Selective Diesel Oxidation Catalysts for Hydrocarbons

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Master of Science Thesis in Chemical Engineering
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KTH Chemical Engineering and Technology
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Abstract

Most vehicles produce emissions containing hydrocarbons (HC), nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO), and particulates (PM), which all affect environment as well as humans. The emissions are regulated by EU Emission Standards, where the latest standard for heavy-duty vehicles is called Euro VI. This has all lead to development of an exhaust aftertreatment system. In short, Scania’s exhaust aftertreatment system consists of diesel oxidation catalyst (DOC), diesel particulate filter (DPF), selective catalytic reduction (SCR) catalyst and ammonia slip catalyst (ASC).

The purpose with this master thesis was to investigate whether it is possible to selectively promote HC oxidation over NO oxidation for a DOC. The work comprised both literature study and experiments in full-scale in engine test bed. Focus was on catalyst distribution of platinum (Pt) and palladium (Pd) as well as the ratio between these two. Generally, zone coated DOCs enable higher conversion than uniformly coated DOCs, especially for exothermic reactions such as the HC oxidation. Pt and Pd have different properties, where Pt has higher overall oxidation performance compared to Pd. Pd has higher thermal stability and lower NO oxidation performance compared to HC oxidation performance. The experiments included testing of six commercially available DOCs with varying Pt:Pd ratios and varying axial distribution. The tests included measurement of HC and NO oxidation performance at different mass flows and temperatures.

The results showed a strong dependence between the HC oxidation and zone-coated DOCs. Whereas the same dependence was not found for NO oxidation. Furthermore, no conclusive results regarding oxidation performance for varying Pt:Pd-ratios were found.
Sammanfattning

Utsläpp från de flesta fordon innehåller bland annat kolväten (HC), kväveoxider (NOₓ), kolmonoxid (CO) och partiklar (PM), vilka påverkar både miljö och människor. EU-standarder reglerar utsläppen och den nyaste lagstiftningen för tunga fordon kallas Euro VI. Detta har lett till utveckling av avgasefterbehandlingen. Scanias avgasefterbehandling omfattar i korthet dieseloxidationskatalysator (DOC), partikelfilter (DPF), katalysator för selektiv reduktion (SCR) samt oxidationskatalysator för ammoniak (ASC).

Syftet med detta examensarbete var att utvärdera möjligheterna att selektivt främja HC-oxidation framför från NO-oxidation för en DOC. Arbetet omfattade både litteraturstudie och fullskaliga experiment i motorprovcell. Fokus var på katalysatorns distribution av platina (Pt) och palladium (Pd) samt förhållandet mellan dessa två metaller. En zonbelagd DOC har generellt en högre omvandlingsgrad jämfört med en jämnt belagd DOC, vilket speciellt gäller för exoterna reaktioner. Pt och Pd har olika egenskaper, där Pt generellt har högre HC- och NO-oxidationsförmåga än Pd. Pd har högre termisk stabilitet samt lägre NO-oxidationsförmåga jämfört med HC-oxidationsförmåga. Experiment med 6 kommersiellt tillgängliga DOC:er utfördes. De olika DOC:erna hade olika Pt:Pd förhållanden och olika axiell distribution i DOC. HC- och NO-oxidationsförmåga testades för olika massflöden och temperaturer.

Acknowledgement

This master thesis was performed during 2012 at Scania CV AB at Research and Development in group NMTF, Particulate Filter Systems and Oxidation Catalysts. This is the diploma work of my Master of Science in Chemical Engineering for the Energy and Environment at KTH.

This diploma thesis work has truly been an interesting time, where I have got the opportunity to learn a lot of things, work with different people and get insight in the work performed at Scania. First of all, I would like to thank my supervisor David Raymand at Scania for all support, guidance and interesting discussions during this time. Thank you for always taking time to help me, your patience, encouragement and continuous feedback throughout this project! Thanks to my boss, Robert Nordenhök, for giving me this opportunity and engagement in my work. Also, thanks to Daniel Hjortborg for all work, contact with suppliers and input into this project. Many thanks to all at NMTF and neighbouring groups for an inspiring work environment, where everyone always is ready to help, answer questions and discuss solutions. Furthermore, thanks to everybody helping me with the experiments in the engine test bed.

Last but not least, I would also like to thank my examiner Lars Pettersson at KTH for support and assistance. Thanks for inspiring courses during my time at KTH, which arouse my curiosity for the world of catalysis.

Thank you all!

Stockholm, September 2012

Karolin Erwe
# Notations and Abbreviations

Explanation of notations and abbreviations used in the report.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Explanation</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Preexponential factor</td>
<td>-</td>
</tr>
<tr>
<td>$A_{c-s}$</td>
<td>Cross-sectional area of substrate</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
<td>mol/dm$^3$</td>
</tr>
<tr>
<td>$C_{i-ii}$</td>
<td>Carbon chains with $i$-$ii$ atoms</td>
<td>-</td>
</tr>
<tr>
<td>$E$</td>
<td>Activation energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant</td>
<td>Depends on reaction</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of substrate</td>
<td>cm</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant</td>
<td>J/mol, K</td>
</tr>
<tr>
<td>$t$</td>
<td>Space time</td>
<td>h$^{-1}$</td>
</tr>
<tr>
<td>$t_i$</td>
<td>Time</td>
<td>h</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_{Eyy}$,$T_{Xyy}$</td>
<td>Thermocouple number $yy$</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Volumetric flow rate</td>
<td>m$^3$/h</td>
</tr>
<tr>
<td>$V_{DOC}$</td>
<td>DOC volume</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Active catalyst site</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_{\text{reaction}}$</td>
<td>Enthalpy of reaction</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Gas density</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td>$X$, $\eta$, $\gamma$, $\kappa$, $\delta$, $\theta$, $\alpha$</td>
<td>Alumina forms (Al$_2$O$_3$)</td>
<td>-</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Explanation</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>ASC</td>
<td>Ammonia slip catalyst</td>
<td></td>
</tr>
<tr>
<td>CDPF</td>
<td>Catalysed diesel particulate filter</td>
<td></td>
</tr>
<tr>
<td>cpsi</td>
<td>Cell per square inch</td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>Diesel oxidation catalyst</td>
<td></td>
</tr>
<tr>
<td>DPF</td>
<td>Diesel particulate filter</td>
<td></td>
</tr>
<tr>
<td>EEV</td>
<td>Enhanced environmentally friendly vehicles</td>
<td></td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
<td></td>
</tr>
<tr>
<td>ELR</td>
<td>European load response</td>
<td></td>
</tr>
<tr>
<td>ESC</td>
<td>European stationary cycle</td>
<td></td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
<td></td>
</tr>
<tr>
<td>GHSV&lt;sub&gt;DOC&lt;/sub&gt;</td>
<td>Gas hourly space velocity of the DOC</td>
<td></td>
</tr>
<tr>
<td>GSA</td>
<td>Geometric surface area</td>
<td></td>
</tr>
<tr>
<td>L-DOC</td>
<td>Large volume oxidation catalyst</td>
<td></td>
</tr>
<tr>
<td>OFA</td>
<td>Open frontal area</td>
<td></td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metals</td>
<td></td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
<td></td>
</tr>
<tr>
<td>RME</td>
<td>Rape Methyl Ester</td>
<td></td>
</tr>
<tr>
<td>TOF</td>
<td>Turnover frequency</td>
<td></td>
</tr>
<tr>
<td>TOR</td>
<td>Turnover rate</td>
<td></td>
</tr>
<tr>
<td>TSA</td>
<td>Total surface area</td>
<td></td>
</tr>
<tr>
<td>TWC</td>
<td>Three way catalyst</td>
<td></td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
<td></td>
</tr>
<tr>
<td>VGT</td>
<td>Variable geometry turbo</td>
<td></td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
<td></td>
</tr>
<tr>
<td>WHSC</td>
<td>World harmonized stationary cycle</td>
<td></td>
</tr>
<tr>
<td>WHTC</td>
<td>World harmonized transient cycle</td>
<td></td>
</tr>
</tbody>
</table>
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1 Introduction
Transportation is an important part of society, but unfortunately most vehicles produce emissions that affect the global air quality. Increasing awareness of emission effects on environment and humans has resulted in necessitating development of the exhaust aftertreatment system.

Catalysts for automotive applications have been developed for over 40 years and the first automotive catalyst was introduced in the mid-1970s. [1,2] Today, catalysis has a central role in the exhaust aftertreatment system and the choice of catalytic system depends on for instance the composition of the exhaust gas. For spark-ignition (for example gasoline) engines, the air-to-fuel ratio is around stoichiometric and the three way catalyst (TWC) is used for simultaneous oxidation of carbon monoxide (CO) and hydrocarbons (HC) and reduction of nitrogen oxides (NO\textsubscript{X}). For compression-ignition (diesel) engines, the air-to-fuel ratio is lean (excess O\textsubscript{2}) and the oxidation/reduction reactions take place in several steps. [1]

In heavy-duty trucks and busses, diesel engines are most commonly used and the exhaust gas contains emissions of CO, HCs, NO\textsubscript{X} and particulate matter (PM). [3,4] These compounds are strictly regulated in order to limit the emissions. [5] Typically, the exhaust aftertreatment system for diesel engines in heavy-duty vehicles includes several catalysts. These must work efficiently together in the wide range of mass flows and temperatures that the engine operates in. [6] There are many aspects to consider when designing the exhaust aftertreatment system such as the vehicle fuel consumption since it affects the emissions as well as cost. Furthermore, development of the engine also affect the emissions, both amount and composition. Other important aspects are the type of emission test cycles that are used since it affects how the engine operates and thereby emissions, what kind of on-board diagnostics that is used for evaluation of the system as well as durability of the exhaust aftertreatment system. [7] Additionally, the final product must meet customers’ demand.

