Interaction effects on deactivated exhaust aftertreatment catalysts run on biofuels

Sandra Dahlin

POKE Summer School

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Sandra Dahlin – that´s me

- 2014 – 201X: Ph.D. student at the division of Chemical Technology, KTH
  - started April 1st

- 2012 – 2014: Development engineer at Scania
  - Engine performance and emissions

- 2012: Graduated as M.Sc. in chemical engineering, KTH
  - Master thesis at Scania – thermal ageing of SCR catalysts

Outline

- Overview
  - Emissions and emission challenges
  - Exhaust aftertreatment system
- Scope of my project
- Input to my project – results from a Scania-project

Emissions from diesel engines

- Nitrogen oxides (NO_x)
- Particulate matter (PM)
- Carbon monoxide (CO)
- Hydrocarbons (HCs)
- Methane CH_4
- Carbon dioxide (CO_2)
- Laughing gas (nitrous oxide, N_2O)

Regulated pollutants

Greenhouse gases

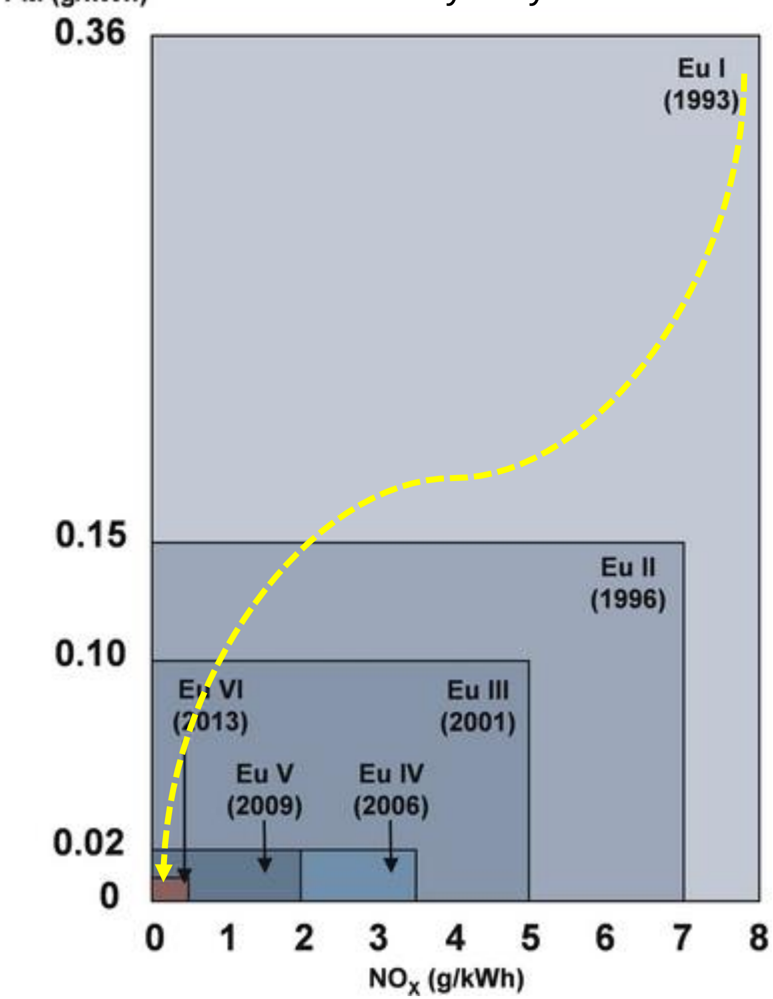
Increasingly stringent emission legislations..

Euro VI
- NOx
- PM (mass and *number*)
- CO
- HC
- *NH_3*

Durability

Beyond Eu VI..
- Greenhouse gases

Heavy-duty trucks



Volvo Trucks Sweden, Utsläpp från lastbilar, http://www.volvotrucks.com/trucks/sweden-market/sv-se/aboutus/environment/our-trucks-and-services/Pages/Emissions-from-trucks.aspx

Emission reduction strategies

- Reduce the production of emissions
  - Engine tuning
  - Exhaust gas recirculation (EGR) to reduce NO_x production
- **Exhaust aftertreatment**
  - Catalysts/traps
  - Filters

Reducing greenhouse gas emissions

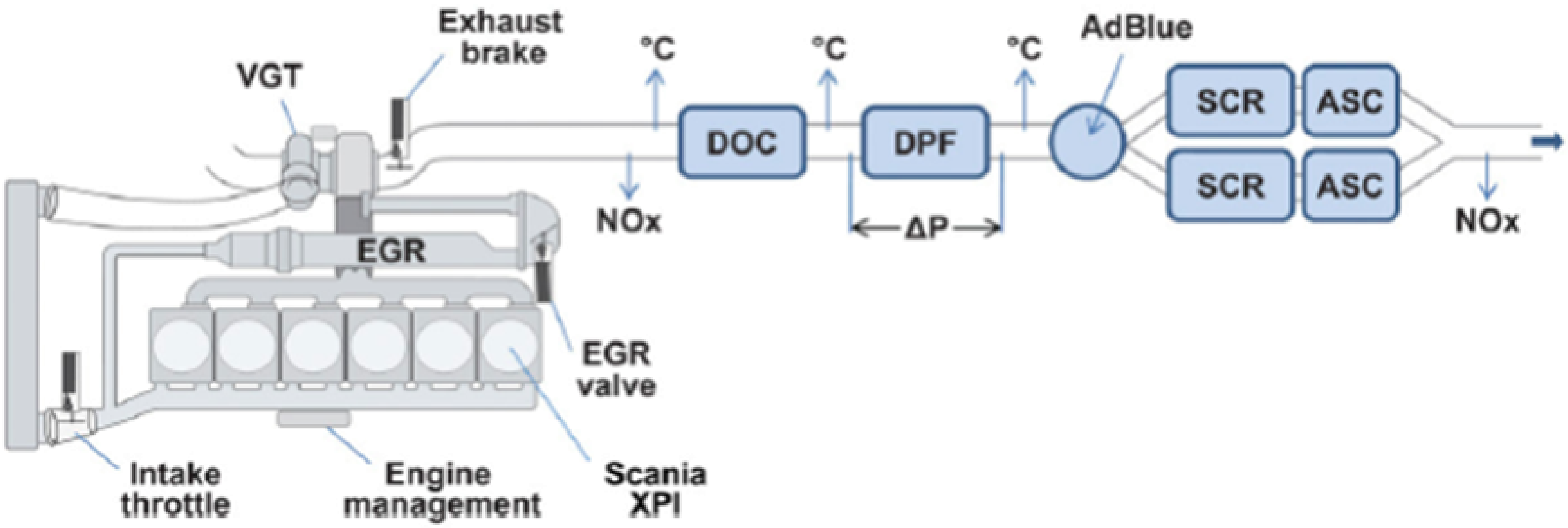
- Improve efficiency
- **Alternative/renewable fuels**

So what do we need to fulfill today and future emission legislations?

