Bimetallic Palladium Catalysts for Methane Combustion in Gas Turbines

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Front cover: Catalytic monolith during combustion
To my family
Abstract

Catalytic combustion is a promising combustion technology for gas turbines, which results in ultra low emission levels of nitrogen oxides ($\text{NO}_x$), carbon monoxide ($\text{CO}$) and unburned hydrocarbons (UHC). Due to the low temperature achieved in catalytic combustion almost no thermal $\text{NO}_x$ is formed. This thesis is concentrated on the first stage in a catalytic combustion chamber, i.e. the ignition catalyst. The catalyst used for this application is often a supported palladium-based catalyst due to its excellent activity for methane combustion. However, this type of catalyst has a serious drawback; the methane conversion decreases severely with time during operation. The unstable activity will result in increasing difficulties to ignite the fuel. The parameters that govern the poor stability and other features of the palladium catalysts are discussed in the thesis.

The objective of the work is to improve the catalytic performance of supported palladium catalysts, with focus on stabilising the methane conversion. A large number of different bimetallic palladium catalysts have been evaluated, where the influence of co-metals, molar ratio and support material is addressed. Results from the activity tests of methane combustion showed that it is possible to stabilise the activity by adding certain co-metals into the palladium catalyst. An extensive characterisation study has been carried out on the various bimetallic catalysts in order to gain a better understanding of how their morphology and physicochemical properties determine the various patterns of combustion behaviour.

The environment inside a gas turbine combustor is very harsh for a catalyst. Since the stability of the catalyst is of great importance for ignition catalysts, it is essential to evaluate the risk of deactivation. In this work special emphasis has been given to thermal deactivation, water inhibition and sulphur poisoning. It was found that a bimetallic Pd-Pt catalyst is significantly more tolerant to the various deactivation processes investigated than the monometallic palladium catalyst.

Finally, the influence of pressure on the catalytic performance has been investigated. The catalysts were assessed at more realistic conditions for gas turbines, in a high-pressure test facility with 100 kW fuel power.

Keywords: activity, bimetal, catalytic combustion, DRIFTS, EDS, gas turbine, methane, morphology, palladium, platinum, pressure, PXRD, stability, TEM, TPO, XPS
Sammanfattning

Katalytisk förbränning är en lovande förbrännningsteknik i gasturbinsammanhang på grund av att förbränningen ger mycket låga halter av kväveoxider (NOₓ), kolmonoxid (CO) och oförbrända kolväten. Tack vare den låga förbränningstemperaturen i en katalytisk brännkammare bildas minimalt med termiskt NOₓ. Denna avhandling fokuserar på det första steget i en katalytisk brännkammare, den så kallade tändningskatalysatorn. Palladiumbaserade katalysatorer används ofta för den här tillämpningen, eftersom de har en utmärkt aktivitet för metanförbränning. Tyvärr har denna typ av katalysator en stor nackdel; metanomsättningen minskar avsevärt med tiden. Den instabila aktiviteten resulterar i att bränslet blir allt svårare att tända. Anledningen till den dåliga stabiliteten och andra egenskaper hos palladiumkatalysatorerna diskuteras i denna avhandling.

Målet med arbetet är att förbättra palladiumkatalysatorernas egenskaper, med fokus på att stabilisera aktiviteten. Ett flertal bimetalliska palladiumkatalysatorer har studerats, med särskild hänsyn till inverkan av olika tillsatsmetaller, molförhållanden och bärarmaterial. Resultatet från denna studie visar att det är möjligt att stabilisera omsättningen genom att tillsätta vissa metaller till palladiumkatalysatorn. De bimetalliska katalysatorerna har genomgått en omfattande karakterisering för att kunna förstå hur katalysatorernas morfologi påverkar deras förbrännningsegenskaper.


I den sista delen av avhandlingen har tryckets inverkan på katalysatorerna undersöks. Katalysatorerna har studerats under mer realistiska förhållanden för gasturbiner, d.v.s. med höga tryck, i en pilotanläggning med 100 kW bränslekapacitet.

Nyckelord: aktivitet, bimetall, DRIFTS, EDS, gasturbin, katalytisk förbränning, metan, morfologi, palladium, platina, PXRD, TEM, TPO, tryck, stabilitet
Publications referred to in the thesis

The work presented in this thesis is based on the following publications, referred to in the text using Roman numerals. The papers are appended at the end of the thesis.

I. *Influence of co-metals on bimetallic palladium catalysts for methane combustion*

II. *Influence of molar ratio on Pd-Pt catalysts for methane combustion*

III. *Catalytic combustion of methane over bimetallic Pd-Pt catalysts: The influence of support materials*

IV. *Characterisation and microstructure of Pd and bimetallic Pd-Pt catalysts during methane oxidation*

V. *Stability of palladium-based catalysts during catalytic combustion of methane: The influence of water*

VI. *Supported palladium-platinum catalysts for methane combustion at high pressure*
Contributions to the papers

I. I am the main author of Paper I, however, significantly assisted by Dr. Kjell Jansson at the Department of Inorganic Chemistry, University of Stockholm, who performed and wrote the text section related to the PXRD and the TEM/EDS analyses. The rest of the experimental work was a joint effort between myself and Nils Iverlund, under my supervision.

II. I am the main author of Paper II, but the interpretation of the results was a shared responsibility between the authors. The TEM/EDS and PXRD analyses were performed by Dr. Kjell Jansson. The XPS evaluation was conducted by Professor José L.G. Fierro at the Catalysis and Petrochemistry Institute (ICP) in Madrid. I had the responsibility for the catalyst preparation, activity measurements and the rest of the characterisation, except for ICP and CO-chemisorption analyses.

III. I am the main author of Paper III. I had the responsibility for preparation of the catalysts, the activity measurements and characterisations, except ICP and CO-chemisorption analyses. The in-situ XRD study was conducted at the University of Udine by me, in close cooperation with Dr. Sara Colussi and Prof. Alessandro Trovarelli.

IV. I am the main author of Paper IV, but the interpretation of the results was a shared responsibility between the authors. The TEM/EDS and PXRD analyses were conducted by Dr. Kjell Jansson, as well as the XPS evaluation. I had the responsibility for the preparation of the catalysts, activity measurements and the remaining characterisation analyses, except for ICP and CO-chemisorption analyses.

V. I am the main author of Paper V. I had the responsibility for preparation of the catalysts, activity measurements and characterisations, except ICP and CO-chemisorption analyses. The DRIFTS study was carried out at Yale University by me, in close cooperation with William Schwartz and Professor Lisa Pfefferle.

VI. I am the main author of Paper VI. I had the responsibility for the sample preparation, lab-scale activity measurements and characterisation, except for the
ICP analyses. The experiments in the high-pressure test facility were carried out in close cooperation between me and the researchers at KTH – Energy Technology, division of Heat and Power Technology.
Other publications

Other publications and conference contributions on catalytic combustion not included in this thesis.


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1
Introduction

Setting the scene

One of the more common approaches for producing electricity is through the use of gas turbines. The primary fuel for stationary gas turbines is natural gas, whose main combustible component is methane. A large share of the pollution released into the air arises from different kinds of combustion processes, which therefore also include pollutants from gas turbines. The effects of these emissions were first noticed in the 1950’s, when phenomena such as smog and acid rain became conspicuous. The awareness of these effects has resulted in various numerous regulations concerning the allowed pollution levels. As the electricity demand is increasing and thereby the amounts of pollution, the regulations become more stringent every year. Therefore, it has become important for the gas turbine manufacturers to develop combustion techniques that comply with the requested emission levels, at the same time being operation and cost efficient.

Catalytic combustion is a very promising combustion technology, which does not require expensive clean-up exhaust systems for reaching ultra low levels of nitrogen oxides (NOx), carbon monoxide (CO) and unburned hydrocarbons (UHC). Other advantages are a stable combustion of the fuel outside the flammability limits and less noisy operation. This combustion technology has been developed during decades and has just recently been commercialised.

One of the main problems with catalytic combustion has been to get the catalysts to ignite the fuel at the compressor discharge temperature of around 350 - 450 °C. For that reason a very active catalyst is necessary. Palladium-based catalysts have been the catalysts in focus due to their excellent combustion activity for methane. However, recent reports have shown that these catalysts are severely deactivated with time. Since palladium-based catalysts initially have a high activity it is desirable to stabilise the activity. One way to achieve this is to include an extra metal into the palladium catalyst, forming a bimetallic catalyst.
1.2 Scope of the thesis

The objective of the work presented in this thesis has been to develop efficient ignition catalysts for catalytic gas turbine combustors. Focus has been on palladium-based catalysts and how to improve the unstable activity. A large number of different bimetallic palladium catalysts have been investigated with particular emphasis on the stability and the level of activity. To gain better understanding of the discrepancies in their catalytic properties, morphology studies have been carried out on both as-prepared and used materials. Special attention has also been given to various deactivation processes.

Additionally, the catalysts have been tested in a high-pressure test facility, which works under more realistic gas turbine conditions than atmospheric lab-scale reactors. The influence of pressure on the methane conversion has been investigated.

The major part of work was conducted at the Department of Chemical Engineering and Technology at the Royal Institute of Technology (KTH), Sweden, and minor parts at KTH – Energy Technology, division of Heat and Power, University of Udine and Yale University.
The first patent for a combustion turbine was issued to the Englishman John Barber in 1791. Since then, gas turbines have been used for a great number of applications. Today, gas turbines are common in airplanes for providing the thrust in a jet engine and, as this thesis will focus on, for heat and power generation in stationary applications. The development of turbines is focused on raising the efficiency and, at the same time, decreasing the harmful emissions produced during operation. A brief introduction to gas turbines and their environmental impact will follow, as it is necessary for understanding the background to the thesis.

2.1 Gas turbine components

A gas turbine in its simplest form consists of three main components, i.e. a compressor, a combustion chamber and a turbine [1]. They are connected as illustrated in Figure 2.1. The first component in a gas turbine is a compressor, which increases the pressure of air from atmospheric to 5 - 30 bar, depending on the type of gas turbine.

When air is compressed, the temperature is simultaneously increased. The compressor discharge temperature is dependent on the pressure ratio over the compressor, and may therefore vary between 350 and 450 °C. This temperature is in some cases increased further by exchanging the heat from the turbine’s warm exhaust gas.

If the compressed air is expanded directly in the turbine, and if there are no losses in any of the components, the power developed by the gas turbine would equal the power supplied to the compressor [1]. Consequently, there would not be any net power produced in the gas turbine. If the temperature of the air is extensively increased prior expansion, the power development is on the other hand significantly improved.
Therefore, the second component in a gas turbine is a combustion chamber, also called a combustor. The compressed air is fed into the combustion chamber, where it is mixed with fuel. One of the more common fuels used in stationary gas turbines is natural gas, whose main combustible component is methane. Natural gas has the advantage of cleaner burning than other fossil fuels, such as oil and coal; it produces less CO\(_2\), which is a greenhouse gas, per unit energy released [2].

The conventional way of combusting the fuel is homogeneously in the gas phase by means of a flame. The combustion generates heat, which is taken up by the gas. As seen in the flowsheet in Figure 2.1, the temperature is raised from 350 - 450 °C before the combustion chamber to above 1500 °C at the exit. This high temperature arises due to the combustion having to occur within the flammability limits of the fuel. However, the temperature may vary with the type of gas turbine. Since the outlet temperature from the combustion chamber often is too high for the turbine materials, the gas has to be cooled prior entering the turbine. The hot gas is therefore mixed with air, which has bypassed the combustion chamber.

The turbine itself consists of blades connected to a shaft, which are cooled by complex systems. The gas, which has reached the desirable pressure and temperature, is expanded through the turbine. Electricity may be extracted from the turbine via a generator. Thereafter, the gas is led either directly out to the atmosphere or via a heat exchanger in order to heat the air before entering the combustion chamber. The levels of pressure and temperature influence the efficiency of the gas turbine. Therefore, the gas turbine manufacturers are aiming for as high values of these two parameters as possible.
possible. Nevertheless, due to material restrictions these levels are limited. Many different types of gas turbines may be found on the market, with a large variety of temperatures and pressures. However, the description of these gas turbines is beyond the scope of this thesis.

2.2 Environmental issues

Even though the exhaust gas from gas turbines should consist only of oxygen-depleted air, carbon dioxide and water when using natural gas, the exhaust gas also comprises many different pollutants. The main pollutants from a gas turbine are formed during combustion, e.g. NO\textsubscript{x}, CO and unburned hydrocarbons (UHC). CO and UHC occur primarily due to incomplete combustion. Much focus today is given to NO\textsubscript{x} formation, since NO\textsubscript{x} leads to acid rain and photochemical smog etc. Acid rain has negative impact on the environment, by causing forest depletion, dissolution of heavy metals into the water, killing off insects and aquatic life forms etc. Photochemical smog also affects human health and the terrestrial and the aquatic ecosystems negatively. In order to reduce the NO\textsubscript{x} emissions, regulations concerning the allowed pollution levels are becoming more stringent every year. In California, the values for the NO\textsubscript{x} limits have been reduced to single digit ppm levels, but vary depending on population density, source of emissions, location and so on. On-going research concerning gas turbines is focusing on meeting the ever more stringent pollution limits, while maintaining existing levels of reliability and keeping costs down.

2.3.1 NO\textsubscript{x} mechanisms

NO\textsubscript{x} may arise from four different mechanisms, i.e. thermal mechanism, prompt mechanism, nitrous oxide mechanism and fuel mechanism [3]. Thermal NO\textsubscript{x} is formed in oxidation of atmospheric nitrogen by radical mechanisms, as proposed by Zeldovich [4].

\[
\begin{align*}
O + N_2 &\leftrightarrow NO + N \\
N + O_2 &\leftrightarrow NO + O
\end{align*}
\]

The concentration of thermal NO\textsubscript{x} depends exponentially on temperature; at 1500 °C the NO\textsubscript{x} concentration may be as high as 1500 ppm [5]. As mentioned above, most gas turbines today employ some kind of flame combustion of natural gas for energy generation. Since the operating flame temperature often is above 1500 °C, thermal
NO\textsubscript{x} is thermodynamically favoured [6]. Hence, thermal NO\textsubscript{x} is an important environmental issue in conventional combustors.

Prompt NO\textsubscript{x} arises when the combustion is running under fuel-rich conditions (more fuel than the stoichiometric reaction requires). The atmospheric nitrogen reacts with CH radicals, derived from the fuel. Unlike thermal NO\textsubscript{x}, prompt NO\textsubscript{x} may be formed at temperatures much below 1350 °C.