1.1 Background
This section describes the engine, fuel, emissions, effects of emissions, legislation and Scania’s exhaust aftertreatment system.

1.1.1 Compression-ignition Combustion Engine
The principle for combustion engines is conversion of the fuel’s chemical energy to mechanical power. Compression-ignition engines are the most common for heavy-duty vehicles. Engines operate in cycles, where a piston moves back and forth in a cylinder resulting in work. The work transfers from the piston via the connecting rod to the crank shaft, where useful work is extracted. Reciprocating engines operate commonly in a four stroke cycle, which consists of the intake, compression, expansion (or power) and exhaust stroke. In the intake stroke, air enters the cylinder and is compressed in the next stroke. The fuel is injected at the end of the compression stroke and the combustion starts as the air-fuel-mixture autoignites. Thereafter follows the expansion (or power) stroke, where the gas expands and generates mechanical work. Finally, the exhaust gas leaves the cylinder. [8]
1.1.2 Diesel and Biodiesel

Diesel originates from fossil fuel and consists of a mixture of hydrocarbons. [9,10] The quality of the fuel is governed by for instance density, content of sulphur and aromatics. [4] Different standards are used in the world and one European standard is EN590 (diesel with up to 7 volume% biodiesel). [11]

Biodiesel has been introduced to decrease CO$_2$ emissions originating from fossil sources and consists mainly of alkyl esters. [12,13] Biodiesel has 10-12% lower energy content and contains around 10% more oxygen than diesel. Blends of diesel and biodiesel are named after its biodiesel content, exemplified blends with 93% diesel and 7% biodiesel are called B7. [13,12]

1.1.3 Emissions

Combustion of diesel in compression-ignition engines result in exhaust gas, a complex mixture of gaseous, liquid and solid compounds. [14] Diesel exhaust consists of hundreds of constituents, but mainly HCs, SO$_X$, NO$_X$, PM, CO, CO$_2$, H$_2$O, O$_2$ and N$_2$. [4,15] The emissions depend primarily on the operation of the engine (air-to-fuel ratio, mixing rate, injection and temperature) and fuel quality. [4] Combustion of biodiesel gives lower emissions of PM, HC and CO but higher emissions of NO$_X$ compared to diesel. [12]

Emissions of HCs are due to incomplete combustion of fuel and lubrication oil. [4] Generally, HCs are both in gaseous from (C$_1$-C$_{15}$) and liquid form (C$_{15}$-C$_{40}$), which means a wide range of HCs. [14,16] Sulphur compounds also originate from fuel and lubricants. SO$_2$ is the main sulphur compound out of the engine, which of a small part is oxidised to sulphates and SO$_3$. [3] NO$_X$ formed in diesel engines are mostly thermal due to high combustion temperature in air. In diesel exhaust more than 90% of the NO$_X$ formed is NO and 5-10% is in form of NO$_2$. [17] PM consists of carbon/ash, soluble organic fraction (SOF) and sulphates. [18,19] The formation of PM is due to incomplete combustion that results in formation of precursor molecules, soot nucleus that agglomerate and forms particulates. [14] CO is formed due to incomplete combustion and complete combustion gives CO$_2$ and H$_2$O. [20]

1.1.4 Effects of Emissions

Emissions from heavy duty diesel engines contribute to air pollution problems such as global warming, photochemical smog and acidification. [15,21] The exhaust gas contains greenhouse gases that contribute to the increased global warming, where CO$_2$ is a major contributor. [15] HC and NO$_X$ in sunlight can form photochemical smog and ozone. [12,21,22] Ozone is a strong greenhouse gas and can damage vegetation as well as affect the health of humans. [21,23] SO$_X$ and NO$_X$ form acids with water, which give acidic rain and acidification of soils and waters. [22,24]

For humans, diesel exhaust is associated with increased risk of respiratory disease, lung cancer and premature mortality. [15,25] Exemplified, SO$_X$, NO$_X$ and HCs irritate the respiratory tract and HCs can be carcinogenic and mutagenic. [15] PM can be carcinogenic, leading to an increased risk for lung cancer. CO is toxic to humans since it blocks uptake of oxygen. [22]
1.1.5 Emission Standards

To limit the negative effects of emissions, there are regulations. In Europe emissions from heavy-duty vehicles are regulated by EU Emission Standards, called Euro I to Euro VI, see Table 1 and Table 2. Euro I came 1992 and thereafter followed stricter legislation with lower emission levels. [5] Euro VI is for all new types of engines and vehicles from 31 December 2012, whereas one year later for all new vehicles sold. Emission standard for Euro VI should be fulfilled for the vehicles during at least 700000 km. [26]

Table 1: Emission standards Euro I to V for heavy-duty diesel engines, where CO, HC, NO\textsubscript{x}, PM and smoke are regulated and the year the standard was introduced. [5,27]

<table>
<thead>
<tr>
<th>Standard</th>
<th>CO [mg/kWh]</th>
<th>HC [mg/kWh]</th>
<th>NO\textsubscript{x} [mg/kWh]</th>
<th>PM [mg/kWh]</th>
<th>Smoke [m\textsuperscript{-1}]</th>
<th>Year</th>
</tr>
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<tr>
<td>Euro I*</td>
<td>4500</td>
<td>1100</td>
<td>8000</td>
<td>612</td>
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<td></td>
<td>4500</td>
<td>1100</td>
<td>8000</td>
<td>360</td>
<td>-</td>
<td>1992 (&gt;85 kW)</td>
</tr>
<tr>
<td>Euro II*</td>
<td>4000</td>
<td>1100</td>
<td>7000</td>
<td>250</td>
<td>-</td>
<td>1996</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>1100</td>
<td>7000</td>
<td>150</td>
<td>-</td>
<td>1998</td>
</tr>
<tr>
<td>Euro III**</td>
<td>1500</td>
<td>250</td>
<td>2000</td>
<td>20</td>
<td>0.15</td>
<td>1999***</td>
</tr>
<tr>
<td></td>
<td>2100</td>
<td>660</td>
<td>5000</td>
<td>100, 130***</td>
<td>0.8</td>
<td>2000</td>
</tr>
<tr>
<td>Euro IV**</td>
<td>1500</td>
<td>460</td>
<td>3500</td>
<td>20</td>
<td>0.5</td>
<td>2005</td>
</tr>
<tr>
<td>Euro V**</td>
<td>1500</td>
<td>460</td>
<td>2000</td>
<td>20</td>
<td>0.5</td>
<td>2008</td>
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</table>

*Emission test cycle ECER-49  
**European stationary cycle (ESC) and European load response (ELR)
***Engines with swept volume below 0.75 dm\textsuperscript{3}/cylinder and rated power speed exceeding 3000 min\textsuperscript{-1}
****For “Enhanced environmentally friendly vehicles” (EEV)

Table 2: Emission standards Euro VI for heavy-duty diesel engines, where CO, HC, NO\textsubscript{x}, NH\textsubscript{3} and PM are regulated and the year the standard will be introduced. [28]

<table>
<thead>
<tr>
<th>Standard</th>
<th>CO [mg/kWh]</th>
<th>HC [mg/kWh]</th>
<th>NO\textsubscript{x} [mg/kWh]</th>
<th>NH\textsubscript{3} [ppm]</th>
<th>PM [mg/kWh]</th>
<th>PM [number/kWh]</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro VI*</td>
<td>1500</td>
<td>130</td>
<td>400</td>
<td>10</td>
<td>10</td>
<td>8.0 x 10\textsuperscript{11}</td>
<td>2012</td>
</tr>
<tr>
<td>Euro VI**</td>
<td>4000</td>
<td>160</td>
<td>460</td>
<td>10</td>
<td>10</td>
<td>6.0 x 10\textsuperscript{11}</td>
<td>2012</td>
</tr>
</tbody>
</table>

*World harmonized stationary cycle (WHSC)
**World harmonized transient cycle (WHTC)
1.1.6 Scania`s Engine and Exhaust Aftertreatment System

Scania`s engine and exhaust aftertreatment system, see Figure 1, must work efficiently together within the operating range of the engine and be reliable over time to fulfill legislation.

