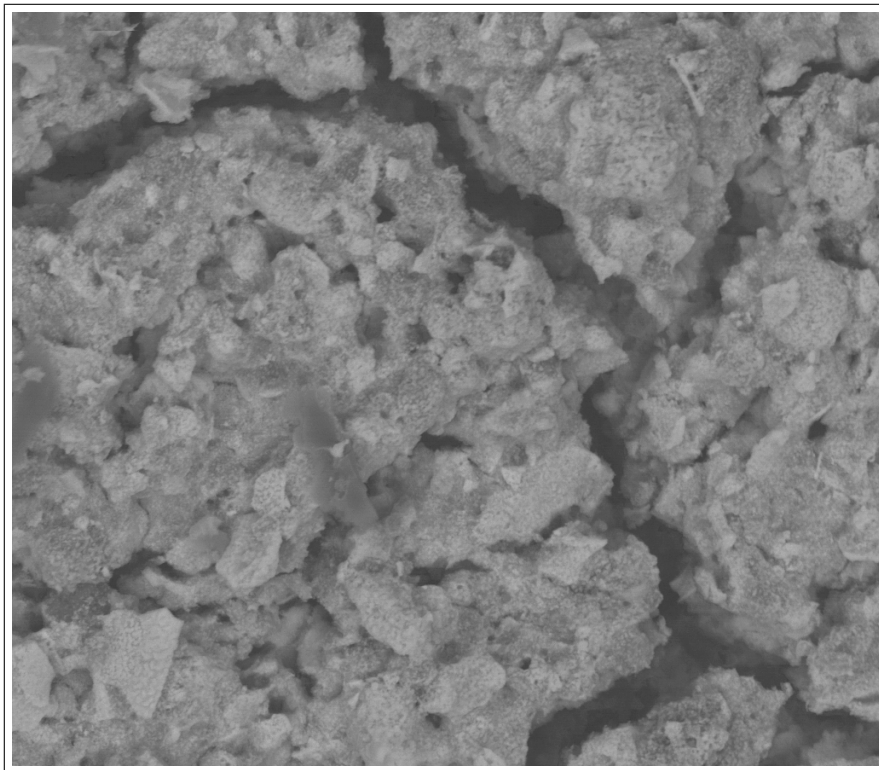


# CHALMERS



## Characterization of Automotive Catalyst Ageing

*Master of Science Thesis*

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Department of Chemical and Biological Engineering  
Division of Chemical Engineering  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2014



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Master of Science thesis  
KBTX05

CHALMERS UNIVERSITY OF TECHNOLOGY  
Department of Chemical and Biological engineering  
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Simon Lindqvist, Göteborg, July 11, 2014



## Abstract

The objective of this thesis work was to study the effect of different ageing methods on catalytic systems for cars. The work was divided into two parts examining three-way catalysts for petrol engines as well as lean NO<sub>x</sub> traps for diesel engines. The first part consisted of an examination of the effect of poison (addition of P, S, Zn and Ca to the fuel) used for rapid ageing of a three-way catalysts (TWC) for petrol systems. The purpose was to investigate how long the catalyst had to be aged thermally to reach the same level of deterioration as a poison aged catalyst. The purpose was also to determine whether it is preferable to use poison as a time-saving measure, or if this affects the result in some way with regards to activity and material characteristics. The second part consisted of a comparison of a fresh and an aged lean NO<sub>x</sub> trap (LNT) with respect to NO<sub>x</sub> storage and conversion capacities. The analysis was done in motor-rigs and flow-reactors as well as with a SEM/EDX equipment analysing the distribution of poisons.

The results showed that 50 h of thermal ageing corresponded well to 20 h of poison ageing of the three-way catalysts with regards to both oxygen storage capacity and conversion capacities. The comparison of the poison ageing and thermal ageing method showed that the poison seemed to have a greater effect on the oxygen storage capacity, while the thermal ageing affected the light-off characteristics more. Both methods did also have a greater effect on the front of the catalyst where the characteristics were more severely deteriorated. The SEM/EDX analysis found most of the poisons in the first part of the catalysts, rapidly declining towards the outlet. The study of the lean NO<sub>x</sub> traps showed that the ageing had reduced both the conversion of HC, CO and NO<sub>x</sub> as well as the NO<sub>x</sub> storage and deNO<sub>x</sub> capacities.

**Keywords:** Three-way catalyst, TWC, Lean NO<sub>x</sub> trap, LNT, catalyst ageing, catalyst characterization





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## 1 Introduction and Background

Emissions from the automotive industry have a direct negative impact on both the environment and our health. These emissions mainly consists of nitrous oxides ( $\text{NO}_x$ ), which contributes to acidification of lakes, carbon monoxide (CO) and hydrocarbons (HC), which can be extremely poisonous, and carbon dioxide ( $\text{CO}_2$ ) which is a greenhouse gas. It is therefore of great importance to reduce the amount of these substances in the exhaust gases. The emissions of the nitrous oxides, carbon monoxides and hydrocarbons are today reduced by the help of different catalytic systems, but it is unfortunately not possible to decrease the emissions of carbon dioxide. However, if alternative fuels are used it would result in a decrease of the net  $\text{CO}_2$  formed.

The most commonly used system for petrol engines is a so called three-way catalyst (TWC), while a lean  $\text{NO}_x$  trap (LNT) is more common for diesel engines. Both of these techniques are very effective at decreasing the emissions of hazardous gases.

Even if the legislations regarding the concentrations are met, one aspect is still in need of further investigation; the ageing process of the catalysts. The required life time for the exhaust gas after treatment system in EU is 160 000 km, and it is therefore crucial that the catalytic converters are able to maintain their high efficiency under this time.

One way to test the catalysts robustness is to mount it on a car and drive it for the required distance, and thereafter analyse the emissions. The problem is that this takes a lot of time, and quicker methods have therefore been developed. One common and very simple procedure is to heat the catalyst in an oven at high temperatures for several hours, which is supposed to represent the thermal ageing from the hot exhaust gases. Another way is to connect the catalyst to a stand-alone engine in a motor-rig, running specially designed cycles for rapid ageing. It is also common to add poisons in the fuel to even further accelerate the ageing process in the motor-rig. Even though it is possible to achieve the same amount of deterioration of the catalyst with regards to emissions through these alternative methods, it is not clear how these methods affect the catalysts in the way of other characteristics and material properties. Further studies are therefore needed in this area, which is the purpose of this thesis work.

### 1.1 Objective

The objective of this thesis work is to analyse the effect of different ageing methods, used in the industry, on catalytic systems. The study is divided in to two parts, examining both three-way catalysts (TWC) for petrol engines and lean  $\text{NO}_x$  traps (LNT) for diesel engines. The effect of thermal- compared to poison-ageing of TWCs will be analysed as well as the impact of ageing of LNTs. It will also be conducted a study to determine the time needed for thermal ageing to correspond to poison ageing. The analysis is done both in motor-rigs and flow-reactors as well as with SEM/EDX equipment.



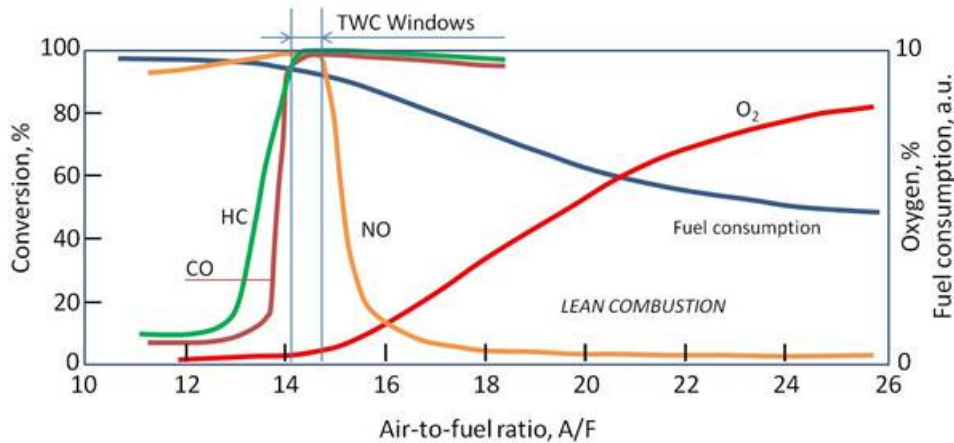
## 2 Theory

Since the purpose of this thesis work is to analyse the effect of different ageing methods on catalysts for different systems, some theory explaining how the different systems work, important characteristics, as well as how this can be analysed, are presented below.

### 2.1 Three-way catalyst

The most common way to decrease the emissions from petrol cars today is to use a so called three-way catalyst, TWC. These catalysts are often in the form of monoliths with around 300-900 cpsi (channels per square inch). The monolith structure often consists of the ceramic material cordierite ( $2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 2\text{MgO}$ ) but can also be made up of corrugated metal [1]. The active sites, often consisting of highly dispersed precious metals such as Pt, Pd and Rh [2, 3], are distributed on the channel walls in the washcoat. The washcoat also contains Ce for oxygen storage capacities and other substances such as Zr, Al and Ba to increase the activity as well as the resistance to ageing [4].

The three-way catalyst is able to simultaneously reduce the emissions of CO, HC (collective name for all hydrocarbons) and  $\text{NO}_x$ , which is from where it got its name. The overall reactions happening in the catalyst are shown in table 1 [5]. This is done most effectively at a stoichiometric air-fuel ratio of 14.7:1, also referred to as  $\lambda = 1$ , which is when the exact amount of air needed to completely oxidise the fuel, is supplied. The dependence of conversion of CO, HC and  $\text{NO}_x$  with respect to the air-fuel ratio is shown in figure 1, together with the operating region of where the catalyst has high conversion of all three species, called the lambda- or TWC-window.



**Figure 1:** The conversion of HC, CO and NO with respect to the air-fuel ratio together with  $\text{O}_2$  and fuel consumption for a three-way catalyst. [6]

A mixture with an air-fuel ratio smaller than 14.7:1 is called rich, which means that there is a deficit of oxygen in the exhaust gases. The lower oxygen concentration results in a lower conversion of CO and HC, but the reductive environment is advantageous

**Table 1:** Overall reactions of a TWC. [5]

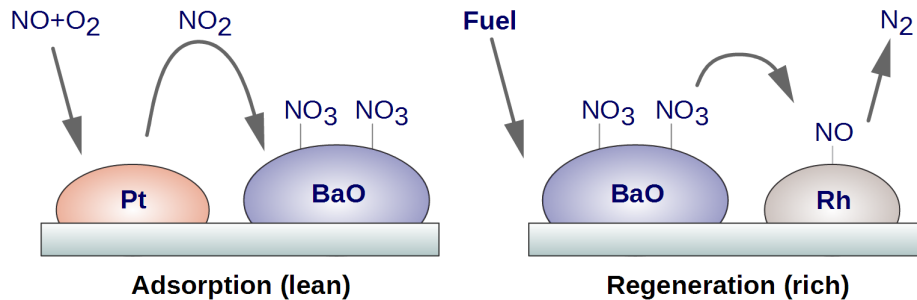
Reactions	Most efficient catalysts
$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	Pt, Pd
$2 \text{HC} + 2 \frac{1}{2} \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{H}_2\text{O}$	Pt, Pd
$\text{NO}_x + x\text{CO} \rightarrow \frac{1}{2} \text{N}_2 + x\text{CO}_2$	Rh, Pd

for the conversion of  $\text{NO}_x$ . Conversely, a mixture with an air-fuel ratio above 14.7:1, called lean, results in an oxygen excess which increases the conversion of CO and HC but decreases the conversion of  $\text{NO}_x$ .

## 2.2 Lean $\text{NO}_x$ trap

Another type of catalytic converter that is common today is the lean  $\text{NO}_x$  trap, LNT. These catalysts are mainly used on diesel systems because of its ability to handle  $\text{NO}_x$  emissions under lean conditions. This also makes it possible to decrease the fuel consumption by running the engine on a lean mixture which increases combustion efficiency, without increasing the  $\text{NO}_x$  emissions.

The LNT is able to do this by adsorbing  $\text{NO}_x$  as nitrates or nitrites under the lean condition cycle and, under the short rich cycle, reduce the adsorbed  $\text{NO}_x$  to  $\text{N}_2$  [7], see figure 2. This is done while continuously oxidising CO and HC in the same way as in a TWC. The LNT is usually composed of three parts; precious metals such as Pt, Pd and Rh for the redox reactions, alkali metals such as Na and K or alkaline earth metals e.g. Ba and Mg for the  $\text{NO}_x$  storage, and a highly porous support material, e.g.  $\text{Al}_2\text{O}_3$ , for large surface area [8]. The major disadvantage with the LNTs is that they are very sensitive to  $\text{SO}_x$  poisoning of the  $\text{NO}_x$  storage sites, which is problematic since all types of petrol and diesel fuels contains significant amounts of sulphur.



**Figure 2:** The process of oxidation of NO and storage of  $\text{NO}_2$  during the lean cycle and reduction of  $\text{NO}_2$  to  $\text{N}_2$  during the rich cycle.

