Marja-Liisa Kärkkäinen

DEACTIVATION OF
OXIDATION CATALYSTS BY
SULPHUR AND
PHOSPHORUS IN DIESEL AND
GAS DRIVEN VEHICLES
MARJA-LIISA KÄRKKÄINEN

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University of Oulu Graduate School; University of Oulu, Faculty of Technology
University of Oulu, P.O. Box 8000, FI-90014 University of Oulu, Finland

Abstract

The combustion of fuels in motor vehicles is one of the most significant causes of air emissions. The use of oxidation catalysts in exhaust gas emission treatment can reduce hydrocarbons (HCs) and carbon monoxide (CO) emissions by more than 90%. Fuels and engine lubricants contain impurities like sulphur (S) and phosphorus (P), which can have a significant effect on the activity and durability of oxidation catalysts.

This thesis aims at increasing the current knowledge of the deactivation phenomena caused by sulphur and phosphorus in diesel and natural/bio gas oxidation catalysts. Accelerated laboratory scale sulphur, phosphorus and thermal treatments in gas-phase conditions were carried out for alumina (Al2O3) based platinum (Pt) and platinum-palladium (PtPd) metallic monolith diesel and natural gas oxidation catalysts. In addition, a vehicle-aged natural gas oxidation catalyst and an engine-bench-aged diesel oxidation catalyst were studied and used as a reference for the laboratory-scale-aged catalysts. BET-BJH, FESEM, TEM, XPS and DRIFT were used as characterization techniques to determine changes on the catalysts. The effect of accelerated deactivation treatments on the catalyst activity was determined using laboratory scale measurements in CO, HC and nitric oxide (NO) oxidation.

Sulphur and phosphorus were found to cause morphological and chemical changes on the studied catalysts. Sulphur was found to be adsorbed vertically throughout the entire catalyst support from the catalyst surface to the metallic monolith, while phosphorus accumulated on the surface region of the precious metal containing catalysts. Both, sulphur and phosphorus, slightly increased the average size of the precious metal particles size and are adsorbed onto the alumina by chemical bonds. In addition, a partial transformation from PdO to Pd and a change in the shape of the precious metal particles due to phosphorus were detected. Due to the detected structural and chemical changes on the catalysts, sulphur and phosphorus treatments reduced the catalytic activity of the studied diesel and natural-gas-oxidation catalysts. Correspondence between real and simulated ageing was found and thus the used accelerated laboratory scale aging method can be stated to be a good tool to simulate sulphur and phosphorus exposure.

Keywords: deactivation, diesel oxidation catalysts, methane, natural gas oxidation catalyst, palladium, phosphorus, platinum, poisoning, sulphur
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Tiivistelmä

Asiasonat: deaktivoituminen, dieselhapetuskatalyyttti, fosfori, maakaasuhapetuskatalyyttti, metaani, myrkytysaine, palladium, platina, rikki
To my beloveds
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Oulu, October 2017

Marja Kärkkäinen
Abbreviations

API  American Petroleum Institute
AsB  Angular selective backscatter
BET  Brunauer-Emmett-Teller method
BJH  Barrett-Joyner-Halenda method
CNG  Compressed natural gas
DOC  Diesel oxidation catalyst
DRIFT  Diffuse Reflectance Infrared Fourier Transform
EB   Engine-bench
EC   European Community
EDS  Energy dispersive spectrometer
EEA  European Environment Agency
EELS Electron energy loss spectroscopy
EPA  Environmental Protection Agency of the United States of America
EU   European Union
FESEM Field emission scanning electron microscopy
FTIR Fourier transform infrared spectroscopy
GHG  Greenhouse gas
GHSV Gas hourly space velocity [h⁻¹]
HC   Hydrocarbon
HPW  High phosphorus concentration treatment
ICP-OES Inductively coupled plasma-optical emission spectroscopy
ILSAC International Lubricants Standardization and Approval Committee
LPW  Light phosphorus concentration treatment
MCT  Mercury Cadmium Telluride detector
NGOC Natural gas oxidation catalyst
PM   Particulate matter
PF   Particulate filter
RT   Room temperature
SAED Selected area electron diffraction
SOF  Soluble organic fraction
SW   Sulphur dioxide-water treatment
TA   Thermal aged
TEM  Transmission electron microscopy
T₅₀  Temperature of 50% conversion of the feed component [°C]
T₉₀  Temperature of 90% conversion of the feed component [°C]
TUT  Tampere University of Technology
TPD  Temperature programmed desorption
USA  United State of America
VOC  Volatile organic compound
W   H₂O-treatment
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
XRF  X-ray fluorescence
ZDDP Zinc dialkyldithiophosphate

**Chemical compounds:**

Al₂O₃  Aluminium oxide, alumina
AlPO₄  Aluminium phosphate
Al₂(SO₄)₃  Aluminium sulphate
CeO₂  Cerium(IV) oxide, ceria
CH₄   Methane
C₃H₆  Propene
CO   Carbon monoxide
CO₂  Carbon dioxide
H₂S   Hydrogen sulphide
NO   Nitric oxide
NO₂  Nitrogen dioxide
NOₓ  Nitrogen oxides
PO₃⁻  Phosphite
SiO₂  Silicon dioxide, silica
SO₂  Sulphur dioxide
SO₃  Sulphur trioxide, sulphite
SO₄²⁻  Sulphate
TiO₂  Titanium dioxide, titania
ZrO₂  Zirconium dioxide, zirconia
Original publications

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:


Kärkkäinen was the first and corresponding author of Papers I, III and V. In Papers II and IV, Kärkkäinen’s contribution was in conducting laboratory scale water, sulphur and phosphorus treatments, activity tests and DRIFT tests as well as in interpreting the obtained data. She also participated in the planning of the contents of the publication with the first author and in writing the article.
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Original publications
1 Introduction

The combustion of fuels in motor vehicles is one of the most significant causes of air emissions. The emissions caused by the incomplete burning of fuels in engines have numerous harmful effects both on the environment and on people’s health. Thus, emission reduction from vehicle engines is a top priority all over the world. Oxidation catalysts have been successfully used in the vehicles since the 1970s to oxidise carbon monoxide (CO) and hydrocarbons (HCs) to release less harmful carbon dioxide (CO₂) and water. In 1980, three-way catalysts were developed and taken into use in stoichiometric conditions (Farrauto & Hoke 2010, Twigg 2011). After that, oxidation catalysts have been used in lean burn vehicles such as trucks in the USA since 1994 and in European diesel light-duty passenger cars and vans since Euro 2 (1996) (Farrauto & Hoke 2010, Lemon 2014). Emission limits for passenger and heavy-duty vehicles have been tightened continuously (EC 2007, EC 2009 c, EPA 2007, EU 2017) together with long-term durability requirements (EC 2009 c). Currently, to meet the emission limits set by the Euro VI (7 years or 700 000 km for heavy-duty vehicles), one key part of the diesel exhaust gas after-treatment system for heavy-duty trucks is the diesel oxidation catalyst (DOC) (Lemon 2014).

Petrol and diesel vehicles are still the most generally used vehicles, but for example, the number of natural gas vehicles is constantly increasing. In January 2017, around 23 million natural gas vehicles existed worldwide (NGV Global 2017) and the forecast is that the number of natural-gas-vehicles (NGVs) will increase to 50 million vehicles by 2020 (Kakaee et al. 2014). Advantages of natural gas compared to petrol and diesel fuels are NG’s lower particulate and nitrogen oxides emissions (Gélin et al. 2003, Kakaee et al. 2014, Korakianitis et al. 2011, Poompipatpong et al. 2011, Papagiannakis et al. 2010). Since natural gas consists mainly of methane, it also has a lower carbon content (Korakianitis et al. 2011, Kakaee et al. 2014) resulting in a reduction in CO₂ emissions (Papagiannakis et al. 2004, Korakianitis et al. 2011, Anderson 2015). Natural gas can be used in stoichiometric and lean burn engines (Korakianitis et al. 2011, Kakaee et al. 2014). Natural gas lean burn engines are used mainly in heavy-duty vehicles such as buses and trucks (Klingstedt et al. 2001). In diesel engines, diesel fuel can be replaced totally by compressed natural gas (CNG) by carrying out engine modifications. The other possibility is to replace the diesel fuel partly by methane (dual-fuel combustion). It is possible to use a dual-fuel system without any modification to diesel engines and CNG is used as the main fuel and the role of the diesel (biodiesel
or other high cetane number fuels can also be used) is to start the combustion and ignite the flame of the CNG in the combustion chamber. (Kakaee et al. 2014, Korakianitis et al. 2011).

The reduction of greenhouse gases (GHGs), e.g. carbon dioxide (CO₂) and methane (CH₄), has been regulated globally in the Kyoto Protocol in 1997 (UNFCCC 1998) and currently strengthened further in the Paris agreement in 2015 (UNFCCC 2015). In addition, the EU has the short-term goal to reduce greenhouse gases by 20% from 1990 levels by the year 2020 (EC 2009 a) and a further target to reduce greenhouse gas emissions by 80% from the 1990 levels by the year 2050 (EEA 2016). The main strategies for reducing GHG emissions of traffic are the development of more fuel-efficient engines, the increased use of the plug-in hybrids and electric vehicles, as well as an increase in the use of biofuels (EEA 2016, REN21). Biofuels mean liquid or gaseous fuels for transport produced from biomass. For example, the European Union’s target for the usage of the share of biofuels in the transportation sector is 10% by 2020 (EC 2009 b).

Biodiesel is considered to be the mostly carbon neutral fuel and it is usually produced by catalytic transesterification of natural oils, such as soybean oil, palm oil and rape-seed oil with low molecular weight alcohols, such as methanol and ethanol (Lee & Shah 2013, He 2016). Biodiesel is used in several countries like Brazil, Argentina, the United States, Germany and France, and can be used in pure form or can be blended with petroleum diesel in different proportions (Amais et al. 2015, Lee & Shah 2013). The disadvantage in the use of edible oils is their high price and competition over food consumption. Therefore, further research has been focused on the development of biodiesel manufacturing using inexpensive waste and non-edible oils (Baskar & Aiswarya 2016, Bhuiya et al. 2016). Biodiesel’s fuel properties vary depending on the source of feedstocks and have a remarkable effect on engine performance and emissions. In general, biodiesel reduces CO₂, PM, CO, and HCs emissions, but increases NOx emissions slightly compared to petroleum diesel fuel (Baskar & Aiswarya 2016, Lee & Shah 2013, Suh et al. 2016).

Biomethane/biogas is a biofuel, which can be manufactured locally from organic waste like the by-products from the anaerobic treatment of wastewaters, organic fractions of municipal solid wastes, livestock residues or organic agro industrial wastes (Munoz et al. 2015, Anderson 2015). Current biomethane production is concentrated primarily in Europe (REN21). The challenge in the use of biomethane as a transportation fuel is in the required standard to purify the fuel in a cost effective and environmental friendly way (Munoz et al. 2015, Korakianitis et al. 2011). As biomethane production increases, it could be blended more with
natural gas, and finally and it could even totally substitute natural gas (Anderson 2015).

The role of oxidation catalysts differs in diesel and natural gas vehicles. The main role of the diesel oxidation catalyst (DOC) is to oxidise CO and unburned HCs and the soluble organic fraction (SOF) of diesel particulates, but often the effective oxidation of nitrogen oxide (NO) to nitrogen dioxide (NO₂) is also desirable (Russell & Epling 2011, Kröcher et al. 2009). In natural gas vehicles, the main challenge for natural gas oxidation catalysts (NGOC) is effective oxidation of unburned methane (CH₄). CH₄ is more difficult to oxidize compared to other hydrocarbons and therefore a higher amount of precious metals and higher temperatures are needed (Gélin & Primet 2002, Barbier & Duprez 2014).

Fuels and engine lubricants contain impurity and additive compounds like phosphorus (P), calcium (Ca), zinc (Zn), magnesium (Mg) and sulphur (S). These compounds are catalyst poisons and they can have a significant effect on the activity and the durability of a catalytic converter (Winkler et al. 2009, Galisteo et al. 2004 and Bartholomew 2001). Sulphur and phosphorus compounds are typically attributed as the main reasons for the exhaust gas catalyst’s chemical deactivation (Rokosz et al. 2001). Both diesel and natural gas fuels contain sulphur. In addition, biogas can contain sulphur. Over the years, it has been possible to reduce the sulphur content in diesel fuel significantly. For example, ultra-low sulphur diesel ($C_S \leq 10$ ppm) is already supplied in all European countries, the USA, Canada, China and Russia (EC 2003, Dieselnet 2017). On the other hand, in many countries in South America, Africa and Asia, high sulphur content diesel ($C_S \geq 350$ ppm) is still available (Global Fuels Specifications 2016, Dieselnet 2017). Phosphorus is a typical additive in engine lubricant oil, but it also a common impurity in biodiesel (Johnson & Hils 2013, Lyra et al. 2009, Sarin 2012, Pietikäinen et al. 2015).

The increasing use of various biofuels and blended fuels can increase the accumulation of impurities on the catalyst surface and thus reduce the long-term durability remarkably. Therefore, there is a demand to develop catalysts with a high resistance to impurities as well as to improve their regeneration potentiality. Thus, it is essential to gain more detailed understanding of the effects of the impurities on the catalyst performance.

### 1.1 Objectives and scope

The main goal of this thesis is to increase the knowledge of the deactivation phenomena caused by sulphur and phosphorus in diesel and bio/natural gas
oxidation catalysts. Various characterization techniques such as BET-BJH, FESEM, TEM, XPS and DRIFT analyses are used to determine the morphological surface changes and the adsorbed sulphur and phosphorus compounds formed. Based on the information acquired, similarity and differences in the sulphur and phosphorus exposure are identified. In addition, the effect of sulphur and phosphorus treatments on catalytic oxidation activity is studied. The objectives of the thesis can be summarized as follows:

- To define the structural and chemical changes on the catalyst surface due to sulphur and phosphorus, separately;
- To illustrate the effect of sulphur and phosphorus, separately, on the activity of diesel and gas oxidation catalysts;
- To evaluate the effect of precious metal composition on the oxidation activity of fresh catalysts as well as on sulphur and phosphorus treated DOC/Pt and DOC/PtPd catalysts;
- To evaluate the correlation between the laboratory-aging and the engine-aging as reliable ageing methods in catalyst deactivation studies.

![Fig. 1. The contributions of the original papers in the thesis.](image)

Paper I deals with the sulphur exposure of the diesel oxidation catalysts. In this paper comparative studies on the characteristic properties and catalytic activity of sulphur on Pt- and PtPd-based catalysts are presented. The activity tests for fresh, water and sulphur treated catalysts are performed with a gas mixture without nitric
oxide. In addition, a comparison between laboratory and engine-bench-aged Pt-based diesel oxidation catalysts are presented. In addition, unpublished DRIFT and activity tests results using a gas mixture with NO are presented in the thesis in Chapters 5.1.3 and 5.2.2.