- *Active* and *durable* catalysts

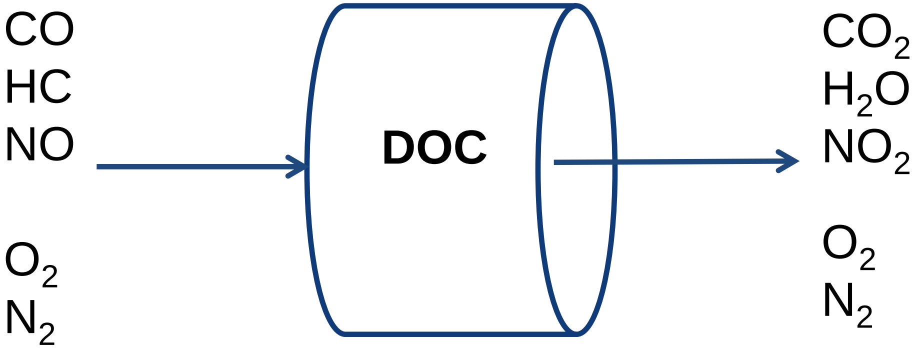
- Change to *renewable* fuel

Scania's aftertreatment strategy



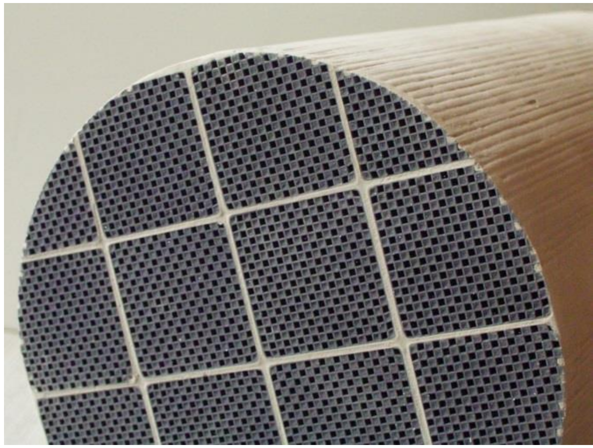
Diesel oxidation catalyst (DOC)

- Oxidizes CO, hydrocarbons and some of the particulates into CO_2 and H_2O
- Oxidizes some NO into NO_2



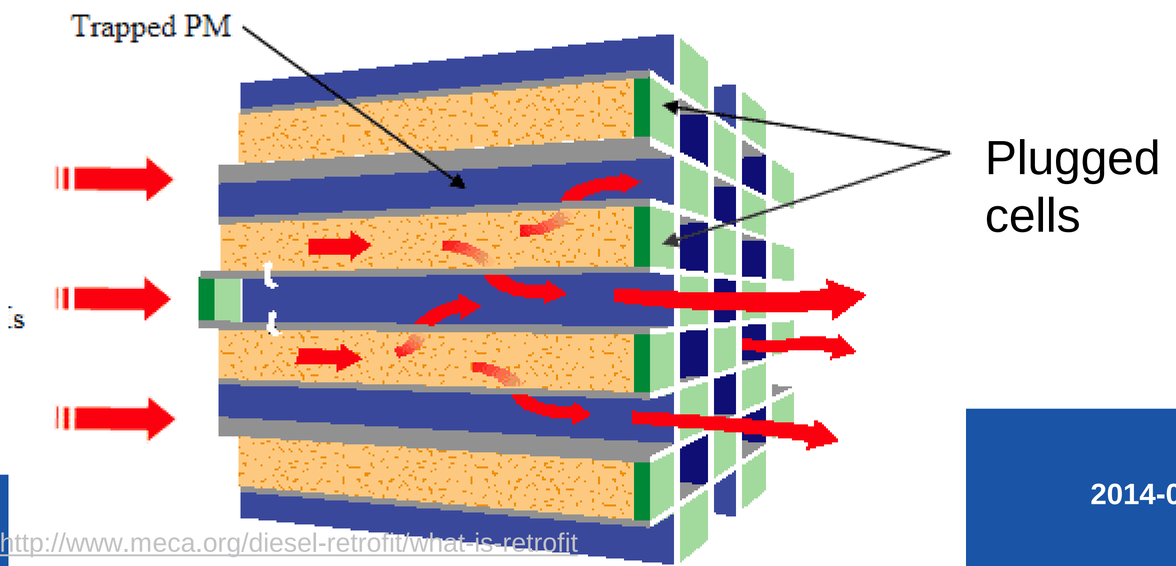
http://www.meca.org/diesel-retrofit/what-is-retrofit

Diesel particulate filter (DPF/CSF)



http://www.cambustion.com/engineering-services/dpf-testing

- Traps particulates (soot and ash)
- Regeneration of filter necessary with time due to pressure build-up
  - Passive (using NO_2)
  - Active
- Catalyzed or non-catalyzed