## 2.3 Characteristics of catalytic converters

Automotive catalysts are characterized through many different measurable characteristics and the most frequently used are presented in brief below.

### 2.3.1 Conversion

One of the most important variable to measure is the conversion of CO, HC and NO<sub>x</sub> over the catalyst. Since it is the catalysts main purpose to decrease the emissions, it is crucial to measure and verify that the conversion is high enough to be able to decrease the emissions below the threshold. This can for example be measured from a real car, in a motor-rig or in a flow reactor.

### 2.3.2 Light-off temperature

A drawback with today's catalysts is that they require a high temperature to function properly. This is not a problem at normal driving conditions but becomes problematic when the car starts with a cold catalyst. This results in a so called cold start, meaning that the temperature of the catalyst is much lower than what is needed for the reactions to take place, resulting in increased emissions.

One way to measure how well the catalyst will be able to handle cold starts is to perform light-off experiments. The light-off curves describes how the conversion depends on the temperature of the catalyst, and can therefore be used to evaluate how well the catalyst performs at lower temperatures. The light-off temperature is usually defined as the temperature at which 50% conversion is achieved [4]. A lower light-off temperature means that the reactions will start earlier after a cold start and lower emissions will be released. Light-off experiments can also be used to evaluate the kinetics of the catalyst in some extent [9].

There have been several proposed solutions to this problem which have included electrical heaters around the catalyst, or re-routing of the exhaust gases to accelerate the heating. Another proposed solution is to use secondary air injections (SAI) which increases the amount of oxygen in gases into the catalyst. This results in an exothermic oxidation of the unburned HC and CO heating the catalyst.

### 2.3.3 Oxygen Storage Capacity

The oxygen storage capacity (OSC) is an important parameter for three-way catalysts and is a measurement of how much oxygen that can be stored in the catalyst material. A TWC system is normally run at an air-fuel ratio of  $\lambda \approx 1$ , as described above, which means approximately stoichiometric conditions. But because of varying engine loads and vehicle speeds, this ratio can differ from  $\lambda = 1$ , resulting in increased emissions. A high oxygen storage capacity can help reduce this effect by storing oxygen in lean conditions and releasing oxygen at rich conditions. This helps to oxidise CO and HC even when there is a deficit of oxygen in the exhaust gases.

The OSC of a catalyst can be measured in several ways, where one way is to use CO or H<sub>2</sub> pulses [10]. This technique will measure the "standard" OSC, that is, it will measure the most loosely bound oxygen. Another kind of oxygen storage capacity, called the oxygen storage capacity complete (OSCC), is a measurement of both the more loosely and strongly bound oxygen [11]. These two differ because of how the oxygen is bound to the catalyst washcoat. The most common materials used in the catalysts to promote the OSC is CeO<sub>2</sub> together with ZrO<sub>2</sub> for thermal stability [12].

### 2.3.4 NO<sub>x</sub> Storage Capacity

The NO<sub>x</sub> storage capacity is one of the most important parameters for an LNT. A high storage capacity means that the car can be run at lean condition for a longer time without releasing too much NO<sub>x</sub>.

NO<sub>x</sub> is a generic term used to describe both NO and NO<sub>2</sub>, but it is only NO<sub>2</sub> that can be stored in the catalyst. This means that NO has to be oxidised for it to be stored. This is often done with the help of precious metals, for example Pt, in the catalyst washcoat. The NO<sub>2</sub> is then stored as nitrates on the BaO.

The NO<sub>x</sub> storage can be measured in several ways, depending on what it is that is of interest. Chaugule et al. [8] measured the fast storage capacity by calculating the amount stored until 1% of the inlet NO<sub>x</sub> escaped the trap. Other methods are to calculate the storage capacity for the time it takes for the conversion to sink to e.g. 70%.

### 2.3.5 deNO<sub>x</sub> Efficiency

The deNO<sub>x</sub> efficiency of a LNT is a measurement of how well it manages to convert NO<sub>x</sub> over a lean-rich cycle. This is, because of how the LNT work, a measurement of both the NO<sub>x</sub> storage capacity and NO<sub>x</sub> reduction activity. For a LNT to achieve high deNO<sub>x</sub> efficiency it needs to have a high storage capacity so that it can store all the NO<sub>x</sub> emissions during the lean period, and a high activity so it can reduce all the stored NO<sub>x</sub> during the short rich period.

## 2.4 Ageing mechanisms

The processes that are believed to contribute to the decreased efficiency of an automotive catalyst over time are usually divided into three areas; thermal, chemical and mechanical. These three mechanisms are described further below.

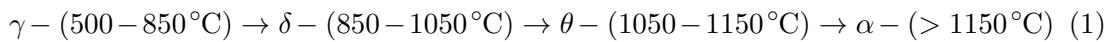
### 2.4.1 Thermal ageing

Catalytic converters for automotive use are subjected to high temperatures under long time, which has a negative effect on the activity of the catalyst. One cause of this is the sintering of the dispersed precious metal particles, which results in a decrease of the number of active sites, and therefore a decrease in catalytic efficiency [13]. The sintering, or agglomeration, can be described through two mechanisms; Ostwald ripening or Smoluchowski ripening, but is mainly movement of atoms between two particles,



merging them together. The difference between sintering and melting is that sintering occurs below the material melting temperature. But it should be noted that the diffusion is accelerated at higher temperatures, meaning that the reduction in precious metal particle dispersion is more severe at higher temperatures.

Another effect of the high temperature is the phase-transition of the support washcoat material. One of the most common support materials is  $\gamma$ - $\text{Al}_2\text{O}_3$ , which changes phase according to the following order [13]:



This phase shift can result in cracks in the washcoat, which might even dislodge parts from the monolith walls, resulting in reduced effectiveness of the catalyst. The phases existing at higher temperatures do also have a lower surface area, decreasing the activity even more.

A third effect of the high temperature is a change of the oxidation states of the precious metals, irreversibly affecting the activity of the catalyst. Palladium decomposes from its most active form, PdO, to metallic palladium when the temperature goes above  $600^\circ\text{C}$ , while rhodium loses its activity in the same way above  $650^\circ\text{C}$  [14].

### 2.4.2 Chemical deactivation

The chemical deactivation of a catalyst is mainly because of substances existing in the fuel and engine oil. Common poisons, such as S, Ca, Mg, Zn and P [15], will attach to the active sites through chemisorption, blocking them from catalytic activity, or even react with the precious metals and support materials, changing the characteristics completely.

Some poisons adsorb or reacts irreversibly with the material and others may only adsorb reversibly. This means that if the catalyst is subjected to certain conditions, the poison will detach, resulting in a regained activity. This can be used effectively for automotive catalysts in the case of sulphur. It is possible to desulphurize the catalyst by utilizing rich pulses at high temperature to reduce the adsorbed sulphur detaching it from the  $\text{NO}_x$  storage sites. Chemical deactivation can also occur because adsorbed species or changed structures blocks pores and thus reduces the active area [16].

### 2.4.3 Mechanical wear

The washcoat on an automotive catalyst has a very high effective area per volume of material. This type of structure makes them sensitive to fouling. Substances such as Mg, Zn and P as well as metal flakes and particles from the engine and exhaust pipe can clog pores and block active sites, reducing the efficiency of the catalyst. This effect can be reduced by decreasing the amount of problematic substances in the engine oils and by using more resilient materials in the engine and exhaust pipe.

There is also a chance that the ceramic material cracks because of large temperature oscillation or thermal shocks, resulting in loss of active substances or decreased active area [16].



### 3 Experimental Method

The catalytic systems analysed and the methods used are described further in this section.

#### 3.1 Catalytic systems

Several catalytic systems were tested and analysed and the two sections below describes their properties and what type of ageing they have been subjected to.

##### 3.1.1 Petrol systems

The catalytic systems analysed for the petrol part of the thesis work consisted of two catalysts connected after each other. The first catalyst had a volume of 1 l and a diameter of 118.4 mm while the second had a volume of 0.568 l and a diameter of 101.6 mm. Both were cylindrical and had a monolith cordierite structure with 400 cpsi. The washcoat consisted of  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2\text{-ZrO}_2$  as support and oxygen storage components and they had a loading mixture of Pd and Rh. The whole system, with both catalysts, was aged according to table 2 and tested in the motor-rig, while only the first catalyst of each system was analysed in the flow reactor and with SEM/EDX. KB-3280 was also analysed before it was aged as reference, additional to the information given in table 2.

**Table 2:** The petrol catalysts analysed.

Catalyst	Ageing
KB-3340	None
KB-3280	12 h poison and 8 h thermal
KB-3310	30 h and 50 h thermal

##### 3.1.2 Diesel systems

The catalytic systems analysed for the diesel part of the thesis work consisted of one catalyst. Table 3 displays the different systems that has been analysed and what ageing they have been subjected to. Both had a precious metal loading mixture consisting of Pt, Pd and Rh.

**Table 3:** The diesel catalysts analysed. Every catalyst was based on a corrugated metal structure.

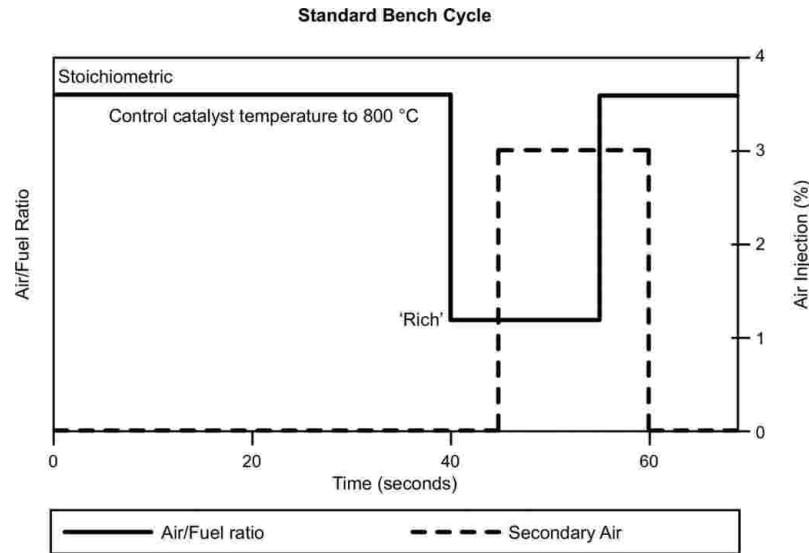
Catalyst	Ageing
LNT-112	None (Stabilized)
LNT-110	Oven and Motor-rig

### 3.2 Ageing methods

Since the objective of the thesis work was to compare and investigate different ageing methods, several different techniques have been used. These techniques are described further in the sections below.

#### 3.2.1 Ageing of petrol systems

The ageing of the petrol TWC systems was done in a motor-rig using a cycle based on the SBC (Standard Bench Cycle), figure 3, issued by the United States Environmental Protection Agency. The cycle is designed for rapid ageing of catalytic systems by changing between rich and lean condition. The cycle consists of four steps which are described in table 4.



**Figure 3:** The Standard Bench Cycle used for ageing of the petrol catalysts [17]

**Table 4:** The four steps of the SBC in figure 3. SAI stands for secondary air injections.

Step	1	2	3	4
Time [s]	40	5	10	5
SAI	NO	NO	YES	YES
Fuel Enrichment	NO	YES	YES	NO
Lambda incl. SAI	1	<1	$\approx 1.05$	$\approx 1.17$

Secondary air injections, used in step 3 and 4 above, means that additional air is added to the exhaust mixture after the engine but before the catalyst. This will produce lean conditions, oxidising the unburned and adsorbed CO and HC, resulting

in a temperature increase. This cycle was used for both the thermal and poison aged catalysts where additional poison was added to the fuel in the latter case. The time used for poison ageing, 20 h (12 with poison and 8 without), was used because of earlier shown accordance of deterioration compared to catalysts aged by cars driven 160 000 km (European standard). The times used for thermal ageing, 30 h and 50 h, was based on qualified guesses to correspond to the poison aged deterioration. The poisons used were a mixture of a primary alkyl zinc dithiophosphate and a synthetic calcium sulfonate.

### 3.2.2 Ageing of diesel systems

LNT-112 was stabilized in an oven at atmospheric pressure and gas composition and was subjected to a couple of deSO<sub>x</sub>-cycles in a motor-rig consisting of high temperature pulses at lean conditions. It was after this seen as a fresh/stabilized active catalyst. LNT-110 was also aged in an oven at atmospheric pressure and gas composition at a higher temperature and for a longer time compared to LNT-112. It was after that also aged in a motor-rig using fuel with high sulphur content and utilizing several deSO<sub>x</sub> cycles. It has been shown that this ageing procedure corresponds well with a LNT aged in a car for 160 000 km, which is why it was used.

