Fuel Cell & Stationary Catalysts

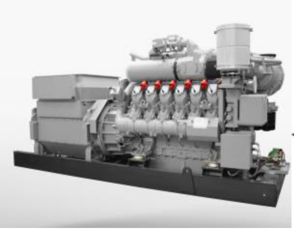
Robust Aftertreatment Systems for Large Engines

Hendrik Noack

11th VERT Forum, 25th March 2021

Agenda

- Introduction
- Catalyst Systems for Large Engines
- Catalysts for high S fuels
- Methane Oxidation Catalyst
- Summary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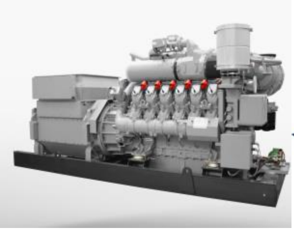


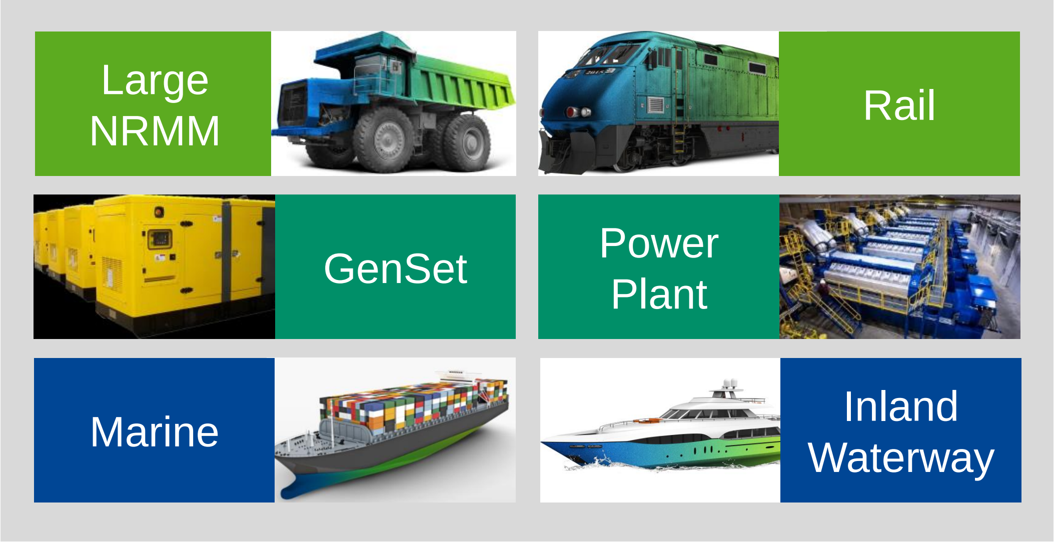

Introduction

Large Engines: P_{eff} > 1MW

Growth in LE market expected from energy production and transportation, including marine

Use of fossil fuels until “green alternatives” are available

Dedicated catalyst solutions required to meet the specific market requirements



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Common EGT Systems for EU Stage V/ Tier 4f

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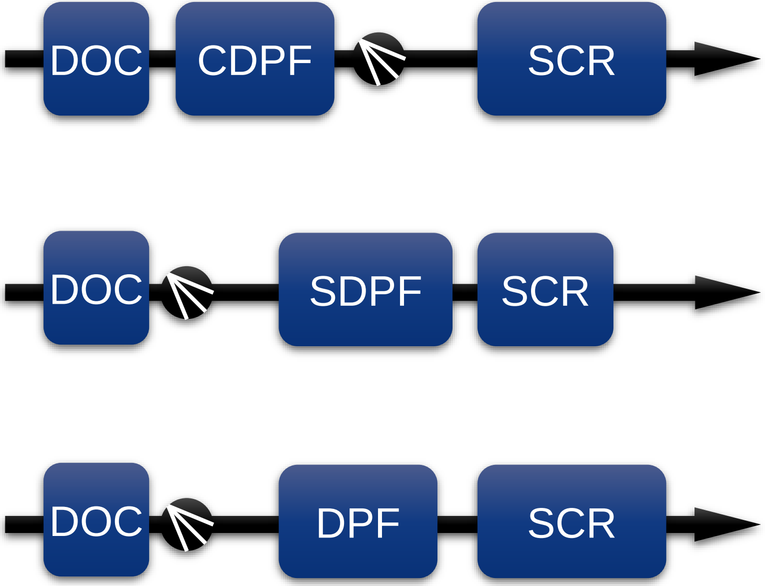
56- 560 kW, Diesel < 10 ppm S



