RARE EARTHS IN AUTOMOTIVE CATALYSTS

Dr. Raoul Klingmann

Umicore Automotive Catalysts

Agenda

Rare Earths in Automotive Catalysts

Three-way Catalysts

Oxygen Storage Materials

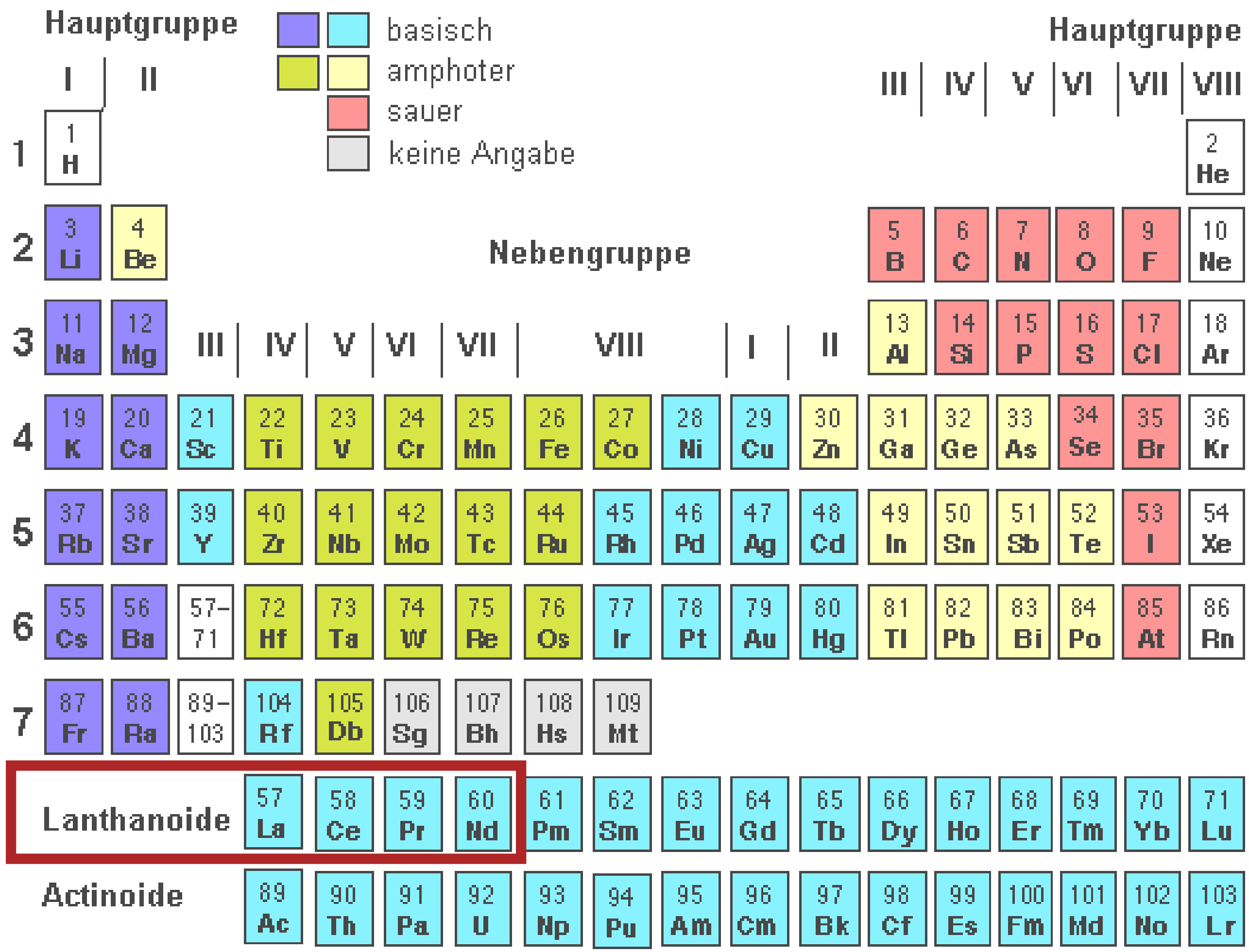
Measurement of Oxygen Storage Capacity

On board diagnosis

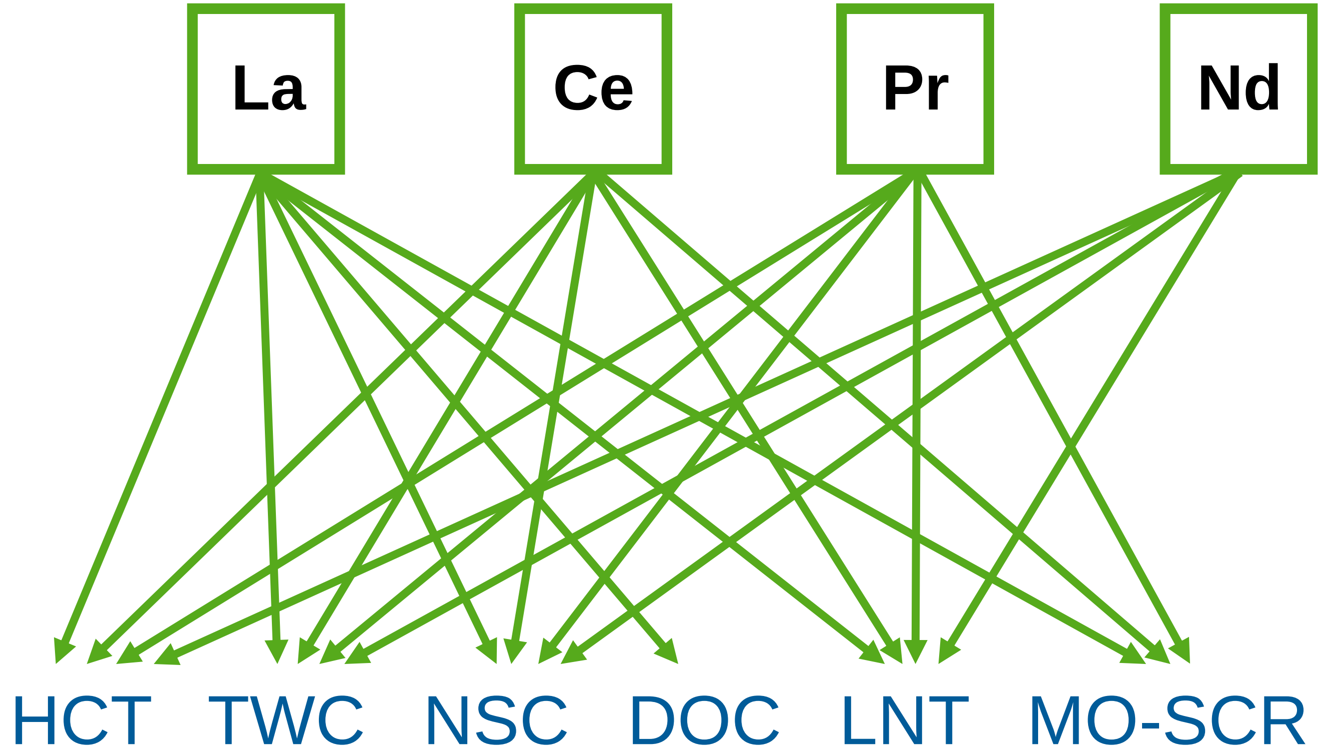
Are there potential substitutes for REE ?

