Catalytic Combustion of Methane over Axially Non-Uniform Pd Catalytic Monoliths Prepared by Chemical Vapour Deposition

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To my beloved parents
“Τῆς παιδείας τῆν μὲν ρίζαν εἶναι πικράν, τὸν δὲ καρπὸν γλυκύν”

“The root of education is bitter yet the fruit is sweet”

Isocrates
Abstract

The escalating demand for electric power is expected to continue in the future. The need to satisfy this demand without sacrifice of environmental quality is a challenging problem facing all forms of power generation including the combustion-based power generating industry. Catalytic combustion is a prevention technology with the potential to achieve low emission gas turbines and thus comply with the advent stringent anti-pollution laws. This technology though continues to face problems due to poor catalyst performance at the high operating temperatures required by modern high efficiency gas turbines, as the catalyst systems are subjected to extreme temperature gradients which induce severe thermal stresses. Improved durability is possible for catalyst utilised in catalytic combustion through the alleviation of axial temperature gradients. There is therefore a need for new catalyst design.

The aim of this work was to examine the potential of axially non-uniform catalyst distribution along monolith reactors for improving catalytic combustor performance. A two-dimensional mathematical model was formulated to investigate the effect of axially non-uniform catalyst distribution on temperature and concentration gradients in catalytic monoliths operating under both steady state and transient methane combustion conditions. It was observed that exponentially decreasing catalyst distributions initiated light-off at the entrance of the monolith. In effect, temperature gradients were lowered as compared to monoliths with uniform catalyst distribution under steady state conditions. Bulk fluid temperature suitable for homogeneous reaction initiation was reached further upstream. For transient conditions, non-uniform distributions alleviated axial temperature gradients but at the expense of large temporal gradients. It was thus concluded that non-uniform catalyst distributions could achieve lower thermal stresses under steady operation yet care should be exercised in their operation during transient conditions.

The potential of chemical vapour deposition (CVD) for preparing axially non-uniform palladium catalytic monoliths was also investigated. The sublimation, deposition and reduction of the metal-organic precursor, palladium (II) acetylacetonate, was investigated through thermogravimetry and XRD. The temperature range for sublimation, avoiding thermal decomposition, was determined to be 100 - 160°C and required to take place in the presence of an inert gas such as helium. The complex was found to be highly unstable in hydrogen. The Clausius-Clapeyron relation determined for
the complex, \( \ln P = -96 \times 10^3/RT + 29.26 \), is indicative of the low vapour pressure of the precursor. Deposition of the metal-organic required the presence of hydroxyl groups. To obtain palladium metal particle deposits, the precursor was reduced under hydrogen at a subsequent stage. Pd on \( \gamma\)-Al\(_2\)O\(_3\)/cordierite catalytic monoliths were subsequently prepared in a CVD reactor. The effects of operating variables such as carrier gas flowrate, sublimation and deposition temperatures and process duration on the catalyst morphology were investigated. All catalyst prepared had exponentially decreasing distribution profiles and palladium particles obtained were small enough to warrant their use in catalytic applications.

The performance of the catalysts was assessed under atmospheric methane combustion conditions. They showed alleviation of temperature gradients along monolith walls and improved methane conversions as compared to uniform catalysts prepared by impregnation. A mathematical model predicted the trends of wall temperature profiles satisfactorily. Non-uniform catalysts achieved lower temperature gradients and higher fuel conversions than uniform catalysts as high reaction rates were present further upstream. Hence, axial catalyst distribution was found to improve performance in the combustion of methane.
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1. Introduction

The present demand for increased electric power is expected to continue to escalate in the future. The need to satisfy this demand without sacrifice of environmental quality is one of the most important problems facing all forms of power generation. With the advent of modern stringent antipollution laws, the combustion-based power generating industry seeks a way for reducing the production of air pollutants such as nitrogen oxides (NOx), carbon monoxide (CO) and unburnt hydrocarbons (UHC) from gas turbine engines. Catalytic combustion, first proposed by Pfefferle (1975) is the technology which offers the potential to achieve low emissions gas turbines. Operating temperatures are well below those typically found in conventional combustors thus inhibiting NOx formation routes in the gas phase. In addition, most of the combustion occurs on the catalyst surface; surface production of NOx is low or non-existent. Homogeneous reactions initiated typically by the end of the catalytic monolith lead to complete CO and hydrocarbon oxidation.

The renewed interest in catalytic combustion has arisen as gas turbine based systems are becoming the preferred approach of electric power generation, particularly for clean burning fuels such as natural gas. Natural gas produces only carbon dioxide and water as the products of combustion but a key problem emanates from the simultaneous emission of NOx during conventional combustion.

Over 30 million tonnes of NOx are vented to the earth’s atmosphere each year world-wide; a key source being power stations (Armor, 1995). Current levels of NOx emissions have been reduced to 15-40 ppm using technologies such as lean premixed dry low NOx (DLN) combustion combined with post exhaust treatment by selective catalytic reduction (SCR). These technologies result though in high capital and operating costs and they are not completely effective options. DLN requires sufficient fuel to maintain a stable flame while SCR is an ‘end-of-pipe’ as opposed to a ‘prevention’ technology, and produces ammonia an equally hazardous pollutant if emitted to the environment (Stambler, 1993).

There is increasing interest in the use of gas turbines for power generation while at the same time more stringent regulations on NOx emissions are being implemented mainly in the US, Europe and Japan. Under guidelines of the 1990 Clean Air Act Amendments, emissions must be further reduced to less than 10 ppm (Cusumano, 1995).
1. Introduction

The goal of the US is to reduce NOx by two million tonnes from 1980 levels. More recently, under the 1997 Kyoto Protocol the EU aim is by 2005 to reduce the greenhouse gases by 8% (based on 1990 emissions) which include NOx and CO (UNFCCC, 1998). For the UK, total NOx emissions in 1990 were about 2.74 million tonnes. This situation provides an opportunity for catalytic combustion and has stimulated much research on catalytic combustors in recent years.

Catalytic combustion of lean premixed fuel and air within the gas turbine is an alternative, prevention technology for achieving emissions levels of 1 ppm (Etemad et al., 1999). Catalytic combustion is thus a means of producing electric power with the formation of virtually no pollution (Cusumano 1994). Pollution prevention is in addition more efficient and thus more cost effective.

However as Etemad et al. (1999) emphasise, this technology continues to face problems due to poor catalyst performance at the high operating temperatures required by modern high efficiency gas turbines. Catalyst systems are subjected to extreme temperature gradients which lead to severe thermal stresses. There is therefore a need for new catalyst design. In addition, issues concerning the system design and how to cope with varying power loads also need to be addressed. The incentive thus exists to overcome the remaining hurdles and develop a commercial unit for industrial gas turbines which achieves single digit NOx emissions with long-term durability.

The market and environmental challenges are thus increasing the demand for improved catalysts, as Kung et al. (1998) comment. There is a need for new materials and synthetic methods to yield catalysts with enhanced activities, selectivities and durabilities. Chemical vapour deposition has attracted the attention of researchers in the field of catalysis as it has shown to be promising (Yoo, 1998). The opportunity therefore arises to utilise this technique for the preparation of novel axially non-uniform palladium catalytic monoliths and utilise them for combustion of methane.
1. Introduction

1.1 Objectives of this Work

It has been suggested that improved durability is possible for catalysts utilised in gas turbine catalytic combustors by alleviating axial temperature gradients. This thesis attempts to provide an insight to the potential of axially non-uniform catalyst distribution for alleviating temperature gradients. Understanding the temperature and concentration fields inside a catalytic monolith with non-uniform catalyst distribution is essential for developing a high performance catalytic gas turbine. The opportunity arises to formulate a comprehensive mathematical model to investigate the effect of non-uniform catalyst distribution in catalytic monoliths on temperature and concentration under gas turbine operation. The focus is on the temperature gradients as they are associated with thermal stresses. Concentration gradients are also investigated as they are useful for assessing further catalyst performance.

The need for preparing such non-uniform catalyst leads to the second aim of the research. Chemical vapour deposition is explored as a method for preparing palladium catalytic monoliths with axially non-uniform distribution. More specifically sublimation, deposition and reduction of the precursor employed are investigated; catalytic monoliths are subsequently prepared and the influence of reactor operating conditions on their distribution is studied. The performance of these catalysts is finally evaluated under methane combustion conditions.

1.2 Structure of this Thesis

In Chapter 1, the fundamental aspects of catalytic combustion in the application of gas turbines for power generation with limited emissions is introduced. The need for new catalyst design is addressed and the novel application of chemical vapour deposition as a method for the preparation of axially non-uniform catalyst is introduced. The objectives of this work are thereafter given. In Chapter 2, an introduction to catalytic combustion and a survey of the state-of-the-art in the field of catalytic combustion for gas turbine application is reported. Attention is given to both experimental and theoretical investigations. The need for improvement of catalyst durability is addressed and the idea of non-uniform distribution of the active element as a way of alleviating
1. Introduction

thermal stresses is introduced. The phenomenon of chemical vapour deposition is reported and its present role in the field of catalysis is discussed. Chapter 3 introduces a mathematical model which has been formulated to investigate the effect of axially non-uniform catalytic monoliths on temperature and concentration profiles under methane combustion conditions. Analysis and discussion of theoretical results are included in the chapter. Chapter 4 deals with an experimental investigation of the sublimation, deposition and reduction of palladium (II) acetylacetonate (the precursor employed for preparing the catalysts) and a Clausius-Clapeyron relation for this complex is presented. In Chapter 5, chemical vapour deposition as a novel technique for preparing axially non-uniform palladium catalysts is investigated under experimental conditions and results are discussed. The experimental investigation of the catalyst performance under methane combustion conditions is presented in Chapter 6. Performance of non-uniform catalyst are compared to uniform in addition to theoretical data provided by the mathematical model. Conclusions and future work are outlined in Chapter 7.
2. Literature Survey

2.1 Gas Turbines

Gas turbines were not a major feature in electricity generation until the present large industrial frames were adopted 10-15 years ago. These have been advanced in size and efficiency and in 1998 gas turbines took a share of 45% of the new power plant market. Recently published data show a staggering year-on-year increase of nearly 100% in the output of sold gas turbines (White, 2000). Total world sales up to 1998 were 33 GW. Sales in 1999 have increased that capacity to 64 GW.

The development of large gas turbines has coincided with the availability of natural gas from an expanding exploration programme. Nevertheless, the predicted growth is such that a quadrupling of present demand by 2020 is expected. Natural gas (which consists mainly of methane) is a resource with reserves according to Burch and Parkyn (1992) expected to last for another 50 years compared with 20 years for crude oil reserves. Reserves at the year 1992 were in excess of $10^{14}$ m$^3$. Gas turbines can run equally well on syngas and the use of low-heating value (LHV) mixtures from biomass gasification is presently considered (Forzatti and Groppi, 1999).

The increase in demand for electric power has led to the increase in popularity of gas turbines. An example of the strong growth of electric power demand world-wide is the case of the United States. As Cusumano (1992) reports, the US Department of Energy anticipates a shortfall in capacity in the United States by the next decade when an additional 100,000 megawatts will be needed. For calibration, a 1000 megawatt plant is required to meet the energy of a typical city of one million people.

The time-frame therefore for retrieving this energy is short but the increase in air pollutants is unavoidable if present technology is to be used. Possible use of nuclear and coal power is not the answer, with eight to twelve years required to license and construct such power plants and most importantly the safety and environmental concerns are vast. Construction time of gas turbine power plants is short, usually two to five years. Furthermore, standard turbine designs allow incremental expansion of power capacity without the enormous capital investments involved in the expansion of typical nuclear and coal plants.
As Rostrup-Nielsen (1994) points out, natural gas is a clean fuel for power generation at high efficiency. Natural gas fired turbine power generation is thus an attractive solution to the emissions problem and there is an abundant supply of natural gas. White (2000) reports that global average energy efficiency in power generation is only 30%; 70% of all the energy input into the power sector is still being wasted. Advanced gas turbines have the potential for higher electric efficiencies but the need to eliminate the formation of NOx remains. Thus the current goal of gas turbines is to reduce emissions while at the same time improve their efficiency.

2.1.1 Gas Turbine Operating Principles

In industry, the use of gas turbines as a source of power generation is already widespread. The theory of gas turbine operation is described in various books such as that by Cohen et al. (1987). The simplified schematic of a gas turbine (Figure 2.1) illustrates their key features.

![Figure 2.1: Simplified schematic of a gas turbine (Kolaczkowski, 1995).](image)

The compressor draws in atmospheric air and adiabatically compresses it to pressures typically in the range of 8-20 atm for industrial gas turbines. The compressor discharge temperature depends on the pressure ratio of the compressor and varies from about 300°C at 9 atm to about 350°C at 12 atm. The compressed air is then fed into a combustion chamber where the fuel is injected and combusted. Gases reaching temperatures in excess of 1800°C, pass through an expansion turbine that provides the
power to the air compressor. Gases are then cooled with bypass air to 1300°C before being passed through to a power turbine, in the case of stationary gas turbines. In the case of aircraft jet engine, the gases are passed through a nozzle to provide the thrust required (Kolaczkowski, 1995). Minimum pressure losses in the combustion system in particular is an important factor in gas turbine operation. Pressure losses have the effect of decreasing the turbine pressure ratio relative to the compressor pressure ratio and thus reduce the net work output from the plant (Cohen et al., 1987).

2.1.2 Production of Nitrogen Oxides Emissions

Even though natural gas is considered a clean fuel as its combustion products are carbon dioxide and water, the NOx emissions associated with its use is a significant problem. The flame temperatures generated in the combustor chamber of a gas turbine are in excess of 1800°C and it is at these temperatures that nitrogen in the air is combusted resulting in the formation of about 150-200 ppm NOx emissions from the turbine. Power plants are major source of nitric oxide emissions. NOx emissions can also be significant in chemical operations such as nitric acid plants.

Nitric oxide is a component of acid rain as it forms nitric acid with the water vapour in the clouds. Furthermore, the NOx formed during gas-phase combustion is the precursor of the nitrogen dioxide; the principle component of photochemical smog. These emissions are also lung irritants and are therefore strictly regulated in many countries. Restrictions are especially severe in areas that have serious air quality problems, including California and Texas in the United States, Japan and parts of Europe.

Miller and Bowman (1989) review the research in NOx production and indicate that there are four principal reaction mechanisms for the formation of NOx in gas-phase combustion. These are: the thermal (Zel’dovich) NOx; the prompt (Fenimore) NOx; the fuel-bound nitrogen mechanism which occurs primarily in the combustion of coal and some liquid fuels; and the NO2 mechanism.

According to Miller and Bowman (1989) in the combustion of clean fuels (that is fuels which do not contain nitrogen components such as methane) oxidation of atmospheric nitrogen (N2) by the ‘thermal’ mechanism is a major source of NOx emissions. At high temperature (above 1550 °C), the usually stable oxygen molecule
(O₂) dissociates to oxygen atoms which are very reactive. The oxygen atom (O) attacks the otherwise stable nitrogen molecule to form NOx. The three principal reactions that comprise the thermal NO formation mechanism are,

\[ O + N_2 \rightarrow NO + N \]  \hspace{1cm} (2.1)

\[ N + O_2 \rightarrow NO + O \]  \hspace{1cm} (2.2)

\[ N + OH \rightarrow NO + H \]  \hspace{1cm} (2.3)

Rates of NO formation in combustion of hydrocarbon fuels can exceed those attributable to direct oxidation of molecular nitrogen by the thermal mechanism especially for fuel-rich conditions. This rapidly formed NO is termed ‘prompt NO’ as its rapid formation is confined to the regions near the flame zone. Some of the hydrocarbon radicals initiating the complex mechanism are given by Miller and Bowman (1989) to be CH, CH₂, C₂, C₂H and C. The mechanism is simplified though as follows,

\[ CH + N_2 \rightarrow HCN + N \]  \hspace{1cm} (2.4)

\[ N + OH \rightarrow H + NO \]  \hspace{1cm} (2.5)

Unlike thermal NOx, prompt NOx is formed at temperatures well below 1500°C.

A principle source of NO emissions in the combustion of fossil fuels is also the nitrogen chemically bound in the fuel. This is a major source of NO emissions for coal and coal-derived fuels which typically contain 0.5-2 % nitrogen by weight. Again the mechanism involved is complex but it includes the formation of HCN. According to Ismagilov and Kerzhentsev (1990), the mechanism is simplified as follows,

\[ HCN + OH \rightarrow HOCN + H \]  \hspace{1cm} (2.6)

\[ HOCN \rightarrow HNCO \]  \hspace{1cm} (2.7)

\[ H + HNCO \rightarrow NH_2 + CO \]  \hspace{1cm} (2.8)

\[ NH_x + H \rightarrow NH_{x-1} + H_2 \]  \hspace{1cm} (2.9)

\[ NH_x + O_x \rightarrow NO + .... \]  \hspace{1cm} (2.10)

\[ NH_x + NO \rightarrow N_2 + .... \]  \hspace{1cm} (2.11)
Finally, the formation of nitrogen dioxide ($\text{NO}_2$) is due to the unreacted NO which reacts with oxygen as follows,

$$\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \quad (2.12)$$

In the combustion of fuels such as methane that do not contain nitrogen compounds, NOx compound (primarily NO) are formed by the thermal and prompt mechanisms. The prompt mechanism predominates at low temperatures under fuel-rich conditions whereas the thermal mechanism becomes important at temperatures above 1550°C.

### 2.1.3 Current Control of Nitrogen Oxide Emissions

The current popular strategy for controlling NOx emissions is through the aftertreatment of combustor exhaust products. The oldest technique for combustion temperature reduction is to provide a heat sink by injecting water or steam into the combustion zone. Examples of other aftertreatment processes are given in Table 2.1 where selective catalytic reduction (SCR) and dry low-NOx (DLN) are those most popular. The various processes currently in use have been reviewed by Siddiqi and Tenini (1981), Armor (1992, 1995) and Heck (1999). For many applications though the emissions achievable are still too high as shown in Table 2.2.

The most effective technologies currently available for controlling NOx emissions from heavy-duty industrial gas turbines are either diluent injection in the combustor reaction zone, or lean premixed dry low NOx combustion. For ultra low emissions requirements, these must be combined with selective catalytic reduction de-NOx systems in the gas turbine exhaust.
2. Literature Survey

<table>
<thead>
<tr>
<th>Reduction of NOx Formation</th>
<th>NOx Removal From Flue Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Combustion Modification</td>
<td>• Dry Process</td>
</tr>
<tr>
<td>Low Excess Air Combustion</td>
<td>Selective Catalytic Reduction (SCR)</td>
</tr>
<tr>
<td>Flue Gas Recirculation</td>
<td>Selective Non-catalytic Reduction (SNR)</td>
</tr>
<tr>
<td>Staged Combustion</td>
<td>Dry Low-NOx (DLN)</td>
</tr>
<tr>
<td>Low NOx Burners</td>
<td></td>
</tr>
<tr>
<td>Catalytic Combustion</td>
<td></td>
</tr>
</tbody>
</table>

| • Use of Low Nitrogen Fuel | • Wet Process |
| Change of Fuel            | Oxidation Absorption |
| Nitrogen Removal of Fuel  | Oxidation Reduction   |

<table>
<thead>
<tr>
<th>Control Technology</th>
<th>Emissions (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncontrolled</td>
<td>100-430</td>
</tr>
<tr>
<td>Wet injection</td>
<td>25-42</td>
</tr>
<tr>
<td>Dry-low NOx</td>
<td>25-42</td>
</tr>
<tr>
<td>Selective catalytic reduction</td>
<td>5-9</td>
</tr>
</tbody>
</table>

Table 2.1: NOx control methods (Siddiqi and Tenini, 1981).

Table 2.2: NOx emissions of natural gas fuelled gas turbines using various control technology (Stambler, 1993).

2.1.3.1 Water or Steam Injection

This method, according to Stambler (1993), decreases the average temperature of the combustion process reducing NOx emissions to typically 25-42 ppm with some loss of efficiency. Although capital costs for this technology are moderate, the operating costs are high due to the requirements for a very high level of water purity prior to injection into the gas combustor.
2.1.3.2 Dry low-NOx

The reaction mechanism which leads to the formation of thermal NOx occurs at temperatures greater than approximately 1550 °C and the rate of NOx production accelerates exponentially with increasing temperature. The new gas-turbine combustor NOx-control strategies are focused on reducing the combustion temperature to below the 1500 °C mark. Dry low-NOx (DLN) combustors achieve a low flame temperature by maintaining a low fuel-to-air ratio in the main combustion zone. The most developed type of DLN technology is lean premixed combustion which reduces NOx emissions to 25-42 ppm.

The concept, according to Zink (1996), of lean premixed combustion is to have a uniform, lean fuel-air mixture throughout the combustion zone with no fuel-rich pockets where high flame temperatures would cause NOx formation. The problems with this technology is having enough fuel to maintain a stable flame while having a uniform lean mixture; achieving the uniform fuel-air mixture over a wide range of power outputs and providing adequate time for CO oxidation to CO₂ and for burnout of unburnt hydrocarbons (UHC). This requires a change in the combustor design which will allow for a large volume downstream of the main combustion zone.