Cummins, DEUTZ, JOHN DEERE, AGCO POWER

CNH INDUSTRIAL, LIEBHERR, JCB

CAT

based on publicly available information, solutions may vary dependent on application and power range

EGT Systems for Engines >560 kW

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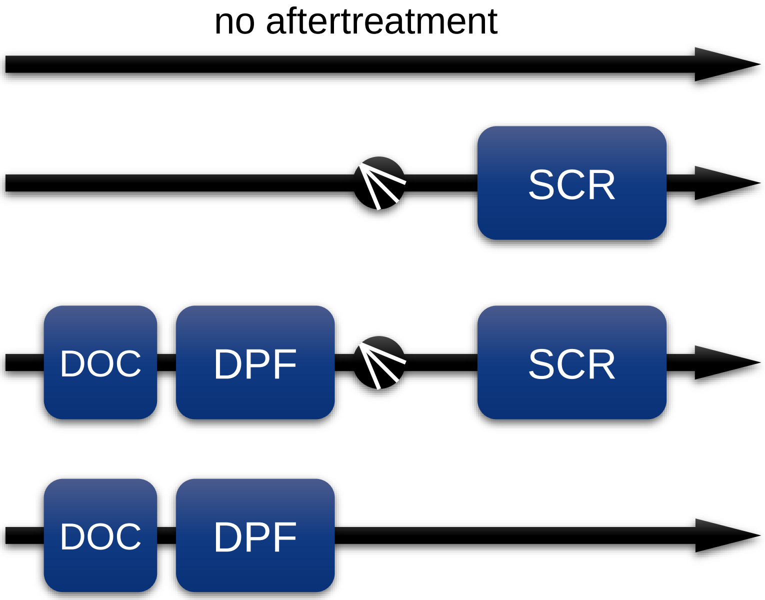

DOC optional

DPF solutions: bare, coated, partial flow

Broad variety of applicable emission classes: IMO, Locomotive, Gensets, IWW

Mostly less demanding NOx and PM standards, no PN limits ➔ wall flow filter partially not required

High share of lean burn gas engines in this segment ➔ low PM, NOx raw emissions

For engines > 1MW substrates with a square X-section are beneficial

Most important requirement

- **Very low back pressure**
- **Durability / poisoning resistance**

Corrugated Catalyst Technology

Features

Key features of Umicore’s corrugated catalyst technology for large engines

- Proven technology in on- and off-road applications
- Low pressure drop
- Light weight
- Low thermal capacity supporting fast light-off
- High poison and pore blocking resistance
- Scalable
- Available with round and square cross sections

Corrugated Catalyst Breakdown

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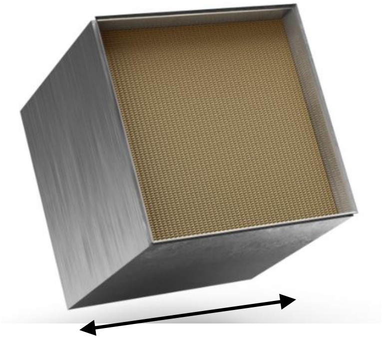
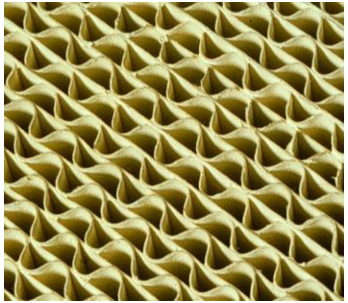
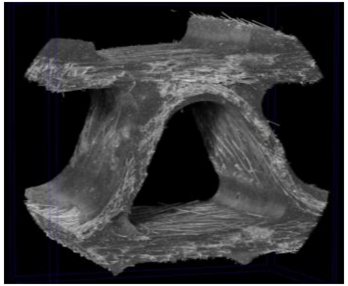
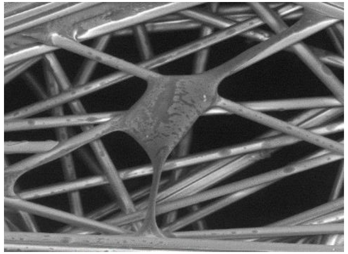
Catalyst element with metal sleeve	Corrugated sheets	Fiber reinforced active material	Fibers
	x10	x250	x2500
			