The nitrous oxide (N\textsubscript{2}O) mechanism is analogous with the thermal mechanism in that oxygen atoms attack atmospheric nitrogen. Instead of directly producing NO\textsubscript{x}, this mechanism produces N\textsubscript{2}O in the first step. N\textsubscript{2}O may then react with another oxygen atom to produce NO. This mechanism may occur at lower temperatures than the thermal mechanism [3].

As the name indicates, fuel NO\textsubscript{x} arises when the nitrogen components in the fuel react with oxygen. Since natural gas contains very small amounts of nitrogen compounds, fuel NO\textsubscript{x} is a minute problem for this fuel [5].

2.3.2 Technologies for reducing NO\textsubscript{x} emissions

Different techniques have been developed for controlling NO\textsubscript{x} formation. The NO\textsubscript{x} problem may be tackled either primarily during the combustion or secondarily by exhaust treatment. A large variety of techniques have been developed and the most common will briefly be presented below. More information regarding these techniques may be found elsewhere [1,3].

By changing the operating conditions during combustion, the NO\textsubscript{x} emissions may be decreased. A common method is to introduce water or steam into the combustion chamber. The purpose of the water is to quench the radicals and lower the flame temperature, resulting in less thermal NO\textsubscript{x}. The higher the water content, the lower the thermal NO\textsubscript{x}. Unfortunately, when the water content increases the formation of CO and UHC increases as well. Furthermore, this technique may be a problem when access to water is inadequate, as it is in many places in the world, or if the ambient temperature is below the freezing point. The water also has to contain low amounts of impurities in order to minimise corrosion. Therefore, many designers of gas turbines prefer a dry method for reducing NO\textsubscript{x} emissions.

By using either fuel rich or lean conditions, the flame temperature may be reduced. One of the dry combustion methods uses both conditions in two separate stages, i.e.
the concept of rich burn/ quick quench/ lean burn. The first stage operates under rich conditions. Thereafter, the combustion reaction is quenched and the hot gas is diluted with air in the second stage. A more common dry method only utilises fuel-lean conditions in which the air and the fuel are intimately mixed prior to entering the combustion chamber. The disadvantage with this method is that it is difficult to maintain stable combustion.

When considering exhaust after-treatment, selective catalytic reduction (SCR) is the most common technique. This technique may also be used together with the primary techniques discussed above. The principle of this method is to reduce NO\textsubscript{x} to N\textsubscript{2} by means of ammonia over a catalyst. However, this system is very complex and expensive.

One of the more promising methods for minimising NO\textsubscript{x} is catalytic combustion. In this method, the combustion reaction takes place on the surface of a catalyst. The catalyst helps the combustion reaction to occur at a lower temperature than would be possible for conventional flame combustion. Since the crucial temperature for the thermal NO\textsubscript{x} formation is not necessarily reached with catalytic combustion, NO\textsubscript{x} levels below 3 ppm may be achieved. Due to the low NO\textsubscript{x} value, no after-treatment of the exhaust gas is necessary when using catalytic combustion. Furthermore, ultra-low emissions of CO and UHC are achieved. This combustion technique will be discussed further in the next chapter.
3 Catalytic combustion in gas turbine applications

The theory of catalytic combustion has been known since the beginning of the 19th century, when Sir Humphry Davy discovered that a platinum wire could induce combustion without a flame of a flammable mixture. Different applications of catalytic combustion have been introduced since then, for example abatement of volatile organic compounds (VOC), small-scale heaters, hair dryers etc. William Pfefferle was the first to propose catalytic combustion for gas turbines in the early seventies [7]. Since then, an increasing number of publications have been published in this field [6,8-15]. As it becomes difficult to reduce the pollution to the required levels, both catalytic companies and gas turbine manufacturers have shown increasing interest in catalytic combustion.

3.1 Catalytic combustion

The basic principle of catalytic gas turbine combustors is to let the combustion reaction take place heterogeneously on or near the catalyst surface instead of in a flame. Flame-based combustion, on the other hand, occurs homogeneously in the gas phase via a range of radical reactions at higher temperatures. Despite the different combustion routes, the reaction products are the same. However, both of these reaction mechanisms are very complex and are not yet fully understood.

Figure 3.1. Picture of a working catalyst during combustion
For the combustion reaction to take place, the temperature must be above a certain value in order to exceed the activation energy. Catalysts are able to reduce the activation energy to levels that are not attainable for flame combustion. As a result, it is possible to combust the fuel over a catalyst at a much lower temperature compared to the conventional flame-based technique. In addition, the catalyst achieves combustion of the fuel outside its flammability limits. Therefore, it is feasible to combust the fuel by catalytic combustion at temperatures below the threshold at which thermal NO\textsubscript{x} is formed. However, it is important to point out that the reduction in combustion temperature does not lead to a decrease in the efficiency of the gas turbine. The turbine inlet temperature largely determines the efficiency and is the same for both combustion techniques. The difference between the two techniques is that no by-pass air is necessary in the catalytic process for reducing the temperature prior to entering the turbine, as illustrated in Figure 3.2. Not only the kinetics affects the combustion rate over a catalyst, but other mechanisms such as the diffusion inside the catalyst pores and mass transport of reactants to the surface and/or products from the surface may affect the overall combustion rate.

### 3.1.1 Advantages with catalytic combustion

The main advantage of catalytic combustion is that it allows combustion at a temperature at which the formation of thermal NO\textsubscript{x} is avoided, and at the same time achieves ultra low emissions of CO and UHC. According to Catalytica Energy Systems, which has developed a catalytic combustor (Xonon Cool Combustion™) for a Kawasaki M1A-13X gas turbine, it is possible to limit the emissions of NO\textsubscript{x} to less than 3 ppm, without compromising the performance of the gas turbine [16]. Since the reduction of NO\textsubscript{x} is very efficient, no exhaust gas treatment is necessary. Catalytic combustion is one of few combustion techniques meeting the low emission limits stated by legislation e.g. in the US and Japan.

The cost for reducing NO\textsubscript{x} is clearly lower for the primary techniques, which include catalytic combustion, compared to the secondary techniques, such as SCR [17]. The disparity in cost is particularly large for small gas turbines.

Other advantages with catalytic combustion are the increased stability of combustion and the ability to combust fuels outside the flammability limits [10]. Additionally, the operation is less noisy and a more even radial temperature profile is obtained.
3.1.2 Requirements

A large number of gas turbines equipped with flame-based combustors are on the market today. If a catalytic combustor is implemented into the system, the operation conditions in the gas turbine are preferably not changed in order to maintain the high efficiency. Some requirements regarding the operation conditions must therefore be met before catalytic combustors can fully replace the conventional flame combustion techniques. Carroni et al. [18] have reviewed some demands, which are summarised in Table 3.1.

One of the more difficult requirements to fulfil is to ignite the fuel at the compressor discharge temperature. If this is not accomplished, the gas has to be preheated in order to reach a temperature at which it is ignited. Preheaters reduce the efficiency of the gas turbine and increase the emissions of NO$_x$. According to Ozawa et al. [19], the main source of NO$_x$ emitted from a catalytic combustor is simply from the preheaters. Hence, a very active catalyst is desirable in order to reduce the need for preheaters. The ignition may also be obstructed by variations in the ambient temperature, which reflect on the compressor discharge temperature.

The operator of the gas turbine will not be pleased by having to change the catalyst inside the combustion chamber too often, since it is a costly and complicated process. Consequently, the catalysts need to have a lifetime of at least 8000 h, but preferably longer. However, the catalysts may easily become deactivated due to the severe environment inside a gas turbine. The high temperature in the combustor may result in thermal degradation of the catalysts and it is therefore essential to have temperature-
Table 3.1. Requirements for a catalytic combustion chamber in gas turbines

<table>
<thead>
<tr>
<th>Issues</th>
<th>Demands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>350 – 450 °C</td>
</tr>
<tr>
<td>Exit temperature</td>
<td>1500 °C</td>
</tr>
<tr>
<td>Ambient condition variations</td>
<td>-25 – +40 °C</td>
</tr>
<tr>
<td>Thermal shocks</td>
<td>&gt; 500 °Cs⁻¹</td>
</tr>
<tr>
<td>Working life</td>
<td>&gt; 8000 h</td>
</tr>
<tr>
<td>Pressure</td>
<td>8 – 30 bar</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>&lt; 3 %</td>
</tr>
<tr>
<td>Mixedness</td>
<td>80 – 85 %</td>
</tr>
<tr>
<td>Multifuel capability</td>
<td>Natural gas / Oil</td>
</tr>
<tr>
<td>Size restrictions</td>
<td>Typically 300 mm length and 180 mm diameter</td>
</tr>
</tbody>
</table>

stable catalysts. This is especially crucial for the last part of the catalytic combustor, where the temperature reaches very high levels. Poisoning, where a substance, e.g. SO₂, blocks the active sites may also deactivate the catalysts. As small amounts of sulphur may be found in natural gas this process is also crucial. Various deactivation processes will be considered in more detail in Chapter 7.

A central difference between utilising catalysts in gas turbine combustors compared to other applications is that gas turbines operate at much higher pressure and flow velocity. All the same, only a few experimental studies concerning the pressure impact on the catalytic performance may be found in the literature. The pressure influence will be covered in more detail in Chapter 8.

Due to the high gas velocity used in gas turbines, there would be a large pressure drop over the catalysts if a packed bed arrangement was used. Since the pressure level is one of the more important parameters for the gas turbine performance, a pressure loss over the combustor would cause an expensive loss of efficiency in the gas turbine. To minimise the pressure drop, the catalysts in a catalytic gas turbine combustor have a monolith structure, also called a honeycomb structure. The monoliths will be discussed more in Section 3.3.

The size of the catalytic combustion chamber should preferably be the size of a conventional combustor. If this is the case, it will be easier to implement the catalytic
combustion chamber in an already existing gas turbine and less reconstruction is needed.

### 3.2 Catalytic combustor configurations

No single catalyst material is today able to work in the entire temperature range of a gas turbine combustor. Therefore, the combustor is divided into different segments according to the activity and the temperature stability of the catalysts. In general, a highly active catalyst is often less temperature stable, whereas a more thermally stable catalyst is less active.

Many different configurations of combustion chambers are suggested in the literature [14]. One is based on fully catalytic combustion, where the temperature is only increased by means of catalysts [20]. Since the catalysts have to stand temperatures as high as 1450 °C, material problems restrict this configuration.

Another common configuration reported in the literature is the hybrid design, in which a fraction of the fuel is first combusted catalytically, followed by a homogeneous combustion zone where the combustion is completed [17,21-23]. In Figure 3.3, the system is illustrated.

The catalyst section is divided into at least two different stages. The first stage is an ignition catalyst. As the name indicates, this catalyst ignites the gas at the compressor discharge temperature and increases the temperature of the gas to a value where the subsequent catalytic stage is able to ignite. If the catalyst is not active enough to ignite

![Figure 3.3. A schematic of a hybrid combustor, adapted from Thevenin [24].](image-url)
the fuel at the compressor discharge temperature, pre-heaters are needed which is not desirable. Therefore, a very active catalyst is preferable in this first stage.

The second stage has a more temperature-stable catalyst, such as a hexaaluminate, which brings the temperature up to the level necessary for initiating the following homogeneous combustion. The remaining fuel components will be combusted homogeneously in the last part of the combustion chamber.

The advantage with the hybrid configuration is that the catalysts will never be exposed to a temperature higher than 950 °C, and the thermal sintering and vaporisation issues will be of less importance [22].

3.3 Catalyst design

A combustion catalyst for gas turbine applications consists of three key components; the monolith increases the mechanical strength and stability, the washcoat brings a high surface area and the active component enables the heterogeneous combustion reaction. A combustion catalyst is schematically shown in Figure 3.4.

To minimise the pressure drop over the catalysts, the catalyst material is supported on a monolith. The monolith consists of a number of parallel channels through which the gas easily may pass with only a small loss in pressure. The catalyst material itself is coated onto the channel walls, in order to enable contact with the reacting gas. A range of various monolith structures may be found on the market, with different shapes and sizes of the channels [12]. The monolith may be fabricated either from ceramic materials, such as cordierite, or metallic materials, such as FeCrAlloy steel. Lately, metallic materials have been given more attention due to their high thermal conductivity and possibility of more sophisticated coating design. A common design is the passive channel structure, where only every second channel is coated with active material and the uncoated channels work as heat exchangers and cool the walls of the monolith [26]. In this way, the temperature over the catalyst may be more easily controlled and temperature run-away is suppressed.

The monolith material is often a low surface area material, which makes it unsuitable for direct application in the combustion chamber. Therefore, a high surface area material, commonly known as the washcoat or support, is attached onto the monolith walls.
The washcoat may be active in itself, which often is the case for the more temperature-stable catalysts, or act as support for another active component, as often is the case for the ignition catalysts. If the washcoat acts as a support, it helps disperse the active components and increases the exposure of active components to reactants. Various washcoat materials will be discussed later in the thesis.

The active component is often a precious metal for ignition catalysts and an oxide, e.g. hexaaluminate, for the more temperature-stable catalysts. This thesis will focus on the ignition catalysts, especially palladium-based catalysts, which will be discussed in the next chapter.
Palladium-based catalysts are often seen as the clear choice for ignition catalysts due to their excellent activity for methane combustion. Other advantages are the unique capability for temperature self-control due to the reversible PdO-Pd metal transformation and the low volatility of Pd species that may be present under the reaction conditions [17]. However, supported palladium catalysts are complex systems, especially when it comes to methane combustion. A great number of papers concerning Pd-based catalysts have therefore been published over the years [6,15,27-31]. In order to better understand the bimetallic palladium catalysts a basic knowledge regarding monometallic palladium catalysts is necessary; a survey of their characteristics will follow.

4.1 Characterisation and microstructure of Pd/Al₂O₃ (Papers I-VI)

In the present work a catalyst consisting of 5 wt% Pd on alumina, Pd/Al₂O₃, has been used as a reference for the bimetallic catalysts. The material was prepared using the incipient wetness technique, where a palladium nitrate solution mixed with deionised water was added to the alumina support in amounts just sufficient to fill the pores and wet the outside of the support particles. Thereafter, the catalyst was calcined at 1000 °C for 1 h. The amount of metals in the catalyst was confirmed by ICP-AES (inductively coupled plasma - atomic emission spectroscopy). More details regarding the physicochemical properties of the catalyst are found in Table 5.1.

According to PXRD (powder X-ray diffraction), which is a characterisation technique for determining the crystal phases in the bulk, the as-prepared Pd/Al₂O₃ consists mostly of PdO. However, small amounts of metallic palladium are also found in the sample. Because of the high calcination temperature the alumina has a δ structure.