2.1.3.3 Selective Catalytic Reduction of NOx

Selective catalytic reduction (SCR) of NOx using NH₃ is, according to Armor (1995), the current best available technology for reducing NOx emissions (5-9 ppm) at many power plants and during the production of chemicals. SCR utilises a catalyst to facilitate reactions between NOx and NH₃ in the presence of oxygen. A simple representation of the complicated sequence of reactions is as follows,

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\]  \hspace{1cm} (2.13)

However this technology has several disadvantages which ultimately make it unattractive. In order to control NOx to approximately 80 % of the inlet values, NH₃ is injected into the flue gas prior to the catalyst. This requires a sophisticated distribution system of pipes and nozzles. The addition of ammonia to reduce NOx involves additional costs and ultimately releases about 5-20 ppm NH₃ (ammonia slip) which is another pollutant. Other issues with regard to this technology is the corrosion and
plugging which arise with the presence of sulphur oxides in the exhaust system. In addition, the large volumes of exhaust being treated necessitate the shipment of NH\textsubscript{3} through residential areas thus leading to concern about public safety.

2.1.3.4 Catalytic Combustion

The need for developing a new generation of combustion systems for gas turbines capable of meeting NO\textsubscript{x} emissions levels below 5 ppm consequently arises. The path for resolving the emissions problem should be through the use of ‘prevention’ technology and not ‘end-of-pipe’ as this can be more efficient and therefore more cost effective. Catalytic combustion is a prevention technology.

In catalytic combustion no pilot flame is required. Combustion is initiated by the interacting catalyst with a fuel-air mixture that is otherwise too lean to burn. Combustion can be carried out at equivalence ratios substantially below 0.5, thus limiting the maximum temperature to less than the threshold of thermal NO\textsubscript{x} production, as shown in Figure 2.2.

Emissions have been reported to be reduced to less than 3 ppm (Dalla Betta et al., 1997). Most of the reaction occurs on the catalyst surface, so gas-phase chemistry - particularly the thermal NO\textsubscript{x} pathway- is suppressed. Griffin et al. (1995) report that the reaction path on the catalyst surface differs significantly from the path in the gas phase; prompt NO\textsubscript{x} formation is therefore diminished. Furthermore, gas-phase chemistry may be inhibited by the catalyst due to adsorption of reactive intermediates. As a result of these effects, an increase in fractional conversion of fuel in the catalyst will produce a decrease in NO\textsubscript{x} emissions. It must be noted though that many unknowns in the current combustion process are the detailed surface reaction mechanisms, the coupling of gas-phase and surface reactions through radical adsorption or desorption and the effects of mass transport to the catalyst surface.
2. Literature Survey

2.2 Catalytic Combustion

Catalytic combustion was first proposed by Pfefferle (1975). It is a process in which a combustible compound and oxygen react on the surface of a catalyst, leading to complete oxidation of the compound. This process takes place without a flame and at much lower temperatures than those associated with conventional flame combustion. Trimm (1983), Pfefferle and Pfefferle (1987), Prasad et al. (1984) and Ismagilov and Kerzhentsev (1990) review this phenomenon as a method of reducing emissions of nitrogen oxides. Catalytic combustion is now widely used to remove pollutants from exhaust gases and there is now a growing interest in its application in power generation, particularly in gas turbine combustors.

2.2.1 The Principles of Catalytic Combustion

Gas-phase combustion can occur only within given flammability limits (5.3 to 15 vol% given by Griffith and Barnard, 1995) and the temperatures produced during combustion can rise to above ca. 1600°C, where the direct combination of nitrogen and oxygen to unwanted nitrogen oxides can occur. Catalytic combustion offers an
alternative means of producing energy. A wide range of concentrations of hydrocarbon can be oxidised over a suitable catalyst and it is possible to work outside the flammability limits of fuel. Reaction conditions can usually be controlled more precisely, with reaction temperatures being maintained below 1500°C. This is important both to minimise the production of NOx and also to avoid thermal sintering of the catalyst.

The objective of introducing a catalyst in the combustor is to carry out heterogeneous oxidation on the surface of the catalyst. By choice of a suitable catalyst, one can ensure that the activation energy for the heterogeneous reaction is much lower than that for the purely homogenous case. Consequently, appreciable heterogeneous oxidation rates can be achieved for temperatures and fuel concentrations much lower than those required for the homogenous reactions to proceed.

The general pattern of catalytic combustion of hydrocarbons is well established and can be found in many review papers such as those previously mentioned. Figure 2.3 shows a typical performance plot of a combustion catalyst: reaction rate versus catalyst surface temperature.

![Reaction rate curve for catalytic combustion](image)

Figure 2.3: Reaction rate curve for catalytic combustion

The premixed gases diffuse to the catalytically active surface such as that of a honeycomb monolith typically used in gas turbines. The reacting species are transferred to the surface by molecular diffusion and the reaction products diffuse back to the main flow and are transported downstream. Near the entrance, where the gas temperature is low, no gas phase reactions are taking place and heat is only released by the catalytic
reactions at the wall. The heat is transported by conduction, radiation and convection to the flow which consequently heats-up. If the gas temperature is high enough, gas phase reactions are initiated leading to a flame type reaction with high reaction rates.

At low catalyst temperatures - for example at the catalyst entrance - the chemical reaction is kinetically controlled and, therefore, exponentially dependent on temperature. In this area the reaction kinetics are determined by the activity of the catalyst. Due to the exponential nature of the reaction mechanism slight changes in surface temperature or flow velocity (convective heat transfer) can lead to extinction or overheating of the catalyst (Lee and Trimm, 1995).

For more active catalysts or those operated at higher temperatures or fuel concentrations, the intrinsic surface reaction rate can be so high that the overall process is limited by the rate of species transport to the surface. The reaction is then mass transfer controlled. This means that the reaction rate at the catalyst surface is much higher than the diffusive transport rate of fuel to the surface. Therefore, diffusion of fuel to the surface dominates the overall reaction rate (increase in catalyst activity does not increase reaction rate). Because the mass transport is only slightly dependent on temperature, the reaction rate is almost constant in this mode of operation. It is therefore impossible to distinguish between catalysts of different activity under these conditions as heterogeneous kinetics play a secondary role in determining the reaction rate.

As the exothermic surface reaction proceeds further, the axial temperature increases and finally, at some point in the bed, the bulk gas temperature is high enough that gas phase reactions occur simultaneously with the catalytic reactions and the combustion goes to completion. The temperature at which these homogeneous reaction are initiated for methane, is 1073 K. (Kolaczkowski, 1999a). The flame temperature - dictated by the efficiency requirements (turbine inlet temperature) of the gas turbine - can be high for modern gas turbine combustors (>1300°C). This illustrates the difficulties in finding materials which can withstand these conditions.

Palladium-based catalysts have been found to be the most efficient catalysts for the catalytic oxidation of methane to carbon dioxide and water (Lee and Trimm, 1995). The catalytic oxidation is dependent on factors such as oxygen to methane feed ratio, the loading of precious metal on the support, the nature of the support, the particle size of the precious metal and the extent and nature of catalyst pre-treatment. The reaction rate
is found to be dependent on the methane concentration, generally to the first order or less. The dependence of rate on oxygen pressure is found to depend on the operating conditions. Because of overheating as a result of high conversions of methane, chemical kinetics are often affected by mass and heat transfer.

To conclude, the features of catalytic combustion as compared to flame combustion are according to Pfefferle (1987), (i) catalytic combustion can be carried out over a wide range of fuel concentrations in air and at low temperatures; (ii) these low temperatures result in attaining NOx emission levels substantially lower than those possible with conventional combustion; (iii) the volumetric heat release rates of catalytic combustors are high to be comparable with the conventional gas turbine combustors.

### 2.2.2 General Applications of Catalytic Combustion

The most common example of catalytic combustion for emissions clean-up is the catalytic converter in the exhaust system of automobiles. According to Saint-Just and der Kinderen, (1996), catalytic combustion has already gone beyond the ‘promising’ status with a number of other commercial applications that take advantage of some of its interesting characteristics. Other present commercial applications of catalytic combustion include:

1. Radiant heaters used in home appliances and burn kerosene type fuels. Radiant heaters insure flexibility (use outdoor is possible) and safety operation, especially in terms of low CO levels in the combustion effluents. They have a higher efficiency than electric radiant heaters for household applications.

2. Catalytic combustion devices used as a convenient means of detecting flammable gases in air. The concentration of the gas of interest is measured through the heat liberated during its combustion.

3. Flameless catalytic burners in kitchen appliances. They are not sensitive to wind, in contrast to conventional burners from which flame stability and efficiency in an outdoor environment is a problem.

4. Natural gas furnaces that feature surface assisted combustion. The heat transfer from the burner to the fluid to be heated is largely by radiation rather than convection. These furnaces offer high efficiency as well as low NOx emission.
2. Literature Survey

Adiabatic lean premixed catalytic combustion fuelled by natural gas is another application concept. In adiabatic lean premixed catalytic combustion, a honeycomb-shaped catalyst is used. A preheated lean fuel-air mixture is introduced into the catalyst system and is burnt under almost adiabatic conditions by both heterogeneous and homogeneous reactions. This concept has attracted a lot of attention as a very low-NOx combustor for gas turbine application. Commercialisation of this concept greatly depends on the development of efficient catalysts with high activities, high durability and low cost. However, it is not easy to develop such catalysts as catalytic activity of natural gas is intrinsically lower than that of petroleum gas. Kolaczkowski (1995) has reviewed the problems specifically associated with gas turbines mainly those associated with catalyst and system design.

2.3 Catalytic Combustors for Gas Turbine Applications

2.3.1 The Catalyst System in a Catalytic Combustor

The catalyst system in a catalytic combustor usually consists of three components (i) the substrate, which acts as a support for the following two components; (ii) washcoat, which provides a high surface area material on which to distribute the active component; and (iii) the catalyst, the active component itself.

2.3.1.1 The Substrate

The substrate in a combustion catalyst system for a gas turbine is usually a ceramic or metal honeycomb monolith because of specific operating requirements such as low pressure drop. Monolithic catalyst supports are an alternative geometry to packed beds of pellets. They are generally made up of an array of parallel channels with the walls coated with a washcoat and with the catalytic material deposited on it. Monolith reactors provide a substrate with high geometric surface area and low pressure drop (high throughput) one or two orders of magnitude lower than packed beds. Cybulski and Moulijn (1994) have published a comprehensive review of monolith catalytic reactors and their applications including catalytic combustion.
Two or three regions may exist in a monolith during catalytic combustion. Near the combustor inlet the fuel conversion is controlled by the intrinsic kinetics of the catalytic reaction. Downstream of the catalytic light-off the conversion becomes limited by the diffusion rate of reactants from the gas phase to the catalyst surface. Eventually, depending on combustor design, the contribution of homogeneous reactions may take place either at the bottom end of the monolith or further downstream, outside the monolith. Catalyst design (cell density, length, catalytically active material) depends on the required operating conditions (entrance velocity, fuel-to-air-ratio, combustion pressure).

Combustion temperatures are greater than what metals can withstand. Ceramic-based catalysts have been used instead but they are subjected to thermal sintering and vaporisation. The ceramic substrate, while able to withstand the high temperatures, cannot stand the temperature gradients it experiences in the structure due to hot spot formation and the thermal cycling of repeated hot and cold conditions. This leads to cracking and the unacceptable risk of sending abrasive particles through the turbine after a few start-up and shut-down cycles. Trimm (1995) reviews the research carried out on materials suitable for high temperatures and Table 2.3 shows the upper temperature limits of various materials.

Ceramic substrates made of cordierite (2MgO·5SiO₂·2Al₂O₃) or mullite (3Al₂O₃·2SiO₂) are examples of substrates which are capable of withstanding the high combustor outlet temperatures (>1300 °C) in the current generation of gas turbines. Details of properties of ceramic materials that have potential to be used in the high temperature environments of catalytic combustors can be found in a review by Zwinkels et al. (1993). The principal disadvantage of ceramic monoliths in gas turbine applications is their relatively low resistance to thermal stresses. Most ceramics will fracture during the very rapid temperature increase and decrease that occurs during a change in turbine load.

The monolith support structure fulfils some demands for application in high temperature combustion (Zwinkels et al., 1993):

1. No chemical reaction between the support and the catalytic component;
2. Capability for high volume throughputs;
3. High geometric area, that is, area per reactor volume;
4. Low pressure drop.
Temperatures of over 1300°C are experienced by monoliths in typical catalytic combustors. Such temperatures subject them to extreme abuse, causing problems such as:

1. thermal sintering of support surface area;
2. thermal sintering and vaporisation of active components such as noble metals;
3. thermal shock fracturing of ceramic supports.

Thermal shock fracture of substrates are particularly experienced during start-up, fuel disturbances during normal operation and shut-down. The importance of the support thus determines the high-temperature behaviour, whereas the catalytic component is major at lower temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Upper temperature limit (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-alumina</td>
<td>1100</td>
</tr>
<tr>
<td>$\alpha$-alumina</td>
<td>2070</td>
</tr>
<tr>
<td>Silica</td>
<td>1100</td>
</tr>
<tr>
<td>Zirconia</td>
<td>2200</td>
</tr>
<tr>
<td>Cordierite</td>
<td>1400</td>
</tr>
<tr>
<td>Fecralloy</td>
<td>1350</td>
</tr>
<tr>
<td>Mullite</td>
<td>1350</td>
</tr>
<tr>
<td>Aluminium titanate</td>
<td>1800</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>1650</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>1540</td>
</tr>
</tbody>
</table>

Table 2.3: Upper temperature limits of various materials (Trimm, 1995).

2.3.1.2 The Washcoat

The substrate is coated with a high surface area material, known as a washcoat, which acts as a support for the active component. The support must be able to maintain its surface area under the operating conditions for the catalyst. However, most oxide supports sinter rapidly above 1200 °C and transform into low-surface-area materials. In particular, neither silica nor alumina, the traditional support materials have the high temperature stability required for catalytic combustion. Alumina undergoes a phase
change above 1000 °C from the high-surface-area γ-phase to the low-surface-area α-phase. Other oxides such as titania and zirconia also undergo phase changes to low-surface-area phases at relatively low temperatures (Thomas and Thomas, 1997).

The washcoat should be inert towards the substrate and the active component of the catalyst at the operating temperature. It should nevertheless have good adhesion with the substrate and excellent cohesion in order to withstand the high gas velocities and the vibration that is associated with gas turbines.

Attempts to prepare washcoats with high temperature stability have centred on stabilising alumina by the addition of other metal oxides. Alkaline earth oxides significantly increase the stability of alumina. Arai and co-workers have studied hexa-aluminates, \( \text{(MO:6Al}_2\text{O}_3) \) where the M can be for example Ba, Sr and Ca, and substituted hexa-aluminates \( \text{(M(M}_2\text{)x Al}_{11-x}\text{O}_{19-x}) \) where \( \text{M}_2 \) can be Cr, Mn, Fe, Co and Ni. Lifetime tests have been reported for \( \text{Sr}_0.6\text{La}_{0.2}\text{MnAl}_{11}\text{O}_{19-x} \) used at 1300 °C for up to 6400 h (Arai et al., 1990; Arai and Machida, 1996; Eguchi and Arai, 1996).

Thermal resistance to maintain large surface area is required to attain high combustion efficiency above 1000 °C. When a metal-supported oxide with large surface area is used as catalyst at high temperatures above 1000 °C, the catalyst undergoes sintering and/or evaporation of the metallic component. Hexa-aluminate compounds are according to Eguchi and Arai (1996) effective in maintaining large surface area but their lifetime is limited to 6400 h. Lifetime of above 8000 h is required for efficient gas turbine operation (Forzatti and Groppi, 1999).

### 2.3.1.3 The Catalyst

The catalyst should have high activity for the oxidation of methane and other hydrocarbons present in natural gas in order to obtain ignition at temperatures close to the compressor outlet temperature of the gas turbine. At the same time the catalyst should maintain high surface area at the operating temperature.

Since Anderson et al. (1961), noble metals, are known to be the most active catalysts for methane combustion. Palladium has popularly been employed as the most active catalyst for methane combustion. The sequence of the catalytic activity for methane oxidation has been reported as \( \text{Pd} > \text{Rh} > \text{Pt} \) (Widjaja et al., 1997). Baldwin et al. (1990a) report that palladium initiates the oxidation of the relatively inactive methane
at a temperature of 350°C. Once the reaction starts, subsequent oxidation is rapid and the heat released is considerable. Another requirement is the catalyst should have very low vapour pressure at the operating temperature in order to avoid loss of catalytic material. The vapour pressure of palladium at 1300 °C is about an order of magnitude lower than that of platinum. Palladium is also more resistant to thermal sintering (Lee and Trimm, 1995).

Currently there is great demand for palladium, platinum and rhodium as legislation on emission control become more stringent. They are mined in a limited number of countries. In 1999, 70 % of the total palladium came from Russia, 20 % from South Africa and the remainder from USA and Canada. Today, 60 % of palladium production is used in car manufacturing. The second biggest application is in the electronics sector. In 1994, 4.87 million ounces were utilised per year while by the end of year 2000 the demand has been estimated to have increased to 8.5 million ounces which is 50 % higher than platinum usage.

A recent article in the German newspaper *Handelsblatt* (2/2/2000) brings forward a current problem with palladium prices which have traditionally been lower than those of Pt ($472/ounce, in 1990) and Rh ($3726/ounce, in 1990). They have currently reached the highest level ever as shown in Figure 2.4. In the beginning of February 2000, the price of palladium was $487/ounce. Palladium prices have in effect reached platinum prices. Exports from the main source of palladium, Russia, have ceased due to domestic problems resulting in a lack of 3 million ounces of palladium. Once Russian exports restart, prices are expected to fall but if the situation is not rectified soon the industry will need to find alternative materials to use.
Figure 2.4: Palladium prices for the past 10 years (Handelsblatt, 2000).

To conclude, any particular catalyst system must also be designed to have a range of conditions over which it will achieve stable operation with low emissions. This operating window is bounded by the following constraints:

1. the inlet gas temperature must be high enough to sustain the requisite catalytic activity;
2. the temperature of the gas leaving the catalyst reactor must be high enough to promote homogeneous combustion and CO burnout within the available residence time;
3. the temperature gradients must be low enough to provide stable, long term reactor operation.

2.3.2 State-of-the-Art Catalytic Combustors

A number of important and fundamental studies have been published addressing catalytically stabilised combustion which was applied to first generation catalytic combustors yet goals set were not achieved. Research such as that carried out extensively by Pfefferle and co-workers (1986; 1987; 1992; 1993; 1995) dealt with the initiation of such reactions early within the catalyst structure. Thus homogeneous combustion was stabilised by the heterogeneous reactions. The problem with this design, as Griffin et al. (1995) point out, is that if complete combustion occurs within a combustor the materials are subjected to the mixture adiabatic flame temperature. Thus material
lifetime is limited. As Schlegel et al. (1996) also comment, catalytically-stabilised combustion is, although extremely lean mixtures can be burnt, accompanied by a narrow operation range (catalyst overheating on one side and extinction of the reaction on the other). This disadvantage of catalytic combustion has had to be taken into consideration along with the increased pressure for further reduction in NOx emissions. Thus a new approach to catalytic combustion has been necessary.

Alternative combustor designs have been developed, in which the catalyst is employed only to preheat the gas to temperatures at which gas phase reactions are initiated but where the gas phase combustion itself takes place downstream of the catalyst bed. Different approaches are possible but the support still favoured though for the catalyst is the monolith as its design plays an important role in developing an efficient and stable catalyst system. Minimum pressure losses in the catalytic reactor in particular is an important factor in gas turbine combustor design. Pressure losses have the effect of decreasing the turbine pressure ratio relative to the compressor pressure ratio and thus reduce the net work output from the plant (Cohen et al., 1987). The design criteria and operating conditions of the new generation gas turbine combustors are summarised in Table 2.4.

<table>
<thead>
<tr>
<th>Design Criteria</th>
<th>Emission targets</th>
<th>NOx &lt; 5 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO &lt; 10 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UHC &lt; 10 ppm</td>
</tr>
<tr>
<td>Pressure drop</td>
<td></td>
<td>&lt; 5 %</td>
</tr>
<tr>
<td>Catalyst durability</td>
<td></td>
<td>8000 h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td></td>
<td>300-450°C</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td></td>
<td>1100°C</td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td>10-20 atm</td>
</tr>
<tr>
<td>Mass flowrate</td>
<td></td>
<td>100-200 kg/m²s</td>
</tr>
<tr>
<td>Residence time</td>
<td></td>
<td>10-30 ms</td>
</tr>
</tbody>
</table>

Table 2.4: Design criteria and operating conditions of gas turbines (Forzatti and Groppi, 1999)
The requirements of a combustor design are:

1. very high catalytic activity in methane complete oxidation to ensure ignition at temperatures as close as possible to that of compressed air, in order to minimise the temperature rise provided by the pre-burner that is responsible for most of NOx formation;
2. high thermal stability of the catalytic materials with respect to deactivation by sintering, phase transformation and volatilisation, and structural integrity upon thermal shocks;
3. coupling of the heterogeneous and homogeneous reactions to guarantee complete conversion of the hydrocarbon and ultra low emissions of CO.

2.3.2.1 Hybrid Design

Furuya et al. (1987; 1995) and Ozawa et al. (1995; 1998) propose a ‘hybrid’ design, where two fuel supply systems are used. As shown in Figure 2.5, only a part of the fuel is mixed to the combustion air upstream of the catalyst. Typically, the fuel is limited to an amount such that catalyst temperature remains below 1000°C. The rest of the fuel is mixed with the hot gases leaving the catalyst, and burns in a premixed type flame downstream of the catalyst. Due to the limited catalyst material temperature (<1000°C), a serious catalyst deactivation is not to be expected.

