Ceria based materials for automotive catalysis: past and future trends

The 2014 EREAN Summer School on Rare Earths
KU Leuven, August 18-21, 2014
OUTLINE

- Introduction to the Automotive Emissions Controls
- Three Way Catalysis for Gasoline Engines – Ceria based materials: role and expectations
- Overview of Ceria based materials for Diesel Exhaust Catalysis
  - Oxidation reactions (Soot...)
  - NOx reduction (LNT, SCR..)
- Conclusions and perspectives
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Road Transportation remains a key source of pollutant emission ....

![Graph showing the percentage contribution of different sectors to NOx emissions. Transport accounts for 58% and road transport exhaust for 33%. Other sectors include non-transport sectors (42%), international shipping, domestic aviation, railways, and domestic shipping. Source: EEA, 2013.]
.....due to uncomplete engine combustion

**Intake**
- air + fuel (HC)

**Exhaust**
- CO$_2$, H$_2$O, N$_2$, O$_2$, Heat

**Regulated pollutants**
- unburnt hydrocarbons HC
- carbon monoxide CO
- nitrogen oxides NOx (NO + NO$_2$)
- particulate matter (PM)

**Non regulated pollutants**
- N$_2$O, NO$_2$, PAH, SO$_2$
- aldehydes (regulate US), ketones....
Exhaust after-treatment has been introduced to reduce air pollution from automotive ....

- **USA**
  - 1975 oxidation catalyst (gasoline)
  - 1981 Three way catalyst TWC (gasoline)

- **Japan**
  - 1980 Three way catalyst (gasoline)
  - 1995 deNOx catalyst (lean gasoline engine)

- **Europe**
  - 1992 Three way catalyst (gasoline)
  - 1996 Diesel oxidation catalyst (DOC)
  - 2000 Diesel Particulate Filter (DPF) with Fuel Borne Catalyst (FBC)
  - 2003 Catalytic DPF & 4way system (DPNR discontinued)
  - 2007 Urea – Selective Catalytic Reduction (NOx SCR)

Housewives calling themselves the Smog-A-Tears carry banners and parade in gas masks through downtown Pasadena in this 1954 air quality protest.
... and to answer pollutants regulations introduced in most of the countries
European Pollutants Regulations for Passenger Cars (Light-Duty)

**DIESEL**

- Euro 3 (2000)
- Euro 4 (2005)
- Euro 5 (2010)
- Euro 6 (2014)

**GASOLINE**

- Euro 3 (2000)
- Euro 4 (2005)
- Euro 5 (2010)
- Euro 6 (2014)

**Euro 4 to Euro 5:**
- PM Filter Required

**Euro 5 to Euro 6b:**
- Focus on NOx
- Euro 6b (2014): -56% / Euro 5

**Gasoline For Euro 6:**
- Focus on Particulate matter
- Euro 6c (2017): $6.10^{11}$ #/km max
Average Engine-out Emissions measured over the European NEDC Cycle

<table>
<thead>
<tr>
<th></th>
<th>HC (g/km)</th>
<th>CO (g/km)</th>
<th>NOx (g/km)</th>
<th>PM (g/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasoline</strong></td>
<td>1.4 - 2.00</td>
<td>7 - 10</td>
<td>2 - 4</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td><strong>Limit Euro6 (&gt;2014)</strong></td>
<td>0.1</td>
<td>1.0</td>
<td>0.06</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Conversion rate (%)</strong></td>
<td>93 - 95</td>
<td>86 - 90</td>
<td>97 - 98</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>HC + NOx (g/km)</th>
<th>CO (g/km)</th>
<th>NOx (g/km)</th>
<th>PM (g/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel DI</strong></td>
<td>0.2</td>
<td>1.2 - 1.4</td>
<td>0.3 - 0.5</td>
<td>0.02 - 0.04</td>
</tr>
<tr>
<td><strong>Limit Euro6 (&gt;2014)</strong></td>
<td>0.17</td>
<td>0.5</td>
<td>0.08</td>
<td>0.0045</td>
</tr>
<tr>
<td><strong>Conversion rate (%)</strong></td>
<td>15</td>
<td>58 - 64</td>
<td>73 - 84</td>
<td>77 - 88</td>
</tr>
</tbody>
</table>
An after-treatment system suited to...

