Tanja Kolli

Pd/Al₂O₃ -BASED AUTOMOTIVE EXHAUST GAS CATALYSTS

THE EFFECT OF BaO AND OSC MATERIAL ON NOₓ REDUCTION

FACULTY OF TECHNOLOGY,
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MASS AND HEAT TRANSFER PROCESS LABORATORY,
UNIVERSITY OF OULU
TANJA KOLLI

Pd/Al$_2$O$_3$ -BASED AUTOMOTIVE EXHAUST GAS CATALYSTS
The effect of BaO and OSC material on NO$_x$ reduction

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Oulu, Finland

Abstract

The aim of the thesis was to find new information on the effect of BaO and oxygen storage capacity material on NOₓ reduction. A total of nine different kinds of Pd/Al₂O₃-based metallic monoliths were studied. Promoters such as oxygen storage capacity material (OSC material in our case Ceₓ₋₁ZrxO₂ mixed oxides) and stabilisers such as barium (BaO) were added into the catalyst alone or together to improve catalyst properties such as catalytic activity, selectivity, and thermal stability.

The key aspects in this thesis can be divided into four parts. First, the behaviour of NO reduction and CO as well as C₂H₄ oxidation over Pd/Al₂O₃-based catalysts in rich, stoichiometric and lean conditions were studied. Secondly, the effect of BaO and the OSC material in NO reduction was considered. Thirdly, the preparation procedure, i.e. the addition order of BaO, OSC material, and Pd on the catalyst was considered. Finally, the effect of ageing on the behaviour of catalysts was investigated.

Several characterization methods (in situ DRIFT, catalytic activity measurements, N₂ physisorption, CO chemisorption, dynamic oxygen storage capacity measurements, and X-ray diffraction (XRD)) were utilised to find answers to the behaviour of these catalysts in the studied model reactions. The Rapid Ageing Hot in Laboratory (RAHLAB) method was used to age the catalyst.

First, it was demonstrated that the CO and hydrocarbon oxidation and NO reduction reactions over the Pd/Al₂O₃-based catalyst behave differently. NO reduction and CO and hydrocarbon oxidation reactions were dependent on the reaction conditions and temperatures. Secondly, the effect of OSC and BaO on NO reduction was studied separately. In the case of OSC material, it was observed that the OSC material has an effect on NO reduction as well as on CO and C₂H₄ oxidation. In the case of BaO, it was observed that BaO has a positive effect on NO reduction as well as CO and C₂H₄ oxidation especially in rich conditions. Thirdly, the effects of the addition order of OSC and BaO on the catalyst was studied separately. It was shown that these have an effect on NO reduction, especially after ageing. First, on the fresh Pd/Al₂O₃ catalyst it was observed that the addition order of OSC on the catalyst has not an influence on catalyst performance. The effect of the BaO addition order on the Pd/OSC/Al₂O₃-based catalyst is found to be insignificant, especially, after the ageing process. Furthermore, it is observed that the effect of RAHLAB ageing was that the catalyst lost its catalytic activity, stability, and selectivity.

Keywords: barium, catalysis deactivation, catalyst, ceria-zirconia mixed oxides, DeNOₓ, oxygen storage capacity, palladium
Acknowledgments

The present study was carried out in the Department of Process and Environmental Engineering, in the Mass and Heat Transfer Process Laboratory at the University of Oulu in 2000-2006.

I am most grateful to my supervisor Professor Riitta L. Keiski, the Head of the Laboratory of Mass and Heat Transfer Process Engineering, for her guidance and the opportunity she provided me to work in the catalyst research group. My warmest and deepest gratitude is expressed for Dr. Katarina Rahkamaa-Tolonen and Dr. Ulla Lassi for their continuous support and scientific directions.

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Oulu, 26 April 2006

Tanja Kolli
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Latin and Greek letters

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>h</td>
<td>Hour(s)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature, °C</td>
</tr>
<tr>
<td>T_{50}</td>
<td>Light-off temperature at which 50% conversion is attained, °C</td>
</tr>
<tr>
<td>T_D</td>
<td>Temperature at which decomposition occurs, °C</td>
</tr>
<tr>
<td>T_R</td>
<td>Temperature at which reformation occurs, °C</td>
</tr>
<tr>
<td>θ</td>
<td>Diffraction angle, °</td>
</tr>
<tr>
<td>λ</td>
<td>Dimensionless air-to-fuel ratio</td>
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</table>

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>A/F-ratio</td>
<td>Air-to-fuel ratio</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller Method</td>
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<tr>
<td>CCC</td>
<td>Close-coupled catalyst</td>
</tr>
<tr>
<td>DRIFT</td>
<td>Diffuse Reflectance Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>ECE-15-Test</td>
<td>European Commission for Europe Test</td>
</tr>
<tr>
<td>EOBD</td>
<td>European limits for OBD</td>
</tr>
<tr>
<td>EUDC</td>
<td>Extra Urban Driving Cycle</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FTP</td>
<td>Federal Test Procedure</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas Hourly Space Velocity</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>HC-SCR</td>
<td>Selective catalytic reduction by hydrocarbons</td>
</tr>
<tr>
<td>MVEG-A</td>
<td>ECE+EUCD cycle for the emission certification of light vehicles used in Europe</td>
</tr>
<tr>
<td>NEDC</td>
<td>New European Driving Cycle</td>
</tr>
<tr>
<td>NH_3-SCR</td>
<td>Selective catalytic reduction by ammonia</td>
</tr>
<tr>
<td>NSR</td>
<td>NO_x storage and reduction</td>
</tr>
<tr>
<td>PDF</td>
<td>Power Diffraction Database File</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metal</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>OBD</td>
<td>On-board diagnostics</td>
</tr>
<tr>
<td>OSC</td>
<td>Oxygen Storage Capacity</td>
</tr>
<tr>
<td>RAHLAB</td>
<td>Rapid Ageing Hot in Laboratory</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SNR</td>
<td>Selective NOx recirculation</td>
</tr>
<tr>
<td>TWC</td>
<td>Three-way catalyst, three-way catalytic converter</td>
</tr>
<tr>
<td>WGSR</td>
<td>Water Gas Shift Reaction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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1 Introduction

Air pollution generated from mobile sources is a problem of public interest. In Finland the fleet of vehicles has increased from 27 000 to nearly 2.5 million in the last 60 years. (Finnish Road Administration, 2005)

The composition of the exhaust from an engine varies with engine type, car’s velocity, engine load and outdoor temperature. There are also variations due to the fuel used and additives in the fuel. (Koltsakis et al. 1997) Table 1 shows that the automotive exhaust gases formed in the gasoline engines contain principally three primary pollutants, which are nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO), and hydrocarbons (HCs). In Table 1 the range of hydrocarbons (HC) is from unburned fuel to methane. (Olsson & Anderson 2004) However, it should be noted that the hydrocarbon range in the literature is dependent on which hydrocarbons are thought to be inert or easily oxidised at higher temperatures. For example Hoebink et al. (2001) argued that C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} are better models for exhaust gas than C\textsubscript{3}H\textsubscript{6} since they are more abundant in exhaust gases and C\textsubscript{2}H\textsubscript{2} imitates the coke formation on the catalyst during cold starts much better. Therefore, it is very difficult to find general information about exhaust gas composition.

Table 1. Typical compositions of car exhaust (taken from Olsson & Anderson 2004, Johnson 2005).

<table>
<thead>
<tr>
<th></th>
<th>CO [%]</th>
<th>HC [ppm]</th>
<th>NO\textsubscript{x} [ppm]</th>
<th>Particulates (g/kW h)</th>
<th>O\textsubscript{2} [%]</th>
<th>(\lambda)</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>0.01–0.05</td>
<td>10–100</td>
<td>50–300</td>
<td>0.01–0.1</td>
<td>3–20</td>
<td>&gt;1</td>
<td>80–500</td>
</tr>
<tr>
<td>Otto lean-burn</td>
<td>0.05–0.5</td>
<td>500–5000</td>
<td>100–1000</td>
<td>0.01–0.1</td>
<td>0.5–5</td>
<td>&gt;1</td>
<td>100–850</td>
</tr>
<tr>
<td>Otto</td>
<td>0.3–1</td>
<td>100–1000</td>
<td>50–2500</td>
<td>-</td>
<td>0.1–1</td>
<td>1</td>
<td>150–1000</td>
</tr>
</tbody>
</table>

Catalytic converters are needed to reduce nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO), and hydrocarbons (HCs), since these compounds contribute to environmental problems via acid rain and the formation of urban smog – and are also linked to many health problems. These compounds are a result of incomplete combustion. In general, the
amount of emissions depends on the air-to-fuel ratio (see Figure 1 in p. 24). The use of noble metal catalysts, such as palladium (Pd), platinum (Pt) and rhodium (Rh) in exhaust gas purification can effectively reduce these problems, since CO, hydrocarbons and NO\textsubscript{x} are converted through catalytic processes to less harmful products (CO\textsubscript{2}, H\textsubscript{2}O and N\textsubscript{2}). It is necessary to simultaneously carry out both reduction and oxidation reactions (see Table 3 in p. 23) over the exhaust catalysts: these can take place through a variety of reactions. (Taylor 1984) The structure of a modern three-way catalyst (TWC) contains a washcoat onto which noble metals, promoters, stabilisers etc. are deposited. Due to this complex structure, continuous research is needed to better understand the reactions between gaseous exhaust compounds and the catalytic surface.

The removal of nitrogen oxides from the exhaust gases of lean burn engines is difficult with three-way catalysts. These catalysts work in an oxygen-rich atmosphere as oxidising catalysts and the reduction of nitrogen oxides is thus restricted. In order to meet new NO\textsubscript{x} and CO emission standards, improved catalysts have to be developed. (Kašpar \textit{et al.} 2003)

Catalytic converters must have high activity and selectivity; this means that conversions of NO\textsubscript{x}, CO and HCs must be over 98 %. In addition, very fast light-off, which means that a catalyst must have a high activity at low temperatures, is needed. For TWCs, thermal stability and high oxygen storage capacity are also required. (Kašpar \textit{et al.} 2003) Successful design of commercial catalytic converters must also take into account the deactivation process, which occurs at high temperatures. This affects the life/activity of the catalyst through the metal and/or support sintering. (Lassi \textit{et al.} 2004)

This thesis work is part of a large research project carried out in the Laboratory of Mass and Heat Process Engineering at the University of Oulu (FT-IR studies and kinetic modelling of catalytic NO-CO-O\textsubscript{2} and NO-hydrocarbon-O\textsubscript{2} reactions). The aim of the project is to improve the present-day understanding of the reactions occurring on the surfaces of noble metal exhaust gas purification catalysts and to find correlations between the results obtained by different experimental methods e.g. \textit{in situ} DRIFT, catalytic activity, N\textsubscript{2} physisorption, CO chemisorption, dynamic oxygen storage capacity (OSC), and X-ray diffraction (XRD).

The purpose of this thesis is to better understand how NO reduction by CO and/or hydrocarbons behaves during rich, stoichiometric and lean reaction conditions over Pd/Al\textsubscript{2}O\textsubscript{3}-based metallic monoliths. Ethene is used to reduce NO in catalytic activity measurements to gain new information about the behaviour of catalytic converters.

Another goal is to investigate the role of co-operation of promoters on Pd/Al\textsubscript{2}O\textsubscript{3}-based catalysts in CO and C\textsubscript{2}H\textsubscript{4} oxidation and NO reduction reactions. For that reason, OSC material (Ce\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} mixed oxides) and stabilisers such as barium oxides (BaO) and lanthanum oxides (La\textsubscript{2}O\textsubscript{3}) are impregnated alone and/or together on the Pd/Al\textsubscript{2}O\textsubscript{3}-based catalyst. Catalytic activity measurements are carried out in very rich, stoichiometric and very lean conditions to determine the effect of these promoters. Recently, barium has been mostly studied as a NO\textsubscript{x} storage compound, the typical content of barium being around 20 wt-%. The relevant aspect in this research is to study the low content of barium (3 wt-%) as a stabiliser.

It is also vital to investigate whether the preparation procedure of a catalyst has an effect on catalytic behaviour. Therefore, the preparation procedure which involves
sequential impregnation steps, i.e. the addition order of Pd, OSC material, and BaO on the catalysts material is studied in greater depth.

Finally, one of the aims of this work is also to study how well barium and OSC material on the Pd/Al₂O₃ catalyst help to maintain the high thermal stability and activity of the catalyst after ageing. In this thesis, catalyst deactivation is done by the RAHLAB (Rapid Ageing Hot in Laboratory) laboratory ageing cycles, which correlate better to real engine conditions.
2 Abatement of nitrogen oxides

The generic formula NO\textsubscript{x} describes the oxides of nitrogen that can be formed in a combustion process. Nitrogen oxides are harmful compounds, dangerous to the natural environment. Since NO\textsubscript{x} emitted to the atmosphere with exhaust gases are harmful, much effort has been placed on eliminating these compounds. The direct decomposition of nitric oxide NO to harmless nitrogen N\textsubscript{2} and oxygen O\textsubscript{2} is an attractive approach for the control of NO emission because of its chemical simplicity; however, it is not yet applied. Selective catalytic reduction (SCR) is an industrially used NO\textsubscript{x} abatement technology. The methods proposed to date that serve the NO\textsubscript{x} abatement purpose can be divided into pre-combustion, combustion, and post-combustion. The first two allow for about 50% abatement of the harmful NO\textsubscript{x}, while the post-combustion methods permit up to 100% of their elimination. The post-combustion methods include the catalytic reactions, of which the direct decomposition of NO\textsubscript{x} to N\textsubscript{2} is one of the most promising method. \cite{teng1996, fritz1997, hayes1997, wojciechowska1999}

The main source of NO\textsubscript{x} emissions is the combustion of fossil fuels such as coal in electrical power plants or petroleum in vehicles. The combustion gases resulting from fossil fuels contain NO\textsubscript{x} pollutants consisting mainly of NO and NO\textsubscript{2}, with NO representing 90 to 95% of the total NO\textsubscript{x}. Three types of NO\textsubscript{x} can be distinguished in a fuel-gas \cite{teng1996, fritz1997, hayes1997, wojciechowska1999}:
Fuel $\text{NO}_x$:
Formed by the oxidation of the nitrogen-containing compounds in the fuel. The oxidation process occurs via the formation of intermediates, with HCN being one of the most common intermediate formed.