In addition to reduction of thermal stresses and stabilisation of homogeneous premixed combustion at lower temperatures, the following major advantages have been claimed:

1. stable combustion is realised under a wider range of combustor operating conditions by controlling the fuel split to the catalyst;
2. a certain degree of lack of uniformity in the fuel-air mixture to the catalytic section is allowed due to the low catalyst temperature.
This configuration was tested by CRIEPI and Kansai Electric in Japan at a scale equivalent to one combustor of a 10 MW class, multi-can type gas turbine (Ozawa et al., 1998). At base load conditions, the performance of the combustor which achieved an outlet gas temperature of 1350 °C is shown in Table 2.5. The catalyst used was PdO promoted with small amounts of Pt and Rh, and supported on an Al₂O₃/ZrO₂ washcoat deposited on a cordierite honeycomb monolith.

<table>
<thead>
<tr>
<th>Full scale tests at 100 % load conditions of a 10 MW GT</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx &lt; 5 ppm</td>
</tr>
<tr>
<td>CO and UHC &lt; 9 ppm</td>
</tr>
<tr>
<td>Pressure drop &lt; 4 %</td>
</tr>
</tbody>
</table>

Table 2.5: Tested performances of hybrid combustor (Ozawa et al., 1998)

A critical issue of this concept is the premixing of the secondary fuel and the hot gases leaving the catalyst. If ignition occurs prior to perfect premixing, increased thermal NOx emissions would be expected to result. The long-term performance of the catalyst and the combustor has also to be estimated. The durability of the catalyst
has not been established and even though maximum temperatures have been reduced, temperature gradients still exist as inlet wall temperatures remain at 300-450°C and outlet wall temperature is approximately 1000°C.

2.3.2.2 Staged Catalytic Combustion

Staged catalyst design is another promising approach for extending catalyst lifetime as temperature rise is limited to a relatively low value. As shown in Figure 2.6 all the fuel, except that required for the pre-burner, is fed to the catalyst section consisting of an inlet stage designed to provide high catalytic activity, low light-off temperature and low catalyst wall temperature, and an outer stage designed to operate at higher wall temperatures in order to provide the required high outlet gas temperature. In a downstream homogeneous section, the combustion of the fuel is completed, CO and UHC are burned out to the levels required to meet the emission standards and the combustor outlet temperature is raised to the levels of modern high efficiency gas turbines, 1300-1500°C.

This design offers the advantage of the use of a wider variety of substrate and catalyst materials as temperature gradients for each catalyst are limited. The technology can in addition be adapted to higher combustor outlet temperatures without changes in catalyst materials. The control of the maximum wall temperature is achieved by means of a proprietary catalyst design based on the temperature self-moderating properties of PdO/Pd catalysts in methane combustion, the use of a monolith metal support with integral heat-exchange capabilities between active and passive channels, and the use of a diffusion barrier over the catalyst surface.

This configuration has been developed by Catalytica in co-operation with Tanaka Kikinzoku Kogyo KK and General Electric (solar Turbines, Allison Engine) and has been described in recent publications (Dalla Betta et al., 1993a, 1994, 1995b, 1995c, 1997a, 1997b; Beebe et al., 1995; Schlatter et al., 1997; Dalla Betta and Rostrup-Nielesen, 1999; Cutrone et al., 1999).
During bench tests at full scale performed in a catalytic combustor system developed by GE for its MS9001E gas turbine, NOx, CO and UHC emissions were documented at levels below emissions targets of 5, 10, and 10 ppm, respectively, at both base load (100%) and part load (78%) as shown in Table 2.6. The tests also documented low pressure dynamics (Schlatter et al., 1997). In a field test performed on a 1.5 MW (Dalla Betta and Rostrup-Nielsen, 1999) Kawasaki M1A-13A machine, the system demonstrated stable performance with limited loss of efficiency and with ultra-low emission of NOx, CO and UHC during the 1000-h operation.
2. Literature Survey

<table>
<thead>
<tr>
<th>Full scale tests on GE MS9001E GT (Schlatter et al., 1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions</td>
</tr>
<tr>
<td>• NOx 3.3 ppm</td>
</tr>
<tr>
<td>• CO 2.0 ppm</td>
</tr>
<tr>
<td>• UHC &lt; 0.1 ppm</td>
</tr>
<tr>
<td>Pressure drop 2.6 %</td>
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<tr>
<th>Field tests on 1.5 MW Kawasaki GT (Dalla Betta and Rostrup-Nielesen, 1999)</th>
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<tbody>
<tr>
<td>Emissions</td>
</tr>
<tr>
<td>• NOx &lt; 3 ppm</td>
</tr>
<tr>
<td>• CO &lt; 5 ppm</td>
</tr>
<tr>
<td>• UHC &lt; 5 ppm</td>
</tr>
<tr>
<td>Efficiency 23.0% (23.6% before introduction of catalyst)</td>
</tr>
<tr>
<td>Load range 50 - 100%</td>
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<tr>
<td>Durability &gt; 1000 h</td>
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Table 2.6: Tested performance of XONON combustor.

The catalyst durability has not been evaluated for above 1000 h. Additional tests are required to improve the reliability of such promising system configurations. Issues which still need to be addressed include long-term performances of the catalyst under such strenuous conditions, enlargement of the load range of operation and improvement of coupling between the heterogeneous and homogeneous sections. There is still a need for catalyst development with enhanced activity to light off the fuel mixture at the temperature of air delivered from the compressor (Forzatti and Groppi 1999).

2.3.2.3 Palladium As A Thermal Regulator

In a state-of-the-art catalytic combustor design the optimal catalyst would need to be active at low temperatures (350 - 400°C), yet not attain the full adiabatic combustion temperature to prevent catalyst deactivation, loss or support melting. Palladium, the most active low temperature methane oxidation catalyst, is a promising candidate, since it experiences a transformation at approximately 750°C, becoming
relatively inactive at higher temperature (Farrauto et al., 1992). This phenomenon leads to a ‘self regulation’ of the palladium surface temperature and could be used to prevent overheating of the catalyst. This is therefore another method for preventing the catalyst surface from adiabatic flame temperature which has also been implemented into other designs such as that of staged combustion.

Methane oxidation on palladium is complex due to palladium oxidation, palladium oxide reduction-decomposition, palladium reoxidation which may occur under reaction conditions. These phenomena are accompanied by dramatic changes in catalytic activity. Due to these effects, the catalyst exhibits unusual hysterisis effects (Farrauto et al., 1992) and ageing behaviour (Baldwin and Burch, 1990a; Baldwin and Burch, 1990b; Briot and Primet, 1991).

The active form of the catalyst is PdO, which is formed from Pd between 200 and 700°C. Farrauto et al. (1992) have found that this active form decomposes in two steps between temperatures of 750 and 850°C in air at 1 atm leading to the nearly completely inactive Pd metal at 850°C. Re-oxidation of the reduced Pd catalyst only at temperatures below 650°C, leading to the observed hysterisis in the catalytic activity temperature.

With this process of deactivation a reactor can be designed where high conversion can be attained in the catalyst at temperatures significantly below those corresponding to adiabatic, mass-transport-controlled operation (Dalla Betta et al., 1993a). The catalyst is composed of a mixture of active PdO and inactive Pd from the catalyst entrance to the location at which the gas temperature has increased beyond the limit for complete decomposition of PdO say, 850°C. The presence of Pd means that portions of the honeycomb surface are catalytically inactive, dissipating heat generated at the active PdO sites and thereby reducing the operating temperature of the catalyst. The self regulating properties of Pd may be integrated into the passive cooling designs to better control of the catalyst surface temperature.

It should be noted that even though significant research has been carried out to investigate in detail this phenomenon and it is commonly agreed that the surface of palladium is more active in an oxidised form, the exact chemical state and morphology of the palladium particles is not known (Lyubovsky and Pfefferle, 1999). Another problem this design faces is the deactivation due to water and carbon monoxide. The combustion products have shown to inhibit the reaction (Burch et al., 1995).
2.3.2.4 Catalyst With Integral Heat Exchange

Another approach to limit catalyst surface temperature has been proposed by Dalla Betta et al. (1993b; 1993d; 1996). All fuel and air needed to reach the required turbine inlet temperature is mixed in front of a honeycomb catalyst. Within the honeycomb (metallic are preferred), a catalytically inactive channel is always located adjacent to catalytically active channel. Even if the surface reaction within the catalytically active channel is diffusion controlled, the surface temperature does not reach the adiabatic flame temperature of the fuel-air mixture, because heat is transferred to the neighbouring, inactive channel. The gas fuel mixture of the neighbouring, inactive channels heats-up and can be burned downstream of the catalyst in a homogeneous combustion zone. There is potential in this line of thought but more research into improving the efficiency is necessary.

2.3.2.5 Diffusion Barriers

The use of diffusion barriers to slow down the rate of reaction in the entrance region by simply applying a thin layer of non-catalytic washcoat over the catalytically active washcoat is described in patent literature (Dalla Betta et al. 1993a; 1993c; 1995a). This barrier is used as a means for introducing diffusion resistances and thus preventing temperature runaway over Pd-based catalysts as it limits the supply of fuel and/or oxidant to the catalyst. A thin diffusion barrier of 4-6 μm can effectively smooth temperature gradients at the entrance through reduction of the apparent activation energy. This leads to a better control of temperature build-up in the catalyst. It also extends the operating range of the catalyst to higher preburner temperatures, lower linear gas velocities, higher fuel/air ratio ranges and higher outlet temperatures.
2.3.3 Challenges Faced by Catalytic Combustors

As Etemad et al. (1999) emphasise, although catalytic combustion has been shown to be beneficial, commercial catalytic combustor development has been restrained by the following:

- Fuel/air preheating required for sustaining catalytic reactivity given available compressor discharge temperatures (generally requiring a preburner, with resulting NOx emissions);
- Limits due to a relatively narrow operating band between minimum required inlet temperature (surface kinetics limited) and maximum survivable catalyst temperature;
- Uniform fuel/air mixture is required to avoid catalyst substrate meltdown as a result of localised rich zone operation;
- High pressure drop associated with conventional catalytic combustion systems, since a long monolith is required to convert most of the fuel/air mixture to products;
- Catalyst and support material durability due to high operating temperatures which lead to thermal stresses. No catalyst system has been demonstrated to operate reliably for at least 8000 h at the turbine inlet temperatures.

Overall, the catalyst must ultimately be designed to:

- have good catalytic activity at or very close to the compressor discharge temperature so that the fuel will react on the catalyst to produce the required heat without the customary use of a preburner which leads to NOx emissions;
- burn enough of the fuel to attain an outlet temperature sufficient to achieve low emissions via downstream homogeneous combustion;
- burn the fuel in a manner that maintains the catalyst temperature below the maximum limit of the constituent materials and achieve low temperature gradients, thus minimising thermal stresses.
2.3.3.1 Thermal Stresses

During start-up, normal operation (when power load may vary) and during shut-down, the catalyst system of all design concepts are exposed to stresses arising from the fluid flow and thermal gradients. Although ceramic based substrates withstand high temperatures, they are brittle and prone to cracking when subjected to restraining forces and/or thermal transients or gradients. Kolaczkowski (1995) identifies the following as major challenges which need to be overcome in the design of the catalytic combustor:

- the thermal mismatch between the reactor operating temperature and the allowable temperature limit of the metal support structure;
- the radial differential thermal growth between the metal support and ceramic reactor substrate;
- the stress due to axial thermal growth and pressure loading when the catalyst is being ignited or shut-down.

Thermal stresses in particular develop when a body is subjected to a varying temperature field. When deformation arising from the change of temperatures is prevented, temperature stresses arise that are proportional to the amount of deformation that is prevented.

Few studies have been published on the interaction between chemical reaction and thermal stresses in monolithic systems. It is a well-known fact that these systems do fail periodically. Mechanical failure of catalyst supports in packed bed reactors have been reported (Thiart et al., 1991; 1993). Catalytic gauzes like platinum used for fast exothermic reactions are prone to metal fatigue, work-hardening and catastrophic failure. Large costs are involved in lost production and catalyst replacement. The creation and propagation of a thermal shock was analysed for a sudden increase of surface temperature, which can occur during the ignition process. Hlavacek et al. (1995) have reviewed several reaction systems where stress distribution may play an important role including car engine operations. They conclude that many experimental research has been carried out which demonstrate the development of stresses during a chemical reaction but it is not always possible to establish the location and magnitude of the various components of the stress system.

In a similar manner, typical reactions which are carried out in monolithic catalysts lead to strong axial temperature gradients in the channels. Although the monolith can
freely expand in the axial direction, it is contained in the radial and azimuthal directions, causing a distributed compressive load on the channel walls. A failure criterion based on the classical plate theory has been derived by Viljoen and van Rensburg (1995). The failure criterion depends greatly upon the axial wall temperature profile.

2.4 Non-Uniform Catalyst Distribution

It has been suggested that improved durability is possible for catalysts utilised in catalytic combustion through alleviating axial temperature gradients. Understanding the temperature and concentration fields inside a catalytic monolith with non-uniform catalyst distribution is thus essential for developing a high performance catalytic gas turbine.

The concept of non-uniform axial catalyst distribution as a method for alleviating temperature gradients in catalytic monoliths has received limited attention. For gas turbine operation, Dalla Betta et al. (1993c) used graded catalyst for the partial combustion of various fuels including methane. The monoliths had a higher concentration of the catalytic metal in the upstream section than the downstream. These catalysts showed low light-off temperatures and hot spots due to excess activity were not experienced. Theoretical studies for monoliths used for automotive exhaust after-treatment showed that the warm-up period is significantly reduced if the catalytic material is distributed non-uniformly along the monolith, in such a way that catalyst loading decreases from the inlet to the outlet of the monolith (Tronci, 1999).

Catalysts with non-uniform distribution in porous supports are known to offer better performance as compared to uniform catalysts. Research regarding the performance and preparation of non-uniform catalyst distribution in pellets has been reviewed by Gavriilidis et al. (1993). The underlying reason for the improvement in the catalyst performance is that the appropriate non-uniform catalyst distribution can induce favourable interaction among mass and heat transfer and reaction. The possibility of improving catalyst performance by suitably distributing the active element within a pellet has been the objective of a number of investigations, both theoretical and experimental, which have been reviewed by Dougherty and Verykios (1987) and Gavriilidis et al. (1993).
Due to the interactions between chemical kinetics and physical transport processes, a spatially non-uniform deposition of the catalytically active material in a support matrix can often lead to improved performance - in terms for example of effectiveness or in the resistance to deactivation - compared to the uniform case. Effective strategies are highly dependent upon specific reaction system characteristics such as reaction kinetics, diffusional resistance, influence of deactivation and thermal properties. Most of the literature dealing with non-uniform catalysts consists of theoretical studies (Becker and Wei, 1977a, 1977b; Morbidelli, 1982) and few experimental studies (Gavrilidis and Varma, 1992).

In the absence of poisoning in a first-order reaction, it can easily be seen that a thin layer of active material deposited in the periphery of the catalyst particle results in optimum catalyst performance. As diffusional effects are minimised, reaction proceeds utilising a higher reactant concentration than in the case in which the same amount of active material has been distributed uniformly throughout a catalyst pellet (Dougherty and Verykios, 1987).

Research on preparation of catalyst with non-uniform distribution has been concentrated on radial distributions in pellets. Lee and Aris (1985) have provided an extensive review of catalyst preparation by impregnation methods. Non-uniform catalyst distribution in pellets are typically prepared by co-impregnation or sequential impregnation techniques (Papageorgiou et al. 1996). A co-ingredient which adsorbs on the support is added in the impregnating solution and it pushes the catalyst precursor inwards in a similar fashion as in a chromatographic process. By utilising the appropriate combination of catalyst precursor and co-adsorbant, a variety of radial catalyst profiles can be obtained (Gavrilidis et al. 1993). These techniques though are not suitable for achieving non-uniform axial distributions. Moene et al. (1993; 1995) showed theoretically that chemical vapour deposition can be applied in the preparation of monoliths with axially non-uniform distribution.

2.4.1 Chemical Vapour Deposition

There is both experimental and theoretical evidence in the literature that chemical vapour deposition (CVD) can be utilised for both uniform and non-uniform catalyst preparation. A fact which is seen as a disadvantage to the electronics industry (the
principle user of CVD) but is an advantage for the preparation of non-uniform catalysts is that precursor concentration is not identical at each point of a simple hot-wall vertical reactor and thus non-uniform deposition can be achieved (Brossa, 1989). Wang et al. (1995) have studied experimentally CVD growth rates of copper films by hydrogen reduction of Cu(hfac)$_{2n}$. They obtained copper films for which the thickness varied monotonically along the substrate. A theoretical investigation of nickel CVD by Moene et al. (1993), indicates that chemical vapour deposition can be used for preparing pellets with non-uniform radial catalyst distribution as well as monolith with non-uniform axial catalyst distribution.

Typical heterogeneous catalyst preparation methods utilised for the general preparation of catalysts include co-crystallisation, ion-exchange and impregnation (Schwarz et al., 1995). They normally require the use of metal complexes to obtain the active, pure metal dispersed on a metal oxide support such as TiO$_2$, SiO$_2$ and Al$_2$O$_3$. Subsequent calcination, required to remove the organic or inorganic ligands, may lead to the oxidation of the supported metal thus requiring a reduction stage to follow in order to regenerate the active metal. During calcination, the catalyst is subjected to temperatures above 400°C. Aggregation of the metal particles may take place at such temperatures consequently affecting activity and selectivity (Hierso et al., 1998). In addition, the micro-structure of the support material itself may be affected as decrease in specific surface area and changes in chemical properties are known to take place (Zwinkels, et al., 1993). Chemical vapour deposition is an alternative catalyst preparation method which offers solutions to the above mentioned problems.

2.4.1.1 Fundamental Aspects of CVD of Metals

Chemical vapour deposition involves the thermally induced reaction of a metal-containing molecule on a heated surface. A schematic representation of the generalised key steps involved in a CVD process is represented in Figure 2.7. A volatile precursor is transported (1) into the reactor and to the substrate, where it adsorbs (2) and reacts (3) to liberate the supporting ligands, which are subsequently desorbed (6) and transported out of the reactor (7). The metal atoms then diffuse (4) to form a stable nucleus, where subsequent growth occurs (5). Under certain circumstances gas-phase reactions (8) can also occur. The details of the surface reactions are likely to be peculiar to a particular
metal-containing precursor, surface, temperature and other deposition conditions (i.e., presence of a reactive gas). Any of these steps may be rate-limiting.

![Diagram of chemical vapour deposition](image)

**Figure 2.7** Key steps involved in chemical vapour deposition (Hampden-Smith and Kodas, 1995a)

The growth of the deposited particles is initiated by exposing a substrate to the precursor. The nucleation process and morphology of the deposit is influenced by the temperature, pressure and gas-phase composition and flowrate. There are several books on CVD which expand on these phenomena (Pierson, 1992; Hitchman and Jensen, 1993). Nucleation occurs at many different points on the surface. Adsorbed species can diffuse at high temperatures to the islands which grow and can coalesce to form a polycrystalline film if sufficient time is allowed for. Transport phenomena govern the access of precursors to the substrate and influence the morphology of the deposit. The reviews by Hampden-Smith and Kodas (1995a; 1995b) give an insight on these phenomena.

Extensive research has been carried out on thin-films deposits on planar substrates for use in electronics. Chen et al. (1988) and Kumar et al. (1989) carried out noble-metal deposition using a reactive gas such as hydrogen or oxygen. This resulted in a significant reduction of deposition temperature and preparation of high-purity deposits.
Gozum et al. (1988) deposited high quality palladium and platinum films, without use of carrier gas, and demonstrated the great importance of choosing the right precursor.

Metal-organic compounds can be used as molecular precursors in the chemical vapour deposition process to deposit, at low temperature (as low as 150°C), a wide variety of materials. An ideal precursor should have according to Maury (1996):

- a good volatility (preferably higher than 10^{-1} torr at ~100°C);
- good thermal stability during its evaporation and transport in the gas phase;
- it should decompose cleanly on pyrolysis without contamination of deposit (e.g. carbon);
- it should have a high purity (be readily purified);
- it should be non-toxic and non-pyrophoric (as should its decomposition by-products);
- it should be stable in its container over a long period since its rate of consumption is usually rather low;
- be readily available in consistent quality and quantity at low cost.

*Metal-organic* chemical vapour deposition (MOCVD) offers advantages such as low deposition temperature and relatively simple equipment (Psaro and Recchia, 1998). A large variety of metal precursors containing halide, carbonyl, allyl, hydride and alkene ligands can be used. For Pd deposition, the number of precursors are limited and they include Pd(allyl)$_2$, Pd(Meallyl)$_2$, Pd(allyl)(Cp), Pd(hfac), [(allyl)PdCl)$_2$ (where allyl is $\eta^3$-C$_3$H$_5$, Cp is the cyclopentadienyl ligand ($\eta^5$-C$_5$H$_5$) and hfac is hexafluoroacetonate) (Hampden-Smith and Kodas, 1995a) and Pd(acac)$_2$ (where acac is the acetylacetonate ligand (CH$_3$COCHCOCH$_3$)) (Pierson, 1992). The latter does not contain halides which can be detrimental to catalytic activity. It is a cheap, air-stable at room temperature yellow powder which is simple to handle and is readily available commercially.

The thermochemical behaviour of Pd(acac)$_2$ adsorbed onto different magnesium oxides has been studied by Dossi et al. (1998) under reducing conditions. The thermal profiles of the different decomposition products were rationalised in terms of chemical interactions with the support. Uemiya et al. (1997) utilised this complex to prepare thin palladium membrane films and only state the sublimation and decomposition temperatures they used. The Clausius-Clapeyron equation of this compound has not been published to-date. It may prove useful to have though when comparing competing
Pd(II) precursors as control of a given CVD process entails knowledge of not only the nature of the deposition process and rate but also the vapour pressures of the precursor.