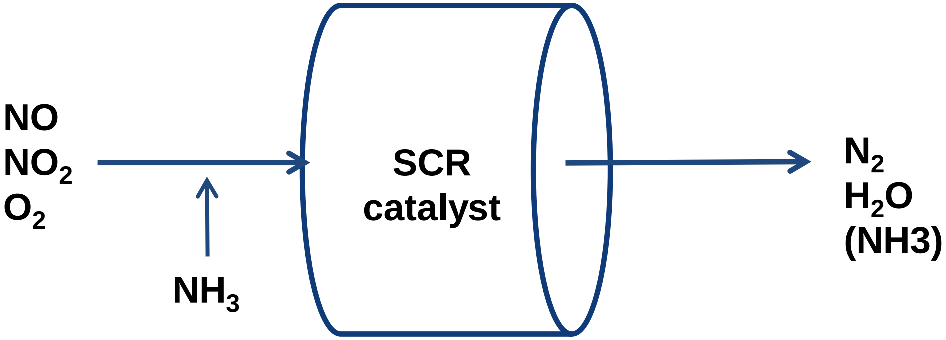


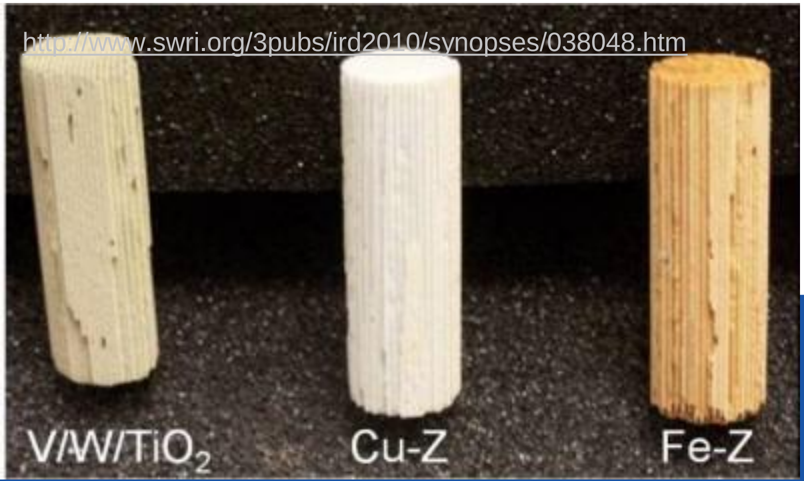
http://www.meca.org/diesel-retrofit/what-is-retrofit

Selective catalytic reduction (SCR) catalyst

http://www.gasgoo.com/auto-images/air-intake-exhaust-system-428/1411353.html

- Reduces NOx to N_2 and H_2O
- Uses NH_3 as reduction agent
  - Water solution of urea (Adblue)used as NH_3 precursor





Standard reaction

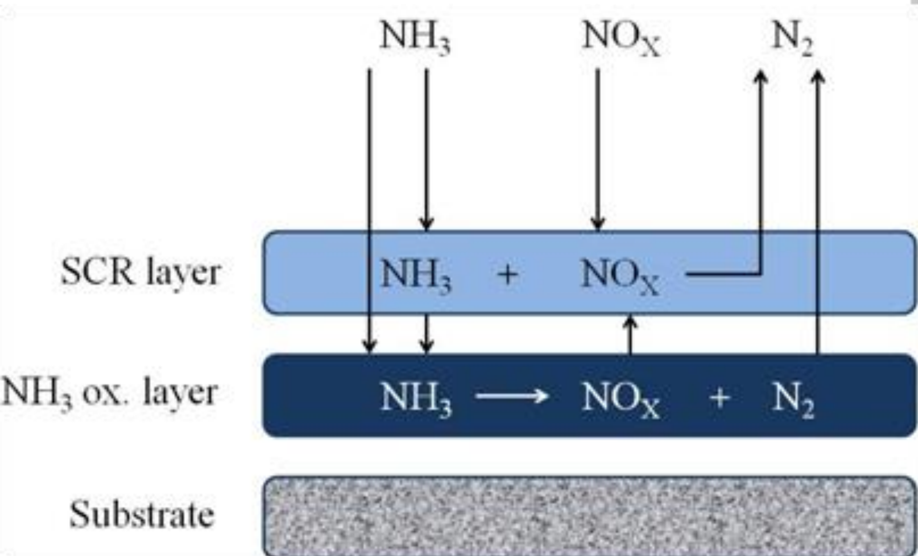
Fast reaction

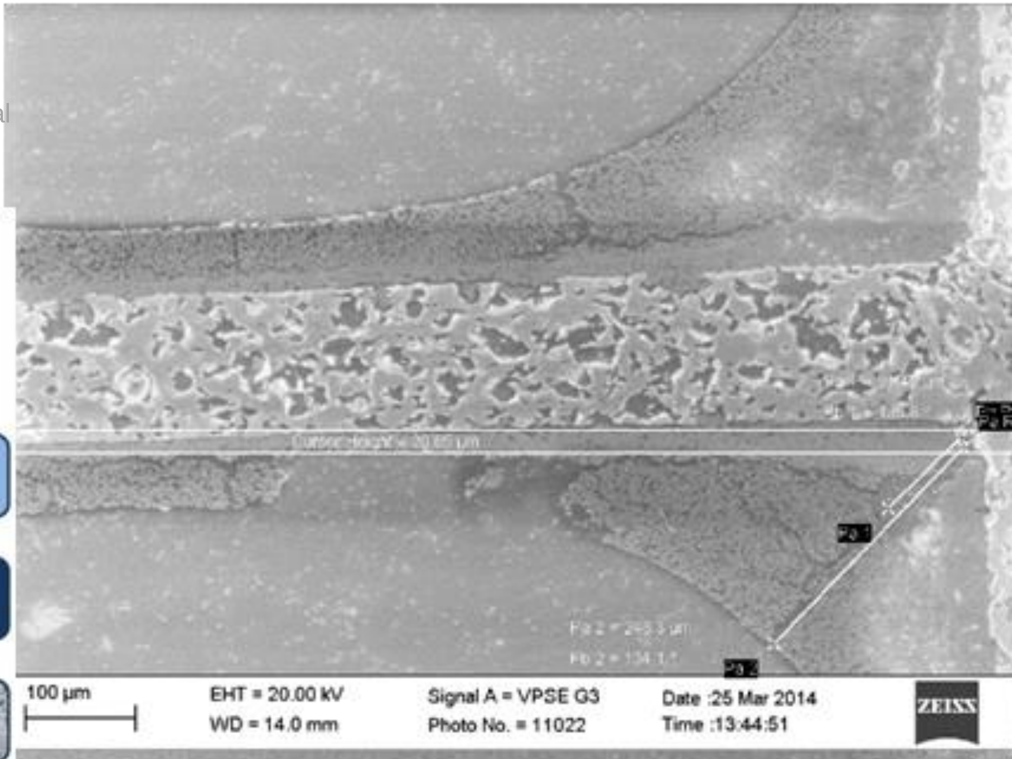
Slow reaction

Ammonia slip catalyst (ASC)

