Interaction effects on deactivated exhaust aftertreatment catalysts run on biofuels

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Sandra Dahlin – that’s me

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

- 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$_2$O)

**Regulated pollutants**

**Greenhouse gases**
Increasingly stringent emission legislations..

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

Beyond Eu VI..
- Greenhouse gases

Heavy-duty trucks

Emission reduction strategies

• Reduce the production of emissions
  – Engine tuning
  – Exhaust gas recirculation (EGR) to reduce NO\textsubscript{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$_2$O
- Oxidizes some NO into NO$_2$
Diesel particulate filter (DPF/CSF)

- 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

http://www.cambustion.com/engineering-services/dpf-testing
Selective catalytic reduction (SCR) catalyst

- Reduces NOx to N₂ and H₂O
- Uses NH₃ as reduction agent
  - Water solution of urea (Adblue) used as NH₃ precursor

*Fast reaction*

*Standard reaction*

*Slow reaction*


http://www.swri.org/3pubs/ird2010/synopses/038048.htm
Ammonia slip catalyst (ASC)

- Excess of NH₃ used for full conversion of NOₓ
- ASC used downstream SCR to prevent NH₃ slip
  - Oxidizes NH₃ into N₂ and H₂O
  - Usually also have an SCR-ability and works thereby as an extension of the SCR catalyst

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 $\rightarrow$ 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..

Interaction effects on deactivated exhaust aftertreatment catalysts run on biofuels
How do the different catalysts in an exhaust treatment system interact when thermally and chemically aged under biofuel operation?
Tasks in the project

• Develop 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 temperature 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

$Na \quad K \quad Ca \quad Mg \quad P \quad S \quad Zn$
Catalysts in focus

DOC, PtPd/Al$_2$O$_3$, samples from commercial monolith
Experimental design

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

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

→ Are there any significant interaction effects?
Experimental procedure

Degreening
Activity fresh catalyst
Contamination
Activity contaminated catalyst

Low level, -1
P, S, Zn, Ca, Na, K, Mg: 0.25 wt%

High level, +1
P, S, Ca: 1.8 wt%
Zn, Na, K, Mg: 1 wt%

ICP analysis

All samples
Selected samples

Further characterization

• BET
• XPS
• CO chemisorption
• XRD
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 solutions

Stock solution 1:
- $(\text{NH}_4)_2\text{HPO}_4$
- $(\text{NH}_4)_2\text{SO}_4$

Stock solution 2:
- $\text{Zn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$
- $\text{NaNO}_3$
- $\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$
- $\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$
- $\text{KNO}_3$

$\text{H}_2\text{O}$

Impregnation in two steps
Drying/Degreening

Chemically aged catalyst
Results

Actual concentrations for contaminated samples in the design

Concentration (% w/w)

Av. High
Av. Low

P
S
Zn
Na
Mg
Ca
K

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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$_2$O$_3$, SiO$_2$, MgO and Na$_2$O
- 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$_2$O$_5$
- Similar compounds were found in the engine-aged samples
Crystalline phases (XRD)

- No crystalline phases formed between poisons and washcoat (i.e. no cryst. AlPO$_4$ or Al$_2$(SO$_4$)$_3$) 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.
Thank you for your attention!

Questions?
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