XPS (X-ray photoelectron spectroscopy) measurements provide valuable information on the composition and oxidation state of the catalyst surface. The binding energy of
Pd$^{3d_{5/2}}$ was determined for the as-prepared material to be 337.1 eV. From the literature it is found that this value is slightly too high for being pure PdO ($\text{Pd}^{2+}$, 336.7 eV [32,33]), indicating the possibility of a mixture with PdO$_2$ ($\text{Pd}^{4+}$, 337.5 eV [34,35]). As PdO$_2$ is not observed in the PXRD pattern, this specie is presumably only found on the surface of the catalyst. PdO$_2$ is commonly known to have poor stability; it has been reported to thermally decompose into PdO at 200 °C [36]. Accordingly, PdO$_2$ is probably not present during the operation of the ignition catalysts.

The morphology and the size of the palladium particles in the alumina washcoat was studied by transmission electron microscopy (TEM), combined with an energy-dispersive X-ray spectroscopy (EDS) detector for element analysis. The palladium particles were found to be homogeneously and well spread in the alumina support. This is depicted in Figure 4.1a, where the palladium particles appear as darker dots in the greyish alumina. In Figure 4.1b, two representative palladium particles are shown. From a number of investigated fragments, the palladium particle sizes were determined to be in the range of 20 - 100 nm. In Figure 4.1c, a close up of a palladium particle is displayed. Lack of facetted crystals indicates that the particles in the as-prepared material are built up of smaller crystals of 3 - 5 nm that are randomly oriented inside the particle. Since both Pd and PdO were present in the sample according to PXRD, the darker areas are most likely attributable to metallic palladium, as an effect of denser material.

![Figure 4.1. TEM images of the Pd/Al$_2$O$_3$ catalyst. (a) distribution of Pd particles on alumina (b) Pd particles and (c) close up of a Pd particle](image-url)
The morphology found in these samples is not necessarily valid for all Pd-based catalysts. Several studies have shown that both the preparation technique [37] and the support material [38,39] affect the morphology and thereby the catalytic performance. A restructuring of the catalysts may also take place during operation. Therefore, in Sections 4.2 and 4.4 the changes in the catalysts under various conditions will be discussed.

**4.2 PdO decomposition / reoxidation (Papers I-IV)**

As the operation temperatures inside a combustor are far from ambient conditions, it is essential to understand how the catalysts are affected by temperature. In order to study the temperature influence on the redox properties of the Pd/Al$_2$O$_3$ catalyst, a series of temperature-programmed oxidation (TPO) experiments have been carried out.

The temperature in this experiment was increased from 300 °C to 900 °C, followed by a decrease to 300 °C. This temperature cycle was repeated twice; the result from the second cycle is presented in Figure 4.2. A broad decrease of the oxygen signal between 450 and 630 °C is observed during heating, indicating that the sample was taking up oxygen from the gas stream. Three positive peaks are located close to each other during the heating ramp; they start at 710 °C and subsist all the way to 900 °C. The first peak is small and appears at around 730 °C. The second peak is by far the largest and has its maximum at 790 °C. The third peak appears at 860 °C, but it is almost not discernible. During the cooling ramp only a single negative peak is detected, which starts around 620 °C.
It is generally known that the positive peaks during heating in the TPO experiments are attributable to palladium oxide decomposing into metallic palladium, according to the formula below [40,41]:

\[
PdO \rightleftharpoons Pd^0 + \frac{1}{2} O_2
\]

This reaction scheme is in line with results from high-temperature XRD measurements, shown in Figure 4.3. The XRD patterns were collected at different temperatures during heating. A large PdO peak at \(2\theta = 33.8^\circ\) is observed for temperatures below 700 °C. At 800 °C the PdO peak starts to decrease along with an increase in the Pd reflection at \(2\theta = 40.1^\circ\). However, the Pd peak is shifted to lower \(2\theta\) value with increasing temperature, most likely due to dilatation of the high temperature chamber. When the temperature has reached 880 °C the Pd peak is even larger while the PdO peak has disappeared, indicating that PdO has fully decomposed into Pd. Only one type of palladium oxide phase was observed for the temperature range used in the experiment. This result is consistent with what others have found [40,42].

At which temperature the PdO decomposition occurs is strongly dependent on the oxygen partial pressure [41,43,44]. According to Forzatti and Groppi [45], the temperature of PdO decomposition in air shifts from 790 °C at atmospheric pressure to 980 °C at 16 bar.

To understand the decomposition behaviour of Pd/Al₂O₃, samples were cooled in helium to ambient temperature at different stages during the heating ramp of the TPO

---

**Figure 4.3.** High-temperature in situ XRD profiles of Pd/Al₂O₃ during heating in 2 vol.% O₂ in helium.
Figure 4.4. TEM images of material taken at (a) 775 °C and (b) 900 °C, after treatment in 5 vol.% O₂ in He.

experiments prior to ex-situ studies by PXRD and TEM/EDS. The first sample was stopped at 775 °C, a temperature at which the PdO decomposition has started but not reached completion. The second sample was taken at 900 °C, after the decomposition is completed. From TEM investigation of the sample taken at 775 °C, it is concluded that the material exhibits individual palladium particles that are completely or partly reduced, but also some particles that appear unaffected. The partly reduced particles imply that the transformation starts with a nucleation of Pd on the PdO crystal, as illustrated in Figure 4.4a.

As shown in Figure 4.4b, at 900 °C the particles are well faceted, indicating that they consist of larger crystals. According to the PXRD results, the particles presumably consist of only metallic palladium. Hence, the decomposition process initiates by nucleation of Pd in close contact to the PdO crystals. As the decomposition progresses the metallic domain grows and result in larger Pd crystals.

Still, this does not explain the appearance of the three decomposition peaks in the TPO experiments. The small Pd patches formed on the PdO surface during decomposition give the idea that the first decomposition peak is due to metallic Pd promoting the decomposition reaction of PdO. If this is the case, the second peak is attributable to bulk PdO decomposition. In order to investigate this, the samples were pre-oxidised for various lengths of time at 500 °C to reduce the amount of metallic Pd in the samples prior to the TPO analyses. The oxidation process is confirmed by high-temperature XRD. In this way, it was possible to investigate if the decreased Pd amount results in a smaller first peak. As seen in Figure 4.5, the first peak slightly decreases with length of oxidation time, simultaneously as the second peak increases. Other parameters that favour reoxidation of Pd metal, such as high partial pressure of
oxygen, addition of oxygen promoters to the support (CeO$_2$) etc., have also been reported to increase the relative extent of the second decomposition peak at the expense of the first peak [40]. All this data signifies that the two TPO peaks are correlated and a possible explanation is that the first peak is due to metallic Pd in contact with PdO promotes the decomposition, whereas the second peak is ascribed to bulk PdO in contact with other PdO crystals. The third TPO peak may be associated to a support-Pd oxide complex [40].

During cooling metallic Pd reoxidises to PdO, which is shown by the negative peak in the TPO profile. The reoxidation process is very complex as major restructuring is required of Pd in order to form PdO due to the different crystal lattices [15]. As shown in the TPO experiments, the metallic particles are not easily reoxidised upon cooling, creating a hysteresis in the PdO/Pd phase transformation; a temperature gap of almost 90 °C is obtained. Several studies have previously reported about this phenomenon [27,28]. The cause of the hysteresis is not very clear and a range of ideas on how the oxidation mechanism occurs is reported in the literature. McCarty [28] has suggested that a passive layer of chemisorbed oxygen hinders the oxidation of Pd by suppressing the nucleation of PdO. The reoxidation, when it does occur, involves the oxide growing in patches on the metal [46]. Progressive oxidation of Pd occurs by transforming more of the Pd metal particles to PdO. According to Lyubovsky et al. [47], the morphology of the palladium particles after the reoxidation are rough and polycrystalline. This description is very similar to the one observed for the as-prepared Pd/Al$_2$O$_3$ (see Section 4.1), which has been calcined above the thermal decomposition temperature of PdO. In Figure 4.6, the proposed redox mechanisms of Pd/PdO are schematically illustrated.

**Figure 4.5.** TPO profiles at various lengths of time at 500 °C over Pd/Al$_2$O$_3$. The black line indicates the as-prepared sample, the dotted line a sample pre-oxidised for 1 h and the grey line a sample pre-oxidised for 10 h.
4.3 Catalytic combustion of methane over Pd-based catalysts (Papers I-VI)

Methane is a stable and highly symmetric molecule with an electronic structure resembling that of a rare gas [15]. It possesses the greatest C-H bond strength among all of the saturated hydrocarbons, resulting in methane being one of the most difficult hydrocarbons to combust. Therefore, the activation of the first C-H bond has been proposed to be a crucial step in methane conversion [48-51]. As soon as this has taken place, the following steps occur rapidly. Many different reaction mechanisms have been suggested over the years. Burch et al. [52] have suggested a heterolytic mechanism where the almost non-polar C-H bonds in the methane molecule are readily activated by the Pd$^{2+}$O$^{2-}$ ions. Other researchers have suggested a redox mechanism or a Mars-van Krevelen mechanism, involving the reaction of methane with PdO and subsequent reoxidation of metallic Pd by oxygen [53,54].

Supported palladium catalysts are the most active noble metal catalysts for methane combustion under lean conditions [55]. Still, the rate of combustion over Pd catalysts
depends on the state of the catalyst surface [52]. Many reports have ascribed greater activity for methane combustion to PdO rather than Pd [27-29,42]. However, it has been suggested that small amounts of metallic Pd enhance the catalytic activity due to increase in the dissociation rate of the first C-H bond [56-58]. It is hypothesised that the products after CH$_4$ adsorption on Pd are H and CH$_n$ (n = 3-1), which rapidly diffuse to the Pd/PdO interface and then reduces the PdO. Nevertheless, it is difficult to sustain the metallic Pd under oxidising conditions.

As the state of the catalysts influence the catalytic activity, the characteristics of the PdO-Pd transformation play an important role in methane combustion, as illustrated in Figure 4.7. The temperature was increased from 300 °C to 950 °C, followed by a decrease down to 300 °C. During heating, the conversion starts to increase at 400 °C. Although the catalyst was continuously heated, the methane conversion falls at around 720 °C. This behaviour has been attributed to PdO decomposing into metallic Pd, which is less active for methane combustion [42]. However, at 810 °C the activity curve reaches a minimum and for higher temperatures the activity increases continuously to 950 °C, where a large contribution most likely comes from homogeneous combustion. During cooling the methane conversion decreases until 800 °C, whereafter the activity is regained and reaches a maximum at 600 °C. This behaviour is ascribed to metallic Pd reoxidising to PdO. Since the temperature was different from that at which the PdO decomposes and that of reoxidisation, a hysteresis was created. These results are in agreement with what other researchers have concluded [27,28].
4.4 Stability issues (Papers I-VI)

Even though palladium-based catalysts have shown promising results when the temperature is varied at a constant rate, it has been reported that palladium catalysts have difficulties in maintaining their high activity for longer periods of time at constant temperature [59-66]. This feature has been observed both at higher pressure and for longer duration of tests. This is in line with results presented in Papers I to VI.

In the activity tests illustrated in Figure 4.8, the methane conversion was measured for 12 h, while the inlet temperature to the catalyst was kept at 500 °C (more information on the reaction conditions may be found in Section 6.1). Pd/Al₂O₃ initially has a high activity for methane conversion. However, the activity declined severely during the course of the experiment, even though the temperature and the other reaction parameters were kept constant. The operation temperature at 500 °C is well below the temperature where PdO decomposes, as previously shown by the TPO and in-situ XRD experiments. Hence, the decrease in activity observed in this experiment is probably connected to some other phenomenon than the PdO to Pd transformation. If the activity decreases to this extent, the ignition of the fuel at the compressor discharge temperature will be increasingly difficult. Therefore, it is desirable to improve the stability of palladium-based catalysts. In the same figure a dotted curve is shown, illustrating the activity of Pd/Al₂O₃ when the temperature was varied between 500, 550 and 600 °C. The unstable activity is shown for all temperature levels, but is slightly more pronounced at the higher temperatures.

![Figure 4.8. Methane conversion versus time on stream over Pd/Al₂O₃. The solid curve represents the activity of the sample kept at 500 °C and the dotted curve represents the activity of the sample at 500, 550 and 600 °C, respectively, when each step is kept for 30 min.](image-url)
Results from Paper V show that it is possible to recover the activity over Pd/Al₂O₃ by exposing the catalyst to a quick increase of methane concentration, resulting in temperatures well above 500 °C. On the other hand, the attempts to regenerate the catalyst by purging the catalyst at 500 °C in atmospheres of nitrogen or air without the presence of methane were unsuccessful. The fact that it is possible to recover the activity indicates that either something desorbs from the catalyst surface that has blocked the active sites or the morphology of the particles changes very fast upon heat treatment. In Sections 4.4.1 and 4.4.2 the different alternatives will be discussed.

4.4.1 The inhibition effect of reaction products (Paper V)

Since the activity tests described above were carried out with high purity gases, the inhibition by impurities in the gases is not the primary source for the deactivation. Hence, if inhibition is the origin for the deactivation it probably arises from species involved in the combustion reaction. Water and carbon dioxide are the reaction products when methane is completely combusted. The impact of these products on the methane activity has extensively been investigated, as both of these products may affect the activity of Pd-based catalysts negatively [49,67,68]. Burch et al. [69] have suggested that water and carbon dioxide inhibit the same active sites on PdO, where water is able to displace carbon dioxide to form an inactive surface hydroxide. For that reason, carbon dioxide will only modestly affect the catalytic combustion over palladium-based catalysts under normal conditions when water is present. The focus will therefore be on the water inhibition in the text below.

The inhibition effect of water is proposed to be due to the formation of palladium (II) hydroxide by the following equilibrium [67,70]:

\[
PdO + H_2O \rightleftharpoons Pd(OH)_2
\]

(Active) \hspace{1cm} (Inactive)

The reason why the activity declines when water is present, is that Pd(OH)₂ is inactive for methane oxidation [48]. The presence of water in the process stream does however not affect metallic palladium, but inhibits PdO strongly [71]. As previously mentioned, the rate-limiting step in methane combustion is to break the bonds in the methane molecule. However, at low to moderate temperatures the rate of combustion of methane is suggested to be limited by recombination of the surface hydroxyl and water desorption [52].
Figure 4.9. In-situ DRIFTS spectra taken at 200 °C over Pd/Al₂O₃ under (a) methane combustion (1 % CH₄, 4 % O₂, balance He) (b) desorption (4 % O₂, balance He)

Since water is produced in the reaction, it will always be present under combustion. The gradual decline of activity observed for palladium-based catalysts has therefore been attributed to the inhibition effect of water generated by the combustion reaction [63,72]. However, most water studies have only included extra water to the feed, without showing that Pd(OH)₂ is really attached onto the catalyst surface. Therefore, in-situ DRIFTS studies have been performed over Pd/Al₂O₃ at 200 °C in the presence of a mixture of methane and oxygen.