![Schematic illustration of Scania´s engine and exhaust aftertreatment system.](image)

Figure 1: Schematic illustration of Scania`s engine and exhaust aftertreatment system. The engine management operates the engine, where VGT, intake throttle, exhaust brake, EGR, EGR valve and Scania XPI are important when operating the engine and for the properties of the exhaust gas. The exhaust aftertreatment system includes DOC, DPF, dosing unit for AdBlue™, SCR and ASC. [6]

Engine management controls how the diesel engine is operated. Air passes the variable geometry turbo (VGT) and then the intake throttle, which can restrict the air intake and thereby increase the exhaust temperature. To increase the temperature of the gas, load can also be applied with the exhaust brake. The purpose of increasing the exhaust gas temperature is to benefit the catalytic reactions in the exhaust aftertreatment system. Scania XPI is the fuel injection system and it operates at high pressure to reduce formation of PM. Exhaust gas recirculation (EGR), regulated by the EGR valve, is used to decrease the combustion temperature and thereby lower the emissions of NOX. [1]

The exhaust aftertreatment system includes a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF), a selective catalytic reduction (SCR) catalyst and an ammonia slip catalyst (ASC), integrated in a silencer. HCs, NO and CO are oxidised over the DOC, while the DPF traps particles. [6] After the DPF, AdBlue™ (urea in water) is injected into a unit, where it decomposes to ammonia (NH₃). [6,29] NH₃ is used to reduce NOX in SCR and excess NH₃ is oxidised in the final step, the ASC. [6,17]

NO₂ has a central role in the exhaust aftertreatment system. This is since NO₂ is essential for regeneration of the DPF (oxidation of soot) and in the right proportion to NO enables faster SCR. [30] This will be explained further in the coming sections 1.1.7 to 1.1.10.
1.1.7 Diesel Oxidation Catalyst

Platinum group metals (PGM) are frequently used as catalysts and the PGMs are platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), osmium (Os) and iridium (Ir). [3,31] Pt and Pd are typically used as DOCs. The reason suitable for DOCs since these are active for oxidation, initiate reactions at low temperature and are more or less thermally stable. [3,40]

Due to the high cost of PGM, alternatives are continuously being developed. However, currently no viable alternative is commercially available. One example recently presented is a catalyst composed of the mixed-phase oxide Mn-Mullite (Sm,Gd)Mn$_2$O$_5$. These new types of mixed-oxide oxidation catalysts promise higher activity, thermal stability and lower cost compared to PGM catalysts. [32] Nevertheless, these developments are still in the future.

In automotive applications, the DOC can be a monolith (substrate with parallel open channels) coated with a catalytic washcoat, see Figure 2. [33] The DOC oxidises mainly HCs, NO and CO in the exhaust gas as it passes, see reactions R-1 to R-3. The enthalpy of reaction ($\Delta H_{\text{reaction}}$ at 25°C and 1 atmosphere) for the exothermic reactions are <$0$ (depends on type of HC), -113 and -288 kJ/mol respectively. [9] DOCs also oxidise SOF of PM, which reduces PM. [33]

\[
\begin{align*}
\text{C}_x\text{H}_y + (x+y/2) \text{O}_2 & \rightleftharpoons x \text{CO}_2 + y/2 \text{H}_2\text{O} & (\text{R-1}) \\
2 \text{NO} + \text{O}_2 & \rightleftharpoons 2 \text{NO}_2 & (\text{R-2}) \\
\text{CO} + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{CO}_2 & (\text{R-3})
\end{align*}
\]

Figure 2: The structure of DOC, where the substrate has parallel open channels with washcoat and catalyst. The exhaust gas passes the DOC and HCs, NO and CO are oxidised. [33]
Other important parameters for the conversion of the oxidation reactions are the amount of PGM. Generally, higher PGM-loading gives higher conversion and lower light-off temperature, see Figure 3. Furthermore, the ratio between Pt and Pd is crucial. [33,44,41,42]

**Figure 3:** Schematic illustration of conversion as function of temperature, where higher PGM-loading generally gives higher conversion and lower light-off temperature. [33,44,41,42]
1.1.8 Diesel Particulate Filter

There are different types of DPFs, but in common is the reduction of PM. Wall-flow filter is one example of a DPF, where the channels are open and closed, see Figure 4. One channel (a) is open at the entrance and closed at the exit, while the adjacent channel (b) is closed at the entrance and open at the exit. The gas enters the DPF in channel (a), passes the filter wall, exits the DPF in channel (b) and PM is trapped in channel (a). The DPF can have a catalytic coating (CDPF) and then the same oxidation reactions as in the DOC take place. [1]

Figure 4: The structure of DPF and in this case a wall-flow filter with open and closed channels. The gas enters channel (a), passes the filter wall and exits the filter in the adjacent channel (b). PM is trapped in channel (a). [1]

The DPF must be regenerated as soot accumulates and the pressure drop gets too excessive. Regeneration comprises combustion of PM to CO₂ and H₂O. [1] Regeneration (passive) takes place during vehicle operation when NO₂ and O₂ oxidise PM. [34] Oxidation by NO₂ has higher PM oxidation rates at lower temperatures than O₂, see Figure 5. [35] The rate of regeneration can be increased by raising the temperature with for instance fuel injection into the exhaust gas or by changing the operation of the engine. After regeneration, ash (unburned PM) is left in the DPF and it must eventually be removed mechanically. [34]

Figure 5: Oxidation of PM by NO₂ or O₂ with relative CO₂ intensity (referring to the amount PM oxidised) as function of temperature, where NO₂ has higher oxidation performance than O₂ at a specific temperature. However, the type of PGM is essential since the properties can vary. [35]
1.1.9 Selective Catalytic Reduction

NO\textsubscript{X} can be reduced by NH\textsubscript{3} over a catalyst, see reactions R-4 to R-6. Reactions R-4, R-5 and R-6 are known as standard SCR, fast SCR and NO\textsubscript{2} SCR, respectively. [33] The general relation between the reaction rate (\(r\)) of these reactions are \(r_{R-5} > r_{R-4} > r_{R-6}\). This means that it is preferred to have the stoichiometry 1:1 between NO and NO\textsubscript{2} to favour fast reduction of NO\textsubscript{X} in reaction R-5. Moreover, an excess of NH\textsubscript{3} is used to enable better reduction of NO\textsubscript{X} since the equilibrium reaction is shifted towards to the products. Other reactions and unwanted side reactions do also take place, such as formation of nitrous oxide (N\textsubscript{2}O). [1,17]

\[
\begin{align*}
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 &\rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} & \text{(R-4)} \\
2 \text{NH}_3 + \text{NO} + \text{NO}_2 &\rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} & \text{(R-5)} \\
8 \text{NH}_3 + 6 \text{NO}_2 &\rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} & \text{(R-6)}
\end{align*}
\]

1.1.10 Ammonia Slip Catalyst

Slip of NH\textsubscript{3} from the SCR is oxidised using an ASC before the exhaust gas can be let out in the atmosphere. NH\textsubscript{3} is toxic to humans (above 50-100 ppm) and regulated by law. NH\textsubscript{3} is oxidised by O\textsubscript{2} which is the desired and strongly exothermic reaction, see reaction R-7. However, there are also undesirable reaction where O\textsubscript{2} and NH\textsubscript{3} can form N\textsubscript{2}O, NO and H\textsubscript{2}O. [24]

\[
4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} \quad \text{(R-7)}
\]

1.2 Purpose

The purpose with this master thesis is to investigate whether it is possible to selectively promote oxidation of HCs over oxidation of NO for a DOC. This means that the DOC should have high HC oxidation performance without too high NO oxidation performance. The reason for developing a selective DOC for HCs is to provide an optimized exhaust aftertreatment system. This is since it enables the possibility to oxidise HCs in a wide range of flows and temperatures to increase the temperature in the exhaust aftertreatment system when necessary and to maintain efficient reduction of NO\textsubscript{X} emissions through the fast SCR reaction. Other properties of the DOC such as thermal and mechanical stability cannot be worsen when selectively oxidising HCs since that would affect the durability of the system.
2 Catalysis

Understanding of catalysis, limitations within the system and properties of the compounds are essential when evaluating how to improve the exhaust aftertreatment system. This chapter describes important catalytic parameters and aspects.

Catalysts enable energetically more favorable reaction paths compared to non-catalysed reaction paths, see Figure 6. [1] The activity of catalysts is defined by turnover frequency (TOF) or turnover rate (TOR), which is the number of catalytic cycle per time unit. [36]

![Figure 6](potential_energy.png)

**Figure 6:** The potential energy as a function of the reaction for catalytic and non-catalytic reaction paths, where R is reactant and P is product. The energy to overcome in the catalysed case \( E_{\text{catalyst}} \) is lower than the non-catalysed case \( E_{\text{no catalyst}} \) and hence the catalysed path is favourable. [1]

Catalysis can be either heterogeneous or homogeneous. In heterogeneous catalysis, the catalyst and reactants are in different phases while in the same phase for homogeneous catalysis. [37] Heterogeneous catalysis with gas phase and solid phase will be considered from now on since it is the principle for the DOC.

In automotive applications, the catalytic system frequently consists of substrate, washcoat and catalyst, see Figure 7. [1,33] The active material is distributed on the washcoat, a material with large surface area to enable good contact between catalyst and gas phase. [1]

![Figure 7](cross_section.png)

**Figure 7:** Schematic illustration of a cross section of a square monolith channel, where substrate, washcoat and active material are marked. [33] The gas passes the channel and comes in contact with the catalyst, which enables faster reaction.
2.1 Catalytic Steps

The catalytic reaction includes the following seven steps, see also Figure 8 [29,38]:

i. External mass transfer (gas diffusion) of the reactants from the bulk (the exhaust gas in automotive applications) to the external surface of the washcoat.

ii. Internal mass transfer (pore diffusion) of the reactants from the inlet of the pore in the washcoat to the catalytic active site.

iii. Adsorption of the reactants to the active sites on the surface of the catalyst.

iv. Surface reaction.

v. Desorption of the products from the catalyst surface.

vi. Internal mass transfer (pore diffusion) of the products to the outlet of the pore.

vii. External mass transfer (gas diffusion) of the products to the bulk.