Rare Earths in Automotive Catalysts

Status



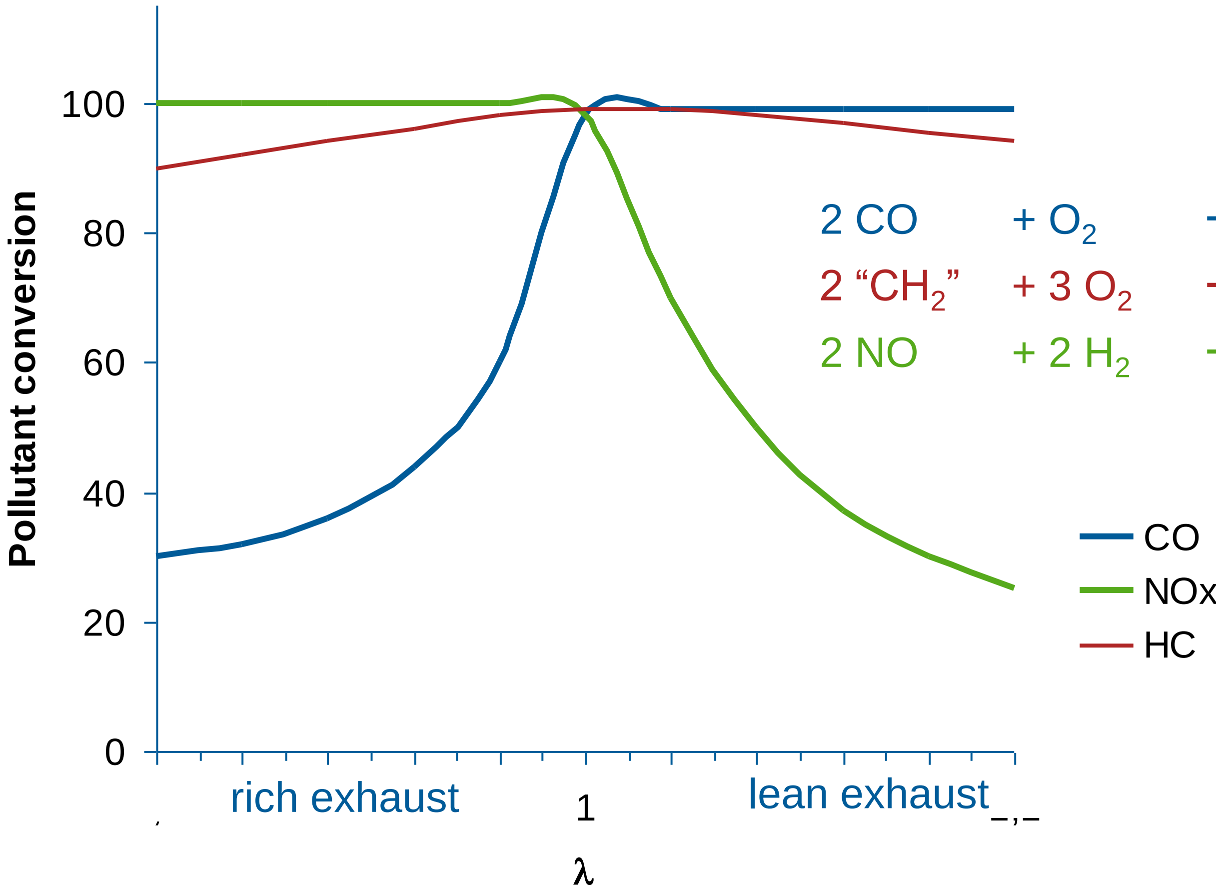
Rare Earths in Automotive Catalysts



Clean air is our business

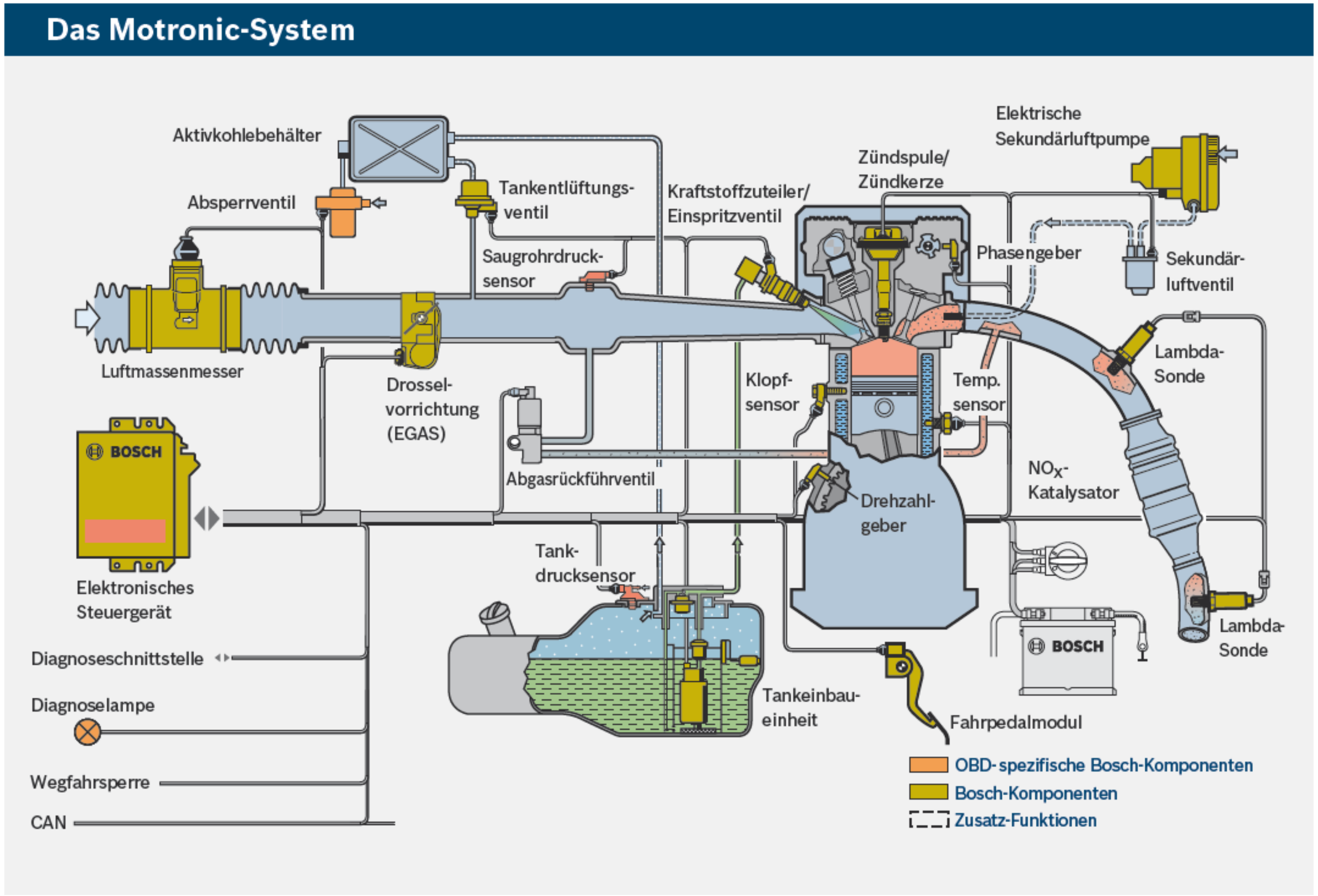
Three-way catalysis

λ-window of a Three-way Catalyst



2 CO	+ O_2	→	2 CO_2
2 “CH_2”	+ 3 O_2	→	2 H_2O + 2 CO_2
2 NO	+ 2 H_2	→	N_2 + 2 H_2O

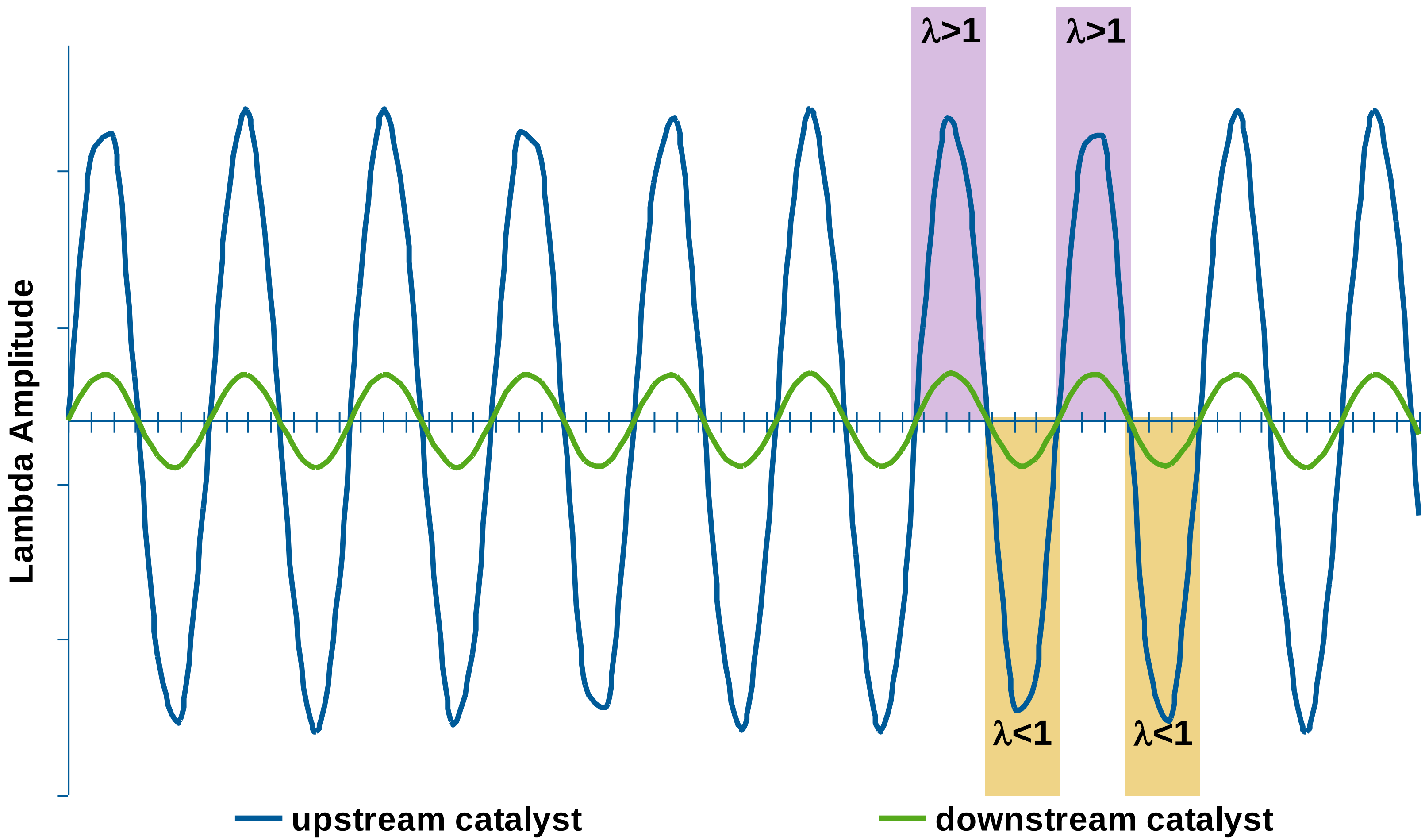
Closed loop air/fuel ratio control



Source: http://www.bosch-kraftfahrzeugtechnik.de/media/de/pdf/antriebssystemepkw/

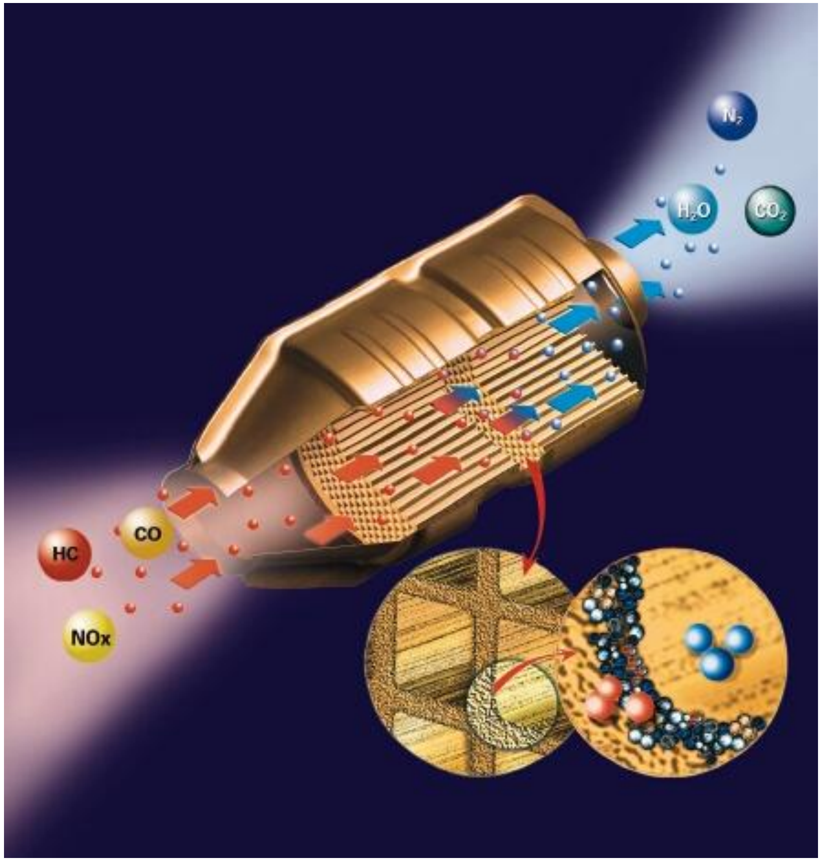
Clean air is our business

Dampening of the oscillations around λ=1



Composition of Three-way catalysts

- oxygen storage materials
- stabilized alumina
- platinum group metals
- promotors
- scavengers
- stabilizers