500 mm	ca. 50 mm	ca. 2 mm	ca. 0.2 mm

Advantages over conventional coated and extruded catalysts at the same activity

- Δp reduction 15-25%
- 30% lower bulk density,
  - Example: 5-6 kg less weight of a standard EU VI HDD SCR catalyst with 27 l of SCR volume

Tri-Modal Pore Structure

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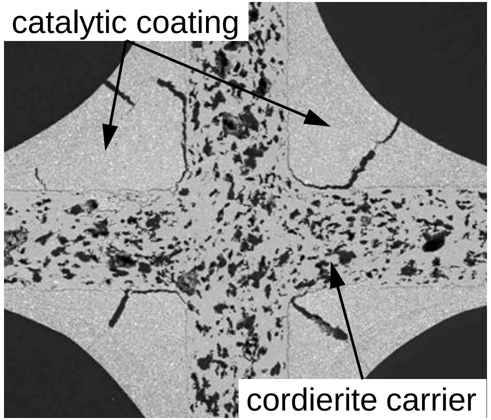
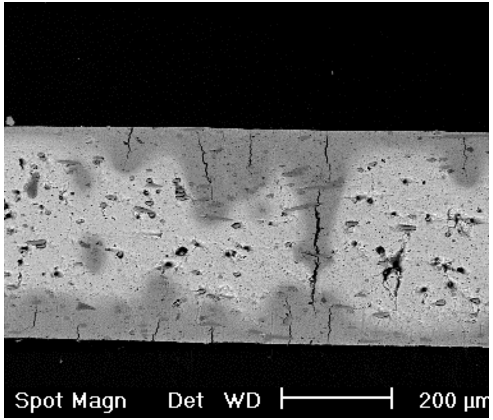
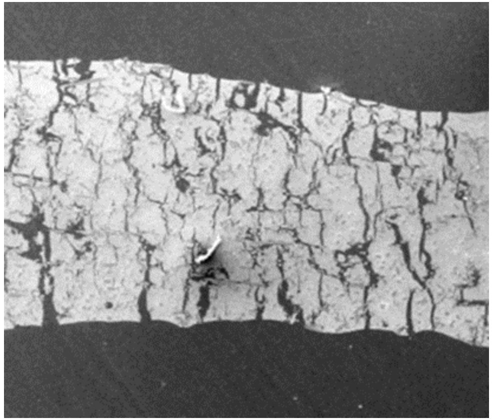
Coated



Extruded



Corrugated



Tri-modal pore size distribution of nano-, meso- and macropores

High catalytic activity and resistance against poisoning and pore blocking

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General Effects of high FSC on Pt Catalysts