## 3.3 Motor-rig

The motor-rigs used consisted of a standalone motor, suspended on a metal rack. The drive shaft was connected to a brake with variable resistance, making it possible to vary the load on the engine. The exhaust after treatment system was connected directly to the engine making it easy to change when another catalyst system was to be tested, and the exhaust gases was vented out through a ventilation system. Temperature and pressure measurements were done at several places inside the engine as well as along the exhaust after treatment system, and exhaust gases could be extracted at several places for composition analysis. The number of measurement points, as well as their position, was chosen specifically for every experiments depending on the type of test and on what information that was of interest. The speed (rpm) of the engine and the resistance of the brake could be controlled and programmed through a computer, making it possible to run tests over a longer time without the need of constant supervision. This customizability made it possible to test many different characteristics of the catalyst.

### 3.3.1 Petrol tests

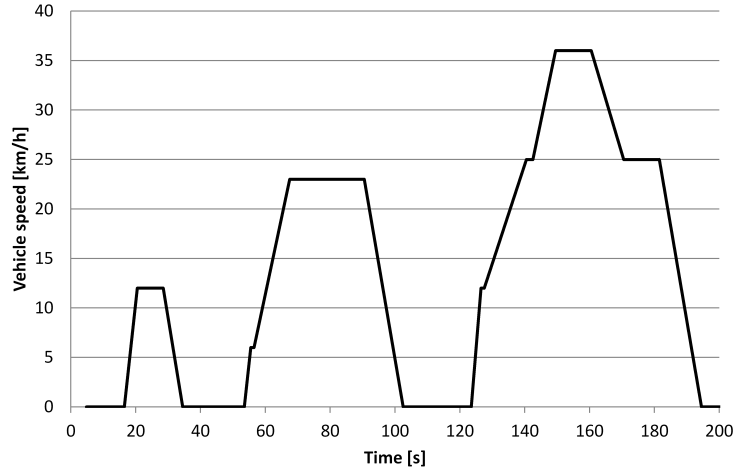
Five different tests were done in the motor-rig, designed to give as much information as possible while keeping the test times short.

#### Light-off test

The light-off test was based on the first 210 seconds of an standard dynamic road cycle (NEDC), figure 4. This means that the engine load and speed was changed according to a predetermined pattern made to simulate ordinary driving. The motor was started

from cold conditions and the emissions of CO, HC and NO<sub>x</sub> and temperature of the catalyst, measured 25 mm into the first catalyst, were monitored giving the conversion with respect to the catalyst temperature. The conversion was calculated as shown in equation 2, where  $C_{EO}$  stands for concentration directly after the engine and  $C_{TP}$  stands for the concentration directly after the second catalyst.

$$Conversion = \frac{C_{EO} - C_{TP}}{C_{EO}} \quad (2)$$



**Figure 4:** The first part of the NEDC cycle, used for the light-off experiment in the motor-rig.

### Oxygen Storage Capacity test

The oxygen storage capacity tests were run at five different load cases, see table 5. The lambda value was switched from rich to lean (RL) and lean to rich (LR) eight times for each case and the switching occurred when the catalyst was full/empty of oxygen determined by achieved steady state of inlet and outlet oxygen. The amount of stored oxygen for the RL and LR test was calculated according to equation 3 and 4 respectively.

$$m_{stored} = \int_{t1}^{t2} X_{O_2} \cdot \dot{m}_{tot} \cdot \left(1 - \frac{1}{\lambda}\right) \quad (3)$$

$$m_{stored} = \int_{t1}^{t2} X_{O_2} \cdot \dot{m}_{tot} \cdot \left(\frac{1}{\lambda - 1}\right) \quad (4)$$

$X_{O_2}$  is approximately 0,23 and is the oxygen/fuel ratio at  $\lambda = 1$ ,  $\dot{m}_{tot}$  is the total mass flow of the exhaust gas and the  $\lambda$ -value is measured before catalyst. The calculation interval starts when the first  $\lambda$ -sensor switches (to rich or lean depending on experiment) and ends when the second sensor after the catalysts switches.

**Table 5:** The five load cases for the OSC test done in the motor-rig.

Load case	Engine speed [rpm]	Engine load [g/rpm]	Expected exhaust temp [°C]
1.	1200	0.2	300-400
2.	1500	0.34	400-500
3.	1900	0.63	500-600
4.	2300	1.13	700-800
5.	2700	1.40	>800

### Dynamic oxygen storage test

The dynamic OSC test performed on the catalysts was done by alternating the lambda value at different frequencies while monitoring the lambda value after the catalyst. The dynamic OSC performance was evaluated by comparing the variation of lambda value before and after the catalyst. The exact test conditions are not possible to display because it is classified.

### 3.3.2 Diesel tests

Two different diesel tests were done in the motor rig, analysing the NO<sub>x</sub> storage capacity and NO<sub>x</sub> conversion.

#### NO<sub>x</sub> storage capacity test

The NO<sub>x</sub> storage capacity test was performed to analyse the amount of NO<sub>x</sub> that could be stored in the catalyst. The NO<sub>x</sub> is stored in the BaO in the washcoat, which is easily poisoned by sulphur from the fuel. Since this type of deactivation is one of the main reasons for LNTs to lose their function over time, it makes this property interesting to study when comparing aged and non-aged catalysts.

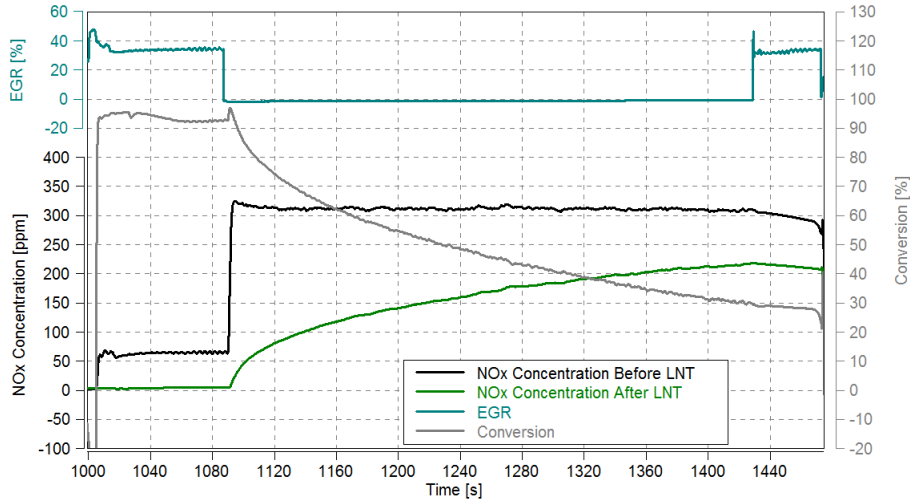
The experiment was conducted both with and without exhaust gas recirculation (EGR). When EGR is turned on, some of the exhaust gases are recirculated back to the engine. This results in a lower combustion temperature and therefore lower NO<sub>x</sub> emissions which made it possible to compare the storage capacity at varying NO<sub>x</sub> concentrations.

The experiment was started by first emptying the catalyst of all previously stored NO<sub>x</sub>. This was done by utilizing several rich pulses, which reduced the NO<sub>x</sub> that had been previously stored. The engine was after that cooled to the right temperature by motoring (i.e. the fuel injections is turned off and the engine is driven by a secondary electric engine). When the right temperature had been achieved, the engine was once again started and the EGR was either turned off or kept on depending on the experiment. This condition was kept until the total conversion had dropped below 70% for the experiment with EGR, or below 30% for the experiment without EGR. The whole

procedure was repeated multiple times at different engine loads and speeds, resulting in varying exhaust gas temperatures and gas flows through the catalyst respectively.

The amount of stored  $\text{NO}_x$  is the difference between the integrals of the  $\text{NO}_x$  concentration before and after the LNT. It was calculated as shown in equation 5, where  $t_1$  is the time where EGR was turned off or fuel injection was started depending on experiment, and  $t_2$  is the time where the conversion reached 30% or 70% respectively. EO stands for engine out which is directly after the engine and TP stands for tail pipe which is after the catalyst. See figure 5 for an example of a typical  $\text{NO}_x$  storage experiment with EGR turned off.

$$m_{\text{stored}} = \int_{t_1}^{t_2} C_{\text{NO}_x, \text{EO}} \cdot \dot{m}_{\text{tot}} - \int_{t_1}^{t_2} C_{\text{NO}_x, \text{TP}} \cdot \dot{m}_{\text{tot}} \quad (5)$$



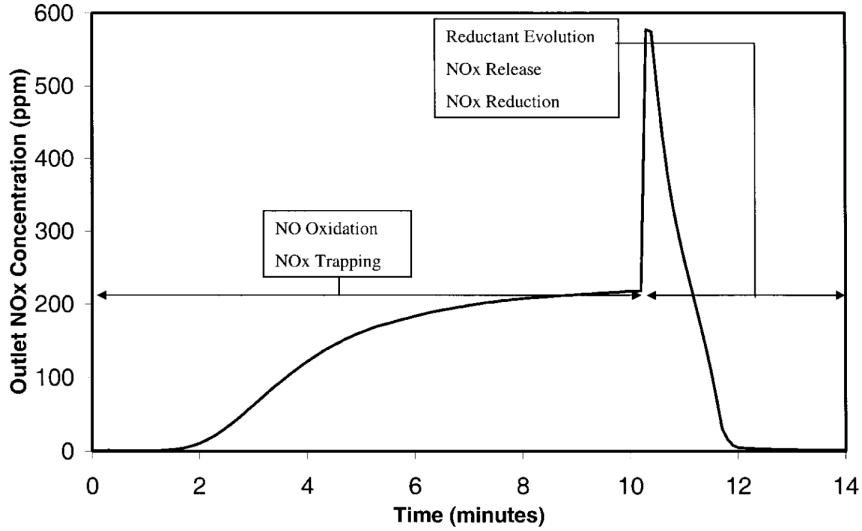
**Figure 5:** Typical concentration profiles from a  $\text{NO}_x$  storage experiment continued down to 30% conversion with EGR turned off.

### $\text{NO}_x$ conversion test

The  $\text{NO}_x$  conversion experiment should be seen as a test of both storage capacity and reduction activity. The experiment is based on several repeated cycles, where one cycle consists of a longer lean period and shorter rich period. The  $\text{NO}_x$  is stored in the LNT during the lean periods, and reduced under the rich pulse. A typical  $\text{NO}_x$  outlet concentration profile is shown in figure 6 from a similar experiment. The conversion is calculated as shown in equation 6, where  $t_1$  is the time where the lean period starts and  $t_2$  is the time where the rich period is finished. EO stands for engine out which is directly after the engine and TP stands for tail pipe which is after the catalyst. Several cycles are repeated at each experimental point for steady state to be a valid assumption and the conversion is only calculated over the last cycle. Table 6 shows the different experimental points.



$$Conversion = \frac{\int_{t_1}^{t_2} C_{NO_x,EO} \cdot \dot{m}_{tot} - \int_{t_1}^{t_2} C_{NO_x,TP} \cdot \dot{m}_{tot}}{\int_{t_1}^{t_2} C_{NO_x,EO} \cdot \dot{m}_{tot}} \quad (6)$$



**Figure 6:** A typical  $NO_x$  outlet concentration profile from a conversion experiment, starting with a longer lean period and finished by a shorter rich period. [18]

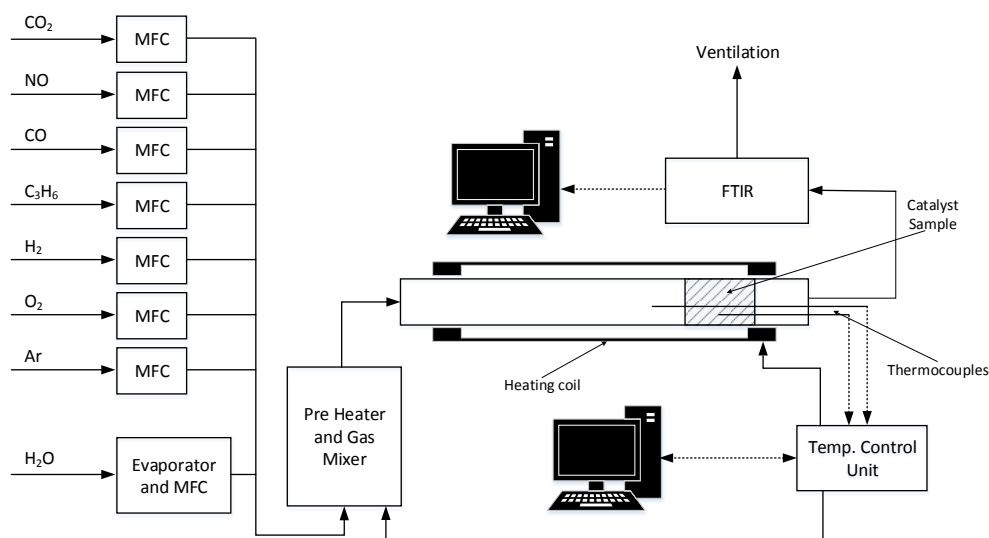
**Table 6:** The different experimental points tested in the  $NO_x$  conversion experiment. The time for the rich pulse was 12 s for all points.