Thermal $\text{NO}_x$ (Zeldovich mechanism):
Formed by the fixation of atmospheric nitrogen. Initiated at temperatures above 1200°C by the oxidation of molecular nitrogen by oxygen radicals. NO is produced by a radical chain mechanism via the following route (M can be a molecule that acts as an energy transfer agent).

\[
\begin{align*}
\text{O}_2 + \text{M} &\leftrightarrow 2 \text{O} + \text{M} \\
\text{N}_2 + \text{O} &\leftrightarrow \text{NO} + \text{N}
\end{align*}
\]

Prompt $\text{NO}_x$ (Fenimore mechanism):
Formed by the oxidation of intermediate HCN. The molecular nitrogen reacts with hydrogen radicals derived from the fuel.

\[
\begin{align*}
\text{N}_2 + \text{CH} &\leftrightarrow \text{HCN} + \text{N} \\
\text{N} + \text{OH} &\leftrightarrow \text{H} + \text{NO}
\end{align*}
\]

The relative contribution of each of the three ways of $\text{NO}_x$ formation depends on the type of fuel, temperature, fuel to air ratio, and the combustion technology employed. With those of low fuel-bound nitrogen content fuels, e.g. natural gas and oil distillates, $\text{NO}_x$ formation in a conventional homogeneous combustion process is almost complete due to thermal $\text{NO}_x$. As catalytic combustion reactions may proceed at substantially lower temperatures than those associated with a flame, it is clear that, for clean fuels, catalytic combustion may be utilised or integrated into a combustion process in order to reduce $\text{NO}_x$ emissions. (Hayes & Kolaczkowski 1997)

The future challenge in automotive emission control is to have lower $\text{NO}_x$ emissions. Such techniques are the direct $\text{NO}_x$ decomposition or $\text{NO}_x$ reduction by hydrocarbons, CO, H2 and other reductants (Kummer 1980). The reduction of $\text{NO}_x$ with hydrocarbons can be achieved by a variety of very different catalysts that are often grouped under the title of the selective reduction of NOx by hydrocarbons (HC-SCR): (1) Pt-catalysts, (2) Ir-catalysts, (3) acid zeolites, and (4) Ag/alumina. The $\text{NO}_x$ storage catalyst is the only concept for $\text{NO}_x$ reduction in lean exhaust gases. This technique is described in more detail in Chapter 3.2.1. Some challenges for $\text{NO}_x$ abatement techniques are summarised in Table 2. (Jobson 2004)
Table 2. Summary of challenges for NO\textsubscript{x} abatement techniques (Jobson 2004).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Challenge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x} storage catalyst</td>
<td>long term durability activity at high temperature</td>
</tr>
<tr>
<td></td>
<td>sulphur resistance or regained activity after sulphur regeneration</td>
</tr>
<tr>
<td></td>
<td>low temperature activity</td>
</tr>
<tr>
<td>HC-SCR by Pt catalyst</td>
<td>improved activity at temperatures below 200°C and above 300°C</td>
</tr>
<tr>
<td></td>
<td>decreased N\textsubscript{2}O formation</td>
</tr>
<tr>
<td></td>
<td>long term durability</td>
</tr>
<tr>
<td>HC-SCR by acid zeolites</td>
<td>catalytic activity (kinetics) in general and at low temperatures in particular</td>
</tr>
<tr>
<td></td>
<td>long term durability</td>
</tr>
<tr>
<td></td>
<td>HC utilisation (fuel penalty)</td>
</tr>
<tr>
<td></td>
<td>sulphur resistance</td>
</tr>
<tr>
<td>NO\textsubscript{x} decomposition</td>
<td>catalytic activity (kinetics) in general and at low temperatures in particular</td>
</tr>
<tr>
<td></td>
<td>long term durability</td>
</tr>
</tbody>
</table>
Three-way catalysts (TWCs) have the ability to simultaneously eliminate three primary pollutants, unburned or partially burned hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxides (NOx). It is necessary to simultaneously carry out both reduction and oxidation reactions over the exhaust catalysts, which can occur through a variety of reactions. Table 3 summarises only some of the desirable reactions. (Taylor 1984)

Table 3. Reactions occurring on automotive exhaust catalysts which may contribute to the abatement of exhaust-containing pollutants (Taylor 1984).

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>2CO + O₂ → 2CO₂</td>
</tr>
<tr>
<td></td>
<td>HC + O₂ → CO₂ + H₂O⁺</td>
</tr>
<tr>
<td>Reduction/three-way</td>
<td>2CO + 2NO → 2CO₂ + N₂</td>
</tr>
<tr>
<td></td>
<td>HC + NO → CO₂ + H₂O + N₂⁺</td>
</tr>
<tr>
<td></td>
<td>2H₂ + 2NO → 2H₂O + N₂</td>
</tr>
<tr>
<td>Water gas shift</td>
<td>CO + H₂O → CO₂ + H₂</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>HC + H₂O → CO₂ + H₂⁺</td>
</tr>
</tbody>
</table>

*a Unbalanced reaction

The amount of NOx, CO, and hydrocarbon emissions in combustion varies depending on the air-to-fuel ratio (A/F-ratio). If an engine is running rich, which means that there is an excess of fuel i.e. λ < 1 or A/F < 14.6, the engine gives the highest power output (see Fig. 1 dashed line). Fuel consumption are, however, very high. Under lean conditions, which mean that the oxygen content is higher than the fuel content, i.e. λ > 1 or A/F > 14.6, NOx emissions are very low. However, in these conditions the emissions of HCs are very high (see Fig. 1). The most important advantage of lean-burn engines is good fuel economy. The other advantage of a lean NOx engine is that the highest exhaust temperatures are typically lower (≤800–850°C) compared to stoichiometric engines. TWCs effectively remove the pollutants only when the A/F values are stoichiometric, i.e. λ = 1 or A/F =
14.6, which means that suitable amounts of reducing and oxidising agents are present in the exhaust to carry out reactions (Fig. 1). (Kašpar et al. 2003)

![Fig. 1. Effect of the A/F ratio (w/w) on engine emissions and engine power (modified from Kašpar et al. 2003).](image)

Engines equipped with TWC operate under stoichiometric conditions. Nowadays the required conversion of pollutants is over 95 %, which is attained only when a precise control of the A/F ratio is maintained. This means that the aim is to maintain the A/F ratio as close to stoichiometric as possible. This narrow operation area is often called the lambda window. For efficient control of the A/F ratio, a computerised system is needed. It controls the fuel injection and measures the amount of air. The oxygen ($\lambda$) sensor located at the inlet of the catalytic converter is controlled by computerised system (see Fig. 2). This $\lambda$ sensor sends a signal which is used as a feedback for the fuel and air injection control loop. At the outlet of the catalytic converter another $\lambda$ sensor is mounted. This configuration constitutes the basis of the so-called engine on-board diagnostics (OBD). (Kašpar et al. 2003)
TWCs typically feature the so-called light-off type conversion vs. temperature behaviour. These curves are characterised by a conversion which steadily increases from 0 to 100 % conversion, the temperature of 50 % conversion being called as the light-off temperature. This means that at this temperature the diffusion rate and reaction rate are the same. At low temperatures the reaction rate is small compared to the diffusion rate. The overall rate of the process is determined by the actual kinetics at the surface, and thus it rises exponentially with the temperature according to the Arrhenius expression. When temperature increases enough, the observed rate of a process is determined entirely by the diffusion control, and its increase with temperature is very small. (Frank-Kamenetskii 1969) The light-off temperature of a typical TWC is around 250–350°C (Kašpar et al. 2003).

### 3.1 Structure of a three-way catalyst

Figure 3 shows a typical design of a modern TWC. A honeycomb monolith or metal is placed in a stainless steel container. Today both ceramic and metal monoliths are used. A key in determining the efficiency of the converter is the choice between ceramic or metal and also the geometrical characteristics of the honeycomb. The major advantage of the metallic substrate is that the wall thickness is not limited by strength. The frontal flow area in the metallic version has 91 % open area while the ceramic monolith has 69 % open area. The other advantages of the metal monoliths are high thermal conductivity and low heat capacity. This allows very fast heating, which minimises the light-off time. Traditionally, cordierite monoliths have been employed quite extensively due to their lower production cost. (Kašpar et al. 2003)
Catalytically active components are usually deposited on a support or carrier. The role of a support is to provide a matrix that stabilises the catalytically active component in small particles, hence increasing the availability of the catalytically active surfaces to reactants. In addition, it increases the thermal stability of the active component. The properties of the support material used are of great importance in determining the performance of the final catalysts. These properties include the support surface area, pore volume, surface acidity and catalytic activity, thermal conductivity, and thermal expansion. (Lox & Engler 1997, Heck & Farrauto 2001, Kašpar et al. 2003, Neyestanaki et al. 2004)

Al$_2$O$_3$ is often chosen as a carrier in a honeycomb monolith to increase the surface area. As can be seen in Figure 4, pure alumina undergoes phase transformation under rising calcination temperatures (Thevenin et al. 2002). γ-Al$_2$O$_3$ is a porous oxide which is employed due to its high surface area, but at higher temperatures, forms such as δ- and θ-Al$_2$O$_3$, are used due to their thermal stability. Non-porous α-Al$_2$O$_3$ is the most stable phase of alumina but has also the lowest surface area compared to the other aluminas. Therefore, additional materials need to be impregnated onto the γ-Al$_2$O$_3$. Many of these additive materials or stabilisers have been reported in the literature – lanthanum, barium, strontium, cerium, and zirconium oxides. BaO and lanthana are the most used and effective stabilisers. (Kašpar et al. 2003)

```
Boehmite    500-850°C → γ   650-1050°C → δ   1050-1150°C → θ   >1150°C → α
```

Fig. 3. a) A typical catalytic converter and b) a metallic honeycomb (adopted and modified from Kašpar et al. 2003).

**3.1.1 Washcoat**

Fig. 4. Modification of the crystal phase of alumina under increasing calcination temperature (Thevenin et al. 2002).
3.1.2 Noble metals

The use of noble metals (synonymous with precious metals or platinum group metals) as catalytically active materials in automotive exhaust gas catalysis is a result of three factors (Shelef & McCabe 2000):

- Very short residence times to remove pollutants dictated by the amount of exhaust in relation to the size of a catalyst.
- Resistance to sulphur oxides.
- Deactivation by high-temperature interaction with insulator oxides, Al, La, Zr, etc. insignificant.

Therefore, conventional three-way catalysts (TWCs) involve noble metals (Pt, Pd, and Rh). The catalytic reactions occur at the noble metal centre (Kašpar et al. 2003). As mentioned above, noble metal catalysts have many beneficial properties compared to base metals. These properties are excellent thermal stability, low tendency to react with support material, and their ability to process gas streams containing upwards of 1000 ppm (by weight) sulphur without being transformed into bulk sulphates. (Gandhi et al. 2003)

However, under exhaust conditions, Pd is inferior to Rh in eliminating NOx (van Santen et al. 1999). Rh initiates the dissociation of NO, which is an important step in the catalytic transformation of NO into less harmful molecules (Di Monte et al. 2002). However, due to the limited supply and increasing cost of Rh, more attention is being paid to modified Pd catalysts. In the 1980s, Pd did not figure prominently in the TWC formulations, largely due to poisoning associated with lead (Pb) and sulphur. Pd is less noble than Pt, and thus more prone to interact with poisonous species. (Gandhi et al. 2003)

Metallic palladium sites are required, for example, for the CO adsorption as well as for the initiation of oxidation reactions. Thus, the activity, selectivity, and stability of the catalyst depend on the state of palladium (Pd, PdO, PdO₂, etc.). The interaction of oxygen on a Pd surface is still poorly known. The PdO ↔ Pd phase transformation is initiated at the surface and causes small domains of Pd metal to be formed on the surface of PdO. These small domains of Pd metal are easily reoxidised upon cooling. However, complete transformation of the PdO → Pd at T > 925°C yields single crystal metal particles that are hard to oxidise during cooling in air. At 900°C the phase transformation (PdO → Pd) has been found to occur in minutes. (Lyubovsky & Pfefferle 1998) Appreciable amounts of bulk oxide are not formed on the transitional alumina-supported Pd unless the sample is cooled below 600°C (Datye et al. 2000).