- Excess of NH_3 used for full conversion of NO_x
- ASC used downstream SCR to prevent NH_3 slip
  - Oxidizes NH_3 into N_2 and H_2O
  - Usually also have an SCR-ability and works thereby as an extension of the SCR catalyst

Image source: Effects of Thermal Aging and Sulfur Poisoning on the Material Properties of Dual-Layer Ammonia Slip Catalysts, Master thesis, Peter Wikholm, 2014





The DOC plays a key role in the system

- Takes care of unhealthy CO and hydrocarbons
- Oxidizes NO into NO_2
  - Facilitates particle filter regeneration
  - Promotes the fast SCR reaction → increases the NOx removal performance

- Often first in the exhaust system – subjected to harsch (chemical) environment

- **Deactivation of the DOC will affect the total performance of the system!!**

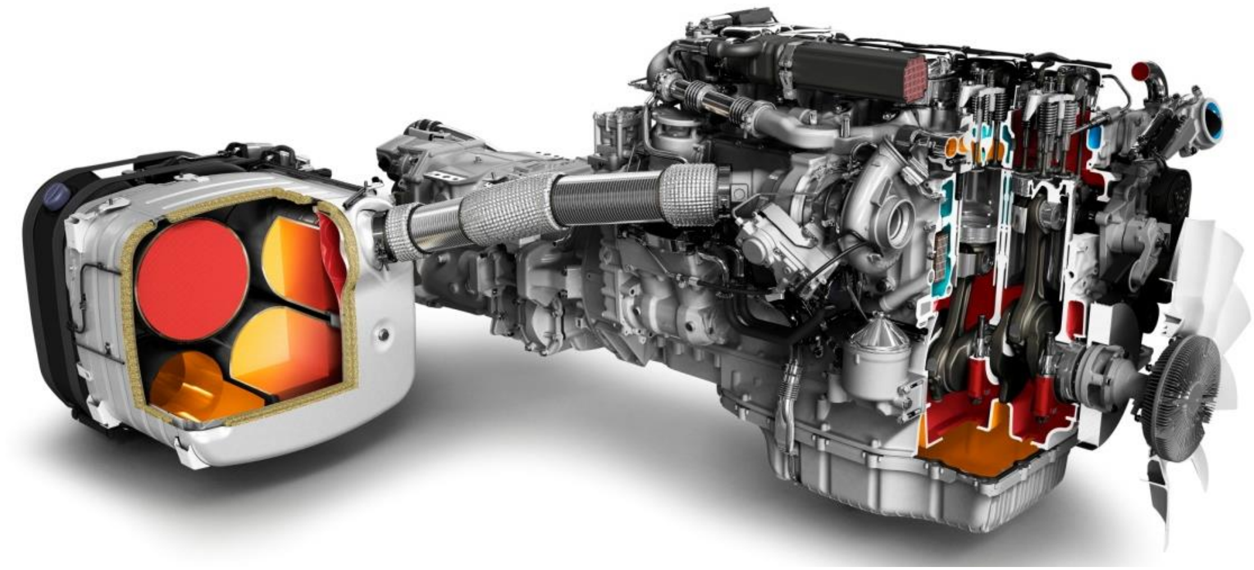
Challenges

- Increased fuel diversity
- Catalyst deactivation
  - Thermal deactivation due to high exhaust temperatures
  - Chemical deactivation due to elements from oil or fuel e.g. Na, K, P
- Interaction between all exhaust treatment components

LIFE TIME

HIGH/LOW TEMPERATURE

CHEMICAL ENVIRONMENT



This project..

KTH Kemivetenskap

CHALMERS

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HALDOR TOPSØE

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SCANIA

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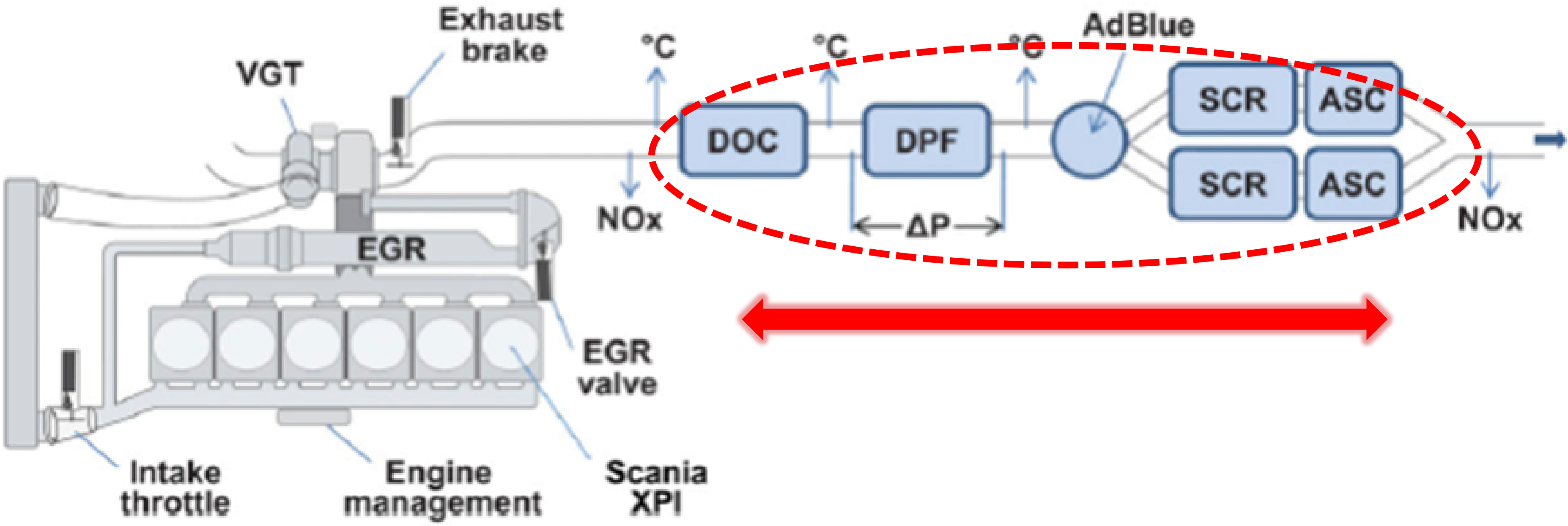
Focus of the project