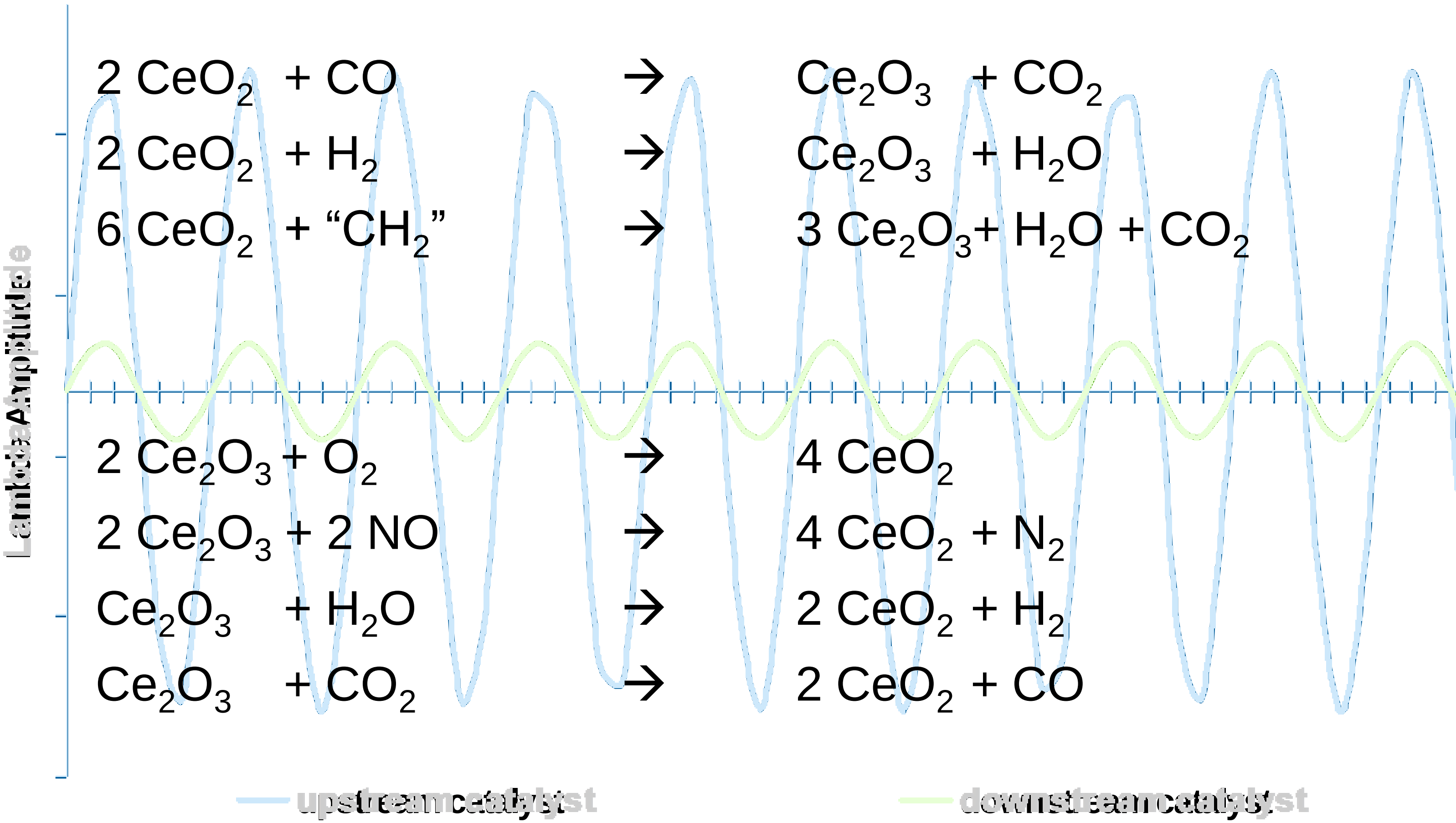


Clean air is our business

umicore
materials for a better life

Oxygen Storage Materials

Oxygen storage and release reactions



$$2\ CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$$

$$2\ CeO_2 + H_2 \rightarrow Ce_2O_3 + H_2O$$

$$6\ CeO_2 + \text{“}CH_2\text{”} \rightarrow 3\ Ce_2O_3 + H_2O + CO_2$$

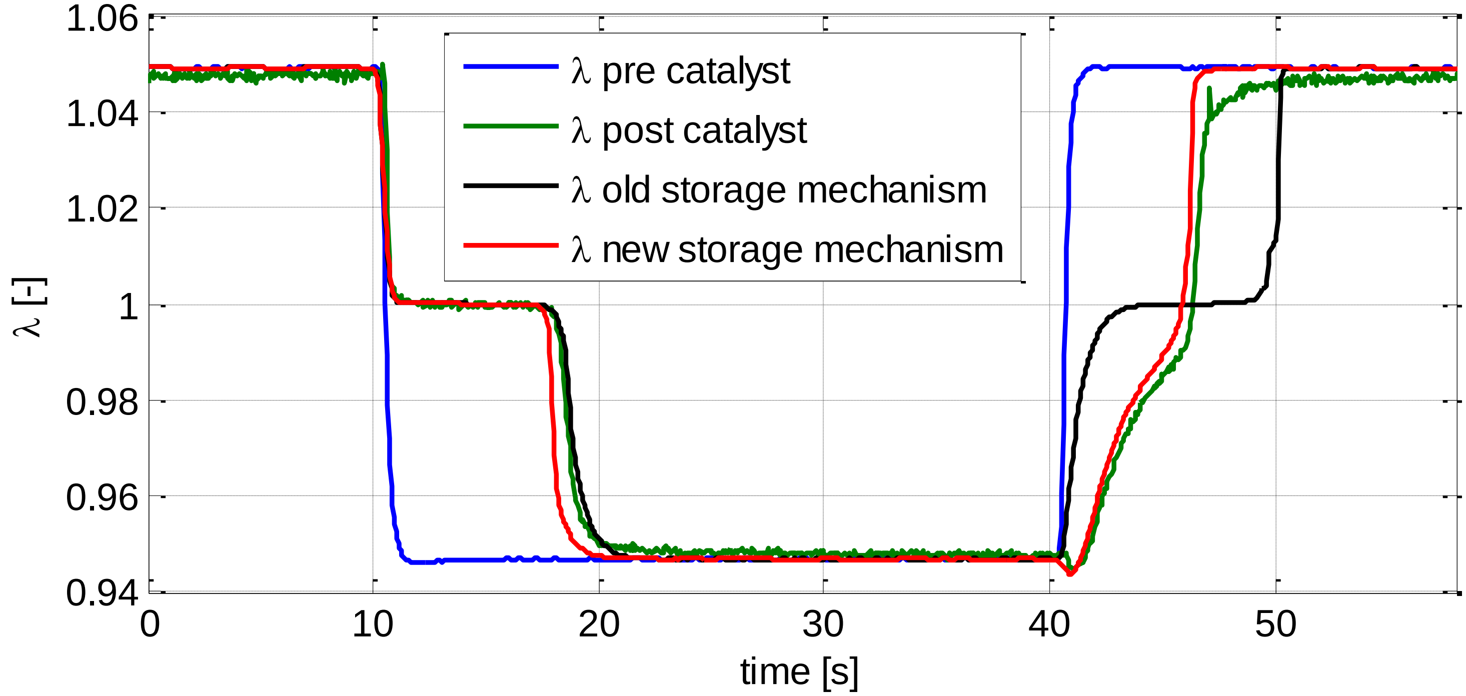
$$2\ Ce_2O_3 + O_2 \rightarrow 4\ CeO_2$$

$$2\ Ce_2O_3 + 2\ NO \rightarrow 4\ CeO_2 + N_2$$

$$Ce_2O_3 + H_2O \rightarrow 2\ CeO_2 + H_2$$

$$Ce_2O_3 + CO_2 \rightarrow 2\ CeO_2 + CO$$

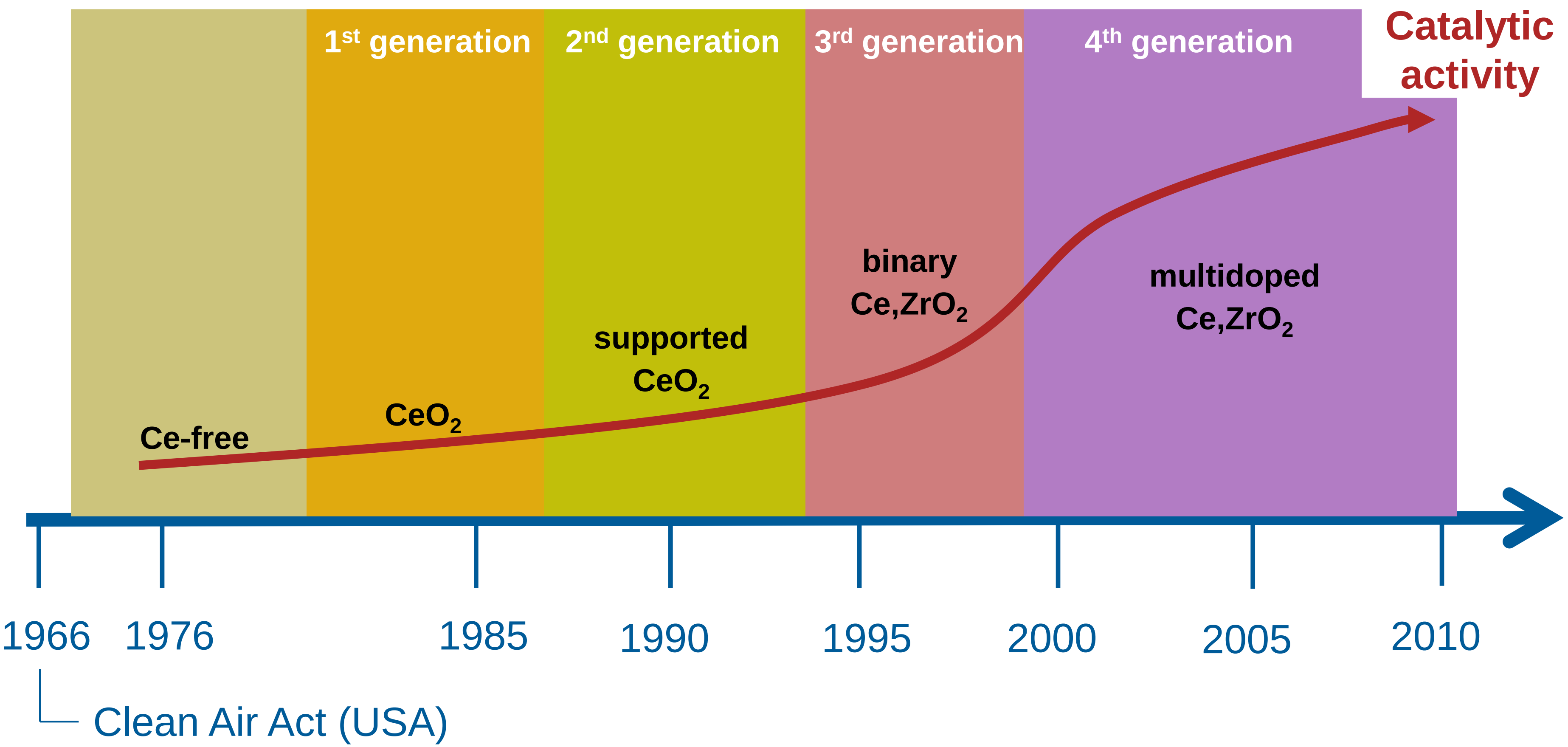
Ceria-Zirconia mixed oxides



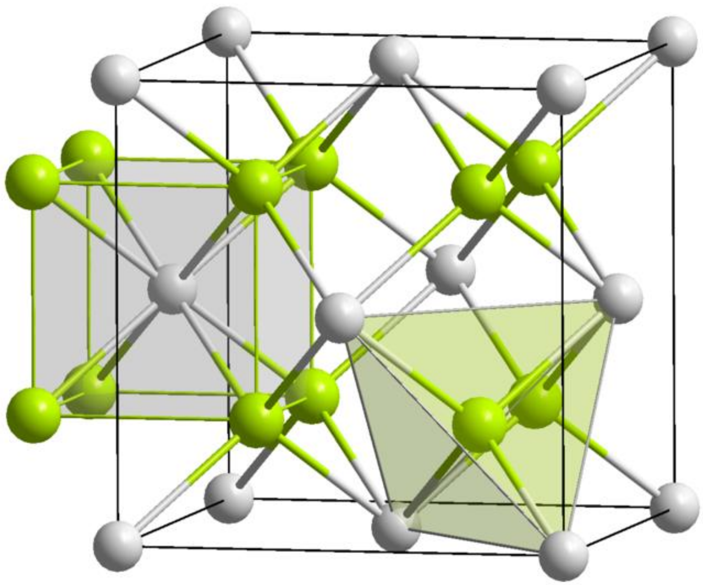
Dynamic behavior of the down stream air-to-fuel ratio for an oxygen storage mechanism including CO_2 and H_2O as oxidizing agents compared to a "traditional" storage mechanism.