A possible mechanism for the thermal cycling in air of palladium oxide to palladium is presented in Figure 5 (Farrauto et al. 1992). In this mechanism it was argued that heating to 770°C results only in decomposition of the PdOₓ (x >1) species. Heating above 800°C converts all PdOₓ to Pd which has a more agglomerated state. (Farrauto et al. 1992)

Generally the reactivity of the support changes the surface structure and chemical composition of a catalyst significantly (Ji et al. 2000). Metal-support interactions may appreciably affect the surface properties, and hence catalytic reactivities of the metal component. The thermal decomposition of PdO and the reformation of Pd to PdO depend on the support upon which they are dispersed, indicating significant metal-support
interactions. For example the addition of 10% of rare earth elements to palladium oxide can increase the PdO decomposition temperature to over 900 °C. It is possible that some of the support components, especially CeO$_2$ and TiO$_2$ provide some structural O to Pd metal during reoxidation. Many different surface states of O:Pd can apparently produce substantially different catalytic behaviour. Dispersed PdO on γ-alumina causes changes in the amount and type of O:Pd interaction. (Farrauto et al. 1995)

Fig. 5. Proposed mechanism for the thermal cycling in air of palladium oxide to palladium dispersed on an alumina support (Farrauto et al. 1992).

Table 4 compares decomposition and reformation temperatures of 4% PdO on various supports. Figure 6 shows a generic thermal profile for the decomposition of supported PdO and reformation of the oxide. $T_D$ is the decomposition onset temperature for PdO to Pd and $T_R$ is the reformation onset temperature of Pd to PdO. In this study, palladium was determined by thermal gravimetric analysis decomposition (TGA) to be present as PdO. In Table 4 it can be seen that TiO$_2$ and CeO$_2$ catalysts show relatively small hysteresis ($T_D-T_R$), indicating a large temperature stability range for PdO. This is quite favourable for catalytic applications where the PdO phase is most desirable for natural gas fuels. (Farrauto et al. 1995)
Table 4. Decomposition and reformation of 4 % PdO on various supports (Farrauto et al. 1995).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_D$ [°C]$^a$</th>
<th>$T_R$ [°C]$^b$</th>
<th>$T_{D-T_R}$ [°C]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO/Al$_2$O$_3$</td>
<td>810</td>
<td>600</td>
<td>210</td>
</tr>
<tr>
<td>PdO/Ta$_2$O$_5$</td>
<td>810</td>
<td>650</td>
<td>160</td>
</tr>
<tr>
<td>PdO/TiO$_2$</td>
<td>815</td>
<td>735</td>
<td>80</td>
</tr>
<tr>
<td>PdO/CeO$_2$</td>
<td>775</td>
<td>730</td>
<td>45</td>
</tr>
<tr>
<td>PdO/ZrO$_2$</td>
<td>682</td>
<td>470</td>
<td>212</td>
</tr>
</tbody>
</table>

$^a$ $T_D$ = The temperature where decomposition occurs.
$^b$ $T_R$ = The temperature where reformation occurs.
$^c$ $T_{D-T_R}$ = Hysteresis temperature between PdO decomposition to Pd and reformation to PdO.

Fig. 6. Generic thermal gravimetric profile (1st cycle) in air for the decomposition of supported PdO (heating) and reformation (cooling) of Pd to PdO. The temperature for decomposition is $T_D$ and the reformation temperature is $T_R$ (Farrauto et al. 1995).

The Pd catalyst supported on alumina can easily undergo a phase transformation between the metallic Pd and the oxidised PdO state during the reaction. The oxidation form of the catalyst is stable at low temperatures (under 400°C) and the reduced form is stable when the temperature is increased. Equilibrium between the reduced and the oxidised forms of Pd catalysts exists at the temperature of approximately 760°C. The change in the oxidation state leads to a change in both the crystal structure and the electronic properties of the catalytic surface. Therefore, it can lead to the change in the catalyst activity. (Lyubovsky & Pfefferle 1999)

Many studies have shown that the activity of a catalyst is influenced by many factors. These factors include precursor and support materials, Pd loading, calcination temperature, Pd crystallite morphology, catalysts pretreatment, and reaction conditions. It has also been demonstrated that the activity of a Pd catalyst initially increases as a function of time. (Epling & Hoflund 1999)
30

3.1.3 Promoters

A promoter is a substance that affects the performance of the catalyst, for example, making it more active, selective, or stable. Promoters may have a physical or chemical role. For example, an additive that reduces the tendency for a Pd catalyst to agglomerate or sinter is described as a physical promoter. (Gates 1992) CeO₂ has been known to have many beneficial effects on TWC performance. This compound has the ability to (Trovarelli 1996, Farrauto & Heck 1999):

- promote the noble metal dispersion,
- increase the thermal stability of the Al₂O₃ support,
- promote the water gas shift and steam-reforming reactions (Equation 1),

\[
\text{Steam reforming: CO or HC} + \text{H}_2\text{O} \xrightarrow{\text{CeO}_2} \text{H}_2 + \text{CO}_2
\] (1)

- favour catalytic activity at the interfacial metal-support sites,
- promote CO removal through oxidation employing a lattice oxygen, and store and release oxygen under, respectively, lean and rich conditions (Equations 2 and 3)

\[
\text{Rich conditions: CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2
\] (2)

\[
\text{Lean conditions: Ce}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CeO}_2
\] (3)

The OSC effectiveness of CeO₂ is greatly enhanced by combining it with ZrO₂. The addition of ZrO₂ into the CeO₂ framework promotes oxygen mobility, enhancing the exchange rate of O₂. CeO₂ is highly unstable at higher temperatures, but ZrO₂ provides thermal stability to CeO₂. Therefore, starting in 1995, CeO₂-ZrO₂ mixed oxides have gradually replaced pure CeO₂ as OSC materials in TWCs. (Fornasiero et al. 1995, Lox & Engler 1997, Kašpar et al. 1999, Farrauto & Heck 1999, Di Monte & Kašpar 2005)

3.2 Problems with TWC

The reduction of NOₓ in lean operation conditions and catalytic deactivation are still two major problems. In addition, the cold start problem and transient driving are connected to the reduction of toxic compounds from the emissions of gasoline engines. (Holmgren 1998 and Olsson 2002)

3.2.1 Lean NOₓ reduction

Lean conditions lead to efficient combustion, resulting in improved fuel economy. However, the excess of oxygen leads to the high oxygen coverage on noble metal sites in exhaust catalysts. Therefore, NOₓ reactions (adsorption, dissociation, and desorption)
cannot occur properly. One solution is to use selective catalytic reduction (SCR), which can be divided into two groups, with ammonia (NH₃-SCR) or hydrocarbons (HC-SCR) as reducing agents. In lean conditions, these catalysts (e.g. Cu and noble metal zeolites, alumina and alumina with base metals) have problems in practical use such as low NOₓ conversion, a narrow temperature window, and insufficient durability. (Takahashi 1996)

A catalyst has been recently developed for lean-burn engines. It consists of noble metals, aluminium oxide and some other metal compounds such as NOₓ storage compounds. These catalysts are called NOₓ storage and reduction catalysts (NSR). (Ambernsson et al. 2001)

Barium oxides are used as a stabiliser especially to inhibit support sintering (Lox & Engler 1997). Barium oxide has also been recently studied as a NOₓ storage compound. These kinds of compounds were found to be necessary, since net-oxidising conditions in three-way catalysts are not effective for NOₓ removal. (Salacs et al. 2002) The NOₓ storage reduction (NSR) concept is based on lean operating and short rich operating cycles in the engine (Olsson 2002). The mechanism for this kind of a catalyst is presented in Figure 7. During the lean period, NOₓ is oxidised over a noble metal catalyst and then stored on a storage compound (such as on BaO, BaCO₃ or Ba(OH)₂) as nitrite and nitrate compounds (Ba(NO₂)₂ and Ba(NO₃)₂). (Lietti et al. 2001, Nova et al. 2002) Nitrates are formed either via the formation of surface peroxides or the oxidation of surface nitrites (Skoglundh et al. 2004).

During the short rich period, these compounds are released and diffused on noble metal sites and reduced to N₂. The NOₓ storage capacity is enhanced with the increasing alkalinity of the element. The problem with a strong alkaline catalyst is that the conversion of hydrocarbons is reduced. (Takahasni et al. 1996) Under lean conditions, NO₂ has been demonstrated to play a crucial role in the storage of NOₓ (Muraki 1991). It functions as an oxidising agent in the NOₓ storage mechanism (Skoglundh et al. 2004). The oxidation of NO is higher on Pt-containing catalysts than on Pd-based catalysts (Muraki 1991). However, Pd catalysts have significant catalytic properties, such as high three-way catalytic activity and excellent light-off characteristics (Nagashima et al. 2004).

The gas composition also affects the NOₓ release mechanism. For example, CO₂ has been found to have a promoting effect on NOₓ release from a noble metal/barium oxide catalyst (Ambernsson et al. 2001). Therefore, CO₂ inhibits NOₓ storage at low temperatures: this phenomenon disappears at higher temperatures (Nova et al. 2002). The promoting effect of CO₂ can be explained by the fact that barium nitrates are replaced with carbonates. The effect of oxygen on the NOₓ release is the opposite. This is due to the fact that nitrate species are stabilised in the presence of O₂. Therefore, based on thermodynamic equilibrium calculations, the NOₓ decomposition occurs at higher temperatures than in the absence of O₂. On the other hand, the high coverage of oxygen on the noble metal suppresses NOₓ decomposition. The presence of oxygen releases NO and oxidises it to NO₂, which is readsorbed on storage sites. However, when water is present, the blocking effect by oxygen is reduced. Hydrocarbon rapidly consumes chemisorbed oxygen: hence the NOₓ release reactions can take place. (Ambernsson et al. 2001)

For the aged catalyst samples containing BaO, it has been noticed that substantial amounts of NOₓ can be stored at low temperatures (about 100°C) on NOₓ storage
compounds, when NO₂, which is an intermediate necessary for NOₓ storage, is present in
the feed. The storage process is inhibited when CO reacts with NO₂. This is a very
important point at the temperatures, at which NO does not react with oxygen over noble
metal sites to form NO₂. When the inlet feed also contains hydrocarbons, the storage of
NO₂ was promoted in the presence of CO. This is due to the NO₂ + CO reaction, which is
inhibited in the presence of a hydrocarbon. (Erkfeldt et al. 2001)

Fig. 7. NOₓ storage and reduction mechanism on NSR catalysts (Takahashi 1996).

For NOₓ purification, the migration process of NOₓ and activated reducing agents from
noble metals to NOₓ storage compounds is very important. XRD studies have proven that
the particle size of a noble metal is a very important factor in NO conversion; the higher
the NO conversion, the smaller the noble metal size. (Takahashi 1996) Accordingly, the
number of active sites for the NOₓ oxidation reaction and reducing agent activation
increases when the noble metal particle size gets smaller. In addition, the interface
between the noble metal and NOₓ storage compound increases. (Takahashi 1996)

Besides NSR, the other category of the NOₓ storage concept is the selective NOₓ
recirculation (SNR) concept. This concept is commercial and patented by Daimler-Benz
in 1994. (Amberntsson et al. 2001)

### 3.2.2 Catalyst deactivation

Catalytic activity and selectivity are very important in three-way catalysis. When a
catalyst looses its activity and/or selectivity over time, it is said to be deactivating. The
mechanisms of catalyst deactivation are numerous; they can be grouped into six intrinsic
mechanisms of catalytic activity decay. Each of the six basic mechanisms is defined
briefly in Table 5. However, it is difficult to give a precise definition of deactivation due
to the complexity of the phenomenon. (Bartholomew 2001)
Table 5. Mechanisms of catalyst deactivation (Bartholomew 2001).

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>Type</th>
<th>Brief definition/description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poisoning</td>
<td>Chemical</td>
<td>Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction</td>
</tr>
<tr>
<td>Fouling</td>
<td>Mechanical</td>
<td>Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores</td>
</tr>
<tr>
<td>Thermal degradation</td>
<td>Thermal</td>
<td>Thermally induced loss of catalytic surface area, support area, and active phase-support reactions</td>
</tr>
<tr>
<td>Vapour formation</td>
<td>Chemical</td>
<td>Reaction of gas with catalyst phase to produce volatile compound</td>
</tr>
<tr>
<td>Vapour-solid and solid-solid reaction</td>
<td>Chemical</td>
<td>Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase</td>
</tr>
<tr>
<td>Attrition/crushing</td>
<td>Mechanical</td>
<td>Loss of internal surface area due to mechanical-induced crushing of the catalyst particle</td>
</tr>
</tbody>
</table>

Deactivation of a three-way catalyst can be due to many ageing phenomena, such as thermal, chemical and/or mechanical, of which the first one is the main cause (Lassi 2003). In this thesis, catalyst samples are fresh but also aged, which means that they go through a high temperature-induced deactivation. This thermally-induced deactivation of catalysts results in (i) the loss of catalytic surface area due to crystalline growth of the catalytic phase, (ii) the loss of support area due to support collapse and loss of catalytic surface area due to pore collapse on crystallites of the active phase, and/or (iii) the chemical transformations of catalytic phases to non-catalytic phases. The first two processes are typically referred to as “sintering”. Three principal mechanisms of metal crystallite growth have been advanced (Bartholomew 2001):

− crystallite migration,
− atomic migration, and
− vapour transport at very high temperatures.