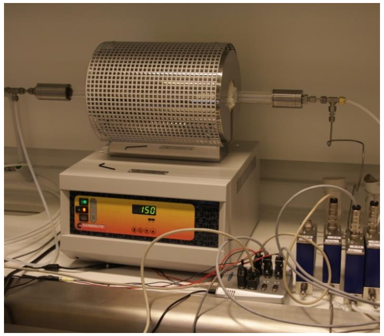


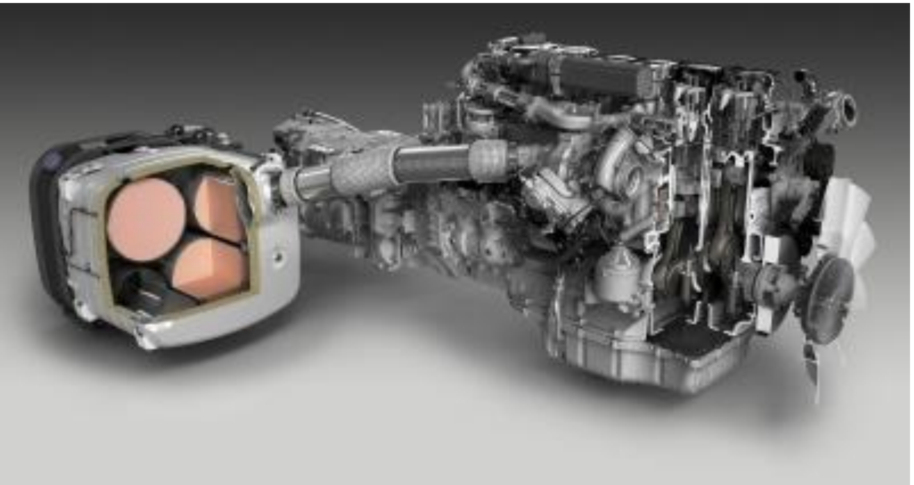
How do the different catalysts in an exhaust treatment system interact when thermally and chemically aged under biofuel operation?

Tasks in the project

- Develope a **lab-scale aging methodology** to verify the **effect of biodiesel** on the **total performance** of the exhaust system

- Map **deactivation** mechanisms and **interaction effects**
  - Qualitatively, quantitatively
  - Identify clear limits regarding temperture and poisoning elements for the whole exhaust aftertreatment system

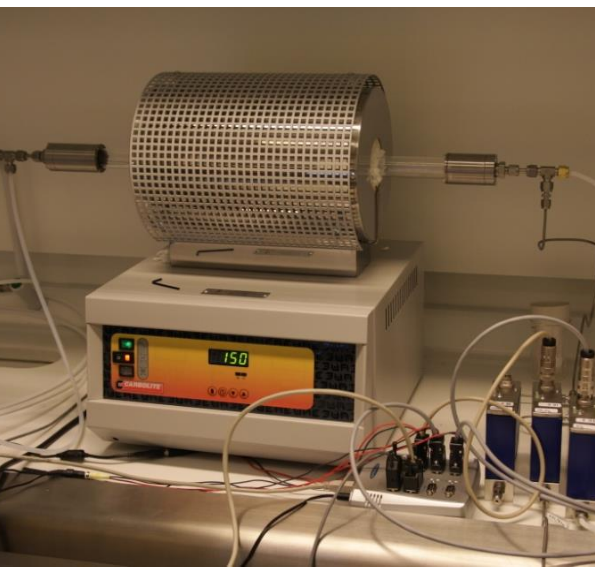




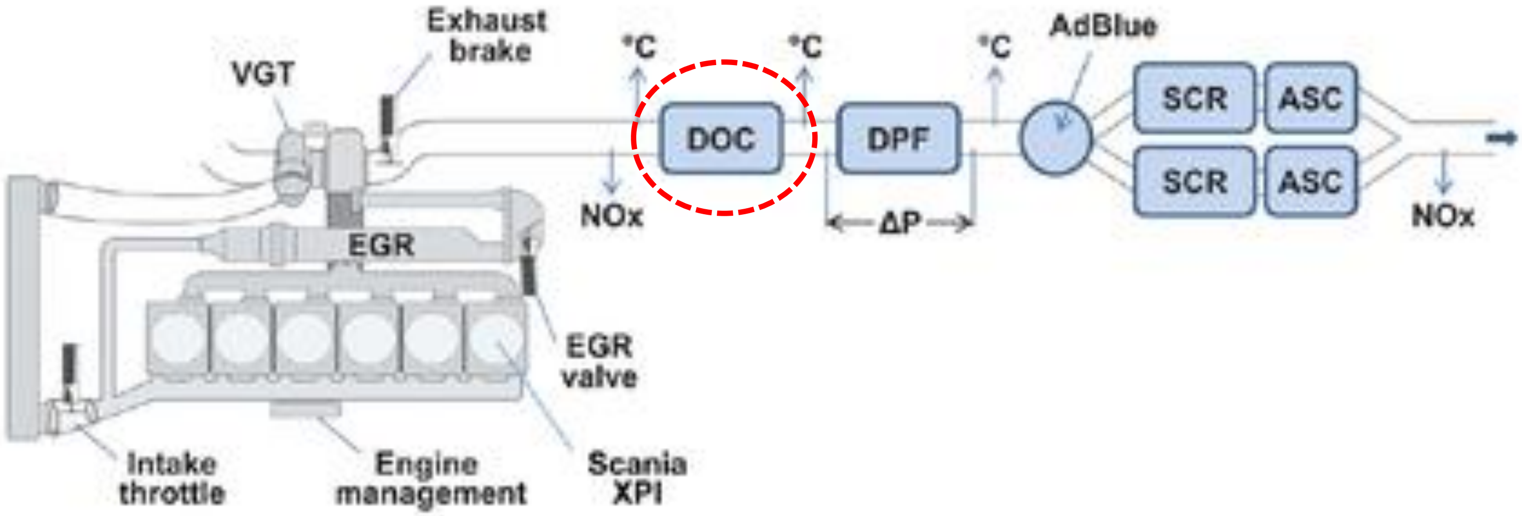
Input to my project

Effect of different fuels, fuel qualities and lube oils on chemical aging of exhaust catalysts