Speed [rpm]	Lean time [s]
1000	900
1000	200
1500	300
1500	75
1750	200

### 3.4 Flow reactor

The flow reactor experiments were done at Chalmers in collaboration with KCK (Competence Center for Catalysis). The experimental set-up is shown schematically in figure 7. It consisted of a gas cabinet where connections to the available gases were located. The gases that were used were connected to individual mass flow controllers (MFC) that were controlled from a computer. The gases were led through the controllers into a mixing and preheating stage, and from there to the reactor. The reactor consisted of a 80 cm

long quartz tube with an inner diameter of 2.2 cm and a heating coil wired around. The catalyst was mounted in the distal portion of the quartz tube and two thermocouples were inserted in the catalyst channels. One was positioned in the middle of the catalyst, measuring the temperature of the catalyst, and the other 10 mm in front of the catalyst, measuring the temperature of the incoming gases. The gas was from here led to the analytical equipment and thereafter to the ventilation. The analytical equipment used was an FTIR equipment (Fourier Transform Infrared Spectroscopy), analysing the gases as they exited the reactor. The FTIR was calibrated with an empty reactor and the signal was compared to the known inlet concentrations of the different gases and it was from this possible to calculate a calibration correlation.



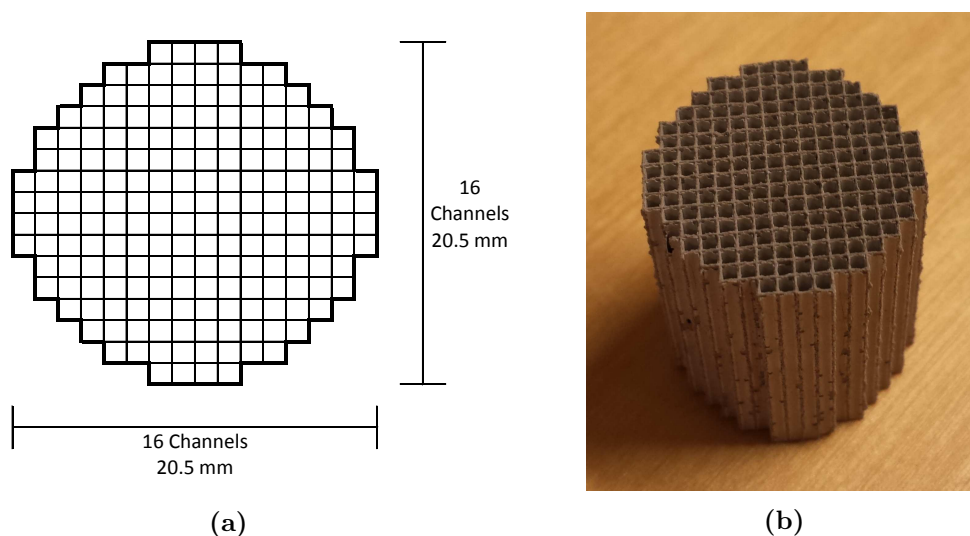
**Figure 7:** A schematic drawing of experimental set up used for the flow reactor experiments.

### 3.4.1 Catalyst preparation

The catalytic systems were split and only the first catalyst of each system was analysed in the flow reactor experiments. The metallic housing surrounding the catalyst was removed and the catalyst itself was cut in four discs with a thickness of 20 mm each. A cube of 20x20 channels was cut out with the help of a utility knife from the middle of each disc. The cube was then formed to a cylinder by carefully cutting away access catalytic material, channel by channel, until the piece shown in figure 8b was achieved.

### 3.4.2 Experiments

The experiments were divided into four different parts, designed to test different characteristics of the catalyst.



**Figure 8:** Figure 8a shows a drawing of the prepared catalyst with dimensions and channel positions. Figure 8b shows a picture of the finished catalyst cylinder.

### Precious metal dispersion

The first part of the test was to analyse the dispersion of the precious metal particles. This was done by first pre-treating the catalyst at 400 °C with oxygen and then reducing it in hydrogen while lowering the temperature. A CO<sub>2</sub> pulse was started when the catalyst reached room temperature. Meanwhile this was kept constant, two separate CO pulses were used with a couple of minutes in between. Detailed steps for the experiment are shown in table 11 in the appendix.

The dispersion calculations were based on the assumption that CO<sub>2</sub> had adsorbed to all the available sites on the oxygen storage material and therefore leaving only the precious metal sites available for CO. It was also assumed that one CO adsorbed corresponded to one available precious metal atom, called on-top configuration. The main idea is to compare the outlet concentration of CO from the two pulses, and from the difference determine the amount adsorbed. But since no difference was shown, it was the desorption of CO at the temperature increase after the pulses that was used. This peak in the outlet concentration was integrated to obtain the total amount of CO released, which corresponds to the total amount adsorbed, directly giving the amount of available precious metal sites. This amount was compared to the total loading of precious metal on the catalyst, giving dispersion measurements in %.

### Oxygen storage capacity

The oxygen storage capacity experiment was conducted by first heating the catalyst in inert Ar to the desired temperature. The catalyst was then oxidised in O<sub>2</sub> and all the excess oxygen not adsorbed to the catalyst was removed by flushing with Ar. A CO pulse was then used to reduce the catalyst. It was then flushed with argon and oxidised

again with an O<sub>2</sub> pulse before the temperature was lowered. This oxidation-reduction-oxidation procedure was repeated at five different temperatures in total. For detailed steps, see table 12 in the appendix.

The oxygen storage capacity is generally given from the total amount of CO reacted, since CO is reacted with one oxygen atom to form CO<sub>2</sub>. To be able to calculate the total oxygen storage capacity, it is important to continue the experiment until the storage sites are saturated. This was not the case in these experiments because of very large oxygen storage capacity in the catalyst, and it was therefore not possible to calculate the oxygen storage capacity. The results were instead used in a comparative manner, comparing the readily available oxygen stored.

#### **CO oxidation with NO light-off**

The CO oxidation together with NO experiment was conducted to investigate the activity of the catalyst. The experiment was started by pre-treating the catalyst to clean it from possible impurities. This was done by first heating the catalyst in Ar, and when the right temperature was achieved, oxidising it in O<sub>2</sub>. It was after that flushed with Ar and reduced in a H<sub>2</sub> pulse before the temperature was lowered. The catalyst was then subjected to a mixture of CO, NO, O<sub>2</sub> and H<sub>2</sub>O while the temperature was increased. For detailed steps, see table 13 in the appendix.

The conversion was calculated by using the outlet concentration of CO and NO respectively and comparing it with the total amount sent in. This was plotted against the corresponding temperature and the light-off temperature was calculated at 50 % conversion.

#### **C<sub>3</sub>H<sub>6</sub> oxidation with NO**

The C<sub>3</sub>H<sub>6</sub> oxidation together with NO experiment was conducted to investigate the activity of the catalyst. It was conducted in the same steps as the CO oxidation experiment, see above. For detailed steps, see table 14 in the appendix.

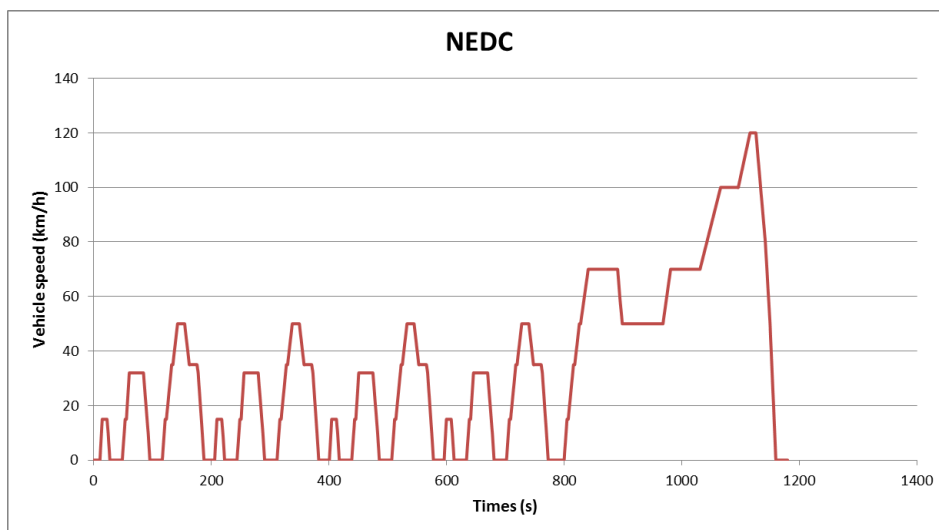
The conversion was calculated by using of the outlet concentration of C<sub>3</sub>H<sub>6</sub> and NO respectively and comparing it with the total amount sent in. This was plotted against the corresponding temperature and the light-off temperature was calculated at 50 % conversion.

### **3.5 Car-dynamo experiment**

One test was performed in a real car positioned on a dynamo. This test procedure makes it possible to analyse the performance of the catalyst with it mounted in the actual car, without having to drive it on the road.

#### **Emission tests**

The total emissions of a LNT are the most important characteristic, since it is a combined measurement of how well the catalyst performs. This was tested in a real car using the NEDC cycle, see figure 9.



**Figure 9:** The full NEDC cycle used in the emission tests of the LNTs.

This cycle was run several times for both the aged and non-aged catalyst while the emissions of CO, HC and NO<sub>x</sub> was measured and the total conversions calculated.

### 3.6 Characterization methods

One characterization method was used during the thesis work to analyse the catalysts. A description of the method and how it was used follows below.

#### 3.6.1 SEM/EDX

The SEM/EDX apparatus used was a Joel, model: JSM-6480 LV with a monochromatic Al K $\alpha$  radiation source. The SEM was mainly used coupled with an EDX to study the distribution and amounts of poisons on the catalyst surface. Some SEM images were also taken to study the structure of the catalyst surface.



## 4 Result and Discussion

The results found from the analyses of the three-way catalysts and lean NO<sub>x</sub> traps together with a discussion follows below.

### 4.1 Petrol results

The following chapter presents and discusses the experimental results and findings obtained through analysis of the petrol catalysts.

#### 4.1.1 Motor-rig experiments and determination of ageing time

Motor-rig experiments were conducted on both the thermal and poison aged catalytic systems as well as a non-aged system for reference. These tests were used to determine if the systems were equally aged. Two different thermal ageing times were compared, 30 h and 50 h, since the time needed for the thermal ageing to correspond to the poison ageing was unknown. The results and discussions for each test, all performed in the same motor-rig, are presented below.

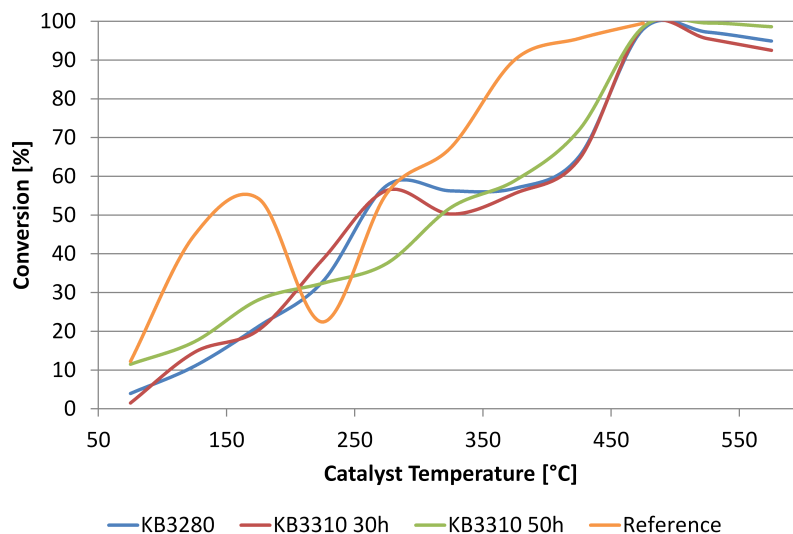
It has to be noted that these results only should be used as a comparison between the systems in the test, and not as a general evaluation of the catalytic performance. The tests showed some uncertain reproducibility with uneven engine speed controls and there were also some experimental problems with leakage in the exhaust system, affecting the results. These shortcomings became apparent first after the tests had been conducted and it was at that time not possible to redo the tests. They are judged, despite this, to be good enough for a comparative analysis in the assessment of the ageing time.

#### Light-off

The light-off test was conducted to compare the activity of the systems at low temperature, which is often used as a measure of deterioration due to ageing.

Figure 10 shows the conversion of CO with respect to catalyst temperature of the four catalytic systems. It is shown that the reference system, the non-aged catalyst, achieves higher conversion for almost the entire temperature range compared to the aged systems, except for a drop at around 240 °C. It is also shown that the reference curve stops at around 470 °C compared to the other systems reaching almost 600 °C. This is because of the uncertain engine control, where some tests ended up with a higher engine speed and therefore a higher temperature, directly effecting the temperature of the catalysts and therefore also the conversion results.

An explanation for the unstable performance of the reference system could be condensation and evaporation of water. Water from the combustion is condensed in the system because of the low temperature in the beginning. Some of the emissions are then dissolved into the water, resulting in lower emissions which are showed as a higher conversion. The water will evaporate because of the increasing temperature, releasing the emissions again which is showed as a decreased conversion. These fluctuations have



**Figure 10:** The conversion of CO with respect to catalyst temperature of the four different petrol systems during the light-off test in the motor-rig.

