and cost.</td>
</tr>
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</table>
Catalyst Synthesis Techniques Employed

Liquid Phase Self Propagating High-temperature Synthesis (LPSHS)

Flame front in the precursor solution

Aerosol Based Synthesis (ABS)

2 μm

Ceria Nanoparticle Coated Filters for Soot Emission Control, PARTEC 2001
K. Karadimitra, G. Macheridou, E. Papaioannou, A. G. Konstandopoulos
Catalyst Evaluation Protocol

Powder Scale

- Thermogravimetric Analysis (TGA)
  - Soot-catalyst mixtures (1:2 in tight contact)
  - Increase of temperature from 150-700 °C with 3 °C/min, under 20% O₂ in N₂.

Monolith Scale

- Diesel Engine Test Cell (1.9L TDI, common rail)
  - Catalyst deposition on wall-flow filter segments
  - Filtration efficiency
  - Soot loading
  - Soot oxidation
Soot oxidation activity – CeO$_2$ Based Oxides

**LPSHS Catalysts**

![Graph showing soot oxidation activity for different CeO$_2$ based oxides at various temperatures.]

- CeZrXY
- CeZrX
- CeZrXYZ
- CeZr
- Ce
- Soot

Temperature (°C) vs. $1/m_0$ (dm/dt) (s$^{-1}$)

SAE-2008-01-417
Soot oxidation activity – $\text{CeO}_2$ Based Oxides

ABS Catalysts

![Graph showing the oxidation activity of different Ce- and Zr-based catalysts. The x-axis represents temperature in Celsius, and the y-axis represents the rate of soot formation $1/m_o (dm/dt)$ in seconds^{-1}. Peaks are labeled for $\text{CeZrX}$, $\text{CeZrXY}$, $\text{CeZrXYZ}$, $\text{CeZrX}$, $\text{CeZr}$, $\text{Ce}$, and soot, indicating the temperature range and peak intensity of each species.]

SAE-2008-01-417
XRD – CeO₂ Based Mixed Oxides

LPSHS:
- well crystallized
- cubic-fluorite cerium oxide, (111) orientation

ABS:
- typical low degree of crystallinity
- cubic-fluorite cerium oxide, (111) orientation
Doping of cerium oxide with other metals generally causes a shift of the cerianite (CeO$_2$) peak to higher diffraction angles.

Crystallite size:
- **ABS**: 4-10 nm with the size decreasing with the increase of the dopants.
- **LPSHS**: crystallites with larger size 10-20nm.
TEM – CeO$_2$ Based Mixed Oxides (ABS)

- Nanocrystalline structure detected by TEM and electron diffraction pattern.
Catalyst Functions

Direct Soot Oxidation Catalyst

Material with redox/oxygen storage ability such as Ce-based metal oxides e.g. Ce/Zr/other metals, referred to as Mixed Oxide Catalysts, MOC.

Indirect Soot Oxidation Catalyst

PGM-based material promoting $\text{NO} \rightarrow \text{NO}_2$ oxidation, CO and HC conversion
• Increase of the clean filtration efficiency with the increase of the catalyst amount.
Filtration Efficiency of Coated DPF

SAE-2008-01-483
Catalyst Amount Effect on Soot Loading

Pressure drop (mbar)

Soot mass load (g/m²)

- uncoated
- 1x g/m²
- 2x g/m²
- 3x g/m²
- 4x g/m²

JSAE-2007-01-7334
Catalyst Amount Effect on Direct Soot Oxidation

![Graph showing the effect of catalyst amount on direct soot oxidation. The x-axis represents temperature in°C, and the y-axis represents 1/mo(dm/dt) in s⁻¹. The graph includes multiple lines for different catalyst amounts: uncoated, 2x g/m², 3x g/m², and 4x g/m². Each line demonstrates a concentration peak at a specific temperature, indicating the optimal temperature for oxidation at different catalyst amounts.](image-url)
PGM addition methods

1. **Simultaneous deposition** of PGM and MOC

2. **Sequential coating-A**: MOC followed by PGM deposition.