Na K Ca Mg P S Zn




Catalysts in focus



DOC, $PtPd/Al_2O_3$, samples from commercial monolith

Experimental design

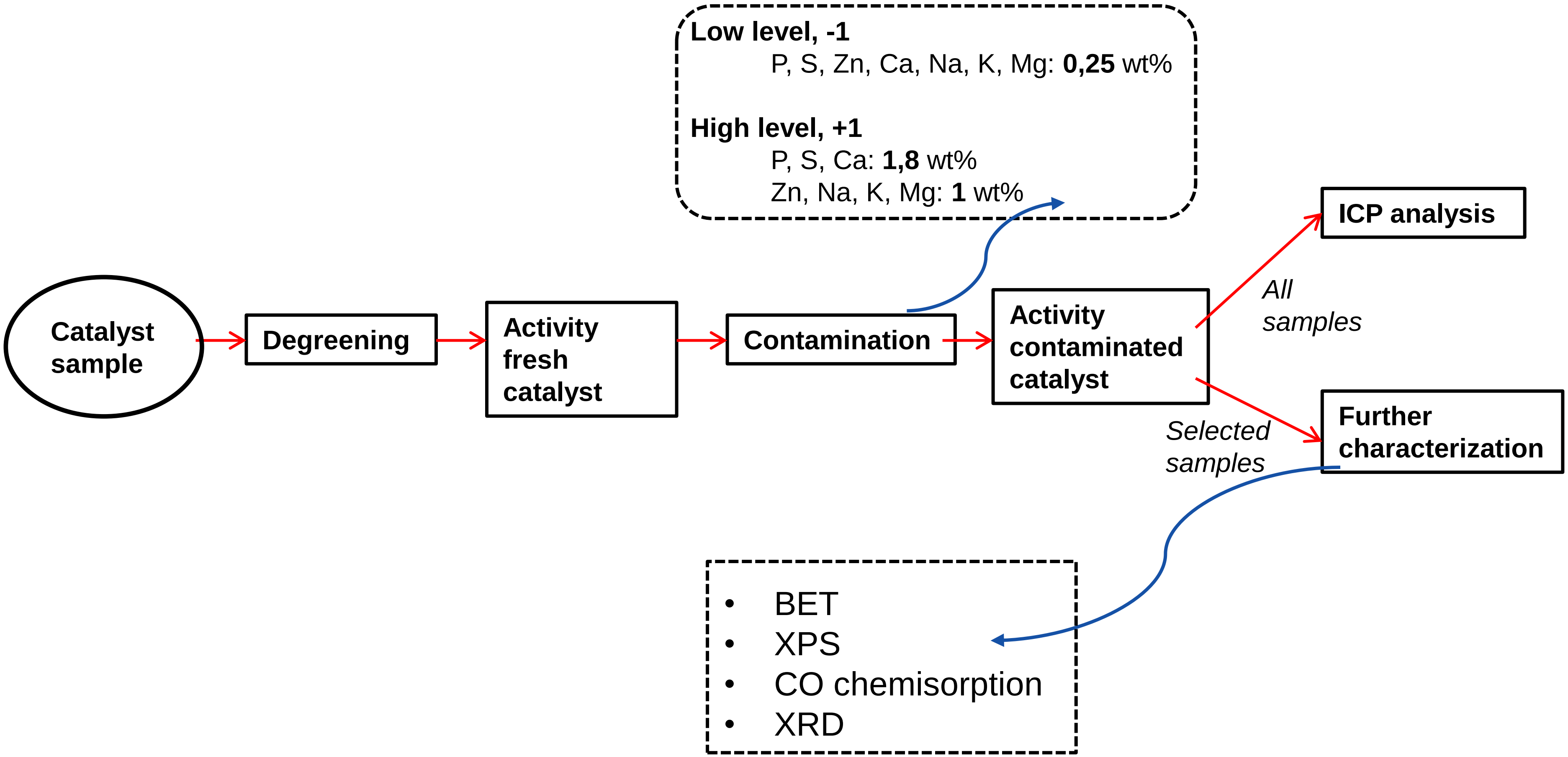
- Poisoning effect
  - -1: Small poisoning effect
  - +1: Large poisoining effect
- Reduced factorial design 2^{7-2}
- Randomized sequence
- 6 replicates
- ∑ 38 observations

→ **Which poisons give rise to a significant effect on NO oxidation?**

→ **Are there any significant interaction effects?**

	P	S	Zn	Na	Mg	Ca	K
1	-1	-1	-1	-1	-1	1	1
2	-1	-1	-1	-1	1	1	-1
3	-1	-1	-1	1	-1	-1	-1
4	-1	-1	-1	1	1	-1	1
5	-1	-1	1	-1	-1	-1	1
6	-1	-1	1	-1	1	-1	-1
7	-1	-1	1	1	-1	1	-1
8	-1	-1	1	1	1	1	1
9	-1	1	-1	-1	-1	-1	-1
10	-1	1	-1	-1	1	-1	1
11	-1	1	-1	1	-1	1	1
12	-1	1	-1	1	1	1	-1
13	-1	1	1	-1	-1	1	-1
14	-1	1	1	-1	1	1	1
15	-1	1	1	1	-1	-1	1
16	-1	1	1	1	1	-1	-1
17	1	-1	-1	-1	-1	-1	-1
18	1	-1	-1	-1	1	-1	1
19	1	-1	-1	1	-1	1	1
20	1	-1	-1	1	1	1	-1
21	1	-1	1	-1	-1	1	-1
22	1	-1	1	-1	1	1	1
23	1	-1	1	1	-1	-1	1
24	1	-1	1	1	1	-1	-1
25	1	1	-1	-1	-1	1	1
26	1	1	-1	-1	1	1	-1
27	1	1	-1	1	-1	-1	-1
28	1	1	-1	1	1	-1	1
29	1	1	1	-1	-1	-1	1
30	1	1	1	-1	1	-1	-1
31	1	1	1	1	-1	1	-1
32	1	1	1	1	1	1	1