Paper II covers sulphur exposure and thermal aging of PtPd natural gas oxidation catalysts in varied combinations. In this study, the focus is to determine the role of sulphur with and without thermal treatment. The results of a solely thermal treated sample are used as a reference. The characterization information from the vehicle-aged PtPd natural gas oxidation catalyst is used as a background for the treatments done on a laboratory scale. These results are presented in this thesis in Chapters 5.1.1.

Papers III and IV focus on obtaining knowledge about phosphorus exposure on Pt- and PtPd-based diesel oxidation catalysts. In both papers, phosphorus treatment results using two different phosphorus concentrations (high and low) are presented. Paper III covers the characterization and performance results except cross-sectional transmission electron microscopy (TEM) characterization results, which are reported in Paper IV.

Paper V presents the effect of the phosphorus exposure on natural gas oxidation catalysts using two different phosphorus concentrations (high and low). The information provided by the characterization and performance results provides new insights into the phosphorus deactivation phenomena for alumina based PtPd catalysts. The NGOC support characterizations are presented in Chapter 5.1.4.
2 Oxidation catalysis

During oxidation, catalysis compounds are oxidized using catalysts. The role of a catalyst is to reduce the activation energy which is needed for the oxidation reaction. Consequently, the desired product can be produced faster, using fewer resources, and generating less waste (Teles et al. 2015, Rothenberg 2010). Oxidation catalysts are widely used in applications such as exhaust gas purification, partial oxidation and in the production of industrial inorganic chemicals like sulphuric acid and nitric acid (Prins et al. 2016). Both, homogeneous and heterogeneous catalysts are used in oxidation catalysis and the catalyst forms vary a great deal. For example, pellets, gauzes and monoliths are used (Twigg & Webster 2006).

The most typical reactions in exhaust gas oxidation catalysis are shown in Equations 1-4. Usually, the CO reaction begins first and subsequently the HC and nitrogen oxide (NOx) reactions take place (Heck et al. 2002). Oxidation of CO, HC and the soluble organic fraction SOF to CO2 and H2O can be described as follows (Hochmuth et al. 2013, Twigg 2011, Heck et al. 2002):

\[ CO + 0.5O_2 \rightarrow CO_2 \]  (1)

\[ C_xH_y + (x + 0.25y)O_2 \rightarrow xCO_2 + 0.5yH_2O \]  (2)

\[ SOF + O_2 \rightarrow CO_2 + H_2O \]  (3)

The oxidation of NO to nitrogen dioxide (NO2) follows the reaction (Martinez-Arias et al. 2012, Olsson & Fridell 2002):

\[ NO + 0.5O_2 \rightleftharpoons NO_2 \]  (4)

2.1 Oxidation catalysts

Heterogeneous monolith-type oxidation catalysts are used widely in air pollution control and for emission mitigation purposes in vehicles, as well as in stationary applications (Twigg & Webster 2006). Oxidation catalysts are mainly used for the oxidation of hydrocarbons and carbon monoxide in vehicle applications and oxidation of volatile organic compounds (VOCs) in stationary applications (Barbier & Dubrez 2014). Two types of monolith substrates are commonly used, i.e. ceramic and metallic monoliths. Ceramic monolith substrates are made of cordierite, i.e. 2MgO.2Al2O3, and they have a good thermal shock resistance and low coefficient of thermal expansion (Williams 2001). Even though ceramic monoliths are the most widely used monolith substrates because of their low price, good corrosive
resistance and good catalyst adhesion, a substantial number of metallic substrates are also used (Gulati et al. 2006, Lemon 2014). Ni and Cr as well as ferritic alloys containing Al are widely used as metallic substrate materials. The advantages of metallic substrates are their higher mechanical resistance, thinner walls and higher thermal conductivity, which allows faster light-off times (Avila et al. 2005, Gulati et al. 2006, Farrauto 2010). In addition, metallic monolith substrates are widely used in the oxidation of VOCs, since with metallic framework materials it is possible to prepare converters on a larger scale and with special monolith shapes (Twigg & Webster 2006, Avila et al. 2005).

The monolithic framework is coated with a thin layer of catalytic material, which consists of highly dispersed active metals on a high surface area support and appropriate promoters (Twigg & Webster 2006). The catalytic materials, which are used especially in DOC and NGOC catalysts are explained in more detail in Section 2.2.

2.1.1 Diesel vehicle application

Diesel emissions from vehicles contain solid, liquid and gaseous components. Solids released from diesel engines are basically soot (carbon-rich particles) which is referred to often as particulate matter (PM). Liquids are generally referred to as the soluble organic fraction (SOF) and are unburned diesel fuel and engine lubricants. SOF can also contain sulphates to some extent, which are formed during combustion from the sulphur compounds present in the diesel fuel. The gaseous components in diesel exhaust gas include carbon monoxide (CO), hydrocarbons (HCs) with a carbon number between C2-C15, and nitrogen oxides (NOx). (Hochmuth et al. 2013, Martinez-Arias et al. 2012, Corro 2002) The composition of diesel exhaust gas is typically: 200-1000 ppm NOx, 10-330 ppm total hydrocarbons, 150-1200 ppm CO, 5-15 vol% O2, 1-7 vol% H2O, 3-13 vol% CO2, 10-100 ppm sulphur oxides, and 50-400 mg m⁻³ particulates (Martinez-Arias et al. 2012). Since diesel engines operate with a large excess of air, exhaust gas purification must be done in lean conditions, not in stoichiometric conditions as it is possible to do in petrol engine applications. Therefore, the exhaust gas temperature of the diesel engine is much cooler than that of a stoichiometrically operated petrol engine (100-500 °C vs. 300-1100 °C) and the exhaust gas temperature in a diesel engine can be around 120–150 °C in urban driving conditions. (Hochmuth et al. 2013 and Twigg 2011)
Currently, a heavy-duty diesel exhaust gas after-treatment system typically contains a diesel oxidation catalyst (DOC), a particulate filter (PF) and units for NOx mitigation. The main goal of the DOCs is to oxidize CO, HCs, and the SOF of particulates completely (Russell & Epling 2011, Lemon 2014, Resitoglu et al. 2015). The oxidation of NO to NO2 in DOC has also become indispensable. In the diesel exhaust gas, NO and NO2 are not in thermodynamic equilibrium and the share of NO2 is only about 5-10%. In diesel particulate filters, NO2 accelerates soot oxidation at low temperatures (Kröcher et al. 2009, Piumetti et al. 2015 Khazanchi et al. 2017). Alternative methods for NOx reduction are selective catalytic reduction (SCR) and NOx storage reduction (NSR). In NOx reduction, the presence of NO2 increases the NOx conversion efficiency in the urea-SCR, making a fast SCR reaction possible and in the NSR system NO2 improves the ability to store NOx as nitrates (Twigg 2011, Kröcher et al. 2009, Rahkamaa-Tolonen et al. 2005).

2.1.2 Natural gas vehicle applications

Lean burn natural gas vehicles (NGV) have lower particulate (PM) and NOx emissions than comparable diesel engines. However, NGVs can emit relatively high levels of unburned methane (CH4), which is a strong greenhouse gas. Therefore, natural gas oxidation catalysts (NGOCs) are necessarily needed to oxidize the unburned CH4. At the same time CO is oxidized to a less harmful compound, i.e. CO2. (Cho & He 2007, Gélin & Primet et al. 2002, Korakianitis et al. 2011, Choudhary et al. 2002). Typically, exhausts of lean NGVs have 500–5000 ppm of CH4, a maximum 15 vol% CO2, 10-15 vol% H2O and ppm levels of SOx and NOx (Gélin & Primet et al. 2002, Zanoletti et al. 2009). CH4 has a higher stability than the other hydrocarbon molecules and therefore it is the most difficult hydrocarbon to oxidize (Barbier & Duprez 2014). The exhaust gas temperature of lean burn natural gas vehicles is relatively low (300–500 °C) and therefore methane oxidation across a natural gas oxidation catalyst is challenging (Liu et al. 2001, Abbasi et al. 2012).
2.2 Materials in oxidation catalysts

2.2.1 Active compounds

Precious metals (Pt, Pd and Rh) as well as transition metal oxides such as copper (Cu), chromium (Cr), nickel (Ni), cobalt (Co) and manganese (Mn) are known to be active in the oxidation of hydrocarbons and carbon monoxide (Neyestanaki et al. 2004, Farrauto 2010). From these, platinum and palladium are the most used active compounds in CO and HCs oxidation in light-duty applications (Farrauto 2010, Russell & Epling 2011). For example, Yu Yao (1980) and Gololobov et al. (2009) have found that Pt has a higher oxidation activity than Pd towards heavier alkanes C3H8, whereas Pd has higher activity towards the oxidization of alkanes (CH4 and C2H6), and CO than Pt. In addition, Yu Yao (1980) found that propene oxidation is much faster than propane oxidation over Pd, and the tendency was the opposite over Pt. If NOx oxidation activity in the diesel oxidation catalyst is desirable, Pt is the preferable choice for that purpose (Watanabe et al. 2007, Wiebenga et al. 2012). Thus, Pt is the most active in diesel applications and Pd is the most active in methane oxidation in lean conditions. Nevertheless, the higher thermal stability of DOC in an oxidative atmosphere is possible when PtPd alloys are used (Kaneeda 2009, Morlang 2005). In methane oxidation, higher resistance against sulphur, water and Pd sintering can be achieved using a PdPt catalyst compared to a Pd only catalyst (Narui et al. 1999, Pieck et al. 2002, Persson et al. 2007, Ozawa et al. 2004). It is widely agreed that PdO is the active phase while metallic palladium is much less active (Farrauto et al. 1995, Burch & Urbano 1995, Datye et al. 2000, Antony et al. 2013). In proportion, metallic Pt is reported to be more active than PtO especially in NO oxidation (Hauff et al. 2012).

2.2.2 Support materials

In the oxidation catalyst, the active compounds are typically deposited on a support (carrier) (Neyestanaki et al. 2004). The support and active compounds form a coating, generally referred to as the catalysed washcoat, on the monolith substrates (Farrauto 2010). The support has several roles and it influences the catalyst activity, selectivity and durability (Heck et al. 2002, Neyestanaki et al. 2004). The main role of the support is to provide the surface to disperse the catalytic substance to maximise the catalytic surface area and increase the thermal stability of the active component. The properties of the support material such as the support surface area,
pore volume, surface acidity and reactivity, thermal conductivity, and thermal expansion, have a strong effect on the performance of the final catalyst. (Heck et al. 2002, Neyestanaki et al. 2004) The support material is quite often a complex mixture of different metals or oxides, which all have a separate role in the support material. The support materials used in CO and HCs oxidation catalysts can consist of several oxides such as alumina (Al₂O₃), titania (TiO₂), ceria (CeO₂), zirconia (ZrO₂), silica (SiO₂) and vanadia (V₂O₅). (Martinez-Arias et al. 2012)

γ-Alumina (γ-Al₂O₃) is commonly the main component in the support material because it has a large surface area, good thermal stability and good interaction with precious metals like Pt (Heck et al. 2002, Kim et al. 2013). γ-Alumina is manufactured from monohydrate (Boehmite) and, to obtain the γ-alumina phase, Boehmite needs to be heated to ~500 °C (Hayes & Kolaczkowski 1997, Prins et al. 2016). Concerning alternative materials, silica-based materials have been investigated to replace γ-alumina. The advantage of silica and SiO₂ZrO₂ are in their inertness towards sulphur (e.g. Kim et al. 2016, Väliheikki et al. 2017).

The support material often contains additives such as promoters and stabilizers. In the γ-alumina based support materials typical additives include metal oxides (e.g. ceria, zirconia and titania). Ceria can have several roles in the oxidation catalyst. Ceria can act as a stabilizer inhibiting the phase transition of alumina (Heck et al. 2002) or it can enhance CO oxidation at the metal-support interface (Barbier & Duprez 2014). Zirconia has been also used to improve the thermal stability of alumina (Russell & Epling 2011). Typically, ceria-zirconia mixed oxide is used as an additive in commercial catalysts (Kim et al. 2016). Other typical thermal stabilizers for alumina are barium oxide (BaO) and lanthanum oxide (La₂O₃) (Hayes & Kolaczkowski 1997, Russell & Epling 2011). Titania is a sulphur resistant material and for that reason it has also been introduced in oxidation catalysts in vehicle applications (Yang et al. 2017).
3 Catalyst deactivation

3.1 General

Catalyst deactivation, the loss of catalytic activity and/or selectivity over time, is a general problem in heterogeneous oxidation catalysis. Typically, the deactivation of automobile oxidation catalysts occurs slowly (Heck et al. 2002, Chorkendorff & Niementsverdriet 2007). The deactivation process is physical or chemical in its nature, but quite often it can be classified as chemical, thermal, or mechanical deactivation. In practice, more than one process or type of deactivation are often present at the same time (Neyestanaki et al. 2004, Bartholomew 2001, Argyle & Bartholomew et al. 2015, Moulijn et al. 2001, Richardson 1989). In addition, deactivation can be classified according to its mechanism. There are several different classifications for this, but Moulijn et al. (2001) and Murzin (2013) have grouped the main mechanisms in heterogeneous catalysis as follows: poisoning, fouling, thermal degradation, mechanical damage, and attrition. Thermal degradation, mechanical damage and attraction are typically irreversible, but poisoning and fouling are at least partly reversible (Moulijn et al. 2001). The principles of various types of mechanical failures, thermal transformations, and deactivation due to impurities are discussed in more detail in the following chapters.