Figure 8: The seven steps in heterogeneous catalysis, where R are reactants and P are products. The reactants are externally diffused from the bulk to the surface of the washcoat (i) and then internally diffused through the pores of the washcoat to the active site (ii), where the reactants are adsorbed to the active sites (iii). The surface reaction takes place (iv) and the products are desorbed (v). Finally, the products are internally diffused (vi) and externally diffused to the bulk (vii). [38]

2.2 Reaction Rate

The Arrhenius equation describes the reaction rate constant \(k\) using the preexponential factor \(A\), activation energy \(E\), ideal gas constant \(R\) and temperature \(T\), see equation E-1. [1]

\[
k = A e^{-E/(RT)}
\]  

(E-1)

The reaction rate is then described by the reaction rate constant and the concentration of the reactants and products.
2.3 Reaction Rate Limitations

Catalytic reactions are limited by the slowest step in the process, which can be any of the seven steps in catalysis (unless thermodynamic equilibrium is achieved). The reaction is kinetically limited at low temperature and at higher temperature the reaction becomes mass transfer controlled, see Figure 9. [1]

![Figure 9: Reaction rate (red line) as a function of temperature with the reaction rate limitations. The reaction rate is controlled by kinetics at low temperature (A$\rightarrow$B) and with increasing temperature the rate-limiting step are internal mass transfer (B$\rightarrow$C) and external mass transfer (B$\rightarrow$C). [39,40]]

Depending on the rate-limiting step, different concentration gradients are formed within the washcoat, see Figure 10. The kinetic controlled case has a uniform reactant concentration (equal to the concentration in the bulk) within the washcoat whereas the reactant concentration decreases for the internal mass transfer controlled case and the reactant concentration is zero for the external mass transfer controlled case. [1]

![Figure 10: Concentration gradients within the washcoat for the different rate-limiting steps. The reactant concentration gradient within the washcoat is uniform for the kinetic controlled case, decreasing for the internal mass transfer controlled case and zero for the external mass transfer controlled case. [1]]
The reaction rate limitations affects when light-off takes place, which is when the reaction rate and thereby conversion increases rapidly with increasing temperature, see Figure 11. The steady state, where the curve flatten out and mass transfer of reactants is rate-limiting. Before light-off, the limiting step is the kinetics. [40]

![Figure 11: Schematic illustration of a light-off curve (also known as ignition-extinction curve) with conversion as function of temperature. [41,42]](image)

All these non-equilibrium processes limit the catalytic conversion that is thermodynamically possible. However, how far a reaction proceeds towards equilibrium is not only determined by kinetics, the residence time ($t$) of the gas inside the catalyst is of equal importance. The $t$ is defined as the volume of the DOC ($V_{\text{DOC}}$) divided by the volumetric flow rate ($v$) at specific temperature and pressure, see equation E-2. [38]

$$t = \frac{V_{\text{DOC}}}{v} \quad (E-2)$$

Gas hourly space velocity of the DOC (GHSV$_{\text{DOC}}$) is then defined as the inverse of $t$, see equation E-3. [38]

$$\text{GHSV}_{\text{DOC}} = \frac{v}{V_{\text{DOC}}} \quad (E-3)$$

Consequently, control of GHSV$_{\text{DOC}}$ during an experiment is of equal importance as to for example temperature control.
2.4 Comparison Between Uniformly and Zone-coated DOCs

The PGM in a catalyst should be distributed optimally, either uniformly or non-uniformly (zone-coated) on the washcoat. For an optimised system, less PGM may be used or higher conversion achieved. [43] This means that a zone-coated DOC may result in an earlier light-off. [33] In general, the oxidation activity of the DOC increases with increasing PGM-loading. [33,44] However, this is also affected by the type of reaction and the reaction rate limitations.

The conversion at a specific temperature and PGM-loading is affected by how the PGM is distributed (uniformly or non-uniformly) for a DOC, see Figure 12 (isothermal reaction) and Figure 13 (exothermic reaction). In this example, both the uniformly distributed and zone-coated DOCs have the same amount of PGM (6A). The uniformly distributed DOC has the PGM-loading 3A in each half of the DOC, while the zone-coated DOC has 5A in the first half followed by 1A in the second half. The reaction rate is assumed to be for a first order reaction, see equation E-4, and the solution to this equation is presented in equation E-5. For the exothermic reaction, the temperature is assumed to increase proportionally to the conversion and the temperature is assumed to double at 100% conversion. Furthermore, the conversion increases proportionally with increasing PGM-loading.

\[
\frac{dc}{dt_i} = kc, \text{ where } k = Ae^{-E_a/(RT)}
\]  
(E-4)

\[
c = c_0e^{-kt_i}
\]  
(E-5)

For an isothermal reaction, the total conversions for the two DOCs are similar, see Figure 12.

For the exothermic reaction, such as HC oxidation, the temperature as well as reaction rate increase along the DOC (this also depends on concentration of the compounds in the gas). For an exothermic reaction, the conversion is higher for the zone-coated DOC compared to the uniformly distributed DOC, see Figure 13. This means that an exothermic reaction and a zone-coated DOC result in a higher conversion faster than a uniformly distributed DOC.
**Figure 12:** Schematic illustration of the conversion for a uniformly distributed DOC compared to a zone-coated DOC at constant temperature in the DOC. The DOCs’ total PGM-loadings are 6A and the DOC is divided into two parts. The conversions are similar for both DOCs.
Figure 13: Schematic illustration of the conversion for a uniformly distributed DOC compared to a zone-coated DOC as temperature increase (exothermic reaction) along the DOC. The DOCs’ total PGM-loadings are 6A. The conversion for the zone-coated DOC increases more rapidly than for the uniformly distributed DOC due to the higher reaction rate at higher temperature. This means that the combination of an exothermic reaction (HC oxidation is strongly exothermic) and a zone-coated DOC enables higher conversions.
3 Oxidation Reactions

Oxidation includes breakage of intramolecular bonds and incorporation of oxygen into the product. [45] However, deeper understanding for the HC, NO and CO oxidation reactions is important when evaluating the performance of the DOC and selectively promote the oxidation of HC and CO while being neutral to NO.

3.1 Reaction Mechanisms

The reaction mechanism is important for the kinetics of the system and two examples of mechanisms are Langmuir-Hinshelwood and Eley-Rideal. The Langmuir-Hinshelwood mechanism includes adsorption of both reactants onto the surface before the chemisorbed species react on the surface. The Eley-Rideal mechanism includes adsorption of one of the reactants onto the surface, whereas the other reactant remains in the gas phase. Consequently, the reaction takes place between the chemisorbed reactant and the reactant in the gas phase. [37]

3.2 Surface Structure, Adsorption and Structure Sensitivity

Catalysts have complicated structures and the surface structure can affect the activity. Three crystal structures are face-centred cubic (fcc), hexagonally close-packed (hcp) and body-centred cubic (bcc), which refer to how the atoms are organised. Pt and Pd have fcc crystal structures, but the crystal surface depends also on the crystal plane exposed. [37] The surface exposed can be in different levels with terraces, kinks and steps, see Figure 14. [46]

![Figure 14: Schematic illustration of the surface structure with terraces, steps and kinks. [46]](image)

The crystal surface influences the adsorption and thereby the reaction. [47] The rate of adsorption depends on the collision rate between gas and surface as well as sticking coefficient. The sticking coefficient describes the probability for adsorption of atoms onto a surface. [37] Compounds adsorb differently onto surfaces and thereby affect the oxidation state of the catalyst. [30] Exemplified, the PGM particles can be oxidised by NO\textsubscript{2} and/or O\textsubscript{2}. NO\textsubscript{2} is a stronger oxidant because it is less kinetically hindered than O\textsubscript{2}. Oxygen coverage can also affect the dissociative adsorption, especially for O\textsubscript{2}. However, NO\textsubscript{2} is less sensitive for oxygen coverage and gives higher oxygen coverage. [48] Oxygen coverage is important for oxidation of HCs, NO and CO since these mainly are oxidised by adsorbed oxygen.