Experimental procedure



Accelerated chemical aging

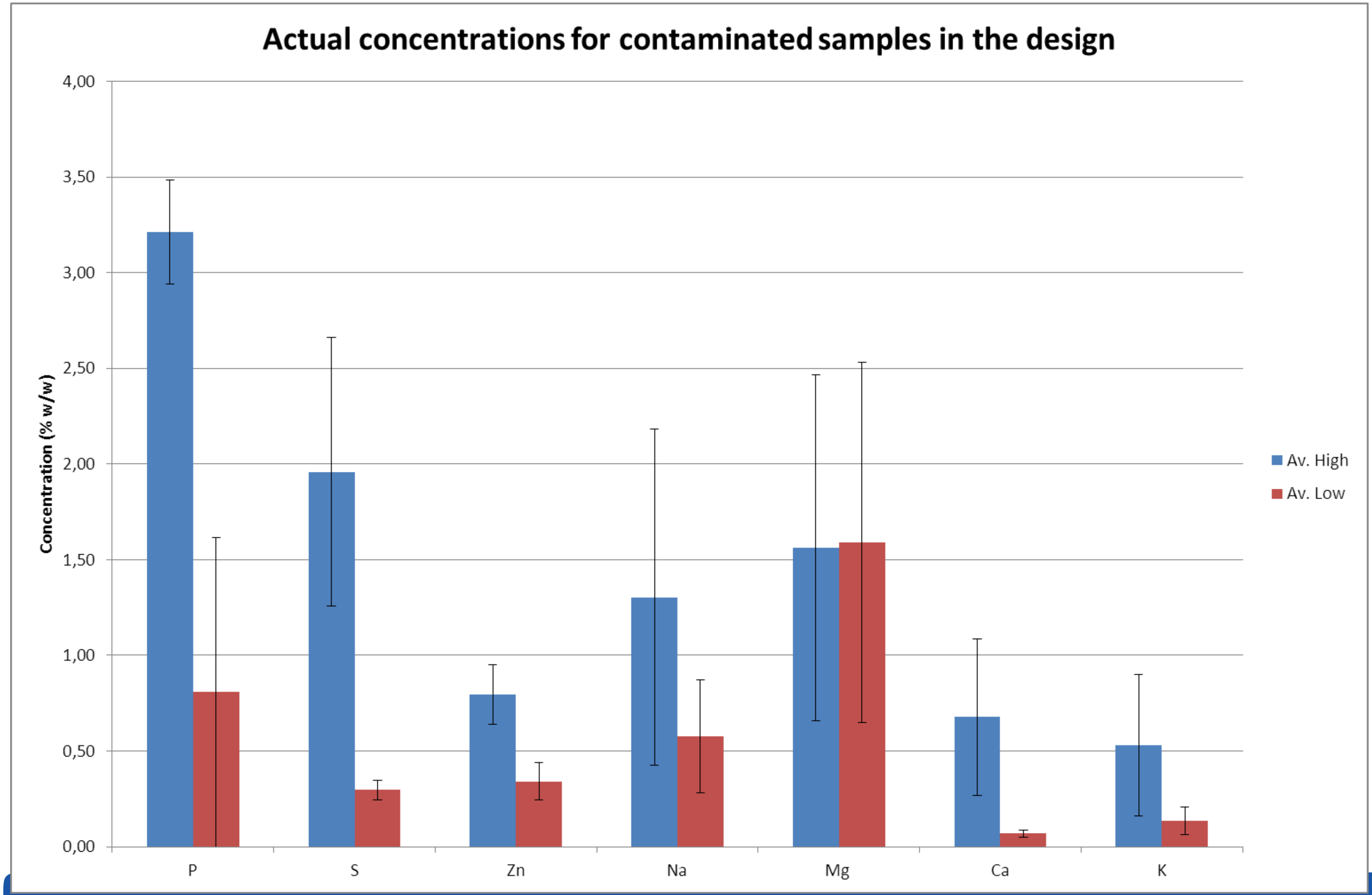
- Gas phase poisoning
  - Injection of aqueous salt solutions to a gas flow
  - Slow accumulation of poisons on the sample
- **Poisoning by impregnation**
  - Wet impregnation of aqueous salt soutions