In Figure 4.9a some representative DRIFTS spectra are displayed, which were collected for various lengths of time after methane introduction. During the course of the experiment the spectra changed considerably. A broad band covering the region between 2800 and 3700 cm⁻¹ was successively built up, due to water being adsorbed on the sample surface [73]. In the same region, peaks of alumina hydroxyls should be located at 3770, 3723 and 3680 cm⁻¹, but these peaks are not distinguishable due to their low intensity [72]. A discrete peak at 3016 cm⁻¹ is identified, which is attributable to gas phase CH₄ [74-76]. This peak is slightly intensified as the reaction proceeds, indicating that the methane conversion decreases, in consistency with the activity tests. Discrete peaks at 3500, 3556, 3697 and 3733 cm⁻¹ are also identified. According to Ciuparu et al. [72] these peaks arise due to hydroxyl groups on the metal oxide surface, i.e. Pd(OH)₂. Since all hydroxyl peaks increased simultaneously with the methane peak, it might be possible that palladium hydroxyls inhibit methane conversion for the conditions used in this experiment. However, the experiment was carried out at much lower temperature than in the activity tests presented in Figure 4.8.
The inhibiting effect of water is strongly dependent on temperature and reaction conditions [77]. According to Card et al. [78], Pd(OH)$_2$ decomposes into PdO at 250 °C in an atmosphere of nitrogen. However, since the concentration of water in the feed stream appears to be essential for when the dehydration occurs [79], the decomposition may occur at higher temperature during combustion. Despite this, the formation of Pd(OH)$_2$ is most likely not very prominent in the activity tests at 500 °C, with the low water concentration produced by the reaction.

The desorption behaviour, when the methane flow is shut off, is illustrated in Figure 4.9b. The two spectra are very alike, except that the methane peak is absent in the spectrum collected after 50 min. The other peaks remain almost the same, even though the large band between 2800 and 3700 cm$^{-1}$ is slightly reduced. Hence, the desorption of water is very slow at this temperature, which is in accordance with the results found in the literature [77,80].

How sensitive the catalyst is to water may depend on the support on which Pd is coated [72]. Either using an additive to the palladium or using a support with high ability to mobilise oxygen might reduce the inhibiting effect of water. Of the commonly used supports, alumina has the lowest oxygen mobility [81].

### 4.4.2 Morphological changes during operation (Paper IV)

The poor stability of methane conversion over monometallic palladium catalysts has been explained by Narui et al. [60] to be a size effect of the Pd particles. By use of in-situ TEM studies they showed that the particles grow during operation. Araya et al. [82] have come to another conclusion; the loss of dispersion of the Pd-based catalyst was too small to be essential.

In order to investigate if the microstructure of the Pd/Al$_2$O$_3$ catalyst changes during operation, the sample was pre-oxidised for 10 h at 500 °C in 5 vol.% O$_2$ in He, followed by ex-situ studies by PXRD and TEM. From the PXRD it is concluded that the small amount of metallic Pd found in the as-prepared sample has vanished along with increasing PdO concentration. This result implies once again that the poor stability of methane conversion is not due to decreasing amounts of PdO phase.

In the TEM images of the pre-oxidised sample, displayed in Figure 4.10, it is shown that the sample have larger crystals than the as-prepared sample.
Fewer particles have the polycrystalline structure, as observed in the as-prepared material. However, the outer diameter of the particles is more or less the same. Several studies concerning the dispersion effect are based on CO/H₂ chemisorption measurements, performed on reduced material. Hence, the particles most likely do not have the polycrystalline structure of the as-prepared sample and therefore less diversion of dispersion is obtained.

Lyubovsky et al. [83] have reported an increase in activity after treating the catalyst above the thermal decomposition temperature. They suggested that this phenomenon is due to the polycrystalline structure formed upon reoxidation being more active than the fully oxidised catalyst. This description of the catalyst is similar to the as-prepared material described earlier. When the sample is losing this structure the activity decreases.

According to Carstens et al. [56] the activity is higher in the presence of both Pd and PdO. Since the sample is becoming more oxidised during operation, less PdO/Pd interfaces are present and the activity may therefore decline. This deactivation process is schematically illustrated in Figure 4.11.

The oxidation process of Pd increases with temperatures, shown by TPO and PXRD. This is consistent with the higher rate of activity loss at the higher temperatures in Figure 4.8. How large the effect of oxidation and the crystal growth are on the catalytic activity is difficult to state. Other deactivation processes may take place simultaneously. However, this effect appears to be a more reasonable cause for the gradually decreasing activity shown in Figure 4.8 than the water inhibition at this high temperature.
One way to maintain a high activity and at the same time stabilise it may be to introduce an extra metal into the palladium catalyst, forming a bimetallic catalyst. In the following chapters the bimetallic catalysts are discussed more closely, as well as their stability and activity.
5
Characterisation and microstructure of bimetallic palladium catalysts

Bimetallic catalyst refers to a catalyst material that is composed of two separate metals joined together. The properties of a bimetallic catalyst may differ from the properties of the metals separately. According to Coq et al. [84], the effect of a co-metal may be interpreted in terms of geometric effects, electronic effects and/or a mixture of the two, depending on the nature of the co-metal and the reaction. However, there is no single interpretation.

The benefit of bimetallic catalysts was early recognised and systematic studies have been carried out for a wide range of applications such as for reforming catalysts [84,85], for selective hydrogenation catalysts [84,86] and for VOC catalysts [87]. Recently, the interest in using bimetallic catalysts in catalytic combustion has increased as well. Different bimetallic palladium catalysts for combustion of methane have been reported to stabilise the activity during combustion [59,60,65,88-92], to increase the level of activity [93-96], to improve the resistance to sulphur poisoning [97,98] etc.

Papers I-VI focus on bimetallic catalysts, including studies of co-metals, molar ratio between Pd and Pt and support materials. In order to gain deeper understanding regarding the behaviour of the bimetallic catalysts morphological studies were carried out, which will be discussed in this chapter.

5.1 The catalysts (Papers I-VI)

A range of different bimetallic catalysts has been studied, which all contained palladium as one of the active components. The catalysts were prepared by the incipient wetness technique, by impregnating the two metal precursors simultaneously. The catalyst powders were thereafter calcined at 1000 °C for 1 h. The bimetallic catalysts were formulated to contain the same molar amount of active components as
the Pd/Al₂O₃ catalyst, i.e. the amounts of noble metals are equal in all catalysts. In Paper I, the co-metals were taken from groups 9-11 in the periodic table, which are close to the location of palladium. The catalysts were prepared to have a composition of equal molar ratio (1:1) between the palladium and the co-metal. The catalysts were supported on alumina. In Paper II the co-metal was chosen to be platinum, but the molar ratio between Pd and Pt was varied ranging from pure Pd to pure Pt. Again, the

Table 5.1. Summary of the catalysts and their physicochemical properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>Metal loadinga (wt %)</th>
<th>BET area (m²/g)</th>
<th>CO-uptake (μmol/g catalyst)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Pd</td>
<td>Pt</td>
<td></td>
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<tr>
<td>Reference catalysts</td>
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<td>1:1PdCo/Al₂O₃</td>
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<td>n.a.</td>
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<tr>
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<td>1:1PdRh/Al₂O₃</td>
<td>n.a.</td>
<td>n.a.</td>
<td>97</td>
</tr>
<tr>
<td>1:1 Pd:Ir/Al₂O₃</td>
<td>1:1PdIr/Al₂O₃</td>
<td>n.a.</td>
<td>n.a.</td>
<td>106</td>
</tr>
<tr>
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<td>1:1PdNi/Al₂O₃</td>
<td>n.a.</td>
<td>n.a.</td>
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</tr>
<tr>
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<td>1:1PdPt/Al₂O₃</td>
<td>n.a.</td>
<td>n.a.</td>
<td>107</td>
</tr>
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<td>n.a.</td>
<td>107</td>
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<td>3.0</td>
<td>91</td>
</tr>
<tr>
<td>2:1 Pd:Pt/LaMnAl₁₉O₁₉</td>
<td>2:1PdPt/LMH</td>
<td>3.1</td>
<td>2.9</td>
<td>18</td>
</tr>
<tr>
<td>2:1 Pd:Pt/ZrO₂</td>
<td>2:1PdPt/ZrO₂</td>
<td>2.6</td>
<td>2.8</td>
<td>15</td>
</tr>
<tr>
<td>2:1 Pd:Pt/Ce-ZrO₂</td>
<td>2:1PdPt/Ce-ZrO₂</td>
<td>2.9</td>
<td>2.8</td>
<td>10</td>
</tr>
<tr>
<td>2:1 Pd:Pt/Y-ZrO₂</td>
<td>2:1PdPt/Y-ZrO₂</td>
<td>2.9</td>
<td>2.8</td>
<td>10</td>
</tr>
</tbody>
</table>

n.a. denotes not analysed

a Determined by ICP-AES
support material was alumina. In Paper III the influence of different support materials was investigated, where the active components were chosen to consist of 2:1 Pd:Pt. A description of the different support materials is found in Section 5.4.

A monometallic palladium catalyst, Pd/Al₂O₃, was used as reference catalyst in all papers and is described in more detail in Chapter 4. Another monometallic palladium catalyst was prepared as well, i.e. ½Pd/Al₂O₃, which contained equal amounts of palladium as the bimetallic catalysts with molar ratio of 1:1. This catalyst was used for comparison in Paper I. The catalysts Pd/Al₂O₃ and 2:1PdPt/Al₂O₃ were also used in Papers IV-VI. More details regarding the different catalysts are given in Table 5.1.

5.2 Influence of co-metals (Paper I)

In Paper I, the influence of various co-metals on the palladium catalyst was investigated. For the bimetallic catalysts studied, three different groups were distinguished depending on how the co-metals interact with the support and/or the palladium:

1) The co-metal reacted with the alumina support to produce a spinel phase (Co and Ni)
2) The co-metal formed separate particles (Rh, Ir, Cu and Ag)
3) The co-metal alloyed with Pd (Pt and Au)

In the first group of bimetallic catalysts, the co-metal reacted with the alumina support to form spinel phases (MeAl₂O₄), as illustrated in Figure 5.1a. This appears to be the case for 1:1PdCo/Al₂O₃ and 1:1PdNi/Al₂O₃.

![Figure 5.1. Schematic illustration of the three groups of bimetallic catalysts (a) group one (b) group two (c) group three](image-url)
The presence of spinel phases is supported by the results from the TPO analyses of these catalysts. As shown in Figure 5.2, the TPO profiles of 1:1PdCo/Al₂O₃ and 1:1PdNi/Al₂O₃ are almost identical to that of ½Pd/Al₂O₃; all three catalysts contain equal amounts of palladium. The peaks observed in the TPO analyses are most likely attributable to the decomposition of PdO, as the co-metals alone do not give rise to any peaks. Since Co and Ni do not affect the oxygen release/uptake of PdO, Pd and the co-metals were most likely not in close contact.

The idea of a spinel phase is also strengthened by the results obtained in the TEM/EDS analyses, in which the co-metals were found to be homogeneously distributed in the alumina, but without forming separate particles. The palladium particles in these catalysts have similar appearance as in the Pd/Al₂O₃ catalyst, with well distributed particles and no major interference with the co-metal. Furthermore, the surface areas are slightly improved in the catalysts from the first group (see Table 5.1). According to the literature, it is possible that Co and Ni react with alumina already at 400 °C [99] and 800 °C [100], respectively, to form the spinel phases. As the catalysts in the present study were calcined at 1000 °C, it is not surprising to find spinel phases in these catalysts.

The second group of bimetallic catalysts produced separate particles of the co-metals, as illustrated in Figure 5.1b. This behaviour is shown for 1:1PdRh/Al₂O₃.

![Figure 5.2. TPO profiles of the (a) Pd/Al₂O₃, (b) ½Pd/Al₂O₃, (c) 1:1PdCo/Al₂O₃, (d) 1:1PdRh/Al₂O₃, (e) 1:1PdIr/Al₂O₃, (f) 1:1PdNi/Al₂O₃ and (g) 1:1PdPt/Al₂O₃, (h) 1:1PdCu/Al₂O₃, (i) 1:1PdAg/Al₂O₃, (j) 1:1PdAu/Al₂O₃](image_url)
Figure 5.3. TEM images of (a) PdO and Ag particles in the 1:1PdAg/Al₂O₃ catalyst (b) Pd₉₅Pt₁₅ particle in the 1:1PdPt/Al₂O₃ catalyst

1:1PdIr/Al₂O₃, 1:1PdCu/Al₂O₃ and 1:1PdAg/Al₂O₃. TEM/EDS analyses revealed that this group of catalysts had well-distributed co-metal particles in the alumina support, as shown in Figure 5.3a for 1:1PdAg/Al₂O₃. The particles appeared in most cases to be enriched near the palladium particles, except for 1:1PdRh/Al₂O₃ which had an even distribution over the entire surface.

1:1PdIr/Al₂O₃ is the only catalyst for which an oxide phase of the co-metal, IrO₂, was detected by PXRD. The other catalysts in this group did not give any signal at all for the co-metal. This may be due to the small particle sizes (1 - 5 nm), as observed in TEM, being below the detection limits of the PXRD instrument.

As seen in Figure 5.2, the TPO profiles of the catalysts from the second group did change the oxygen release/uptake of the PdO. For 1:1PdRh/Al₂O₃, 1:1PdCu/Al₂O₃ and 1:1PdAg/Al₂O₃, the decomposition peak appears more or less at the same temperature as for the ½Pd/Al₂O₃ catalyst. However, the reoxidation temperature is slightly shifted, in most cases to a higher temperature. For 1:1PdIr/Al₂O₃, the peaks are distinctly shifted.

As illustrated in Figure 5.1c, the co-metals are alloyed with palladium in the third group of bimetallic catalysts. This may be the case for 1:1PdPt/Al₂O₃ and 1:1PdAu/Al₂O₃. In Figure 5.2, a clear shift in decomposition and reoxidation temperatures is observed for 1:1PdPt/Al₂O₃. For 1:1PdAu/Al₂O₃, no signal for either the decomposition or the reoxidation is recorded. The absence of peaks in the TPO experiments may be explained by the results from PXRD analyses, where almost no PdO was detected.
The TEM study indicated that the co-metals in the third group did not form separate particles and were only to be found in the close vicinity of Pd. This is shown in Figure 5.3b for 1:1PdPt/Al₂O₃.