- engine type (gasoline vs diesel mainly)
- pollutants to be treated
- industrial constraint of automobile
  - cost
  - efficiency
  - durability

CO
HC
NOx
PM

CO₂
H₂O
N₂

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Three Way Catalyst (TWC) is converting CO, HC and NOx

- CO + O₂ → CO₂ OXIDATION
- HC + O₂ → CO₂ + H₂O OXIDATION
- NOx + HC/H₂/CO → N₂ + H₂O/CO₂ REDUCTION
TWC Catalytic Converter

Canning

Ceramic Support monolithe

Inside a channel

"Washcoat"
Large Surface area to disperse active components (Alumina)

Active Components
Noble Metals (Pd, Rh)
OSC Materials (CeO₂)

Impregnation

Bosch Source

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To convert to large extend the 3 pollutants, Noble Metals need stoechiometric conditions: \([\text{CO} + \text{HC}] = [\text{NOx} + \text{O}_2]\)

Cerium Oxide is acting as \(\text{O}_2\) buffer allowing large “richness” operation thanks to Ce\(^{3+}/\text{Ce}^{4+}\) Redox Couple
Ceria is a needed component of TWC converters

- Provides oxygen storage capacity (OSC)
  
  Oxygen release: \[ x \text{ CO} + \text{CeO}_2 \rightarrow x \text{ CO}_2 + \text{CeO}_{2-x} \]
  
  Oxygen storage: \[ 1/2x \text{ O}_2+ \text{CeO}_{2-x} \rightarrow \text{CeO}_2 \]

- Stabilizes noble metals dispersion at high temperature

- Promotes water/gas shift reaction
  
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

- Promotes steam reforming reaction
  
  \[ (\text{HC}) + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
TWC Challenges are related to reduction of noble metals (PGM)

NEEDS

- Disperse and stabilize PGM as small nanoparticles
- Facilitate Efficiency at low temperature
- Allow Close Coupled position to get early light-off
- Allow TWC catalyst without Pt and with low Rh content
- High efficiency at low washcoat amount (Gasoline Filter)

MATERIAL Impact

- Porous materials with High thermal Stability (> 1050°C)
- Improved Oxygen Storage Capacity (OSC) thermodynamic (TPR) and kinetics (OSC switch)
- Affinity with PGM, in particular Pd and Rh
- Facilitate deNOx reactions with Pd (Pt free TWC)
Main parameters to improve the efficiency of OSC materials for low PGM TWC

Materials have to be fine tuned to each type of PGM (Pd, Rh)

<table>
<thead>
<tr>
<th></th>
<th>Thermal Stability</th>
<th>OSC</th>
<th>PGM affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallographic structure</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Composition (Zr, dopants)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Textural properties</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Benefit of Zirconium changes with Ce/Zr ratio

Improved Thermal Stability

Lower Temperature Reduction

Improved Ce$^{4+}$ reduction

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Change in Crystal Structure can explain benefit of Zirconium introduction for OSC

CeO$_2$ cubic

Ce-rich cubic

Zr-rich tetragonal

environnement $8 \times 2.34$ Å

anti-prism square base $4 + 4$

2 tétrahèdres $4 + 4$

$4 \times 2.12$ Å

$4 \times 2.39$ Å

Zr content increase

Reducibility increase
CeO$_2$ replaced by CeO$_2$/ZrO$_2$ in the 90’s

Due to more stringent pollutant regulations, higher thermal stability and reactivity CeO$_2$-ZrO$_2$ has been introduced in TWC washcoat
Dopant is also improving thermal stability and OSC