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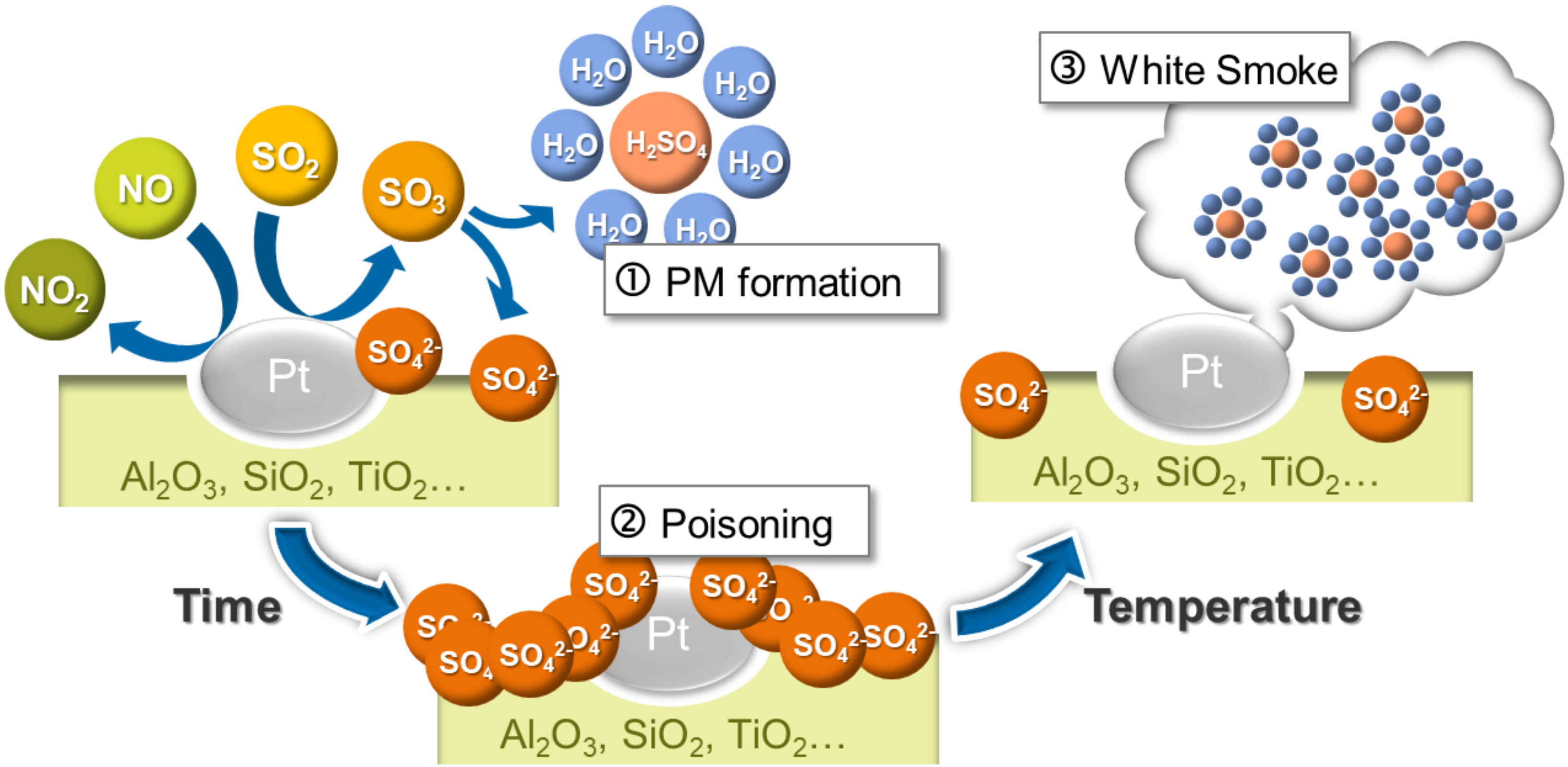

Sulfur Impact on NO_2 Formation

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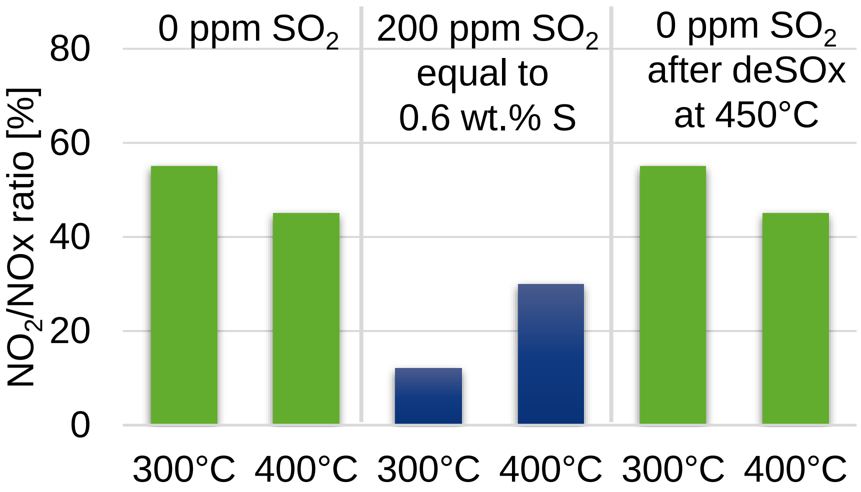
Model gas test, DOC with 10 g/ft³ Pt, aged 100 h, 550°C