Source: Roman Möller, Martin Votsmeier, Christopher Onder, Lino Guzzella, Jürgen Gieshoff
Applied Catalysis B: Environmental 91 (2009) 30–38

Development of OS-materials for TWC



Stabilized Ceria-Zirconia mixed oxides

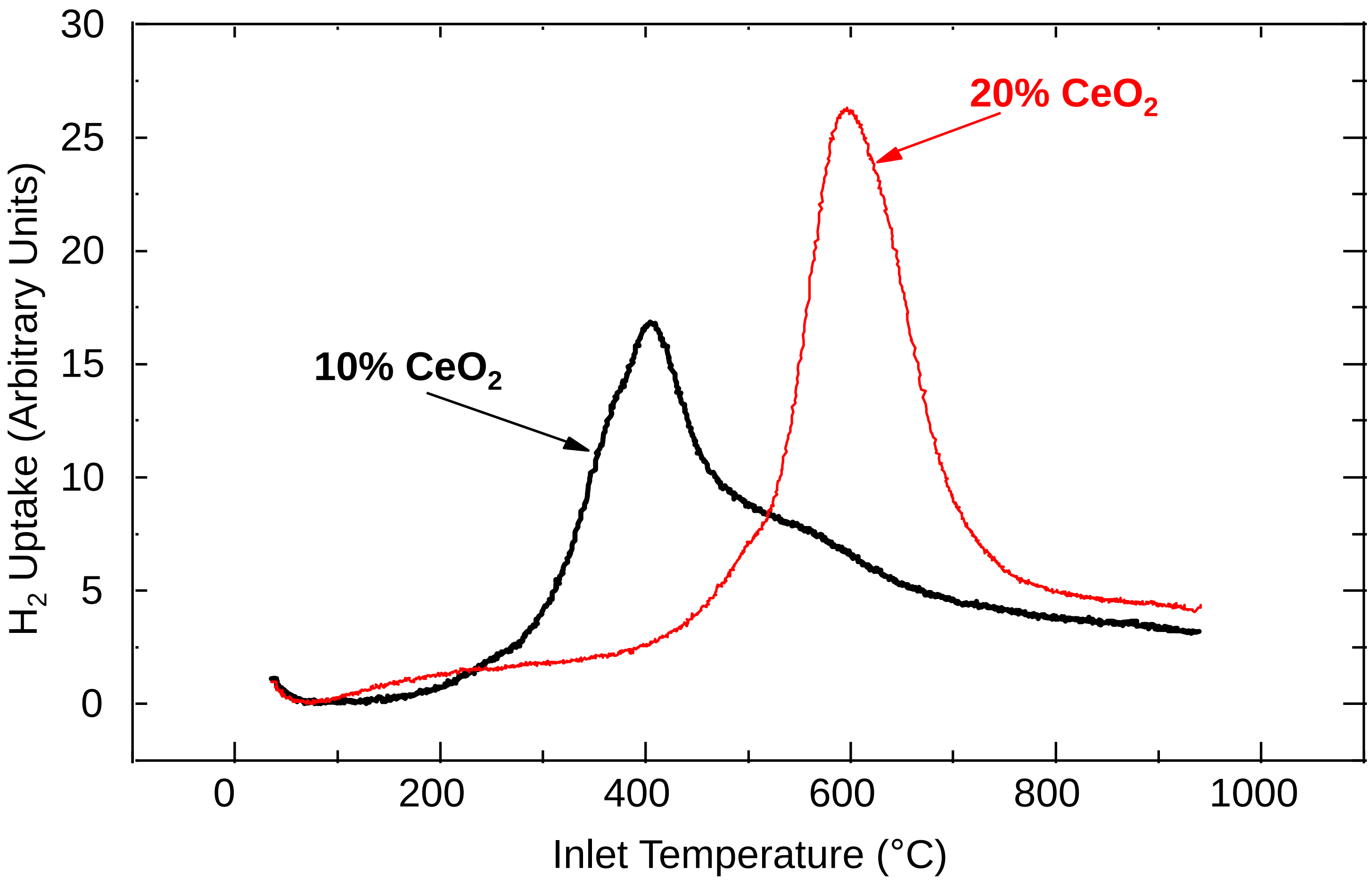


Fluorite Structure
Ce,Zr O

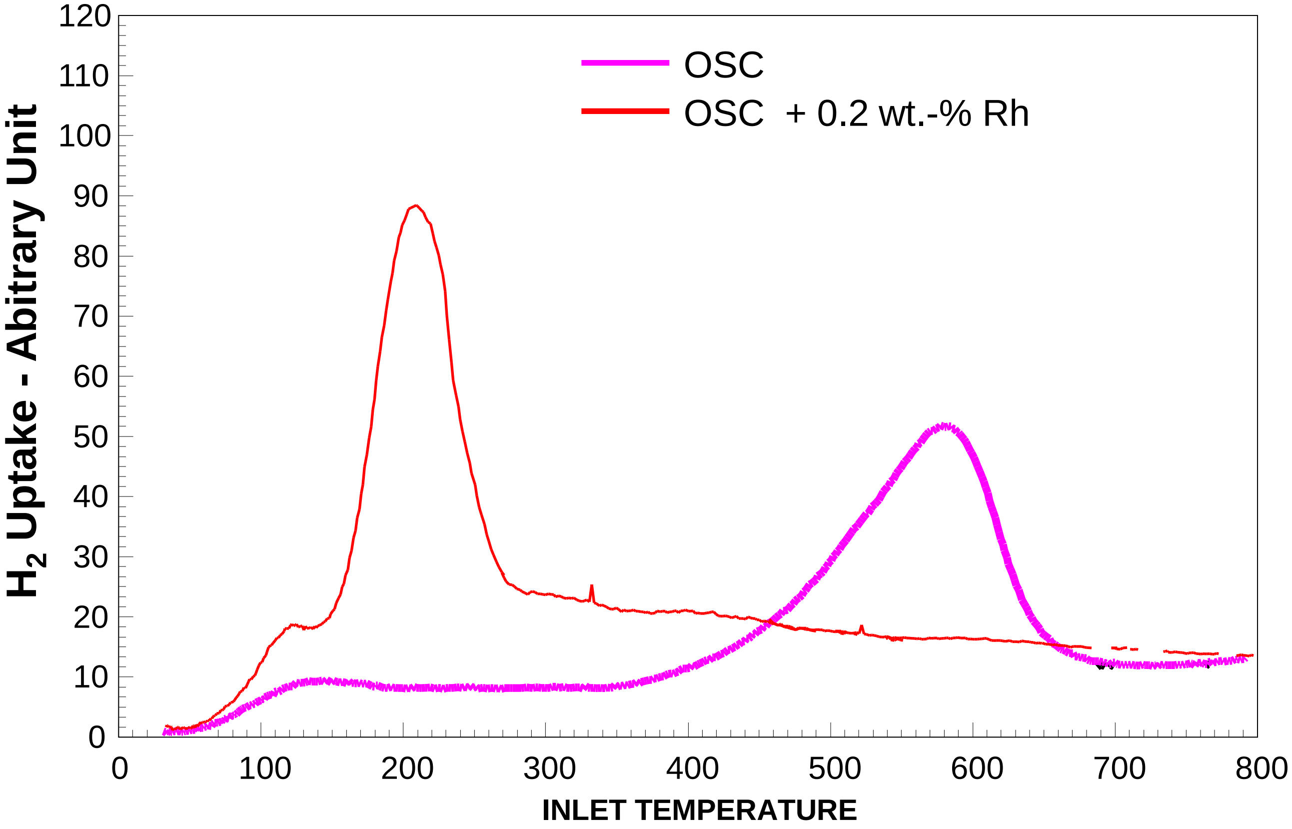
- cubic crystal structure
- typical dopants: La, Pr, Nd, Y, Sm
- improved redox behaviour
- improved thermal stability
- improved phase stability

Source: Wikimedia commons

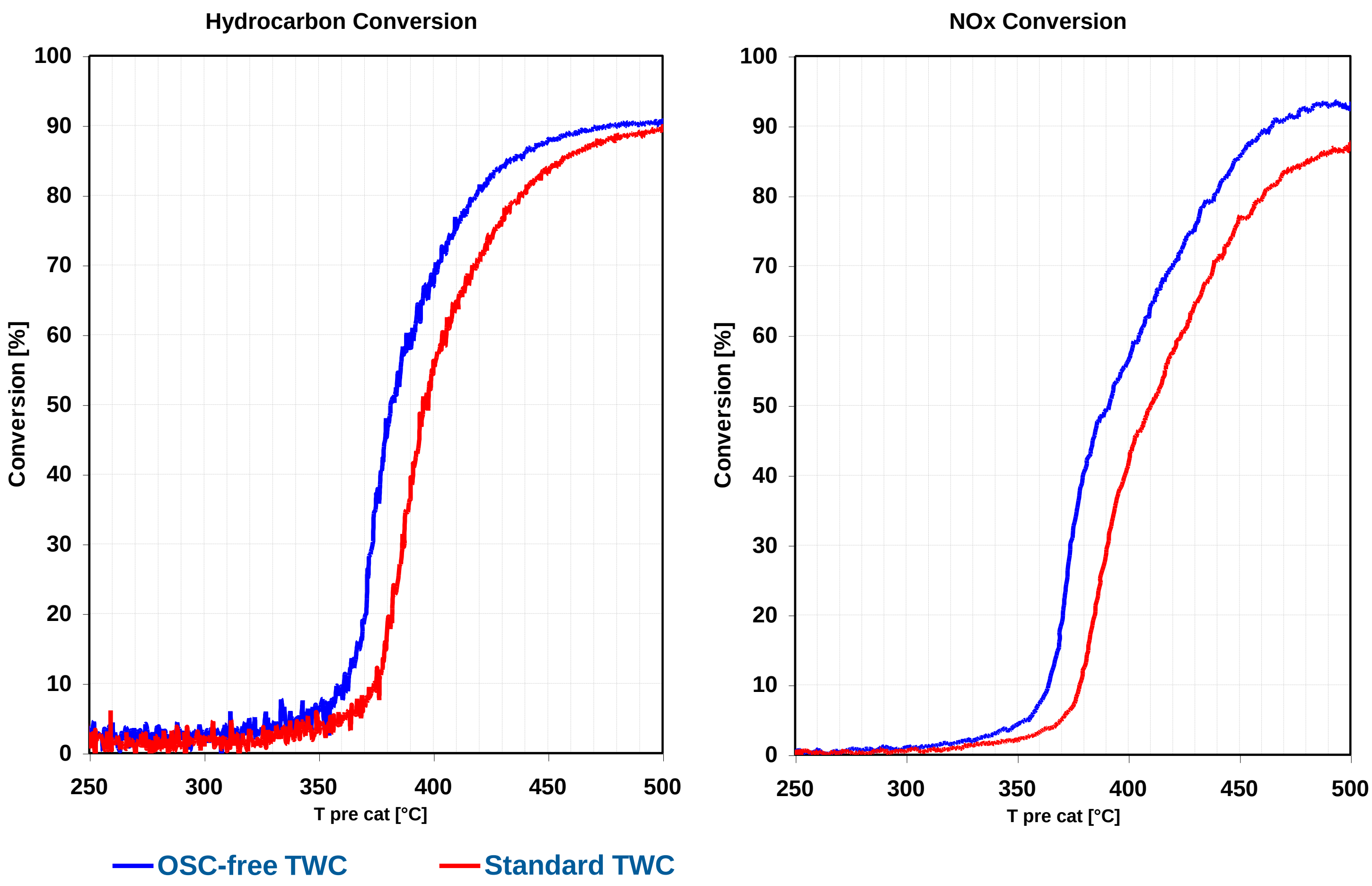
Influence of Ceria/Zirconia ratio on OSC