### 5.3 Influence of molar ratio between Pd and Pt (Papers II and IV)

The molar ratio between the active metals may have major effects on the catalytic activity and stability [65,101]. In Paper I, only catalysts with a molar ratio of 1:1 Pd:co-metal were studied. Therefore, it is valuable to continue the catalyst survey by evaluating the impact of molar ratio. The most promising catalyst from the study was 1:1Pd:Pt/Al₂O₃ (see Section 6.2 for more detail). Therefore, the influence of molar ratio between Pd and Pt is described in this section, ranging from pure Pd to pure Pt.

According to the TEM/EDS analyses shown in Figure 5.4a-b, the particles of the bimetallic catalysts with ≥50 at% Pd are split into two different domains; one with PdO and one likely consisting of an alloy between Pd and Pt. It is interesting to note that the two domains are always found in close contact, suggesting that the PdO phase persistently interacts with a metallic phase. However, it should be pointed out that no core shell structure was obtained, but the domains are located next to each other as illustrated in Figure 5.5. The PdO domain has a more homogeneous structure than observed for the palladium particles in Pd/Al₂O₃; presumably no metallic Pd is present in the PdO domain. The size of the alloy domain increases with the amount of platinum at the expense of the PdO domain. This results in no PdO remaining in the catalysts with lower concentration of palladium than equimolar. This is in line with the results presented in Paper I, where almost no PdO phase was detected.

![Figure 5.4. TEM images of (a) 2:1PdPt/Al₂O₃ and (b) 1:1PdPt/Al₂O₃](image-url)
The size of the noble metal particles were estimated from numerous investigated fragments to be between 30 and 80 nm, except for 1:2PdPt/Al₂O₃ that exhibited a very wide size distribution of 20 - 200 nm. In all catalysts, the noble metal particles were well distributed in the alumina support.

From PXRD analyses it is suggested that a Pt₁₋ₓPdₓ alloy is present in all bimetallic catalysts in the current study, but the composition varied with the platinum content. For the bimetallic catalysts with >50 at% Pd, PdO was observed together with the alloy, whereas for catalysts with <50 at% Pd no PdO was detected. By using Vegard’s law for solid solution, the composition was determined to be in the range of 0.33 < x < 0.55. Generally, the x value is closer to x = 0.5 than the nominal value indicates, as displayed in Figure 5.6. Due to these feature the remaining palladium forms the PdO domain, as pure metallic palladium is difficult to sustain for longer periods of time in an oxidising atmosphere. For the Pt-rich catalyst, all of the palladium is located in the alloy and therefore no separate PdO domain is formed.

The TPO experiments also indicate a decreasing amount of PdO in the sample with increasing Pt amounts. As shown in Figure 5.7, the decomposition peak was shifted towards lower onset temperature with increasing Pt content, at the same as the intensity of the peak decreases. The shift in decomposition temperature is not due to the lower concentration of palladium in the sample, since the decomposition of ½Pd/Al₂O₃ (shown in Figure 5.2) appears at the same temperature as that in Pd/Al₂O₃. Hence, Pt promotes the PdO decomposition. For the catalyst with <50 at% Pd, no peaks were detected in the temperature range used in the TPO analyses, indicating that no PdO is present.
Common for all samples that give a response in the TPO analysis was slow reoxidation that continues during heating. This is seen in the TPO profiles as a broad negative peak before the reduction peak.

XPS provides valuable information on the surface state of the catalysts in this study. The binding energies of Pd3d\textsubscript{5/2} and Pt4d\textsubscript{5/2} were evaluated. Two different methods were used in order to determine the surface phases of Pd3d\textsubscript{5/2}. In Paper II, the data processing was performed using the XPS peak program. The spectra were deconvoluted using the least squares fitting routine by a Gaussian/Lorentzian (90/10) product function provided with the software. In this way two different components of the Pd3d\textsubscript{5/2} were established: one at 336.0 eV and one between 337.3 eV and 337.7 eV, as seen in Table 5.2.

**Figure 5.6.** Nominal composition versus surface determined by XPS (□), Pt\textsubscript{1-x}Pd\textsubscript{x}-alloy determined by PXRD (○) and total composition determined by ICP-AES (▽), in as-prepared catalysts. The dashed line represents the theoretical values.

**Figure 5.7.** TPO profiles of (a) Pd/Al\textsubscript{2}O\textsubscript{3} (b) 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} (c) 2:1PdPt/Al\textsubscript{2}O\textsubscript{3} and (d) 1:1PdPt/Al\textsubscript{2}O\textsubscript{3} in 5 vol.% O\textsubscript{2} in helium.
Table 5.2. Binding energies of core electrons of the different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd3d$_{5/2}$</th>
<th></th>
<th>Pt4d$_{5/2}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>Intensity (%)</td>
<td>BE (eV)</td>
<td>Intensity (%)</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>337.1</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4:1PdPt/Al$_2$O$_3$</td>
<td>337.3</td>
<td>100</td>
<td>314.4</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>316.8</td>
<td>28</td>
</tr>
<tr>
<td>2:1PdPt/Al$_2$O$_3$</td>
<td>336.0</td>
<td>22</td>
<td>314.4</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>337.3</td>
<td>78</td>
<td>317.0</td>
<td>22</td>
</tr>
<tr>
<td>1:1PdPt/Al$_2$O$_3$</td>
<td>336.0</td>
<td>41</td>
<td>314.5</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>337.5</td>
<td>59</td>
<td>317.1</td>
<td>23</td>
</tr>
<tr>
<td>1:2PdPt/Al$_2$O$_3$</td>
<td>336.0</td>
<td>65</td>
<td>314.5</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>337.7</td>
<td>35</td>
<td>317.1</td>
<td>18</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>314.5</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>317.1</td>
<td>23</td>
</tr>
</tbody>
</table>

The binding energy of the first component was the same for the bimetallic samples, independent of the molar ratio. This may be attributable to Pd$^{2+}$, but according to the literature this value is slightly too low (PdO, 336.7 eV [32,33]). The binding energy of the second component increased with platinum content from 337.3 eV for the 4:1PdPt/Al$_2$O$_3$ to 337.7 eV for 1:2PdPt/Al$_2$O$_3$. According to the literature, a component at this high binding energy may be attributable to a higher oxidation state of palladium than Pd$^{2+}$, probably Pd$^{4+}$ [34,35]. The ratio between the two components varies with molar ratio.

In Paper IV a second way of determining the surface composition was carried out by assuming that all three oxidation states, i.e. Pd$^{0}$, Pd$^{2+}$ and Pd$^{4+}$, might be present on the catalyst surface. The amount of each state was determined by convolution using the binding energies of Pd$^{0}$, Pd$^{2+}$ and Pd$^{4+}$ taken from the literature as being 335.2 eV [102,103], 336.7 eV [32,33] and 337.5 eV [34,35], respectively. By performing the XPS evaluation in this way it was revealed that all three species were present on the catalyst surface of the as-prepared material. Pd$^{4+}$ was most likely only present on the surface of the catalyst, since this specie was not detected by PXRD. In order to investigate if this was the case, depth profiling by argon etching was carried out. As expected, after etching of the material Pd$^{4+}$ disappeared and the only oxidation states
detected in the bulk materials were Pd$^0$ and Pd$^{2+}$. The etching also indicated that all three phases were present on the surface of the as-prepared bimetallic catalysts.

For platinum, the Pt4d$_{5/2}$ was recorded. Again, two different components were detected; a major one at 314.4 - 314.5 eV, associated with metallic platinum [104,105], and a minor one at 316.8 - 317.1 eV, signifying the presence of oxidised platinum species, probably PtO$_2$ [104,106].

To study whether the Pd and Pt atoms are homogeneously distributed on the catalyst surface, the surface composition derived from XPS was plotted versus the nominal Pd composition, shown in Figure 5.6. The data appear to fit a straight line reasonably, suggesting that both metals are uniformly distributed on the catalyst surface and none of the metals is segregated. The bulk composition of Pd determined from ICP analyses is included in the same graph in order to investigate the possibility of XPS data agreeing with the bulk composition.

**5.4. Influence of support materials (Paper III)**

Several researchers have shown that the behaviour of monometallic Pd catalysts is strongly affected by the type of support material, especially during oxidation and reduction of Pd. The support material may also have significant impact on the thermal stability of the catalysts. Al$_2$O$_3$ is one of the most common support materials due to its high surface area, but at higher temperature it experiences phase transformations resulting in decreased surface area [107]. In recent years ZrO$_2$ has received considerable attention. It has, for example, been shown to enhance the rate of PdO reoxidation compared to Al$_2$O$_3$ [71]. Another possibility to improve the reoxidation process is to add ceria to the catalysts [39,108-111]. Concerning the thermal stability, it is possible to improve the stability of ZrO$_2$ by doping the material with yttrium oxide [112,113]. Another very thermally stable material is manganese-substituted lanthanum hexaaluminate (LaMnAl$_{11}$O$_{19}$) [114-116]. Ersson et al. [115] have reported that this material has a surface area of as high as 28 m$^2$/g after calcination for 4 h at 1200 °C.

While the influence of different support materials is well-documented for monometallic palladium catalysts, few studies have addressed the impact of support materials on bimetallic Pd-Pt catalysts. As the reoxidation process has been reported to
be slow for the bimetallic catalysts it is of interest to study the impact of support materials, especially for the reoxidation after thermal decomposition. Therefore, the study presented in Paper III focuses on Pd-Pt bimetallic catalysts and the influence of support materials. Five different support materials were chosen for this investigation, i.e. Al$_2$O$_3$, ZrO$_2$, ceria-stabilised ZrO$_2$, yttria-stabilised ZrO$_2$ and LaMnAl$_{11}$O$_{19}$.

The surface areas of all catalyst powders were determined by nitrogen adsorption at liquid N$_2$ temperature, according to the BET (Brunauer-Emmett-Teller) theory. The results are presented in Table 5.1. A large disparity in surface area between the samples are observed, where the alumina-based catalyst has considerably higher surface area (91 m$^2$/g) than the other samples (10 - 18 m$^2$/g). Despite this, 2:1PdPt/Al$_2$O$_3$ has the lowest CO-uptake, whereas 2:1PdPt/ZrO$_2$ has almost three times as high a value.

It is evident that the support material has a major impact on the Pd-Pt catalysts, as shown in Figure 5.8. It has been confirmed both by high-temperature in situ XRD and TPO. Both the temperature of PdO decomposition and the temperature of reoxidation are affected by the support material. When considering the decomposition, the reduction of the 2:1PdPt/Al$_2$O$_3$ catalyst occurs at 560 °C, while for 2:1PdPt/LaMnAl$_{11}$O$_{19}$ the reduction peak starts at 590 °C. All zirconium samples have an onset temperature of the reduction at 630 °C, some 70 °C higher than for 2:1PdPt/Al$_2$O$_3$. The high-temperature in situ XRD confirms that the peak observed during heating in the TPO experiments is due to PdO decomposition, as in the case of Pd/Al$_2$O$_3$. 

**Figure 5.8.** TPO profiles of (a) 2:1PdPt/Al$_2$O$_3$, (b) 2:1PdPt/LMH, (c) 2:1PdPt/ZrO$_2$, (d) 2:1PdPt/Ce-ZrO$_2$ and (e) 2:1PdPt/Y-ZrO$_2$. The O$_2$ concentration is displayed as a function of temperature when 2 vol.% O$_2$ in helium is flowing over the sample.
The TPO profiles of the bimetallic catalysts also diverge significantly during cooling. The temperatures where reoxidation is initiated are for all catalysts lower than the onset temperature of the reduction during heating, which creates a hysteresis. The size of the hysteresis differs between the catalysts and appears to be influenced by the nature of the support material. Additionally, the temperature range over which the reoxidation takes place differs between the samples. 2:1PdPt/Al₂O₃ has the widest hysteresis of all Pd-Pt catalysts, with a temperature difference of 80 °C; it is still some 20 °C less than for the monometallic palladium catalyst. The peak representing oxidation is not easily distinguished because it is very wide and reaches all the way to 330 °C. The hysteresis of the 2:1PdPt/LaMnAl₁₁O₁₉ is somewhat narrower than for the alumina-supported catalyst, i.e. 60 °C. The zirconium-based catalysts reoxidise at higher temperatures than the other two bimetallic catalysts. 2:1PdPt/Ce-ZrO₂ and 2:1PdPt/ZrO₂ have the narrowest hysteresis of all tested catalysts, 30 and 40 °C, respectively. However, 2:1PdPt/Ce-ZrO₂ reoxidises much faster since the oxidation peak reaches the baseline at higher temperature than for 2:1PdPt/ZrO₂. 2:1PdPt/Y-ZrO₂ has more difficulties in reoxidising and a hysteresis of 70 °C is obtained. This means that the support material has a great influence on the reoxidation of Pd; Ce-ZrO₂ appears to be the best and Al₂O₃ to be the worst. The reoxidation is most likely to increase with the oxygen partial pressure, since only 2 vol.% O₂ is used in these TPO experiments.

The superior reoxidation properties for the monometallic palladium catalysts when Ce is present have been ascribed to the ability to shift easily between reduced (Ce³⁺) and oxidised (Ce⁴⁺) states, which enhances the oxygen mobility in the material [117]. This would enable oxygen to be transported to the palladium particles and improve the reoxidation process, resulting in a smaller temperature gap between the decomposition and reoxidation of PdO. This is in line with the findings presented in this study for the bimetallic 2:1PdPt/Ce-ZrO₂ catalyst.

5.5. Changes in microstructure during operation (Papers III and IV)

Previously discussed characterisation studies have been carried out on the as-prepared catalyst materials. Even though these studies give a good indication of the structure of the catalysts, it is not certain that the morphology remains constant under the reaction conditions. Therefore, the morphology after treatments at different oxidation conditions and temperatures has been investigated and is described in this section.
In order to investigate what happens with the sample when the temperature is maintained at 500 °C, high-temperature in situ XRD studies were carried out over 2:1PdPt/Al₂O₃. The temperature was kept at 500 °C and a continuous flow of air was passed over the sample. A diffractogram was collected every hour; in Figure 5.9 some representative XRD patterns are shown. The sample initially has a relatively large Pd-Pt peak at between 2θ = 39.9° and 40.1° and only a small PdO peak at 2θ = 33.8°. With time the peak of PdO increases along with a decrease in the Pd-Pt peak. Hence, more PdO is formed with time, under the reaction conditions used in the experiments. After 10 h the sample appeared to have stabilised, as the area of the peaks does not change anymore.

Figure 5.9. High-temperature in situ XRD profiles at 500 °C of 2:1PdPt/Al₂O₃ in air.

In Figure 5.10 the TPO profiles of 2:1PdPt/Al₂O₃ in 5 vol.% O₂ in helium are shown. The sample was either as-prepared or pre-oxidised at various temperatures for 1 h.