NO_2 needed for passive soot removal

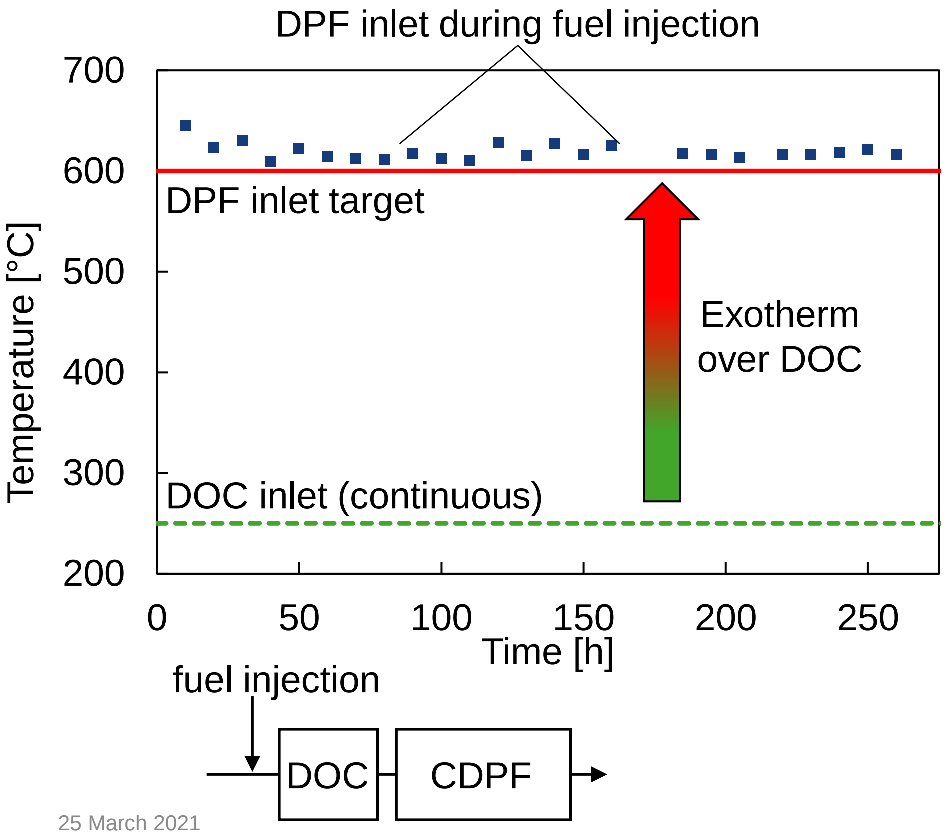
Sufficient NO_2 formation w/o S

NO_2 formation of the DOC is reduced with high S fuels ➔ **passive soot regeneration is limited, but can still work at temperatures of 400°C+**

Sulfur poisoning is reversible at elevated temperatures of 450°C

Feed gas: 1000 ppm NO, 200 ppm C_3H_6/CO, 0/200 ppm SO_2, GHSV=50.000 h^{-1}

Heat-Up Tests with high fuel sulfur content



Durability run on a Diesel burner

- Test duration: 250 h
- Fuel sulfur content: 1.600 ppmw
- Fuel injection: 15 min every 10 h

No degradation of the DOC heat-up function!

Active regeneration with high S fuel possible

Precious Metal Free Coating for PM Reduction

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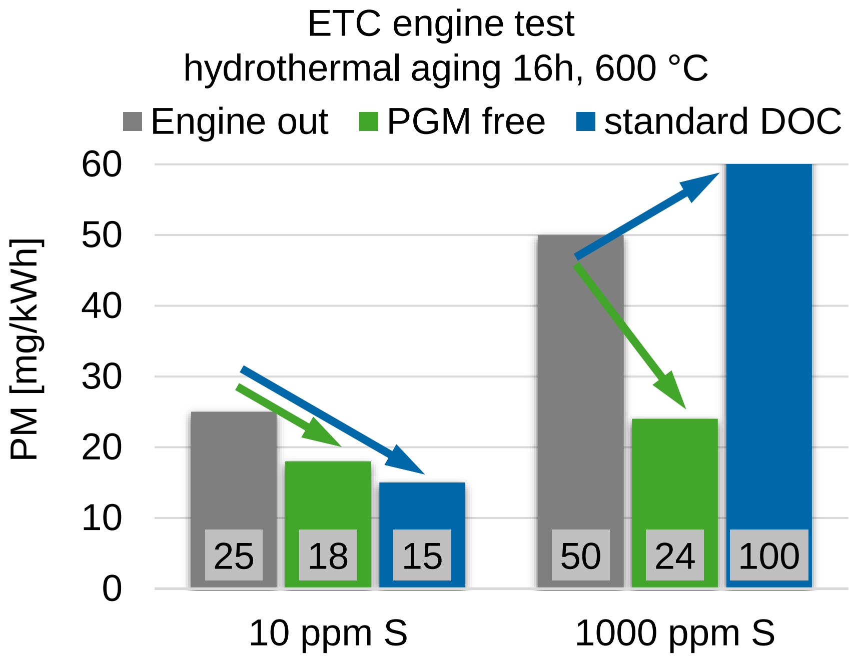