All these mechanisms can take place simultaneously. Temperature, atmosphere, metal type, metal dispersion, promoters/impurities and support surface area, texture and porosity, are the principal parameters affecting rates of sintering and redispersion. MgO or BaO are promoters which have the ability to slow sintering rates by decreasing metal atom mobility. In general, sintering processes are slow at moderate reaction temperatures and are either irreversible or difficult to reverse. Thus, sintering is more easily prevented than cured. (Bartholomew 2001)

3.2.3 Cold start and transient driving

The cold start problem occurs after starting the engine, when the catalyst is at the same temperature as the surroundings (-30°C to 30°C) and thus no conversion can take place. This means that the majority of the total HC and CO is emitted before the light-off of the catalyst. For HC this is roughly 50-80 %. A solution for this is a close-coupled catalyst (CCC), which reduces the heat-up time. (Shelef & McCabe 2000) However, as a
consequence of this location of the catalyst, temperatures up to 1050°C are common. For this reason, TWCs must be developed to have good thermal stability. (Heck & Farrauto 2001) As was discussed in the oxygen storage materials (section 3.1.3) there is a lot of effort being put into designing catalysts that can withstand extreme gas temperatures. Close coupled technology designed for cold-start emissions uses carriers such as Zr-based materials with low Ce content that resists deactivation due to sintering, and platinum group metals (PGMs) encapsulation after high temperature ageing. Nevertheless, the low Ce content (~20 wt-%) of these materials limits the total oxygen availability. (Rohart et al. 2004)

The technology race to develop suitable methods to control cold start HCs include both catalytic and some unique approaches which all contain catalysts of various compositions (Heck & Farrauto 2001):

1. close-coupled catalyst,
2. electrically heated catalysed metal monolith,
3. hydrocarbon trap,
4. chemically treated catalyst,
5. exhaust gas ignition,
6. pre-heat burners,
7. cold start spark retard or post manifold combustion,
8. variable valve combustion chamber,
9. double walled exhaust pipe.

During transient driving modes (accelerations and decelerations) the shortcomings were manifested in “breakthrough” emissions of CO and NOx (and sometimes HC) and could be traced to a loss in oxygen storage capacity (OSC) with time in service (Gandhi et al. 2003). For CO, HC, particulates, and other products of incomplete combustion, the highest emissions occur at low average speeds, whereas emissions of nitrogen oxides generally increase with an increase in average speed (Boulter et al. 1999).

European Union (EU) emission regulations for new vehicles force continuous improvements in both engines and the TWC concept. The EU’s limits for gasoline engines from Euro 1 to Euro 5 are presented in Figure 8. Emissions are tested by using test cycles that contain city and highway portions. The test cycles that are used most frequently include the American Federal Test Procedure (FTP), which simulates typical city and highway usage in Los Angeles, and the European ECE-15 test (ECE = European Commission for Europe). (Krahl et al. 1996)
The ECE+EUDC cycle, also known as the MVEG-A cycle for the emission certification of light vehicles, is used in Europe. The entire cycle includes four ECE segments (Fig. 9 a), repeated without interruption, followed by one EUDC (Extra Urban Driving Cycle) segment (Fig. 9 b). Before the test, the vehicle is allowed to soak at least 6 hours at a test temperature of 20 to 30°C. It is then started and allowed to idle for 40 s. Effective since 2000, that idling period has been eliminated, i.e., engines start at 0 s and the emission sampling begins at the same time. This modified cold-start procedure is also referred to as the New European Driving Cycle or NEDC. ECE represents city driving conditions, i.e. low vehicle speeds, and a low exhaust gas temperature. Meanwhile the EUDC represents far more aggressive, high speed driving modes. (http://www.dieselnet.com/standards/eu/ld.html)

Starting from the Euro 3 stage, vehicles must be equipped with an onboard diagnostic system (OBD) for emission control. The driver must be notified in the event of a malfunction or deterioration of the emission system that would cause emissions to exceed mandatory thresholds. The thresholds are based on the cold start ECE+EUDC test. To distinguish from the US OBD, the European limits are also referred to as the EOBD (European OBD). (http://www.dieselnet.com/standards/eu/ld.html)
Fig. 9. Speed versus time for the a) ECE and b) EUDC driving cycles (Directive 98/69/EC, further amendments in 2002/80/EC).
4 Experimental

4.1 Catalysts

The catalysts used in this study were metallic monoliths. The model catalyst consisted of a thin metal foil coated with a washcoat mainly containing Al₂O₃. The washcoat material content of the catalyst was 55 g/m². All the studied catalysts contained palladium (Pd) as an active metal. The content of Pd in the catalyst was 1 wt-%. In *in situ* DRIFT experiments the content of Pd was 1 and 3 wt-%. The active metal, Pd, was added on different washcoats of the catalyst. In addition to the Al₂O₃ washcoats, the washcoat contained in some cases 20 wt-% La₂O₃. The OSC material was used as a promoter (additive), with BaO and La₂O₃ as stabilisers. CeₓZr₁₋ₓO₂ mixed oxides were used as OSC materials in the catalyst. The compositions of the studied catalysts and the papers in which their behaviour is described are presented in Table 6.

<table>
<thead>
<tr>
<th>Catalyst/composition</th>
<th>Pd [wt-%]</th>
<th>BaO [wt-%]</th>
<th>La₂O₃ [wt-%]</th>
<th>OSC [wt-%]</th>
<th>Used in Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>1 and 3*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>I</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>II, IV</td>
</tr>
<tr>
<td>Pd/BaO/Al₂O₃</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>IV</td>
</tr>
<tr>
<td>Pd/(OSC+Al₂O₃)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>II, III</td>
</tr>
<tr>
<td>(Pd+OSC)/Al₂O₃</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>III</td>
</tr>
<tr>
<td>Pd/(Al₂O₃-OSC-La₂O₃)</td>
<td>1</td>
<td>-</td>
<td>20</td>
<td>23.6</td>
<td>V</td>
</tr>
<tr>
<td>Pd/(BaO-OSC)/Al₂O₃</td>
<td>1</td>
<td>2.9</td>
<td>-</td>
<td>19.8</td>
<td>V</td>
</tr>
<tr>
<td>(Pd-BaO-OSC)/Al₂O₃</td>
<td>1</td>
<td>2.9</td>
<td>-</td>
<td>19.8</td>
<td>V</td>
</tr>
<tr>
<td>(BaO-Pd-OSC)/Al₂O₃</td>
<td>1</td>
<td>2.9</td>
<td>-</td>
<td>19.8</td>
<td>V</td>
</tr>
</tbody>
</table>

*3wt-% Pd/Al₂O₃ has been used in *in situ* DRIFT studies.

The catalyst samples consisted of flat (Fig. 10 a) and corrugated metal foils (Fig. 10 b) coated with a support material, on which the noble metal was impregnated in an aqueous...
solution. The catalysts were mainly prepared by mixing the washcoat materials with precursor salts in a water slurry with relevant noble metal loadings. This slurry was then sprayed on the foil. Finally the catalysts were dried and calcined in air at 550°C for 4 hours. The dried and calcined catalysts are referred to as ‘fresh’ in the following text.

![Fig. 10. The catalyst sample: a) flat foil, b) corrugated foil, c) fresh catalyst, and d) reduced catalyst.](image)

The conditions in which the three-way catalysts are exposed during the real driving or engine ageing conditions are more or less transient (rapid temperature and atmosphere changes). Therefore, the laboratory ageing method (RAHLAB, Rapid Ageing Hot in Laboratory), which has been provided to correlate well with real engine conditions (Kallinen et al. 2005), was used to age the catalysts.

This was done by subjecting the fresh sample to cyclic conditions consisting of the following phases and temperatures: stoichiometric phase at 930°C for 60 s, CO enrichment phase for 15 s during which the temperature was raised from 930°C to 1020°C, additional air + CO phase at 1020°C for 7 s followed by 3 s during which the temperature was reduced from 1020°C to 930°C, and finally the oxidising phase for 1 s at 930°C. The total ageing time was 1 hour. The gas compositions during the laboratory ageing cycle are presented in Table 7. The laboratory ageing procedure is described in Kallinen et al. 2005.

**Table 7. Gas composition used during the laboratory ageing cycle in different ageing phases (Kallinen et al. 2005).**

<table>
<thead>
<tr>
<th>Gas/phase</th>
<th>O₂</th>
<th>NO</th>
<th>H₂O</th>
<th>CO₂</th>
<th>CO</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric</td>
<td>0.06</td>
<td>0.06</td>
<td>13</td>
<td>15</td>
<td>0.14</td>
<td>0.003</td>
<td>0.0013</td>
</tr>
<tr>
<td>+ CO³</td>
<td>0.06</td>
<td>0.04</td>
<td>13</td>
<td>13</td>
<td>4</td>
<td>0.075</td>
<td>0.025</td>
</tr>
<tr>
<td>+ O₂ + CO⁶</td>
<td>3.5</td>
<td>0.04</td>
<td>13</td>
<td>13</td>
<td>4</td>
<td>0.075</td>
<td>0.025</td>
</tr>
<tr>
<td>Oxidising</td>
<td>3.5</td>
<td>0.06</td>
<td>13</td>
<td>13</td>
<td>0.14</td>
<td>0.003</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

³ CO enrichment

⁶ additional air + CO enrichment
4.2 Catalyst characterization techniques

4.2.1 In situ DRIFT experiments

To study reaction intermediates during NO reduction by propene, Pd/Al₂O₃-based catalysts were investigated in lean and rich conditions by in situ DRIFT spectroscopy at Ecocat Oy, Oulu, Finland. The spectra were measured on a Perkin Elmer 1760X FTIR with a heated reaction chamber at a resolution of 4 cm⁻¹ by accumulating 20 scans. The oxidation pretreatment was done to ensure that the surface is clean enough and the adsorbed species have desorbed. The pretreatment procedure was started by heating the catalyst from room temperature to 400°C in vacuum for 25 minutes. Then the reaction chamber was evacuated at 400°C for 15 minutes. Oxygen was introduced to the reaction chamber at the same temperature for 20 minutes. A small oxygen flow during the cooling to room temperature was kept in the reactor chamber to prevent self-reduction of the catalyst. Finally, the catalyst was evacuated at room temperature for 20 minutes to clean the chamber of oxygen species.

The experiment was started by inserting the reaction gas mixture into the reaction chamber. The spectra were measured at 25, 220, and 260°C. The measurement does not give reliable data for the formation of CO₂ in the cell because the IR beam goes through the laboratory air. The reaction gas mixture contained NO, C₃H₆, and/or O₂ according to Table 8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>NO [%]</th>
<th>C₃H₆ [%]</th>
<th>O₂ [%]</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + O₂</td>
<td>5</td>
<td></td>
<td>2.5</td>
<td>stoich.</td>
</tr>
<tr>
<td>NO+C₃H₆</td>
<td>8.2</td>
<td>0.9</td>
<td></td>
<td>stoich.</td>
</tr>
<tr>
<td>NO+C₃H₆+O₂</td>
<td>6.9</td>
<td>1.5</td>
<td></td>
<td>rich</td>
</tr>
<tr>
<td>NO+C₃H₆+O₂</td>
<td>5.7</td>
<td>0.7</td>
<td>1.4</td>
<td>lean</td>
</tr>
</tbody>
</table>

4.2.2 Catalytic activity measurements

The catalytic activities of the fresh and aged catalysts were compared with laboratory scale experiments. To specify the efficiency of an automotive exhaust gas catalyst, the light-off temperature of the catalysts (T₅₀-value) was determined. This means the temperature at which 50 % conversion is reached. The lower the light-off temperature is, the more active the catalyst.

Catalytic activity measurements were performed with a laboratory apparatus consisting of mass flow controllers (Brooks 5850TR), magnetic valves for flow selection and insertion, and a tubular quartz reactor inside an electrically heated furnace. The whole system of the gas mixer and temperature controller (thermocouple in front of the monolith) were overseen and controlled by a PC via a LabView program designed...
specially for this equipment. The concentrations of gas compounds and spectrometric data were collected on a separate PC. Figure 11 shows the experimental set-up for the activity experiments. Table 9 presents the reactions used to determine catalytic activities and the papers in which they are used. In Paper I catalytic activities were determined by using the model reactions presented in Table 8.

The redox properties of the gas mixtures were identified by the stoichiometric number, S (oxidising-reducing components ratio), calculated in Equation 4.

\[
S = \frac{\left[O_2\right] + \left[NO\right]}{\left[CO\right] + 3 \cdot \left[C_2H_4\right]}
\]  \hspace{1cm} (4)

When \(S < 1\), \(S = 1\), or \(S > 1\), the redox property is net reducing, stoichiometric, or net oxidising, respectively (Yamazaki et al. 2004).