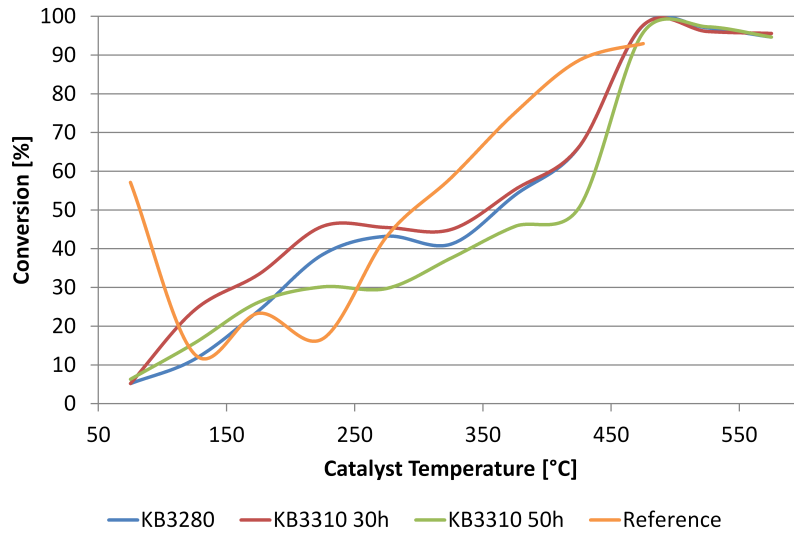
nothing to do with the performance of the catalyst, but are shown as uneven performance, which is why they have to be taken into account. A temperature spike, because of for example insufficient engine control, can make more water evaporate at the same time, even further enhancing this effect. Another explanation is that CO adsorbs to the catalyst surface, and is shown as a high conversion. But the adsorbed CO is released when the temperature is increased which is shown as a decreased conversion. This effect would be most severe for the reference catalyst since it has the least degree of sintering.

When studying the aged systems, a close similarity is shown between KB-3280 and KB-3310 30 h indicating similar degree of ageing, whereas KB-3310 50 h shows some deviation. The largest difference is in the temperature range of 240-340 °C, where KB-3310 50 h shows a lower conversion. This could indicate a higher degree of deterioration because of too long thermal ageing time. This hypothesis is further strengthened when studying the light-off curves for HC and NO<sub>x</sub> shown in figures 11 and 12.

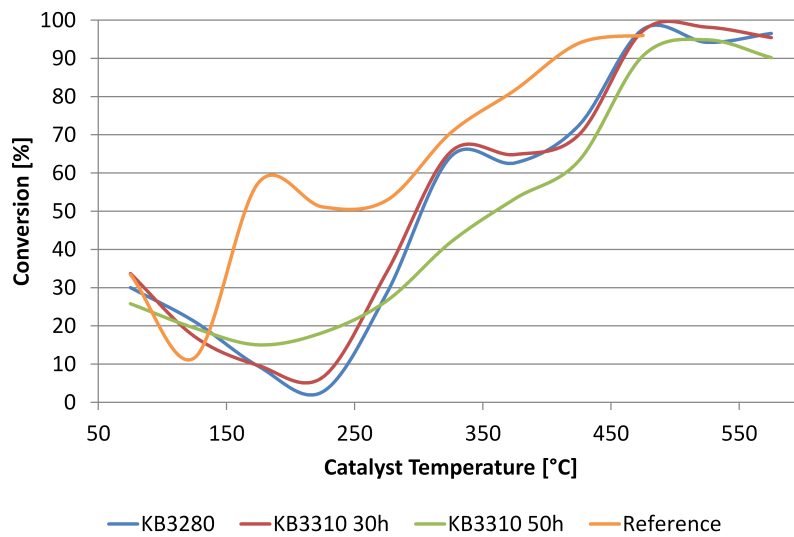
Figure 11 and 12 both shows a lower conversion for KB-3310 50 h, ever further indicating that 50 h of thermal ageing might was too long compared to the poison aged catalyst. However, one exception is shown in the temperature range of 150-250 °C of the NO<sub>x</sub> light-off test, figure 12, where KB-3310 50 h achieves a higher conversion. A possible explanation for this could be that KB-3310 50 h was subjected to a high temperature spike in the beginning of the test because of the uncertain engine controls mentioned earlier. This would start the reactions earlier on KB-3310 50 h compared to the other catalysts, and when the temperatures was lowered again it could keep the higher reaction rates.

It could also be noted that the conversion achieved by KB-3310 30 h in the HC, and in some extent the NO<sub>x</sub>, light off test is somewhat higher compared to KB-3280,





**Figure 11:** The conversion of HC with respect to catalyst temperature of the four different petrol systems during the light-off test in the motor-rig.



**Figure 12:** The conversion of  $\text{NO}_x$  with respect to catalyst temperature of the four different petrol systems during the light-off test in the motor-rig.

indicating that 30 h might be too short.

It is also shown in figure 10 and 12 that the largest difference between the reference and the aged systems are in the lower temperature intervals, indicating that the ageing has a large impact on the light-off temperatures and not so much on the performance at higher temperatures.

**Table 7:** The light-off temperatures at 50 % conversion of CO, HC and NO<sub>x</sub> from motor-rig experiments for the differently aged petrol systems.

Catalyst	CO light-off [°C]	HC light-off [°C]	NO <sub>x</sub> light-off [°C]
KB-3280	257	362	302
KB-3310 30 h	252	352	293
KB-3310 50 h	317	425	360
Reference	140/265	295	165

Table 7 displays the light-off temperatures at 50 % conversion for the different species, showing a significantly higher light-off temperature for KB-3310 50 h and a slightly lower for KB-3310 30 h compared to KB3280. The reference shows some varying values because of the reasons mentioned above, and two values are displayed for the CO light-off since the curve passes 50 % conversion two times, see figure 10.

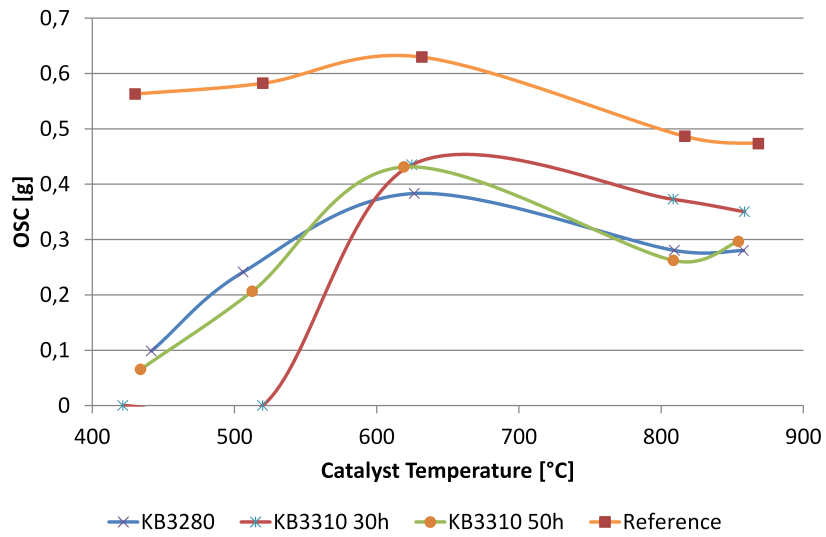
It should again be noted that these values are based on the total conversion of the system, that is of two catalysts, and should therefore not be used in comparison with single catalyst light-off temperatures presented further below.

### Oxygen storage capacity

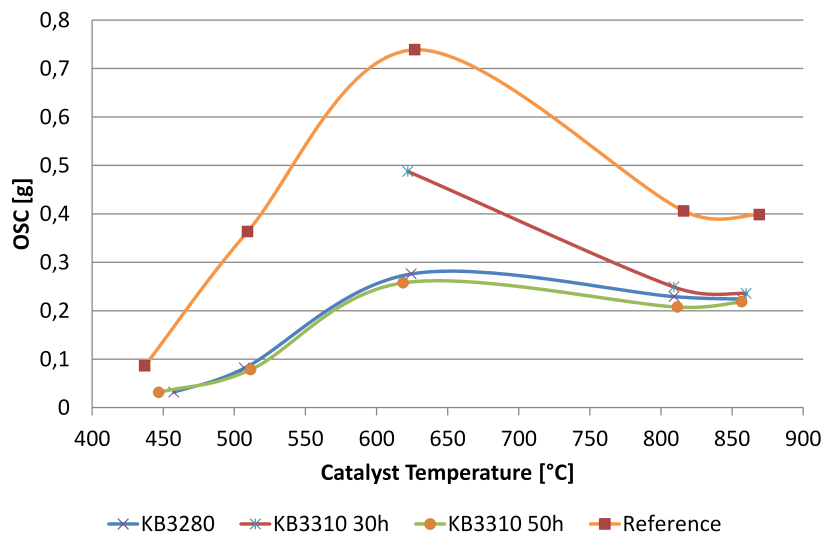
The OSC test was conducted to compare the oxygen storage capacity of the catalysts since this is one of the most important characteristic and is often greatly affected by the ageing.

Figure 13 shows the oxygen storage capacity of the three aged catalysts and the reference at different temperatures when changing from rich to lean conditions. It can be seen that all the aged catalysts have significantly lower OSC compared to the reference, where the largest drop is at lower temperatures. This indicates that the ageing has a larger impact at the low temperature performance, something that was also shown in the light-off tests. It can also be seen that KB-3280 and KB-3310 50 h has equal performance while KB-3310 30 h has lower OSC at lower temperature but somewhat higher at higher temperature. This could be due to a leakage that was found after the experiment had been conducted which influenced the reading of the oxygen sensors.

Figure 14 also indicates a large difference between the aged catalysts and the reference, but it is here more pronounced in the middle of the temperature range instead of in the lower range as was shown in figure 13. It is because of experimental problems missing results from KB3310 30 h making it difficult to compare it to the other systems, but it can be seen that KB-3280 and KB3310 50 h performs very similar.



**Figure 13:** The oxygen storage capacity at different temperatures of the three differently aged petrol catalysts and reference, when changing conditions from rich to lean.



**Figure 14:** The oxygen storage capacity at different temperatures of the three differently aged petrol catalysts and reference, when changing conditions from lean to rich.

The missing results make it hard to draw some definite conclusions, but there are at least indications that KB-3280 and KB-3310 50 h have achieved the same amount of ageing.

### Dynamic OSC

The dynamic OSC is another way to test how the OSC capacity of the catalysts has been effected by the ageing. The reference system is not included because of experimental problems.

**Table 8:** The dynamic OSC capacities of the three catalytic systems presented as difference between lambda value before and after. Test 1, 2 and 3 have been conducted at different conditions. A low value indicates a good dynamic oxygen storage capacity.

Catalyst	Test 1 [%]	Test 2 [%]	Test 3 [%]
KB-3280	72,2	56,9	18,5
KB-3310 30 h	14,7	21,0	11,9
KB-3310 50 h	88,1	40,8	17,7

It is shown in table 8 that KB-3280 and KB-3310 50 h have a similar dynamic OSC performance, while KB-3310 30 h shows a significantly better performance. This could be an indication of that the ageing time of 30 h thermal is too short to achieve the same amount of ageing compared to the poisoning ageing method, at least with respect to the dynamic OSC capacity.

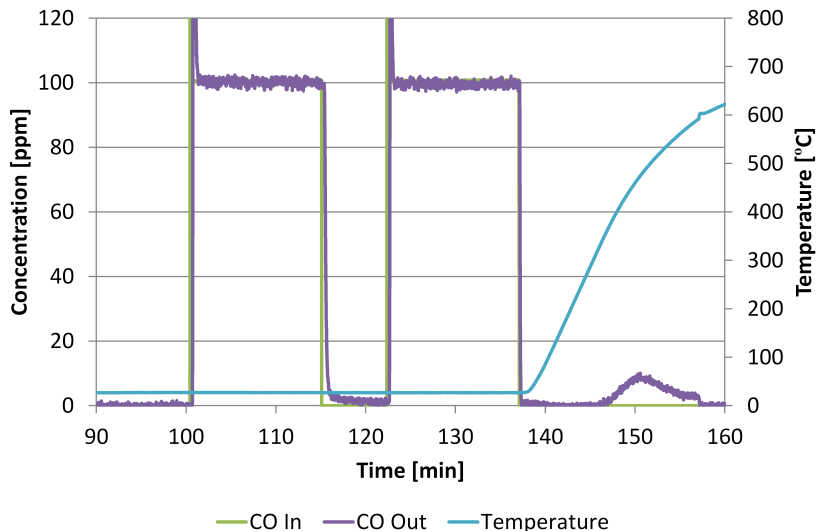
#### 4.1.2 Flow reactor

The flow reactor experiments were conducted because of its precise controls and ability to analyse characteristics at different positions axially for each catalyst. This enabled a detailed analysis of how and where the two different ageing methods affected the catalysts. The first three discs of the first catalyst from the catalytic systems KB-3280 (poison aged) and KB-3310 50 h (thermal aged) was analysed and the results from the different experiments are shown below.