$(NH_4)H_2PO_4$
$(NH_4)_2SO_4$ $\xrightarrow{\textit{H2O}}$ Stock solution 1

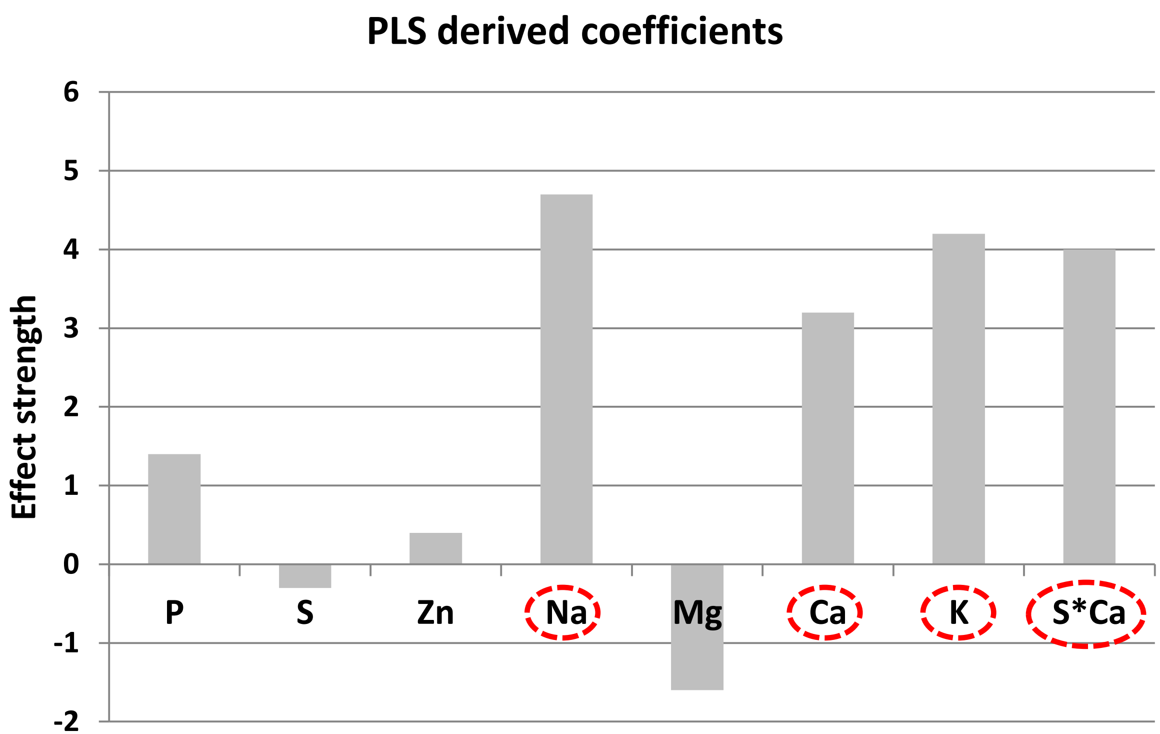
$Zn(NO_3)_2.4H_2O$
$NaNO_3$
$Mg(NO_3)_2.6H_2O$
$Ca(NO_3)_2.4H_2O$
KNO_3 $\xrightarrow{\textit{H2O}}$ Stock solution 2

Impregnation in two steps
Drying/Degreening
→ Chemically aged catalyst

Results

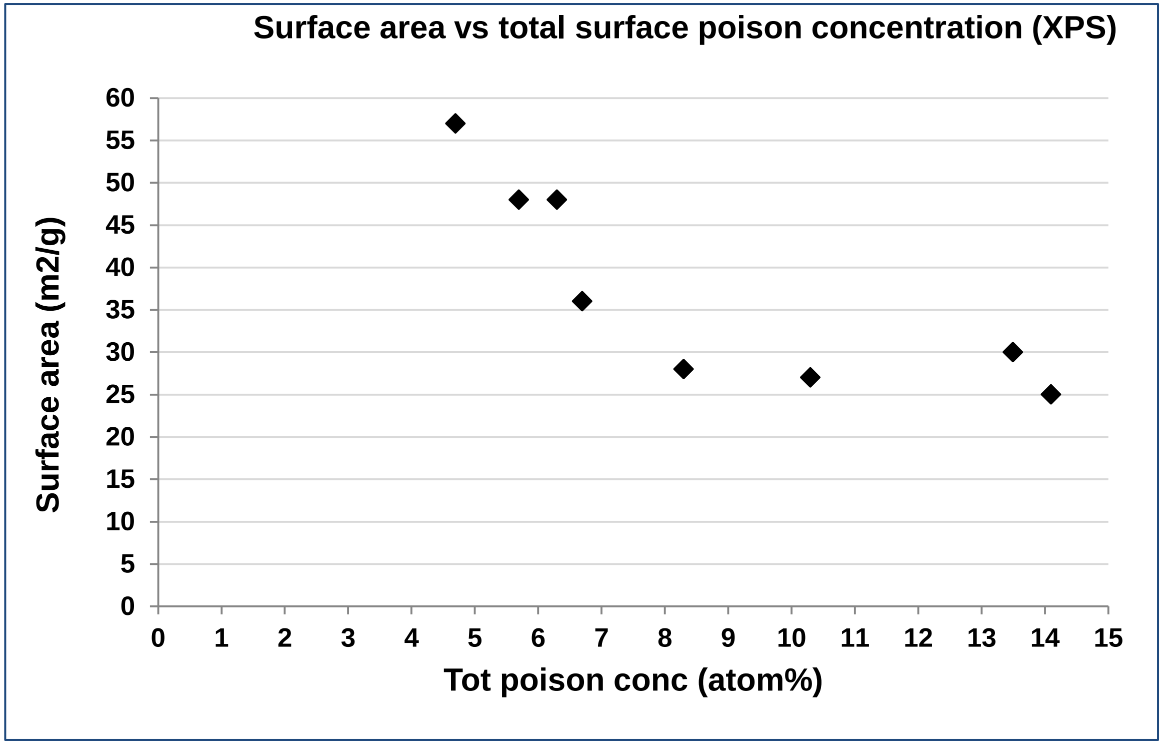

Actual concentrations for contaminated samples in the design
Concentration (% w/w)
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
P
S
Zn
Na
Mg
Ca
K
Av. High
Av. Low

Effect strength of the different poisons and interaction effects



High values - stronger poisoning effect
Low values - less poisoning effect

Catalyst characterization – surface area vs total poison concentration



Increased poison amount on the catalyst
→ decreased surface area

Type of species on surface (XPS)

- Fresh samples - Al_2O_3, SiO_2, MgO and Na_2O
- Lab contaminated samples - besides the above mentioned also Ca^{2+}, Zn^{2+}, S and P
  - S is present as sulfate
  - P is likely present as P_2O_5
- Similar compounds were found in the engine-aged samples

Crystalline phases (XRD)

- No crystalline phases formed between poisons and washcoat (ie no cryst. $AlPO_4$ or $Al_2(SO4)_3$) in the lab-aged or engine-aged samples

- In some of the lab-aged and both the engine-aged samples some extra peaks not related to washcoat or cordierite substrate found
  - $CaSO_4$
  - SiO_2

Results summary

- Large variation related to the contamination procedure and higher than expected experimental variation somewhat limits the conclusions which can be drawn from the experiments

- Na, K, and Ca and Ca*S exhibit strong poisoning effects on the DOC catalyst

- Important for future work
  - More reliable contamination procedure
  - Reduced experimental variation so that lower contamination levels can be studied

Acknowledgements

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Swedish Energy Agency

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Thank you for your attention!

Questions?

KTH ROYAL INSTITUTE
OF TECHNOLOGY

Sandra Dahlin

sanj@kth.se
+46 8 553 854 95