3.1.1 Mechanical failures

Catalyst deactivation by mechanical damage or attrition can inhibit catalyst activity in several ways. First, mechanical damage, e.g. monolith failure, blocks the pores and inhibits or even prevents catalyst functionality. In automobile applications, monolith failure can be caused by a sudden mechanical impact or thermal shock (Bartholomew 2001, Moulijn et al. 2001). Secondly, high gas flow velocity and rapid temperature changes (thermal stress) can cause attrition, leading, for example, to the loss of the support and precious metals. This can happen in particular when a metal substrate is used, since the thermal expansion difference between the support material and substrate can cause the loss of support material. (Heck et al. 2002, Moulijn et al. 2001, Argyle & Bartholomew et al. 2015)
3.1.2 Thermal transformations

Thermally induced deactivation is a physical process, which can be caused by volatilization, sintering, or phase transformation. Due to elevated temperatures, the active component can react with the surrounded medium and form volatile compounds. (Moulijn et al. 2001) Sintering can cause the loss of the active material surface due to particle growth of the catalytic phase (catalyst sintering) and/or the loss of the support area due to collapse of the support (support sintering). The sintering process takes place at elevated temperatures and is accelerated in hydrothermal conditions. (Bartholomew 2001, Argyle & Bartholomew et al. 2015) Sintering is a strongly temperature dependent phenomenon and the underlying mechanism is surface diffusion or mobility of large aggregates (crystal growth). Hüttig and Tamman temperatures can be used to estimate the temperature at which sintering could occur. At the Hüttig temperature (T\textsubscript{Hüttig} = 0.3T\textsubscript{melting}) atoms at defects become mobile indicating surface diffusion whereas at the Tamman temperature (T\textsubscript{Tamman} = 0.5T\textsubscript{melting}) atoms of the bulk exhibit mobile indicating crystal growth. (Moulijn et al. 2001) In practice, the real temperature where a solid becomes mobile depends on several factors such as texture, particle size and the morphology of the material. Generally, highly porous materials are more sensitive to sintering than less porous materials and small particles are more sensitive to sintering than large particles. In addition, structural promoters (or impurities) may inhibit the surface migration of atoms of active particles (Moulijn et al. 2001).

In the case of active material sintering, it is generally proposed that metal particle growth can happen by crystallite migration and due to Ostwald ripening (atom migration) (Forzatti et al. 1999, Hansen et al. 2013). In crystallite migration crystallites migrate along the support surface, and the collision and coalescence of two crystallites forms a large particle. In Ostwald ripening metal atoms escape from one crystallite and migrate along the support and are captured by larger crystallites (Hansen et al. 2013, Neyestanaki et al. 2004, Sehested et al. 2004, Forzatti et al. 1999).

Support sintering can be accompanied by phase transformations. A good example of this is Al\textsubscript{2}O\textsubscript{3}, where γ-alumina is gradually transformed via δ-alumina and θ-alumina to α-alumina at high temperatures (over 1000°C) resulting in a loss of surface area (Honkanen et al. 2017, Neyestanaki et al. 2004). The normal operating temperature in diesel and lean-natural-gas engines are moderate compared to petrol engines and thus thermal deactivation in normal operation conditions (100-500 °C) is not a crucial problem for DOC or NGOC (Heck et al. 2004).
Nevertheless, the repeated misfiring or particulate filter regeneration in the case of a diesel engine can lead to sudden temperature increases and unexpectedly high values (up to 900 °C) in the oxidation catalyst (Cavataio et al. 2009, Chorkendorff & Niementsverdriet 2007).

### 3.1.3 Deactivation due to impurities

Selective or non-selective poisoning can cause a loss of catalyst activity and selectivity caused by the adsorption of impurities (Heck et al. 2002). Selective poisoning (poisoning) is a typical form of chemical deactivation and arises from the chemisorption of species on catalytic sites inhibiting or altering the sites for catalytic reactions (Hayes & Kolaczkowski 1997, Bartholomew 2001). Usually, chemisorption is strong and causes a permanent loss of the active site (irreversible poisoning). In some cases, it is possible that the poison is desorbed over time once the impurity in the feed is reduced (reversible poisoning) (Hayes & Kolaczkowski 1997).

Non-selective poisoning (fouling) arises as a result of physical adsorption of species/impurities on catalytic sites blocking access to active sites (Hayes & Kolaczkowski 1997, Heck et al. 2002). Fouling is classified as mechanical deactivation (Richardson 1989, Bartholomew 2001, Argyle & Bartholomew et al. 2015). The most common example of fouling is carbon deposition on the catalyst surface (coking), but it is a relevant mechanism also in the case of the impurities like Mg, Ca and Zn, S and P (Bartholomew 2001, Winkler et al. 2009).

In summary, impurities such as sulphur and phosphorus can cause both poisoning and fouling. Fouling can be irreversible or reversible, like poisoning. Typically, carbon fouling is reversible, since carbon deposition can be burned off the catalyst surface in oxygen rich conditions at elevated temperatures. (Bartholomew 2001, Hayes & Kolaczkowski 1997, Moulijn et al. 2001)

### 3.2 Impurities and their effects

#### 3.2.1 The origin of impurities

A catalyst’s impurities originate from engine lubricant additives and fuels. Engine lubricants contain several types of oil additives, which aim to improve the performance and extend the lifetime of the lubricant (Finnish National Board of
Education 2017). Detergents are surface-active materials and are used in engine lubricants to keep engine parts clean. Typically, detergents contain alkaline earth metals like calcium (Ca), sodium (Na) and magnesium (Mg). To prevent foaming of engine lubricants silicon containing anti-foaming additives are primarily used. (Finnish National Board of Education 2017, Winkler et al. 2010) Antiwear resistance is a critical feature in engine lubricants. Zinc dialkyldithiophosphate (ZDDP) has been used as an antiwear resistance additive from the mid-1940s and it is still commonly used, because of ZDDP’s very good antiwear features and low price (Faring & Jao 2017, Johnson & Hils 2013, Spikes 2004). ZDDP is a metal containing phosphate ester, which contains Zn, P and S (Johnson & Hils 2013). The phosphorus concentration in engine lubricants differs from 600 ppm to 2000 ppm. The International Lubricants Standardization and Approval Committee (ILSAC) is the organization responsible for setting the lubricant specifications for passenger cars and the current standard GF-5 (introduced in 2010) sets the phosphorus concentration between 600 ppm minimum and 800 ppm maximum for passenger car engine lubricants (Faring & Jao 2017, ILSAC 2017). Generally, the phosphorus concentration limits in different standards are higher for heavy duty engine oils (Faring & Jao 2017). The sulphur concentration in engine oils can be up to ~ 4000 ppm (Wiebenga et al. 2012), but engine oils with very low sulphur concentrations (~ 15 ppm) are also available (API 2017). Sulphur concentration limits for engine oils have been set, for example, by the American Petroleum Institute (API) (API 2017).

The use of ultra-low sulphur diesel is spreading all over the world, so sulphur’s significance as a catalyst impurity in diesel vehicles will diminish gradually (Global Fuels Specifications 2016). Natural gas fuel always contains sulphur, even if the SO\textsubscript{2} content is very low (ppm level) (Kakaee et al. 2014, Gélin & Primet 2002). Feedstocks for biogas (sewage sludge, livestock manure or agro-industrial biowaste) can contain inorganic and organic sulphur, which is converted into dissolved sulfides and are transferred to biogas mainly in the form of hydrogen sulphide (H\textsubscript{2}S) (Arrhenius et al. 2017, Munoz et al. 2015). The European standard on automotive fuel specifications for natural and biomethane gas specifies 20 mgm\textsuperscript{-3} without odorization and 30 mgm\textsuperscript{-3} with odorization as maximum limits for sulphur concentrations; even though the goal should be 10 mgm\textsuperscript{-3} with odorization (EN 2017). Currently, the quality that the gas industry can provide is 30 mgm\textsuperscript{-3} with odorization and therefore that value is within the standard (EN 2017).

In biodiesel, phosphorus, calcium and magnesium are typical impurities, whereas the sulphur content is typically very low (Amais et al. 2015, Lyra et al. 2015).
Phosphorus originates from the feedstocks used in biodiesel production, such as phospholipids in vegetable oils or animal fats or alternatively from the inorganic salts in used frying oil (Lyra et al. 2009, Sarin 2012). For example, low-quality, untreated rapeseed oil can contain very high amounts of phosphorus (~350 mgkg⁻¹) (Pietikäinen et al. 2015). Currently the maximum permissible concentration of phosphorus set by biodiesel standards in Europe is 4 mgkg⁻¹ (EN 2012) and in the USA 10 mgkg⁻¹ (Amais et al. 2015).

### 3.2.2 Sulphur contamination

Typically, sulphur is in the exhaust in the form of SO₂. In oxygen rich conditions and in the presence of precious metal containing catalysts, SO₂ is further oxidized to SO₃ at temperatures above 300 °C (Neyestanaki et al. 2004, Corro 2002). Sulphur compounds are bound tightly on the active sites of the catalyst forming stable precious metal surface sulphates (NMSO₄, in which NM is the precious metal). The formed sulphates inhibit reactants from adsorbing on the active sites (Neyestanaki et al. 2004). Even very small amounts of sulphur reduce the methane oxidation activity over Pd-based catalysts. A low sulphur concentration also inhibits ethane, propane, and CO oxidations but to a lesser extent than the oxidation of methane (Gélin & Primet 2002). In methane oxidation, one way to prevent adsorption of sulphur on the Pd surface species is to use a bimetallic PtPd catalyst. The role of metallic Pt⁰ surface species is to adsorb sulphur compounds and preventing the adsorption of sulphur on the Pd surface species leaves the Pd surface available for methane oxidation (Corro et al. 2010).

The support materials can be sulphur sensitive like alumina (Al₂O₃) and sulphur resistant like silica (SiO₂). It is generally agreed that SO₂ inhibition of Pd has a different mechanism on sulphur sensitive and sulphur resistant support materials (Lampert et al. 1997, Colusii et al. 2010, Konsolakis et al. 2013, and Mowery & McCormick 2001). In both cases, Pd first oxidizes SO₂ to SO₃. With a sulphur sensitive support, SO₃ is adsorbed on both Pd and the support material, but with a sulphur resistant support, SO₃ is adsorbed only on Pd. Therefore, the sulphur sensitive support acts like a sink and prevents the rapid deactivation of Pd. Recently, Hamzehlouyan et al. (2016) have studied adsorption and desorption of SO₂ over γ-alumina and Pt/γ-alumina. Based on DRIFT and temperature programmed desorption (TPD) data, they suggest the following reaction steps for the SO₂ adsorption and desorption on/from γ-alumina: 1) SO₂ is molecularly adsorbed on the Al sites; 2) SO₂ adsorbs onto coordinated oxygen atoms on the alumina; 3) the
adsorbed SO₂ forms surface sulphites/sulphates; and 4) the formation of bulk aluminium sulphites occurs. In addition, they found that Pt has an increasing effect on the sulphate formation and the migration of the surface sulphates to the bulk alumina. The migration of sulphates from the bulk back to the alumina surface was found to happen at lower temperatures in the case of Pt supported alumina compared to bare alumina (Hamzehlouyan et al. 2016). Nevertheless, Pt only or Pt-rich catalysts are found to be less effective in sulphate formation than the Pd only or Pd-rich catalysts (Wilburn & Epling 2017). Konsolakis et al. (2013) reported that the acidity of Pd/γ-alumina catalyst changes during SO₂-treatment. When fresh Pd/γ-alumina catalysts have only Lewis acid sites, SO₂-treated catalysts also have a significant amount of Brönsted acid sites on the Pd/γ-alumina support. This in particular can have a diminishing effect on the methane oxidation activity (Wischert et al. 2011).

The presence of water alone has been reported to have a decreasing effect especially on the methane conversion by forming Pd(OH)₂ (Burch & Urbano 1995, Roth et al. 2000). In addition, Mowery & McCormick et al. (2001) have shown that the joint effect of water and sulphur increases the formation of PdSO₄, since the spill over of SO₂ from PdO to the alumina is inhibited. Sulphur poisoning is typically reversible and SO₂ from the catalyst surface can desorbed already at temperatures below 400 °C (Kröcher et al. 2009). The decomposition of more stable aluminium sulphate at lean conditions (excess of O₂) takes place at 700-750 °C (Arosio et al. 2006, Kröcher et al. 2009).

Regeneration can be achieved using short reductive pulses (e.g., CH₄) and, for example, Arosio et al. (2006) have reported that complete regeneration is already possible at a temperature of 600 °C. During regeneration, sulphur can quickly and directly be desorbed from the Pd surface with a sulphur resistant support. With a sulphur sensitive support, regeneration is much more difficult because of the SO₃ spill over from the support on the Pd surface during the regeneration (Lampert et al. 1997). According to Kinnunen et al. (2017), a sulphur poisoned catalyst can be regenerated by decomposing PdSO₄ to PdSO₃ followed by the release of oxygen and SO₂. As a result of the decomposition of PdSO₄, metallic Pd is formed, which is an inactive phase for methane combustion (Kinnunen et al. 2017).

3.2.3 Phosphorus contamination

In phosphorus contamination, a phosphate-containing layer can be formed on the support (fouling), which blocks the support pores and covers the precious metals.
(Matam et al. 2012, Mowery et al. 1999, Winkler et al. 2009). In addition, phosphate compounds can form bonds and compounds directly with the support elements (poisoning) (Matam et al. 2012). With an alumina support, phosphate typically forms aluminium phosphate (AlPO₄) compounds (Galisteo et al. 2004, Kröger 2007, Rokosz 2001, Matam et al. 2013), which can modify the chemical properties of the surface as well as the electronic properties of the Pt particles (Ramis et al. 1989). Phosphorus has been observed to also form compounds with Ce, Zn and Mg forming CePO₄, Zn₂P₂O₇ and Mg₃(PO₄)_2, respectively (Larese et al. 2003, López et al. 2005, Winkler et al. 2009). It is possible that a glassy phosphorus containing layer, which blocks active sites, is formed on the catalyst surface (Klimczak et al. 2010) Phosphorus has been mostly detected in the front part of vehicle-aged DOC and NGOC catalysts (Angove & Cant 2000, Lanzerath et al. 2009, Mowery et al. 1999, Wiebenga et al. 2012, Winkler et al. 2009).

Regeneration of a catalyst that has been contaminated with phosphorus is much more difficult than that of a sulphur contaminated catalyst, since phosphorus cannot desorb or can be evacuated through heating. However, Rokoz et al. (2001) and Christou & Efstathiou (2007), for example, have found phosphorus compound removal by oxalic acid to be a good method for phosphorus regeneration.
4 Materials and methods

Individual impurities (sulphur and phosphorus) were studied using a laboratory scale deactivation procedure. Bench- and engine-aged catalysts were used as references for the laboratory scale-aged catalysts. This work was done in the project funded by the Academy of Finland, and in close co-operation with three universities and one industrial partner, Dinex Ecocat Ltd. Figure 2 illustrates the tasks and the roles of the partners in this work. Dinex Ecocat Ltd provided the fresh catalyst materials. The laboratory scale deactivation treatments used in this study were done at the University of Oulu (UOulu). X-ray fluorescence (XRF) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analyses were done as purchased services. The other characterizations and analyses were done in co-operation with UOulu, Tampere University of Technology (TUT) and Aalto University (Aalto).