2.4.1.2 Catalyst Preparation

Chemical vapour deposition (CVD) has been used extensively for preparation of thin films which find applications in electronics (Hampden-Smith and Kodas, 1995a; Hampden-Smith and Kodas, 1995b; Maury, 1996) and in high performance materials (Brossa, 1989). CVD is a versatile method for depositing a great variety of elements and compounds with a minimum number of steps and in addition possible to vary the composition and structure of the deposited material applied. However, CVD can be utilised for deposition of metal particles and is thus of interest in catalyst preparation. This method allows direct deposition of the active material onto catalyst supports. It reduces the number of steps typically encountered in conventional preparation methods such as impregnation and precipitation which involve washing, drying, calcination etc. Complications caused by the solvents during liquid-phase preparation, for example redistribution of the active material during drying, are also avoided (Schwarz et al, 1995).

In recent years increasingly more studies on the application of CVD in the field of catalysis have been reported. The chemical vapour deposition technique for metal deposition from volatile metal-organic precursors onto oxide support surfaces or inside zeolite cages has been proved to be extremely advantageous in the preparation of catalysts.

Dossi and co-workers (1993-1998) have carried out extensive work on the application of CVD for depositing active metal into zeolite channels. They have shown that metal-organic compounds are suitable and flexible precursors for preparing highly dispersed metal particles supported on metal oxides and zeolites. The metal phase is usually obtained by simple ligand removal under mild conditions, preventing, to a large extent, sintering to large crystallites or carbide formation. CVD-based catalysts showed the additional advantage of a very clean metal phase, due to the absence of any contamination from solvents or anions containing halogens or sulphur (Ugo et al., 1996).

Dossi et al. (1993b) described the preparation of a proton-free Pd/NaY catalyst, obtained by CVD of [Pd(η³-C₅H₅)(η⁵-C₃H₅)], characterised by a high dispersion and
uniform distribution of the metal particles inside the zeolite channels with a good thermal stability towards sintering in hydrogen at 500°C. The CVD process was carried out in two stages, deposition of the precursor and subsequent reduction to the active metal by hydrogen utilising a quartz hot wall reactor. Platinum hexafluoroacetylacetonate was selectively introduced inside the channels of KL zeolites (Dossi et al., 1994) and HL zeolites (Dossi et al., 1996) via CVD in another investigation and small non-acidic platinum clusters were formed. These catalyst showed remarkably high activities in the conversion of methylcyclopentane to benzene at 500°C. Long catalyst life was in addition achieved due to the reduced coke formation and slow sintering rate.

Preparation of platinum supported on SiO₂, Al₂O₃ and TiO₂ after decomposition of Pt(acac)₂ at 300°C was carried out by Köhler et al. (1995) utilising a fluidised bed. The adsorbed precursor was decomposed in nitrogen. They determined that surface properties of the support material influence the adsorption sites of Pt(acac)₂ as well as the decomposition pathways of the adsorbates and finally the dispersion of the catalytic compound. The deposited particles were found to be more mobile on silica and hence more capable to agglomerate. Alumina-supported Pt may be stabilised by coordinatively unsaturated Al³⁺ surface ions. Their attempts to prepare palladium on supported material using Pd(acac)₂ failed as the temperatures they used were high and the complex decomposed in the gas phase before adsorption was accomplished.

A fluidised bed was utilised by Hierso et al. (1998) for carrying out metal-organic chemical vapour deposition for preparing metal-supported catalysts. Various metal precursors (Rh(allyl)₃, Pd(allyl)(hfac), Pt(COD)(CH₃)₂) and supports (SiO₂, Al₂O₃) were used. They concluded that fluidised beds are applicable for preparation of metal aggregates homogeneously dispersed on the substrates.

CVD has been utilised to prepare thin palladium membranes for hydrogen separation applications. Yan et al. (1994) and Kusukabe et al. (1996) formed thin palladium membranes inside the porous wall of α-alumina support tubes. Palladium (II) acetate was decomposed in argon and the best membranes were obtained under reduced pressure. High performance palladium membranes were obtained with respect to their hydrogen permeability. Uemiya et al. (1997) prepared palladium, ruthenium and platinum membranes in support tubes with a thin γ-alumina layer. The precursors used were acetylacetonato complexes which they sublimed and decomposed in nitrogen under
atmospheric pressure. For palladium (II) acetylacetonate they used a sublimation temperature of 160°C and a decomposition temperature of 270°C. They determined suitable operating conditions for thin metal layers utilised for hydrogen permeation.

CVD has thus attracted the attention of researchers in the field of catalysis. Further research is still necessary to understand specific aspects of the CVD of metals, ranging from the design requirements and thermal chemistry of metal-containing compounds to the surface reaction kinetics and mechanisms which are both physical and chemical in nature. In addition, CVD reactor design and operation is an active area of research in which advances are required to allow reliable deposition of particles. This technique has shown to be a promising method for catalyst preparation at a time when new catalyst preparation methods are sought to improve overall catalyst performance. The opportunity therefore exists to utilise this technique for the preparation of novel axially non-uniform palladium catalytic monoliths.

2.5 Mathematical Modelling of Catalytic Combustors

The understanding of the temperature and concentration fields inside a catalytic monolith with non-uniform catalyst distribution not only in steady state but also in transient conditions is indispensable for developing a high performance catalytic gas turbine.

In principle the following phenomena occur in the monolith channels: heterogeneous reactions on the walls and homogeneous reactions in the gas phase (initiated at temperatures above 1073 K for methane combustion); heat, mass and momentum transfer by convection and diffusion in the gas phase and at the gas-solid interface; mass diffusion in the catalyst pores; heat transfer by conduction and radiation in the solid. Strong interactions occur between these phenomena due to the intense thermal effects associated with the heat of combustion.

Computer simulation can be an effective tool for revealing phenomena present during catalytic combustion in a monolith provided that the underlying mathematical model is realistic. To develop an appropriate model, some decisions must be made concerning the number of space dimensions to consider. The most realistic model, especially for non-circular cross-section channels, would be a three dimensional model.
This may be computationally prohibitive and is probably not justified in terms of accuracy. As Groppi et al. (1995a) emphasise, it is important to strike the appropriate balance between model reliability and complexity.

Most reported work on catalytic combustion, both computational and experimental, has been done under steady state conditions as this is the simplest type of operation to model. Of the few transient modelling studies, most are directed towards the simulation of conditions found in automobile converters. They are based on one dimensional simplification of the governing equations and may exclude important parameters. Transient operation in gas turbines is encountered in practice during start-up and shutdown or when the loading is changed. During such operation, the thermal stresses which develop are quite important.

2.5.1 Automobile Converters

Some of the first models were investigated by Young and Finlayson (1976a; 1976b). Phenomena studied included axial conduction in the wall, diffusion and conduction in the gas phase. Constant physicochemical properties of the gas were assumed in spite of significant temperature variations. Oh and Cavendish (1982) used Nusselt and Sherwood numbers obtained during nonreacting flow of a fully developed fluid with constant properties. This is questionable as the flow profile continues to evolve when reaction is taking place. Conduction and radiation in the solid phase were ignored. A reasonable assumption was the gas to be at pseudo-steady state with the wall temperature slowly evolving. This is justified due to the relative heat capacities of the gas and solid and also due to the high gas velocities encountered. Most models assume uniform distribution of variables at the inlet including velocity.

Zygourakis (1989) on the other hand used a two dimensional model, in which the multichannel reactor was modelled as a continuum to simulate transient behaviour with flow maldistribution in the channels. Axial conduction in the gas phase was neglected while another commonly employed assumption used was that the transient term in the gas phase was neglected due to the small thermal capacity of the fluid. Both transient and steady state conditions produced virtually identical results. It was determined that non-uniform flow distributions characterised by high fluid velocities in an inner core of the reactor may substantially degrade its light-off performance. Results also showed that
a step decrease in the feed stream temperature can lead to large and highly localised overtemperature excursions.

The effect of radiation on wall temperature gradients was principally examined by Lee and Aris (1977) by utilising a two-dimensional model. Axial conduction and diffusion in the fluid were ignored while aside from radiation, axial conduction in the wall was taken into account. It was shown how the effect of radiation is to ameliorate steep gradients. Various approximations on how to represent radiation in mathematical models were discussed.

Previous work on non-uniform catalyst distribution has been limited. All simulation investigations have been based on catalytic converters for cars and have used lumped models. Oh and Cavendish (1982) using the one dimensional model discussed above, examined the light-off behaviour of three axial distributions: uniform, linearly increasing and decreasing. The carbon monoxide cold-start emissions were found to be reduced when more catalyst is concentrated at the inlet than the outlet. This was due to the light off being shifted further upstream of the converter. Psyllos and Philippopoulos (1992, 1993a; 1993b) studied the performance of the catalytic converters with various parabolic axial catalyst distributions using a one-dimensional transient model. Heat and mass transfer coefficients were represented by average values. Temperature dependency of physical properties for gas and solid phases were not taken into account. They showed that such monoliths have shorter warm-up periods than those with uniform catalyst distribution. Tronci et al. (1999), as opposed to the previous studies, determined an optimal catalyst distribution which would minimise emissions due to cold-start. The model employed was the one originally proposed by Oh and Cavendish (1982). They determined the optimal distribution to have a large amount of catalyst in the upstream section of the monolith to ensure that the hot spot is kept at the monolith inlet. The local surface area of the optimal distribution in the downstream section of the converter was reduced yet steady state performance was not affected.

2.5.2 Gas Turbine Combustors

The above studies are related to automotive conditions but significant work has also been carried out on catalytic monoliths for power applications. A comparison of mathematical models of catalytic combustors for gas turbine application has recently
been carried out by Groppi et al. (1999). Significant work dealing with catalytic combustion in monoliths with uniform catalyst layer has been carried out including modelling of various levels of sophistication. Most work in recent years has been carried out by Hayes, Kolaczkowski and co-workers (1992-1999) and Groppi, Forzatti and co-workers (1993-1999).

An early, one dimensional transient model which addressed conditions found in gas turbines was that formed by Ahn et al. (1986). The pseudo-steady state gas assumption was also used. The correlations considered for the Nusselt and Sherwood numbers were based on the entrance conditions but were applied throughout the channel. Studies by Hayes and Kolaczkowski (1994; 1999) and Groppi et al. (1995b) showed that values of the Nusselt and Sherwood numbers depend on the reaction rate at the wall and thus show strong perturbations at the light off point.

Hayes et al. (1996) carried out both experimental and theoretical work for the transient behaviour of a honeycomb monolithic reactor in which methane was combusted. Both start-up and shut-down procedures were investigated. Their comprehensive unsteady state, two-dimensional model included axial diffusion in the gas phase, radiation and axial conduction in the solid. The gas was assumed to be at pseudo-steady state and the wall to have a slowly evolving temperature. A developing velocity profile and temperature dependent properties were considered. It was observed that under laminar flow conditions, heat losses by convection are substantially larger than heat losses by radiation and conduction. It was shown that radiation from the monolith ends can be of importance at high temperatures but it is difficult to be precise in modelling this phenomenon as environment radiation temperatures and the emissivity of the monolith are difficult to determine.

In the two and three-dimensional models for gas turbines developed by Groppi et al. (1993; 1995a; 1995b; 1996), negligible axial diffusion and radial pressure drop have been assumed. Their aim was to find the simplest, adequate model with substantial savings of computational time. Their assumption of negligible homogeneous reactions is justified as the model relates to monoliths used in hybrid and staged combustors where temperatures are limited and residence times are very short. The outlet bulk temperature though is high enough (above 1073K) to sustain the homogeneous reactions further down the combustor system. They determined that the entrance effects are critical because of the short length of the catalytic monolith; however the hydrodynamic
development plays a less important role compared to the development of temperature and concentration profiles. Groppi et al. (1999) also emphasise the importance of the temperature dependence of the gas properties as it seriously affects the prediction of the combustor performance.

The concept of diffusion barriers has been investigated theoretically by Leung et al. (1996). Their investigation mainly involved the influence of diffusion on the reaction rate in the washcoat of a catalytic monolith reactor. They demonstrated that the rate of reaction may be strongly influenced by the diffusion limitations at temperatures at which such reactors may operate. This was attributed to the presence of fillets of washcoat in the corner of the channel. Thus they determined that the diffusion resistance of the washcoat material may be used advantageously in controlling sharp temperatures gradients at the inlet of the reactor and this can be enhanced by applying a thin layer of inactive washcoat on top of the active layer.

To develop an appropriate model, decisions must be made concerning the number of space dimensions to consider. The most realistic model, especially for non-circular cross-section channels, would be a three-dimensional model. This may be computationally prohibitive and is probably not justified in terms of accuracy. As Groppi et al. (1995b) emphasise, it is important to strike the appropriate balance between model accuracy and complexity. Simple one-dimensional models require less computer time but may lead to incorrect predictions of light-off behaviour due to the difficulty in estimating local interphase transfer coefficients (Groppi et al., 1995b).

In the case of two-dimensional models, the need for heat and mass transfer correlations does not exist and it is possible to impose correctly the flux boundary condition at the monolith wall. Thus, a single monolith channel may be modelled in two dimensions by considering it to be cylindrical. This closely approximates the geometry of a coated channel as the application of washcoat tends to ‘round’ the corners (Hayes and Kolaczkowski, 1994).

The opportunity thus arises to formulate a comprehensive mathematical model to investigate the effect of non-uniform catalyst distribution in catalytic monoliths for gas turbine operation. The focus on the temperature gradients is necessary as they are associated with the thermal stresses arising during gas turbine operation. Concentration gradients may also be useful for investigating further catalyst performance.
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

3.1 Introduction

The need to reduce toxic emissions produced by gas turbines such as nitrogen oxides (NOx), carbon monoxide (CO) and unburned hydrocarbons (UHC) is an important issue as exemplified by the guidelines of the 1990 Clean Air Act Amendments. The goal of the US is to reduce NOx by two million tonnes from 1980 levels. According to Cusumano (1995), NOx emissions must be reduced to less than 10 ppm. More recently, under the 1997 Kyoto Protocol the EU aim is by 2005 to reduce the greenhouse gases by 8% (based on 1990 emissions) which include NOx and CO (UNFCCC, 1997). For the UK total NOx emissions in 1990 were about 2.74 million tonnes. Catalytic combustion of lean premixed fuel and air within gas turbines is an alternative, prevention technology for achieving NOx emission levels as low as 1 ppm and simultaneously minimising emissions of UHC and CO to less than 2 ppm (Dalla Betta et al., 1994). However, as Kolaczkowski (1995) points out, this technology still requires catalyst performance to be improved, since catalyst lifetime is limited by thermal stresses and deactivation.

The general principles and developments in the field of catalytic combustion can be found in many review articles and books (cf. Trimm, 1983; Prasad et al. 1984; Ismagilov and Kerzhentsev, 1990; Hayes and Kolaczkowski, 1997). Research in this area has also been carried out by Pfefferle et al. (1986; 1987; 1995) with particular emphasis on catalytically stabilised combustion. Furuya et al. (1987; 1995) and Ozawa et al. (1995; 1998) proposed a ‘hybrid’ design where two fuel supply systems are used. Only part of the fuel is mixed to the combustion air upstream of the catalyst. Typically the amount is limited such that the catalyst temperature remains below 1000°C. The rest of the fuel is mixed with the hot gases leaving the catalyst and burns under homogeneous reactions. Dalla Betta et al. (1994-1999) have shown that catalytic combustion can achieve ultra-low emissions of NOx, CO and UHC on a large scale utilising a combustor configuration where the catalyst temperature is limited to below 1000 °C and employing two catalyst stages. In such a configuration all the fuel, with the exception of that
required for the preburner, is fed to the catalyst section. At the end of the second stage a heterogeneous reaction section exists so that fuel oxidation proceeds to completion achieving higher temperatures. This configuration however requires two types of catalysts. It may be preferable to have a single catalytic monolith, thus minimising system complexity but thermal stresses may still be a problem. It is suggested that improved catalyst durability is possible by alleviating axial temperature gradients which result to thermal stresses (Kolaczkowski, 1995; Groppi et al., 1996).

It is well known that ceramics used in severe high-temperature environments such as engine parts and gas turbine applications fail periodically. Mechanical failure of catalytic monoliths has been reported (Thiart et al., 1993). A body subjected to a varying temperature field develops thermal stresses. Typical reactions carried out in monolith reactors lead to strong axial temperature gradients in the channels. Viljoen et al. (1995) have used a failure criterion which depends on the axial temperature profile. The axial temperature profile is implemented into a thermal stress model and stresses are examined in order to determine whether they exceed the breaking strength of the material. Kolaczkowski et al. (1999b) recently developed a three-dimensional mathematical model for thermal stress analysis of monoliths with square, triangular or hexagonal cross-sections.

Non-uniform axial catalyst distribution has been shown to offer better performance as opposed to uniform distribution in various applications. There is experimental evidence that there are advantages in using such distributions for monolith reactors. For catalytic combustion Dalla Betta et al. (1993c) used graded catalyst for partial combustion of various fuels including methane. The monoliths had a higher concentration of catalytic metal in the upstream section. These catalysts showed low light-off temperatures, and hot spots due to excess activity were not experienced. Theoretical investigations of automotive catalytic converters such as those carried out by Oh and Cavendish (1982); Psyllos et al. (1992; 1993a; 1993b); Tronci et al. (1999) have indicated that non-uniform distributions can shift the light-off position towards the inlet of the monolith. Research regarding the performance and preparation of non-uniform catalysts has been reviewed by Gavriilidis et al. (1993). The underlying reason for this improvement is that the appropriate non-uniform catalyst distribution can induce favourable interaction among mass and heat transfer and reaction.
Computer simulation is an effective tool for studying phenomena present during catalytic combustion. A plethora of mathematical models with uniform catalyst distribution can be found in literature. Young and Finlayson (1976a; 1976b) employed multidimensional models to study axial conduction in the wall, diffusion and conduction in the gas phase. Constant physicochemical properties of the gas were assumed in spite of significant temperature variations. Lee and Aris (1977) examined the effects of radiation with a two-dimensional model. It was shown that radiation ameliorated steep temperature gradients. Various approximations on how to represent radiation in mathematical models were discussed. Zygourakis (1989) examined the effects of flow maldistribution among channels using a transient two-dimensional model. Results showed that a step decrease in the feedstream temperature can lead to large and highly localised overtemperature excursions.

The above studies are related to automotive conditions but significant work has also been carried out on catalytic monoliths for power applications. Studies by Hayes and Kolaczkowski (1994; 1999) and Groppi et al. (1995b) demonstrated that values of the Nusselt and Sherwood numbers depend on the reaction rate at the wall and thus show strong perturbations at the light off point. Hayes et al. (1996) carried out both experimental and theoretical work for the transient behaviour of a honeycomb monolithic reactor in which methane was combusted. Both start-up and shut-down procedures were investigated. The unsteady state, two-dimensional model included axial diffusion in the gas phase, radiation and axial conduction in the solid. The gas was assumed to be at pseudo-steady state and the wall to have a slowly evolving temperature. A developing velocity profile and temperature dependent properties were considered. It was observed that under laminar flow conditions, heat losses by convection are substantially larger than heat losses by radiation and conduction. It was shown that radiation from the monolith ends can be of importance at high temperatures but it is difficult to be precise in modelling this phenomenon as environment radiation temperatures and the emissivity of monolith are difficult to determine.

In the two and three-dimensional models for gas turbines developed by Groppi et al. (1993; 1995a; 1995b; 1996), negligible axial diffusion and radial pressure drop have been assumed. The aim was to find the simplest, adequate model with substantial savings of computational time. The assumption of negligible homogeneous reactions is
justified as the model relates to monoliths used in hybrid and staged combustors where temperatures are limited and residence times are very short. Outlet bulk temperature though is high enough (above 1073K) to sustain homogeneous reactions further down the combustor system. They determined that entrance effects are critical because of the short length of the catalytic monolith; however the hydrodynamic development plays a less important role compared to the development of temperature and concentration profiles. In a recent review paper, Groppi et al. (1999) also emphasise the importance of the temperature dependence of the gas properties as it seriously affects the prediction of the combustor performance.

The concept of diffusion barriers has been investigated theoretically by Leung et al. (1996). The investigation mainly involved the influence of diffusion on the reaction rate in the washcoat of a catalytic monolith reactor. They demonstrated that the rate of reaction may be strongly influenced by diffusion limitations at temperatures at which such reactors may operate. This was attributed to the presence of fillets of washcoat in the corner of the channel. Thus they determined that the diffusion resistance of the washcoat material may be used advantageously in controlling sharp temperatures gradients at the inlet of the reactor and this can be enhanced by applying a thin layer of inactive washcoat on top of the active layer.

To develop an appropriate model, decisions must be made concerning the number of space dimensions to consider. The most realistic model, especially for non-circular cross-section channels, would be a three-dimensional model. This may be computationally prohibitive and is probably not justified in terms of accuracy. As Groppi et al. (1995a) emphasise, it is important to strike the appropriate balance between model accuracy and complexity. Simple one-dimensional models require less computer time but may lead to incorrect predictions of light-off behaviour due to the difficulty in estimating local interphase transfer coefficients (Groppi et al., 1995a).