Figure 5.10. TPO profiles of 2:1PdPt/Al₂O₃ in 5 vol.% O₂ in helium. The sample was either as-prepared or pre-oxidised at various temperatures for 1 h.
A similar observation was made from TPO analyses, where the decomposition peak during heating increased with pre-oxidation. From these studies it was demonstrated that both the length of the run and the temperature affect the amount of PdO formed.

As seen in Figure 5.10, the formation of PdO increases with temperature until the temperature exceeds that of the PdO decomposition. After pre-oxidation at 400 °C only a small variation in the reduction peak is observed, but at 600 °C the peak is significantly increased. When the pre-oxidation took place at 800 °C no changes of the PdO decomposition peak was obtained.

The exact composition of the solid solution of Pd-Pt was difficult to state from the in-situ XRD studies due to the shift with temperature. For that reason, the TPO experiments after pre-oxidation were stopped at given temperatures and cooled in helium prior to ex-situ studies. By mean of PXRD performed at ambient temperature it was determined that the solid solution composition changed from $x = 0.57$ for the as-prepared sample to $x = 0.52$ for the sample that had been pre-oxidised at 500 °C for 10 h. Consequently, by pre-oxidising the sample below the temperature of PdO decomposition the material obtains a solid solution closer to $x = 0.5$. This is most likely the reason for the ability of 2:1PdPt/Al$_2$O$_3$ to form more PdO during reaction. Some palladium diffuses out from the alloy. Since PdO is the thermally stable phase in this temperature range, metallic Pd will quickly oxidise into PdO. However, one should point out that the ability to form PdO is most likely a finite process and the leaching of Pd from the alloy will not go below $x = 0.5$.

When the material was pre-oxidised at 800 °C, a temperature above the PdO decomposition temperature in the TPO experiments, the ex-situ studies illustrated a solid solution composition close to the nominal value of the catalysts, i.e. $x = 0.67$. From the TEM/EDS studies of the same sample only well facetted particles were found, see Figure 5.11b. According to the EDS analysis, Pd and Pt were evenly spread in the noble-metal particles; palladium was never found without platinum. This indicates that once the PdO decomposes the metallic palladium is incorporated in the solid solution. When the catalyst is reoxidising, Pd must diffuse out from the solid solution in order to become oxidised, which may explain the slow reoxidation process.
Figure 5.11. TEM images of Pt$_{1-x}$Pd$_x$/PdO particles in the 2:1PdPt/Al$_2$O$_3$ catalysts after (a) pre-oxidation at 500 °C for 10 h (b) pre-oxidation at 800 °C for 10 h

of 2:1PdPt/Al$_2$O$_3$. However, this activation will most likely only occur after the catalyst is treated under conditions favourable for PdO decomposition.
An ignition catalyst must have high combustion activity in order to ignite the gas at the compressor discharge temperature. Therefore, it is important that the catalyst maintains its combustion activity during operation. In this chapter, the combustion performances of the bimetallic catalysts discussed in Chapter 5 is evaluated. The levels of both activity and stability will be addressed and are discussed in the following.

6.1 Experimental parameters

6.1.1 Experimental equipment

A tubular reactor, working close to atmospheric pressure, was used to evaluate the activity and the stability of the catalysts. The laboratory reactor consists of a quartz tube, which was located inside a programmable furnace. The activity tests were performed on cordierite monoliths (400 cpsi, φ 14 mm and length 10 mm), coated with 20 wt% of catalyst material. The gas mixture supplied to the reactor consisted of air and methane, both gases adjusted by mass flow controllers. The composition of the outlet gas from the reactor was analysed with an on-line gas chromatograph, equipped with a TCD detector. The temperature was recorded by a thermocouple placed upstream of the monolith.

6.1.2 Reaction conditions

All lab-scale tests described in this chapter were performed at a gas hourly space velocity (GHSV) of 250 000 h⁻¹. The feed provided to the reactor consisted of 1.5 vol.% methane in air. Four types of activity tests were carried out. The first type of activity test, the transient test, was accomplished by varying the temperature at a constant rate from 300 °C up to 950 °C, whereafter the temperature was returned to 300 °C. Two consecutive temperature cycles were conducted, but only results from the
second cycle are used in the figures. In the second type of activity test, the steady-state tests, the temperature was increased stepwise by 50 °C; each temperature step was held constant during an hour. In the third type of activity tests the temperature was varied between 500, 550 and 600 °C, where each step was maintained for 30 min. In the last type of activity test the catalytic performance was evaluated for 12 h when the temperature was maintained at 500 °C.

An uncoated monolith has also been evaluated in order to investigate the role of homogeneous combustion in the temperature range of the transient activity tests. During heating the uncoated monolith first showed activity above 920 °C. During cooling the activity continually dropped until 815 °C, where no methane conversion was observed at all. The methane conversion never exceeded 58 %. Based on these results, the contribution to methane conversion is mostly catalytically induced combustion for temperatures below 920 °C during heating and below 815 °C during cooling.

6.2 Influence of co-metals on the catalytic activity (Paper I)

In order to understand the influence of co-metals on methane conversion, a series of activity tests was performed over the bimetallic catalysts described in Section 5.2. Figure 6.1a-b shows the behaviour in the transient activity tests of some representative catalysts. All bimetallic catalysts, except 1:1PdCu/Al₂O₃, have similar combustion profiles as the Pd/Al₂O₃ catalyst, in which the PdO decomposition has strong impact on the methane conversion. However, the appearance during PdO decomposition is slightly modified by the co-metals. From the morphology study presented in Section 5.2, the bimetallic catalysts were divided into three groups. For the first group (Co and Ni), where the co-metal formed a spinel phase with alumina, the PdO decomposition takes place at a higher temperature than for Pd/Al₂O₃. This is likely associated to the slightly larger surface area of the spinel-containing catalysts. For the rest of the catalysts, the drop in conversion is less pronounced than that of Pd/Al₂O₃. The lower effect of PdO decomposition in the second group (Rh, Ir, Cu and Ag), in which separate particles of the co-metals are formed, may to some extent be induced by the activity of the co-metals themselves. From the literature it is found that the individual co-metals are active for methane combustion, but first at higher temperatures [98,118,119]. Therefore, it is possible that their activity may suppress the impact of PdO decomposition on the methane conversion. The alloy formation in the third group (Pt and Au) is also likely to stabilise the decomposition.
Figure 6.1. Transient activity tests for Pd/Al₂O₃ (■), 1:1PdNi/Al₂O₃ (○), 1:1PdPt/Al₂O₃ (▲), 1:1PdAg/Al₂O₃ (●) and 1:1PdCu/Al₂O₃ (◇) during (a) heating ramp (b) cooling.

The reoxidation of Pd during the cooling ramp of the transient activity tests, shown in Figure 6.1b, follows the TPO results well. The catalysts containing alloys have a slow reoxidation process, whereas the catalysts with separate particles obtain a much faster reoxidation. The catalysts with a spinel structure are unaffected, presumably due to the fact that the co-metals in this group do not interact with the palladium.

Since there was no clear temperature when the catalysts were ignited, the temperature at a methane conversion of 10% is used for measuring the activity. The monometallic palladium catalyst obtained the lowest temperature, and was therefore the most active of the tested catalysts. When considering only the bimetallic catalysts, 1:1PdNi/Al₂O₃ was the most active. However, this catalyst had similar activity as ½Pd/Al₂O₃, indicating that the nickel does not influence the activity of Pd catalysts.

If a catalyst is very active initially but shows declining methane conversion during operation, the fuel will be increasingly difficult to ignite. Therefore, it is desirable to have a catalyst with stable activity. The stability over the bimetallic catalysts with various co-metals was evaluated by step-wise steady state tests. The results are presented in Figure 6.2.

As discussed previously, the methane conversion over Pd/Al₂O₃ declines with time, regardless of the temperature. Similar behaviour is also shown for some of the bimetallic catalysts, i.e. 1:1PdCo/Al₂O₃, 1:1PdRh/Al₂O₃ and 1:1PdNi/Al₂O₃. The rest of the bimetallic catalysts presented a stable activity for methane combustion.
When considering both the level and the stability of activity, 1:1PdPt/Al₂O₃ is the most promising catalyst for catalytic combustion of methane. This is in line with results of other researchers [59,60,65,88,89,91]. The activity of 1:1PdPt/Al₂O₃ even increases during operation. Additionally, 1:1PdAg/Al₂O₃ has very stable activity but is less active at the higher temperatures.

The stability of the methane conversion appears to be dependent on how the co-metals interact with the palladium and/or the support material. For the first group of catalysts, the activity is just as unstable as for Pd/Al₂O₃. This is probably due to a fairly stable spinel structure that does not allow the co-metals to interact with the palladium. Catalysts from the second group may obtain a stable activity if the co-metal is in close contact with palladium. Otherwise the catalysts will have an unstable behaviour. The third group presents a stable activity for all catalysts.

Whether the activity and stability are improved or not when a co-metal is included is not clear from the literature, but a range of results may be found. The preparation technique may influence the morphology and thereby the catalytic activity of the bimetallic catalysts [120,121], and might therefore be a reason for the divergent results.

6.2. Influence of the Pd-Pt molar ratio on the catalytic activity (Paper II)

The opinion is divided regarding the effect on the level of methane oxidation when platinum is added to the palladium catalysts. A considerable part of the papers appear to come to a positive conclusion [59,60,89,95]. However, it has also been reported that
the initial activity is lower for the bimetallic Pd-Pt catalysts compared to the monometallic palladium catalysts [92]. An explanation for the diversity of the results might be the different molar ratios between palladium and platinum used in the experiments. This is supported by the results from the present study, where the molar ratio significantly affects the catalytic properties.

The results from the transient activity tests for the catalysts in Section 5.3 with various molar ratios are shown in Figure 6.3a-b. The characteristic behaviour of Pd-based catalysts, with a drop in activity at around 750 °C, is observed for all bimetallic catalysts, except for 1:2PdPt/Al₂O₃. 1:2PdPt/Al₂O₃ has a combustion profile similar to that of Pt/Al₂O₃, although the activity of 1:2PdPt/Al₂O₃ is considerably lower. The behaviour during PdO decomposition is affected by the molar ratio, where 1:1PdPt/Al₂O₃ has a less pronounced drop of activity.

The 4:1PdP/Al₂O₃ catalyst has the highest activity among the bimetallic catalysts; it is even slightly more active than Pd/Al₂O₃ for temperatures up to 540 °C. Conversely, the bimetallic catalysts with higher platinum content show lower activity than Pd/Al₂O₃. The diverse activities indicate that the amount of platinum added is crucial for the level of activity, which may explain the large variation of results reported in the literature.

![Figure 6.3. Transient activity tests for Pd/Al₂O₃ (■), 4:1PdPt/Al₂O₃ (●), 2:1PdPt/Al₂O₃ (▲), 1:1PdPt/Al₂O₃ (△), 1:2PdPt/Al₂O₃ (○) and Pt/Al₂O₃ (□) during (a) heating ramp (b) cooling](image-url)
When considering monometallic Pd catalysts, small amounts of metallic Pd on the PdO particles have been proposed to give an enhanced activity compared to fully oxidised PdO particles [56,58]. However, it is difficult to sustain the metallic phase of palladium for longer periods of time in an oxidising atmosphere because of the metallic particles being oxidised back to PdO [56]. In the case of bimetallic Pd-Pt catalysts, it appears that the metallic phase is preserved even in an oxidising atmosphere due to the alloy; it is preserved even after calcination in air. The presence of the alloy may therefore result in an improved activity compared to Pd/Al₂O₃, despite the slightly lower palladium content in the 4:1PdPt/Al₂O₃ catalyst.

Even though small amounts of Pd-Pt alloy appear to be beneficial for the activity for methane combustion, high amounts of alloy cannot compensate for significantly lower palladium content in the catalyst. In this study the amount of noble metal was kept constant for all catalysts, resulting in a considerably lower palladium content in the 2:1PdPt/Al₂O₃ and 1:1PdPt/Al₂O₃ catalysts. Furthermore, the amount of the Pd-Pt alloy is higher in these catalysts at the expense of the PdO phase. It is generally known that pure PdO catalysts are much more active than pure metallic palladium catalysts as well as Pt catalysts [8,42]. Therefore, it is not surprising that the 2:1PdPt/Al₂O₃ and 1:1PdPt/Al₂O₃ catalysts have lower activity, in spite of the high metallic fractions.

As shown in Section 5.2, 1:2PdPt/Al₂O₃ has a very uneven structure with large particles and almost no PdO present in the catalyst. The poor activity of this catalyst indicates that the alloy itself most likely has very low activity for methane conversion.

Figure 6.4. Steady-state activity tests for Pd/Al₂O₃ (■), 4:1PdPt/Al₂O₃ (●), 2:1PdPt/Al₂O₃ (▲), 1:1PdPt/Al₂O₃ (△), 1:2PdPt/Al₂O₃ (○) and Pt/Al₂O₃ (□). The dotted line represents the temperature.
The results from the steady-state activity tests are presented in Figure 6.4. Again, a wide distribution of methane conversion among the catalysts is seen. 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} initially gives an excellent methane conversion, close to the values achieved for Pd/Al\textsubscript{2}O\textsubscript{3}. However, the activity of 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} is unstable and just as for the Pd/Al\textsubscript{2}O\textsubscript{3} catalyst decreases with time for all temperatures. Nevertheless, the loss in conversion is not as pronounced, resulting in the 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} becoming more active at the end of each temperature step. All other catalysts in this test series achieved a stable conversion, even though the level of activity is lower.

2:1PdPt/Al\textsubscript{2}O\textsubscript{3} and 1:1PdPt/Al\textsubscript{2}O\textsubscript{3} are significantly more stable for temperatures below 640 °C. Above this temperature the methane conversion decreases as well, probably due to the PdO decomposition. For the platinum-rich catalyst, 1:2PdPt/Al\textsubscript{2}O\textsubscript{3}, the conversion is very low although stable. Pt/Al\textsubscript{2}O\textsubscript{3} also has poor activity at the lower temperatures, but at 695 °C the methane conversion is improved.

These results reveal that not only the level of activity is influenced by the molar ratio of palladium and platinum, but the ability to keep a constant activity with time is also affected. Even though 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} showed an excellent activity, its stability is insufficient. Nevertheless, it achieves a better stability than the monometallic Pd catalyst, indicating that the Pd-Pt alloy hampers the loss in activity but the amount of alloy in 4:1PdPt/Al\textsubscript{2}O\textsubscript{3} is not enough to stabilise the conversion. By increasing the amount of platinum in the catalysts and thereby the amount of alloy, the stability becomes improved. 2:1PdPt/Al\textsubscript{2}O\textsubscript{3} has a very stable conversion with time, even though the amount of PdO is still fairly high. This is most likely due to the close contact between the alloy and the PdO domains.