Impact of precious metals on oxygen storage behaviour of ceria-zirconia mixed oxides

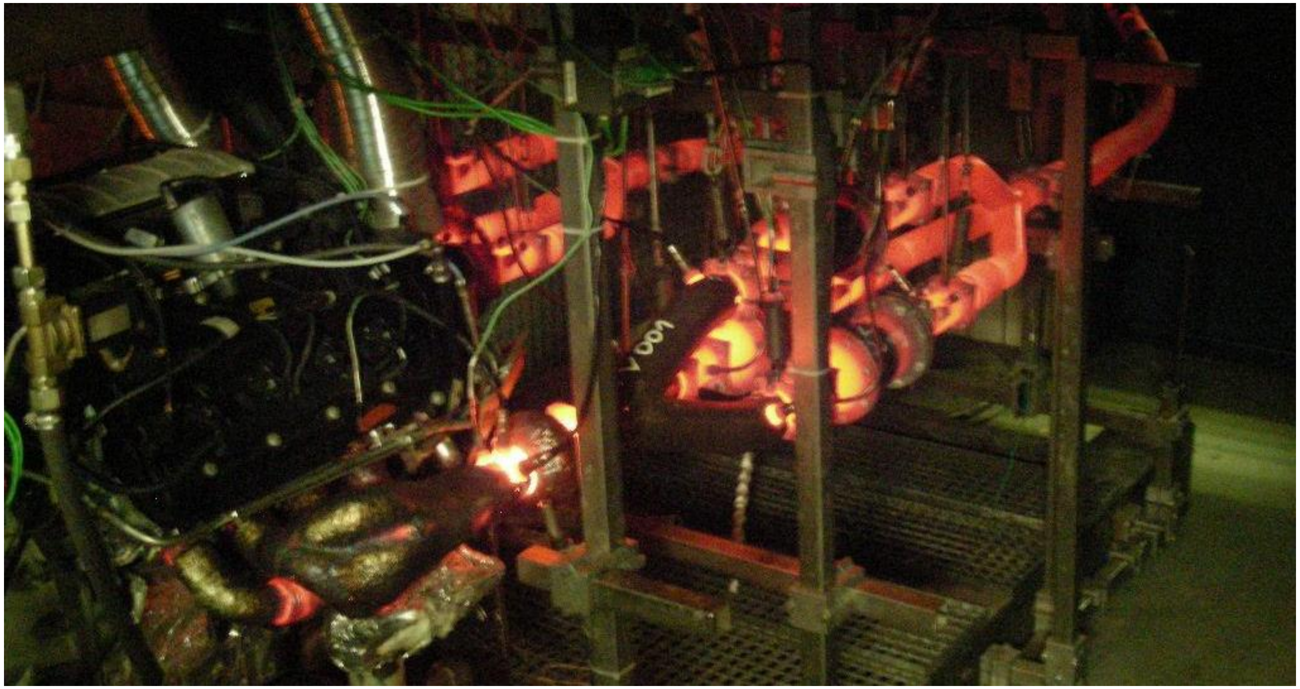


Impact of OS materials on lightoff of an aged TWC



Clean air is our business

Temperature Requirements for TWC

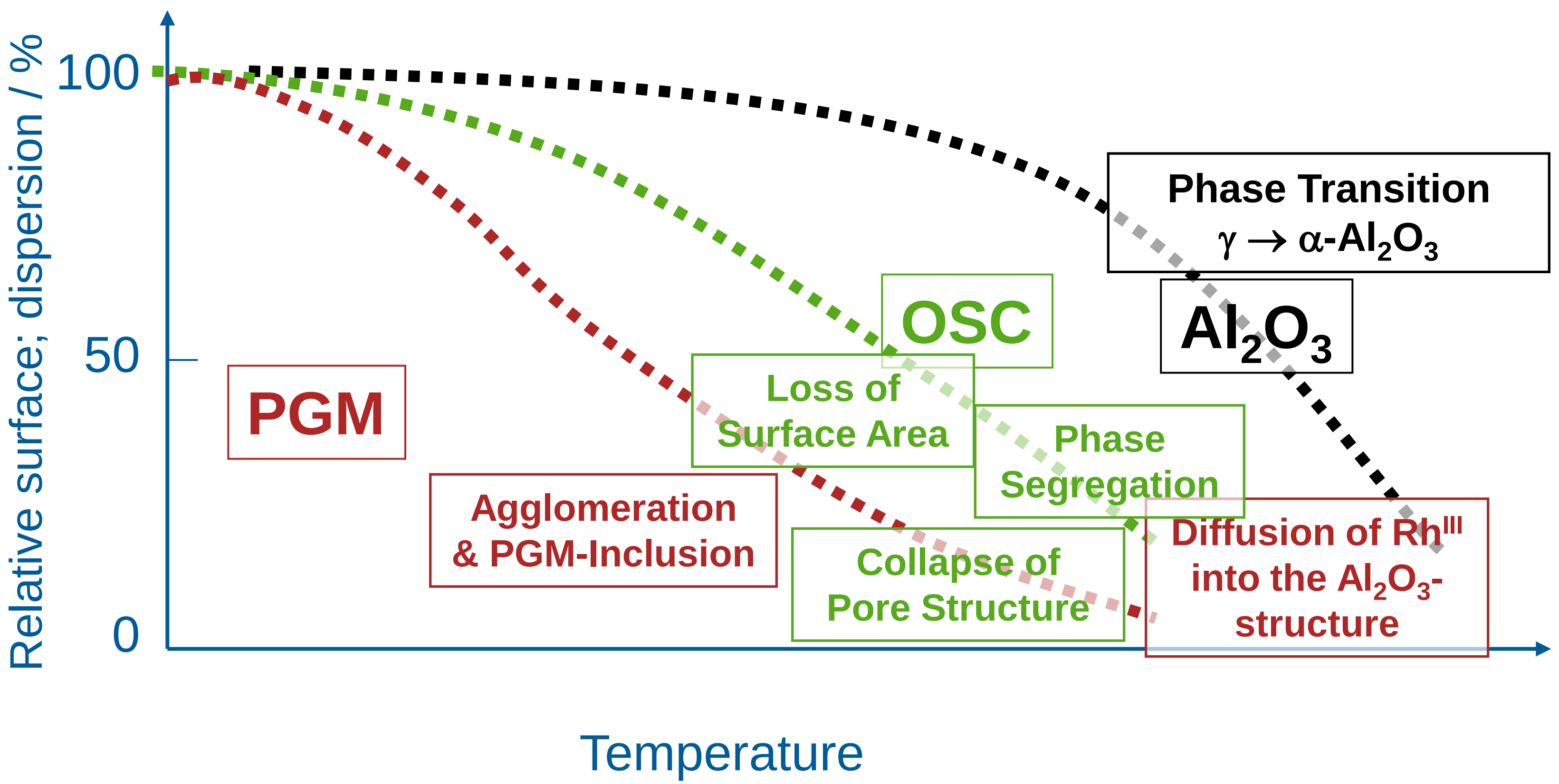


Typical aging temperature in front of catalyst (fuel cut aging cycle)

850°C 870°C 890°C 930°C 950 °C

1996 1997 1998 1999 2000 2001 2002 2003 2004 2005

Temperature Stability of TWC components



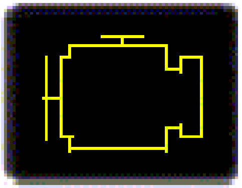
On-board diagnosis

Regulatory need for on-board diagnosis

<u>Directive 70/220/EEC:</u>

8.1. Vehicles with positive-ignition engines

8.1.1. Petrol fuelled engines

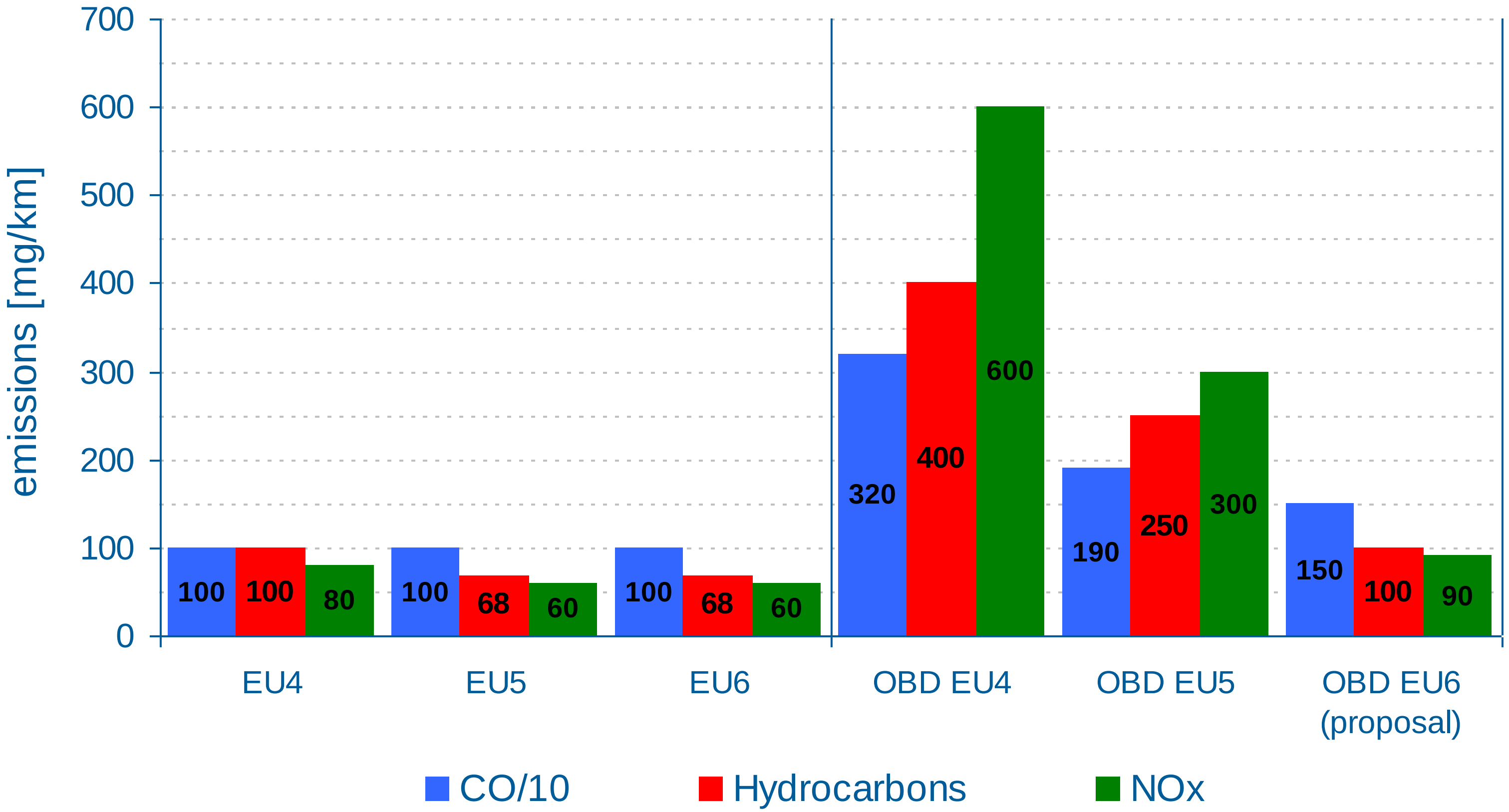


With effect from 1 January 2000 for new types and from 1 January 2001 for all types, vehicles of category M1 - except vehicles the maximum mass of which exceeds 2 500 kg - and vehicles of category N1 class I, must be fitted with an on-board diagnostic (OBD) system for emission control in accordance with Annex XI.