PM decrease by means of VOC oxidation

FSC influencing engine out PM emissions

Standard DOC

- good for low FSC
- PM increase at high FSC due to $SO_2 \rightarrow SO_3$ oxidation

Umicore PGM free coating

- avoiding SO_3 formation
- significant PM mass reduction at high and low FSC

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LNG as a Marine Fuel

Significant reduction of PM, SOx, NOx compared to HFO and MGO fueled engines undisputed

LNG is considered as alternative fuel to reduce CO_2 emissions through lower carbon content of CH_4, especially for marine propulsion

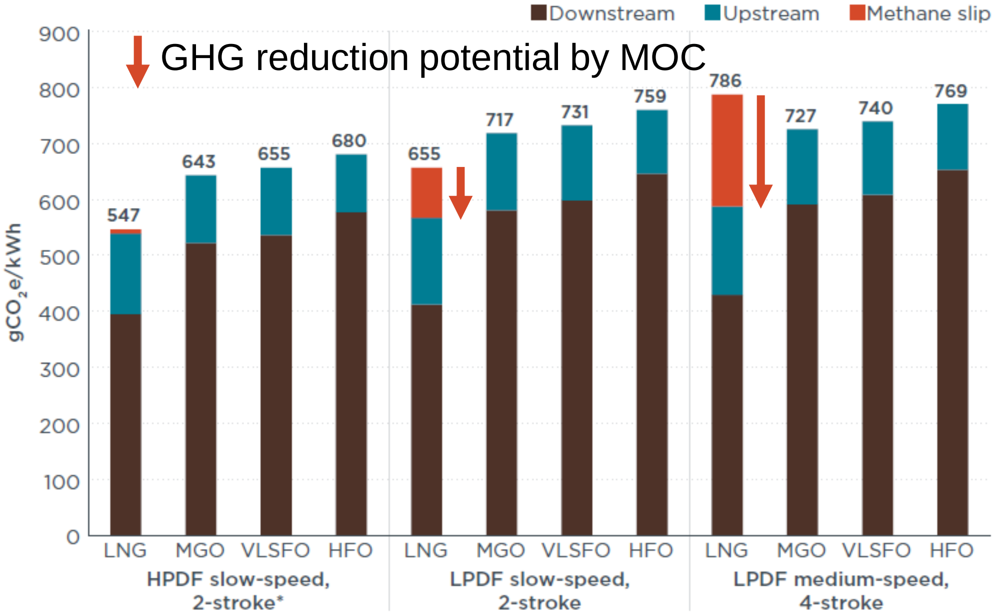
Methane: GWP (100 yrs)=28, GWP (20 yrs)=84

Key factors for the exploitation of the GHG mitigation potential (Well-to-Wake balancing)

- leakage rates in LNG production and distribution
- **methane slip during combustion**