3. **Sequential coating-B**: MOC followed by PGM deposition (lower temperature process)

4. **Sequential coating-C**: MOC followed by PGM deposition (different solution properties)

5. **Optimized coating-D**: Combination based on above knowledge

PGM loading is the same in all cases
Effect of PGM addition method on soot loading behavior

Filtration velocity = 1.36 cm/s

$T_{\text{loading}} = 250 \, \text{C}$
Effect of PGM addition method on soot oxidation

10% O₂, 300 ppm NO in N₂

Temperature (°C)

$\frac{1}{m_0} \frac{dm}{dt}$ (s⁻¹)
CO conversion

![Graph showing CO conversion vs. Temperature (C) with two lines: one for state of the art and another for advanced coating.]
Addition of NOx storage material on soot oxidation

10% O₂, 300 ppm NO
DPF Digital Materials
Tailored Aggregate Generator

$k_f = 1.5 \quad N_a = 500$
Soot loading simulation with actual soot aggregate geometry
Soot loading simulation with actual soot aggregate geometry
True to geometry studies of coatings

Coupled transport/reaction/separation phenomena
Simulation of 3-D DPF wall

\[ y = 10 \quad y = 20 \quad y = 30 \quad y = 40 \quad y = 50 \]

\( \text{NO}_2 \) concentration through wall with catalyst at 300 C

SAE-2008-01-0442
NO₂ turnover, R: analytical vs. 3-D simulation

![Graph showing NO₂ turnover comparison between analytical and 3-D simulation methods. The graph includes data points for different temperatures (T = 300 C and T = 350 C).]
NEDC Testing of C-DPFs

Number emissions according to PMP protocol

Ogyu et al., GPC 2008
NEDC Testing of C-DPFs

Number emissions according to PMP protocol

- **uncoated**: $1.2 \times 10^{10}/\text{km}$
- **state of the art**: $4.5 \times 10^{10}/\text{km}$
- **advanced**: $4.2 \times 10^{9}/\text{km}$

Ogyu et al., GPC 2008
Effect of Structure on Flow Distribution

<table>
<thead>
<tr>
<th>Pore structure</th>
<th>SEM</th>
<th>Digital Material</th>
<th>3-D reconstruction</th>
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<td>Narrow pore distribution</td>
<td><img src="image1" alt="SEM" /></td>
<td><img src="image2" alt="Digital Material" /></td>
<td><img src="image3" alt="3-D reconstruction" /></td>
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<tr>
<td>Broad pore distribution</td>
<td><img src="image4" alt="SEM" /></td>
<td><img src="image5" alt="Digital Material" /></td>
<td><img src="image6" alt="3-D reconstruction" /></td>
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Ogyu et al., GPC 2008
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<tr>
<th>A-ΔP</th>
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<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>z</td>
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Narrow Gas flow

Broad Gas flow

Ogyu et al., GPC 2008
Evolution of the soot oxidation rate with temperature

Conclusions

- A direct soot oxidation catalyst formulation (designated as MOC) was developed and tested at the powder scale and on wall flow monoliths.

- The MOC coated filter exhibited lower pressure drop during soot loading than the uncoated filter. Increase of the catalyst amount increases significantly the filtration efficiency of the filters, while the filtration efficiency attains rapidly a high value with the accumulation of only a small amount of soot on the filter.

- Total soot oxidation consists of the NO$_2$ oxidized soot plus the direct-catalytically oxidized soot. Optimization of PGM-MOC based multifunctional coatings must take into account the composite effect of the indirect and direct-catalytic soot oxidation. The method of preparing PGM-MOC catalytic coatings and the sequence of the material deposition on the filters plays an important role on the NO to NO$_2$ conversion.

- In depth understanding of the coupled transport – reaction phenomena occurring inside the microstructure of the coated walls of DPFs is highly aided by employing computational approaches based on realistic representations of all “actors” involved: nano and microstructured porous substrates/filters, catalyst coatings and dispersions and soot nanoparticle aggregates.
Acknowledgements

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