With effect from 1 January 2001 for new types and from 1 January 2002 for all types, vehicles of category N1 classes II and III and vehicles of category M1, the maximum mass of which exceeds 2 500 kg, must be fitted with an OBD system for emission control in accordance with Annex XI.

Clean air is our business

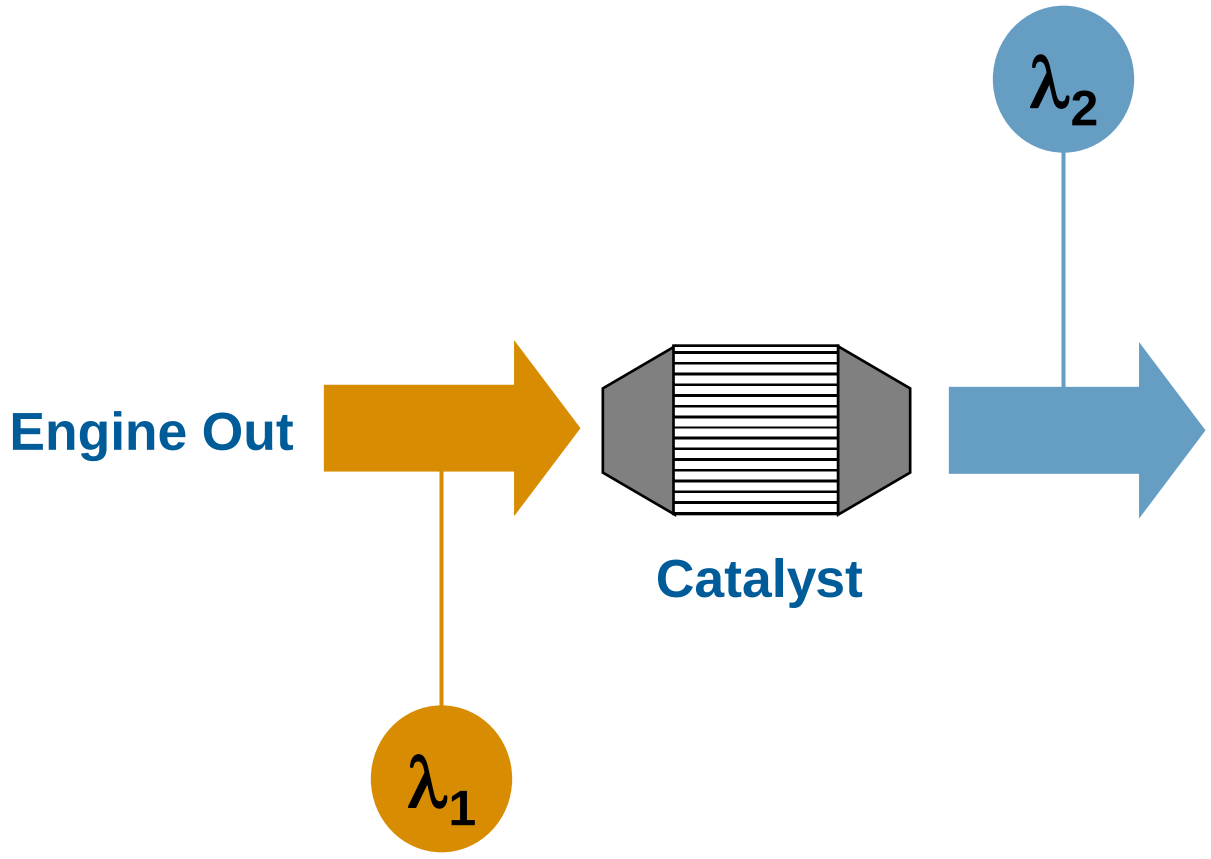
Legal emission and OBD limits in Europe



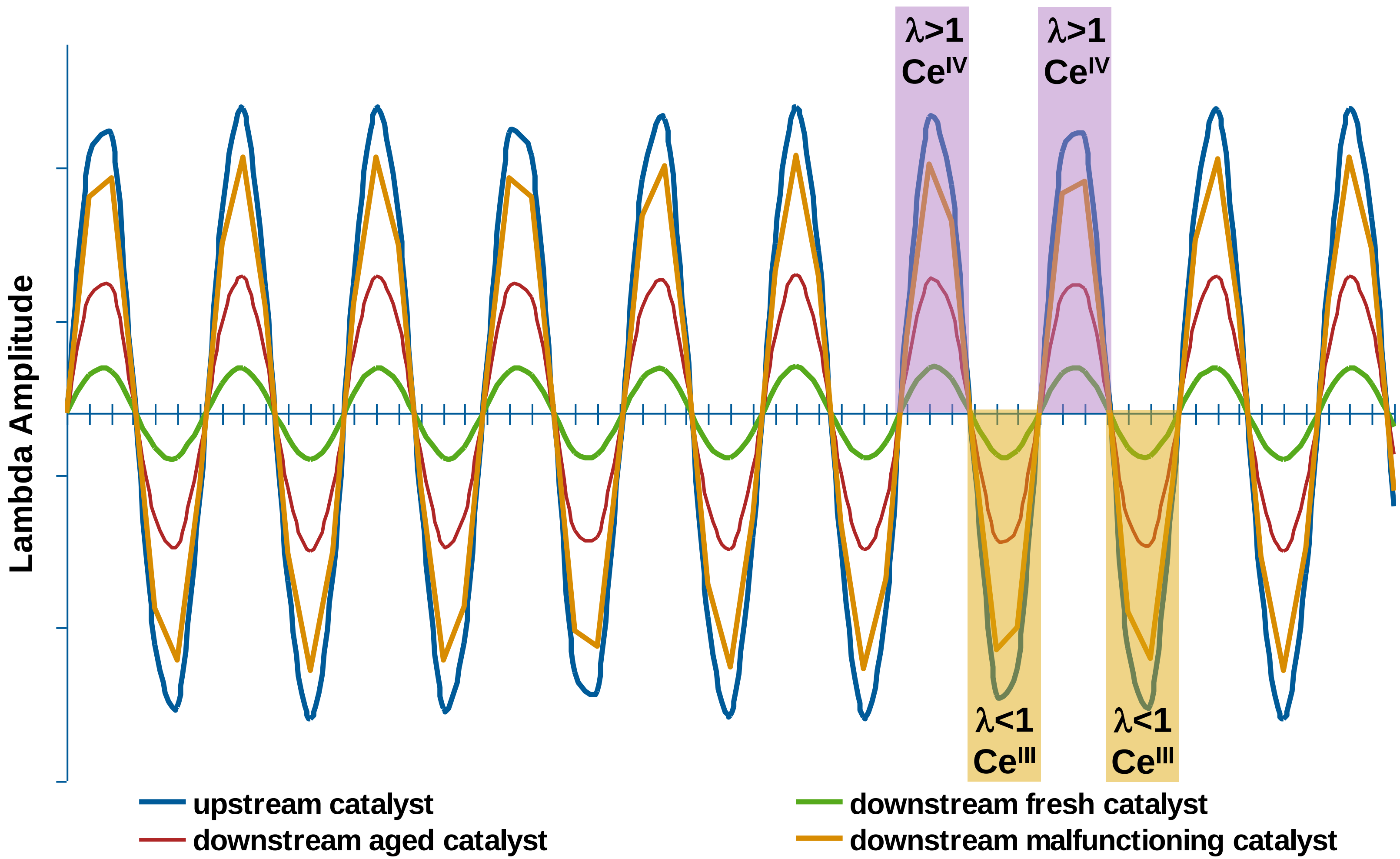
Clean air is our business

Measurement of Oxygen Storage Capacity on a Vehicle

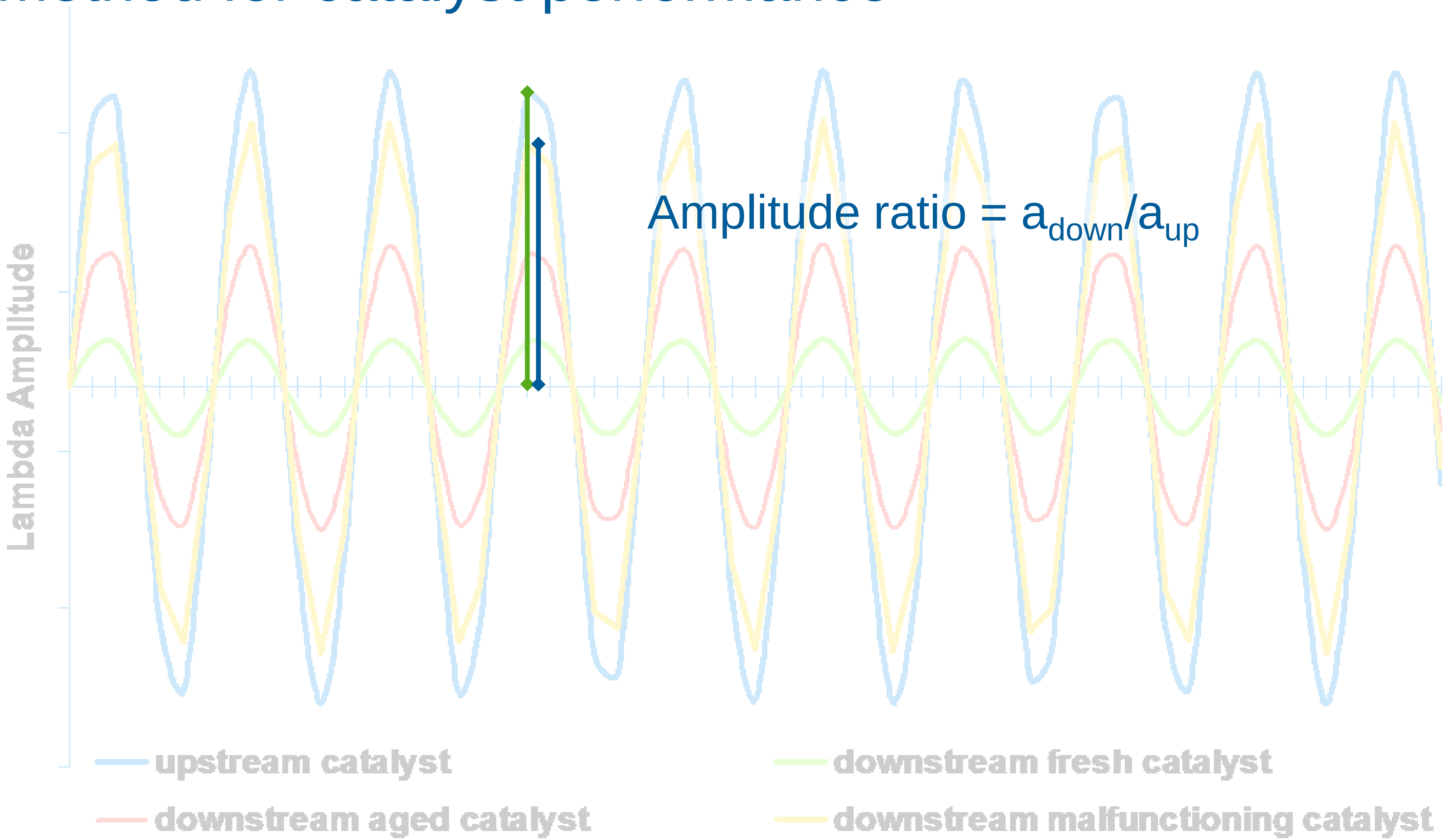
Oxygen Storage Test Setup for OBD



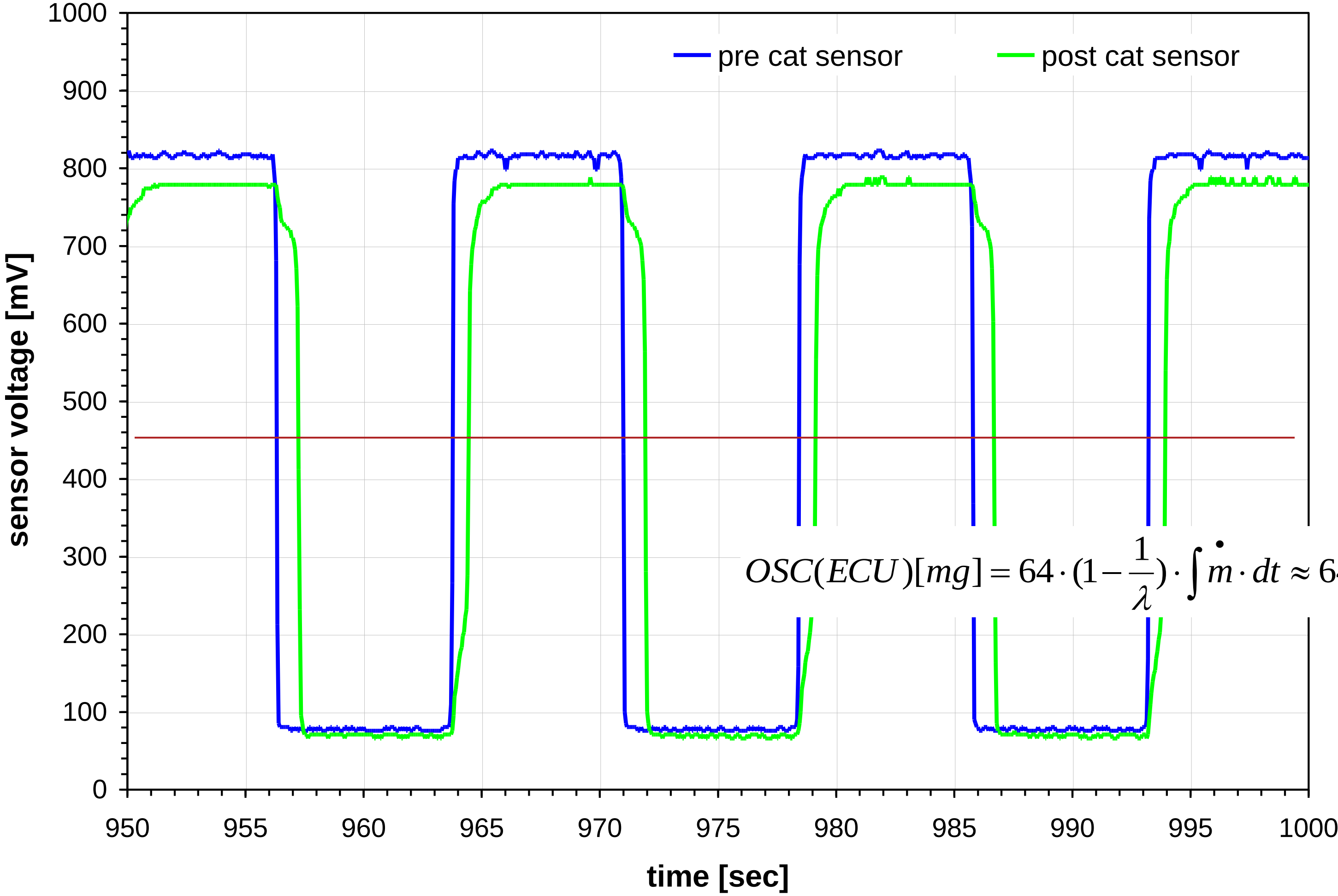
Degradation of "Lambda Absorption" Capacity