#### Precious metal dispersion

The precious metal dispersion experiment was conducted to compare how the ageing had affected the dispersion, and if there were any difference axially along the catalysts.

Figure 15 shows the results from the dispersion experiment on the first disc of KB-3310. No visual adsorption of CO is shown which should be apparent in the beginning of the first pulse of CO. This was the case for all experiments which is why the desorption peak after the two pulses was used for dispersion measurements instead. A single-point adjustment was done on the KB-3310 experiments to correct the FTIR-signal because of insufficient calibration in that specific concentration region.



**Figure 15:** The precious metal dispersion experiment for the first disc of the first catalyst of KB-3310 50 h (thermal aged).

**Table 9:** The precious metal dispersion for the different discs in percent of available metal sites compared to total amount.

Catalyst	Dispersion
KB-3280-1	0.22 %
KB-3280-2	0.28 %
KB-3280-3	0.30 %
KB-3310-1	0.71 %
KB-3310-2	0.87 %
KB-3310-3	0.77 %

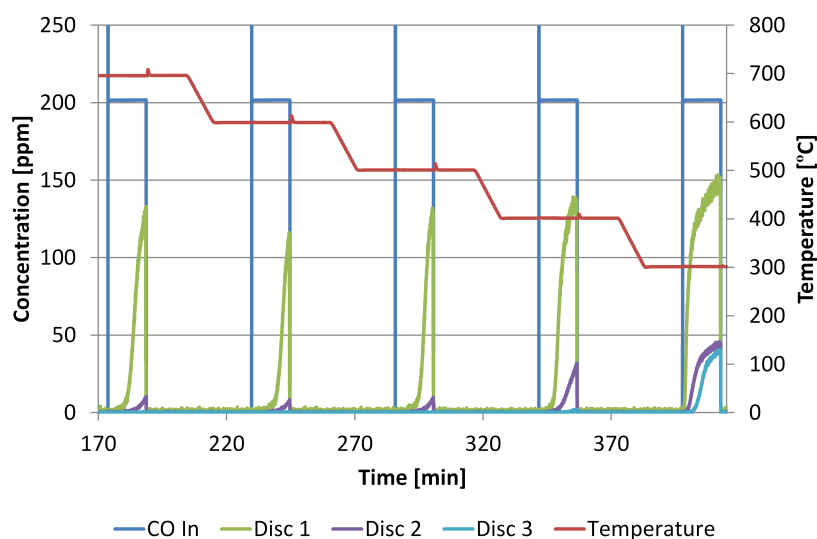
Table 9 shows the results of the dispersion experiments in percent of available precious metal compared to total precious metal on the catalyst. The values are very low compared to similar studies [19]. There can be different reasons for these low values, for example the high  $\text{CO}_2$  level used for decreasing the influence from the OSC material, might influence the noble metals. Secondly, the cooling is done in hydrogen and it is possible that palladium hydrides are formed and that CO is not attached to them.

It is also shown that KB-3310 has a higher total dispersion compared to KB-3280, which is something that was not expected. It was because of the longer ageing time of KB-3310 believed that it would have a higher degree of sintering, since this is the main deterioration type of thermal ageing, but it is the opposite of what is shown. It could maybe be so that the high amount of poison on the washcoat surface of KB-3280 covers

the precious metal, showing as a lower dispersion. It should be noted that the values are very low for all samples, as discussed above, which makes the analysis difficult.

### Oxygen storage capacity

Since the oxygen storage capacity is regarded as one of the most important parameters of an automotive catalyst, an experiment was conducted analysing this property. The general procedure is to have a CO pulse long enough for saturation to occur, which makes it possible to calculate total OSC. But the pulses showed to be too short for this to be possible, so a comparative analysis will be conducted instead. It should be noted that it, because of the short pulses, is the standard oxygen storage capacity that is compared and not the complete oxygen storage capacity.

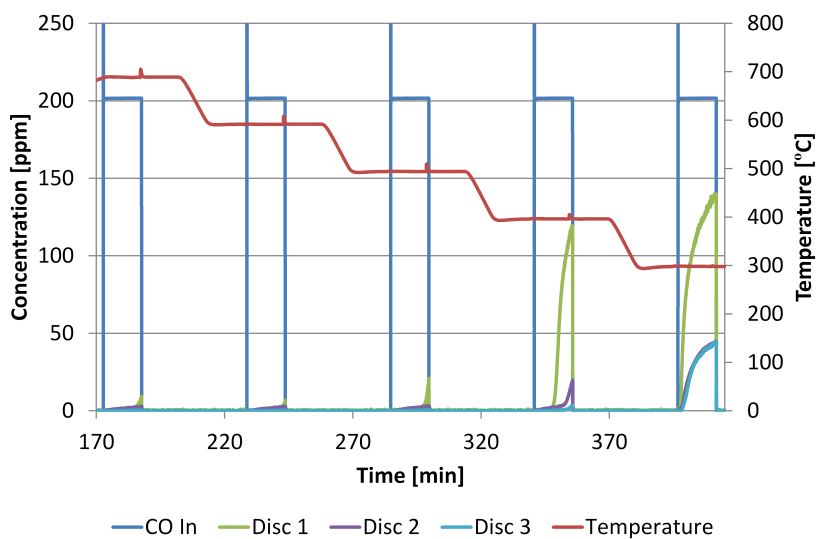


**Figure 16:** The oxygen storage capacity experiment for the three discs of the first catalyst of KB-3280 (poison aged), showing the concentration of CO in and out from each disc.

Figure 16 shows the results from the experiments on KB-3280. It can be seen that the first disc has a significant CO slip for all temperatures, compared to the second and third. This indicates that the oxygen storage capacity of the first 20 mm of the catalyst have been affected by the ageing in a higher degree. Some slip can also be seen from the second disc, while the third shows it first at the lowest temperature.

Figure 17 shows a similar behaviour for KB-3310 but not as severe slip for the first disc. It seems like the poison had a greater effect on the oxygen storage capacity compared to the thermal ageing, but both methods had a greater effect on the inlet of the catalyst compared to the outlet.

One explanation for the poison ageing to have a larger impact on the OSC compared to the thermal ageing could be that the poisons stick to the catalysts surface, covering not only the active metal sites but also the cerium oxide which is one of the main oxygen storage components, while the thermal ageing mostly contributes to the agglomeration

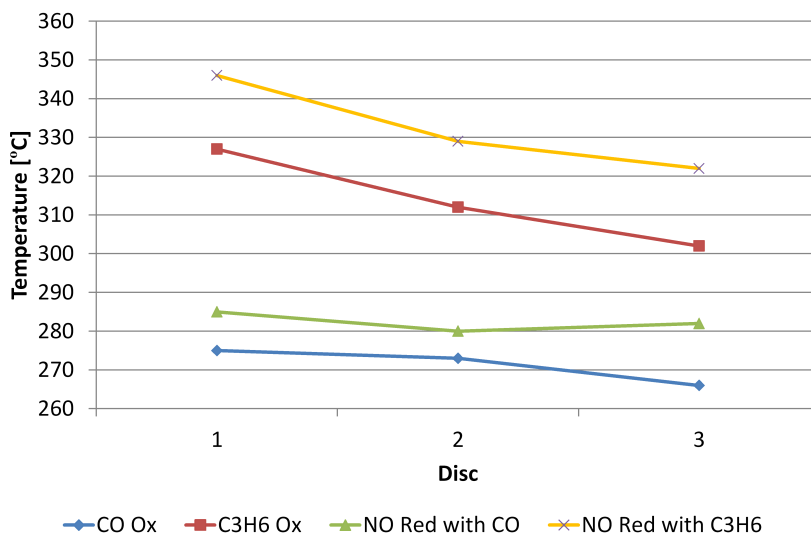


**Figure 17:** The oxygen storage capacity experiment for the three discs of the first catalyst of KB-3310 50 h (thermal aged), showing the concentration of CO in and out from each disc.

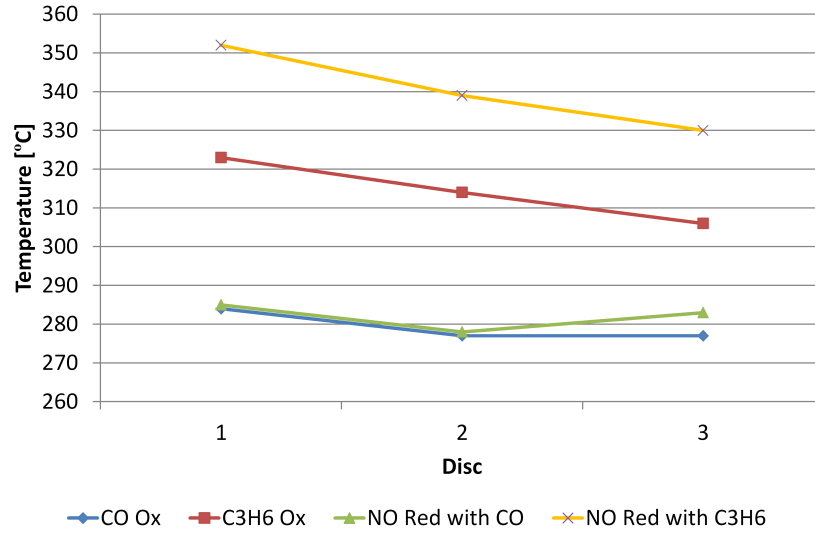
of the active metal particles, not having as large effect on the OSC.

### Light-off experiments

The light-off experiments were conducted to determine the low temperature activity of the catalysts at different locations axially.



**Figure 18:** The light-off temperatures at 50% conversion for the three discs of the first catalyst of KB-3280 (poison aged).



**Figure 19:** The light-off temperatures at 50% conversion for the three discs of the first catalyst of KB-3310 (thermal aged).

Figure 18 and 19 both shows a similar behaviour for the light-off temperature, a lower temperature i.e. a higher activity further away from the inlet. This indicates that both ageing methods had a greater effect on the inlet of the catalysts.

**Table 10:** The light-off temperatures at 50% conversion for the different discs from the light-off experiments in the flow reactor.

Catalyst	CO [°C]	C <sub>3</sub> H <sub>6</sub> [°C]	NO with CO [°C]	NO with C <sub>3</sub> H <sub>6</sub> [°C]
KB-3280-1	275	327	285	346
KB-3280-2	273	312	280	329
KB-3280-3	266	302	282	322
KB-3310-1	284	323	285	352
KB-3310-2	277	314	278	339
KB-3310-3	277	306	283	330

Table 10 shows the light-off temperatures for the different species and discs. The CO light-off temperatures are somewhat lower in comparison to what Gonzáles-Velasco et al. [20], who have performed light-off experiments on Pd–Rh catalysts, have found, while the C<sub>3</sub>H<sub>6</sub> and NO are in good accordance. The differences are likely due to that different catalysts are used. In addition, Gonzales-Velasco et al. had an experimental setup where two gas mixtures were used alternately during the temperature increase.

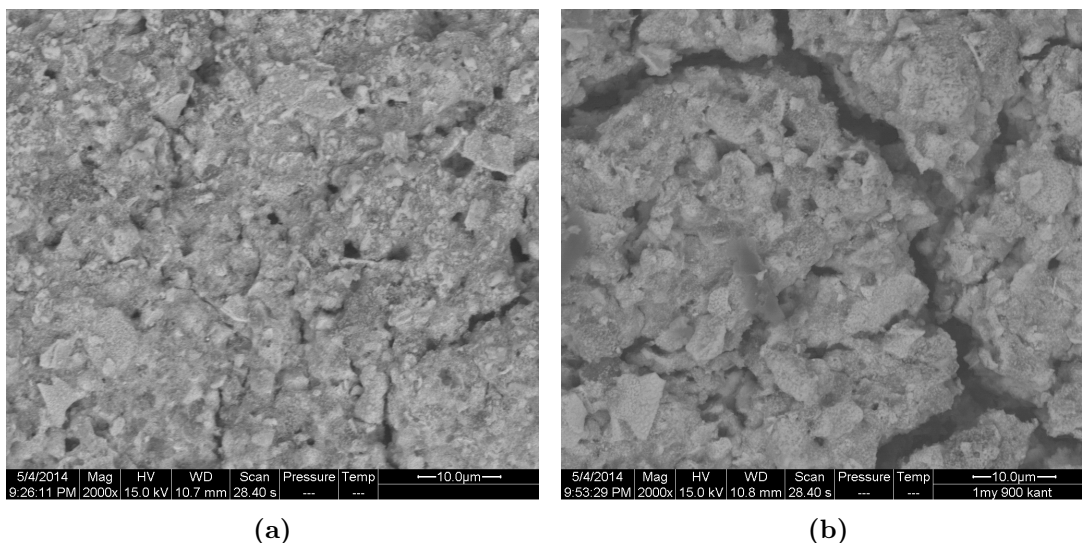
It can be seen from the table that KB-3280 performs better at CO oxidation and NO reduction with C<sub>3</sub>H<sub>6</sub> for all discs compared to KB-3310, while the C<sub>3</sub>H<sub>6</sub> oxidation and



NO reduction with CO are very similar. These findings are in accordance with what was found in the motor-rig tests which showed worse light-off performance for the thermally aged catalyst.