In the case of two-dimensional models, the need for heat and mass transfer correlations does not exist and it is possible to impose correctly the flux boundary condition at the monolith wall. Thus, a single monolith channel may be modelled in two dimensions by considering it to be cylindrical. This closely approximates the geometry of a coated channel, as the application of washcoat tends to ‘round’ the corners (Hayes and Kolaczkowski, 1994).
In this work, results on the effect of axially non-uniform catalyst distribution on temperature and concentration profiles for methane combustion conditions are presented, for applications in both hybrid and staged combustors. A two-dimensional model is formulated considering adiabatic operation, axial and radial diffusion in the gas phase, conduction in the solid, radiation, flat inlet velocity profile and temperature dependent physical properties. Simulations are performed both for steady state and transient conditions representative of start-up, fuel interruption and shut-down of a gas turbine.

3.2 Mathematical Model

The simulation of the whole monolith reduces to the analysis of a single channel and is similar to the model proposed by Groppi et al. (1995a). This is based on the hypotheses of global adiabaticity, perfectly uniform distribution of variables at the inlet section and identical conditions prevailing in all channels. Heterogeneous reactions at the catalytic wall are irreversible and first order with respect to the fuel (methane) concentration and zero order with respect to oxygen due to fuel lean conditions (Spivey, 1987). Intraphase diffusion is taken into account through the effectiveness factor which is calculated according to the analytical solution of the reaction-diffusion problem for a first-order kinetics in an isothermal slab (Froment and Bischoff, 1990). The validity of isothermality was verified by calculation of the Prater number which was close to zero (Appendix 1). Contribution of homogeneous reactions has been neglected in order to keep the model simple. This assumption is realistic due to the short residence time of the gas stream within the monolith channel (Groppi et al., 1995) and also because in certain cases the exit temperature was low (<1073 K) (Kolaczkowski, 1999a). When these temperatures are high, the downstream monolith portion can in principle be reduced up to the point where homogeneous reactions are initiated after the monolith. In addition to steady state simulations, the effect of non-uniform catalyst distribution is investigated for transient conditions that are typically encountered in gas turbine operation.
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

3.2.1 The Governing Equations

The model is based on mass, energy and momentum balances (cf. Bird et al., 1960) for the gas phase and energy balance for the solid phase, while reactions are incorporated through boundary conditions.

More specifically the gas phase material balance is,

\[
\rho u \frac{\partial m_f}{\partial z} + \rho v \frac{\partial m_f}{\partial r} = \frac{\partial}{\partial z}(D_f \rho \frac{\partial m_f}{\partial z}) + \frac{1}{r} \frac{\partial}{\partial r}(D_f \rho r \frac{\partial m_f}{\partial r}) \tag{3.14}
\]

The mean bulk mass fraction is given by,

\[
m_{f, \text{bulk}} = \frac{\int_0^R \rho u m_f \, r \, dr}{\int_0^R \rho u \, r \, dr} \tag{3.15}
\]

The gas phase energy balance is,

\[
\rho u C_{pr} \frac{\partial T_f}{\partial z} + \rho v C_{pr} \frac{\partial T_f}{\partial r} = \frac{\partial}{\partial z}(k_f \frac{\partial T_f}{\partial z}) + \frac{1}{r} \frac{\partial}{\partial r}(k_f r \frac{\partial T_f}{\partial r}) + u \frac{\partial P}{\partial z} + v \frac{\partial P}{\partial r} \tag{3.16}
\]

The mean bulk temperature is given by,

\[
T_{f, \text{bulk}} = \frac{\int_0^R \rho u T_f \, r \, dr}{\int_0^R \rho u \, r \, dr} \tag{3.17}
\]

The momentum balance in the axial direction is,

\[
\rho u \frac{\partial u}{\partial z} + \rho v \frac{\partial u}{\partial r} = -\frac{\partial P}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial u}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial v}{\partial z} \right)
+ \frac{\partial}{\partial z} \left( \frac{2}{3} \mu \left( \frac{1}{r} \frac{\partial v}{\partial r} + \frac{\partial u}{\partial z} \right) \right) + \frac{\partial}{\partial z} \left( 2 \mu \frac{\partial u}{\partial z} \right) \tag{3.18}
\]

The momentum balance in the radial direction is,
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

\[
\rho u \frac{\partial v}{\partial z} + \rho v \frac{\partial v}{\partial r} = - \frac{\partial P}{\partial r} + \frac{2}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial v}{\partial r} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial u}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{2}{3} \mu r \left[ \frac{1}{r} \frac{\partial v}{\partial r} \frac{\partial u}{\partial z} \right] + \frac{\partial}{\partial z} \left( \mu \frac{\partial v}{\partial z} \right) \right) \tag{3.19}
\]

The momentum equation is constrained by the equation of continuity,

\[
\frac{\partial \rho u}{\partial z} + \frac{1}{r} \frac{\partial \rho vr}{\partial r} = 0 \tag{3.20}
\]

The boundary conditions used for the momentum, mass and energy balances are as follows. Dirichlet boundary conditions at the inlet i.e., flat velocity profile, fixed temperature, fuel mass fraction and pressure.

\[z = 0, \; \forall \; r\]

\[T_r = T_f^0, \quad m_f = m_f^0, \quad P = P^0\]  \tag{3.21}

\[u = u^0 \quad \text{except at } r = R, \quad v = 0\]  \tag{3.22}

Zero flux conditions are applied to the wall temperature at the inlet while no slip conditions are assumed at the wall.

\[z = 0, \; \text{at } R\]

\[\frac{\partial T_w}{\partial z} = 0, \quad u = 0\]  \tag{3.23}

Zero flux boundary conditions are applied at the outlet as viscous effects are no longer important and temperature and mass fraction profiles are fully developed.

\[z = L, \; \forall \; r\]

\[\frac{\partial T_r}{\partial z} = 0, \quad \frac{\partial m_f}{\partial z} = 0\]  \tag{3.24}

\[v = 0, \quad \frac{\partial u}{\partial z} = 0\]  \tag{3.25}

Zero flux conditions are applied to the wall temperature at the outlet.

\[z = L, \; \text{at } R\]

\[\frac{\partial T_w}{\partial z} = 0\]  \tag{3.26}
Symmetry conditions are applied along the monolith centre.
\[ r = 0, \forall z \]
\[
\frac{\partial T_r}{\partial r} = 0, \quad \frac{\partial m_r}{\partial r} = 0, \quad \frac{\partial u}{\partial r} = 0 \quad (3.27)
\]
\[
v = 0, \quad \frac{\partial P}{\partial r} = 0 \quad (3.28)
\]

At the wall the rate of diffusion from the bulk to the surface is equal to the rate of catalytic reaction. By performing a material balance at the wall we obtain,
\[
D_r \rho \frac{\partial m_r}{\partial r} = -\eta K_c \delta p m_f ^T \quad (3.29)
\]

At the wall, the rate of heat dissipation to the fluid is equal to the rate of energy generation due to reaction, conduction in the solid and radiation. The steady state energy balance at the wall is thus,
\[
k_f \frac{\partial T_f}{\partial r} = -\Delta H_r \eta K_c \delta p \frac{m_f}{\text{RMM}} + \frac{(1-e)}{4} \frac{d_{eq}}{\partial z} \left( \frac{m_f}{\text{RMM}} \right) + \frac{(1-e)}{4} \frac{d_{eq}}{\partial z} \left( \left[ k_t + k_r \right] \frac{\partial T_w}{\partial z} \right) \quad (3.30)
\]

For transient simulations it is sufficient to consider only the unsteady state wall energy balance. Due to the high gas velocity the gas is considered to be at steady state while the wall temperature is slowly developing.
\[
\frac{(1-e)}{4} \frac{d_{eq}}{C_p w \rho_w} \frac{\partial T_f}{\partial t} = -k_f \frac{\partial T_f}{\partial r} - \Delta H_r \eta K_c \delta p \frac{m_f}{\text{RMM}} + \frac{(1-e)}{4} \frac{d_{eq}}{\partial z} \left( \left[ k_t + k_r \right] \frac{\partial T_w}{\partial z} \right) \quad (3.31)
\]

For the transient calculations simulations were initiated utilising
\[
T_w = T^o \quad (3.32)
\]
for the whole monolith and after the steady state temperature profile was obtained the disturbance on the fuel (or total) flowrate was introduced.

The reaction rate coefficient is obtained from
\[
K_c = K_c^o \exp \left( \frac{-E_s}{R} \left[ \frac{1}{T} - \frac{1}{T^o} \right] \right) \quad (3.33)
\]

while the effectiveness factor by
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

\[ \eta = \frac{\tanh \varphi}{\varphi} \quad (3.34) \]

The Thiele modulus, \( \varphi \), is defined for slab geometry and first order reaction as

\[ \varphi = \delta \sqrt{\frac{K_c}{D_{\text{eff}}}} \quad (3.35) \]

### 3.2.2 Physical Properties

Physical properties are considered to be temperature dependent with the exception of gas heat capacity for which a constant value is utilised (1080 J/Kg. K).

The molecular diffusion coefficient is determined by the Fuller equation (Perry and Chilton, 1984) which for an air-methane mixture becomes,

\[ D_f = 9.99 \times 10^{-5} \left( \frac{T^{1.75}}{P} \right) \quad (3.36) \]

and the Knudsen diffusion coefficient by (Satterfield, 1970),

\[ D_k = 97 r_p \sqrt{\frac{T}{RMM}} \quad (3.37) \]

The effective diffusivity is obtained by (Froment and Bischoff, 1990),

\[ \frac{1}{D_{\text{eff}}} = \left( \frac{1}{D_f} + \frac{1}{D_k} \right) \tau_p \epsilon_p \quad (3.38) \]

The thermal conductivity and viscosity of the gas are taken to be that of air and are expressed as a linear function of temperature, based on values from Incropera and de Witt (1990),

\[ k_f = 1.679 \times 10^{-2} + 5.073 \times 10^{-5} T_f \quad (3.39) \]

\[ \mu = 5.53 \times 10^{-11} T^2 + 8.523 \times 10^{-8} T - 1.865 \times 10^{-5} \quad (3.40) \]

The gas is assumed to be ideal, and its density is given by,

\[ \rho = \frac{P \left( \frac{RMM}{m} \right)}{RT} \quad (3.41) \]

The density of the cordierite is taken to be 1710 kg/m³ and its heat capacity and thermal conductivity are
These correlations for a cordierite system are obtained from Hayes et al. (1992).

Radiation is taken into account through an equivalent conductivity as proposed by Lee and Aris, (1977),

\[
k_r = \frac{16}{3} \sigma r T_w^3 \psi(\chi)
\]  

(3.44)

where

\[
\psi(\chi) = 1 + \frac{\chi^3}{4} - \frac{\chi^2 \sqrt{\chi^2 + 1}}{4} + \frac{\sqrt{\chi^2 + 1}}{8} - \frac{9}{8\chi} \ln(\chi + \sqrt{\chi^2 + 1})
\]

(3.45)

and

\[
\chi = \frac{L}{d_e} e^{r}
\]

(3.46)

The remaining physicochemical parameters, monolith characteristics and operating conditions utilised in the calculations are adopted from Groppi et al. (1995a) and are given in Table 3.1.
### Table 3.1: Operating conditions, monolith characteristics and physicochemical parameters used for the calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas temperature at the inlet of catalyst, $T_f^0$</td>
<td>723 K</td>
</tr>
<tr>
<td>Fuel (CH$_4$) molar fraction at catalyst inlet, Y</td>
<td>0.02</td>
</tr>
<tr>
<td>Pressure, P</td>
<td>$10.15 \times 10^5$ N/m$^2$</td>
</tr>
<tr>
<td>Inlet gas velocity (referred to the cross section immediately upstream the catalyst inlet), $u^0$</td>
<td>7.75 m/s</td>
</tr>
<tr>
<td>Open frontal area, $e$</td>
<td>0.68</td>
</tr>
<tr>
<td>Radius of channel, $R$</td>
<td>$6 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Channel length, $L$</td>
<td>0.1 m</td>
</tr>
<tr>
<td>Uniform thickness of active catalyst layer, $\delta_0$</td>
<td>$2 \times 10^{-5}$ m</td>
</tr>
<tr>
<td>Inlet reaction rate coefficient, $K_c^0$</td>
<td>200 s$^{-1}$</td>
</tr>
<tr>
<td>Pore radius, $r_p$</td>
<td>$1 \times 10^{-8}$ m</td>
</tr>
<tr>
<td>Void fraction, $\varepsilon_p$</td>
<td>0.5</td>
</tr>
<tr>
<td>Tortuosity factor, $\tau_p$</td>
<td>3</td>
</tr>
<tr>
<td>Hydraulic diameter, $d_{eq}$</td>
<td>$12 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Activation energy, $E_a$</td>
<td>90.16 KJ/mol</td>
</tr>
<tr>
<td>Reaction enthalpy, $\Delta H_r$</td>
<td>-802 KJ/mol</td>
</tr>
</tbody>
</table>
3.2.3 Catalyst Distribution

The non-uniform catalyst distribution is implemented in the model by considering a washcoat of constant catalyst loading but of variable thickness, \( \delta \), as a function of axial location \( z \). Such catalyst can in principle be prepared by sequential slip casting (cf. Dalla Betta, 1993c).

\[
\frac{\delta(z)}{\delta_0} = a \left( \frac{z}{L} \right)^2 + b \left( \frac{z}{L} \right) + c
\]

(3.47)

\[
\frac{\delta(z)}{\delta_0} = c \exp\left( \frac{z}{\xi} \right)
\]

(3.48)

The overall amount of catalyst is considered to be the same for all distributions and equal to that of the uniform distribution, \( \delta_0 \).

\[
\frac{1}{L} \int_0^L \delta(z) dz = \delta_0
\]

(3.49)

Utilising equation 3.49 along with the constraint that catalyst thickness must remain non-negative throughout the reactor the constants, \( a \) and \( b \), can be calculated (Psyllos and Philippopoulos, 1993a).

\[
a = \frac{c - 1}{\xi - 1/3}
\]

(3.50)

\[
b = -2\xi \frac{(c - 1)}{\xi - 1/3}
\]

(3.51)

\[
\delta(z) \geq 0 \quad \text{for} \quad 0 \leq z \leq L
\]

(3.52)

where \( c \) is the dimensionless catalyst thickness at the monolith inlet, \( \delta(0)/\delta_0 \), \( \xi \) is the dimensionless axial location along the monolith where the function \( \delta(z) \) is minimised, \( (z/L)_{\text{min}} \), and \( \xi \) determines how sharply the exponential distribution decreases. Distribution profiles investigated in this work are decreasing and parabolic profiles (see Figure 3.1).
3.2.4 Numerical Methods and Model Validation

The set of PDEs of both models are solved using the general PROcess Modelling System (gPROMS) simulation package (Oh and Pantelides, 1996). gPROMS is a software designed for modelling and simulating processes with both discrete and continuous characteristics. It allows model developers to write the detailed mathematical equations using a sophisticated natural language. It distinguishes two fundamental types of modelling entity. MODELS describe the physical and chemical laws that govern the intrinsic behaviour of a system, while TASKs are descriptions of the external actions and disturbances imposed on such a system. A third type of entity, the PROCESS is formed by a TASK driving a MODEL, thereby defining a complete simulation of the process. The gPROMS input files for steady state and transient models can be found in Appendix 2.

For the steady state model, orthogonal collocation on finite elements is adopted for the radial direction as the model is predominantly dispersive in that direction.
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

(Finlayson, 1980). Third-order polynomials over three finite elements are used. Satisfactory convergence is achieved with overall ten grid points. Increasing the total number of grid points up to twenty five increased significantly computational time yet made no significant difference to temperatures obtained (maximum difference of 0.2 % at the monolith inlet). To further minimise computational time, the central finite difference method is adopted for the axial direction. Twenty one points are found to be sufficient to achieve satisfactory convergence. This number of points has been shown to be sufficient as use of an extra point improved the wall temperature value at the monolith inlet by 0.3 %. In the unsteady state model the gas velocity is high and as a result the gas phase is assumed to be in steady state with a slowly evolving wall temperature. Orthogonal collocation on finite elements is again adopted for the radial direction using third-order polynomials over two finite elements. Central finite difference method is employed for the axial direction using sixteen points. For integration with time, finite difference is utilised. Steady state temperature profiles obtained using the transient model compared satisfactorily with those obtained using the steady state one (temperature difference never exceeded 5 %).

The wall and bulk temperature profiles for a uniform catalyst layer compare well to the profiles obtained by Groppi et al. (1995a) (Figure 3.2 and Figure 3.3). Both models predict the same inlet temperatures even though the inlet boundary condition of the wall in the current model is a zero flux condition as opposed to a Dirichlet boundary condition used by Groppi et al.. Bulk temperature profiles are relatively similar as they predict an outlet bulk temperature of approximately 1073-1080 K. The main difference between the two models is their prediction of wall temperature. More specifically, the light-off experienced by their reactor is steeper than the one predicted by the current model. Wall temperature at $z = 0.01$ m is approximately 980 K for their model while it is 890 K for this work. This difference arises from the fact that the present model is more comprehensive. Groppi et al. (1995a) consider only the axial momentum balance and utilise instead a global mass balance to determine the radial change in velocity. They consider negligible axial diffusion in both mass and energy balances while they consider heat transfer at the wall by conduction and radiation as well as the dependency of gas properties on temperature is taken into account. The current model considers the full axial and radial momentum balances as well as diffusion both in the radial and axial
direction. Physical properties were considered to be temperature dependent but certain physical properties such as and tortuosity factor may differ from theirs. Groppi et al. do not specify whether they considered Knudsen diffusivity and do not specify all parameter values used such as tortuosity factor. Thus if diffusional resistances are higher in the current model, this would lead to a smoother development of the light-off and a lower maximum wall temperature by approximately 15 K.
Figure 3.2: Wall and bulk temperature profiles predicted for a monolith with characteristics and operating conditions as in Table 1.

Figure 3.3: Wall and bulk temperature profiles predicted by Groppi et al., (1995a) for a monolith with characteristics and operating conditions as in Table 1.
3.3 Results and Discussion

3.3.1 Steady State Conditions

During catalytic combustion fuel and air flow down the channel, the reactants are transported to the catalyst surface, they diffuse into the porous structure and react on catalytically active sites. The products from the reaction subsequently diffuse through the pores back into the bulk. As the reaction proceeds in the catalyst layer, energy is released and is transferred to the solid and gas phases by conduction, convection and radiation. For the uniform catalyst distribution, the rate of heat production at the entrance is low and convective heat removal due to the inlet gases does not allow the inlet wall temperature to increase much above the bulk. Light-off is experienced further along the monolith where heat released by reaction more than compensates heat removed by the various heat transfer mechanisms. When the temperature of the wall is higher than the bulk gas, energy is transferred to the latter and gas temperature increases along the axial direction. However radial heat transfer in the gas phase is relatively slow and radial temperature gradients appear as shown in Figure 3.4. In the same figure it is shown that there is a portion of the bulk phase close to the wall where temperature exceeds 1073 K. In this region homogeneous reactions can potentially be initiated since temperatures are sufficiently high (Kolaczkowski, 1999a). Furthermore, it is expected that homogeneous reactions can be sustained beyond the monolith outlet since a significant portion of the exiting fluid has temperature exceeding 1073 K. At steady state the wall temperature increases from 723 K to 1095 K within the first 2 cm. The sharp wall temperature gradient which develops can lead to stresses in the substrate, catalyst deactivation and subsequent degradation (Thiart et al., 1993; Viljoen et al., 1995; Kolaczkowski et al., 1999b). Alleviation of the sharp temperature gradients can potentially improve catalyst durability and lifetime.

The effect of non-uniform catalyst distribution on axial wall temperature gradients is investigated for decreasing and parabolic profiles shown in Figure 3.1. The total catalyst amount in the monoliths is kept constant. Distribution 1 is the uniform distribution (20μm). Distribution 2 has an inlet catalyst thickness of 25 μm and outlet of 17.5 μm. Distributions 3 and 4 have an exponentially decreasing nature. Distribution 3 has an inlet catalyst thickness of 70 μm and outlet of 2.5 μm, while distribution 4 an inlet of 123 μm and outlet of 0.26 μm. Finally distribution 5 has a parabolic profile with an
inlet and outlet catalyst thickness of 50 $\mu$m and a minimum thickness at the middle of the monolith length of 5 $\mu$m. The following constraints are used in assessing performance improvement in such reactors. (i) wall temperatures do not exceed 1300 K (the upper operation limit for ceramic monolith, Trimm, 1995); (ii) wall temperature gradients are lower than those experienced by the monolith with uniform catalyst distribution and (iii) exit gas temperatures are high enough to initiate homogeneous reactions and CO burnout downstream of the monolith (above 1073 K).

Figure 3.4: Two-dimensional temperature profile in a monolith channel with uniform catalyst distribution.
and Figure 3.6a. Inlet wall and bulk temperatures are similar for the uniform distribution 1. Inlet catalyst loading is relatively low and the temperature of the inlet gases is not high enough to allow for substantial increase in wall temperature. However, wall temperature progressively increases leading to high reaction rates which in turn result to higher heat production and eventually light-off is obtained. The maximum wall temperature gradient experienced by monolith with distribution 1 is 275 K/cm. Exit wall temperature is 1205 K.