![Diagram showing tasks and roles of partners](image)

**Fig. 2.** Tasks and roles of the partners in this work. University of Oulu (UOulu), Tampere University of Technology (TUT), Aalto University (Aalto).
4.1 Materials

The catalysts used in this study were three precious metal loaded catalysts mounted on a metallic foil (monolith type catalysts) (Figure 3), two being diesel oxidation catalysts (marked as DOC/PtPd and DOC/Pt) and one a natural gas oxidation catalyst (marked as NGOC/PtPd). DOC/PtPd and DOC/Pt catalysts were used in Papers I, III and IV and NGOC/PtPd catalysts were used in Papers II and V. In addition, the DOC support material without precious metals was used to indicate the roles of Pd and Pt for phosphorus exposure (Paper III). Detailed information about the used catalysts is presented in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support material</th>
<th>Active materials</th>
<th>Active material content of catalyst (gdm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC support</td>
<td>γ-alumina with additives (zeolites and e.g. Ce, Zr and Ti oxides)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DOC/Pt</td>
<td>see above</td>
<td>Pt</td>
<td>1.8</td>
</tr>
<tr>
<td>DOC/PtPd</td>
<td>see above</td>
<td>Pt:Pd (4:1)</td>
<td>1.8</td>
</tr>
<tr>
<td>NGOC support</td>
<td>γ-alumina</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NGOC/PtPd</td>
<td>see above</td>
<td>Pt:Pd (1:4)</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Fig. 3. Picture of a catalyst sample.

4.2 Deactivation treatment procedures

4.2.1 Laboratory scale treatments

Gas phase sulphur, phosphorus and water treatments of the studied catalysts were performed at UOulu using a laboratory scale tubular quartz reactor. The diameter of the sample monolithic catalyst was 1.0 cm and the length was 3.8 cm. The conditions of the laboratory scale treatments using water (W), sulphur dioxide-water (SW), low phosphorus-water (LPW), high phosphorus-water (HPW) and
thermal aged (TA) are shown in Table 2. All the treatments were completed at 400 °C for 5 h with the total gas flow of 1 dm³. The gas hourly space velocity (GHSV) was 20 000 h⁻¹ during the treatments. Water and SO₂-treatments (Papers I and II) were performed using the setup shown in Figure 4. 0.065 M and 0.13 M aqueous P-solutions or pure water were added through a peristaltic pump into the gas feed before the tube furnace, and the solution was evaporated in a furnace before entering the catalyst bed (monolith). The gaseous compounds were controlled by mass flow controllers (Brooks 5280S). Water and P-treatments (Papers III-V) were done with a similar setup but the furnace, reactor pipe and the sample inside were aligned vertically. In addition, the thermal treatments were done at TUT for the NGOC/Pt catalyst (Paper II).

Table 2. Laboratory scale treatments and corresponding markings used.

<table>
<thead>
<tr>
<th>Marking</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>10 vol% H₂O, 10 vol% air and N₂ (bal.) at 400 °C 5h</td>
</tr>
<tr>
<td>SW</td>
<td>100 ppm SO₂, 10 vol% H₂O, 10 vol% air and N₂ (bal.) at 400 °C 5h</td>
</tr>
<tr>
<td>LPW</td>
<td>10 vol% 0.065 M (NH₄)₂HPO₄ (aq.), 10 vol% air and N₂ (bal.) at 400 °C 5h</td>
</tr>
<tr>
<td>HPW</td>
<td>10 vol% 0.13 M (NH₄)₂HPO₄ (aq.), 10 vol% air and N₂ (bal.) at 400 °C 5h</td>
</tr>
<tr>
<td>TA</td>
<td>100 vol% synthetic air (80 % N₂ and 20 % O₂) at 1000 °C 5h</td>
</tr>
<tr>
<td>TA+SW</td>
<td>TA-treatment followed SW-treatment</td>
</tr>
</tbody>
</table>

Fig. 4. Schematic of the SO₂ treatment equipment.
4.2.2 Vehicle and engine-bench-aged treatments

The long-term field ageing for the NGOC/PtPd catalyst was done in a lean-burn natural gas heavy duty vehicle for 160,000 km. The engine-bench-aging for the DOC/Pt catalyst was performed with a diesel passenger car engine for ~30 h using a diesel fuel with a high sulphur content (C₅ ≥ 350 ppm). For the engine-bench-aged catalyst the accumulated soot was burned in air for 4 h at 600 °C before activity experiments and analyses. The vehicle and engine-bench-aged samples were provided by Dinex Ecocat Ltd.

4.3 Catalyst characterization

4.3.1 Bulk analyses

*Inductively coupled plasma optical emission spectroscopy (ICP-OES)*

The phosphorus content analysis in bulk was done on an ICP-OES device (Thermo Fisher Scientific, iCAP 6500 Duo) (Papers III, IV). The catalyst powders from two monoliths were diluted with a solution of HNO₃ and HCl and then digested using microwaves. After digestion, the samples were diluted with water and analysed. The ICP-OES analyses were done as a purchased service by Suomen Ympäristöpalvelu.

*X-ray photoelectron fluorescence (XRF)*

The sulphur content of sulphur treated catalyst samples was analysed by a Philips MagiX apparatus containing Super Q Analytical software (Paper I). The amount of catalyst in the analyses was ~30 mg. XRF analyses were done as a purchased service by Kemiantutkimuspalvelut Oy.

4.3.2 Physisorption analyses

To determine the effect of deactivation treatments on the specific surface area, pore size and pore volume, physisorption analyses were carried out using a Micrometrics ASAP 2020 device (Papers I-III and V). Specific surface areas (m²g⁻¹) were measured from the N₂ adsorption isotherms at -196 °C according to the BET
(Brunauer-Emmett-Teller) method. The pore size and pore volume distributions of catalysts were calculated from N\textsubscript{2} desorption isotherms using the BJH (Barrett-Joyner-Halenda) method. The measurements were performed using catalyst powders, so before the analyses the catalysts were scraped from the metal foil.

4.3.3 Electron microscopy, spectroscopy and diffraction analyses

Field-emission scanning electron microscopy (FESEM)

The microstructures of the fresh and treated monolith catalysts were studied with an FESEM (Zeiss ULTRA plus) equipped with an energy dispersive spectrometer (EDS, INCA Energy 350 with INCAx-act silicon-drift detector (SDD), Oxford Instruments) using cross-sectional FESEM samples (Papers II, III and V). A conventional metallographic sample preparation technique (including the moulding of a catalyst monolith in a resin, grinding and polishing) was used in the sample preparation. Finally, the sample was coated by carbon to avoid sample charging in the FESEM studies. The images were taken with an angular selective backscatter (AsB) detector to maximize the Z-contrast.

Transmission electron microscopy (TEM)

TEM was used to characterize the microstructure and composition of the samples as well as to determine structural changes in the support and the precious metal. A TEM (Jeol JEM-2010) equipped with an energy dispersive X-ray spectrometer (EDS, Noran Vantage with Si(Li) detector Thermo Scientific) was used for imaging and elemental analysis. In addition, a high resolution TEM (HRTEM, FEI Titan 80-300) was used for high-resolution imaging, electron energy loss spectroscopy (EELS), and elemental analysis. In Paper I, the TEM samples used were catalyst powders scraped from the metallic foil. First, the powder was crushed between glass slides and then the crushed powder was dispersed with ethanol onto a carbon-covered Cu grid. Cross-sectional samples were used in Papers II, IV and V. The sample preparation was started so that two small pieces of the catalyst monolith were attached to catalyst layers face-to-face to a titanium grid by carbon glue. The grid was pre-thinned by hand to a thickness of ~100 \textmu m and then thinning was continued with a dimple grinder (Model 656, Gatan Inc.) to the thickness of ~20
µm. The final thinning was done with a precision ion polishing system (PIPS, Model 691, Gatan Inc.).

**X-ray photoelectron spectroscopy (XPS)**

Chemical states and atomic concentrations of phosphorus and noble metals were characterized with an XPS (Surface Science Laboratories SSX-100) using monochromatic Al Kα radiation (Papers I-III and V). Samples from the fresh catalyst and the inlet and outlet sections of the treated catalysts were measured. The samples were made by scraping the catalyst surface and pressing the scraped powder against indium films. This resulted in samples where the charging was small. The binding energy was calibrated by setting carbon 1s line at 284.6 eV. During the quantitative analysis, Shirley background subtraction was applied (Shirley 1972, Aronniemi et al. 2005). The contribution from carbon and indium was omitted in the compositional analysis.

**X-ray diffraction (XRD)**

XRD was used for identifying the phase composition of fresh and treated catalysts. In the XRD analyses scraped catalyst powders were also used. The XRD patterns were recorded with a Siemens D5000 diffractometer, and nickel-filtered Cu Kα radiation was applied (Papers III and V). The patterns were acquired in the angle diffraction range of $15^\circ \leq 2\theta \leq 90^\circ$, with a 5s count accumulation per step. Diffraction patterns were assigned using a PDF database supplied by the International Centre of Diffraction Data. For the XRD analysis, the phosphorus exposure to the support material NGOC was applied using 0.2 M phosphorus feeding in order to obtain better detectability. In addition, PANanalytical Empyrean diffractometer using Cu Kα radiation with the PIXcel3D detector was used in Paper II. Crystallite sizes were determined from the XRD patterns using the HighScore plus software based on the Scherrer equation (shape factor 0.9). Diffraction patterns were assigned using the database (PDF-4 + 2014) from the International Centre of Diffraction Data.

**Diffuse reflectance infrared Fourier transform (DRIFT)**

An FTIR spectrometer ( Bruker Vertex V80) equipped with a DRIFT unit and liquid nitrogen-cooled Mercury Cadmium Telluride (MCT) detector were utilized to
determine the bonding of the compounds on the scraped catalyst powder (Papers II, III and V). The DRIFT analyses were performed at room temperature under atmospheric conditions. A mirror was used as a background spectrum. The spectra were recorded by using the resolution of 4 cm$^{-1}$.

4.3.4 Activity measurements

Activity tests were performed on a laboratory scale using gas mixtures which simulate the exhaust gases of diesel (Papers I and III) and natural gas (Papers II, V) vehicles. In addition, two different gas mixtures, with and without nitric oxide (NO) were employed for the diesel oxidation catalysts. The used gas mixtures are presented in Figure 5. The tests were carried out for the fresh and treated metallic monolith catalysts at atmospheric pressure in a horizontally aligned tubular quartz reactor (i.d. 0.8 cm). In the diesel activity tests, the gas mixture was inserted into the reactor at room temperature (RT), while in the natural gas activity tests, the mixture was added at 100 °C. Water feeding was started for all the experiments at 110 °C using a peristaltic pump. The sample was heated at a heating rate of 5 °C min$^{-1}$ for the DOC and 10 °C min$^{-1}$ for the NGOC up to the desired temperature (300 °C and 600 °C for the DOC and the NGOC, respectively). The catalyst was kept at 300 °C and 600 °C for 15 min for the DOC and NGOC, respectively, and after that the temperature was reduced to RT under an N$_2$ flow. The procedure was repeated to determine the stability of the catalyst during the test and to ensure the reliability of the results. Gas flow rates were controlled with mass flow controllers (Brooks 5280S). The outlet gas composition was measured by an FTIR gas analyser (Gasmet™ CR2000). The oxygen concentration was determined with a paramagnetic oxygen analyser (ABB Advanced Optima). The total gas flow was 1 dm$^3$, resulting in a gas hourly space velocity (GHSV) of 31 000 h$^{-1}$ for a monolith.
Fig. 5. The gas compositions and conditions in the activity tests.

Without NO:
500 ppm CO, 300 ppm C\textsubscript{3}H\textsubscript{4}, 12 vol% O\textsubscript{2} and 10 vol% H\textsubscript{2}O, and N\textsubscript{2} as the balance gas (Paper I)

With NO:
1000 ppm NO, 500 ppm CO, 300 ppm C\textsubscript{3}H\textsubscript{4}, 12 vol% O\textsubscript{2} and 10 vol% H\textsubscript{2}O, and N\textsubscript{2} as the balance gas (Paper III)

600 ppm CH\textsubscript{4}, 500 ppm CO, 10 vol% CO\textsubscript{2}, 12 vol% O\textsubscript{2} and 10 vol% H\textsubscript{2}O and N\textsubscript{2} as the balance gas (Papers II and V)
5 Results and discussion

5.1 Characterizations

5.1.1 The vehicle-aged oxidation catalyst

Aging in a real application using an actual size catalyst provides realistic information about the overall deactivating effect caused by oil- and fuel-derived contaminants and high operating temperatures. Therefore, a vehicle-aged natural gas oxidation catalyst (NGOC/PtPd) was studied (Honkanen et al. 2013) and used as a reference for the laboratory-scale-ageing.

It was found that the vehicle-aged NGOC/PtPd catalyst had been exposed to thermal deactivation together with poisoning and fouling. Information on the accumulation of sulphur, phosphorus, calcium and zinc on the support was collected using FESEM-EDS. In the inlet part of the catalyst (Figure 6a), the surface was totally covered by a Ca- and S-rich layer detected by FESEM-EDS. Phosphorus had also penetrated the top layer of the catalyst. The following contaminants were found in the inlet part of the vehicle-aged catalyst with XPS measurements: calcium (19 wt%), sulphur (12 wt%), phosphorus (8 wt%) and zinc (5 wt%). In the outlet part the amount of these impurities was significantly lower: calcium (0.8 wt%), sulphur (1.3 wt%), phosphorus (0.2 wt%) and zinc (0.1 wt%) (Honkanen et al. 2013). The FESEM-EDS line analysis (Figures 6b-c) shows that sulphur accumulated throughout the support (from the surface to the bottom), but phosphorus was located mainly in the region of 10 μm from the surface. Similar behaviour as with phosphorus was observed with calcium, but zinc accumulated mainly on the surface, at a penetration depth of ~5 μm. In Figure 6b-c, it can also be seen that the sulphur concentration (from the 10 μm region) increased while the concentration of phosphorus decreased.
Binding energies were measured by XPS to determine the chemical compositions of the elements. S 2p was found with a binding energy value of ~168.9 eV (Figure 7a). This suggests that sulphur appeared on the vehicle-aged catalyst or the support surface mainly in the form of sulphates (SO$_4^{2-}$) (Moulder et al. 1992). P 2s was observed with a binding energy of ~190.4 eV (Figure 7b) indicating phosphorus mainly in the form of phosphate (PO$_4^{3-}$) (Naumkin et al. 2012). The results are in good agreement with the results by Galisteo et al. (2004), Wiebenga et al. (2012) and Andersson et al. (2007).
5.1.2 The fresh catalysts and effect of water

Structures of the fresh diesel and natural gas oxidation catalysts were studied by cross-sectional transmission electron microscopy (TEM). The fresh diesel oxidation catalysts’ cross-sectional TEM characterization is reported in Paper IV. The fresh DOC/PtPd had very small-grained (< 5 nm) Pt/Pd particles supported on a fine grained γ-alumina, titania, ceria and zirconia containing support material. Furthermore, monocrystalline alumina-rich and amorphous silica-rich areas without Pt or Pd particles were found. The fresh DOC/Pt consisted of small (5-10 nm) Pt particles supported on fine grained γ-alumina and titania containing areas (Paper IV). The fresh NGOC/PtPd catalyst had a small-grained γ-alumina support with well distributed, small-grained (< 5 nm) Pt and Pd particles (Paper II).