Table 9. Characteristics of the experiments carried out with dissimilar feedstream compositions and the papers in which they have been used. Symbol X means that the compound is present in the feedstream. \(S\) means the stoichiometric number calculated by Equation (4).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(C_2H_4)</th>
<th>NO</th>
<th>CO</th>
<th>(O_2)</th>
<th>(N_2) (balance)</th>
<th>(S)</th>
<th>Used in Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>5.73</td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>0.60</td>
<td></td>
<td>II, IV</td>
</tr>
<tr>
<td>3</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>6.33</td>
<td></td>
<td>II, IV</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.86</td>
<td></td>
<td>II, III</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.09</td>
<td></td>
<td>II, III, V</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.95</td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>7</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.75</td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>8</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.08</td>
<td></td>
<td>II, IV</td>
</tr>
<tr>
<td>9</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.83</td>
<td></td>
<td>II, IV</td>
</tr>
</tbody>
</table>

FT-IR (Gasmet™ FT-IR Gas Analyser, see Figure 11) was used to analyse the following gas compounds: \(C_2H_4\), \(H_2O\), \(CO\), \(CO_2\), \(NH_3\), \(NO\), \(N_2O\), and \(NO_2\). The nitrogen balance was calculated as follows: \(N_{\text{bal}} = NO_{\text{inlet}} - NO_{\text{outlet}} - NO_2_{\text{outlet}} - 2 \cdot N_2O_{\text{outlet}}\) (Salas 2002). The oxygen concentration was determined by using a paramagnetic oxygen analyser (ABB Advance Optima, see Figure 12).
Prior to measurements, the catalysts were oxidised in an air flow at 500°C for 20 minutes, and then cooled down to room temperature under an air flow. The reaction chamber was rinsed with a nitrogen flow for a few minutes. Activity measurements were carried out at atmospheric pressure using a cylindrical catalyst with a volume of 1.4 cm³ (length 28 mm and diameter 8 mm). The total gas flow during the experiments was 1 dm³/min corresponding to the feed gas hourly space velocity (GHSV) of 43 000 h⁻¹. The GHSV was based on the flow rate (dm³/min) and monolith volume (dm³) in the reactor.

The reaction chamber was rinsed with the reaction gas mixture for 5 minutes (in Paper I this was not done) at room temperature before raising the temperature up to 500°C with a linear heating rate of 10°C/min. The concentrations of reactants and products as a function of temperature were measured every 5 seconds by an FT-IR gas analyser, and the fluctuation of oxygen was measured with a paramagnetic oxygen analyzer (Figure 12).
4.2.3 Physisorption analyses

Specific surface area (m$^2$/g) was measured for fresh and aged catalyst samples by using the non-specific Brunauer-Emmett-Teller (BET) method (Coulter Omnisorp 360CX). Surface area is an attribute that is used by catalyst manufacturers and users as a measure of the activity and stability of catalysts. The determination of surface area is most commonly performed by measuring the amount of gas adsorbed (typically nitrogen) at cryogenic temperatures (liquid nitrogen). Based on the amount of gas adsorbed (adsorbate) at a given pressure, the BET equation is used to calculate the number of adsorbed gas molecules that form a monolayer on the catalyst surface.

4.2.4 Chemisorption analyses

The dispersion of Pd and the particle size of Pd were determined by using chemisorption measurements. Carbon monoxide was used as the adsorbate gas. CO-chemisorption measurements were carried out close to room temperature (30°C) by a volumetric adsorption method by using a sorptometer (Carlo Erba Sorptomatic 1990) at Ecocat Oy, Oulu, Finland. The active metal particle size and dispersions were calculated by assuming the stoichiometric factor between a chemisorbed gas molecule and metal atoms to be 1:1, regardless of the particles size. Noble metal particle sizes were calculated from the dispersion measurement results. For the dispersion measurement the pretreatment was done with hydrogen at 300°C for 30 min, after which the sample was held in vacuum for 30 min. (Kallinen et al. 2005).

Chemisorption analysis is a valuable technique for the rapid evaluation of the active metal dispersions and consequently the particle size of supported metals (Gasser 1985). However, the chemisorption method can be criticized due to the assumptions of the stoichiometry between the adsorbate gas and the noble metal and in the case of small
particles, the particle geometry may not be true (Di Monte et al. 2000). Because of this fact one should be careful when comparing the dispersion values of different catalysts. Furthermore, when metal oxides, such as CeO$_2$ and Ce$_{x}$Zr$_{1-x}$O$_2$, are in close contact with the active metal, CO can also be adsorbed on ceria (Ciuparu et al. 2000), which results in excessively high CO dispersion values.

### 4.2.5 Dynamic OSC measurements

Oxygen storage capacity values can be presented in two different ways according to the developed method of measurement (Lambrou et al. 2004):
- OSC (oxygen storage capacity, $\mu$mol-O/g) related to the more reactive oxygen species and the most readily available lattice oxygen, and
- OSCC (oxygen storage capacity complete, $\mu$mol-O/g) related to the total or maximum oxygen storage capacity at the conditions of the experiment, not necessarily to the equilibrium oxygen uptake.

OSC was measured for fresh and aged monoliths. The experimental procedure was used for measuring the OSC by alternating the step concentration switches of gas compositions (CO or O$_2$). The total oxygen storage capacity (OSC) was measured with the laboratory equipment using a quartz reactor and a ceramic furnace (Maunula et al. 1999). The storage capacity (O$_2$ ml) of the OSC material was measured and calculated from the difference between the totally CO-adsorbed and O$_2$-adsorbed catalyst surfaces (Kallinen et al. 2005). The measurements were done by changing the flow between 2 vol-% CO and 1 vol-% O$_2$ from 2 to 2 s at 400°C or from 5 to 5 s at 400°C (2 to 2 s means first 2 s CO and then 2 s O$_2$). The same measurements were done also at 600°C and 700°C. The gases were analysed using the OmniStar mass spectrometer. Oxygen storage capacity (OSC) was studied at Ecocat Oy, Oulu, Finland.

### 4.2.6 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive and quick technique to determine the existence of materials crystalline structures and phases in a sample. In this thesis, XRD was used for studying the ageing-induced solid-solid phase transformation.

The XRD diffractograms presented in this study were recorded on a Siemens D5000 diffractometer employing the nickel-filter Cu Ka radiation ($\lambda$= 1.5406 Å, 40 kV, 30 mA) at 0.020° intervals in the range of 20° ⩽ 20 ⩽ 75° with 1 s count accumulation per step directly from the catalyst foils. To clarify the results one measurement was done by employing nickel-filtered Cu Ka radiation ($\lambda$= 1.5406 Å, 40 kV, 40 mA) at 0.010° intervals in the range of 20° ⩽ 20 ⩽ 75° with a 1 s count accumulation per step.

Diffraction patterns were assigned using a PDF database supplied by the International Centre for Diffraction Data (PDF2 - Diffraction Database File). XRD resources of the Institute of Electron Optics at the University of Oulu were used.
5 Results and discussion

This thesis examines several Pd/alumina-based catalysts (see Table 6). Several activity and characterization analyses were conducted on fresh and laboratory-aged (RAHLAB) catalysts. The main ideas can be presented in four different parts. The first idea was to study the basic reaction mechanism for NO reduction by hydrocarbons over a Pd/Al₂O₃ catalyst. Then, the behaviour of BaO and OSC materials on the performance of Pd/Al₂O₃-based catalysts was assessed. A study was also done to find out if the addition order of the OSC material and/or BaO into the catalysts has an effect on the catalytic behaviour. Finally, the effect of ageing on catalytic activity, selectivity, and stability was assessed. This chapter presents the main findings of the results.

5.1 NO reduction by hydrocarbons over Pd/Al₂O₃ catalysts

*In situ* DRIFT spectroscopy and FT-IR gas analyser were used to investigate a possible reaction mechanism for NO reduction by hydrocarbons [Paper I]. In this study the main intermediates observed in the reduction of NO by propene near the light-off temperature of NO were: isocyanates (-NCO), acetates (-COO⁻), formates (-HCOO⁻), nitrites (-NO₂⁻), and nitrates (-NO₃⁻). According to Di Monte *et al.* (2002) palladium has been found to be a relatively inefficient metal for the dissociative chemisorption of NO compared to Rh. However, NO adsorption and dissociation reactions to nitrite and nitrate species have been found to occur according to the following Equations 5-9 (* denotes a free active site) (Shimizu *et al.* 1998, Fritz & Pitchon 1997, Freysz *et al.* 2001, Macleod *et al.* 2001, Almusaiter & Chuang 1998 and Burch & Watling 1997):

\[
\begin{align*}
\text{NO} + \* & \leftrightarrow \text{NO}\* \quad (5) \\
\text{NO}\* + \* & \rightarrow \text{N}\* + \text{O}\* \quad (6) \\
\text{NO}\* + \text{N}\* & \rightarrow \text{N}_2\text{O} \quad (7) \\
\text{NO}\* + \text{O}\* & \rightarrow \text{NO}_2\* \\
\text{NO}\* + \text{O}_2 & \rightarrow \text{NO}_3\* 
\end{align*}
\]
According to our experiment, the amounts of these intermediates depend on the reaction conditions (rich or lean) and temperature. The nitrite and nitrate species are typically observed at low temperatures, which is evident from the formation of unwanted N₂O during the measurement of catalytic activity (Fritz & Pitchon 1997 and Freysz et al. 2001). Thus, there are not enough noble metal active sites for the formation of N₂ as it is presented in Equation 10 (Rahkamaa & Salmi 1999):

\[
2N^* \rightarrow N_2 + 2^* \quad (10)
\]

At a temperature below 327°C, the formation of N₂ can also occur via Equation 11 (Rahkamaa & Salmi 1999):

\[
NO^* + N^* \rightarrow N_2 + O^* + ^* \quad (11)
\]

Propene adsorption and dissociation on the catalyst surface with the presence of NO lead to partially oxidised hydrocarbons (CₓHᵧOₓ⁻), such as formates and acetates (Fritz & Pitchon 1997, Tanaka et al. 1994). It was observed in our study that these reactions depend on the reaction conditions, since during the rich conditions, the formation of formates was more probable than in lean conditions. The formation of cyamide or isocyanide species and organic nitro compounds (R-ONO, where R refers to hydrocarbon) are observed to be surface intermediates when formates (partially oxidised hydrocarbons) react with nitrite or nitrate species or oxygen. Depending on the reaction conditions, the reaction between nitrates and isocyanides or cyanides produces nitrous oxide, and the desired products, N₂ and CO₂, according to Equations 12-14 (Bamwenda et al. 1995, Freysz et al. 2001, Cowan et al. 1998, Burch & Watling 1997 and Captain & Amiridis 1999). However, N₂O, NH₃, and CO can also be formed, especially, in rich conditions and in the presence of water, as in Equations 15-16 (Cowan et al. 1998 and Cant & Liu 2000). NH₃ is also formed in reactions between hydrocarbons with nitrogen oxides.

\[
-NCO^* + NOx^* \rightarrow N_2 + CO_2 + N_2O \quad (12)
\]
\[
-C≡N^* + NOx^* \rightarrow N_2O + N_2 + CO_2 \quad (13)
\]
\[
N_2O^* + CO^* \rightarrow N_2 + CO_2 \quad (14)
\]
\[
-NCO^* + H_2O \rightarrow NH_3 + CO_2 \quad (15)
\]
\[
-C≡N^* + H_2O \rightarrow NH_3 + CO \quad (16)
\]

Figure 13 presents a plausible simplified reaction mechanism for the C₃H₆ assisted SCR of NO, derived by integrating the information on the reaction intermediates and the side products detected by in situ DRIFT and gas phase analyses (Huuhtanen et al. 2005). The reduction of NOₓ by hydrocarbons depends on the choice of the platinum group metal (PGM) and on the chemical nature of the hydrocarbon reactant (Burch et al. 2002). The study of the reaction mechanism of the reduction of NO by propene over a Pd/alumina catalyst provides information about the reaction intermediates. The catalytic reduction of NO by ethene or propene over Pt-based catalysts is reported to be almost similar (Burch & Millington 1995). Therefore, in this thesis, ethene was chosen to be the reductant {[Papers II and IV]} in NOₓ reduction over Pd/Al₂O₃-based catalysts.
5.2 Effect of OSC on NO reduction

Promoters are used to improve the properties of catalysts, such as activity and selectivity, during the catalytic processes. Several dissimilar reactions (see Table 10) were studied for comparing the catalytic activities of metallic Pd/Al₂O₃ and Pd/(OSC+Al₂O₃) [Paper II]. A FT-IR gas analyser was used to follow the reactions, by monitoring the concentration changes of reactants and products as a function of temperature. A summary of the light-off temperatures of NO, CO, and C₂H₄ on Pd/Al₂O₃ and Pd/(OSC+Al₂O₃) catalysts in the studied reactions are presented in Table 10.

Table 10. Light-off temperatures ($T^{50}$-values [°C]) for C₂H₆, NO, and CO in the studied reactions over Pd/Al₂O₃ and Pd/(OSC+Al₂O₃) catalysts.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>C₂H₆</th>
<th>NO</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Al₂O₃</td>
<td>Pd/(OSC + Al₂O₃)</td>
<td>Pd/Al₂O₃</td>
</tr>
<tr>
<td>C₂H₆ + O₂</td>
<td>227</td>
<td>229</td>
<td>-</td>
</tr>
<tr>
<td>C₂H₆ + NO</td>
<td>409</td>
<td>284</td>
<td>355</td>
</tr>
<tr>
<td>C₂H₆ + NO + O₂</td>
<td>272</td>
<td>262</td>
<td>n.d</td>
</tr>
<tr>
<td>CO + O₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO + NO</td>
<td>-</td>
<td>-</td>
<td>217</td>
</tr>
<tr>
<td>CO + NO + O₂</td>
<td>-</td>
<td>-</td>
<td>n.d</td>
</tr>
<tr>
<td>C₂H₆ + CO + O₂</td>
<td>182</td>
<td>119</td>
<td>-</td>
</tr>
<tr>
<td>C₂H₆ + CO + NO</td>
<td>430</td>
<td>314</td>
<td>375</td>
</tr>
<tr>
<td>C₂H₆ + CO + NO + O₂</td>
<td>217</td>
<td>187</td>
<td>n.d</td>
</tr>
</tbody>
</table>

*a Defined as the temperature of 50 % conversion of C₂H₆, NO, and CO.

n.d. not detected, because no light-off occurred.
The effect of OSC on the Pd/Al₂O₃ catalyst was analysed by comparing the light-off temperatures of C₂H₄, NO, and CO (Table 10). In addition, details concerning reaction products were followed, such as formation temperatures and concentration of products, and curve shapes of product yields (see Figure 14). In this study it was observed that these variables depend on the presence of OSC material in the catalyst, and on the reaction conditions, varying from lean to rich. The concentrations of the reaction products (H₂O, CO₂, N₂O, NO₂, and NH₃) were monitored during the activity test, and the selectivity to N₂ was calculated according to the following equation: \( N_{\text{bal}} = \text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}} - \text{NO}_2_{\text{outlet}} - 2\cdot\text{N}_2\text{O}_{\text{outlet}} \) (Salasc 2002). In addition, the amount of inlet oxygen consumption during the measurement was calculated.