### 4.1.3 SEM/EDX

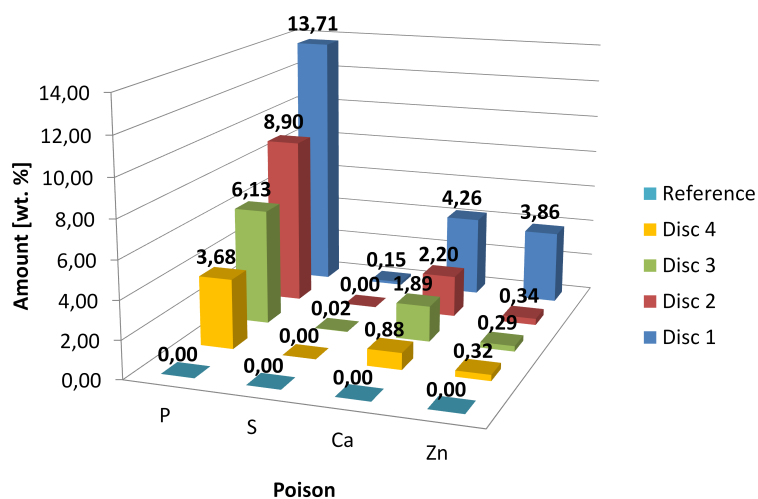
A SEM apparatus coupled with an EDX equipment was used to study the surface of the catalyst, analysing both agglomeration of particles as well as deposits of poisons.



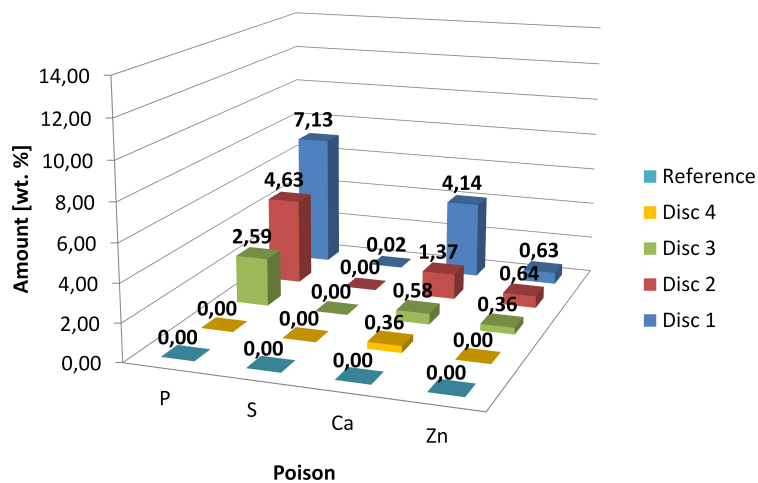
**Figure 20:** SEM pictures of the catalyst surface of (a) KB-3280 (poison) and (b) KB-3310 (thermal).

Figure 20 shows two SEM pictures of the surface of the catalysts, where large cracks can be seen on KB-3310, which are not found on KB-3280. This kind of physical deterioration is most likely because KB-3310 have been subjected to high temperatures for a longer time, 50 h compared to 20 h, resulting in a phase shift of the  $\gamma$ - $\text{Al}_2\text{O}_3$  support material which causes cracks in the washcoat. This effect of thermal ageing have been shown in several studies [16], [22], [14].

Figure 21 and 22 shows the distribution of poisons on the four discs of KB-3280 and KB-3310. It is clearly shown that the inlet of both catalysts contain higher amounts of poisons, which decreases with a sharp gradient towards the outlet. It can also be seen that KB-3280 contains higher amounts of poison on all discs, except for Zn on the second and third discs, compared to KB-3310. The poisons found on KB-3310 are from the normal use of engine oil and fuel. These values are similar to what Winkler et al. [22] have found from doing tests with real cars run on ordinary fuel for 40 000 km. The large difference in poison amounts between the discs could be an explanation for the difference in activity and OSC between the discs that was found in previous tests.



**Figure 21:** The poison amounts found on the catalyst surface from EDX analysis on the four discs of the first catalyst of KB-3280 (poison).



**Figure 22:** The poison amounts found on the catalyst surface from EDX analysis on the four discs of the first catalyst of KB-3310 (thermal).

## 4.2 Diesel results

The results found from the experiments on the lean NO<sub>x</sub> traps will be shown and discussed in the sections below.

### 4.2.1 Motor-rig

Three different characteristics have been tested in the motor-rig; the total conversion of HC, CO and NO<sub>x</sub>, the NO<sub>x</sub> storage capacity and the NO<sub>x</sub> conversion capacity. These results are presented in the following paragraphs.

#### Total conversion

The total conversions can be used for measuring how aged the catalyst is, since the conditions of all the other characteristics are influencing the emissions. It was not LNT-112 that was analysed in this test, but another stabilized LNT with the same composition. These are estimated to produce the same results which are why this comparison can be made. The aged catalyst is LNT-110 which is analysed further below.

The results showed that the stabilized catalyst only performs slightly better for HC and CO, while the difference is larger for the conversion of NO<sub>x</sub>, around 45 %, but that both the stabilized and aged catalyst manage to get above 50 % conversion. The drop in HC and CO conversion is most likely because of sintering of precious metals or poisoning of active sites. The difference in NO<sub>x</sub> performance could depend on several different characteristics which will be analysed further.

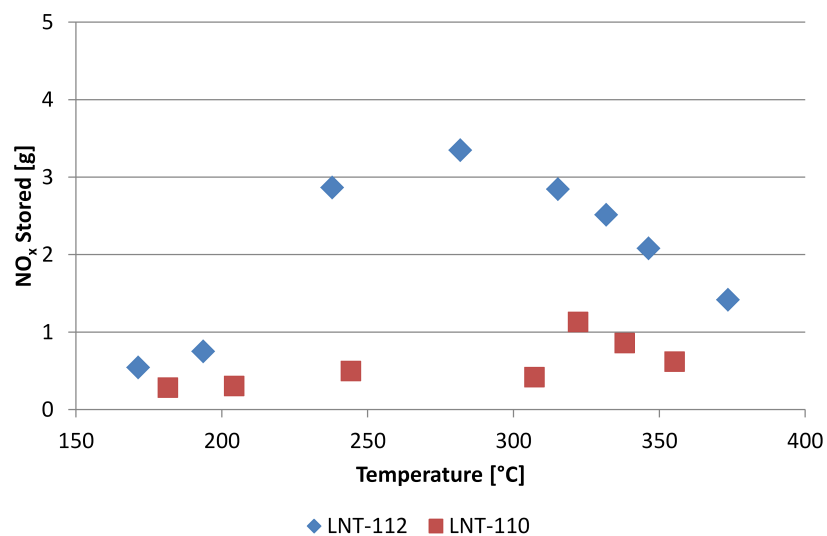
#### NO<sub>x</sub> storage capacity

The NO<sub>x</sub> storage capacity was analysed because of its importance on the overall performance of the LNT and its sensitivity to ageing, mainly because of sulphur in the fuel. Three experiments were conducted, two without EGR at 1650 rpm and 1000 rpm, and one with EGR and variable engine speed. The results are shown in figure 23, 24 and 25.

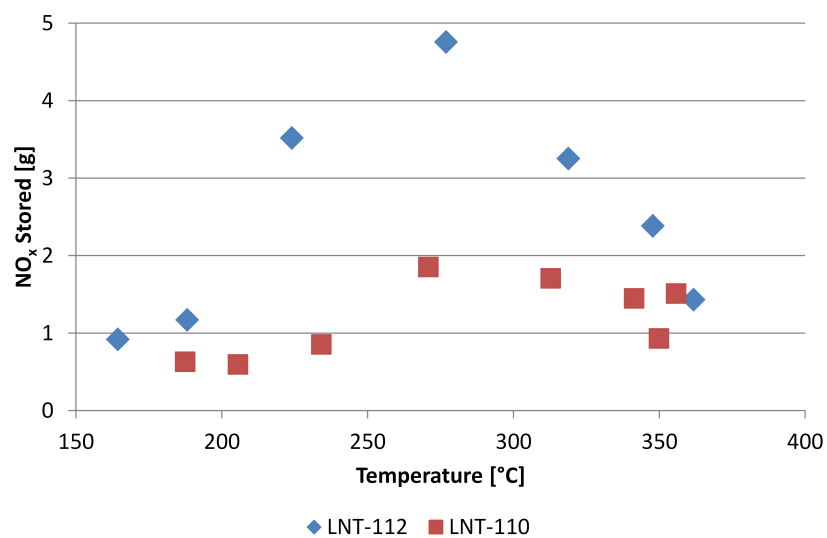
Figure 23 shows a clear difference between the aged and stabilized LNT. The stabilized catalyst performs better over the whole temperature range and reaches almost 3.5 g of storage capacity, where the aged catalyst only reaches slightly above 1 g. It could also be noted that the maximum is shifted to a higher temperature for the aged catalyst.

This trend is continued for lower engine speed, shown in figure 24. It is once again shown a much higher storage capacity for the stabilized catalyst compared to the aged, with a maximum capacity of 4.76 g and 1.85 g respectively. It can also be seen that the overall storage capacity is increased for both catalysts compared to the higher engine speed. This is probably because of the smaller volume flow through the catalyst, resulting in a longer residence time, giving the NO<sub>x</sub> more time to chemisorb to the surface.

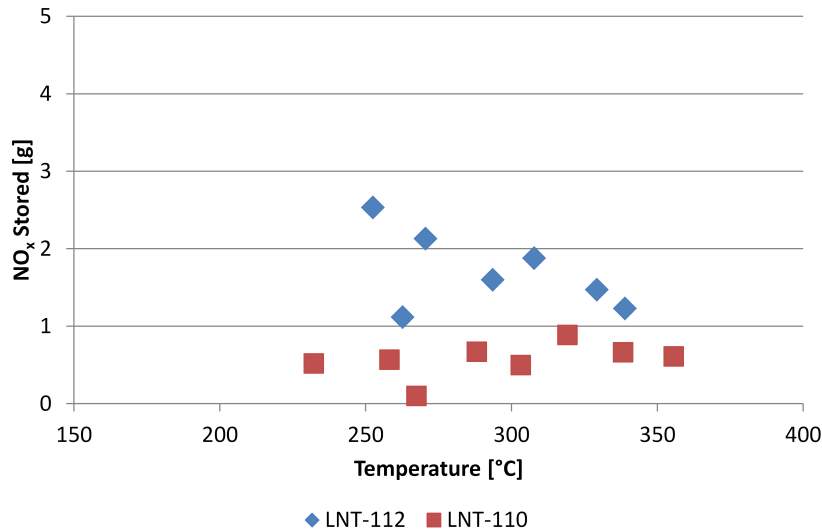
Figure 25 shows the NO<sub>x</sub> storage capacity when EGR is used. The same overall picture is shown, where the stabilized catalyst performs better, but the difference is not as pronounced as it was in the other experiments. A reason for this could be that, when the EGR is on, it lowers the combustion temperature in the engine, resulting in lower NO<sub>x</sub> production. The lower concentration is not as demanding on the LNT, which makes



**Figure 23:** The NO<sub>x</sub> storage capacities for the stabilized (LNT-112) and aged (LNT-110) catalysts at 1650 rpm without EGR.



**Figure 24:** The NO<sub>x</sub> storage capacities for the stabilized (LNT-112) and aged (LNT-110) catalysts at 1000 rpm without EGR.



**Figure 25:** The NO<sub>x</sub> storage capacities for the stabilized (LNT-112) and aged (LNT-110) catalysts at variable engine speed with EGR.

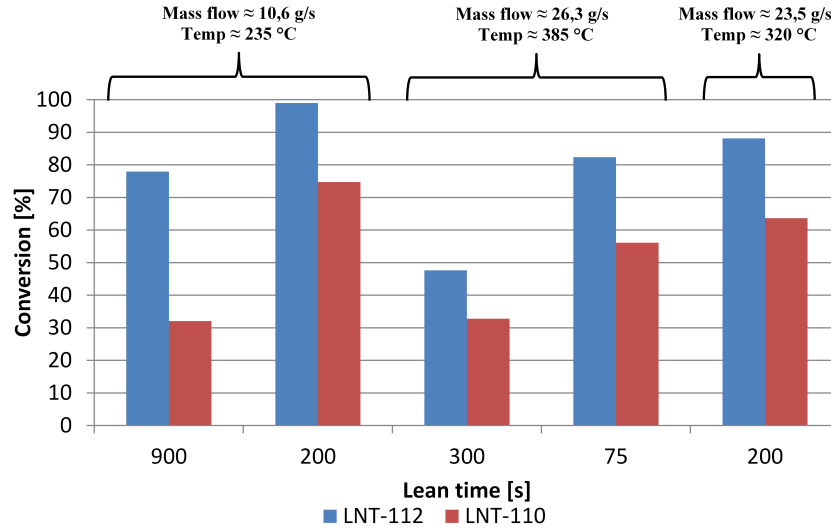
it possible for the aged catalyst to perform similar to the stabilized. It should also be noted that this experiment was stopped at 70% conversion, instead of at 30%, which makes the experiment shorter and does therefore not show the differences as clearly. This is also the reason to why the maximum values are lower compared to previous experiments without EGR.