The chemical composition of elements of the fresh diesel and gas oxidation catalysts was studied by XPS (Papers I and II). According to the binding energies of Pt (Table 3), platinum was found in a metallic form (Pt) in the fresh DOC/Pt samples (Moulder et al. 1992, Serrano-Ruiz et al. 2006, Olsson & Fridell 2002, Talo et al. 1995). In the case of fresh DOC/PtPd and NGOC/PtPd, platinum and palladium were found in oxide form (PtO and PdO, respectively), which is in agreement with results by Brun et al. (1999) and Shyu & Otto (1988).
Table 3. Binding energies (eV) measured by XPS over fresh, H₂O (W-) and SO₂+H₂O (SW-) treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts. In addition, results of engine-bench-aged (EB-aged) DOC/Pt catalyst as well as thermal aged (TA-) and TA-treatment followed by SW-treatment (TA+SW) NGOC/PtPd catalyst (Modified from Paper I).

<table>
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<th>S</th>
<th>Al</th>
<th>O</th>
</tr>
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<td>4d_{5/2}</td>
<td>2p_{3/2}</td>
<td>1s</td>
<td>1s</td>
<td></td>
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<td>-</td>
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<td>531.0</td>
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<td>118.3</td>
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<td>-</td>
<td>169.1</td>
<td>119.0</td>
<td>530.9</td>
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n.d.= not determined

The laboratory scale sulphur and phosphorus treatments were carried out in the presence of water. In order to determine the role of water during the sulphur and phosphorus treatments, water treatments of DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts were conducted (Paper I and Paper V). It was observed that the water treatment did not have any significant influence on the S_BET value, total pore volume or average pore size of the studied catalyst (Table 4). This suggests that hydrothermal sintering did not take place. Based on the XPS results, the water treatment did not cause any significant changes in the oxidation stage of platinum or palladium on the DOC catalyst (Table 3). For the water treated NGOC catalyst the XPS measurement was not done.

### 5.1.3 The effect of sulphur

According to the XRF results, the sulphur content in the SW-treated DOC/PtPd and DOC/Pt catalysts was determined to be 1.9 and 1.8 wt%, respectively (Table 4, Paper I). The XPS analyses results support the XRF results although the sulphur concentrations were systematically higher due to differences in the surface versus bulk analyses. The concentration of sulphur on the SW-treated NGOC/PtPd catalyst was detected by XPS (Table 4, Paper II) to be ~ 4 wt% and a little bit less (~3.5
wt%) on the TA+SW-treated NGOC/PtPd catalyst. Based on the XPS results, the catalyst surface adsorbed quite the same amount of sulphur over all the studied catalysts. According to the physisorption results (Table 4, Papers I and II), the SW-treatment reduced the specific surface area ($S_{BET}$) and the pore volume of the DOC/PtPd and DOC/Pt catalysts. The $S_{BET}$ values of the DOC/PtPd and DOC/Pt catalysts decreased by 13% and 15%, respectively. The $S_{BET}$ value of the SW-treated NGOC/PtPd decreased only slightly (5%) and no changes in pore volume were detected. The TA-treatment of the NGOC/PtPd catalyst caused a significant change to the catalyst support structure reducing the specific surface area by ~40% and increasing the average pore size by ~40% compared to the fresh NGOC/PtPd catalyst (Table 4, Paper II). The $S_{BET}$, total pore volume and average pore size values were identical between the TA and TA+SW-treated NGOC/PtPd catalyst, so the SW-treatment was not observed to have any decreasing effect on these values after thermal treatment.

Table 4. Sulphur contents (wt%) measured by XRF and XPS, specific surface area ($S_{BET}$), total pore volume and average pore size values of fresh, H$_2$O (W-) and SO$_2$+H$_2$O (SW-) treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts. In addition, the results are presented for the engine-bench-aged (EB-aged) DOC/Pt catalyst as well as thermal aged (TA-) and TA-treatment followed by SW-treatment (TA+SW) NGOC/PtPd catalysts (Modified from Paper I and II).

<table>
<thead>
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<th>S average XPS (wt%)</th>
<th>Specific surface area ($m^2g^{-1}$)</th>
<th>Total pore volume ($cm^3g^{-1}$)</th>
<th>Average pore size (nm)</th>
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<td>-</td>
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<tr>
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<td>W</td>
<td>-</td>
<td>-</td>
<td>223</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>0.40</td>
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<td>192</td>
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<td></td>
<td>EB</td>
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<td>2.3</td>
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<td>7.1</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>154</td>
<td>0.40</td>
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</tr>
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<td></td>
<td>W</td>
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<td>-</td>
<td>160</td>
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<td>10.0</td>
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<tr>
<td></td>
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<td>0.40</td>
<td>10.0</td>
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<tr>
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<td>96</td>
<td>0.34</td>
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<td>TA+SW</td>
<td>n.d.</td>
<td>3.3</td>
<td>96</td>
<td>0.33</td>
<td>14</td>
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</table>

n.d. = not determined
Figure 8 presents the TEM images of the fresh and SW-treated DOC/PtPd catalysts. No significant changes were observed in the alumina-based support, or the sizes of precious metal particles (palladium or platinum). More detailed FESEM-EDS and TEM-EDS analyses showed that in the SW-treated NGOC/PtPd catalyst, sulphur accumulated uniformly throughout the whole catalyst structure horizontally from the inlet part to the outlet part and vertically from catalyst surface to the metallic monolith (Paper II). In addition, electron energy loss spectroscopy (EELS) maps indicated that sulphur accumulated mainly close to the precious metal particles (Paper II).

A slight increase in the precious metal particles was detected by TEM as well as in the PdO crystal size (from 3 to 6 nm) detected by XRD for the NGOC/PtPd catalyst and these are noted in (Paper II). The amount of platinum in the fresh and SW-treated samples were, however, too small to be detected by XRD. Lee et al. (1999) found that SO2 induced sintering of Pt/Al2O3 particles. They explained that a reaction of SO2 with oxygen at the Pt-O-support interface reduces the Pt-O interaction, which promotes the migration and sintering of Pt particles. Similar phenomena could also take place with Pd particles. Significant morphological changes due to the TA-treatment were observed when compared to the fresh and SW-treated NGOC/PtPd catalysts. The phase transformation of alumina (from γ-alumina to α-alumina) and formation of the PdPt alloy was detected by XRD and TEM and significant increases in the precious metal particle size (from ~5 nm to 50-60 nm) were observed by FESEM and TEM (Paper II). According to the XRD, FESEM and TEM studies, no further morphological changes were detected after the TA+SW-treatment compared to the TA-treatment. Based on the EELS maps (Paper II), sulphur was found to be distributing randomly in the TA+SW-treated NGOC/PtPd catalyst in contrast to the SW-treated NGOC/PtPd catalyst.
Based on the XPS-measurements, the SW-treatment did not cause significant changes in the chemical compositions of platinum, palladium or the support material in the DOC/PtPd, DOC/Pt or NGOC/PtPd catalysts compared to the fresh catalysts (Table 3). The chemical composition of sulphur on the surfaces of all the SW-treated catalysts was observed to be the same form as that of the vehicle-aged catalyst, namely $\text{SO}_4^{2-}$ (Figure 9, Figure 7a).

The DRIFT spectra of the fresh and SW-treated catalysts are presented in Figure 10. The SW-treatment had an effect on the binding of the compounds on the surface of the catalyst. The SW-treated DOC/Pt has a very broad band at around
1300 cm$^{-1}$ most probably representing the surface sulphate species on alumina (Konsolakis et al. 2013, Abdulhamid et al. 2006) or alternatively physisorped SO$_2$ on alumina (Şentürk et al. 2012, Pieplu et al. 1998, Hamzehlouyan 2016, Mitchell & Sheinker 1996). The broad band at around 1280 cm$^{-1}$ of the SW-treated DOC/PtPd can be attributed to sulphate species interacting with the surface OH-groups (Yao et al. 1981, Şentürk et al. 2012, Gracia et al. 2005). The SW and TA+SW-treated NGOC/PtPd catalysts (Figure 10) have a broad band at around 1200–1100 cm$^{-1}$ indicating the bulk aluminium sulphate species (Paper II, Abdulhamid et al. 2006, Mitchell & Sheinker 1996, Şentürk et al. 2012). No sulphur compounds on palladium (Pd-SO$_4$) or platinum (Pt-SO$_4$) were observed, because an absorbance band at 1435 cm$^{-1}$ (Paper II, Hoyos et al. 2010, Mowery & McCormick 2001) was missing. The absence of SO$_4^{2-}$ species on the Pd with an alumina support has also been reported by Colussi et al. (2010), Yu & Shaw (1998) and Konsolakis et al. (2013). As mentioned in the theory part of this paper, this is due to the nature of alumina, which acts as a sulphur sink inhibiting the sulphating of Pd sites (Konsolakis et al. 2013, Lampert et al. 1997). It can thus be concluded that SO$_2$ is first oxidized to SO$_3$ over the Pd entities and then it migrates to the alumina support forming Al$_2$(SO$_4$)$_3$ (Colussi et al. 2010, Konsolakis et al. 2013). The band at 1640 cm$^{-1}$ in all spectra indicates the presence of surface-bound water (Yu & Shaw 1998, Konsolakis et al. 2013). The bands at 1240 and 1190 cm$^{-1}$ of the DOC catalysts as well as the band at 1033 cm$^{-1}$ of the NGOC catalysts originate from the catalytic material.
Fig. 10. DRIFT spectra of the fresh and SO₂+H₂O (SW-) treated DOC/PtPd, DOC/Pt and NGOC/PtPt catalysts. In addition, the spectra of the thermal aged (TA-) and TA-treatment followed by SW-treatment (TA+SW) NGOC/PtPt catalyst (Modified from Paper III).

In summary, sulphur caused minor morphological and chemical changes on DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts. Based on XPS analysis, the quantity of the accumulated sulphur was detected to be quite similar (3.3-4.6 wt%) in the SW-treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts as well as in the TA+SW-treated NGOC/PtPd catalysts. Sulphur was found to adsorb vertically throughout the whole catalyst support material from the catalyst surface to the metallic monolith, and not only on the surface of the catalytically active material. Only a minor (~15%) decrease in the $S_{BET}$ and pore volume values was observed over the SW-treated DOC/Pt and DOC/PtPd catalysts, and no notable changes on the NGOC/PtPd catalysts were detected. According to the detailed structural inspection of the SW-treated NGOC/PtPd catalyst, a slight increase in the size of the precious metal particles was observed. In addition, sulphur accumulation mainly close to the precious metal particles was observed. The TA-treatment was found to cause significant morphological changes on the NGOC/Pt catalyst, but no
further morphological changes were detected after the TA+SW-treatment compared to the TA-treatment. Based on the DRIFT results, sulphate species on the alumina and surface OH-groups in DOC/Pt and DOC/PtPd catalysts, were found respectively, as well as bulk aluminium sulphate in the SW- and TA+SW-treated NGOC/PtPd catalysts.

**Correlation between laboratory and engine aged samples (Paper I)**

The correlation between the laboratory exposed and engine-bench-aged DOC/Pt catalyst was evaluated. The content of sulphur on the engine-bench-aged catalyst by XRF was found to be ~1 wt%, which is a bit lower than the SW-treated sample (Table 4). The difference in the sulphur amount is probably caused by different conditions during the accelerated deactivation of the catalyst compared to the engine-bench-aged procedure. In the laboratory scale accelerated procedure, the sulphur exposure was done in stable conditions using a higher sulphur content than in the engine-bench-aging. No substantial amounts of other impurities were identified. Table 4 shows that the engine-bench-aged catalyst’s specific surface area results correlate well with the results of the SW-treated catalyst. Based on the XPS results, sulphur was also found in the form of sulphate on the engine-bench-aged catalyst and it did not cause any significant changes in the chemical composition of platinum (Table 3). Instead, minor growth in Pt particles, i.e. sintering, on the engine-bench-aged catalyst was observed (Figure 8c). The size of the largest detected particle was approximately 20 nm. No growth in particle size was detected on the SW-treated DOC/Pt samples (Figure 8b). Based on the characterization results, the results of the laboratory scale SW-treated catalysts correspond well to the results of the engine-bench-aging.

**5.1.4 The effect of phosphorus**

**Diesel oxidation catalyst (Paper III and IV)**

The phosphorus accumulation of DOC/PtPd and DOC/Pt catalysts and their bare support material was studied. The phosphorus content of the DOC samples was measured by implementing an ICP-OES, XPS and FESEM-EDS analyses. Based on ICP-OES results, the accumulation of phosphorus was higher on the DOC/Pt and NGOC/PtPd catalysts compared to the DOC/PtPd catalyst (Table 5). In
addition, the phosphorus content was found to be substantially higher for both the DOC and NGOC bare support materials than the correspondingly treated precious metal containing DOC and NGOC catalysts. The systematically higher phosphorus contents (Table 5) measured by XPS compared to those from the ICP-OES analysis can be explained by the surface sensitivity of XPS indicating that phosphorus accumulates mainly on the surfaces of the catalyst particles.

Table 5 also presents the results of the N₂-physisorption analyses. The results show that the phosphorus treatment had a diminishing effect on the $S_{\text{BET}}$ and total pore volume values for both DOC and NGOC catalysts. The LPW-treatment reduced the $S_{\text{BET}}$ and the total pore volume of the DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts by ~13%, ~28% and ~16%, respectively. After the HPW-treatment, the reduction in the $S_{\text{BET}}$ values of the DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts were ~26%, ~39% and ~31%, respectively. The decrease of the $S_{\text{BET}}$ values from the phosphorus treatments was higher on the DOC and NGOC bare support materials compared to the samples with precious metals, which may be due to the higher phosphorus concentration of the bare support materials versus samples with precious metals. The decrease in the $S_{\text{BET}}$ and the total pore volume values are in good agreement with the amount of phosphorus accumulated on the DOC/PtPd and DOC/Pt catalysts. As supposed, the specific surface area ($S_{\text{BET}}$) values for the fresh samples with precious metals were slightly lower in comparison to the bare support material.
Table 5. Phosphorus contents (wt%) measured by ICP-OES and XPS, specific surface area ($S_{BET}$), total pore volume and average pore size of fresh, low (LPW) and high (HPW) P-solution treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts. In addition, the results are presented for the fresh and HPW-treated DOC-support material as well as fresh, LPW- and HPW-treated NGOC support (Modified from Paper III).