According to our results, catalytic activity was enhanced in the presence of the OSC material. For example, during the CO+O₂ reaction over the Pd/(OSC+Al₂O₃) catalyst the
conversion of CO was around 8% at room temperature. The formation of CO₂ was also enhanced at ambient temperature. According to Fernández-Carcía et al. (1999) the presence of metallic Pd⁰ sites is required for CO adsorption as well as for the initiation of the CO oxidation reaction. It should be remembered that the Pd oxidation state (Pd²⁺) is less effective for CO activation than the Pd⁰ state (Fernández-Carcía et al. 1999). CO activation efficiency is related to the effectiveness of the active sites in initiating CO oxidation. It indicates how easily CO forms a bond with an active site after which the C–O bond weakens. (Fernández-Carcía et al. 1999) The OSC material enhances the catalytic properties of the noble metal by favouring the formation of the metallic state and through creation of anionic vacancies in the OSC component at room temperature. (Fernández-Carcía et al. 2001). The reaction between adsorbed CO and oxygen from the lattice of the OSC material enhances oxygen adsorption from the feedstream by lowering the inhibiting effect of adsorbed CO (Monteiro et al. 2001).

The formation of CO₂ was the result of the oxidation reactions of CO and C₂H₄. In our study it was observed that in cases where the reaction conditions were lean, the formation of CO₂ was started at lower temperatures on the Pd/(OSC+Al₂O₃) catalyst than on the Pd/Al₂O₃ catalyst. In addition, the oxygen consumption over the Pd/(OSC+Al₂O₃) catalyst was lower than over the Pd/Al₂O₃ catalyst. According to Liotta et al. (2002) ceria favours the transfer of the lattice oxygen from the bulk to the surface of the catalyst, thus increasing the oxygen availability on the Pd surface. This effect may explain why in our experiments the oxygen consumption from the feedstream was weaker over the Pd/(OSC+Al₂O₃) catalyst than over the Pd/Al₂O₃ catalyst.

Thus, it can be concluded that during the oxygen pretreatment, the OSC material stored oxygen that was released in oxidation reactions. Therefore, it was concluded that OSC material activates the oxidation reactions of CO and C₂H₄.

In our study the formation of H₂O was observed in the C₂H₄ oxidation reactions. Further studies are needed to determine why the formation of water was lower over an OSC-containing catalyst than over the ones without OSC.

Our results indicated that, as expected, the formation of N₂ was higher in rich conditions than in very lean conditions. The OSC material improves the NO adsorption and dissociation reactions, and thus there are enough available sites for N₂ formation (Di Monte et al. 2002). However, NO inhibits the C₂H₄ and CO oxidation reactions by competing with O₂ for metallic adsorption sites (Martínez-Arias et al. 2001, Fernández-García et al. 2000).

NH₃, CO, and N₂O are not desired products in exhaust gas purification: therefore, the amount of these compounds in the product stream should be as low as possible. In our study the formation of NH₃ and CO was observed only during the C₂H₄+NO and C₂H₄+CO+NO reactions, when the reaction conditions during the measurement were rich (S = 0.6 and 0.08, respectively). This indicates that ethene is adsorbed and dehydrogenates on the catalyst surface. The explanation for the formation of NH₃ and CO is maybe the limited availability of adsorbed oxygen.

Under really lean deNOₓ conditions a substantial amount of N₂O is formed at temperatures below 300°C and, in Europe at least, this is perceived to be the major problem. However, N₂O could be a key intermediate in the formation of gaseous N₂ at least at low temperatures. (Burch et al. 2002) Also our study revealed that N₂O starts to be formed at low temperatures. The OSC material was found to promote the formation of
N₂O, CO, and NH₃ in rich conditions. The difference was relatively small for the formation of N₂O regardless of whether the conditions were lean or nearly stoichiometric.

As mentioned above, the formation of N₂O and N₂ was more reliable on the Pd/(OSC+Al₂O₃) catalyst than on the Pd/Al₂O₃ catalyst at low temperatures. As concluded by Di Monte et al. (2002), this effect suggests that NO reduction is promoted by the OSC-containing material, which presumably involves reactive oxygen species at the Pd/OSC interface generated by the redox Ce⁴⁺/Ce³⁺ couple. These kinds of reactive oxygen species, which move from ceria to the metal surface, are responsible for the formation of reduced Ce³⁺ sites on which NO dissociation promptly occurs and generates N₂O and nitrite/nitrate species. (Di Monte et al. 2002)

According to Burch & Sullivan (1999) the reaction mechanism for the formation of NO₂ is either via NO+O* → NO₂* (Eley-Ridel) or via NO*+O* → NO₂* (Langmuir-Hinselwood), where * denotes a surface site. Both mechanisms can occur at the same time. However, the latter mechanism is more common than the former one. (Olsson 2002) Therefore, the detection of NO₂ is a sign of Pd-O species on the surface (Burch & Sullivan 1999). In our study, the detection of NO₂ was done only when oxygen was present in the feedstream. Apparently, there is a lack of reduced active adsorption sites for NO. This might explain why in our study the conversion profile of NO decreased at higher temperatures (around 400°C). The other possible explanation for the decrease in the NO₂/NO ratio is thermodynamic limitation. It has also been discovered that the OSC material reduces the formation of NO₂ and according to Hu et al. (1996) ceria has been shown to keep palladium in the Pd²⁺ or Pd⁺ forms even at higher temperatures. Thus, the lower concentration of NO₂ over the Pd/(OSC+Al₂O₃) catalyst might be explained by the oxidised Pd state, which prevents NO adsorption.

5.3 Effect of OSC addition order and ageing on NO reduction

The effects of the Pd addition method on alumina or the OSC material in the NO reduction and CO oxidation reactions were studied by light-off experiments performed in a tubular reactor and analyzed by a FT-IR gas analyser, CO chemisorption, BET surface areas, and a dynamic OSC technique. In addition, the effect of ageing on the light-off performance of the Pd/(OSC+Al₂O₃) and (Pd+OSC)/Al₂O₃ catalysts during the CO + NO and CO + NO + O₂ reactions was determined [Paper III]. The main difference between the catalysts was that in the case of the (Pd+OSC)/Al₂O₃ catalyst, Pd was preimpregnated to the OSC material and in the case of the Pd/(OSC+Al₂O₃) catalyst, Pd was added to the washcoat slurry in the final stage. A summary of the light-off temperatures of NO and CO, as well as BET surface areas, and CO chemisorption results on the fresh and aged (Pd+OSC)/Al₂O₃ and Pd/(OSC+Al₂O₃) catalysts are presented in Tables 11 and 12, respectively.
Table 11. The light-off temperatures* of NO and CO in the studied reactions for the fresh and aged Pd/(OSC+Al2O3) and (Pd+OSC)/Al2O3 catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pd/(OSC+Al2O3)</th>
<th>(Pd+OSC)/Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Aged</td>
</tr>
<tr>
<td>Reaction/T50 [°C]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO+NO</td>
<td>n.d.</td>
<td>108</td>
</tr>
<tr>
<td>CO+NO+O2</td>
<td>123</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* defined as the temperature of 50 % conversion of CO and NO
n. d. = not detected, because no light-off occurred

Table 12. BET surface areas, particle sizes of Pd, and dispersions of the fresh and aged Pd/(OSC+Al2O3) and (Pd+OSC)/Al2O3 catalysts.

<table>
<thead>
<tr>
<th>Analysis results</th>
<th>Pd/(OSC+Al2O3)</th>
<th>(Pd+OSC)/Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET-surface area [m2/g]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>154</td>
<td>61</td>
</tr>
<tr>
<td>Aged</td>
<td>&gt;100</td>
<td>5</td>
</tr>
<tr>
<td>Particle size of Pd [nm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>3</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Aged</td>
<td>&gt;100</td>
<td>5</td>
</tr>
</tbody>
</table>

a In the case of (Pd+OSC)/Al2O3 catalyst, Pd and OSC material were mixed and added together.
b CeZr1-xO2 mixed oxides were used as OSC.
c The CO dispersion values for the fresh studied catalysts are probably too high, because CO can also adsorb on ceria.

A dynamic OSC technique enables the detection of the oxygen available for redox processes on a time scale of seconds (Kašpar et al. 2003). As can be seen in Figure 15, in the case of a fresh Pd/(OSC+Al2O3) catalyst, the dynamic oxygen storage capacity is somewhat lower than in the case of the (Pd+OSC)/Al2O3 catalyst regardless of temperature or a varying CO and O2 gas insertion time (2 to 2s or 5 to 5 s). Instead, for aged catalysts, the difference in dynamic oxygen storage capacity is insignificant at 600°C and 700°C. The only clear difference is at 400°C where the Pd/(OSC+Al2O3) catalyst stored oxygen better than the (Pd+OSC)/Al2O3 catalyst (see Fig. 15). This can be due to the Pd particle size (see Table 12), which is an important parameter under dynamic conditions (Boaro et al. 2003).
Fig. 15. Dynamic oxygen storage for the fresh catalysts: defined as the volume of O₂ in the washcoat for the fresh and aged Pd/(OSC+Al₂O₃) and (Pd+OSC)/Al₂O₃ catalysts.

Based on the activity test, the differences in the fresh catalysts were insignificant compared to the aged catalysts. Figure 16 presents as an example the CO+NO reaction over the fresh and aged Pd/(OSC+Al₂O₃) catalysts. For fresh catalysts, the Pd addition method has only a slight effect on the light-off temperature of NO (see Table 11). As expected, during the CO+NO reaction the NO selectivity to N₂ was 100% at 500°C due to rich conditions. However, when reaction conditions were changed from rich to lean in the CO+NO+O₂ reaction, the conversion of NO was low. Therefore, the formation of N₂ was not observed. This can be explained by the lack of adjacent vacant sites for NO dissociation (Rahkamaa & Salmi 1999). It was observed that during the CO+NO reaction the conversion of CO decreased at around 350°C. This effect is probably due to the oxidised state of Pd caused by NO adsorption and dissociation reactions.

The activity of CO oxidation decreases when the PdO phase is present (Ciuparu et al. 2000). Pd particles that are in close contact with alumina are readily reduced to metallic Pd (Martínez-Arias et al. 2001, Fernández-Carcía et al. 2001). In addition, because the amount of CO in our study was much higher than the amount of NO, all NO was reduced during the CO+NO reaction. Therefore, alumina-supported PdO particles can be reduced by CO already at room temperature. CO is adsorbed more strongly on metallic palladium than on Pd oxide. (Ciuparu et al. 2000) High surface coverage of CO consumed the active surface, which is sometimes referred to as CO poisoning (Church et al. 1989). In our study the CO conversion was higher over the fresh Pd/(OSC+Al₂O₃) catalyst than over the fresh (Pd+OSC)/Al₂O₃ catalyst.
According to our activity results the formation of CO$_2$ was observed in the beginning of the measurement. This is probably a result of the direct reaction of CO with oxygen originating from the oxygen storage material (Cordatos & Gorte 1996). It was observed that the maximum amount of CO$_2$ formed at higher temperatures was finally the same over all the studied catalysts. In Pd-OSC based catalysts, the most active sites involve interactions between Pd and Ce-Zr mixed oxides (Kašpar et al. 2003, Heck & Farrauto 2001). Vacant sites for NO adsorption are formed as a result of the reduction of ceria (from Ce$^{4+}$ to Ce$^{3+}$) during oxygen transfers. NO decomposes readily on reduced ceria (Ce$^{3+}$) (Cordatos & Gorte 1996).