Amplitude Ratio measurement as diagnosis method for catalyst performance

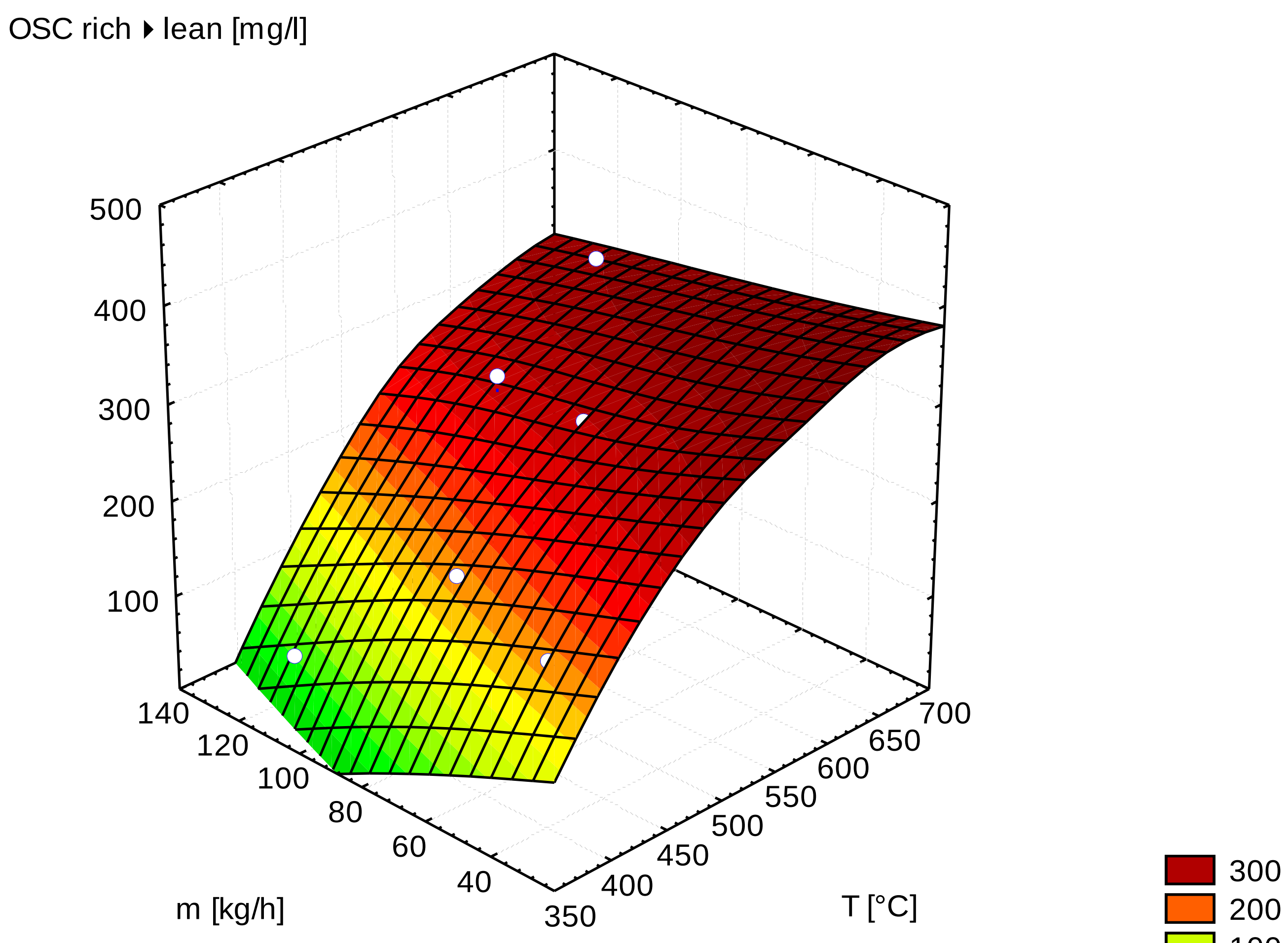


Catalyst diagnosis by λ-step test

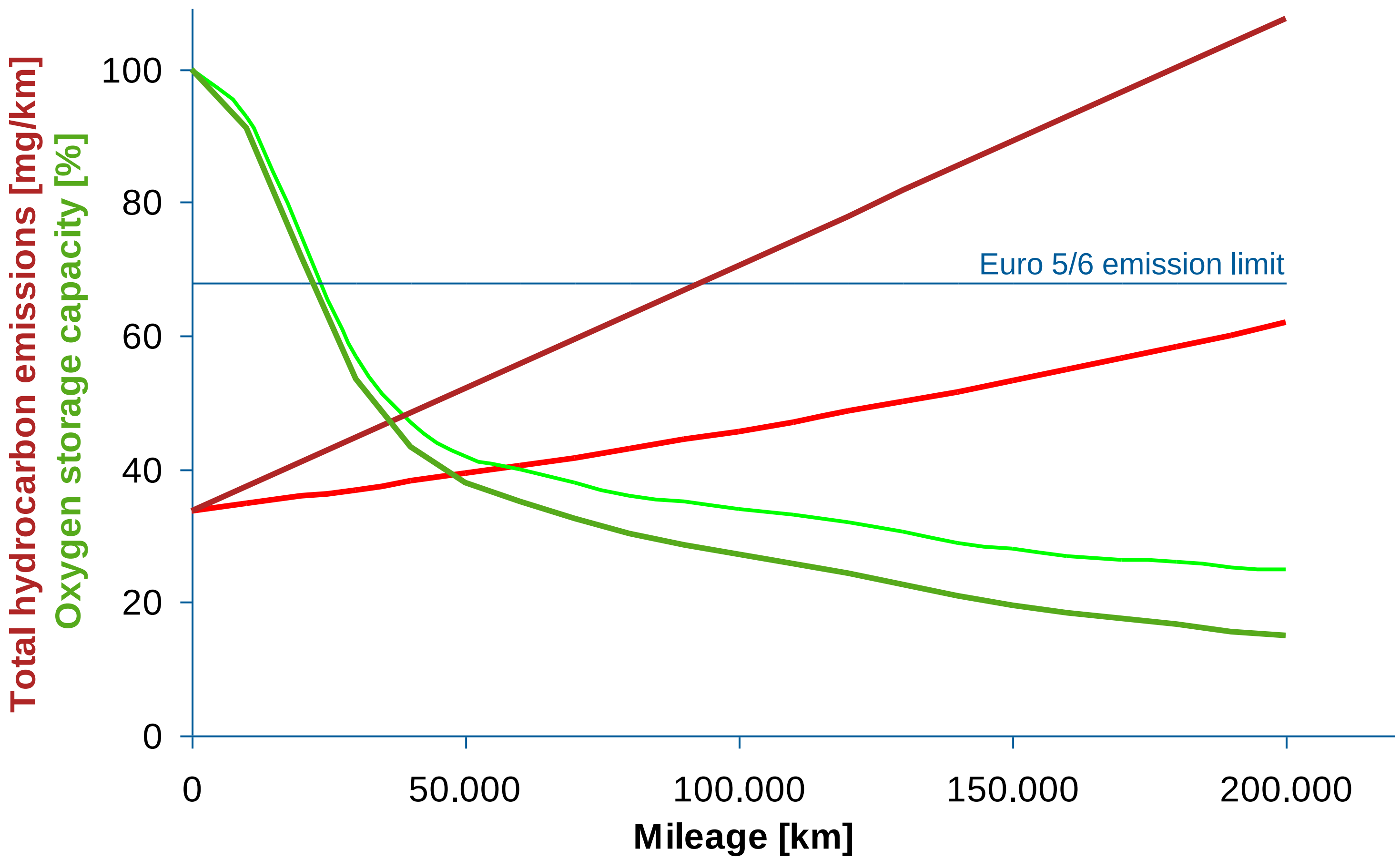


$$OSC(ECU)[mg] = 64 \cdot (1 - \frac{1}{\lambda}) \cdot \int \dot{m} \cdot dt \approx 64 \cdot (1 - \frac{1}{\lambda}) \cdot \dot{m} \cdot \Delta t$$

Relation of Oxygen Storage and Engine Map

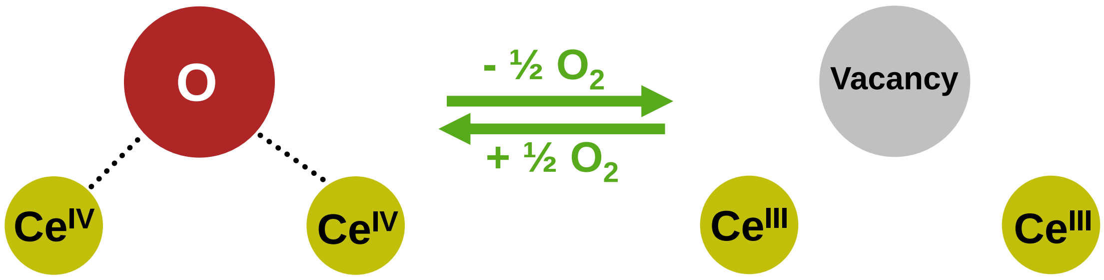


Correlation between OSC and performance



Substitutes for ceria in oxygen storage materials

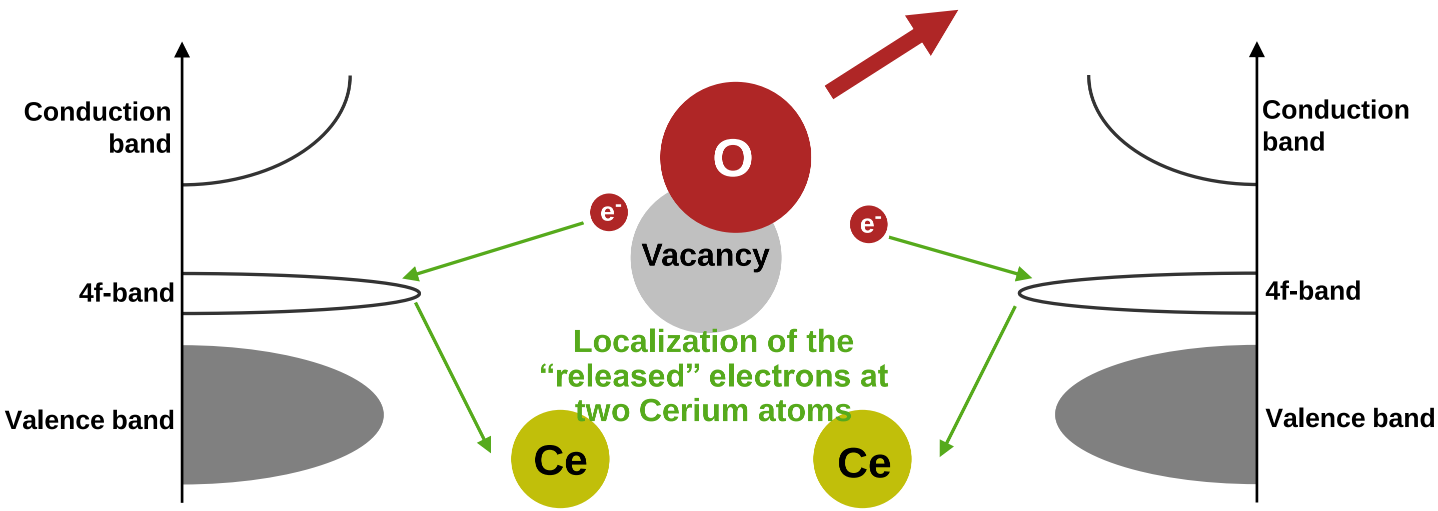
What makes ceria so special for OS ?



Electron configuration of cerium: [Xe] $6s^2 5d^1 4f^1$

What makes ceria so special for OS ?

The density of states of CeO_2 shows the presence of a narrow, empty Ce f band in the gap between the valence and conduction bands. In perfect CeO_2, every oxygen atom is situated in the center of a tetrahedron, surrounded by four Ce atoms. All four valence electrons of Ce nominally leave the host atoms and transfer into the p bands of oxygen atoms.
The process of oxygen-vacancy formation in ceria: An oxygen atom moves away from its lattice position leaving behind two electrons, which may occupy the lowest possible empty state, which is the f band of Ce. As was shown by Skorodumova et al., a substantial energy gain is achieved by their further condensation to localized f states on nearest Ce atoms, turning Ce^{4+} into Ce^{3+}. In Ce_2O_3 the Ce f electron is fully localized.