If the reaction rate changes markedly with different catalyst particle sizes, a catalytic reaction is structure sensitive. [46] Particle size affects the surface structure since smaller particles often have more corners and edges than larger particles. [33,46]
3.3 Oxidation of Hydrocarbons

For oxidation of HCs, the reaction rates vary depending on type of HC. Exemplified, the oxidation rate of alkanes tends to increase with increasing length of the carbon chain. When it comes to modelling of HC oxidation, propane and propylene are most often used to represent saturated and unsaturated HCs. [33]

Complete oxidation of HCs follow the Langmuir-Hinshelwood mechanism, see reactions R-8 to R-11 where $\sigma$ denotes active catalyst sites. [33]

\[
\begin{align*}
\text{HC} + \sigma & \rightleftharpoons \text{HC}\sigma \\
\text{O}_2 + \sigma & \rightarrow \text{O}_2\sigma \\
\text{O}_2\sigma + \sigma & \rightarrow 2\text{O}\sigma \\
\text{O}\sigma + \text{HC}\sigma & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\sigma
\end{align*}
\]

The rate-limiting step for HC oxidation is the surface reaction between HC and oxygen. Below light-off, oxygen on the surface is the limiting reactant because adsorption of HC is stronger than that of oxygen. This means that HCs self-inhibit the surface and thereby the oxidation, especially at high concentrations. [33] \(\text{H}_2\text{O}\) can also inhibit the catalyst, causing deactivation of catalyst surface area as underactive OH-compounds are formed. This inhibition affects Pd above 300$^\circ$C, but not Pt over this temperature because hydroxyls are less stable than chemisorbed oxygen on Pt. [57] Furthermore, \(\text{H}_2\text{O}\) competes with \(\text{O}_2\) for vacant sites. [33] Additionally, CO inhibits HC oxidation on Pd and especially Pt. [49]

HC oxidation is structure sensitive. Exemplified, the reaction rate for oxidation of propylene increases with decreasing Pt particle size. [33]

HC oxidation gives rise to oscillations due to shifting between the oxidised form (PtO) and the reduced form (Pt). In lean exhaust more of the less active PtO is formed until an upper limit, where the activity recovers when for instance HC reacts with oxygen in PtO and Pt is formed. [33] Moreover, temperature influences the adsorption/desorption of \(\text{O}_2\) since adsorption is higher at lower temperature and desorption is higher at higher temperature. [50] This can also give rise to hysteresis or inverse hysteresis, see Appendix A.
3.4 Oxidation of Nitric Oxide

The catalytic oxidation reaction of NO follows the Langmuir-Hinshelwood mechanism, see reactions R-12 to R-15. [54, 42]

\[
\begin{align*}
\text{NO} + \sigma & \rightleftharpoons \text{NO}^\sigma \quad \text{(R-12)} \\
\text{O}_2 + \sigma & \rightarrow \text{O}_2^\sigma \quad \text{(R-13)} \\
\text{O}_2^\sigma + \sigma & \rightarrow 2\text{O}^\sigma \quad \text{(R-14)} \\
\text{NO}^\sigma + \text{O} & \rightleftharpoons \text{NO}_2 + 2\sigma \quad \text{(R-15)}
\end{align*}
\]

The rate-limiting step is adsorption/desorption of \( \text{O}_2 \) in reaction R-13. [33, 42]

The NO oxidation reaction can be inhibited by HCs and CO due to competition of vacant sites. [33] The reaction rate for NO oxidation on Pt/Al\(_2\)O\(_3\)/SiO\(_2\) is also affected by inhibition of the product NO\(_2\). [33, 42] This is since NO\(_2\) preferentially adsorbs on Pt due to its high sticking coefficient, which makes it an effective source for surface oxygen. This means that NO\(_2\) results in an oxidised Pt surface as well as preventing other species from getting adsorbed. Thereby, most of the oxygen on the surface originates from dissociation of NO\(_2\) rather than \( \text{O}_2 \). [42]

Several researchers have found that the NO oxidation over Pt/Al\(_2\)O\(_3\) or Pt/SiO\(_2\) is structure sensitive, which in this case means that the NO oxidation reaction rate per site increases with increasing particle size. [33, 51, 52] The reason for this is that the larger Pt particles adsorb oxygen more weakly and thereby less Pt oxides are formed. [33] Despite thermal aging the activity of the catalyst increases due to increasing particles and the effect is stronger for Pt/Al\(_2\)O\(_3\) than Pt/SiO\(_2\). [51] NO oxidation over Pd is also structure sensitive. The reaction rate increases with increasing PdO cluster sizes, but the structure sensitivity is modest for clusters over 6 nm. [57] The reason for this is that weaker oxygen bonds are formed onto the surface of larger particles due to less corners and edges, which facilitate more vacancies. [33, 57]

NO oxidation over Pt/Al\(_2\)O\(_3\) give rise to both normal and inverse hysteresis and a possible explanation is reversible oxidation/reduction of Pt. Hence, at high temperatures Pt is oxidised by NO\(_2\) or \( \text{O}_2 \) to a less active oxide and reduced most likely by NO to its monometallic form at lower temperatures. [30]
3.5 Oxidation of Carbon Monoxide

Langmuir-Hinshelwood mechanism is the accepted reaction mechanism for oxidation of CO on Pt and Pd, see reactions R-16 to R-19. [33]

\[
\begin{align*}
\text{CO} + \sigma & \rightleftharpoons \text{CO}^\sigma & (\text{R-16}) \\
\text{O}_2 + \sigma & \rightarrow \text{O}_2^\sigma & (\text{R-17}) \\
\text{O}_2^\sigma + \sigma & \rightarrow 2\text{O}^\sigma & (\text{R-18}) \\
\text{O}^\sigma + \text{CO}^\sigma & \rightarrow \text{CO}_2 + 2\sigma & (\text{R-19})
\end{align*}
\]

CO adsorbs with the carbon atom towards the surface of Pt. On the surface CO migrates to chemisorbed O atoms due to its better mobility. The rate-limiting step over Pt is the surface reaction between CO and O, while the rate-limiting step over Pd is desorption of CO at high CO concentrations. At temperatures between 225 and 425°C, O\textsubscript{2} promotes the oxidation reaction while CO inhibits it by blocking active sites for adsorption of O\textsubscript{2}. The inhibition decreases with increased temperature and is not significant at temperatures above 370-425°C. At temperatures between 475 and 775°C, the mass transport of reactants to the surface is the limiting step. [33]

The adsorption of oxygen is in principle irreversible, which can result in a fully oxygenated surface and CO cannot adsorb. [33] However, CO\textsubscript{2} is rapidly formed when gaseous CO is introduced to an oxygen covered surface and the other way around does not result in any reaction. For this reason an additional Eley-Rideal step can be added, where adsorbed oxygen reacts with CO in the gas phase, see reaction R-20. [47,53]

\[
\text{O}^\sigma + \text{CO} \rightarrow \text{CO}_2 + \sigma & \quad (\text{R-20})
\]

CO oxidation is structure sensitive and faster on larger particles. However, this is not observed when Pt particles are larger than around 5 nm. [33]

Oxidation of CO over Pt shows hysteresis, but if NO is present the result is instead inverse hysteresis. [30] Oscillations appear for CO oxidation and affect the reaction rates at “steady-state”. [33]

The oxidation of CO is an exothermic reaction, which results in extra heat that can promote the HC oxidation. However, this depends strongly on the CO concentration. [41]
4 Diesel Oxidation Catalyst – Platinum Group Metals

The choice of PGMs is essential for the application. Other important factors are catalyst preparation, loading, distribution, dispersion, alloy/monometallics and uniform/non-uniform distribution. [33] Dispersion of the active material is important for the characteristics of the catalyst. Given the same amount of active material is dispersed, low dispersion is when the particles are fewer and larger compared to high dispersion when the particles are more and smaller. [37] Generally, higher dispersion is desirable and gives higher oxidation activity.

4.1 Platinum and Palladium

Pt has higher molar mass and melting point than Pd, see Table 3. [31]

Depending on particle size and oxidation temperature in presence of oxygen, possible species on the Pt surface are PtO, PtO₂ and chemisorbed oxygen. [54] Generally, the active form for oxidation reactions is metallic Pt and palladium oxide (PdO). [3,33] However, Pd is more active than PdO when it comes to oxidation of volatile organic compounds (VOC) excluding methane. [55,56]

Pd is more likely to form oxides in small particles due to more corners and edges compared to larger particles. [57] Compared to metal particles, oxide particles have irregular shapes. [58] At temperatures above 600-800°C PdO decomposes. [3]

Pd has higher thermal stability than Pt. [41,59,60] By combining Pd with Pt, thermal stability of bimetallic alloys are enhanced compared to the monometallic forms. [41] Generally, alloying metals may result in new active sites that modify activity and selectivity of the catalyst. [46]

The metal dispersion is greater for Pd than alloys of Pt-Pd and even lower for Pt. [59] When the active material is an alloy of both Pt and Pd the bimetallic particles consist of Pt with Pd dispersed on the surface. In other words, Pd segregates towards the surface of the alloy and the segregation depends on the atmosphere the catalyst is exposed to. [61,62]

Additionally, cost of PGMs (Pt and Pd) reduces with higher fraction of Pd and this is since the average price (March 2011-March 2012) of Pt was 54 US$/g and Pd 23 US$/g. [41,63]

Table 3: Molar mass and melting point of Pt and Pd. [31,64]

<table>
<thead>
<tr>
<th>Category</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass [g/mol]</td>
<td>195</td>
<td>106</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>1755</td>
<td>1555</td>
</tr>
</tbody>
</table>
4.2 Oxidation Activity of Platinum Group Metals

The HC oxidation activity of Pt and Pd depends on HC concentration as well as type of HC. [33] Generally, Pt is more active for oxidation of saturated hydrocarbons, while Pd is more active for oxidation of unsaturated hydrocarbons. [40] However, when it comes to oxidation of methane (CH₄), Pd is more active than Pt. [3] Overall, Pt has the most efficient light-off performance for HCs of the two. Furthermore, small amounts of Pt can promote Pd catalysts to enable a better HC oxidation. [33]