<table>
<thead>
<tr>
<th>Improved Thermal Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>La (wt%)</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>(S_{\text{BET}}) at 900°C aging</td>
</tr>
<tr>
<td>(S_{\text{BET}}) at 1100°C aging</td>
</tr>
</tbody>
</table>

Low Temperature Ce\(^{4+}\) reduction

<table>
<thead>
<tr>
<th>Low Temperature Dynamic OSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>350°C</td>
</tr>
<tr>
<td>400°C</td>
</tr>
<tr>
<td>450°C</td>
</tr>
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</table>

Rh based
Aged 1050°C/Redox

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Adjust dopants of OSC material can also improve PGM efficiency

Dopants Tuning can Boost Noble metals efficiency and allow Noble Metal Content reduction

Lean Light-off (r=0.98) conversion CO

Sweep test conversion NO (450°C)

Pd based powder model catalyst (1wt %) over CeZr – Redox aging at 1100C-6h
Change of textural properties of OSC materials improves thermal stability

**Actalys**
CeZr Mixed Oxide
Homogeneous Texture
More Compact

**Optalys**
CeZr Mixed Oxide
Open texture

Ageing:
- 900°C to 1000°C
- Actalys: 45 m²/g to 15 m²/g
- Optalys: 60 m²/g to 40 m²/g
For extremely high temp. demanding applications, new highly mesoporous Mixed Oxides have been developed …

Hg porosimetry analysis on Mixed Oxides aged at different temperatures
Control of textural properties and composition of OSC materials allow reduction of Noble metals

Testing of powder model catalysts at lab: Rh from 0.2 to 0.05 wt%
Redox aged catalysts: 6h/1100 C
Conversion: CO/NO at Cross Over Point (COP) – T = 470° C
Ceria based components in TWC – trends

- TWC for gasoline powered engines is
  - A mature technology with proven technical solutions
  - Ceria based component is the key Oxygen Storage Capacity Component
  - Need further innovation to reduce noble metal content (and therefore the cost of catalytic converters)

- Next regulation will drive Filter introduction
  - Euro 6.c (2017) with Particule Number of \(6 \times 10^{11}\) # /km max
  - To manage Low Back Pressure / Efficiency trade-off, introduction of TWCF (Filter with TWC washcoating).

- As a consequence, requests for the OSC material keep the trend:
  - Higher thermal Stability
  - High Reactivity OSC material (large O exchange at lower temperature)
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Diesel Exhaust treatment is more challenging due to lean atmosphere (Oxygen rich)

Due to large $O_2$ content in the exhaust, TWC cannot convert the pollutants and dedicated catalysts are requested.
Diesel Exhaust is becoming more complexe

Ceria Materials are included in all the functions

- ✓ CO, HC
- ✓ Particulate Matter
- ✓ NOx

Lean Diesel Engine

Euro4 and before

Euro5 2010

Euro6b 2014

deNOx

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Principle of Diesel Particulate Filter function (filtration)

Physical filtration through a porous ceramic structure

- Porous wall
- Particules cake
Diesel Particulate Filter operation cycle during cold operations

DPF operation cycle:
– Succession of soot loading (= increase of exhaust back pressure)
– and Regenerations phases (= combustion of diesel particulates)

A – Soot filtration

B – Soot combustion:

\[
\text{Soot} + \text{O}_2 + T^\circ\text{C} \rightarrow \text{CO}_2
\]
Strategies to get reliable DPF Regeneration: $T^\circ C$ & $O_2$

"$T^\circ C$" Methods:
- In-Cylinder Post-Injection
- Electric Heating
- HC-Vaporizer + DOC
- Diesel Fuel Burner
- Exhaust throttling...