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<th>Catalyst</th>
<th>Treatment</th>
<th>$P_{\text{bulk ICP-OES}}$ (wt%)</th>
<th>$P_{\text{average XPS}}$ (wt%)</th>
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<td>DOC/PtPd</td>
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<td></td>
<td>LPW</td>
<td>5.7</td>
<td>12</td>
<td>133</td>
<td>0.35</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>8.6</td>
<td>14</td>
<td>111</td>
<td>0.27</td>
<td>9.6</td>
</tr>
</tbody>
</table>

n.d. = not determined

Based on the cross-sectional FESEM analyses, most of the phosphorus is accumulated on the catalyst surface layer and the phosphorus decrease is evident through the catalyst layer from top to bottom of the phosphorus treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts (Paper III and V). Figure 11 illustrates the cross-sectional FESEM images and phosphorus content extracted from the selected measurement points (around 5 μm interval) on the LPW- and HPW-treated DOC/PtPd and DOC/Pt catalysts (Paper III). Most of the phosphorus, ~13-15 wt% in the HPW-treated DOC/PtPd and DOC/Pt catalysts, accumulated down to 10 μm from the surface over the HPW-treated PtP (Figure 11a-b, Paper III). The phosphorus concentration is similar (15-20 wt%) throughout the bare support material layer from top to bottom (Figure 11c, Paper III). The amount of phosphorus on the catalyst surface was ~10 wt% on the LPW-treated NGOC/PtPd catalyst and ~15 wt% on the HPW-treated NGOC/PtPd (Paper V). The amount of phosphorus decreased almost linearly through the catalyst from top to bottom. The results correlate well with the phosphorus accumulation results over the vehicle-
aged NGOC/PtPd catalyst (Figure 6c). The phosphorus concentration was higher on the surface region of the bare support (~20 wt%) of the NGOC than on the NGOC/PtPd catalyst, and the phosphorus concentration decreased only slightly from the surface region towards the metallic monolith, which is concurrent with the DOC results.

Fig. 11. Cross-sectional FESEM images and phosphorus content information from the selected measurement points: a) DOC/PtPd catalyst after high (HPW) and low (LPW) P-solution treatment, b) DOC/Pt catalyst after HPW- and LPW-treatment, and c) support material after HPW-treatment (Paper III, published by permission of Springer).

The detailed structural characterization was done by TEM. Paper IV reports the cross-sectional TEM results for the LPW- and HPW-treated DOC/Pt and DOC/PtPd
catalysts. The deactivation behaviour of phosphorus for both catalysts was found to be similar. LPW- and HPW-treatments increased the precious metal particle size slightly and changed the shape of the particles from irregular to spherical. Phosphorus accumulated mainly in the alumina-rich areas. In the case of HPW-treated DOC catalysts, the phosphorus content was even 20 wt% in the alumina-rich areas and below 5 wt% in the silica rich areas. After the HPW-treatment of both the DOC catalysts, the amorphous form of alumina rich area was detected in the selected area electron diffraction (SAED) pattern. The cross-sectional TEM studies (Figure 12) of the HPW-treated NGOC/PtPd catalyst, reported in Paper V, indicate a denser structure in comparison to the fresh catalyst. On the surface of the HPW-treated NGOC/PtPd catalyst, the size of the PtPd particles increased slightly compared to the fresh catalyst. Based on the SAED patterns, the nanocrystalline $\gamma$-alumina in the fresh NGOC catalyst changed to an amorphous structure in the HPW-treated catalyst (Figure 12). The results are in good agreement with the DOC results.

![Fig. 12. Cross-sectional TEM images and SAED patterns of a) the fresh NGOC/PtPd catalyst and b) the high P-solution (HPW) treated NGOC/PtPd catalyst (Paper V, published by permission of Springer).](image)

In order to determine the chemical compositions of elements before and after phosphorus exposure, XPS, DRIFT and XRD analyses were done. In Table 6, binding energies of the fresh and phosphorus treated DOC and NGOC samples are presented. In all the phosphorus treated DOC and NGOC samples, P 2s was found in a binding energy range between 190.1 eV and 191.8 eV. This suggests that phosphorus is attached to the precious metal or to the support surface in the form
of phosphate form (PO$_4^{3-}$) (Naumkin et al. 2012). The phosphate form of phosphorus was also detected in the vehicle-aged sample (Figure 7b). The phosphorus treatments did not change the platinum or palladium oxidation states (Table 6).

Table 6. Binding energies (eV) measured by XPS for fresh, low (LPW) and high (HPW) P-solution treated DOC/PtPd, DOC/Pt and NGOC/PtPd catalyst. In addition, the results are presented for the fresh and HPW-treated DOC-support material as well as fresh, LPW- and HPW-treated NGOC support (Modified from Paper III).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>Pd</th>
<th>Pt</th>
<th>P</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3d$_{5/2}$</td>
<td>4d$_{3/2}$</td>
<td>2s</td>
<td>1s</td>
<td>1s</td>
</tr>
<tr>
<td>DOC/PtPd</td>
<td>Fresh</td>
<td>336.4</td>
<td>315.5</td>
<td>-</td>
<td>119.2</td>
<td>531.2</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>337.3</td>
<td>315.4</td>
<td>191.2</td>
<td>119.2</td>
<td>531.7</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>336.9</td>
<td>315.0</td>
<td>190.1</td>
<td>118.1</td>
<td>530.8</td>
</tr>
<tr>
<td>DOC/Pt</td>
<td>Fresh</td>
<td>-</td>
<td>314.8</td>
<td>-</td>
<td>119.7</td>
<td>531.4</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>-</td>
<td>314.2</td>
<td>191.4</td>
<td>119.2</td>
<td>531.4</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>-</td>
<td>313.2</td>
<td>190.4</td>
<td>118.2</td>
<td>530.3</td>
</tr>
<tr>
<td>DOC/Support</td>
<td>Fresh</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>119.1</td>
<td>531.2</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>-</td>
<td>-</td>
<td>191.3</td>
<td>118.5</td>
<td>531.3</td>
</tr>
<tr>
<td>NGOC/PtPd</td>
<td>Fresh</td>
<td>336.3</td>
<td>315.3</td>
<td>-</td>
<td>118.3</td>
<td>530.2</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>336.9</td>
<td>315.0</td>
<td>191.0</td>
<td>119.0</td>
<td>531.1</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>336.6</td>
<td>315.3</td>
<td>190.9</td>
<td>118.7</td>
<td>531.4</td>
</tr>
<tr>
<td>NGOC/Support</td>
<td>Fresh</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>118.6</td>
<td>530.9</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>-</td>
<td>-</td>
<td>191.3</td>
<td>119.1</td>
<td>531.8</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>-</td>
<td>-</td>
<td>191.8</td>
<td>119.5</td>
<td>532.0</td>
</tr>
</tbody>
</table>

n.d. = not determined

The DRIFT spectra of the fresh and HPW-treated DOC and NGOC catalysts are presented in Figure 13 (Papers III and V). For the fresh DOC samples, two broad bands were identified at 1190 cm$^{-1}$ and 960 cm$^{-1}$ and for the fresh NGOC sample only one sharp band was observed at 1033 cm$^{-1}$. These bands can be attributed to be material originated and, thus, are not due to the phosphorus adsorption. The band at 1640 cm$^{-1}$ in all spectra shows the presence of surface-bound water (Yu & Shaw 1998, Konsolakis et al. 2013). In the case of the HPW-treated DOC and NGOC catalysts, a very broad band is detected at ~1300 cm$^{-1}$, and the band at 1190 cm$^{-1}$ for the DOC samples and the band at 1033 cm$^{-1}$ for the NGOC sample have almost disappeared. A very broad band at ~1300 cm$^{-1}$ was observed also for the HPW-treated NGOC bare support material (Paper III). The band in the area around 1300
cm⁻¹ can be attributed to phosphite (PO₃⁻) and especially aluminium metaphosphate Al(PO₃)₃ (Nyquist et al. 1971). Wiebenga et al. (2012) have found that phosphorus, in the form of PO₃⁻, is typically found in vehicle-aged catalyst samples.

Fig. 13. DRIFT spectra of fresh and high P-solution (HPW) treated DOC/PtPd, DOC/Pt, NGOC/PtPd and DOC/Support (Modified from Paper III).

The XRD patterns of the fresh and HPW-treated DOC/support and DOC/PtPd catalyst are presented in Figure 14. The XRD analyses for the fresh DOC/PtPd and DOC/support have main peaks at 23.5° (peak b), 25.5° (peak c) and around 29° (peak d) indicating a silica phase, anatase phase of titania and CeₓZr₁₋ₓO₂ phase, correspondingly (Rashad et al. 2013, Wang 2013, Wu et al. 2017). In addition to these peaks, a low shoulder in the phosphorus treated catalysts at around 20° was detected, which most probably indicates the presence of an amorphous aluminium phosphate (AlPO₄) phase (Galisteo et al. 2004, Poojary et al. 1993, PDF-2 Powder Diffraction File Database). In the cross-sectional TEM analysis, alumina was found in an amorphous form in the HPW-treated DOC/PtPd and DOC/Pt catalysts. In addition, phosphorus was found to accumulate mainly on the alumina-rich areas. The results gained by TEM suggest the formation of dense and amorphous AlPO₄.
Therefore, the TEM results correspond and support the XRD results well. The formation of amorphous AlPO₄ is very likely, since the transformation of AlPO₄ from an amorphous to a crystalline phase has been earlier reported (Scaccia et al. 2003, Youssif et al. 2004) to happen at >500 °C and the temperature in our aging procedure was only 400 °C.

Fig. 14. The XRD pattern of (1) the fresh DOC support material, (2) the DOC support material after treatment with high P-solution (HPW), (3) the fresh DOC/PtPd catalyst and (4) the DOC/PtPd catalyst after the HPW treatment; a = AlPO₄, b = SiO₂, c = TiO₂, d = CeₓZr₁₋ₓO₂ (Paper III, published by permission of Springer).

The XRD analyses for the fresh NGOC/PtPd catalyst shows the main peaks at 33° (peak b) and 46° (peak d) (Figure 15) indicating the PdO phase and the γ-alumina phase, correspondingly (PDF-2 Powder Diffraction File Database). The detection of the phosphorus compounds of the samples was possible only from the high phosphorus concentration samples. Therefore, only the HPW-treated NGOC/PtPd-catalyst and the 0.2 M P-solution-treated bare support material results with fresh samples are presented in Figure 15. The quite broad peak at around 20° (peak a) in the phosphorus treated catalysts indicates the presence of an amorphous AlPO₄ phase (PDF-2 Powder Diffraction File Database, Galisteo et al. 2004). The result corresponds well with the TEM results as well as the results obtained with the
HPW-treated DOC/PtPd catalyst. In addition, the found amorphous AlPO₄ phase explains why such a high amount of phosphorus is needed until it can be detected by XRD. When analogous samples with precious metals are compared, it can be seen, that they both have a peak at 2θ=34°, which corresponds to PdO (PDF-2 Powder Diffraction File Database). However, the peak is lower in the HPW-treated NGOC/PtPd catalyst compared to the fresh sample. Furthermore, the HPW-treated NGOC/PtPd catalyst shows a peak at 2θ=40° (peak c), indicating the presence of elemental Pd. Usually the transformation of PdO to elemental Pd has been reported to occur by sintering (Lampert et al. 1997, Persson et al. 2007, Euzen et al. 1999, Gholami & Smith et al. 2015a). In the study by Honkanen et al. (2017), it was found that PdO sintering to Pd in air starts at 700 °C in the NGOC/PtPd catalyst and the temperature used in the aging procedure was only 400 °C. It is therefore possible, that some form of interaction with phosphorus caused this partial reduction of PdO, as AlPO₄ was formed. Based on N₂ physisorption, CO chemisorption and STEM-analysis, Matam et al. (2012) concluded that mono- to multilayer amorphous aluminium phosphate-like species are formed at 700 °C. Phosphorus species can potentially affect the strength of interactions between PdOx nanoparticles and the support and hence, can alter the electronic and catalytic properties of the surface Pd sites.
In summary, based on the characterization results, phosphorus treatments (LPW- and HPW) change the morphological and chemical structures of DOC/PtPd, DOC/Pt and NGOC/PtPd catalysts. It was found, that when more phosphorus was present in the feed-stream, higher amounts of phosphates were found on the studied catalysts. In the case of the precious metal containing catalyst (DOC/Pt, DOC/PtPd and NGOC/PtPd), phosphorus was detected to accumulate only on the surface region of the catalyst. The phosphorus accumulation on the catalyst surface reduces the $S_{BET}$ and pore volume values, and this phenomenon was more severe after HPW- than after the LPW-treatment. Phosphorus treatments were found to slightly increase the average size of precious metal particles, and the shape of the metal particles changed from an irregular form to a mainly spherical form. Phosphorus was adsorbed mainly on the alumina by chemical bonds and most likely formed dense amorphous aluminium phosphate. It was also found, that phosphorus can cause the partial transformation from PdO to Pd. The deactivation behaviour of phosphorus differed between precious metal containing catalysts and bare support.
materials. The amount of accumulated phosphorus was found to be significantly higher in the bare support material than in the precious metal containing catalysts. In addition, the accumulation of phosphorus on the bare support materials was almost uniform from the surface towards the bottom.

5.2 Activity measurements

5.2.1 Fresh and water treated diesel oxidation catalysts

The laboratory scale activity measurements for fresh and water (W-) treated DOC/PtPd and DOC/Pt catalysts were done using a gas mixture without and with NO (Papers I and III, respectively). In this study, all of the activity tests were done in the presence of water. The used gas compositions are presented in Figure 5. C$_3$H$_6$ and CO conversions over the fresh DOC/PtPd and DOC/Pt catalysts of the gas mixture without NO and with NO are presented in Figure 16. In addition, in Figure 16, NO conversions as well as NO$_2$ and N$_2$O formations are shown for the fresh DOC/PtPd and DOC/Pt catalysts using a gas mixture with NO. The light-off temperatures (T$_{50}$ and T$_{90}$) over the fresh and water treated DOC/PtPd and DOC/Pt catalysts are summarized in Table 7. The activity measurement results of the water treated catalysts indicate that the water treatment has no effect on the activity of the studied catalysts. The only exception was the C$_3$H$_6$ oxidation temperature increase by ~20 °C for the DOC/PtPd catalyst in the case when the gas mixture without NO was used (Table 7, Papers I and III). This could be due to the formation of Pd(OH)$_2$, which inhibits the hydrocarbon oxidation at low temperatures (<190 °C) (Burch & Urbano 1995, Roth et al. 2000, Gholami et al. 2015b).