Pt has higher NO oxidation activity than Pd. [59] NO oxidation mainly depends on Pt content, meaning that higher Pt loading gives higher NO oxidation within the temperature range the reaction occurs. [33,41] Moreover, Pd-only catalysts are nearly inactive for NO oxidation below 300°C. [41]

Pd has higher CO oxidation activity than Pt. [60]

4.3 Light-off Temperatures for Oxidation in Pt:Pd Systems

Pt has higher HC (xylene and propene) oxidation activity than Pd, whereas it is the other way around for oxidation of CO, see Figure 15. However, a small amount of Pt can promote HC oxidation for Pd. The CO light-off temperature for Pd is lower than for Pt. Furthermore, the light-off temperature decreases with increasing loading of Pd and Pt but only to an upper limit since it depends on the reaction limitations. However, this does also depend on the catalyst and the compound to be oxidised. [44]

\[ \text{Figure 15: Light-off temperatures for 220 ppm xylene (Δ), 900 ppm propene (□) and 4600 ppm CO (○) at GHSV}_{\text{DOC}} 144000 \text{ h}^{-1} (20°C) for different catalyst ratios of Pd:Pt. In all cases the PGM-loading was 10 μmol/g catalyst. The catalysts were thermally aged at 550°C for two hours. The light-off temperature was defined as the DOC inlet temperature where half of the compound was converted.} \]
When the gas contained CO the light-off temperature of propene decreased for higher mass fraction of Pd of the total PGM-loading, see Figure 16. Furthermore, the amount of NO$_2$ decreased with higher mass fraction of Pd. [41] Light-off temperatures of HCs are lower for Pt than for Pd when there is no CO in the gas. If CO is present, the oxidation of HCs occurs at higher temperatures for Pt and especially Pd. [33]

![Figure 16](image1.png)

**Figure 16:** Light-off temperature of propene in 200 ppm NO, 260 ppm propene and 90 ppm propane (□) and the gas contained 500 ppm CO as well (o) at GHHSV$_{DOC}$ 30000 h$^{-1}$. The catalyst was severely aged by hydrothermally treatment with 10% water in flowing air at 750°C for 72 h. [41]

NO to NO$_2$ conversion decreases with increasing mass fraction of Pd, see Figure 17. [41]

![Figure 17](image2.png)

**Figure 17:** NO to NO$_2$ conversion at steady-state for a mildly aged catalyst (left) and a severely aged catalyst (right) for the ratios of Pt:Pd [wt] 1:0 (▲), 7:1 (●), 2:1 (o), 1:2 (▲), 1:5 (□) and 0:1 (●). The mildly aged catalyst was hydrothermally treated with 10% water in flowing air at 750°C for 2.4 h, while the severely aged catalyst was treated in the same condition for 72 h. [41]
4.4 Catalyst Deactivation of Platinum Group Metals and Washcoat

Deactivation of catalysts needs to be considered since it affects the performance of DOCs. Catalysts can be thermally, chemically and/or mechanically deactivated. [1] Catalysts in exhaust aftertreatment systems are mainly thermally and chemically deactivated during normal vehicle operation. [19] Thermal deactivation is sintering of the active metals and/or washcoat due to increased temperature, see Figure 18. The driving force is the lower surface energy. [3] Regeneration of catalysts is possible if the deactivation is reversible. [46]

![Figure 18](image18.png): Fresh catalyst, washcoat and substrate (left), sintered catalyst (middle) and sintered washcoat (right). [1]

Chemical deactivation can be selective or nonselective, see Figure 19. [3] Selective deactivation is when the poison chemisorbs irreversibly to the active site and thereby blocks it, which results in decreased activity towards the desired reaction. [3,65] Examples of catalyst poisons are sulphur, phosphorus, zinc and magnesium originating from fuel and lubrication oil. [3,66] The active site can be reversible inhibited, which is a weaker interaction with the active site than poisoning. [3,65] The nonselective poisoning, known as masking or fouling, is deposition of compounds onto the washcoat surface. [3] Additionally, poisoning is often more extensive in a zone where it first comes in contact with the catalyst. [66]

![Figure 19](image19.png): Selective poisoning of catalytic active sites and nonselective poisoning of catalytic active sites by masking. [67]

Mechanical deactivation can be caused by thermal shock, attrition/abrasion and/or crushing. [19,68] Thermal stress can result in breakage of the washcoat and/or separation of the washcoat from substrate. [69] Attrition is grinding down caused by friction and abrasion is superficial friction often only a few micrometers into the surface, which can be caused by PM when passing the catalyst. [68] Moreover, the structure can be physically blocked. [19]
4.5 Washcoat

The washcoat does not only provide large surface area, but it also affects the activity and selectivity of catalysts and may catalyse the reaction itself. \[1,70,71\] Some important parameters for the washcoat are thermal stability, mechanical stability, surface area, porosity, pore size distribution and reactivity. \[33,44,72\]

Pore size distribution of the washcoat affects whether or not a molecule can or cannot diffuse into the structure to the active site. Smaller molecules are less sensitive. \[44\] Exemplified, HCs, NO, NO\(_2\) and O\(_2\) have different sizes that affect the diffusion into pores. HCs can be large (compared to the other mentioned molecules), which can result in difficulty to reach the active site in the washcoat and thereby lower oxidation rate.

The distribution of the washcoat on the substrate depends on the shape of the cell. An example of this is that square cells tend to have more washcoat in the corners compared to the sides, while hexagonal cells have more uniform thickness of the washcoat. \[7\] This means that the internal mass transfer may be affected due to a longer transportation distance within washcoat, here in the corners of square cells.

The washcoat can contain promoters that facilitate reaction and stabilizers. \[33\] Structural promoters can change surface structure, which often affects the catalyst selectivity. \[46\] The washcoat can be either sulphating or non-sulphating, meaning that sulphur compounds adsorb or not to the washcoat. The advantage of having a sulphating support is the damping effect that gives slower deactivation of the active material. \[33\]

There are numerous washcoats that can be used for catalysis applications. The most commonly used washcoat is alumina (Al\(_2\)O\(_3\)) and other examples of washcoats are silica (SiO\(_2\)), titanium dioxide (TiO\(_2\)) and zeolites. \[1,33\] Al\(_2\)O\(_3\) can exist in several forms and these are chi (\(\chi\)), eta (\(\eta\)), gamma (\(\gamma\)), kappa (\(\kappa\)), delta (\(\delta\)), theta (\(\theta\)) and alpha (\(\alpha\)). The manufacturing (material and temperature) and operation conditions determine the form of Al\(_2\)O\(_3\). The most common form in catalytic pollution control is \(\gamma\)-Al\(_2\)O\(_3\) due to high thermal and mechanical stability, which has high surface area (50-300 m\(^2\)/g). Crystalline and non-porous \(\alpha\)-Al\(_2\)O\(_3\) is formed due to calcination above 1000°C and can be used as ceramic support. \[72\] If Al\(_2\)O\(_3\) is used as the washcoat, the catalyst can tolerate more SO\(_X\) because it works as a scavenger. \[3\]
4.6 Substrate Geometry and Material

The geometry and material of the substrate influence mass and heat transfer, which in turn affect the performance of the DOC. When optimizing the substrate geometry there are several parameters to consider such as length, diameter, pressure drop, cell shape, cell density and material. [1]

In applications for heavy-duty vehicles, ceramic monolith with honeycomb structure with square cells is commonly used due to its relatively large surface area combined with low pressure drop. [1,43,7] Furthermore, space limitations must be considered since the component must fit onto the vehicle. [1] Substrate materials can for instance be ceramics, metals and plastics. [39]

Pressure drop represents energy loss, hence the substrate design is of interest to consider. [39] Cell density is defined as the number of cells per unit frontal surface area, often measured in cells per square inch (cpsi). [18,39] The cell density depends on number of cells/channels, diameter of these and wall thickness. [39] The channels can be in form of square, triangular, hexagonal and round. [1] Thinner walls or lower cell density result in lower pressure drop and shorter heating, but lower mechanical strength. [7] Thinner walls improve the light-off performance due to faster heating. Moreover, the conversion increases with higher cell density due to better external mass transfer. [73]

The geometric surface area (GSA) of the substrate is the area of the channels per unit substrate volume, where the washcoat and catalyst are deposited. [39,74] Increasing the geometric surface area gives higher conversion, but the pressure drop usually increases. Furthermore, larger open frontal area (OFA) of the substrate gives lower pressure drop. [39] Total surface area (TSA) of the substrate with a specific volume depends on GSA and substrate volume (V), which depends on cross-sectional area (A_{c-s}) and length (L), see equations E-6 and E-7. [1]

\[
\text{TSA} = \text{GSA} \times V 
\]

\[
V = A_{c-s} \times L 
\]
5 Working Hypotheses

Based on previous chapters, the work has proceeded from following the two working hypotheses:

[A] Does the HC conversion increase if the amount of active material is higher in a zone at the beginning and less in a zone at the end of the catalyst compared to if the same amount is dispersed equally?

[B] Is it possible to selectively increase HC oxidation by increasing the relative amount of Pd (and lowering the relative amount of Pt to decrease the NO oxidation) in the catalyst without endangering the total oxidation performance of the DOC?
6 Method
This master thesis comprised both theoretical and experimental work followed by analyses and evaluation.