"$O_2$" Methods:
- Fuel Borne Catalyst (In-situ "$O_2$")
- Catalytic Coating (In-Situ "NO_2")
- CRT (NO_2 in the Exhaust Gas)

Combined Regeneration Methods
- Post-Injection + Fuel Borne Catalyst
- Post-Injection + Catalytic Coating
- Post-Injection + HC-Vaporizer + Catalytic Coating
- Diesel Burner + Catalytic Coating or Fuel-Borne Catalyst
- Throttling + Fuel Borne Catalyst ....
Catalytic Mechanisms for Soot Oxidation

• Via NO2 (local CRT)
  2 NO + O2 → 2 NO2
  2 NO2 + C → CO2 + 2 NO
  NO2 + C → CO + NO

• Via direct oxidation by “activated oxygen” (from surface or bulk) and oxygen spill over
  \[ \text{O}_2 \rightarrow 2 \text{O}^* \]
  \[ 2 \text{O}^* + \text{C} \rightarrow \text{CO}_2 \]
  \[ \text{O}^* + \text{C} \rightarrow \text{CO} \]
Direct observation of soot oxidation shows soot oxidation at ceria-soot interface and continuous movement of soot to interface.

Environmental TEM photos show soot shrinking into ceria washcoat during oxidation.

(2 mbar O2 at 550°C, time interval between each image = 2 min, scale bars = 90 nm)

- Soot-ceria interface re-established itself. Interface might be mobile, or oxygen surface diffuses. More likely van der Waal forces re-established the interface.

Particle diameter (open symbols) remains fixed, but distance of center from catalyst decreases with oxidation.

Source: Haldor Topsoe Group (2008)
Example of Coated Diesel Particulate Filters (c-DPF, CSF)

- A special soot burning catalyst is distributed very finely over the inside walls of the DPF
- PGM (Pt) is used to enhance Oxygen Storage Capacity of the Ceria-based coated materials at lower temperatures

Catalytic Coating

Source: Ford 2003
Ceria Based Oxide are key components of c-DPF to reduce Soot combustion temperature.

Importance of composition

From Mazda SAE 2007-01-1919

At low Temp, soot reacts with the lattice oxygen of the OSM. CePr MO shows the highest reactivity.

Importance of Porous Texture

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A fuel-borne catalyst (FBC) is an efficient approach to facilitate soot combustion

Continuous supply of fresh catalyst,

Homogeneous catalyst dispersion and intimate contact of the catalyst with soot.

- To lower the temperature of soot ignition, decreasing thus the engine stress (oil dilution…)
- To allow a fast regeneration, whatever the driving cycle
- To favor the diffusion of the combustion process to the entire soot layer, due to a complete regeneration, avoiding thus pyrolytic carbon formation
- To limit secondary emissions
  - (No impact on NO2/NOx ratio)
The Eolys™ FBC: a colloidal dispersion

- The first Eolys™ generation was based on a colloidal dispersion of Ceria, stabilized by an organic shell designed to insure a perfect dispersion and stability in diesel fuels.

- The organic solvent is a pure aliphatic solvent (C11-C15) fully compatible with diesel fuel.

- It shows a high catalytic activity at low dosing rates (15 to 30 ppm in fuel).
The first Series Production in 2000

- **First Serial Application** on Peugeot 607 model (2.2 HDI) in May 2000, with Diesel Common Rail Injection System

- Since May 2000, more than 10 Mio vehicles have been sold in the European market

Extension of DPF system to all HDI engines (DV4, DV6, DW10, DW12, DT17) from Year 2001

System demonstrated robustness, reliability and durability, including at the EURO5 step
System of the FBC Ceria-based Eolys application from Year 2000

Filtre à particules (FAP)
Particulate filter

DPF Regeneration:
- Post-injection
- DOC
- FBC

Diesel Oxidation Catalyst
Diesel Particulate Filter

Ceria-based Eolys storage and release system
(rigid tank with electronics)

1 Ensemble filtre "pré-catalyseur et filtre à particules"
Particulate filter and pre-catalyser filter assembly
2 Capteurs de pression et de température
Temperature and pressure sensors
3 Calculateur moteur
Engine ECU
4 Injection de produit additif dans le gazole du réservoir principal si nécessaire
Injection of an additive into the fuel in the main tank if necessary
5 Information spécifique à la tâche
Specific information sent to the task
6 Pré-catalyseur
Pre-catalyst
7 Filtre à particules (FAP)
Particulate filter

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Faster and Efficient DPF Regeneration are Required for Applications in Urban Conditions

- **% DPF Regeneration**
  - **FBC**: >90% after 5 min.
  - **CSF**: 22% after 10 min.
  - **DPF**: 20% after 10 min.