Our study revealed lower NO reduction and CO oxidation activities for the aged catalysts than for the fresh catalysts, as expected. If the light-off temperatures of CO and NO are compared (see Table 11), Pd on OSC-containing alumina was more active than Pd.
on OSC material after ageing. In addition, NO was reduced to N₂O at low temperatures and was oxidised to NO₂ at higher temperatures in lean conditions more likely over the Pd/(OSC+Al₂O₃) catalyst than over the (Pd+OSC)/Al₂O₃ catalyst. Martínez-Arias et al. (2004) have reported that Pd loading has an effect on the NO reduction reaction in activity tests over PdO/γ-Al₂O₃ catalysts. They deduced from their results that NO dissociation is favoured over the large Pd particles. The Pd particle size is increased during the ageing process as a consequence of the sintering of Pd and Ce-Zr mixed oxides (Kašpar et al. 2003, Martínez-Arias et al. 2002). According to our experiments the activity decline from fresh to aged is due to a decrease in the number of active sites on the surface, which was observed as a larger Pd particle size for the aged catalysts than for the fresh catalysts (see Table 12). In addition, the oxygen storage capacity of the aged Pd/(OSC+Al₂O₃) catalyst was higher at 400°C than that of the (Pd+OSC)/Al₂O₃ catalyst (see Figure 15). Sintering explains the lower catalytic activity by decreasing the number of active sites on the aged catalysts. On the other hand, our ageing procedure was done at rather high temperatures (from 930°C to 1020°C), which also changes the BET surface areas and possibly also the chemical state of palladium (Lassi et al. 2004). This kind of thermal deactivation of the catalysts is due to the collapse of surface area, the sintering of Pd particles and the phase transitions observed in the bulk material (Lassi et al. 2004b). In our study, oxygen consumption in the CO+NO+O₂ reaction was higher for the aged catalysts than over the fresh ones. This effect is due to the loss of active sites on the surface by thermal deactivation.

### 5.4 Effect of BaO on NO reduction

The removal of nitrogen oxides from exhaust gases is a major goal when designing new catalytic materials for lean-burn applications. For this reason, attention has been drawn to studying the N-containing compounds such as NO, NO₂, N₂O, and N₂. The effect of BaO on C₂H₄ and CO oxidation as well as on NO reduction was studied [Paper IV]. The FT-IR gas analyser and CO chemisorption results were used to compare the catalytic activities of metallic Pd/Al₂O₃ and Pd/BaO/Al₂O₃. Four model reactions, C₂H₄+NO, C₂H₄+NO+O₂, C₂H₄+CO+NO, and CO+C₂H₄+NO+O₂, were followed by monitoring the changes in the concentrations of reactants and products as a function of temperature. A summary of the light-off temperatures of NO, CO, and/or C₂H₄ as well as BET surface areas, and CO chemisorption results on the Pd/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts is presented in Tables 13 and 14, respectively.
Table 13. Light-off temperatures (T<sub>50</sub>-values [°C])* for NO, CO, and C<sub>2</sub>H<sub>4</sub> in studied reactions over Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction / T&lt;sub&gt;50&lt;/sub&gt;-value</th>
<th>Pd/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Pd/BaO/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>NO</td>
<td>CO</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;+NO</td>
<td>409</td>
<td>355</td>
<td>-</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;+NO+O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>272</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;+CO+NO</td>
<td>430</td>
<td>375</td>
<td>n.d.</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;+CO+NO+O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>217</td>
<td>n.d.</td>
<td>214</td>
</tr>
</tbody>
</table>

* Defined as the temperature of 50% conversion of C<sub>2</sub>H<sub>4</sub>, NO, and CO
n. d. = not detected, because no light-off occurred.

Table 14. BET surface areas, particle sizes of Pd, and dispersions of the Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

<table>
<thead>
<tr>
<th>Catalysts/analysis results</th>
<th>Pd/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Pd/BaO/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET-surface area [m&lt;sup&gt;2&lt;/sup&gt;/g]</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>Particle size of Pd [nm]</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Dispersion value [%]</td>
<td>18</td>
<td>12</td>
</tr>
</tbody>
</table>

According to our results the differences between the Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts during the C<sub>2</sub>H<sub>4</sub> + CO + NO and C<sub>2</sub>H<sub>4</sub> + CO + NO + O<sub>2</sub> reactions are relatively small, as can be seen in Figures 17 and 18. The formation of NH<sub>3</sub> was not observed in the C<sub>2</sub>H<sub>4</sub> + NO + O<sub>2</sub> (Figure not presented) and C<sub>2</sub>H<sub>4</sub> + CO + NO + O<sub>2</sub> reactions because the reducing agent (C<sub>2</sub>H<sub>4</sub>) was completely oxidised (reaction conditions are lean). Together with the formation of CO, the formation of NH<sub>3</sub> indicates that C<sub>2</sub>H<sub>4</sub> is adsorbed and dehydrogenated on the catalyst surface. Therefore, the limited availability of oxygen explains the formation of NH<sub>3</sub> and CO. Thus, in our study the formation of CO was not detected during the C<sub>2</sub>H<sub>4</sub>+O<sub>2</sub> reactions.

It can be concluded from the light-off temperatures of NO, CO, and C<sub>2</sub>H<sub>4</sub> (Table 13) that the reducing agents favour reacting with oxygen over NO. Thus, there is a lack of reductants for the NO reactions. When comparing the light-off curves of NO and C<sub>2</sub>H<sub>4</sub> in Figures 17 and 18 it was observed that CO was a more effective reductant than ethene at low temperatures (<200°C). Based on our studies [Paper I] NO reduction by propene over the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst occurs via intermediates such as NCO, acetates, formates and nitrates. According to Fridell et al. (2000), BaO enhances HC oxidation by improving the resistance of platinum against propene (or propene-derived species) poisoning. This self-poisoning effect is due to the blocking effect of active sites by components such as NO and CO or propene-derived species. This means that neither NO nor CO may be adsorbed on the Pt metal sites. However, barium oxide provides a site for CO to form BaCO<sub>3</sub>. Therefore, on the barium-containing catalyst there are more active sites for CO and C<sub>2</sub>H<sub>4</sub> adsorption. (Salacs et al. 2002) This effect explains why the light-off temperature of C<sub>2</sub>H<sub>4</sub> is lower for the Pd/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst than for the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.
Fig. 17. The conversion curves of NO, CO, and C\textsubscript{2}H\textsubscript{4} (on the right) and the concentration curves of N\textsubscript{2}O, NH\textsubscript{3} or NO\textsubscript{2}, and N\textsubscript{2} (on the left) for a) C\textsubscript{2}H\textsubscript{4}+CO+NO and b) C\textsubscript{2}H\textsubscript{4}+CO+NO+O\textsubscript{2} reactions as a function of temperature over the Pd/Al\textsubscript{2}O\textsubscript{3} catalyst (Paper IV).
Our results showed that the formation of NO₂ was as much as fifty percent less over the Pd/Al₂O₃ catalyst than over the Pd/BaO/Al₂O₃ catalyst. This means that during lean operation conditions Ba is more likely present in the form of Ba(OH)₂ and/or BaCO₃. NO is first oxidised over the noble metal, and the NO₂ formed reacts with Ba(OH)₂ or BaCO₃ to form nitrates (Lietti et al. 2001). Ba(OH)₂ is more probable than BaCO₃ in our case because the amount of CO₂ formed during the reaction was not so high. Thus, NO is
adsorbed and stored to BaO, which explains low NO₂ formation over the Pd/BaO/Al₂O₃ catalyst.

NO₂ is a very significant compound in several NOₓ removal techniques, such as in NOₓ traps (Olsson & Fridell 2002b). The adsorption and desorption of oxygen are important steps in NO oxidation. The acidity or alkalinity of the support material has an effect on the formation of Pd-O and Pd-O₂ species, which are intermediates for the formation of NO₂ (Olsson & Fridell 2002b). Large amounts of Pd-O and Pd-O₂ species can deactivate the surface of the catalyst in NO oxidation and NO₂ dissociation reactions (Olsson & Fridell 2002b). In NO₂ storage reactions the participation of active oxygen species is significant (Lietti et al. 2001).

Olsson & Fridell (2002b) noticed in their XPS studies that more PtO₂ was formed on the Pt/BaO/Al₂O₃ catalyst than on the Pt/Al₂O₃ catalyst. They explained this effect by the fact that Al₂O₃ is an acidic support material which receives electrons from platinum, and thus the electron density in Pt decreases. During oxidation platinum donates electrons to oxygen. BaO is a more alkaline compound than alumina. When BaO is added to the Pt/Al₂O₃ catalyst, it favours the oxidation of platinum (Olsson & Fridell 2002b). In our case, Pd particles on Al₂O₃ or on BaO/Al₂O₃ are quite large (6-10 nm) for the electron transfer between Pd and Al₂O₃ or BaO/Al₂O₃. However, more studies are needed to clarify this effect.

This study revealed that the oxidised form of barium (BaO) consumed less oxygen from the feedstream than the Pd/Al₂O₃ catalyst. For the Pd/BaO/Al₂O₃ catalyst, however, the maximum amount of water formed was high. According to Prinetto et al. (2001) this effect may be caused by the formation of BaCO₃ and Ba(OH)₂ adsorption sites on the oxidised surface during the reaction. The fresh, calcined catalyst contains BaCO₃, which in a dry environment leads to the formation of BaO. The presence of hydrogen leads to the formation of Ba(OH)₂. Lietti et al. (2001) reported that NOₓ storage occurs primarily at BaO, then at Ba(OH)₂, and finally at BaCO₃. However, during the NOₓ storing process for nitrates or nitrites over the last two mentioned adsorption sites it is accompanied by the release of CO₂ and H₂O. The displacement of surface carbonate species by NOₓ is likely due to the fact that CO₂ is less acidic than NOₓ species. (Nova et al. 2002)

5.5 Effect of BaO addition order and ageing on NO reduction

The effects of the BaO addition order on the fresh and aged Pd-BaO-OSC/Al₂O₃ were studied. The Pd/(Al₂O₃-OSC-La₂O₃) catalyst was used as the reference catalyst, even though the support material contained La₂O₃ [Paper V]. The model reaction CO + NO was used for comparing the catalytic properties such as activity and selectivity to N₂ and N₂O. A FT-IR gas analyser was used to follow the gaseous reaction products as a function of temperature. CO chemisorption and N₂ physisorption analyses were also done over fresh and aged catalysts. These results are summarised in Table 15. A dynamic OSC technique was used to detect the oxygen availability for redox processes (see Figures 19 and 20). In addition, the effect of thermal ageing treatment was studied by XRD (see Figure 21).
Table 15. BET surface areas and CO chemisorption measurements of the fresh and aged Pd/(Al₂O₃-OSC-La₂O₃), Pd/(BaO-OSC)/Al₂O₃, (Pd-BaO-OSC)/Al₂O₃, and (BaO-Pd-OSC)/Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd/(Al₂O₃-OSC-La₂O₃)</th>
<th>Pd/(BaO-OSC)/Al₂O₃</th>
<th>(Pd-BaO-OSC)/Al₂O₃</th>
<th>(BaO-Pd-OSC)/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis results</td>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
<td>Aged</td>
</tr>
<tr>
<td>BET-surface area [m²/g]</td>
<td>75</td>
<td>30</td>
<td>139</td>
<td>54</td>
</tr>
<tr>
<td>Particle size of Pd [nm]</td>
<td>5</td>
<td>377</td>
<td>3</td>
<td>negative</td>
</tr>
<tr>
<td>Dispersion value [%]²</td>
<td>23</td>
<td>&lt;2</td>
<td>34</td>
<td>negative</td>
</tr>
</tbody>
</table>

¹ Reliable calculation of the Pd size was impossible due to enormous growth of particle size during ageing.
² The CO dispersion values for the fresh catalysts are probably too high because CO is also adsorbed on ceria.

The results of the characterization techniques indicate that the difference between the fresh and aged catalysts is apparent. This effect was expected due to high temperatures used during the ageing process.

Comparing the results of fresh catalysts it can be observed that the addition of BaO has increased slightly the dispersion values of Pd. The BaO addition did not have a significant effect on the particle size. The reason for almost a twofold higher BET-surface area (see Table 15) could be due to fact that the content of alumina is higher for the barium-containing catalyst than for the Pd/(Al₂O₃-OSC-La₂O₃) catalysts, as can be seen in Table 6. However, even if the surface area is an important parameter under dynamic conditions (Boaro et al. 2003), it does not totally explain why, in our study, the presence of barium on the fresh catalysts has a positive effect on the oxygen storage capacity (OSC) at 400°C and 600°C (see Fig. 19). Instead, at 700°C only small differences were observed between the studied catalysts. This provides a clue about the structural changes due to thermal ageing or PdO/Pd transformation mentioned in Chapter 3.1.2 (Farrauto et al. 1992).

It should also be noted that in the case of the fresh Pd/(Al₂O₃-OSC-La₂O₃) catalyst, the dynamic oxygen storage capacity was lower at 400°C and 600°C than over the fresh (Pd+OSC)/Al₂O₃ catalyst. However, at 700°C the dynamic oxygen storage capacity was almost the same as in the case of the Pd/(OSC+Al₂O₃) catalyst (see Figure 15). This was interesting even if in the latter case the amount of OSC was lower than in the Pd/(Al₂O₃-OSC-La₂O₃) catalyst (see Table 6). Therefore, the conclusion can be withdrawn that La₂O₃ inhibits the capability to store oxygen.
Fig. 19. Dynamic oxygen storage for the fresh catalysts: defined as the volume of O\textsubscript{2} in the washcoat for Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}), Pd/(BaO-OSC)/Al\textsubscript{2}O\textsubscript{3}, (Pd-BaO-OSC)/Al\textsubscript{2}O\textsubscript{3}, and (BaO-Pd-OSC)/Al\textsubscript{2}O\textsubscript{3} catalysts.

According to our results, the particle size of Pd increased after ageing, as expected, and the dispersion values decreased. From Table 15, it can be calculated that the decrease in specific surface area was similar for the aged Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst and the BaO-containing catalyst. The loss of surface area was expected due to a high ageing temperature. For the aged catalysts, the oxygen storage capacity was lower for the BaO-containing catalyst than for the catalyst without BaO at 400°C (see Figure 20). This effect is probably due to a lower OSC content in the BaO-containing catalysts than in the OSC catalyst stabilised by La\textsubscript{2}O\textsubscript{3}.