In the case of fresh DOC/Pt and DOC/PtPd when a gas mixture without NO was used (Figure 16a and c), the C$_3$H$_6$ oxidation started at around 110 °C and at 135 °C, respectively. Both catalysts adsorbed and desorbed C$_3$H$_6$ at low temperatures (below 120 °C), which was a consequence of the presence of zeolites in the DOC catalysts (Paper I). For example, Kröger et al. (2007) and Huhtanen et al. (2005) have reported that the fresh zeolite samples have the ability to adsorb propene at low temperatures. Above 135 °C, the C$_3$H$_6$ oxidation activity of the fresh DOC/Pt catalyst was only slightly better compared to the fresh DOC/PtPd catalyst: the T$_{50}$-values were equal, but the T$_{90}$-value of DOC/Pt was slightly (~15 °C) lower compared to that of the DOC/PtPd catalyst (Figure 16a and c, and Table 7). A small difference can be seen in CO oxidation where the T$_{50}$-value of the fresh DOC/Pt
was ~20 °C and T90 10 °C lower compared to the fresh DOC/PtPd catalyst (Figures 16a and c, and Table 7). CO adsorption on Pt and Pd was very strong even at low temperatures (<100 °C) (Zhou et al. 2015), which explains the remarkable CO conversions (~20%) already at 110 °C for the fresh DOC PtPd and Pt catalysts. (Paper I)

Fig. 16. Conversion as a function of temperature for different gas mixtures: a) and c) without NO (w/o NO) and b) and d) with NO over the fresh DOC/PtPd and DOC/Pt catalysts. For a gas mixture with NO, NO2 and N2O formation is also presented (Paper I and III, published by permission of Springer).
Table 7. Light-off temperatures ($T_{50}$ and $T_{90}$) for C$_3$H$_6$ and CO oxidation and maximum conversion of NO over the fresh, H$_2$O- (W-) treated DOC/PtPd and DOC/Pt catalysts. (Modified from Papers I and III).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>$T_{50}$ (°C)</th>
<th>$T_{90}$ (°C)</th>
<th>Maximum conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_3$H$_6$</td>
<td>CO</td>
<td>C$_3$H$_6$</td>
<td>CO</td>
</tr>
<tr>
<td>Without NO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC/PtPd</td>
<td>Fresh</td>
<td>144</td>
<td>138</td>
<td>169</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>166</td>
<td>140</td>
<td>191</td>
</tr>
<tr>
<td>DOC/Pt</td>
<td>Fresh</td>
<td>141</td>
<td>122</td>
<td>151</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>135</td>
<td>120</td>
<td>143</td>
</tr>
<tr>
<td>With NO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC/PtPd</td>
<td>Fresh</td>
<td>192</td>
<td>178</td>
<td>212</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>194</td>
<td>182</td>
<td>219</td>
</tr>
<tr>
<td>DOC/Pt</td>
<td>Fresh</td>
<td>176</td>
<td>129</td>
<td>186</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>180</td>
<td>117</td>
<td>192</td>
</tr>
</tbody>
</table>

For the fresh DOC/PtPd and DOC/Pt catalysts, the presence of NO in the gas mixture shifted CO and C$_3$H$_6$ oxidation to higher temperatures (Figure 16b and d, and Table 7). In addition, NO increased the temperature difference of CO and C$_3$H$_6$ oxidation activity over the fresh DOC/Pt catalyst compared to the fresh DOC/PtPd catalyst (Paper III). A closer inspection of the fresh DOC/PtPd and DOC/Pt catalysts using a gas mixture with NO (Figure 16b and d) indicates that the oxidation of CO started first, followed by that of C$_3$H$_6$. NO$_2$ formation started after the CO was totally converted and C$_3$H$_6$ had converted by more than 90% (Paper III). The observations are in good correspondence with the results reported e.g. by Khosravi et al. (2014) and Haufl et al. (2012). Above 140 °C, a small amount (~10 ppm) of N$_2$O was observed, which was caused by the reaction of C$_3$H$_6$ with NO based on Equation (5) (Khosravi et al. 2014):

$$C_3H_6 + 2NO + 4O_2 \rightarrow N_2O + 3H_2O + 3CO_2 \quad (5)$$

A comparison between the fresh DOC/PtPd and DOC/Pt catalysts illustrates that the activity for CO, C$_3$H$_6$ and NO oxidation over the fresh DOC/Pt catalysts was higher than over the PtPd catalysts for the entire temperature range. In the NO conversions, the difference between the fresh catalysts was the most significant. The maximum conversion of NO over the DOC/Pt catalyst was 50% and over the DOC/PtPd catalyst only 13%. Based on the XPS measurements (Table 3), Pt was found in a metallic form (Pt) on the fresh DOC/Pt catalyst and in an oxidized form (PtO) on the DOC/PtPd catalyst. Metallic Pt has been reported to be more active than oxidized Pt especially in NO oxidation (Haufl et al. 2012). Thus, the detected
PtO in this study most probably explains the lower NO conversion over the DOC/PtPd catalyst compared to the DOC/Pt catalysts (Paper III).

### 5.2.2 The effect of sulphur on diesel oxidation catalysts

The gas mixtures without and with NO were also used to verify the role of sulphur dioxide-water (SW-) treatment on the oxidation activity of DOC/PtPd and DOC/Pt catalysts. In the case of SW-treatment and a gas mixture without NO (Paper I), the C₃H₆ oxidation activity decreased over the DOC/PtPd and DOC/Pt catalysts (Figure 17a and c, and Table 8). Desorption of C₃H₆ after the water feeding was significantly stronger over the SW-treated DOC/PtPd catalyst than the fresh DOC/PtPd catalyst and therefore propene oxidation did not start until a temperature of ~170 °C. Nevertheless, the light-off temperatures (T₅₀ and T₉₀) were equal in the C₃H₆ oxidation over the SW-treated DOC/PtPd and DOC/Pt catalysts (Paper II). This means that the deactivation effect of the SW-treatment is considered equal (an increase of 32 °C) at the light-off temperature T₅₀ for the activity of DOC/PtPd and DOC/Pt catalysts. However, the effect is stronger for the activity over the DOC/Pt (35 °C) catalysts than that of DOC/PtPd (18 °C) at the light-off temperature of T₉₀. Quite similar effects can be seen for the CO oxidation activity (Figure 17a and c, and Table 8) (Paper I).
Fig. 17. Conversion as a function of temperature for gas mixtures: a) and c) without (w/o NO) and b) and d) with NO over the SO₃+H₂O- treated (SW) DOC/PtPd and DOC/Pt catalysts. For a gas mixture with NO, NO₂ and N₂O the formation is also presented. (Figures a and c modified from Paper I).
Table 8. Light-off temperatures ($T_{50}$ and $T_{90}$) for $C_3H_6$ and CO oxidation, and the maximum conversion of NO over the fresh, $H_2O-$ (W-), $SO_2+H_2O-$ (SW-) DOC/PtPd and DOC/Pt catalysts. In addition, the results are presented for the engine-bench-aged (EB-aged) DOC/Pt catalyst (Modified from Papers I and III).

<table>
<thead>
<tr>
<th>Catalyst Treatment</th>
<th>$T_{50}$ (°C) $C_3H_6$</th>
<th>$T_{50}$ (°C) CO</th>
<th>$T_{90}$ (°C) $C_3H_6$</th>
<th>$T_{90}$ (°C) CO</th>
<th>Maximum conversion (%) NO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Without NO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC/PtPd Fresh</td>
<td>144</td>
<td>138</td>
<td>169</td>
<td>153</td>
<td>-</td>
</tr>
<tr>
<td>SW</td>
<td>176</td>
<td>170</td>
<td>187</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>DOC/Pt Fresh</td>
<td>141</td>
<td>122</td>
<td>151</td>
<td>143</td>
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</tr>
<tr>
<td>SW</td>
<td>173</td>
<td>143</td>
<td>186</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>EB-aged</td>
<td>162</td>
<td>152</td>
<td>182</td>
<td>179</td>
<td>-</td>
</tr>
<tr>
<td><strong>With NO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC/PtPd Fresh</td>
<td>192</td>
<td>178</td>
<td>212</td>
<td>193</td>
<td>13</td>
</tr>
<tr>
<td>SW</td>
<td>194</td>
<td>172</td>
<td>226</td>
<td>192</td>
<td>17</td>
</tr>
<tr>
<td>DOC/Pt Fresh</td>
<td>176</td>
<td>129</td>
<td>186</td>
<td>160</td>
<td>50</td>
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<tr>
<td>SW</td>
<td>190</td>
<td>147</td>
<td>201</td>
<td>185</td>
<td>46</td>
</tr>
</tbody>
</table>

The SW-treatment of the gas mixture with NO influences the oxidation activity of DOC/Pt more than DOC/PtPd as shown in Table 8 and Figure 17b and d. The CO oxidation is identical over the fresh and SW-treated DOC/PtPd catalysts. $C_3H_6$ oxidation over the SW-treated DOC/PtPd (Figure 17b) starts at the same temperature as over the fresh DOC/PtPd (Figure 16b) and the SW-treatment does not decrease the $C_3H_6$ oxidation activity until the higher temperatures are reached (above 190 °C). No change in the NO oxidation activity compared to the fresh DOC/PtPd catalyst was observed. For the DOC/Pt catalyst, the SW-treatment shifts the CO oxidation temperature to higher temperature (by 10-20 °C) compared to the fresh catalyst (Figure 17d and 16d). Therefore, the oxidation of $C_3H_6$ and NO over the SW-treated DOC/Pt catalyst shifts the $T_{50}$ values by ~20 °C and ~10 °C, respectively, to higher temperatures than over the fresh DOC/Pt catalyst.

Based on the results, the SW-treatment was found to especially shift the propene light-off temperature ($T_{50}$ and $T_{90}$) to higher temperatures. Since only a minor reduction in the $S_{BET}$ and pore volume values and no change in the pore size were detected over the SW-treated DOC/PtPd and DOC/Pt catalysts, it can be assumed that the loss of the active sites is the main reason for the higher oxidation temperature needed (Heck et al. 2002).
Correlation between laboratory and engine aged samples

The correlation between the laboratory and engine aged samples was studied using sulphur dioxide-water (SW) treated and engine-bench-aged DOC/Pt catalysts (Paper I). Figures 18 presents the CO and C₃H₆ oxidation activity over the fresh, SW-treated and EB-aged DOC/Pt catalysts. In addition, the T₅₀ and T₉₀ values are presented in Table 8.

![Fig. 18. a) CO and b) C₃H₆ conversions over the fresh, SO₂+H₂O- (SW-) treated and engine-bench aged (EB-aged) DOC/Pt catalysts using a gas mixture without NO (Modified from Paper I).](image)

The results show that the laboratory scale SW-treatment corresponds relatively well to the EB-aged results. In Figure 18a, it can be seen, that there are no significant differences in the CO oxidation activity between the EB-aged and the SW-treated catalysts. C₃H₆ oxidation over the SW-treated sample (Figure 18b) starts at ~35 °C higher temperatures compared to the EB-aged catalysts, but only slight (10 °C) and not significant differences in the light-off temperatures T₅₀ and T₉₀, respectively, were observed. The slightly better activity of EB-aged catalysts in C₃H₆ oxidation can be explained by the XRF results, which show that the sulphur accumulation on the bulk analysis of the EB-aged DOC/Pt is lower than on the SW-treated catalyst (S content 1 wt% and 2 wt%, respectively).

5.2.3 The effect of phosphorus on diesel oxidation catalysts

To determine the effect of phosphorus on the DOC/PtPd and DOC/Pt catalyst activity, two different phosphorus concentrations, low (marked as LPW) and high (HPW), were used in activity tests (Paper III). The activity tests were done with a
gas mixture with NO (Figure 5) C₃H₆, CO and NO conversions. The NO₂ and N₂O formation over the fresh and phosphorus treated (LPW and HPW) DOC/PtPd and DOC/Pt catalysts are shown in Figure 19.

The LPW-treatment had a negligible effect on the DOC/PtPd and DOC/Pt catalysts’ CO oxidation activity and the oxidation of C₃H₆ started at the same temperature as it did with the fresh catalysts. Propene conversion of ~100% was observed over the fresh DOC/PtPd, fresh and LPW-treated DOC/Pt catalysts and ~90% for the LPW-treated DOC/PtPd catalysts. A decrease in the C₃H₆ oxidation activity compared to the fresh catalysts can be seen at above 170 °C. The light-off temperature T₉₀ increased by ~50 °C and by ~20 °C for the LPW-treated DOC/PtPd and DOC/Pt catalyst, respectively, compared to the similar fresh catalysts. Based on the cross-sectional TEM analysis, a minor precious metal particle size increase and a change in the shape of the particles over the LPW-treated DOC/PtPd and DOC/Pt catalysts could be one reason for the observed changes. In addition, only a slight decrease in the S_BET, pore size and pore volume values over the LPW-treated DOC/PtPd catalyst was seen. Thus, most probably, the main reason for the activity loss of the LPW-treated DOC/PtPd catalysts is the reduced accessibility of reactants to the catalyst pores and on the active surface.
Fig. 19. Conversion as a function of temperature for the gas mixture with NO over the fresh, low (LPW) and high (HPW) P-solution treated DOC/PtPd and DOC/Pt catalysts (Paper III, published by permission of Springer).
Table 9. Light-off temperatures ($T_{50}$ and $T_{90}$) for the $C_3H_6$ and CO oxidation and the maximum conversion of NO over the fresh, low (LPW) and high (HPW) P-solution treated DOC/PtPd and DOC/Pt catalysts (Modified from Paper III).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>$T_{50}$ (°C)</th>
<th>$T_{90}$ (°C)</th>
<th>Maximum conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$C_3H_6$</td>
<td>CO</td>
<td>$C_3H_6$</td>
</tr>
<tr>
<td>DOC/PtPd</td>
<td>Fresh</td>
<td>192</td>
<td>178</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>196</td>
<td>170</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>207</td>
<td>173</td>
<td>-</td>
</tr>
<tr>
<td>DOC/Pt</td>
<td>Fresh</td>
<td>176</td>
<td>129</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>179</td>
<td>145</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>197</td>
<td>168</td>
<td>295</td>
</tr>
</tbody>
</table>

The results in Figure 19 and Table 9 show that the HPW-treatment has a more severe effect on the DOC/PtPd and DOC/Pt catalysts’ oxidation activity than the LPW-treatment. The HPW-treatment reduced the $C_3H_6$ conversions so that the maximum $C_3H_6$ conversions were 78% and 90% (at 300 °C) for the DOC/PtPd and DOC/Pt catalysts, respectively. In addition, the HPW-treatment reduced the maximum CO conversion over the HPW-treated DOC/PtPd catalyst by ~10% compared to the fresh catalyst. Furthermore, the HPW-treatment caused a significant reduction in the maximum conversions of NO over the DOC/PtPd and DOC/Pt catalysts (reduced by 67% and 100%, respectively). It is possible that the uncompleted oxidation reactions of CO and $C_3H_6$ over the PtPd catalyst inhibit the NO reactions in the studied temperature area (Khosravi et al. 2014, Hauff et al. 2012).