Methane oxidation catalyst (MOC) is an enabler

Life-cycle GHG emissions by engine and fuel type, 100-year GWP



Source: The climate implications of using LNG as a marine fuel, ICCT, 2020

The big challenge of deactivation

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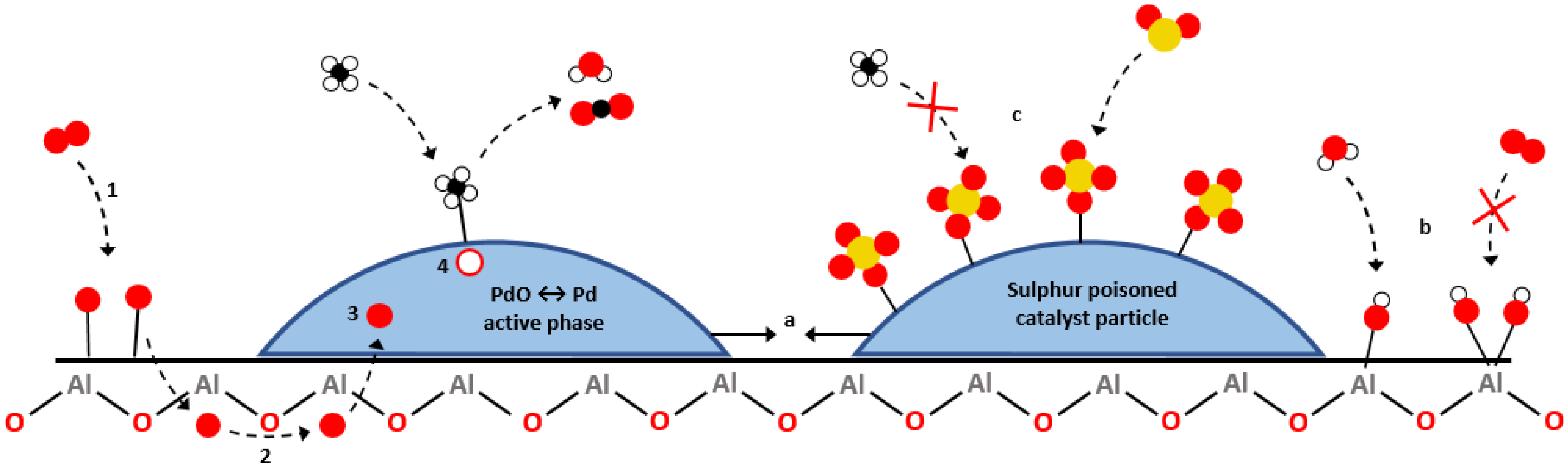
Working principle and deactivation of classic Pd/Al_2O_3 catalyst for complete methane oxidation



Al_2O_3 support

Support-assisted Mars-van Krevelen mechanism:

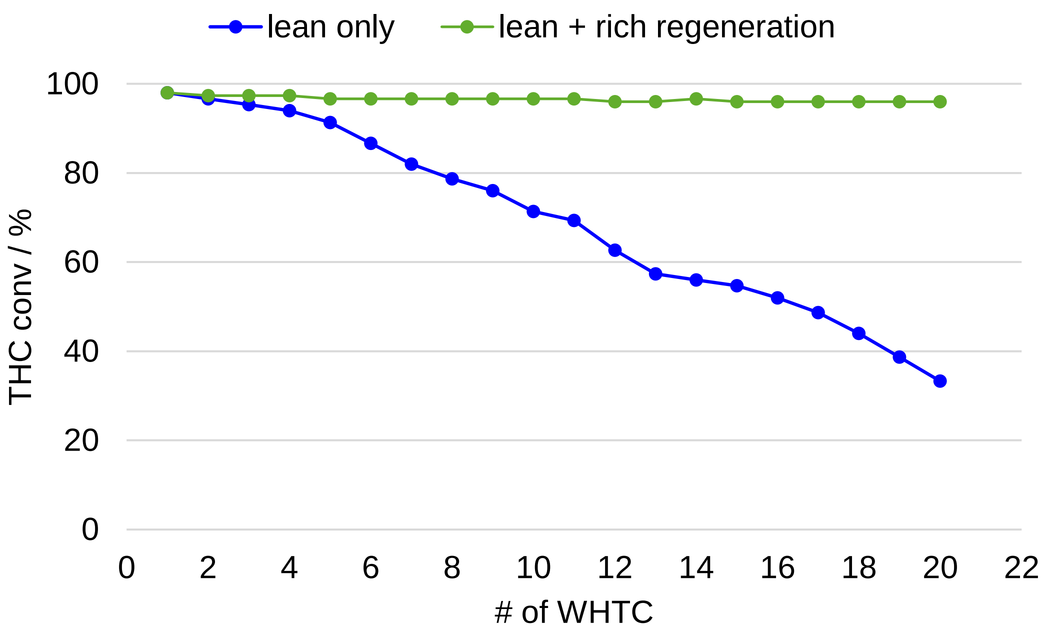
1. Oxygen is adsorbed on support surface
2. Oxygen is transported through support
3. Oxygen fills O-vacancies in PdO particles
4. PdO oxidizes CH_4, forming new O-vacancy

Deactivation in Pd-based methane oxidation catalysts:

a) Thermal deactivation caused by metal particle sintering.
b) Chemical deactivation caused by the presence of water which forms hydroxyls that block support oxygen uptake.
c) Chemical deactivation caused by the presence of SO_2 which forms inactive $PdSO_4$ on the catalyst surface.