The experimental work consisted of full-scale experiments in engine test bed and testing different parameters affecting the oxidation of HCs by using different DOCs. An engine test bed includes engine and exhaust gas aftertreatment system in a soundproof room and control room, from where the engine is operated.

6.1 Test Objects
To test the effect of zone-coated catalysts and varying Pt:Pd ratio, six commercially available DOCs were tested, see Table 4 and Table 5. DOC I, II,III and IV are zoned-coated DOCs. The first two DOCs were labelled as references since these had been used in previous tests at Scania. In these previous tests they were found to have good HC oxidation performance and NO oxidation performance, respectively.

Table 4: Specification of the DOC substrate (material, volume and cell density/wall thickness) and the coating (supplier, PGM-loading and ratio Pt:Pd) for the reference DOC for oxidation of HC and NO, respectively.

<table>
<thead>
<tr>
<th>DOC</th>
<th>HC ref</th>
<th>NO ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Ceramic</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Volume [dm$^3$]</td>
<td>$V_1$</td>
<td>$V_1$</td>
</tr>
<tr>
<td>Cell density/wall thickness [cpsi]/[mil]</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplier</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>PGM-loading [g/ft$^3$]</td>
<td>High</td>
<td>low</td>
</tr>
<tr>
<td>Ratio Pt:Pd [wt]</td>
<td>Pt&gt;Pd</td>
<td>Pt&gt;&gt;Pd</td>
</tr>
</tbody>
</table>

Table 5: Specification of the DOC substrate (material, volume and cell density/wall thickness) and the coating (supplier, PGM-loading and ratio Pt:Pd) for DOC I-IV.

<table>
<thead>
<tr>
<th>DOC</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Ceramic</td>
<td>Ceramic</td>
<td>Ceramic</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Volume [dm$^3$]</td>
<td>$V_1$</td>
<td>$V_1$</td>
<td>$V_1$</td>
<td>$V_1$</td>
</tr>
<tr>
<td>Cell density/wall thickness [cpsi]/[mil]</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Coating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplier</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>PGM-loading [g/ft$^3$]</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Ratio Pt:Pd (total) [wt]</td>
<td>Pt&gt;&gt;Pd</td>
<td>Pt&gt;Pd</td>
<td>Pt&gt;Pd</td>
<td>Pt&gt;Pd</td>
</tr>
</tbody>
</table>
6.1.1 Large Volume Oxidation Catalyst

A large volume oxidation catalyst (L-DOC) was used downstream the DOC. This catalyst was mounted downstream the DOC to oxidize any HC-slip leaving the DOC and the specifications of L-DOC is presented in Table 6.

Table 6: Specification of the L-DOC substrate (material, volume and cell density/wall thickness) and the coating (supplier and PGM-loading).

<table>
<thead>
<tr>
<th>L-DOC</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Material</td>
<td></td>
</tr>
<tr>
<td>Volume [dm$^3$]</td>
<td>$V_2$</td>
</tr>
<tr>
<td>Cell density/wall thickness [cpsi]/[mil]</td>
<td>C</td>
</tr>
<tr>
<td>Coating</td>
<td></td>
</tr>
<tr>
<td>Supplier</td>
<td>D</td>
</tr>
<tr>
<td>PGM-loading [g/ft$^3$]</td>
<td>Very low</td>
</tr>
</tbody>
</table>
6.2 Test Setup

The test setup after the engine consisted of pipes, insulated inlet cone, DOC, ring, L-DOC and outlet cone, see Figure 20 and Figure 21. Just before the inlet cone, a mixing unit with baffles was used to enable good mixing of the exhaust gas before it reached the DOC and downstream components. This was chosen to facilitate comparison between the performance of the DOCs.

![Diagram](image)

**Figure 20:** Experimental setup with insulated inlet cone (with baffles to enable better mixing), DOC, ring, L-DOC and outlet cone. TE09 and TX11, TE10 and TX12, and TE11 and TX13 refer to the gas temperature pre DOC, post DOC and post L-DOC.

![Image](image)

**Figure 21:** Experimental setup with insulated inlet cone, DOC, ring, L-DOC, outlet cone and pipes. The picture at the top to the right is the inlet cone with the bafflers mix of the exhaust gas.
To evaluate the temperature profile inside the centre of the DOCs, four thermocouples were placed inside the DOC at the centre, see Figure 22 and Figure 23. The thermocouples were placed at 10, 25, 50 and 90% of the length of the DOC from the inlet because it would give some information about the temperature profile within the DOCs with different loaded zones.

![Figure 22: Axial placement of four thermocouples inside the DOC.](image)

![Figure 23: Placement of the four thermocouples at the centre (marked with ×) of the DOC.](image)

### 6.2.1 Engine and Fuel

The engine used in the tests was a six cylinder 13L diesel engine and the fuel was EN590 diesel with 10% Rape Methyl Ester (RME).
6.3 Testing
The testing of the DOCs included both measuring of HC and NO oxidation performance.

6.3.1 Degreening of the DOCs
First, the DOCs were degreened for 4 h with a DOC inlet temperature of 450°C before any tests were performed (Scania standard). DOC HC ref and DOCs I-IV were new catalysts while DOC NO ref had been used in tests before but this DOC was also degreened in the same way as the other ones.

6.3.2 Automatic Tests for Measuring HC and NO Oxidation Performance
The automatic test TST_DOC_TempTrappa_V02 (TempTrappa) was used to evaluate both HC and NO oxidation performance of the DOCs, see Figure 24. This test was developed and tested by Olof Svensson, NMOD. The reason for using an automatic test was to ensure that all tests were performed in the same way aiming at good repeatability.

In short, the test TempTrappa uses predetermined load, speed and mode to operate the engine. These parameters were listed in a Design of Experiment file (DOE-file). During testing, the point was first stabilised so the temperature after DOC was within 1°C/min (dTE10/dt<1°C/min). Thereafter were values measured and stored before DOC, after DOC and after L-DOC measured (average during 30 s). FTIR was used to measure the gas composition. Next, the program evaluated if it was possible to start internal post-injection of diesel (HC-dosing). HC-dosing started if the DOC inlet temperature was less than 30°C lower than the desirable DOC outlet temperature. If not, the program moved to the next point. If the difference was larger than 30°C, HC-dosing was initiated. The HC-dosing amount injected aimed at reaching a target temperature after the DOC using a feedback mechanism. Values were measured and stored (average during 30 s). Thereafter, the program moved to the next point. If the HC slip after L-DOC was larger than 100 ppm the HC-dosing was ended and the system cleaned by increasing the mass flow rate. The program used both average values and recorder.

The points (speed and torque) in the DOE-file was chosen to evaluate different flow rates (GHSV$_{DOC}$ X1<X2<X3<X4 ) at varying DOC inlet temperatures. DOC I was the first to be tested followed by DOCs II, III, IV, HC ref and NO ref. After the first test a number of points were added to the test series (DOC II) to cover a wider temperature range and some of these points were adjusted after the second test. Thereafter (DOC III, DOC IV, DOC HC ref and DOC NO ref) was the same points used when testing the performance. The criteria of acceptance for the GHSV$_{DOC}$ was ±5% of the targeted GHSV$_{DOC}$.

The emissions in the gas was measured with Fourier transform infrared spectroscopy, which can detect compounds that absorb infrared radiation. In the tests performed, FTIR was used for evaluation of HCs, NO, NO$_2$ and CO among other compounds. This instrument also had a flame ionization detector (FID) for better analysis of the HCs.
**Figure 24:** Schematic illustration of the automatic test TempTrappa. The test used a list of speed and torque to operate the engine, resulting in different GHSV$_{\text{DOC}}$ and DOC inlet temperature. The program measured before DOC, after DOC and after L-DOC as well as initiating HC-dosing when possible.


7 Results and Discussion

In this chapter, results from the engine test beds are presented and discussed. The first part describes HC oxidation performance of the DOCs and thereafter follows NO oxidation performance of these. The selectivity of the DOCs are then discussed. Finally, the repeatability and uncertainty of measurements are commented.

7.1 HC Oxidation Performance of the DOCs

The HC conversion is normally calculated by measuring the HC-concentration upstream and downstream the DOC. This was not possible due to limitations of the gas analysers (FTIR and FID) used. The used gas analysers can measure HC-concentrations up to several hundred ppm. During HC-dosing, the concentration is of the order 10000 ppm. Therefore the conversion was analysed using thermocouples upstream and downstream the DOC and L-DOC. If all HC (>99%) is oxidised in the DOC, no additional exotherm will occur in the L-DOC. If only half (50%) of the HC is oxidised in the DOC an additional exotherm will occur in the L-DOC. The heat created will be proportional to the HC conversion. If the following effects can be understood it is possible to calculate the conversion using the measured temperatures:

(i) DOC and L-DOC are able to achieve >99% conversion in all test points

(ii) No effect of thermal mass of the system.

(iii) The system is adiabatic, which means that no heat loss occurs to the surroundings.