Distribution 2 exhibits light-off further towards the entrance. Distributions 3, 4 and 5 similarly initiate high reaction rates at the entrance of the monoliths (Figure 3.5b). Catalyst loading is high enough to achieve a build-up of heat at the wall inlet and thus inlet wall temperatures (1075-1090 K) are higher than bulk gas temperature (723 K). Maximum wall temperature gradients are significantly reduced even by the moderate distribution 2 which achieves a value of 67 K/cm. Distributions 3, 4 and 5 achieve 43, 41 and 43 K/cm respectively. Care must be taken though that catalyst distributions are not highly exponential as distribution 4. These experience decrease of reaction rates and finally extinction at the outlet as catalyst amount in that location is low. Distribution 5, even though it has a highly exponential profile from the inlet up until the middle of the monolith length, succeeds in avoiding extinction of reactions as catalyst layer increases again significantly from the middle to the monolith exit. Conduction through the walls help maintain the temperature to above 1000 K at the middle of the monolith and exit temperature is approximately 1215 K. For distribution 3 maximum wall temperature is found to be 10 K higher than the uniform case but well below 1300 K. It is worth noting that the temperature profiles in the light-off region are similar for distributions 3-5 even though the corresponding loadings in that region are different.

It is evident from the above that favourable distributions for alleviating wall temperature gradients are those with high enough catalyst loading at the entrance to sustain a high temperature in that position, and adequate loading at the exit in order to avoid extinction, such as distributions 3 and 5.
Figure 3.5: Steady state wall temperature profiles.
Figure 3.6a and Figure 3.6b show that bulk temperatures in all monoliths are higher than the uniform case as there is more heat generated at the entrance and its transport to the bulk is efficient enough to maintain wall temperatures at the level of 1100-1200 K. Bulk temperatures by the exit of all monoliths are approximately 1100-1190 K. Homogeneous reactions can therefore be initiated further upstream. In a hybrid or a stage combustor, homogeneous reactions take place in a separate section. Thus, the length of monoliths studied can in principle be reduced to the point where bulk temperature is sufficient for sustaining homogeneous reactions (1073 K). For the distributions of this works this would lead to a decrease in monolith length of ca. 50\%. According to Cohen (1987) and Etemad et al. (1999) a shorter catalytic monolith leads to a reduction in pressure drop and thus an increase in overall gas turbine efficiency.

Figure 3.7a illustrates how increasing the catalyst amount at the entrance by a small amount as compared to the uniform case, results in high diffusional resistances for the system studied and thus effectiveness factors at the entrance drops to ca. 0.2. Thus, distribution 2 operates close to mass transfer control throughout the monolith whereas distribution 1 operates close to kinetic control in the first centimetre.

In Figure 3.7b, the effectiveness factor for distributions 3 and 4 increases gradually towards the value of 1.0 along the monolith as catalyst thickness is decreased. This is opposite to the trend of the uniform case. Distributions such as 3 and 4 have limited amount of catalyst at the monolith exit and thus the controlling mechanism moves from mass transport to kinetics from inlet to outlet. For distribution 5, effectiveness factor attains a maximum where catalyst loading is at a minimum. It is worth noting that at the monolith exit, distributions 3 and 5 exhibit values of the effectiveness factors at the opposite limits of the range 0 - 1.0. However, catalyst overall behaviour (see Figure 3.5 and Figure 3.6) is not significantly different. Both distributions though have small effectiveness factors at the entrance region.
Figure 3.6: Steady state bulk temperature profiles.
3. Theoretical Investigation of Axially Non-Uniform Catalytic Monoliths for Methane Combustion

Figure 3.7: Effectiveness factor along monoliths at steady state.
It is interesting to compare this behaviour with that experienced when using diffusion barriers for alleviation of temperature gradients such as those proposed by Dalla Betta et al (1993a; 1993b) and Leung at al., 1996. The diffusion barriers slow down the rate of reaction at the entrance region. They can be prepared by applying a thin layer of non-catalytic washcoat over the uniform catalytic washcoat. This leads to a smoothening of the S-type temperature profile and a more linear development of the wall temperature along the monolith with maximum temperature gradient 160 K/cm (Leung at al., 1996). In this work, S-type temperature profiles are maintained but axial temperature gradients are alleviated by increasing the entrance wall temperature through non-uniform catalyst distribution. Since wall temperature is kept at a high level for most of the monolith, the bulk temperature attained at the outlet is close to the corresponding wall temperature. Unfortunately, comparison cannot be made with the above works since outlet bulk temperatures are not reported.

Figure 3.8 shows the fuel mass fraction at the wall for all distributions studied. For the uniform distribution the sharp decrease of mass fraction coincides with the light-off region. For all other distributions the mass fraction axial profiles at the entrance are similar and exhibit a sharp decrease in the first centimetre. For distribution 4, reaction rates at the monolith outlet are very low due to insufficient amount of catalyst. Hence, fuel diffusing from the bulk results to a rise of the wall mass fraction.

The profiles of bulk mass fractions along the monoliths are shown in Figure 3.9. Distributions 1 and 2 exhibit the same profile, even though the corresponding wall mass fractions are different. This is due to the fact that diffusion from the bulk to the wall is not fast enough to replenish fuel consumed. Bulk fuel mass fraction for distribution 4 stabilises after ca. 0.06 m because, as mentioned before, reaction rates are low towards the monolith outlet. This results in a final conversion of 73.6 %. Conversion obtained by the uniform distribution is 81.5 % while it is further increased by distributions 2, 3 and 5 (conversions in the range 83-84 %).
Figure 3.8: Fuel mass fraction at the wall as a function of monolith location.
Figure 3.9: Mean fuel mass fraction in the bulk as a function of monolith location.
From all distributions examined, distributions 3 and 5 show the best performance, with the former marginally better since the outlet wall temperature is slightly lower while the outlet bulk temperature higher than the latter. The two-dimensional temperature profile for distribution 3 is shown in Figure 3.10. Comparing this figure with Figure 3.4, it is evident that the temperature region 1100 - 1200 K is larger, while the temperature region 700-800 K is smaller for the monolith with distribution 3. Thus, it is possible to sustain homogeneous reaction using distribution 3 further upstream as compared to the uniform distribution. Maximum wall temperatures are well below the material limit of 1300 K. Wall temperature gradients are lower compared to the uniform distribution as inlet temperatures are high while maximum temperatures remain at similar levels as the uniform distribution.

Figure 3.10: Two-dimensional temperature profile in a monolith channel with catalyst distribution profile 3.
3.3.2 Transient Conditions

In the above, it has been shown that decreasing catalyst profiles are preferable to uniform under steady state conditions since they reduce wall temperature gradients as high reaction rates are initiated further upstream at the monolith. At the same time, they can sustain outlet wall temperatures to levels similar to those of the uniform profile.

During gas turbine operation changes in fuel loading take place during start-up and shut-down. In addition, under normal operation, disturbances such as fluctuations in the inlet fuel concentration can occur (Kolaczkowski, 1995). Therefore, below we examine how a non-uniform distribution (distribution 3) which exhibits improved steady state performance, as compared to the uniform, behaves under transient conditions.

3.3.2.1 Start-up Conditions

Start-up conditions are simulated by introducing a step increase of methane concentration from 0-2 vol % at time $t = 0$ in an air stream preheated at 723 K which flows within the monolith. Figure 3.11 shows how axial wall temperature profiles evolve with time for distributions 1 (uniform) and 3.

For the uniform distribution reaction rates progressively increase in the upstream region and the heat produced is used both to heat up the monolith wall and the incoming gases. However, the inlet wall temperature is pinned at 723 K throughout the transient period because of the significant cooling effect of the inlet stream. Even though sharp wall temperature gradients are present, heat conduction is not sufficient to compensate the heat lost by convection. This is in accordance with Groppi et al. (1996) who state that for a ceramic monolith with uniform catalyst distribution, despite large temperature gradients, heat conduction is negligible, due to low ceramic thermal conductivity. The temperature profile in the downstream section (2-10 cm) remains practically flat throughout the transient period, indicating a balance between heat production and heat dissipation in that region. Steady state is achieved in 15 s.

For distribution 3, catalyst loading in the entrance region is so high that a significant amount of heat is generated. This not only compensates for the convective cooling from the inlet gases but also raises the wall temperature at the inlet, as shown in Figure 3.11b. In addition, temperature increase with monolith length in the first centimetre is always lower as compared to the uniform case. A hot spot develops
between 2-8 s because as the amount of catalyst decreases along the monolith heat generation is exceeded by heat removal and thus temperature drops. Eventually at steady state, which is reached in 14 s, the hot spot disappears as heat removal rate decreases and a favourable balance between heat removal and heat generation is accomplished.

By comparing Figure 3.11a and Figure 3.11b it is evident that overall axial wall temperature gradients experienced by the non-uniform catalyst are lower as compared to the uniform distribution, throughout the transient period. It is worth noting that temperature gradients with respect to time now appear and they are typically larger for the non-uniform distribution. These gradients are equivalent to thermal shocks which can be detrimental to catalyst durability.
Figure 3.11: Wall temperature profiles during start-up conditions. (a) Uniform distribution; (b) Distribution 3.
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3.3.2.2 Disturbance during Steady State Conditions

Disturbances are simulated by considering the extreme case where there is a 3 s cut-off of methane supply while the rest of the feed stream continues to flow. The effect on wall temperature after interrupting the methane flow momentarily is shown in Figure 3.12a and Figure 3.12b for the uniform and non-uniform catalysts respectively.

Wall temperatures change significantly with time, due to strong convective cooling by the inlet gases. The behaviour though is different for the two distributions. For the uniform catalyst the wall temperature at the inlet is always fixed and axial temperature gradients are lower both during cooling as well as re-heating, as compared to the steady state. For the non-uniform catalyst inlet wall temperature changes, and even though axial temperature profiles shift in an approximately parallel fashion, larger axial temperature gradients as compared to the steady state condition are observed at 1 and 2 s.

In addition, the temperature changes observed at the entrance are higher than the corresponding ones at the outlet (see Figure 3.12b). This is due to the fact that the most significant decrease in heat generation is experienced at the monolith inlet where the highest amount of catalyst is located. It is worth noting that the temperature profiles at 3 s are similar for both distributions and they would approach a flat temperature profile at 723 K if the fuel disruption lasted longer. Similarly, in the case of start-up simulations, significant temporal temperature gradients appear in both cases and they are more substantial for the non-uniform distribution. The time taken for both monoliths to achieve steady state is similar (approximately 20 s).
Figure 3.12: Wall temperature profiles during fuel disturbance. (a) Uniform distribution; (b) Distribution 3.
3.3.2.3 Shut-down Conditions

Shut-down conditions are simulated by imposing the flows of air and fuel to cease at time $t = 0$. It is worth re-iterating that the boundary conditions employed are the same as for the steady state simulations. As such, the fluid temperature at the monolith inlet remains at 723 K.

In Figure 3.13 the evolution of wall temperature profiles with time is shown for distributions 1 (uniform) and 3. At time $t = 0$, there exist radial and axial temperature profiles in the monolith channel. These result to heat transfer from the wall to the bulk and axially along the monolith due to conduction and radiation. The temporal temperature gradients observed are smaller than in Figure 3.12 because no convective heat transfer mechanism is present during shut-down, which is in accordance with the observations of Hayes et al. (1996).

Overall the performance of uniform distribution seems to be better than the non-uniform, since for the former, the maximum axial wall temperature gradient diminishes with time, while the opposite trend is observed for the non-uniform distribution. This is due to the fact that the bulk inlet temperature is kept at 723 K and this results in substantial heat losses at the entrance of the significantly hotter wall entrance of distribution 3, as compared to the uniform distribution. Obviously catalyst performance during shut-down will be affected by the boundary conditions employed; for example it is conceivable that the bulk inlet temperature is a decreasing function of time.

For the time period simulated, the uniform distribution does not cool down significantly at the monolith ends as radiation losses from the ends are not considered. If such heat losses were to be accounted for, wall temperature gradients for both distributions would be sharper especially at the outlet as observed by Hayes et al. (1996). For both distributions, axial temperature gradients during shut-down are higher than those exhibited during fuel disturbance while the opposite is observed for temporal temperature gradients. During fuel disruption, convective cooling is fast and heat losses are relatively uniform throughout the monolith length while in the former, slow conduction cooling gives rise to less uniform heat dissipation.
Figure 3.13: Wall temperature profiles during shut-down conditions. (a) Uniform distribution; (b) Distribution 3.
4. Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate

4.1 Introduction

Chemical vapour deposition (CVD) has been used extensively for preparation of thin films which find applications in electronics (Hampden-Smith and Kodas, 1995a, 1995b; Maury, 1996) and in high performance materials (Brossa, 1989). However, CVD can also be utilised for deposition of metal particles and is thus of interest in catalyst preparation. This method allows direct deposition of the active material onto catalyst supports. It reduces the number of steps typically encountered in conventional preparation methods such as impregnation and precipitation which involve washing, drying, calcination etc.. Complications caused by the solvents during liquid-phase preparation, for example redistribution of the active material during drying, are also avoided (Schwarz et al., 1995).

CVD is a versatile method for depositing a great variety of elements and compounds with a minimum number of steps. In addition it is possible to vary the composition and structure of the deposited material applied (Brossa, 1989). Dossi and co-workers (1993-1999) have carried out extensive work on the application of CVD for depositing active metal into zeolite channels. They have shown that metal-organic compounds are suitable and flexible precursors for preparing highly dispersed metal particles supported on metal oxides and zeolites. The metal phase is usually obtained by simple ligand removal under mild conditions, preventing sintering to large crystallites or carbide formation. CVD-based catalysts showed the additional advantage of a clean metal phase, due to the absence of any contamination from solvents or anions containing halogens or sulphur (Ugo et al., 1996).

Dossi et al. (1993b) described the preparation of a proton-free Pd/NaY catalyst, obtained by CVD of \([\text{Pd(}\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)]\). It was characterised by a high dispersion and uniform distribution of the metal particles inside the zeolite channels with a good thermal stability towards sintering in hydrogen at 500°C. The CVD process was carried out in two stages, deposition of the precursor and subsequent reduction to the active metal by hydrogen utilising a quartz hot wall reactor. Platinum hexafluoroacetylacetonate was selectively introduced inside the channels of KL zeolites.
Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate (Dossi et al., 1994) and HL zeolites (Dossi et al., 1996) via CVD and gave rise to small non-acidic platinum clusters. These catalysts showed remarkably high activity and selectivity in the conversion of methycyclopentane to benzene at 500°C. Long catalyst life was in addition achieved due to the reduced coke formation and slow sintering rate.

Preparation of platinum supported on SiO₂, Al₂O₃ and TiO₂ after decomposition of Pt(acac)₂ at 300°C was carried out by Köhler et al. (1995) utilising a fluidised bed. The adsorbed precursor was decomposed in nitrogen. They determined that surface properties of the support material influence the adsorption sites of Pt(acac)₂ as well as the decomposition pathways of the adsorbates and finally the dispersion of the catalytic compound. The deposited particles were found to be more mobile on silica and hence more capable to agglomerate. Alumina-supported Pt may be stabilised by co-ordinatively unsaturated Al³⁺ surface ions. Their attempts to prepare palladium on supported material using Pd(acac)₂ failed as the temperatures they used were high and the complex decomposed in the gas phase before adsorption was accomplished.

A fluidised bed was utilised by Hierso et al. (1998) for carrying out metal-organic chemical vapour deposition for preparing metal-supported catalysts. Various metal precursors (Rh(allyl)₃, Pd(allyl)(hfac), Pt(COD)(CH₃)₂) and supports (SiO₂, Al₂O₃) were used. The Clausius-Clapeyron relations for the above compounds were determined. They concluded that fluidised beds are suitable for preparation of metal aggregates homogeneously dispersed on the substrates.

CVD has been utilised to prepare solid metal membranes for hydrogen separation applications. Yan et al. (1994) and Kusukabe et al. (1996) formed thin palladium membranes inside the porous wall of α-alumina support tubes. Palladium (II) acetate was decomposed in argon and the best membrane were obtained under reduced pressure. The membranes high hydrogen permeability. Uemiya et al. (1997) prepared palladium, ruthenium and platinum membranes in support tubes with a thin γ-alumina layer. The precursors used were acetylacetonato complexes which they sublimed and decomposed in nitrogen under atmospheric pressure. For palladium (II) acetylacetonate they used a sublimation temperature of 160°C and a decomposition temperature of 270°C. They determined suitable operating conditions for thin metal layers utilised for hydrogen permeation.

In the above studies deposition of the active material was uniform. The present work focuses on the preparation of monolithic catalysts with non-uniform active metal
distributions which have been shown theoretically to offer better performance as compared to uniform catalysts (Oh and Cavendish, 1982; Psyllos and Philippopoulos, 1993; Gavrilidis et al., 1993; Tronci et al., 1999). They initiate reactions further upstream of the monolith and as long as there is sufficient catalyst downstream to sustain the reactions, overall conversion is improved. Moene et al. (1993; 1995) demonstrated theoretically that CVD can be utilised for non-uniform catalyst preparation.

Metal-organic chemical vapour deposition (MOCVD) is adopted in this study as it offers advantages such as low deposition temperature and relatively simple equipment (Psaro et al., 1998). A large variety of metal precursors containing halide, carbonyl, allyl, hydride and alkene ligands can be used. For Pd deposition, precursors include Pd(allyl)$_2$, Pd(Meallyl)$_2$, Pd(allyl)(Cp) (Hampden-Smith and Kodas, 1995a) and Pd(acac)$_2$ (palladium (II) acetylacetonate) (Pierson, 1992). Pd(acac)$_2$ is employed in the current work, since it does not contain halides which can be detrimental to catalytic activity. It is a cheap, air-stable at room temperature yellow powder which is simple to handle and is readily available commercially.

Irrespective of the uniformity of the deposit, control of a given CVD process entails knowledge of vapour pressures of the precursor and the nature of the deposition process and rate. This work deals with experiments designed to study sublimation, deposition and reduction of Pd(acac)$_2$ as a function of operating parameters such as carrier gas flowrate and composition, sublimation and deposition temperatures. The Clausius-Clapeyron relation for Pd(acac)$_2$ is determined. The temperature range for deposition on a cordierite monolith with γ-alumina washcoat and the importance of hydroxyl groups in the CVD of the metal-organic complex are in addition investigated.
4.2 Experimental

4.2.1 Sublimation of Pd(acac)\textsubscript{2}

Pd(acac)\textsubscript{2} (Pd(C\textsubscript{3}H\textsubscript{7}O\textsubscript{2})\textsubscript{2}) is a palladium complex in powder form with a palladium content of 33%. It has a purity above 97% as supplied by Fluka Chemicals. Sublimation was investigated using a Cahn thermogravimetric analyser (TGA), model TG131. A carrier gas (helium or hydrogen) was used to control the sublimation atmosphere while a purge gas (nitrogen) was employed to avoid contamination of the balance mechanism. The sample boat was suspended in the TGA furnace by a nichrome wire, 0.25 mm in diameter (see Figure 4.1a). Throughout the entire study, it was necessary to clean the glass parts of the TGA regularly using concentrated HCl/HNO\textsubscript{3} (3:1) mixture as deposits would build up. The solid which condensed onto the walls of the TGA at room temperature during helium sublimation experiments was identified by X-ray diffraction (XRD) to be Pd(acac)\textsubscript{2} while in a hydrogen atmosphere shiny deposits, indicative of metallic palladium, were observed.

The mass of the sample boat initially containing 50-100 mg of Pd(acac)\textsubscript{2} was recorded as a function of time for various temperatures and flowrates under atmospheric pressure. The sublimation temperature in a helium environment (99.999% purity, BOC CP grade) was fixed at values in the range 100 - 190 °C and flowrates of 20 - 200 ml/min. In a hydrogen environment (99.99% purity, BOC zero grade) temperatures ranged from 27 - 41 °C under a fixed flowrate of 80 ml/min. The first 30 min of sublimation experiments were required to stabilise the sample temperature. Mass loss occurring during this stabilisation step was eliminated from thermogravimetric measurements. Additional sublimation runs were carried out at temperatures of 160 °C and 170 °C at helium flowrates of 160 ml/min and 55 ml/min respectively, but with direction of flow opposite to that shown in Figure 4.1a, in order to investigate whether flow configuration influenced the sublimation rate of the complex.

4.2.2 Deposition of Pd(acac)\textsubscript{2}

The deposition of Pd(acac)\textsubscript{2} on monoliths was also investigated by thermogravimetry. A sublimer consisting of a stainless steel vessel, oil bath and heating plate was connected to the TGA. The sublimed precursor was transported by the helium carrier gas to the substrate which hung in the TGA balance as shown in Figure 4.1b.
Teflon tubing connected the sublimer to the TGA. It was short and insulated so that condensation of the sublimed precursor was avoided.

The sublimation temperature was fixed at 140 °C as a result of the experiments described in the previous section. Once the temperature stabilised the monolith was hung in the TGA balance and the data acquisition was initiated. The gain in mass was recorded as a function of time for a range of deposition temperatures and flowrates under atmospheric pressure. The deposition temperature was varied between 100 - 150 °C and helium flowrate between 55 - 200 ml/min. The first 30 min of the deposition experiments were required to stabilise the temperature of the monolith samples. The mass gain during this stabilisation step was eliminated from thermogravimetric measurements. Cordierite monoliths with square channels of size 1.2 mm were used as substrates and contained a 200 μm thick γ-alumina washcoat. Their size was 0.8 cm x 0.8 cm x 5 cm.