**EU4 DW12TEDA engine** (97.5 kW- 2.18L)
- Pt based DOC/4.2L SiC DPF DPF
- soot load 4.5g/l
- Coated-DPF: 3.2 L EURO5 design

(@ Fe/Soot %w/w = 1.20%)

**at 500°C**
Lean NOx-Trap (LNT) and NH₃-Selective Catalytic Reduction (SCR) catalysts are Euro 6 technologies.
Lean NOx-Trap (LNT) and NH₃-Selective Catalytic Reduction (SCR) catalysts are Euro 6 technologies.
Ceria based MO is a low Temperature NOx Storage component and will help NOx reduction in rich LNT after 1 min NOx Storage.

- Ceria efficient NOx Storage below 300°C
- Dopants further improve NSC
- Dopants tune Temperature Storage

Fast NOx reduction in rich with Ceria:
- Ceria is promoting in situ H₂ production (WGS reaction) to enhance NOx reduction during rich purge

Pt based model catalyst – hydrothermally aged at 700°C – model gas test

More in MinNOx 2014 conference
Lean NOx-Trap (LNT) and NH₃-Selective Catalytic Reduction (SCR) catalysts are Euro 6 technologies.

**LNT CATALYSTS**

- **Adapted PGM based TWC**
  - PtPd/Alumina + NOx Storage component
  - Rh/Alumina + OSC material

**NH₃-SCR CATALYSTS**

- **Oxide Catalyst without PGM**
  - Vanadia based / TiO₂
  - Cu or Fe exchanged zeolite
  - Acidic Ce-Zr mixed oxide

**Reactions**

- **Hydrolysis catalyst (H)**
  - \((\text{NH}_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2)\)

- **Oxidation catalyst (O)**
  - \(4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}\)

- **Oxidation catalyst (V)**
  - \(2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2\)
  - \(4\text{HC} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}\)
  - \(2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2\)
Ce based Catalyst is a balanced alternative to Zeolithe based Catalyst

Maintain High Temp deNOx

Efficient at low Temp

NO-only

Source: UMICORE_DEER 2010
Dedicated Acidic CeZr for SCR

High Selective DeNOx after severe ageing in NO only
Strong resistance to deactivation (T°, H2O, CO/HC) and S resistance

Source: IAV-Solvay MinNOx 2014
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Ceria is definitively a unique material with tunable properties to meet gasoline and diesel depollution.

Repeated Fast Redox Cycle

Tunable Basicity

Tunable Acidity
New market drivers to consider for future exhaust architectures

**Drivers**

- **Stringent Pollutants regulations**
  - New Test Cycle / Cold Start...
  - Real Driving Emission

- **CO₂ 95 g/km in 2020**
  - Low Temp. Combustion mode
  - Hybridization...
  - Reduced exhaust temperature

- **Integration / Cost**
  - Compact lay-out
  - Multifunctional system (LNT in DOC or SCR in DPF)

**Material Needs**

- **Higher Efficiency**
  - In particular at low Temp.

- **Higher PGM affinity**
  - Pd, Rh for TWC
  - Pt, Pd for diesel

- **Better Surface Chemistry control**
  - Reactivity
  - Poisons / inhibitors

- **Higher Thermal Stability**

- **Multifunctional materials**
Conclusions

- Ceria based materials are definitively key materials for automotive depollution

- Coming challenges of automotive depollution to consider are:
  - New pollutants regulations
  - Reduced Exhaust Temperature to meet CO$_2$ regulation
  - Cost efficient solutions

- For material, future means
  - More Efficient
  - More Durable,
  - Smart solutions including multifunctional materials
Thank you for your attention

Any questions?

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