Hence, the catalysts must contain sufficient PdO to be active at the lower temperatures and sufficient amount of Pd-Pt alloy to achieve stable conversion. Therefore, 2:1PdPt/Al\textsubscript{2}O\textsubscript{3} and 1:1PdPt/Al\textsubscript{2}O\textsubscript{3} have the most promising catalyst compositions in terms of molar ratio of the catalysts tested. These catalysts obtain very stable conversion and fairly high activity.

6.4 Influence of support materials on the catalytic activity (Paper III)

The effect of support material on the catalytic performance for methane combustion has been studied for the catalysts described in Section 5.4. Dissimilarities in activity and combustion profiles are observed between the various support materials.
Figure 6.5. Transient activity tests for Pd/Al₂O₃ (■), 2:1PdPt/Al₂O₃ (▲), 2:1PdPt/LMH (●), 2:1PdPt/ZrO₂ (○), 2:1PdPt/Ce-ZrO₂ (□) and 2:1PdPt/Y-ZrO₂ (△) during (a) heating ramp (b) cooling.

2:1PdPt/Al₂O₃ is the most active catalyst in the low-temperature region; 2:1PdPt/Ce-ZrO₂ is the most active between 620 and 800 °C, whereas 2:1PdPt/LMH is superior for temperatures above 800 °C.

The performance of the catalysts during the transient activity tests is presented in Figure 6.5a-b. Similar combustion behaviour as for the Pd/Al₂O₃ catalyst is observed for 2:1PdPt/Al₂O₃, although it is not as active as the monometallic catalyst. By changing support material the drop in activity due to PdO decomposition may be suppressed. The PdO decomposition features are less pronounced for the three zirconia-containing catalysts. Narui et al. [38] have observed similar behaviour for monometallic Pd catalysts. They speculated that presence of stable PdO species in the PdO/ZrO₂ interface may stabilise the PdO decomposition. The suppressed effect of PdO decomposition may also be an effect of the higher oxygen mobility in ZrO₂ materials compared to alumina support, as discussed in Section 5.4. 2:1PdPt/LMH is even less affected by the PdO decomposition; its activity significantly increases in the temperature range of PdO decomposition.

2:1PdPt/Al₂O₃ exhibits the highest activity of the bimetallic catalysts at lower temperatures, but for temperatures above 720 °C the conversion of bimetallic catalysts on other supports surpasses that of the alumina catalyst. The three zirconium-based catalysts present similar activities at the lower temperatures, but at the higher temperatures the conversion of 2:1PdPt/Y-ZrO₂ is slightly lower.
Above 800 °C, 2:1PdPt/LMH is superior among the bimetallic catalysts. This catalyst differs in many aspects from the other bimetallic catalysts. When temperature is increased, the support material itself becomes active towards methane oxidation [122,123]. Sekizawa et al. [124] showed that the high catalytic activity of the Mn-substituted hexaaluminates results in a suppressed drop of activity in the range of PdO decomposition temperature. Hence, a support with high activity is superior for temperatures above the PdO decomposition, although it might be discussed whether the noble metals have any essential effect in this temperature range. However, at lower temperatures 2:1PdPt/LMH shows poor activity.

The recovery of activity during cooling corresponds to the reoxidation of Pd. Similar combustion profiles are shown for the Pd-Pt catalysts as for Pd/Al₂O₃. Recovery of activity occurs at a lower temperature for the alumina catalyst than for the zirconia-based samples. This is most likely due to the improved reoxidation capacity of the material, as previously discussed.

Regardless of the support material, all bimetallic Pd-Pt catalysts have considerably more stable methane conversion than the monometallic palladium catalyst. In Figure 6.6a-b the steady-state activity tests are presented in terms of methane conversion when temperature is increased stepwise from 470 to 720 °C. 2:1PdPt/Al₂O₃ gives a stable conversion up to 620 °C, whereafter the conversion starts to drop with time. Similar observations are made for all bimetallic catalysts, except for

![Figure 6.6](image_url). Steady state activity tests for (a) Pd/Al₂O₃ (■), 2:1PdPt/Al₂O₃ (▲), 2:1PdPt/LMH (○); (b) 2:1PdPt/ZrO₂ (□), 2:1PdPt/Ce-ZrO₂ (△) and 2:1PdPt/Y-ZrO₂ (△). The dotted line represents the temperature.
2:1PdPt/ZrO$_2$ that manages to keep a stable conversion also at 670 °C. The 2:1PdPt/LMH shows rather low activity in the tested temperature interval. When considering the zirconia-based catalysts, the methane conversions over 2:1PdPt/ZrO$_2$ and 2:1PdPt/Y-ZrO$_2$ follow each other closely up to 570 °C. 2:1PdPt/Ce-ZrO$_2$ is superior at all temperatures, especially at high temperatures. Its activity even surpassed the activity of 2:1PdPt/Al$_2$O$_3$ at 620 °C.

The support material clearly affects the catalytic performance of the catalyst. Zirconia-based catalysts appear to be beneficial in suppressing the effect of PdO decomposition; zirconia also enhances PdO reoxidation during cooling. However, the activity at the lower temperatures is much lower than for the alumina catalysts. This may be due to the almost five times higher surface area of the 2:1PdPt/Al$_2$O$_3$ catalyst compared to the other bimetallic catalysts.

6.5 Key aspects of the Pd-Pt catalysts (Papers I-VI)

In Paper IV, the stability over 2:1PdPt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ was further investigated. The results are displayed in Figure 6.7.

The unstable activity over the monometallic palladium catalyst is once again demonstrated. A drop in methane conversion of this magnitude is not acceptable in gas turbine applications. On the other hand, 2:1PdPt/Al$_2$O$_3$ managed to keep its activity during the entire test. Even though 2:1PdPt/Al$_2$O$_3$ started with a lower level of activity at the beginning of the test, the bimetallic catalyst surpassed Pd/Al$_2$O$_3$ after only 6.6 h, for the conditions used in the experiments. In agreement with the results in the other

![Figure 6.7](image-url) Figure 6.7. Activity test when temperature was kept at 500 °C for (■) Pd/Al$_2$O$_3$ and (▲) 2:1PdPt/Al$_2$O$_3$. The dotted line represents the activity of 2:1PdPt/Al$_2$O$_3$ when the temperature was varied in steps between 500 and 600 °C.
papers in this thesis, 2:1PdPt/Al$_2$O$_3$ is superior as an ignition catalyst compared to the monometallic palladium catalyst.

The higher combustion stability of 2:1PdPt/Al$_2$O$_3$ is confirmed at pressure up to 15 bar in a high-pressure test facility, which will be described in more detail in Chapter 8. After a while, 2:1PdPt/Al$_2$O$_3$ showed a higher activity for methane combustion than Pd/Al$_2$O$_3$ also in this test facility. The higher stability of Pd-Pt catalysts has also been demonstrated for greater lengths of time [59].

It is interesting to note that the activity of the 2:1PdPt/Al$_2$O$_3$ catalyst is increased with time, as illustrated in Figure 6.7. As previously shown, more PdO is formed with time in the 2:1PdPt/Al$_2$O$_3$ under oxidative conditions. Accordingly, the increased PdO amount is most likely the reason for the increasing activity since PdO is more active and the alloy appears to have poor activity. The formation of PdO is increased at higher temperatures, resulting in a faster activation process. However, as shown in Figure 6.7 the activity increase appears to level out after 12 h, indicating that the formation of PdO is limited. The catalyst is most likely to stagnate at the activity obtained at this point.

No clear answer is found in the literature to why the activity becomes more stable when certain co-metals are included in the palladium catalyst. An explanation may however be that the co-metals improve the resistance to water inhibition. As discussed in Section 4.4.1, Pd(OH)$_2$ is produced at lower temperatures, but the production is not established for the temperatures used in the activity tests. Some representative DRIFTS spectra of 2:1Pd:Pt/Al$_2$O$_3$ collected both under reaction and desorption are presented in Figure 6.8. By comparing Figure 6.8 and Figure 4.9 it is clear that less surface hydroxyls are adsorbed on 2:1PdPt/Al$_2$O$_3$ than on Pd/Al$_2$O$_3$. Otherwise the features in the spectra are very similar. Since no additional peaks for the Pd-Pt alloy or Pt are found in the spectra it may be concluded that the alloy is less affected by the hydroxyls. If this is the case, the alloy may have higher ability to dissociatively adsorb CH$_4$. The reason for the water inhibition is suggested to be the cleavage step becoming even slower if surface hydroxyls are formed since they are considered to be inactive for splitting the C-H bond [48]. Consequently, the bimetallic catalysts may be less affected by hydroxyl formation at 200 °C as it has other ways of splitting the methane molecule than PdO due to the alloy. Nevertheless, this is not ascertained for the temperatures used in the activity tests.
Figure 6.8. In-situ DRIFTS spectra taken at 200 °C over 2:1PdPt/Al₂O₃ under (a) methane combustion (1 % CH₄, 4 % O₂, balance He), (b) desorption (4 % O₂, balance He)

From the morphological studies it is shown that the PdO part in the bimetallic catalysts consists of only PdO, without interference of metallic Pd as in the case of the monometallic catalysts. As no metallic crystals are able to oxidise in the PdO part, the structure in the active PdO phase is more durable compared to that of Pd/Al₂O₃. In addition, the close contact between the PdO and the alloy domain results in the bimetallic catalysts always having a metallic phase for splitting the C-H bond, independent of the oxidation time. These features probably make the bimetallic catalysts to be more stable catalysts than the Pd/Al₂O₃ catalysts.

Independent of which reason is the correct answer to the stability issue the close contact between the PdO part and the Pd-Pt alloy is most likely the cause for the higher stability.

Just as for the monometallic catalysts, the reaction mechanism for methane combustion over 2:1PdPt/Al₂O₃ is not yet known. The alloy part may both help with the splitting of the methane molecule and the oxygen molecule, resulting in a higher activity compared to the two metals separately.
It is essential for an ignition catalyst to maintain a constant conversion at the same time as the level of activity is high. The environment inside a gas turbine combustor is very harsh for a catalyst, with high temperature, pressure, flow velocity and large temperature fluctuations. Therefore, other deactivation processes may take place than previously considered in this thesis. As the durability of the catalysts is one of the most crucial factors for a successful commercial application, various deactivation processes must be taken into account when designing a catalytic system. In this chapter, different deactivation phenomena are discussed and special attention is given to thermal deactivation, water inhibition and sulphur poisoning.

### 7.1 Thermal deactivation (Paper IV)

Deactivation after prolonged exposure to high temperatures has been extensively investigated in catalysis contexts [125-129]. The deactivation process is far from trivial and various phenomena may occur simultaneously such as phase changes, sintering, compound vaporisation etc. Since the temperature inside the gas turbine combustor is very high, information about thermal deactivation is of great importance.

In order to study the thermal stability, the catalysts were aged in an furnace at 1000 °C for 10 h in an air stream with 15 vol.% of water vapour. This is a very harsh treatment as the temperature is above the normal operation temperature of the catalysts and above the temperature window of PdO. Furthermore, hydrothermal treatment is much more severe than thermal ageing without water vapour. However, these conditions enhance the ageing and give an indication of the long-term stability of the catalysts. The monoliths and the catalyst powders were aged at the same time to be able to link the activity results with the changes of the catalysts. The catalytic activity was evaluated in the same way as the second type of activity tests, described in Section 6.1.2.
Figure 7.1. Steady-state activity tests of (a) Pd/Al₂O₃ and (b) 2:1PdPt/Al₂O₃. The black line indicates the activity of the as-prepared samples and the dotted line the activity of the aged samples.

The activities of as-prepared and aged Pd/Al₂O₃ catalysts are presented in Figure 7.1a. The curves show that the thermal treatment has a strong impact on the catalytic performance, where the aged catalyst has considerably lower activity than the as-prepared one. The conversion decreases with time for both samples, as previously has been discussed, even though that of the aged sample decreases less.

In Figure 7.1b the activities of the as-prepared and aged 2:1PdPt/Al₂O₃ catalysts are shown. The loss of activity due to thermal deactivation is significantly lower than that for the monometallic Pd catalyst, although small variations are observed. Fortunately, the ability to keep a constant activity is sustained upon ageing.

In order to clarify the discrepancy in the activity loss between the two catalysts, their textural properties were determined and are compiled in Table 7.1. Decreasing surface area upon ageing may to some extent reduce the activity of both catalysts. From PXRD diffraction patterns it is revealed that the aged samples have higher θ-Al₂O₃ content than the as-prepared samples. Hence, the thermal treatment gives rise to a phase transformation from δ-Al₂O₃ to θ-Al₂O₃. It is generally known that phase transformation of alumina is accompanied by a loss of surface area [107], and therefore results in a lower surface area after thermal treatment. The restructuring of the alumina lattice may result in pore collapse and encapsulation of the active phase, in this case the noble metals, rendering them inaccessible to the gas molecules and thereby lowering the activity. However, since the loss of surface area is in the same
range for both catalysts, the differences in activity are most likely not associated to changes in the surface areas.

Due to the high temperature treatment it is likely that the metallic crystals sinter into larger crystals, reducing the active surface available for the combustion reactant. As seen in Table 7.1, the average crystal size of PdO, determined from the PXRD data, is smaller in the 2:1PdPt/Al₂O₃ catalysts than in Pd/Al₂O₃ independently of the treatment. However, no major changes are observed upon ageing. The reason for the higher thermal degradation of Pd/Al₂O₃ is most likely not connected to the crystal growth. The catalysts in the present study were calcined at considerably higher temperature than used in most ageing studies, resulting in larger initial sizes of the palladium-containing particles. Due to the larger particles, and thus the larger distance between them, the ability of moving in the alumina matrix to cause crystal growth and sintering is reduced. Nevertheless, atomic migration via the surface or the gas phase by the so-called Ostwald ripening process is still possible.

Vaporisation of the noble metals is also a phenomenon that may decrease the activity. Vaporisation may either contribute to the sintering of the supported metals through the Ostwald ripening process or lead to significant loss of catalytic material in the effluent gas stream. In either case, the number of active sites is decreased. As the noble metal loading is slightly reduced for both catalysts after ageing, as seen in Table 7.1, at least the last phenomenon is most likely occurring. For the Pd/Al₂O₃ catalyst the Pd loading is decreased from 5.1 to 4.8 wt%. In 2:1PdPt/Al₂O₃ the Pd content remains constant, but the platinum content is decreased. Since palladium in the form of PdO appears to be the active phase in the bimetallic catalysts, the loss of Pt will not probably severely decrease the activity. According to the literature, Pt is more easily vapourised than Pd, especially in the form of PtO₂ [127]. Small amounts of PtO₂ on the catalyst surface
were detected by XPS, which may explain the lower stability of platinum. It is interesting to note that the alloy appears to stabilise the Pd phase, which is probably related to the solid solution formation at higher temperatures having the nominal composition value. This is in line with what previously has been reported in the literature [130].