It is from these experiments clear that the ageing of LNT-110 have had a significant effect on the NO<sub>x</sub> storage capacity. Benramdhane et al. [23] found similar results analysing the storage capacity of fresh and thermally aged LNTs. His explanation for the loss of storage capacity is the agglomeration of Pt particles. A lower dispersion of the Pt particles will decrease the activity for NO oxidation, which is a necessity since NO has to be oxidised to NO<sub>2</sub> before it can be stored, directly effecting the storage capacity. The agglomeration will also decrease the Pt/Ba interface, hindering the transport of NO<sub>2</sub> from the oxidation sites to the storage sites. This, together with the sulphur poisoning of the storage sites, which have been showed to have a great effect [24], lowered the capacity significantly.

### NO<sub>x</sub> conversion

The NO<sub>x</sub> conversion experiment was conducted on both the stabilized and aged catalyst, analysing a combination of storage capacity together with NO<sub>x</sub> reduction activity. Six different experimental points were tested, where either the lean time, engine speed or both was changed.

Figure 26 shows the total conversion of NO<sub>x</sub> over one lean-rich cycle. It can be seen that the stabilized catalyst, LNT-112, achieves higher conversion at every experimental point, where the largest difference is shown at a lean time of 900s and a mass flow



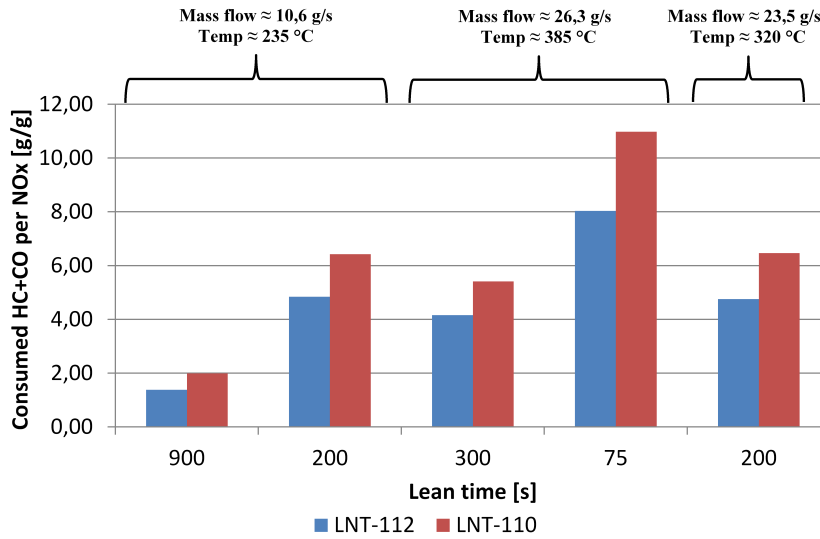
**Figure 26:** The  $\text{NO}_x$  conversions for the stabilized (LNT-112) and aged (LNT-110) catalysts calculated over one lean-rich cycle at varying lean times and engine speeds.

of  $10.6 \text{ g s}^{-1}$ . The long lean time in combination with the small mass flow makes this experimental point dependent on the maximum storage capacity, and as was shown in the storage capacity experiment, this characteristic was reduced for the aged catalyst. The low temperature of around  $235 \text{ }^\circ\text{C}$ , which is lower than what was found to be optimal (see figure 23 and 24) may further increase the difference since the aged catalyst might have even harder to maintain higher storage capacity away from the optimal temperature compared to the stabilized catalyst.

It can also be seen that a shorter lean time is preferable. A shorter lean time before the rich pulse results in less  $\text{NO}_x$  that has to be stored, which in turn results in less  $\text{NO}_x$  that can slip. This also means that the experimental points that has shorter lean time is more likely a measurement of activity, and the longer lean times are more dependent on storage capacity.

One way to analyse the activity of the catalyst without the influence of the storage capacity is to study the amount of reductants (HC and CO) used per reduced  $\text{NO}_x$ . It needs to be noted that not all of the consumed HC and CO is because of the reduction of  $\text{NO}_x$ , since the catalyst will oxidise these species even without the  $\text{NO}_x$  present. But it can still act as a comparison if the amount of consumed reductants is assumed to be somewhat equal for the different experimental points. A lower amount of consumed reductants per consumed  $\text{NO}_x$  will be an indication of a more effective catalyst. The amount of consumed reductants per consumed  $\text{NO}_x$  for each experimental point is displayed in figure 27.

It can be seen from figure 27 that the stabilized catalyst uses less reductants per reduced  $\text{NO}_x$ , indicating a better activity. It can also be seen that the experimental point with a lean time of 900 s needs significantly less reductants, compared to the other



**Figure 27:** The amount of reductants (HC and CO) used per amount  $\text{NO}_x$  reduced for the stabilized (LNT-112) and aged (LNT-110) catalysts calculated over one rich pulse at varying lean times and engine speeds.

experimental points. This indicates that a longer lean time together with a small mass flow and lower temp, is advantageous for a higher activity. A reason for this could be that the consumed amount of reductants because of the oxygen in the exhaust gases, is a larger part of the total consumed amount for the shorter lean times. This is because a longer lean time will store more  $\text{NO}_x$  and therefore consume more reductants, which makes the other consumption a smaller part.

The differences between the stabilized and aged catalyst is probably because of agglomeration of Pt and Rh particles during the ageing procedure, reducing the number of active sites and therefore the total activity. Poisoning of active sites by sulphur has also been showed to greatly decrease the activity [24].





## 5 Conclusions

The thesis work was divided into two parts, analysing the effect of ageing on both three-way catalysts for petrol engines as well as lean  $\text{NO}_x$  traps for diesel engines. The catalysts have been analysed by both motor-rig tests and flow-reactor experiments as well as by SEM/EDX.

It was through motor-rig tests on the three-way catalysts found that 50 h of thermal ageing corresponded well with 20 h poison ageing, especially with regards to the oxygen storage capacities. The emission tests did show some slight indication of 50 h being too long, shown as somewhat higher light-off for HC and  $\text{NO}_x$ , but the differences were only small.

The flow reactor experiments found a higher degree of deterioration at the inlet of the catalysts for both types of ageing. This was shown through lower precious metal dispersion, lower oxygen storage capacities and higher light-off temperatures. The thermal aged catalyst showed better oxygen storage capacity for the first two discs, while the third disc performed almost identical to the third disc of the poison aged catalyst. The light-off temperatures for CO oxidation and NO reduction with  $\text{C}_3\text{H}_6$  were somewhat lower for the poison aged catalyst. These results indicate that the poison ageing method had a greater effect on the oxygen storage while the thermal ageing method impairs the light-off characteristics. SEM/EDX analysis found significant amounts of poison on the thermal aged catalyst, even though no poison was added in the fuel, but the poison aged catalyst contained even higher amounts. It also showed a sharp gradient of the poison distribution where the highest amounts were found at the inlet, decreasing rapidly to almost no poison at the outlet, which could be an explanation for why the catalysts were more deteriorated at the inlet.

The study of the stabilized and aged lean  $\text{NO}_x$  traps showed significantly reduced performance for the aged catalyst. The total conversions of HC, CO and  $\text{NO}_x$  were all affected, and the largest decrease was for the conversion of  $\text{NO}_x$ . The  $\text{NO}_x$  storage capacity was also found to be significantly lower over the whole temperature range, something that was shown to have a direct effect on the  $\text{NO}_x$  conversion over the lean-rich cycles. It was also found, by studying the consumption of HC and CO, that the activity of the aged LNT was significantly lowered.



## 6 Future work

The mechanisms of ageing of catalytic systems for the automotive industry are still in great need of further investigation. This work showed the different effects of poison and thermal ageing, but a more extensive analysis is still needed to fully understand the processes behind the ageing.

The study of the three-way catalytic systems in this work was focused on the first catalyst and how the ageing methods affected this. The second catalyst was not analysed separately. An analyse of the second catalyst might give more understanding of the ageing process and behaviour of the total system.

Further analysis of both the petrol and diesel systems might give even more understanding of how the ageing methods affect the catalyst. Characterization methods such as BET for surface area and pore size measurements, XRD for crystal size information and XPS for chemical and electronic states of the washcoat material could give even more information on the ageing procedure. More information about the ageing of the lean  $\text{NO}_x$  traps can also be obtained by analysing characteristics such as  $\text{NO}_x$  storage and reduction capacity at other engine speeds, engine load and temperature.



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## A Flow reactor experiments

**Table 11:** The steps for the precious metal dispersion experiment. The time for cooling in step 5 was achieved by removing the insulation. Argon is used as balance.

Step	Time [min]	Temperature [°C]	Concentrations	Flow [ml min <sup>-1</sup> ]
1.	10	40 °C min <sup>-1</sup> to 400	100 Ar	3500
2.	10	400	8% O <sub>2</sub>	3500
3.	5	400	100% Ar	3500
4.	20	400	2% H <sub>2</sub>	3500
5.	40	27	2% H <sub>2</sub>	3500
6.	20	27	0.5% CO <sub>2</sub>	1000
7.	15	27	0.5% CO <sub>2</sub> , 0.01% CO	1000
8.	7	27	0.5% CO <sub>2</sub>	1000
9.	15	27	0.5% CO <sub>2</sub> , 0.01% CO	1000

**Table 12:** The steps for the oxygen storage capacity experiment. Step 7, 13, 19 and 25 are cooling steps. The flow was  $3500 \text{ ml min}^{-1}$  with Argon used as balance.

Step	Time [min]	Temperature [c]	Concentrations
1.	20	$40 \text{ }^\circ\text{C min}^{-1}$ to 700	100% Ar
2.	15	700	8% O <sub>2</sub>
3.	0.5	700	100% Ar
4.	15	700	0.02% CO
5.	0.5	700	100% Ar
6.	15	700	8% O <sub>2</sub>
7.	10	$10 \text{ }^\circ\text{C min}^{-1}$ to 600	100% Ar
8.	15	600	8% O <sub>2</sub>
9.	0.5	600	100% Ar
10.	15	600	0.02% CO
11.	0.5	600	100% Ar
12.	15	600	8% O <sub>2</sub>
13.	10	$10 \text{ }^\circ\text{C min}^{-1}$ to 500	100% Ar
14.	15	500	8% O <sub>2</sub>
15.	0.5	500	100% Ar
16.	15	500	0.02% CO
17.	0.5	500	100% Ar
18.	15	500	8% O <sub>2</sub>
19.	10	$10 \text{ }^\circ\text{C min}^{-1}$ to 400	100% Ar
20.	15	400	8% O <sub>2</sub>
21.	0.5	400	100% Ar
22.	15	400	0.02% CO
23.	0.5	400	100% Ar
24.	15	400	8% O <sub>2</sub>
25.	10	$10 \text{ }^\circ\text{C min}^{-1}$ to 300	100% Ar
26.	15	300	8% O <sub>2</sub>
27.	0.5	300	100% Ar
28.	15	300	0.02% CO
29.	0.5	300	100% Ar
30.	15	300	8% O <sub>2</sub>



**Table 13:** The steps for the CO oxidation experiment. The time for the first heating step is dependent on the amount of heating supplied and the time for step 5 on the amount of insulation. The flow was  $3500 \text{ ml min}^{-1}$  with Argon used as balance.

Step	Time [min]	Temperature [°C]	Concentrations
1.	Until heated	400	100% Ar
2.	10	400	8% O <sub>2</sub>
3.	5	400	100% Ar
4.	20	400	2% H <sub>2</sub>
5.	Until cooled	50	100% Ar
6.	15	50	0.5% CO, 0.05% NO, 0.225% O <sub>2</sub> , 5% H <sub>2</sub> O
7.	120	$5 \text{ min}^{-1}$ to 650	0.5% CO, 0.05% NO, 0.225% O <sub>2</sub> , 5% H <sub>2</sub> O

**Table 14:** The steps for the C<sub>3</sub>H<sub>6</sub> oxidation experiment. The time for the first heating step is dependent on the amount of heating supplied and the time for step 5 on the amount of insulation. The flow was  $3500 \text{ ml min}^{-1}$  with Argon used as balance.

Step	Time [min]	Temperature [°C]	Concentrations
1.	Until heated	400	100% Ar
2.	10	400	8% O <sub>2</sub>
3.	5	400	100% Ar
4.	20	400	2% H <sub>2</sub>
5.	Until cooled	50	100% Ar
6.	15	50	0.0555% C <sub>3</sub> H <sub>6</sub> , 0.05% NO, 0.225% O <sub>2</sub> , 5% H <sub>2</sub> O
7.	120	$5 \text{ min}^{-1}$ to 650	0.0555% C <sub>3</sub> H <sub>6</sub> , 0.05% NO, 0.225% O <sub>2</sub> , 5% H <sub>2</sub> O