(i) can be tested by measuring the concentration of HC downstream the L-DOC. (ii) can be minimized by performing tests in stationary points (constant GHSV$_{DOC}$ and temperature). (iii) can be evaluated by calculating the temperature drop across DOC and L-DOC prior to HC-dosing. Using (i)-(iii), the HC conversion can be calculated using equation E-8, where TE10 is the temperature after DOC and TX13 is the temperature after L-DOC.

\[
X = \frac{TE10(dosing) - TE10(not
dosing)}{TX13(dosing) - TX13(not
dosing)} \quad \text{(E-8)}
\]

Important to notice is that this system is not adiabatic and due to the heat loss of the system, the calculated HC conversions after the DOC exceed 100% in some of the cases. However, the HC oxidation performance of the DOC can be compared between the different DOCs.
HC oxidation performance of the DOCs are similar where it was possible to perform HC-dosing and the HC conversion decreases with increasing GHSV$_{\text{DOC}}$ in all cases, see Figure 25. In other words, the HC slip increases with increasing GHSV$_{\text{DOC}}$ causing a larger exotherm across the L-DOC. A longer residence time in the DOC (lower GHSV$_{\text{DOC}}$) enables higher conversion of HCs. To enable higher HC conversion after the DOC at the higher flow rates, a larger DOC is needed (to improve the mass transfer and thereby the HC conversion). Furthermore, the HC conversion increases with increasing DOC inlet temperature due to higher reaction rate.

Figure 25: HC conversion after the DOCS as function of the DOC inlet temperature for the four GHSV$_{\text{DOC}}$ X1, X2, X3 and X4 1/h. Lower GHSV$_{\text{DOC}}$ and higher DOC inlet temperature give higher HC conversion after the DOC.
The differences in HC conversion are small between the DOCs at a specific GHSV\textsubscript{DOC}, see Figure 26. However, the temperature intervals where it is possible to dose HCs vary, see Figure 27.

![Figure 26](image)

**Figure 26**: HC conversion after the DOCs as function of the DOC inlet temperature for the six DOC at the GHSV\textsubscript{DOC} X1. All HC conversion over the DOCs are similar, but the range where it is possible to perform HC-dosing are different. This is especially valid for the DOC NO ref.

It was possible to achieve successful HC-dosing for a range of DOC inlet temperatures for the six DOCs, see Figure 27. DOC I-IV have similar HC oxidation performance as DOC HC ref, while the DOC NO ref has the lowest HC oxidation performance of the six DOCs.

The zone-coated DOCs HC ref and I-IV enable better light-off of the HCs in the exhaust gas compared to DOC NO ref.

There is no noticeable effect of lower HC oxidation performance by increasing the ratio of Pd (compare for DOC I with DOC II and DOC III) even though Pd has less oxidising properties than Pt. Additionally, the HC oxidation performance is not noticeably affected by the PGM loading when comparing DOC I and DOC IV. Consequently, the HC oxidising performance for the new prototypes is limited by mass transfer.
Figure 27: HC oxidation performance for the DOCs for the GHSV_{DOC} (the flow is increasing in the y-direction in each graph) as function of DOC inlet temperature. The round points represent where measurements with HC-dosing were tested and the black triangles represents the points where it was possible to successfully dose and oxidise HCs. The red lines mark the lower temperature where it was possible to oxidise HCs during dosing for the evaluated points. DOC I-IV have similar HC oxidation performance as the DOC HC ref, while DOC NO ref has the lowest HC oxidation performance.
7.2 NO$_2$/NO$_x$ after the DOCs

The NO$_2$/NO$_x$ oxidation performance vary for the different DOCs, see Figure 28. All NO$_2$/NO$_x$-quotas presented are measured while not dosing diesel. At low temperature the system is limited by the kinetics and with increasing temperature, the limitation is the internal mass transfer followed by the external mass transfer. The thermodynamic equilibrium is the upper limit for how much NO$_2$/NO$_x$ that can be formed at the specific conditions.

There are a number of parameters to evaluate. First, the DOC NO ref has the lowest NO oxidation performance while DOC HC ref has the highest. This was expected since it is the two DOCS with the lowest and highest PGM-loading, respectively. DOC I-IV have the NO oxidation performance between the two reference DOCS, where DOC IV is the closest to DOC NO ref for the evaluated GHSV$_{DOC}$. Moreover, DOC III is quite close to DOC IV and thereby also DOC NO ref (especially at GHSV$_{DOC}$ X3 and X4 1/h).

![Figure 28: NO$_2$/NO$_x$ after the DOCS as function of the DOC inlet temperature for the four GHSV$_{DOC}$ X1, X2, X3 and X4 1/h.](image)

NO$_2$/NO$_x$ at the DOC inlet temperature 280°C and GHSV$_{DOC}$ X1 was analysed as function of Pt content, Pd content and total PGM content, respectively. The same correlation was found in all three cases, increasing content increases the NO oxidation. As such, these results do not clearly indicate that Pt has a higher activity for NO oxidation than Pd as was previously shown in the literature. However, it is likely that the variations in Pt:Pd ratios for the DOCS tested here are too small to result in a significant change. The NO oxidation is also affected by for instance type of washcoat and PGM-loading.
7.3 Repeatability for Measuring DOC IV

To test the repeatability DOC IV used and both HC oxidation performance and NO$_2$/NO$_X$ performance was tested at GHSV$_{DOC}$ of X1, see Figure 29. The temperature was first decreased, then increased and finally randomly selected twice (by using Excel), see Figure 30. The repeatability is good regarding there is a lot of parameters affecting the performance of the DOC. The NO$_2$/NO$_X$ is somewhat higher in Figure 29 compared to Figure 28. However, the order of the points measuring may explain this.

Figure 29: HC conversion after DOC as function of DOC inlet temperature and NO$_2$/NO$_X$ after DOC as function of DOC inlet temperature for the GHSV$_{DOC}$ X1. Here the repeatability for the points is evaluated as the temperature first was decreased, then increased and then randomly selected order twice. The repeatability is in both cases high, regarding there is a lot of different parameters affecting the results such as the stability of the engine.

Figure 30: The order of the measured points with the DOC inlet temperature for the GHSV$_{DOC}$ X1 1/h. Points 1-12 are while decreasing the temperature, points 13-24 are while increasing the temperature, points 25-36 are the randomly selected order the first time and points 37-48 is the randomly selected order the second time.
7.4 Uncertainty of Measurements

Non-uniform flow distribution affects the oxidation performance by changing the external mass transport and thereby the temperatures created by HC oxidation. This may also affect the temperatures measured, but the thermocouples were placed in the same way in all tests.

To eliminate differences caused by hysteresis between the DOCs, the tests were performed in the same way and the steady-state points were measured by decreasing the DOC inlet temperature.

The post injection of diesel has also certain margin of error since partial oxidation upstream the DOC may change the DOC inlet temperature and HC composition, which in turn affect the oxidation performance.
8 Conclusion

A non-uniform PGM distribution enables higher HC oxidation performance compared to uniform PGM distribution, which means that working hypothesis A about HC oxidation with non-uniform distribution can be accepted.

The overall HC oxidation performances for DOC I-IV compared to DOC HC ref were not significantly affected by changes in ratio between Pt:Pd for the evaluated mass flow rates and temperatures, which confirm working hypothesis B. However, no conclusive results showing a significant difference in the NO oxidation between Pt and Pd were found. This is even though Pd generally has lower oxidation activity than Pt.

In summary, it is possible to selectively promote the HC oxidation over the NO oxidation performance of a DOC. This means that the oxidation properties of the DOC can be custom made for a specific application.
References


Appendix A – Hysteresis

Exhaust aftertreatment systems operate under transient temperature conditions due to how the engine operates. For this reason, hysteresis is a phenomenon of interest to consider since it can arise under transient temperature conditions. Oxidation reactions usually show hysteresis behaviour, where the conversion is higher during the cooling phase compared to the heating phase, see Figure A-1. The phenomenon can also be inverse hysteresis, where the conversion is higher during the heating phase compared to the cooling phase, see Figure A-1. [A1]

Figure A-1: Illustration of hysteresis, where conversion is higher during cooling than heating (left), and inverse hysteresis, where conversion is higher during heating than cooling (right). [30]

Hysteresis can be caused by both physical and chemical effects. [A1] It can for instance be caused by thermal resistance within the catalyst, multiple steady states caused by exothermic reactions or surface inhibition, pore structure and oxidation state of the catalyst. [A1,A2] Hysteresis attributed to thermal resistance within the catalyst is due to higher inlet temperature than the average temperature of the catalyst during heating and the other way around for cooling. The exothermic heat of reaction enables reaction even when the inlet temperature is lower than the ignition temperature resulting in the possibility for hysteresis. Surface inhibition depends on which compounds adsorb onto the catalyst at what operating conditions and thereby changes may give rise to hysteresis. [A1] Adsorption depends on the pore structure among other things and thereby the structure may give rise to hysteresis. [A2] Another explanation is reversible oxidation of the catalyst, where the catalyst gets oxidised or reduced depending on conditions, which affects the activity. [A1]

To sum up, hysteresis and/or inverse hysteresis are vital to consider for the exhaust aftertreatment system. This is since the reaction rate, besides gas composition and temperature, depends on the history of the catalyst. Engine control systems usually use look-up tables to predict conversion, which do not regard hysteresis or inverse hysteresis. [A1]
References – Appendix A