For both the studied catalysts, based on their characterizations, the HPW-treatment caused chemical and structural changes on the catalyst surface by forming amorphous AlPO$_4$, increasing the particle sizes of the precious metals slightly and changing their shape from irregular to mainly spherical. It is suggested that phosphorus may cover some of the surface sites and may partly block the pores. It is worth noting, that based on the ICP-OES, XPS and physisorption analyses (Table 5), the phosphorus concentration was lower and changes in $S_{BET}$ and pore volume were minor in the DOC/PtPd catalyst after the HPW-treatment in comparison to the correspondingly treated DOC/Pt catalyst. However, the HPW-treatment similarly or even more severely affects the DOC/PtPd catalyst’s oxidation activity than that of the DOC/Pt catalyst. It is most probable, that in the case of the HPW-treated DOC/PtPd catalyst, oxidized Pt together with morphological and chemical changes caused the lower activity for the DOC/PtPd catalyst.
5.2.4 The effect of sulphur and phosphorus on a natural gas oxidation catalyst

The effect of water (W-), sulphur (SW-), low (LPW-) and high (HPW-) phosphorus treatments on the CH$_4$ and CO oxidation activity over the NGOC/PtPd catalyst was studied (Paper II and V). Experiments were also done to find out the combined effect of the thermal aging (TA) followed by sulphur exposure (SW) on the NGOC/PtPd catalyst’s activity in CH$_4$ and CO oxidation (Paper II). As a reference, the activity of the TA-treated NGOC/PtPd catalyst was also studied (Paper II). The light-off temperatures ($T_{50}$ and $T_{90}$) of CO and CH$_4$ over the fresh and treated NGOC/PtPd catalysts are summarized in Table 10 and the CH$_4$ conversions are presented in Figure 20. Water treatment was found to have a negligible effect on the CO and CH$_4$ oxidation activity.

Figure 20 clearly shows the diminishing effect of the SW-treatments on the methane oxidation activity of the studied catalyst. Over the SW-treated catalyst, methane oxidation started at ~120 $^\circ$C higher temperatures compared to the fresh catalyst and the light-off temperatures ($T_{90}$) were observed to increase by 50 $^\circ$C compared to the fresh catalyst. For the fresh catalyst, ~100% CH$_4$ conversion was achieved and after the SW-treatment the maximum conversion was around 90%.

The SW-treatment was found to increase the carbon monoxide $T_{90}$ value by over 50 $^\circ$C of the NGOC (Table 10). However, 90% CO conversion was still achieved at low temperatures (~150 $^\circ$C) (Paper II). Based on a physisorption analysis, no notable changes in the $S_{BET}$ and pore volume values of the NGOC/PtPd catalysts were detected (Table 4). Higher sulphur concentrations were detected by STEM-EELS near the precious metal particles than in those regions without Pt and Pd particles. A slight increase in precious metal particles analysed by XRD was also observed. Thus, the reduced activity detected by the temperature shift in the light-off curves to higher temperatures was most probably caused due to a combination of structural changes (particle transformation) and chemical deactivation (sulphates).

TA-treatment was carried out to determine the effect of sulphur exposure on a thermally aged NGOC/PtPd catalyst. Characterizations indicate that the TA-treatment caused drastic sintering of the precious metals and support material. Figure 20 and Table 10 show that the effect of the TA-treatment alone on the CH$_4$ oxidation activity is quite similar to the SW-treated NGOC/PtPd catalyst. Nevertheless, the SW-treatment following the TA-treatment (TA+SW) significantly reduces the CH$_4$ oxidation activity compared to the TA-treated catalyst.
Based on the XRD, FESEM and TEM studies, morphology changes on the catalyst after the TA- and TA+SW-treatments were observed to be similar, as well as changes in the $S_{\text{BET}}$-values and the pores sizes compared to the fresh catalyst. Therefore, it seems that the formation of aluminium sulphate distributed randomly over the TA+SW-treated catalyst surface in addition to the sintered catalyst was the reason for the dramatic catalyst deactivation.

All the activity tests included two similar temperature ramps (run 1 and run 2). Significant differences were only noticed with the TA+SW-treated NGOC/PtPd catalyst, between run 1 and 2 and therefore these results are included in Figure 20. The difference in the CH$_4$ oxidation activity between run 1 and run 2 indicates that partial regeneration of the catalyst took place during the first run removing sulphur compounds from the catalyst (Paper II).

Fig. 20. Conversion of CH$_4$ as a function of temperature for the NGOC/PtPd catalyst after different treatments: fresh, H$_2$O- (W-), SO$_2$+H$_2$O- (SW-), low (LPW) and high (HPW) P-solution, thermal aged (TA) and TA-treatment followed by SW-treatment (TA+SW) (Modified from Papers II and V).
Table 10. Light-off temperatures (T50 and T90) for the CH4 and CO oxidation over the fresh NGOC/PtPd catalyst with the following treatments: H2O- (W-), SO2+H2O- (SW-), low (LPW) and high (HPW) P-solution, thermal aged (TA-) and TA-treatment followed by SW-treatment (TA+SW) (Modified from Paper II).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>T50 (°C)</th>
<th>T90 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH4</td>
<td>CO</td>
<td>CH4</td>
</tr>
<tr>
<td>NGOC/Pt</td>
<td>Fresh</td>
<td>390</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>393</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>SW</td>
<td>437</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>LPW</td>
<td>420</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>HPW</td>
<td>503</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>TA</td>
<td>445</td>
<td>&lt; 110</td>
</tr>
<tr>
<td></td>
<td>TA+SW run 1</td>
<td>564</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>TA+SW run 2</td>
<td>498</td>
<td>&lt; 110</td>
</tr>
</tbody>
</table>

The phosphorus treated NGOC has a lower methane oxidation activity compared to the fresh natural gas oxidation catalyst (Figure 20). For the fresh catalyst, ~100% CH4 conversions were achieved, but after the LPW- and HPW-treatments the maximum conversions were only 86% and 63%, respectively. The deactivation effect of the HPW-treatment on the NGOC/PtPd catalysts is stronger compared to the LPW-treatment in the whole temperature range. The increase in the light-off temperature (T50) of CH4 was moderate (~30 °C) over the LPW-treated catalyst and significant (~110 °C) over the HPW-treated catalyst (Table 10). In addition, both phosphorus treatments increased the T90-values of the CO conversion, resulting in a difference of ~25 °C and ~100 °C for the LPW- and HPW-treated catalyst, respectively, compared to the fresh catalyst (Paper V). In the case of the LPW-treated NGOC/PtPd catalyst the significant decrease in the maximum CH4 conversion and smaller pore sizes compared to the fresh catalyst suggest that the pore diffusion could be hindered. For the HPW-treated NGOC/PtPd catalyst, the pore size was similar, but the accumulated phosphorus content was higher than for the LPW-treated catalyst. This is most probably caused by formation of a fouling layer on the catalyst surface hindering further CH4 oxidation.
6 Summary and conclusions

Emission limits for passenger and heavy-duty vehicles have been tightened continuously together with the long-term durability requirements. Fossil fuels and engine lubricants contain impurities which can have a significant effect on the activity and durability of a catalytic converter. In addition, the increasing use of various biofuels and blended fuels can increase the accumulation of impurities on the catalyst surface and thus remarkably reduce the long-term durability.

In this thesis, deactivation phenomena due to sulphur and phosphorus in diesel and natural gas oxidation catalysts were studied with the aim to increase knowledge about the effects of impurities on the catalyst performance. The main objectives of the research were to define the structural and chemical changes on the catalyst surface caused by sulphur and phosphorus, as well to illustrate the effect of these impurities on the activity of diesel and natural gas oxidation catalysts. In addition, the goal was to evaluate the effect of precious metal composition (Pt vs. PtPd) on the oxidation activity of diesel oxidation catalysts, and to define the correlation between real and simulated ageing.

The sulphur exposure was studied in Papers I and II, respectively. Sulphur was found to especially shift the C₃H₆ light-off temperature (T₅₀ and T₉₀) to higher temperatures on diesel and natural gas oxidation catalysts. The analyses indicated that sulphur was adsorbed vertically throughout the entire catalyst support material from the catalyst surface to the metallic monolith. Only a minor or negligible reduction in the S_BET and pore volume values were observed. Sulphate species were detected on alumina or they were chemically bound as bulk aluminium sulphate, not on the precious metals. A more detailed inspection of the sulphur treated natural gas oxidation catalysts indicated a sulphur accumulation close to the noble metal particles and a slight increase in precious metal particle sizes. Thus, reduced activity is most probably caused by combination of minor structural changes and chemical deactivation (sulphates).

The thermally aged natural gas oxidation catalyst was also sulphur treated (Paper III). The effect of the thermal aging alone on the CH₄ oxidation activity is quite similar to the sulphur treated natural gas oxidation catalyst. Nevertheless, the sulphur treatment following the thermal aging significantly reduces the CH₄ oxidation activity compared to the thermal aged catalyst alone. Based on the analyses, thermal deactivation caused drastic sintering of the precious metal and support material, but no further morphology changes were observed after the sulphur treatment. Therefore, the formation of aluminium sulphate distributed
randomly over the thermal aged and the sulphur treated catalyst surface in addition to the sintered catalyst is most probably the reason for the drastic catalyst deactivation.

Phosphorus exposure was studied in Papers III-V. The phosphorus treatments were done using two different phosphorus concentrations (low and high). Both treatments reduced the catalysts activity, but the high phosphorus concentration treatment was found to have a more significant decreasing effect on the CO and hydrocarbons (C\textsubscript{3}H\textsubscript{6} and CH\textsubscript{4}) oxidation activity than the low phosphorus concentration treatment. In the case of diesel oxidation catalysts, the most drastic decrease was detected in the maximum conversion of NO. Based on the analyses, the phosphorus accumulation on the catalyst surface was higher and the decrease in the S\textsubscript{BET} and pore volume was more severe after the high-concentration phosphorus treatment than after the low-concentration phosphorus treatment. Phosphorus was observed to accumulate only on the surface region of the precious metal containing catalysts, forming a fouling layer on the catalyst surface, which hindered the surface reactions. In addition, phosphorus was mainly found to adsorb on the alumina by forming chemical bonds and was most likely to form dense, amorphous aluminium phosphate. Phosphorus treatments were found to slightly increase the average size of the precious metal particles, and the shape of the metal particles changed from an irregular form to a mainly spherical form. Therefore, these significant structural changes together with chemical deactivation (aluminium phosphates) can be assumed to reduce oxidation activity.

In Papers I, III and IV, the effect of precious metal composition (Pt vs. PtPd) on the oxidation activity on fresh as well as on sulphur and phosphorus treated diesel oxidation catalysts (DOC/PtPd and DOC/Pt catalysts) was studied. Two different gas mixtures, with and without NO were used in the diesel oxidation catalyst tests. For both gas mixtures, the oxidation activity of fresh and treated catalysts was higher than that of the DOC/PtPd catalysts over the entire temperature range. The difference in the oxidation activities between the DOC/PtPd and DOC/Pt catalysts with a gas mixture without NO was much smaller than with the gas mixture with NO. It is worth noting that the deactivation effect on the C\textsubscript{3}H\textsubscript{6} oxidation activity with both gas mixtures was found to be more severe on the sulphur treated DOC/Pt catalyst than the DOC/PtPd catalyst. The phosphorus treatments reduced the CO and C\textsubscript{3}H\textsubscript{6} oxidation activity more on the DOC/PtPd catalyst than on the DOC/Pt catalyst especially at higher temperatures (above 170 °C). According to TEM, XPS, XRD and DRIFT analyses, the structural and chemical changes between the DOC/PtPd and DOC/Pt catalysts were observed to
be similar after sulphur and phosphorus treatments. Nevertheless, based on the ICP-OES results, the amount of the accumulated sulphur was determined to be identical in the DOC/PtPd and DOC/Pt catalysts, but the amount of phosphorus was higher in the DOC/Pt catalyst than in the DOC/PtPd catalyst. Thus, in the case of fresh, sulphur and phosphorus treated DOC/PtPd catalysts, oxidized Pt most probably lowers the activity for the DOC/PtPd catalyst and is at least one reason for the lower activity of the DOC/PtPd catalyst compared to the DOC/Pt catalyst.

The correlation between laboratory aging and engine-aging was studied using the sulphur treated and engine-bench-aged DOC/Pt catalysts (Paper I). The C\textsubscript{3}H\textsubscript{6} and CO oxidation activity of the sulphur treated DOC/Pt catalysts corresponds relatively well to the results of the engine-bench-aged catalyst. Based on the XPS results, sulphur was detected to appear mainly as sulphate (SO\textsubscript{4}^{2-}) on both catalysts. In addition, the S\textsubscript{BET} and total pore volume values had a relatively good correlation between the laboratory and engine-bench-aged DOC/Pt catalysts. In addition, good correlation between the characterization results (chemical state results by XPS and phosphorus accumulation depth by FESEM-EDS) of the vehicle and laboratory aged natural gas oxidation catalyst can be seen. In summary, it can be concluded that the laboratory scale deactivation aging method is a useful tool for simulating deactivation phenomena caused by sulphur and phosphorus.

To conclude, this thesis provides valuable knowledge about the effect of sulphur and phosphorus on Pt or PtPd containing alumina based catalysts. This information can be used to develop more impurity resistant catalytic materials. In addition, the information gained, the developed catalytic materials and accelerated ageing procedures can further be used in other applications to abate methane emissions from fugitive emissions, flue gases, methane filling stations, storing fuels, and from exhaust gases originating from transportation.

Nevertheless, there is still a need for further research into catalyst deactivation. In this thesis, exposures to impurities (sulphur and phosphorus) were studied separately and the next step would be to investigate the combined effect of impurities on the catalyst. Besides experimental studies, modelling studies could also bring forth new knowledge that would beneficial in understanding the deactivation phenomena and the regeneration possibilities of these complicated materials.
List of references


PDF-2 Powder Diffraction File Database International Centre of Diffraction Data, 12 Campus Boulevard Newton Square, PA 19073-3273, USA (PDF cards: 70-4689 (AlPO₄), 43-1024 (PdO) and 65-6174 (Pd), 10-0425 γ-Al₂O₃).


Wang R, Mutinda SI & Fang M (2013) One-pot hydrothermal synthesis and high temperature thermal stability of Ce0.5Zr0.5O2 nanocrystals. RSC Advances 3: 19508–19514.


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DEACTIVATION OF OXIDATION CATALYSTS BY SULPHUR AND PHOSPHORUS IN DIESEL AND GAS DRIVEN VEHICLES