4.2.3 Reduction of Pd(acac)₂

For the preparation of palladium catalysts the metal-organic precursor is first sublimed, then deposited onto the substrate and finally decomposed to give palladium particles. Decomposition can be accomplished thermally or through a reducing agent. In this work it is carried out under hydrogen atmosphere in order to avoid carbon contamination which is characteristic of thermal decomposition (Rand, 1973). The reduction of the deposited Pd(acac)₂ to palladium was thus investigated by thermogravimetry. Mass of the monolith was recorded as a function of time for a range of temperatures under atmospheric pressure. The decomposition temperature was varied between 25 - 45 °C using hydrogen gas as the reducing agent at a flowrate of 80 ml/min. Similarly as before, the first 30 min of the decomposition experiments were needed to stabilise the temperature of the samples. Mass loss during this stabilisation step was eliminated from thermogravimetric measurements. It must be noted that in order to observe better the reduction process, the deposition process was extended for 16 hours, at a deposition temperature of 150°C and flowrate of 120ml/min, in order to have enough deposit for the hydrogen reduction experiment.
4. Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate

Figure 4.1: (a) Positioning of sample boat with respect to the direction of carrier gas flow for sublimation experiments; (b) Schematic of set-up used for deposition experiments.
4.3 Results and Discussion

4.3.1 Investigation of Precursor Sublimation

4.3.1.1 Effect of Carrier Gas Composition

The mass loss of the cylindrical, round-bottom sample boat (227 mm² cross-sectional area) filled with 50 mg of palladium complex was recorded as a function of time at constant temperature under atmospheric pressure. Typical thermogravimetric curves are given in Figure 4.2 and Figure 4.3 for helium and hydrogen atmospheres respectively.

The rate of weight change remains constant throughout the period of time investigated under a helium atmosphere for temperatures varying from 100 - 160 °C. It can be seen in Figure 4.2 that at 190 °C the rate of weight loss is significantly increased but there is a change in the rate after approximately 20 min. This indicates the presence of a second process affecting weight loss. A solid residue approximately 28 % of the initial mass of Pd(acac)₂ was found in the sample boat after the experiment at 190 °C. The residue was identified by XRD to contain metallic palladium. This indicates that thermal decomposition is the main cause for weight loss at this temperature. It is worth noting that a brown carbonaceous coating was observed on the boat as well as parts of the TGA glassware after the 190°C helium experiment.

In a hydrogen environment, experiments lasted 150 min after temperature stabilisation. As shown in Figure 4.3, the sample mass reached a constant value for experiments at 31 - 41 °C. The sample boat was never entirely empty at the end of these experiments. A black residue, on average 34 % of the initial weight, was found in the boat for experiments carried at 31 - 35 °C in H₂. At 27 °C the residue was 89 % of the initial weight whereas at 41 °C, 43 %. XRD analysis of the residues showed the presence of metallic palladium indicating that hydrogen reduction of Pd(acac)₂ occurred under these experimental conditions.

Comparing rates of weight loss for experiments where precursor decomposition occurs, different behaviour is observed depending on the environment. Namely in helium atmosphere there is a decrease in rate at 190 °C while in a hydrogen atmosphere there is a continuous increase in rate almost up to the point where weight loss ceases. This rate acceleration suggests that in the presence of hydrogen, decomposition may involve a more complex mechanism.
Figure 4.2: Weight change with time for sublimation of 50 mg Pd(acac)$_2$ at various temperatures and helium flowrate 160 ml/min.

Figure 4.3: Weight change with time for sublimation of 50 mg Pd(acac)$_2$ at various temperatures and hydrogen flowrate 80 ml/min.
Figure 4.2 and Figure 4.3 show that sublimation can take place at much lower temperature in hydrogen than in helium but the metal-organic complex is unstable in a hydrogen environment and reduction of the complex starts from an early stage. For the period of time investigated, the onset of the thermal decomposition of Pd(acac)$_2$ occurred between 160 °C and 190 °C in helium and reduction of the complex started as early as 27 °C in H$_2$.

In an attempt to lower sublimation temperature while avoiding precursor decomposition, experiments were performed using hydrogen diluted in helium. In Figure 4.4, initial rates of weight loss (i.e. immediately after the 30 min stabilisation period) are shown as a function of temperature for various concentrations of hydrogen in helium. It can be seen that when hydrogen was present even at small amounts the rate of weight loss was higher throughout the temperature range investigated than when only helium was present.

![Graph showing initial rate of weight loss vs. 1000/T (K$^{-1}$) for different carrier gas compositions](image)

**Figure 4.4: Effect of carrier gas composition on initial rate of weight loss of 50 mg Pd(acac)$_2$ and total gas flowrate 80 ml/min.**

XRD analysis of the residues from all runs involving hydrogen though showed the presence of metallic palladium. The existence of precursor reduction is further
supported by the fact that the slopes of the Arrhenius plot for the sublimation experiments at 100 % helium changes when hydrogen is introduced. Thus, reduction of the complex takes place even at very low concentrations of hydrogen. This is in contrast with the results of Pauleau and Fasasi (1991) whose complex Cu(acac)₂ was highly stable in the presence of hydrogen and the Arrhenius plots obtained using hydrogen as carrier gas had the same slope as those obtained using argon.

The Pd(acac)₂ molecule undergoes structural changes when exposed to the temperatures required for sublimation. This is evident from the XRD profiles shown in Figure 4.5 and Figure 4.6. In Figure 4.5 pattern a, corresponds to the precursor as received is shown and all peaks are identified to belong to the Pd(acac)₂ structure. In Figure 4.5 patterns b, c and Figure 4.6, pattern a, corresponds to the precursor residues after it has been exposed for four hours in a helium atmosphere at 100 °C, 160 °C and 190 °C respectively. The low angle section of the diffractograms (2θ = 10 - 30°) indicates the partly amorphous nature of the compound (Figure 4.5a). With increasing temperature, there is a rearrangement of the lattice reflected as a “swelling” in Figure 4.5b and Figure 4.5c. At even higher temperatures, 190 °C, the peaks corresponding to Pd(acac)₂ disappear and peaks for Pd metal appear indicating decomposition of the precursor (Figure 4.6a). In Figure 4.6 pattern b, corresponds to the precursor after being exposed to 1 % hydrogen in helium at 100 °C for four hours. In this case peaks for both Pd(acac)₂ and Pd metal are observed. It must be noted though that the Pd peaks are shifted to the left indicating that the Pd lattice has not reached a stable arrangement. In addition the peaks are rather broad and this can be attributed to the presence of small Pd particles.

As the ultimate aim is to prepare catalysts, we wish to avoid carbonaceous deposits which can be present when thermal decomposition takes place. Hence, further investigations were carried out using helium as carrier gas at the lower temperatures of 100 - 160 °C.
Figure 4.5: (a) XRD profile of pure Pd(acac)$_2$; (b) XRD profile of residue after sublimation run under helium at 100 °C; c) XRD profile of residue after sublimation in helium at 160 °C.
Figure 4.6: (a) XRD profile of residue after sublimation in helium at 190 °C; (b) XRD profile of residue after sublimation run under 1 % hydrogen in helium at 100 °C.
4.3.1.2 Effect of Sublimation Surface Area

Experiments were performed using two different sample boats in order to investigate the effect of sublimation surface area, i.e. the cross-sectional area of the boat. The boats had cross-sectional areas 126 mm$^2$ and 227 mm$^2$. The smaller diameter boat had a flat bottom while the larger diameter one had a round bottom. Mass loss was recorded at 140 °C in 200 ml/min helium flowrate and initial sample mass was fixed at 100 mg. As shown in Figure 4.7 the rate of sublimation increased proportionally with increasing surface area. The percentage weight loss after 130 min for the boat with cross-sectional area 126 mm$^2$ was 1.34 % while for the bigger boat with cross-sectional area 227 mm$^2$ it was 2.20 %.

![Figure 4.7: Effect of cross sectional area of sample boat on sublimation rate of 100 mg Pd(acac)$_2$ at 140 °C and helium flowrate 200 ml/min.](image)

Pauleau and Fasasi (1991) used a similar complex, Cu(acac)$_2$, to prepare copper deposits. They concluded that the sublimation zone is limited to the surface area of the macroscopic gas-solid interface and observed similar dependence of sublimation rate on boat surface area. Sublimation rate was independent of the internal surface area of the powdery compound and thus of the initial sample mass. Nevertheless, in all further
sublimation experiments in the present work the initial amount of metal-organic complex was always kept at 50 mg.

**4.3.1.3 Effect of carrier gas flowrate and sublimation temperature**

The energy associated with the phase change is the enthalpy of sublimation of the solid. Sublimation occurs when the solid molecules experience collisions with the carrier gas molecules and above a specific temperature their energy is sufficient to overcome the surface binding energy and they desorb. The energy required to sustain the sublimation comes from the internal energy of the solid which then must experience a reduction in temperature. The latent heat lost by the solid because of sublimation is replenished by the energy transfer to the solid from the furnace (Atkins, 1994).

A series of experiments were conducted to investigate the effect of flowrate on sublimation rate. As can be seen from Figure 4.8 the sublimation rate is independent of carrier gas flowrate above 20 ml/min for all temperatures investigated (100 - 160 °C). It must be noted that the flow is laminar (at a flowrate of 160 ml/min and based on the TGA tube diameter of 3.5 cm, Re = 0.63).

![Figure 4.8: Effect of helium flowrate on sublimation rate of 50 mg Pd(acac)₂ at various temperatures.](image)

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**Figure 4.8: Effect of helium flowrate on sublimation rate of 50 mg Pd(acac)₂ at various temperatures.**
These results indicate that the concentration gradient responsible for transfer of precursor molecules by diffusion from the gas-solid interface to the carrier gas stream is not affected by flowrate. However it is influenced by the direction of carrier gas flow. As shown in Figure 4.9, for helium flow of 160 ml/min and temperature 160 °C, when the direction of flow is from top to bottom the sublimation rate is 1.7 times higher as compared to that for a flow in the opposite direction. For experiments carried out under different conditions (helium flowrate 55 ml/min, temperature of 170 °C) the same ratio of initial sublimation rates for the two flow directions was observed (0.00175 mg.s\(^{-1}\) / 0.00102 mg.s\(^{-1}\), shown in Appendix 3). The above results demonstrate that for sublimation experiments attention must be paid to the flow pattern of the system. Flow from top to bottom in the TGA configuration leads to the formation of a thinner boundary layer, mass transfer of the precursor molecules is thus faster.

![Graph showing the effect of flow direction on sublimation rate](image)

**Figure 4.9: Effect of flow direction with respect to sample boat, on the sublimation rate of 50 mg Pd(acac)\(_2\) at 160 °C and helium flowrate 160 ml/min.**

If one plots sublimation rate as a function of reciprocal temperature an Arrhenius relationship is obtained as shown in Figure 4.10. When no decomposition takes place the apparent activation energy calculated from the diagram is effectively the enthalpy of sublimation as will be shown later. From the same figure this is found to be 96 kJ/mol. This value as expected is independent of flow direction. Even though sublimation rates increase when flow direction is from top to bottom, the slope of the Arrhenius plot (not
shown) remains the same. The apparent activation energy found compares well with literature values for similar metal-organic complexes. Arndt et al. (1995) found an apparent activation energy for Pt(acac)₂ of 113 kJ/mol and Pauleau and Fasasi (1991) calculated the apparent activation energy for Cu(acac)₂ to be 105 kJ/mol.

![Figure 4.10: Arrhenius plot for the sublimation of Pd(acac)₂ under atmospheric pressure and helium flowrate 160 ml/min, flow direction from bottom to top.](image)

**4.3.1.4 Clausius-Clapeyron Equation**

In order to determine operating conditions for a CVD process, it is desirable to know the concentration of the metal-organic precursor in the fluid surrounding the support. This can be accomplished utilising the Clausius-Clapeyron equation which is developed in this section for Pd(acac)₂.

Two main steps are involved in the sublimation process of Pd(acac)₂: (1) desorption of Pd(acac)₂ molecules; (2) diffusion of these molecules in the carrier gas phase.

The gas-phase diffusion step can be considered to occur in one direction only along the axis y (see Figure 4.1a) which is the axis of the vertical cylindrical tube of the TGA. The sample boat is placed at the centre of the TGA isothermal zone.
The sublimation rate of Pd(acac)$_2$ can be expressed as,

$$S_R = -\frac{dn}{dt}$$  \hspace{1cm} (4.53)

where $dn$ is the number of Pd(acac)$_2$ molecules per m$^2$ leaving the gas-solid interface during time $dt$. It is assumed that the precursor vapour at the gas-solid interface is in equilibrium with the solid and hence the gas-phase diffusion is the rate-limiting step. Furthermore, the precursor containing carrier gas is treated as an ideal gas mixture.

Following similar treatment as Pauleau and Fasasi (1991), which is based on the kinetic theory of gases (cf. Alberty, 1980) the vapour pressure of Pd(acac)$_2$ at the gas-solid interface is given by the Clausius-Clapeyron equation,

$$\frac{dP_0}{dT} = P_0 \left( \frac{\Delta H_{\text{sub}}}{RT^2} \right)$$  \hspace{1cm} (4.54)

which when integrated gives,

$$\ln P_0 = -\left( \frac{\Delta H_{\text{sub}}}{RT} \right) + a$$  \hspace{1cm} (4.55)

where $P_0$ is the vapour pressure at temperature $T$, $R$ is the ideal gas constant, $\Delta H_{\text{sub}}$ the enthalpy of sublimation and $a$ is a constant.

The sublimation rate is equal to the diffusion flux,

$$S_R = -\frac{dn}{dt} = -D \frac{dC}{dy}$$  \hspace{1cm} (4.56)

where $D$ is the diffusion coefficient of Pd(acac)$_2$ in the carrier gas. According to Atkins (1994) for short flight paths of molecules the diffusion coefficient can be calculated from,

$$D = v \frac{\lambda}{2}$$  \hspace{1cm} (4.57)

where $v$ is the mean velocity based on the Maxwellian distribution and $\lambda$ is the mean free path of the molecules. $dC/dy$ is the concentration gradient of Pd(acac)$_2$ which is approximated by the linear gradient,

$$dC/dy = -C_0/L$$  \hspace{1cm} (4.58)

where $C_0$ is the concentration of Pd(acac)$_2$ at the gas-solid interface and $L$ is the position along the $y$-axis where Pd(acac)$_2$ concentration becomes negligible. Since ideal gas behaviour is assumed then concentration is calculated by,

$$C_0 = \frac{P_0 N_A}{RT}$$  \hspace{1cm} (4.59)

where $N_A$ is the Avogadro number.
The sublimation rate can thus be expressed as,

\[ S_R = -\frac{dn}{dt} = \frac{C_0 \nu \lambda}{2L} \quad (4.60) \]

The mean velocity and mean free path of precursor molecules for a Maxwellian distribution is given by Alberty et al. (1980),

\[ \nu = \sqrt{\frac{8RT}{\pi M_1}} \quad (4.61) \]

\[ \lambda = \sqrt{\left(\frac{Z_{11} + Z_{12}}{2}\right)} \quad (4.62) \]

where \( M_1 \) is the molar mass of \( \text{Pd(acac)}_2 \), \( Z_{11} \) is the frequency at which a given \( \text{Pd(acac)}_2 \) molecule collides with others and \( Z_{12} \) is the frequency at which a \( \text{Pd(acac)}_2 \) molecule collides with molecules of the carrier gas. These collision frequencies and the total collision frequency, \( Z_T \), are given by,

\[ Z_{11} = \frac{4\sigma_1^2}{\pi} \left(\frac{\pi RT}{M_1}\right)^{1/2} \left(\frac{N_A P_0}{RT}\right) \quad (4.63) \]

\[ Z_{12} = 2\sqrt{2} \left(\sigma_{12}\right)^2 \left(\frac{\pi RT}{\mu_{12}}\right)^{1/2} \left(\frac{N_A P_2}{RT}\right) \quad (4.64) \]

\[ Z_T = Z_{11} + Z_{12} \quad (4.65) \]

where \( P_2 \) is the pressure of the carrier gas. The collision diameter of \( \text{Pd(acac)}_2 \), \( \sigma_1 \), of the carrier gas, \( \sigma_2 \), can be used to obtain the collision diameter between \( \text{Pd(acac)}_2 \) and the carrier gas molecules, \( \sigma_{12} \).

\[ \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad (4.66) \]

while the reduced mass is calculated from,

\[ \mu_{12} = \frac{M_1 M_2}{M_1 + M_2} \quad (4.67) \]

where \( M_2 \) is the molar mass of the carrier gas. During sublimation experiments, the carrier gas pressure is considerably higher than the saturation vapour pressure of the precursor complex \( (P_0 << P_2 \approx P) \) and hence from equations (4.63) and (4.64), \( Z_{11} << Z_{12} \), and

\[ \lambda = \nu/Z_{12} \quad (4.68) \]

Combining equations (4.61), (4.64), (4.67) and (4.68) we obtain,
4. Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate

\[ \lambda = \frac{1}{N_\lambda (\sigma_{12})^2 \pi} \left( \frac{M_2}{M_1 + M_2} \right)^{1/2} \frac{RT}{P} \quad (4.69) \]

Using equations (4.59), (4.61) and (4.68), equation (4.60) becomes,

\[ S_R = -\frac{dn}{dt} = k \left( \frac{P_0}{P} \right) \sqrt{(RT)} \quad (4.70) \]

where

\[ k = \sqrt{\frac{2 \left[ M_2 / (M_1 + M_2) \right]}{L(\pi)^{3/2} (\sigma_{12})^2 \left( \frac{M_1}{M} \right)^{1/2}}} \quad (4.71) \]

The change in number of molecules, \( dn \), is related to the change in mass of precursor, \( dm \), as follows:

\[ \frac{dn}{dt} = \frac{dm}{dt} \frac{N_\lambda}{M_1} \quad (4.72) \]

Integration of equation (4.72) using equations (4.55) and (4.70) gives,

\[ \Delta m = \frac{k M_1}{N_\lambda P} (RT)^{1/2} \exp \left[ -\left( \frac{\Delta H_{\text{sub}}}{RT} \right) + a \right] \Delta t \quad (4.73) \]

Thus,

\[ \frac{\Delta m}{\Delta t} = K \quad (4.74) \]

where \( \Delta m \) is the change of mass of the precursor complex with change in time \( \Delta t \), per \( m^2 \) of the sublimation area. \( K \) is the rate of sublimation and is given by,

\[ K = \frac{k M_1}{N_\lambda P} (RT)^{1/2} \exp \left[ -\left( \frac{\Delta H_{\text{sub}}}{RT} \right) + a \right] \quad (4.75) \]

From equation 4.74 it is evident that at constant temperature and pressure, the change in precursor weight is proportional to time. By determining the rate of mass loss as a function of temperature, the enthalpy of sublimation can be calculated from equation 4.75.

\[ \ln K = G \ln T - \left( \frac{\Delta H_{\text{sub}}}{RT} \right) + a \quad (4.76) \]

where \( G \) is a constant (at constant pressure). Since the temperature range of our experiments is narrow, 100 - 160 °C, the variation of \( \ln T \) is neglected and hence plotting \( \log K \) versus \( T^{-1} \) (see Figure 4.10) the enthalpy of sublimation is calculated to be 96 kJ/mol.
Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate

From the Clausius-Clapeyron equation, 4.55, the vapour pressure of Pd(acac)_2 as a function of temperature can be calculated if P_0 is known for a specific temperature. Powell, (1966) gives a vapour pressure for Pd(acac)_2 of 0.1 Torr at 160 °C. Thus the Clausius-Clapeyron equation for palladium (II) acetylacetonate takes the form,

$$\ln P_0 = -\frac{96 \times 10^3}{RT} + 29.26 \quad (4.77)$$

The dependence of vapour pressure on temperature is given in Figure 4.11.

In Table 4.1, Clausius-Clapeyron equations for other organometallic compounds are given. The enthalpies of sublimation range from 65 - 83 kJ/mol. Hence, the enthalpy of sublimation for Pd(acac)_2 is comparable to those of other organometallic compounds. Pd(acac)_2 exhibits a low vapour pressure as compared to the other precursors. This is a disadvantage when high palladium loading is required but it may be counter balanced by the fact that Pd(acac)_2 is a cheap, readily available and easy to handle material.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Clausius-Clapeyron</th>
<th>Vapour pressure at 433K (Pa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(acac)_2</td>
<td>lnP = -96 x 10^3/RT + 29.26</td>
<td>13.37</td>
<td>this work</td>
</tr>
<tr>
<td>Rh(acac)(CO)_2</td>
<td>lnP = -9887/T + 31.9</td>
<td>8658</td>
<td>Hierso et al. (1998)</td>
</tr>
<tr>
<td>Rh(allyl)_3</td>
<td>lnP = -8476/T + 29.49</td>
<td>20230</td>
<td>Hierso et al. (1998)</td>
</tr>
<tr>
<td>[Rh(Cl)(CO)_2]_2</td>
<td>lnP = -10052/T + 32.8</td>
<td>14548</td>
<td>Hierso et al. (1998)</td>
</tr>
<tr>
<td>(MeCp)PtMe_3</td>
<td>lnP = -71 x 10^3/RT + 26.1</td>
<td>588</td>
<td>Xue (1992)</td>
</tr>
<tr>
<td>Cp_2Ni</td>
<td>lnP = -65 x 10^3/RT + 22.4</td>
<td>77</td>
<td>Dormans et al. (1991)</td>
</tr>
<tr>
<td>Cu(hfac)_2</td>
<td>log_{10}P = - 3180/T + 9.46</td>
<td>17440</td>
<td>Hitchman and Jensen (1992)*</td>
</tr>
</tbody>
</table>

Table 4.1: Clausius-Clapeyron equations for various compounds.