Source: N.V. Skorodumova, S. I. Simak, B. I. Lundqvist, I. A. Abrikosov and B. Johansson Phys. Rev. Lett 89/16 (2002) 166601

Development of low Rare Earth Three-way Catalysts

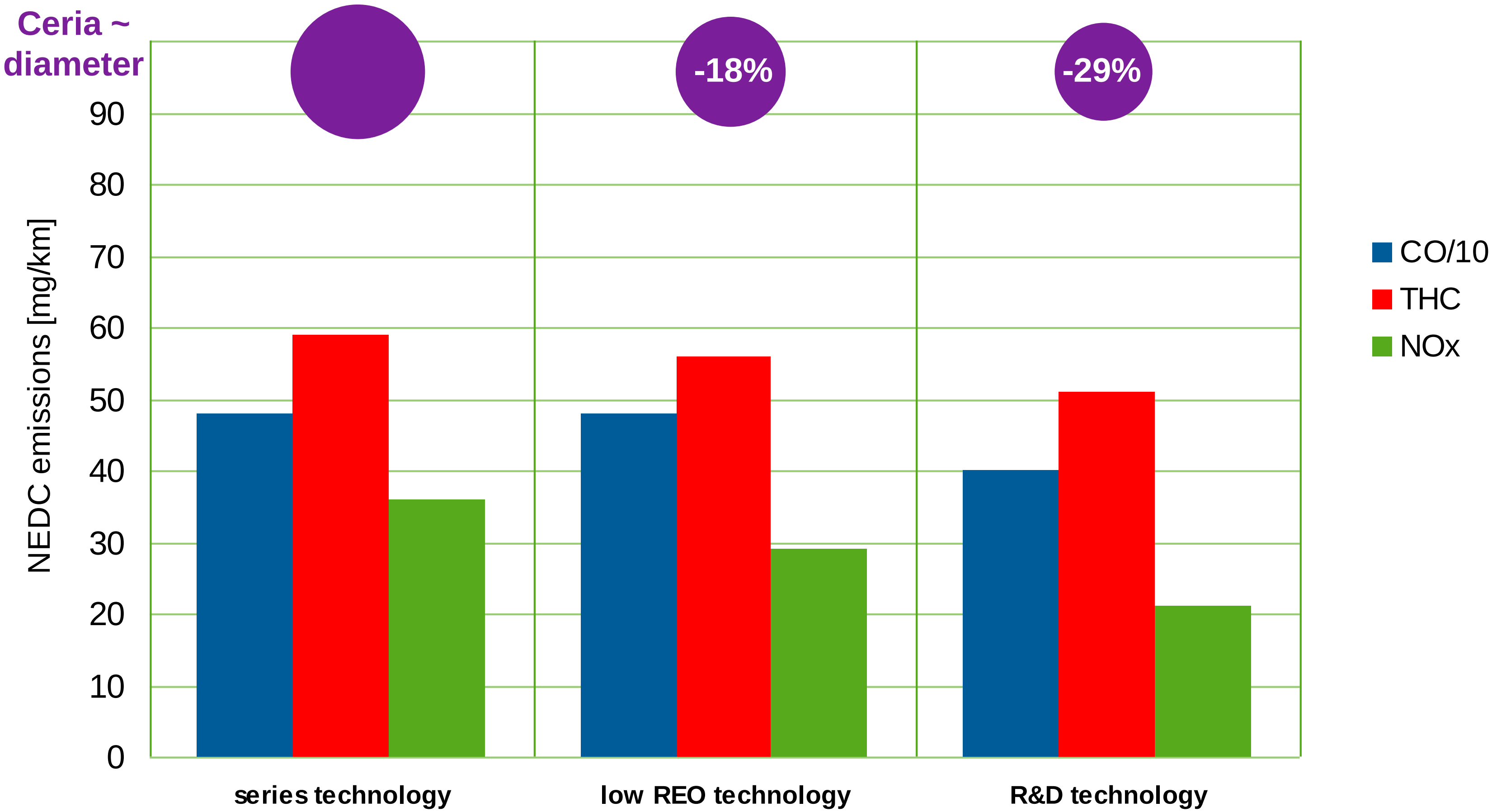
Can we at least omit some Rare Earth Oxides ?

Design Features of low REO Three-way Catalysts:

- Less oxygen storage material needed compared to standard TWC
- Highly dynamic OSC material type needs to be used
- Highly aging-robust OSC material type needs to be used
- OSC materials „make room“ for other ingredients
- Different processing possible

Performance of low Rare Earth TWC

tested on a EURO-5 calibrated 1.4l Opel Corsa



Summary

Summary

- Rare Earth Oxides are important part of exhaust aftertreatment catalysts, especially for gasoline aftertreatment.
- Ceria as essential part of mixed oxide oxygen storage materials is the most important REO for emission catalysis.
- Oxygen storage materials play a vital role for on-board diagnosis of emission control devices.
- Currently no equivalent substitute for ceria in oxygen storage materials is available.
- Development of low-OSC and in turn low-REO Three-way catalysts has been demonstrated to be feasible.

umicore
materials for a better life

THANK YOU