From TEM studies of the aged Pd/Al₂O₃ materials it has been shown that the particles have more faceted structures and almost no metallic Pd is found in the sample. The reconstruction into a less active morphology may therefore be another explanation of the poor stability against thermal ageing. According to TEM analyses of the aged 2:1PdPt/Al₂O₃ sample the alloy part is unaffected by ageing, although the PdO part is larger. However, the changes in the morphological structure after ageing may also be due to the TEM images being obtained after the activity tests.

In summary, the thermal deactivation is worse for Pd/Al₂O₃ than for 2:1PdPt/Al₂O₃. Hence, Pt prevents the ageing of Pd catalysts. The stability difference may be attributed both to changes in the morphology and to the loss of palladium of the monometallic catalyst, which is not observed for the bimetallic catalyst.

### 7.2. Water inhibition (Paper V)

The effect of water has also been studied over the two catalysts, as small amounts of water may be found in natural gas. In Figure 7.2 the activity is presented in terms of methane conversion plotted versus time on stream when 5 vol.% water vapour periodically was added to the feed stream. The behaviour is clearly different over the monometallic and the bimetallic catalysts when extra water is present in the feed. As previously shown, Pd/Al₂O₃ gradually loses activity with time, even under dry conditions. When extra water is introduced into the feed the catalyst continues losing activity, but the rate of activity loss is increased and the slope of the activity curve becomes steeper. When water is removed the activity increases slightly, but not to the initial level before the introduction. It appears as it the Pd/Al₂O₃ catalyst has difficulties to recover after water exposure, which is in agreement with findings of Araya et al. [82] that water enhances the deactivation process of Pd-catalysts.

The bimetallic catalyst behaves differently in presence of water. When water vapour is added to the feed stream the activity decreases abruptly to a lower level, which is kept during the entire water step. When the vapour is removed the activity fully recovers to
the level before the introduction, suggesting that water does not affect the bimetallic catalyst to the same extent as Pd/Al$_2$O$_3$.

The two different behaviours observed for the monometallic and the bimetallic catalysts indicate that two different deactivation processes occur during the water exposure. The stepwise deactivation observed for the bimetallic catalyst indicates that water molecules are weakly absorbed on the catalyst surface and cover some of the active sites. This feature will most likely be wholly reversible as soon as the water is removed, as shown in the experiments. This process is also possible to some extent for Pd/Al$_2$O$_3$, but this catalyst also experiences another deactivation process as the conversion decreases continuously during the whole water step. One explanation is that it might be possible that water enhances the oxidation/sintering process, described earlier. Another possibility may be that Pd(OH)$_2$ is actually formed at 500 °C due to the high water concentration in the feed. As the alloy part of the bimetallic catalyst appears to be less affected by the hydroxyls produced, at least at 200 °C (see Section 6.5 for more details), the additional water in the feed stream may not affect the activity of 2:1PdPt/Al$_2$O$_3$ in the same way.

### 7.3. Sulphur poisoning (Unpublished results)

Depending on the origin of the natural gas, some sulphur species may be present in various concentrations, usually in the form of SO$_2$ or H$_2$S. These sulphur compounds have been reported to have a dramatic effect on the catalytic performance, especially for Pd-based catalysts [131-135]. The deactivation is attributed to irreversible
Figure 7.4. Activity test performed at 500 °C at various concentrations of SO₂. The GHSV was 300 000 h⁻¹ during the experiment. The dashed line represents 2:1PtPd/Al₂O₃ and the solid line Pd/Al₂O₃.

adsorption of sulphate species on the metal, blocking the active sites for further methane conversion [136,137]. The impact of sulphur on activity is temperature dependent [138], and is therefore more severe on the catalysts located near the inlet of the combustor.

The sulphur tolerance was investigated for Pd/Al₂O₃ and 2:1PdPt/Al₂O₃; the result is presented in Figure 7.4. The activity tests were performed in the Perstorp Formox test facility, a tubular reactor similar to the one described in Section 6.1.1 but the product gas was analysed by a FID detector. The experiments were carried out by periodically adding SO₂ in various concentrations to the feed stream. The catalysts were allowed to stabilise in the reaction mixture (1.5 vol.% CH₄ in air) prior to the sulphur tests.

During exposure to the lower SO₂ concentration levels, i.e. 9 and 15 ppm, the methane conversion over 2:1PdPt/Al₂O₃ remained almost unchanged. In contrast, the Pd/Al₂O₃ catalyst exhibited a clear deactivation, even at such a low SO₂ concentration as 9 ppm. When the concentration was increased, the bimetallic catalyst was also affected by the sulphur, but not to the same extent as the monometallic palladium catalyst. Hence, 2:1PdPt/Al₂O₃ appears to be more resistant against sulphur than Pd/Al₂O₃.

This result is not very surprising since platinum has been reported to be more resistant against sulphur, and in some cases the activity is even enhanced by the presence of sulphur [133,139]. Whether the morphology, with a PdO part in close contact with a Pd-Pt alloy, improves the sulphur tolerance or not is difficult to determine from these data.
A gas turbine operates at pressures between 5 and 30 bar, depending on the type of gas turbine. Despite this, most activity tests reported in the literature for ignition catalysts have been carried out close to atmospheric pressure. The scale-up from atmospheric to elevated pressure is not a straightforward task [140]. Therefore, the catalytic performance in a real gas turbine is hard to predict from atmospheric tests. For that reason it is important to investigate what happens with the catalytic activity of methane combustion when pressure is increased. In order to gain more understanding about the pressure impact, catalysts have been tested in a high-pressure test facility. The test rig operates more closely to real gas turbine conditions, with high pressures and flow velocities. In this chapter the pressure impact on the catalytic activity is discussed.

### 8.1 Experimental equipment

The high-pressure test facility allows tests to be conducted at pressures up to 35 bar with inlet temperatures up to 600 °C. A catalytic combustor, electrical heaters and fuel injection system are all placed inside a pressure vessel with diameter 300 mm and height 3 m. A compressor increases the pressure of ambient air. Thereafter, a group of electrical heaters preheats the gas to the desirable inlet temperature of the catalytic combustor. The methane is supplied through a fuel injection system located upstream the catalysts. A number of thermocouples measure the temperatures in different locations in the system. A picture of the high-pressure test facility is shown in Figure 8.1. More details regarding this test facility may be found elsewhere [141].
8.2 Influence of pressure on methane conversion (Paper VI)

The pressure impact on methane combustion was evaluated by lowering the pressure stepwise from 15 bar down to 5 bar. As discussed in previous chapters, one of the more efficient ignition catalysts is 2:1PdPt/Al₂O₃. This catalyst was compared to the monometallic palladium catalyst, Pd/Al₂O₃, at high pressure. Monoliths of size \( \phi \) 35 mm, length 20 mm, were used in the tests. The inlet temperature was kept at 500 °C and the linear gas velocity was kept at 6.5 m/s. To keep the linear velocity constant is of great practical interest, since commercial gas turbines are operated at constant linear velocity; pressure is varied when changing load.

Figure 8.1. Picture of the high-pressure test facility
The results concerning the pressure influence are displayed in Figure 8.2. Both catalysts show similar trends, i.e. a decrease in methane conversion with increasing pressure. A more clear variation of methane conversion is shown for the lower pressures, but when the pressure surpassed 10 bar the variation in methane conversion levels out.

Other research groups have also investigated the pressure impact, with widely dissimilar results [142-146]. The variation in the results may be due to differences in the operating conditions, such as keeping the mass flow instead of the linear velocity constant.

Chou et al. [144] have numerically investigated the pressure impact and found that two competing factors affect the overall methane conversion when pressure is changed. First, the diffusion of reactants through the gas to the catalyst surface decreases with increasing pressure as the diffusion coefficient decreases. Consequently, methane conversion is expected to decrease with pressure. Second, surface reaction rate increases with pressure due to the increased heat released from the combustion reaction, resulting in higher methane conversion. By evaluating these two factors it was found that a decrease in methane conversion with pressure is to be expected for levels above 2 bar due to the combustion being largely controlled by gas phase diffusion rate of the fuel at higher pressures.

The elevated pressure has not only negative effects. Ozawa et al. [147] have shown that the NO\textsubscript{x} level tends to decrease with pressure. Furthermore, no major difference in the pressure drop over the monolith was observed for the various pressures.
This thesis describes the development of ignition catalysts for gas-turbine combustors. When designing an ignition catalyst for this application, both the level and the stability of the activity for methane combustion must be considered. It is well known that supported monometallic palladium catalysts have an excellent initial activity for methane combustion. However, this type of catalysts suffers from severe deactivation with time, making it increasingly difficult to ignite the methane. Based on the experimental results presented in this thesis, the poor stability may be attributable to morphological changes of the palladium particles during operation. The particles of the as-prepared catalyst consist of small crystals of both PdO and Pd. During operation the crystals become more oxidised, as well as more sintered. From the literature it is suggested that small amounts of metallic palladium increase the methane conversion, because of the metal having high ability to split the first C-H bond in the methane molecule. Hence, the polycrystalline structure observed for the as-prepared catalyst is most likely more active than the fully oxidised catalysts obtained during operation. The deactivation may also to some extent be due to water inhibition from the surface hydroxyls generated in the combustion reaction. Still, this feature is most likely only significant at very low temperatures and is a very small contribution to the deactivation in the temperature window of the ignition catalysts.

In order to stabilise the activity over the palladium catalysts, a range of different compositions of bimetallic catalysts has been evaluated, which all contain palladium as one of the active components. Special emphasis has been given to the influence of co-metals, molar ratio and support materials.

Through morphology studies the bimetallic catalysts have been divided into three different groups, depending on where the co-metals were found in the catalyst, i.e. the co-metal reacted with the alumina support to form spinel structures, the co-metal formed separate particles and the co-metal alloyed with palladium.
It was proven that it is possible to stabilise the activity by adding certain co-metals into the palladium catalyst. The catalysts that acquired a stable conversion contained either a co-metal that forms separate particles in close contact with the Pd particles (e.g. Ir, Cu and Ag) or a co-metal that is alloyed with Pd (e.g. Pt and Au). The co-metals forming a spinel structure with alumina (e.g. Ni and Co) had similarly unstable activity as the monometallic palladium catalyst. The most promising catalyst tested was a Pd-Pt catalyst, when considering both the level and the stability of the activity. Even though the initial activity was lower for the Pd-Pt catalyst compared to the Pd catalyst, the Pd-Pt catalyst has been shown to be superior in the long run due to its higher stability.

As a combination of Pd and Pt appears to be a promising candidate for the ignition catalyst, the catalyst survey was continued by investigating the molar ratio between Pd and Pt. From morphological studies it was revealed that the particles of the Pd-Pt catalysts was split into two different domains; one consisted of only PdO and one likely consisted of an alloy between Pd and Pt. These two domains were always found in close contact for catalysts rich in palladium. The size of the alloy increased with the amount of platinum in the catalysts at the expense of the PdO domain. It was found that the molar ratio had major impact on the catalytic performance. Small amounts of alloy increased the activity of palladium catalysts. However, considerably more Pt was required to stabilise the activity, but the level of activity became lower. Hence, it is a balance between the amount of PdO and Pd-Pt alloy in order to obtain an ignition catalyst with high activity and stability.

When the bimetallic Pd-Pt catalysts are exposed to a higher temperature than the stability window of PdO, the PdO decomposes and the metallic Pd is most likely incorporated into the alloy. When the catalysts are reoxidised the palladium presumably has to diffuse out from the alloy in order to be oxidised. For that reason, the bimetallic catalysts have a slow reoxidation process. In order to improve the reoxidation properties, various support materials have been evaluated. Zirconia-based support materials appear to be promising, especially the cerium-doped zirconia. However, due to the low surface area of the zirconia samples, the alumina catalyst is more active at the lower temperatures.

The reason for the higher stability of the Pd-Pt catalysts has been investigated. For lower temperatures, the superior stability of Pd-Pt catalysts may be ascribed to the higher water tolerance since the alloy is presumably less affected by the surface hydroxyls. However, this is not verified for the higher temperatures. Another possible explanation arises from the morphology of the PdO domain, which does not contain
any metallic Pd crystals. Hence, no oxidation of metallic Pd is possible during operation. In addition, the PdO domain will always be in close contact with a metallic phase, which may increase the rate of splitting of the first C-H bond in the methane molecule.

Since the environment inside a gas turbine combustor is very harsh, various deactivation processes may take place simultaneously. Therefore, it is important to evaluate the risk of deactivation when designing an ignition catalyst. Results from this thesis signify that the Pd-Pt catalyst is clearly more tolerant compared to the monometallic palladium catalyst as to thermal deactivation, water inhibition and sulphur poisoning.

The higher stability of the Pd-Pt catalyst was confirmed in a high-pressure test facility, working at pressures up to 15 bar, i.e. more realistic operation conditions for a gas turbine. The pressure influence on the combustion activity is negative, when the linear velocity is kept constant. However, the pressure impact is much more prominent at lower pressures, but levels out for pressures above 10 bar.

From the results presented in this thesis it has been shown that the bimetallic Pd-Pt catalyst is a promising ignition catalyst; it has high stability during operation, as well as high tolerance for thermal deactivation, water inhibition and sulphur poisoning. This results in an improved lifetime of the Pd-Pt catalyst compared to that of the monometallic palladium catalyst.
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Last, but not least, I wish to express my deepest gratitude to my family and my boyfriend Andreas for their help and encouragement.
# Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionisation detector</td>
</tr>
<tr>
<td>GHHSV</td>
<td>Gas hourly space velocity</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma – atomic emission spectroscopy</td>
</tr>
<tr>
<td>In-situ XRD</td>
<td>In-situ X-ray diffraction</td>
</tr>
<tr>
<td>LMH</td>
<td>Manganese-substituted lanthanum hexaaluminate</td>
</tr>
<tr>
<td>n</td>
<td>Number of H atoms in hydrocarbon species</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Nitrogen oxides (includes both NO and NO$_2$)</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TPO</td>
<td>Temperature programmed oxidation</td>
</tr>
<tr>
<td>UHC</td>
<td>Unburned hydrocarbons</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>x</td>
<td>Solid solution coefficient of Pt$_{1-x}$Pd$_x$</td>
</tr>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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References


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