Lean Operation and Regeneration

Engine bench demonstration



Cycle conditions:

- T_min = 200°C
- T_max = 550°C
- T_avr = 450°C
- EN590 Diesel (<10 ppm S)

Regeneration strategy:

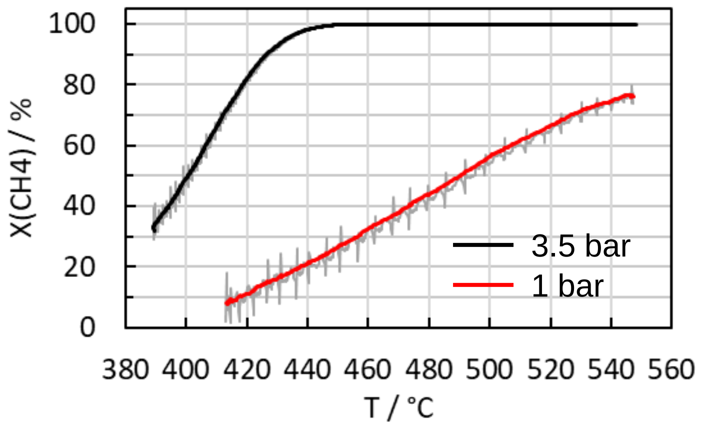
- λ < 1 for a few seconds (PdOH ➔ Pd)
- λ > 1 (Pd ➔ PdO)

Lean MOC operation is possible when applying adequate regeneration measures

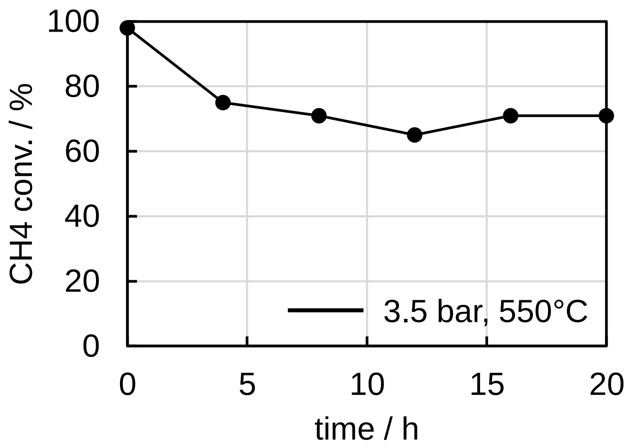
MOC Lean Operation Upstream T/C

Influence of Pressure

Light-off with H_2O, no SO_2



Const. temp. with H_2O, 20 ppm SO_2



1000 ppm CH_4, 250 ppm CO, 60.000 1/h, 10% O_2, 10% H_2O, 5% CO_2

- Positive effect of elevated pressure on MOC activity
- Water inhibition reduced

- Sulfur poisoning less pronounced
- 60-70% CH_4 conversion seem possible if p and T are high enough

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Customized catalyst solutions needed to satisfy the requirements of large engines

Umicore's corrugated SCR catalyst technology

- high performance, well proven, light-weight, low pressure drop
- Dual function SCR for CO, HC and NH_3 control

High sulfur fuels

- NO_2 based DPF regeneration limited, but possible if temperatures are adequate
- Active DPF regeneration based on fuel injection upstream a DOC is a feasible solution
- PGM free solutions available for soot reduction and SO_3 (H_2SO_4) suppression

Methane oxidation catalyst

- MOC products available for pre-turbine installation ($T \geq 500°C$, p_{abs} >1 bar) and post turbine with engine regeneration measures
- Still a long way to go for a durable MOC for post turbine installation and lean only operation (T_{50}<450°C, S and H_2O resistant)

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materials for a better life

Questions and feedback are welcome!

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