When comparing the oxygen storage capacity results for the aged catalysts (in Figure 20) an interesting phenomenon occurs when temperature is increased from 400°C to 600°C and 700°C. At higher temperatures the oxygen storage capacity was much higher than at 400°C. The same effect is observed also in the case of aged Pd/(OSC+Al\textsubscript{2}O\textsubscript{3}) and (Pd+OSC)/Al\textsubscript{2}O\textsubscript{3} catalysts in Figure 15. Instead, the oxygen storage capacity for the aged Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst at 600°C was even higher than it was for the fresh Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst (see Fig. 19). Thus, for the aged Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst, the ageing process had a positive effect probably due to the sintering of the active particles i.e. the particle size of Pd is increased high enough. For the aged Pd/(OSC+Al\textsubscript{2}O\textsubscript{3}) and (Pd+OSC)/Al\textsubscript{2}O\textsubscript{3} catalysts the particle size is smaller (Table 12) than for the aged Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst (Table 15). Meanwhile, for the aged (BaO-Pd-OSC)/Al\textsubscript{2}O\textsubscript{3} catalyst, the oxygen storage capacity at 600°C and 700°C was the worst compared to the other studied catalysts after ageing.

When comparing the dynamic oxygen storage capacities of the aged Pd/(OSC+Al\textsubscript{2}O\textsubscript{3}) catalyst (Fig. 15) and the aged Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst (Fig. 20), it can be observed that the higher OSC content on the Pd/(Al\textsubscript{2}O\textsubscript{3}-OSC-La\textsubscript{2}O\textsubscript{3}) catalyst did not affect the result this time either. It seems that also in this case La\textsubscript{2}O\textsubscript{3} lowers the dynamic oxygen storage capacity, which explains why there were not great differences between
the results. These are interesting phenomena and more studies are needed to find explanations.

Fig. 20. Dynamic oxygen storage for the aged catalysts: defined as the volume of O₂ in the washcoat for Pd/(Al₂O₃-OSC-La₂O₃), Pd/(BaO-OSC)/Al₂O₃, (Pd-BaO-OSC)/Al₂O₃, and (BaO-Pd-OSC)/Al₂O₃ catalysts.

From Table 9 it can be seen that during the activity measurement the studied reaction CO+NO was occurring in rich conditions (S = 0.09). In the case of the fresh catalysts, the catalysts were behaving similarly to those in Figure 16 except that the NO and CO conversions below 100°C were quite poor compared to the Pd/OSC/Al₂O₃-based catalysts. Therefore, both BaO and La₂O₃ retard the NO and CO adsorption and diffusion on the catalyst surface at low temperatures due to the lack of active Pd⁰ sites for CO adsorption.

It was observed that catalytic activity of fresh catalysts was dependent on the addition order of BaO on the catalyst support. However, the catalyst performance (activity and selectivity) between these BaO-containing catalysts is relatively small and most likely due to differences in the Pd-BaO-OSC interactions.

As can be seen in Table 6, the OSC content on the Pd/(Al₂O₃-OSC-La₂O₃) catalyst was higher than on the Pd/OSC/Al₂O₃-based catalysts [Paper III]. Therefore, it was assumed that the CO conversion followed the same trend or was even higher than in the case of Pd/OSC/Al₂O₃-based catalysts at around 300°C [Papers II and III]. However, the CO conversion on the Pd/(Al₂O₃-OSC-La₂O₃) catalyst acted in the same way as it did over the Ba-containing catalysts.

From Table 16 it can be observed that for the barium-containing catalysts the difference between the light-off temperatures of the fresh and aged catalysts was higher than for the catalyst without barium. Barium (normally ~20wt-%) is a well-known stabiliser due to its ability to retain large surface areas of alumina effectively because the added cations occupying the surface sites or bulk sites prevent atomic diffusion (surface diffusion and bulk diffusion), which generates the α phase transformation from the γ-, δ-, and θ-alumina phases. (Arai & Machida 1996 and Liotta et al. 2003)
It seems that in the case of the barium-containing catalysts, which have a lower content of alumina than the Pd/(Al₂O₃-OSC-La₂O₃) catalysts (see Table 6), the ability to stabilise alumina was not good enough. However, this can also be due to the low barium content. In addition, small differences can be observed between the light-off temperatures of the barium-containing catalysts.

Table 16. The light-off temperature\(^a\) of NO for the fresh and aged Pd/(Al₂O₃-OSC-La₂O₃), Pd/(BaO-OSC)/Al₂O₃, (Pd-BaO-OSC)/Al₂O₃, and (BaO-Pd-OSC)/Al₂O₃. \(\Delta T^{50}\) refers to the difference between the light-off temperatures.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(T^{50}) (NO) [°C]</th>
<th>(\Delta T^{50}) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/(Al₂O₃-OSC-La₂O₃)</td>
<td>136</td>
<td>125</td>
</tr>
<tr>
<td>Pd/(BaO-OSC)/Al₂O₃</td>
<td>124</td>
<td>136</td>
</tr>
<tr>
<td>(Pd-BaO-OSC)/Al₂O₃</td>
<td>103</td>
<td>155</td>
</tr>
<tr>
<td>(BaO-Pd-OSC)/Al₂O₃</td>
<td>113</td>
<td>142</td>
</tr>
</tbody>
</table>

\(^a\) The temperature of 50 % conversion of NO.

Our XRD results revealed the ageing-induced solid-solid phase transformation. The fresh catalyst contains amorphous material and the crystallite sizes were small, and, therefore, no clear diffraction peaks were observed (see Fig. 21). Due to the sufficient temperature during the ageing process, the oxide phases i.e. Al₂O₃ (alumina), CeAlO₃, and LaAlO₃ were found according to X-ray diffraction data (PDF-2 Diffraction Database). Pd and BaO were well dispersed on the catalyst surface and/or the crystallite sizes were small, and, therefore, they were not observed by XRD.

Our study revealed that the formation of LaAlO₃ occurs after the ageing of the catalysts for the Pd/(Al₂O₃-OSC-La₂O₃) catalyst, which is both lanthana-rich and contains \(\gamma\)-Al₂O₃ (Bogdanchikova et al. 1998). The peak of LaAlO₃ is closely related to the phase transformation of Al₂O₃ (Ozawa & Nishio 2004). According to Hietikko et al. (2004) the presence of the LaAlO₃ phase at high temperatures prevents deactivation between alumina and the catalytically active noble metal and increases the stability of the \(\gamma\)-Al₂O₃ phase.

For the barium-containing catalysts, the temperature or ageing time was high enough for the formation of the CeAlO₃ phase (see Fig. 21). This means that the surface area remains high and no formation of low surface area \(\alpha\)-Al₂O₃ takes place. In our case the crystal structure for Al₂O₃ is orthorhombic, which according to Bhattacharya et al. (2004), refers to the \(\kappa\)-Al₂O₃ metastable phase formed at around 900°C. Based on our XRD results, our CeO₂-ZrO₂-binary system is tetragonal (Kašpar et al. 1999).

As can be observed in Figure 21, the LaAlO₃ peak for the Pd/(Al₂O₃-OSC-La₂O₃) catalyst is stronger than the CeAlO₃ peak for the other studied catalysts. This could explain why for the Pd/(Al₂O₃-OSC-La₂O₃) catalyst, the specific surface area loss is 60 %, which for the barium containing catalysts, is 61 %, 62 % and 65 % (for the Pd/(BaO-OSC)/Al₂O₃, (Pd-BaO-OSC)/Al₂O₃, and (BaO-Pd-OSC)/Al₂O₃ catalysts, respectively).

Therefore, the aluminates (LaAlO₃ and CeAlO₃) and alumina oxygen layers are similar in terms of anion packing (Arai & Machida 1996), which results in a strong
interaction that inhibits crystal growth and provides a higher thermal stability (Di Monte & Kašpar 2005).

Fig. 21. X-Ray powder diffraction data for the (1) fresh Pd/(Al₂O₃-OSC-La₂O₃), (2) aged Pd/(Al₂O₃-OSC-La₂O₃), (3) aged Pd/(BaO-OSC)/Al₂O₃, (4) aged (Pd-BaO-OSC)/Al₂O₃, and (5) aged (BaO-Pd-OSC)/Al₂O₃ catalysts. A = LaAlO₃, B = Ce₉.₇Zr₂.₃O₂₅, C = La-Zr-O₂, D = Al₂O₃, and E = CeAlO₃ (OSC refers to Ce₁₋ₓZrxO₂) (Paper V).
6 Conclusions

Four principal goals have been dominant throughout the course of this work and the writing of this thesis. These were: (1) the behaviour of NO reduction and CO as well as C₂H₄ oxidation over Pd/alumina-based catalysts, (2) the effect of OSC material and BaO on the NO reduction, (3) the effect of the addition order of OSC material and BaO during the preparation procedure and finally, (4) the effect of ageing on the catalytic activity, selectivity and stability of the catalysts.

First, it was demonstrated that the CO and hydrocarbon oxidation and NO reduction reactions over the Pd/Al₂O₃-based catalyst behave differently. NO reduction and CO and hydrocarbon oxidation reactions were dependent on the reaction conditions and temperatures. It was discovered that the amount of intermediates, such as nitrates, NCO, acetate, and formates depends on the reaction conditions (rich, stoichiometric, and lean). Nitrate and nitrite species, for example, are typically found at low temperatures and are responsible for the formation of unwanted N₂O. At higher temperatures and especially at stoichiometric and lean conditions, the surface reactions occur fast enough to form active sites for N₂.

Secondly, the effect of OSC and BaO on NO reduction was studied separately. In the case of OSC material, it was observed that the OSC material has an effect on NO reduction as well as on CO and C₂H₄ oxidation. The reason why the OSC material improved the activity of these reactions is that the OSC material provides oxygen for oxidation reactions, while the reduced sites provide adsorption sites for NO. When oxygen is present in the feedstream, the promoting effect of OSC material is observed only at low temperatures. In the case of a reaction gas mixture without oxygen, the promoting effect can be observed in a wider temperature window.

Then, in the case of BaO, it was observed that BaO has a positive effect on NO reduction as well as CO and C₂H₄ oxidation especially in rich conditions. One explanation for this phenomenon could be that barium oxide seems to prevent the self-poisoning of the reaction by NO or by ethene-derived species (CO, carbonaceous products). This means that neither NO nor CO may be adsorbed on the Pd metal sites because of the blocking effect of other components. Barium oxide offers a site for CO to form BaCO₃. Therefore, on the barium-containing catalyst there are more active sites for CO and C₂H₄ adsorption.
Thirdly, the effects of addition order of OSC and BaO on the catalyst was studied separately. It was shown that these have an effect on NO reduction. First, on the fresh Pd/Al₂O₃ catalyst it was observed that the addition order of OSC on the catalyst has no influence on catalyst performance. However, the situation changes when the catalysts were aged. Ageing has an effect on catalytic activity especially on NO adsorption and dissociation reactions at low temperatures. It seems that a stronger Pd-OSC interaction was formed when Pd was added into the OSC material than when it was added into the mixture of alumina and the OSC material. Strong Pd-OSC interaction forms oxygen vacancies for further reactions.

Then, the effect of the BaO addition order on the Pd/OSC/Al₂O₃-based catalyst was found to be insignificant, especially, after the ageing process. A comparison of catalytic activities and selectivities for the fresh Pd-BaO-OSC-containing catalysts revealed that the NO adsorption and dissociation reactions occur a bit faster when the BaO and Pd impregnation into the catalyst material was done during the last production step. This means that Pd and BaO are on the top layer of the catalyst.

Furthermore, it was observed that the effect of the RAHLAB ageing was that the catalyst lost its activity, stability, and selectivity. Upon ageing the number of active sites decreased due to thermal deactivation, which was caused by sintering of the Pd particles. This effect was seen as a small decrease in catalytic activity and selectivity. At low temperatures, the smaller Pd particle sizes have an effect on the oxygen storage capacity. The formation of LaAlO₃ and CeAlO₃ was observed on the XRD-results. The presence of these compounds indicates that both La₂O₃ and OSC retard the alumina transformation to α phase. Thus LaAlO₃ and CeAlO₃ compounds keep alumina in more active γ-, δ-, and θ-alumina phases for catalysis.

In this thesis, scientific experimental methods and information gathered from the literature have been used to ascertain that the effect of OSC and BaO on Pd/Al₂O₃-based catalysts on NO reduction is significant. One future challenge that requires a further study is to determine why less water is formed over an OSC-containing catalyst than over a Pd/Al₂O₃ catalyst. In addition, it would be interesting to know why barium addition on the Pd/OSC/Al₂O₃ catalyst has a positive effect on the oxygen storage capacity (OSC) at 400°C and 600°C but no longer at 700°C. Finally, further studies, e.g. in situ DRIFT studies, are recommended to better understand and explain surface phenomena during the catalytic reactions.
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234. Laitinen, Risto (2006) Improvement of weld HAZ toughness at low heat input by controlling the distribution of M-A constituents


Tanja Kolli

Pd/Al₂O₃ -BASED AUTÔMÔVİTE EXHAUST GAS CATALYSTS

THE EFFECT OF BaO AND OSC MATERIAL ON NOₓ REDUCTION

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