*pressure is in torr.
Figure 4.11: Dependence of vapour pressure of palladium (II) acetylacetonate on temperature.
4.4 Precursor Deposition

For the deposition experiments the precursor was sublimed in helium at 140 °C in order to avoid possible decomposition. Unfortunately, it was not possible to measure precursor concentration at the TGA inlet. In addition, due to the sublimer geometry it could not be ensured that the carrier gas exiting the sublimer was saturated with precursor.

4.4.1 Effect of Carrier Gas Flowrate

Figure 4.12 shows the effect of the total flowrate on the deposition rate over the monolith sample. At low flowrates, deposition rate increases almost linearly while at higher flowrates a plateau is reached. Furthermore, deposition rates at low flowrates are similar for both temperatures examined. This can be due to deposition of all the precursor entering the monolith channels. As flowrate increases there may not be sufficient time for all the precursor to deposit, and thus a certain portion leaves the channels. In fact this loss becomes more pronounced with increasing flowrate since deposition rate above ca. 120 ml/min remains constant. It must also be noted that significant precursor losses occur due to flow in the annulus between the sample and the quartz tube of the TGA. It is worth pointing out that a flowrate increase of 33 %, from 60 ml/min to 80 ml/min, at 150 °C results in an increase in deposition rate by 86 %, from $1.24 \times 10^{-5} \text{ mg/s}$ to $2.31 \times 10^{-5} \text{ mg/s}$ which is disproportionally high. A possible explanation for this behaviour is that the precursor concentration in the carrier gas increases with flowrate and consequently leads to higher deposition rates.
4. Sublimation and Deposition Behaviour of Palladium (II) Acetylacetonate

4.4.2 Effect of deposition temperature

As seen in Figure 4.12, at high flowrates a temperature increase of 30 °C (from 120 - 150 °C) results in a modest increase in deposition rate (5.3 x 10^-6 mg/s). If the deposition is kinetically controlled this would be an indication of low activation energy while if the deposition is controlled by external mass transfer such weak dependence would be expected due to the power law relation of mass transport coefficient to temperature. Since a first order dependence on precursor concentration can be observed for both kinetically and mass transfer limited deposition, the best way to discriminate between the two regimes is to vary temperature and observe its effect on deposition rate (Pierson, 1992; Hampden-Smith and Kodas, 1995). This is shown in Figure 4.13 where the change from kinetic to mass transfer control occurs at ca. 130 °C at 80 ml/min (Re = 0.32, based on the TGA tube diameter of 3.5 cm). This transition temperature is not expected to be affected significantly by the carrier gas flowrate since the flow is laminar and the flow developing length is small (1% of total length).

From the slope of Figure 4.13 an apparent activation energy of 61 kJ/mol is calculated for the low temperature region where the reaction is kinetically controlled. Arndt et al. (1995) found for deposition of Pt(acac)₂ on alumina an activation energy of
204 kJ/mol. The large difference between these values may be due to the fact that in our experiments a concentration gradient exists along the substrate and hence the activation energy calculated is not the true one of the deposition reaction.

![Deposition Rate vs. Temperature](image)

**Figure 4.13:** Temperature dependence of deposition rate of Pd(acac)$_2$ on cordierite monoliths with $\gamma$-alumina washcoat at a helium flowrate of 80 ml/min.

### 4.4.3 Nature of deposition and reduction of Pd(acac)$_2$

The main steps involved in CVD of a species onto the surface of a substrate are diffusion of the precursor from the bulk fluid to the substrate surface, adsorption of reactants on the substrate, chemical reaction where the organometallic precursor undergoes decomposition, desorption of reaction products and subsequent diffusion to the bulk fluid (Pierson, 1992). It is worth noting that common practice is to carry out all the above steps in a single stage (Hampden-Smith and Kodas, 1995; Pierson, 1992). However Pd(acac)$_2$ is very sensitive to hydrogen and can decompose in its presence even in the gas phase. For this reason the CVD process in our work is divided into two stages. So far we have concentrated on the first stage which is the deposition of precursor on the support. In order to obtain the Pd particles, a second stage is required, namely reduction of Pd(acac)$_2$. 

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Precursor reduction was achieved in pure hydrogen atmosphere (cf. Dossi et al., 1993; Wang et al., 1995; Bhaskaran et al., 1997). Using this method the ligands are removed by hydrogen and Pd is left on the substrate without any carbon deposit. Similar procedure was employed by Dossi et al. (1993) during CVD of Pd and Pt organometallic precursors in zeolites. In order to establish when decomposition was initiated hydrogen was passed over the substrate on which Pd(acac)₂ had previously been deposited, over a continuous temperature range of 25 to 45 °C. As shown in Figure 4.14, approximately 1 mg of the metal-organic complex was reduced by hydrogen at 25 °C in approximately 30 min. Increasing the temperature to 35 °C accelerated the decomposition. Further increase to 45 °C did not make a significant difference as most of the precursor had already been reduced. Based on the above experiment it is concluded that room temperature Pd(acac)₂ reduction is sufficient for catalyst formation.

 Attempts were made to deposit the precursor on α-alumina and Fecralloy but were not successful. This is attributed to the absence of hydroxyl groups on these supports which can act as anchors for the precursor molecules. Babich et al., (1997) investigated possible interactions between support surface and Cr(acac)₃ and argued that

![Figure 4.14: Effect of hydrogen on Pd(acac)₂ deposited on substrate and flowrate of 80 ml/min.](image)
the organometallic compound is attached to the support through hydrogen bonding with surface hydroxyl groups. Thus the presence of these groups is necessary for catalyst preparation using Pd(acac)$_2$ by CVD.
5. Preparation of Axially Non-uniform Pd Catalytic Monoliths by Chemical Vapour Deposition

5.1 Introduction

Some of the common heterogeneous catalyst preparation methods are impregnation, co-crystallisation and ion-exchange (Schwarz et al., 1995). They normally require the use of metal complexes to obtain the active, pure metal dispersed on a metal oxide support such as Al₂O₃, SiO₂ and TiO₂. Subsequent calcination to remove the organic or inorganic ligands, may lead to oxidation of the supported metal thus requiring a reduction stage to follow in order to regenerate the active metal. During calcination, the catalyst is subjected to temperatures typically above 400°C. Aggregation of the metal particles may take place at such temperatures consequently affecting activity and selectivity (Hierso et al., 1998). Alternative catalyst preparation methods such as metal-organic chemical vapour deposition (MOCVD) can overcome some of these problems. This technique allows deposition of pure metal particles at temperatures as low as 150°C. It is a versatile method for depositing a great variety of elements and compounds with a minimum number of steps and in addition it is possible to vary the composition and structure of the deposited material. In recent years increasingly more studies on the application of MOCVD in the field of catalysis have been reported.

Dossi and co-workers (1993-1999) have carried out extensive work on the application of MOCVD for depositing active metal into zeolite channels. They have shown that metal-organic compounds are suitable and flexible precursors for preparing highly dispersed metal particles supported on metal oxides and zeolites. The metal phase is usually obtained by simple ligand removal under mild conditions, preventing sintering to large crystallites or carbide formation. MOCVD-prepared catalysts showed the additional advantage of a clean metal phase, due to the absence of contamination from solvents or anions containing halogens or sulphur (Ugo et al., 1996). Dossi et al. (1993b) described the preparation of a proton-free Pd/NaY catalyst, obtained by MOCVD of [Pd(η³-C₅H₅)(η²-C₅H₃)]. It was characterised by a high dispersion and uniform distribution of the metal particles inside the zeolite channels with a good thermal stability towards sintering in hydrogen at 500°C. The MOCVD process was carried out in two stages, deposition of the precursor and subsequent reduction to the active metal.
5. Preparation of Axially Non-uniform Pd Catalytic Monoliths by Chemical Vapour Deposition

by hydrogen utilising a quartz hot wall reactor. Platinum hexafluoroacetylacetonate was selectively introduced inside the channels of KL zeolites (Dossi et al., 1994) and HL zeolites (Dossi et al., 1996) via MOCVD and gave rise to small non-acidic platinum clusters. These catalysts showed remarkably high activity and selectivity in the conversion of methylcyclopentane to benzene at 500°C. Long catalyst life was in addition achieved due to reduced coke formation and slow sintering rate.

Preparation of platinum supported on SiO₂, Al₂O₃ and TiO₂ after decomposition of Pt(acac)₂ at 300°C was carried out by Köhler et al. (1995) utilising a fluidised bed. The adsorbed precursor was decomposed in nitrogen. They determined that surface properties of the support material influence the adsorption sites of Pt(acac)₂ as well as the decomposition pathways of the adsorbates and finally the dispersion of the catalytic compound. The deposited particles were found to be more mobile on silica and hence more capable to agglomerate. Alumina-supported Pt may be stabilised by co-ordinatively unsaturated Al³⁺ surface ions. Attempts to prepare palladium supported catalysts using Pd(acac)₂ failed as the temperatures used were high and the complex decomposed in the gas phase before adsorption was accomplished.

A fluidised bed was utilised by Hierso et al. (1998) for preparing metal-supported catalysts. Various metal precursors (Rh(allyl)₃, Pd(allyl)(hfac), Pt(COD)(CH₃)₂) and supports (SiO₂, Al₂O₃) were used. The Clausius-Clapeyron relations for the above compounds were determined. It was concluded that fluidised beds are suitable for preparation of metal aggregates homogeneously dispersed on the substrates.

MOCVD has been utilised to prepare solid metal membranes for hydrogen separation applications. Yan et al. (1994) and Kusukabe et al. (1996) formed thin palladium membranes inside the porous wall of α-alumina support tubes. Palladium (II) acetate deposited and decomposed in argon and the best membrane was obtained under reduced pressure. The membranes showed high hydrogen permeability. Uemiya et al. (1997) prepared palladium, ruthenium and platinum membranes in support tubes with a thin γ-alumina layer. The precursors used were acetylacetonato complexes which they sublimed and decomposed in nitrogen under atmospheric pressure. For palladium (II) acetylacetonate, a sublimation temperature of 160°C and a decomposition temperature of 270°C were used.

In the above studies, deposition of the active material has been uniform. The focus of the present work is the preparation of palladium catalytic monoliths with non-
uniform distribution of the active metal utilising Pd(acac)$_2$. These catalysts have been shown theoretically to offer better performance as compared to uniform distributions (Oh and Cavendish, 1982; Psyllos et al, 1993, Tronci et al., 1999). They induce high reaction rates further upstream and overall conversion can be improved. Preparation of catalytic pellets with radial non-uniformity can be carried out using techniques such as sequential and co-impregnation (Papageorgiou et al., 1996). Preparation of axially non-uniform catalysts cannot be carried out using these methods. Moene et al., (1993; 1995) demonstrated theoretically that MOCVD can be utilised for preparing axially non-uniform catalysts, and this is explored experimentally in the current work.

5.2 Catalyst Preparation

Palladium (II) acetylacetonate, Pd(acac)$_2$, was employed for catalyst preparation as it is a cheap, air-stable at room temperature powder which is simple to handle. It was supplied by Fluka with 33 % palladium content and 97 % purity. The monolith support (supplied by Johnson Matthey) was cordierite (2MgO.2Al$_2$O$_3$.5SiO$_2$) with γ-alumina washcoat. It had dimensions 8 x 8 x 50 mm (without corner channels as shown in Figure 5.1) and an average weight of 1.7 x 10$^{-3}$ kg. The square channels had 1.2 mm hydraulic diameter. The cell density was 400 cells/inch$^2$ and the open frontal area taking into account the washcoat thickness was 69 %. From a scanning electron micrograph the average thickness of the washcoat at the side of the channel was determined to be approximately 200μm and the thickness of the cordierite wall to be 300μm (Appendix 4). Prior to every experiment, each monolith was heated in a furnace for 48 hours at a temperature of 100 °C to remove any contaminants.

Sublimation and deposition took place in the same reactor in order to avoid loss of precursor between the sublimation and deposition regions. Decomposition of the precursor was carried out in a subsequent stage. 50 mg of the precursor Pd(acac)$_2$ was placed on quartz wool positioned 230 mm inside a quartz reactor (I.D. 10 mm and length 600 mm) from the inlet of the gas carrier stream (Figure 5.2). The quartz wool was supported by two small indents in the tube. Glass beads of 1 mm in diameter and 0.6 x 10$^{-3}$ kg in total were placed on quartz wool 20 mm above the precursor again supported by two small indents in the tube. This arrangement was found to improve radial
uniformity of the catalyst in the monolith. The monolith sample was weighed and hung in the reactor tube by cotton thread 20 mm above the glass beads. The small gap between the monolith external walls and the quartz tube (ca. 1 mm each side) was plugged at the bottom end of the monolith in order to assist in achieving radial uniformity. The quartz tube was heated by a vertical resistance furnace (Carbolite CST 10/70) and the monolith was positioned at the centre of the uniform temperature zone (50 mm) shown in Figure 5.3.

The deposition of the metal-organic precursor onto the substrate was carried out by heating the reactor to deposition temperature in a helium environment (99.999 % purity, BOC CP grade). Based on thermogravimetric analysis of the behaviour of the precursor complex (Chapter 4) it was decided to use low sublimation and deposition temperatures (100-120 °C and 130-150 °C respectively). In this way risk of carbon contamination due to thermal decomposition of the complex was avoided. Helium flowrates ranged from 80-240 ml/min and the duration of the process varied from 2-4 hours. For most experiments, the precursor was placed at position 1 (as shown in Figure 5.3). For sublimation experiments, to achieve a temperature of sublimation, 100°C, with a deposition temperature of 130°C, the reactor temperature was lowered by 10°C as compared to previous experiments. To achieve a temperature of sublimation, 110°C, the precursor was placed in position 2. For the deposition experiments, the precursor was initially placed at position 2 and for every 5°C increase in reactor temperature, the precursor was lowered 5 mm with respect to position 2. These changes were based upon the furnace temperature profile obtained under a helium flow of 160 ml/min and deposition temperature of 140°C given in Figure 5.3.

The deposition stage ceased when the carrier gas flowrate and furnace were shut-down and the monolith was removed immediately and allowed to cool down to room temperature away from the precursor to avoid any further deposition. It must be noted that for the preparation of catalysts 1 and 3, monoliths were allowed to cool within the reactor. All monoliths were subsequently heated to 30 °C in a hydrogen flow of 80ml/min for 2 hours. This reduction process was necessary to obtain metallic palladium particles. After each experiment the reactor was cleaned using aqua regia.
**Figure 5.1:** Typical dimensions of catalytic monolith.

**Figure 5.2:** Chemical vapour deposition set-up.
Figure 5.3: Temperature profile in the MOCVD reactor.
5.3 Catalyst Characterisation Methods

The total palladium loading was determined using Atomic Absorption Spectroscopy (AAS). Distribution profiles were obtained using Electron Probe X-ray Microanalysis (EPMA). Palladium particle size was determined using Transmission Electron Microscopy (TEM).

5.3.1 Atomic Absorption Spectroscopy

In order to determine the overall amount of palladium present on each monolith, analyses were carried out by Atomic Absorption Spectroscopy (AAS) using a Philips PU9100 atomic absorption spectrophotometer, working at a wavelength of 248 nm.

This technique uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids the analyte atoms or ions are vaporised in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Concentration is determined from a working curve after calibrating the instrument with standards of known concentration (Wachs et al., 1992).

Palladium from the catalysts was dissolved using aqua regia. A calibration curve (r = 0.999) was obtained in the Pd concentration range of 1.0 - 14 μg/ml and is given in Appendix 5. Effectiveness of the extraction methodology was tested using Pd on γ-alumina pellets with a known loading of 0.5 wt% obtained from Johnson Matthey and was found to be satisfactory as the loading was determined to be 0.481 wt%.

The chemical extraction of palladium involved grinding the sample very finely in order to minimise possible mass transfer limitations inside the small pores of the porous material which is insoluble in the aqua regia (Dossi et al., 1993a). The sample was then weighed and placed in 50 ml of (3:1) 0.1 M HCL/0.1 M HNO₃ solution. The resulting mixture was then heated to gentle boiling while being stirred continuously. The volume of the solution was significantly reduced and the slurry was left to cool down to room temperature. It was subsequently filtered and diluted in a volumetric flask with 0.1 M HCl until a final Pd concentration between 1 and 13 μg/ml was reached.
5.3.2 Electron Probe X-ray Microanalysis

The axial distribution of palladium on the washcoat surface was determined by EPMA. Analyses were carried out using a JEOL 8600 microscope and applying an acceleration voltage of 20 keV. Catalysts were carbon coated prior to analysis.

EPMA is an elemental analysis technique based upon the bombardment of a specimen with a focused beam of energetic electrons (beam energy 5 - 30 keV) to induce emission of characteristic X-rays (0.1 - 15 keV). The X-rays are measured by Energy-Dispersion X-ray analysis (EDX). The X-ray spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak is converted into elemental atomic weight (Wachs et al, 1992). Results in this work are expressed as percentage weight of palladium with respect to Al₂O₃ washcoat. It should be noted that if no palladium was detected on a specific location along a monolith then no symbol is shown on the graphs.

5.3.3 Transmission Electron Microscopy

The size of palladium particles was determined by Transmission Electron Microscopy (TEM) and Energy Dispersion X-ray Analysis (EDX) and was carried out at BP Amoco Chemicals (Sunbury). The monolith end with the highest palladium loading was embedded in araladite resin overnight at 60 °C. Thin sections (<100 nm) were then cut with a diamond knife. A JEOL 2000FX TEM and a LINK ultra-thin window EDX detector were utilised.

In TEM a thin solid specimen (≤ 200 nm thin) is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons. The beam is strong enough to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the samples. Analysis of transmission electron image yields information on atomic structure (Wachs et al, 1992).
5.4 Results and Discussion

Non-uniform catalysts were prepared using a constant amount of Pd(acac)\(_2\) (50 mg) under varying helium flowrates (80-240 ml/min), precursor sublimation and deposition temperatures (100-120 °C and 130-150 °C, respectively) and duration of the process (2-4 hours), as shown in Table 5.1. The total amount of palladium deposited on each monolith is also given. The palladium loading is based on the total weight of support (\(\gamma\)-Al\(_2\)O\(_3\) and cordierite).

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Flowrate (ml/min)</th>
<th>Tsub (°C)</th>
<th>Tdep (°C)</th>
<th>Time (h)</th>
<th>Mass of Pd (µg)</th>
<th>Pd Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 1</td>
<td>80</td>
<td>110</td>
<td>140</td>
<td>3</td>
<td>206</td>
<td>0.012</td>
</tr>
<tr>
<td>Catalyst 2</td>
<td>160</td>
<td>110</td>
<td>140</td>
<td>3</td>
<td>267</td>
<td>0.016</td>
</tr>
<tr>
<td>Catalyst 3</td>
<td>200</td>
<td>110</td>
<td>140</td>
<td>3</td>
<td>583</td>
<td>0.037</td>
</tr>
<tr>
<td>Catalyst 4</td>
<td>240</td>
<td>100</td>
<td>130</td>
<td>2</td>
<td>88</td>
<td>0.005</td>
</tr>
<tr>
<td>Catalyst 5</td>
<td>240</td>
<td>110</td>
<td>130</td>
<td>2</td>
<td>221</td>
<td>0.013</td>
</tr>
<tr>
<td>Catalyst 6</td>
<td>160</td>
<td>120</td>
<td>138</td>
<td>4</td>
<td>338</td>
<td>0.018</td>
</tr>
<tr>
<td>Catalyst 7</td>
<td>160</td>
<td>120</td>
<td>145</td>
<td>4</td>
<td>608</td>
<td>0.034</td>
</tr>
<tr>
<td>Catalyst 8</td>
<td>160</td>
<td>120</td>
<td>150</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst 9</td>
<td>160</td>
<td>110</td>
<td>140</td>
<td>2</td>
<td>192</td>
<td>0.012</td>
</tr>
<tr>
<td>Catalyst 10</td>
<td>160</td>
<td>110</td>
<td>140</td>
<td>4</td>
<td>328</td>
<td>0.019</td>
</tr>
<tr>
<td>Catalyst 11</td>
<td>160</td>
<td>110</td>
<td>140</td>
<td>2</td>
<td>190</td>
<td>0.012</td>
</tr>
<tr>
<td>Catalyst 12</td>
<td>160</td>
<td>110</td>
<td>140</td>
<td>2</td>
<td>187</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 5.1: Operating conditions used for catalyst preparation and amount of palladium deposited.
5.4.1.1 Deposition Reproducibility and Radial Catalyst Profiles

The reproducibility of catalyst deposition was examined by preparing three different catalysts (9, 11, 12) under the same sublimation and deposition conditions (see Table 5.1). The overall palladium loading of the catalyst was the same to the third decimal place. The distribution profiles are given in Figure 5.4 and are found to be similar even when one looks closer to the first 10 mm of the monolith length (Figure 5.4b).

Catalyst deposition in each individual channel was determined to be similar for all samples by visual inspection. Catalyst 4 was in addition characterised by EPMA after being cut along its length (see Figure 5.5). Palladium loading drops to 0 at the cordierite walls of each channel. The average distance where no palladium is detected is approximately 300 μm which coincides with the cordierite wall thickness. A linear increase of Pd/Al₂O₃ weight ratio is observed between the valleys and the peaks and this corresponds to the cross section of the alumina washcoat layer. The plateaus in Figure 5.5 correspond to the external surface of the washcoat. This pattern is repeated for each channel, indicating that all channels have the same palladium amount and radial catalyst distribution. As can be seen from the same figure, palladium does not deposit uniformly inside the washcoat. The precursor is prone to attach onto the active sites (hydroxyl groups, Babich et al., 1997) along the external surface of the wall first and a limited amount of precursor diffuses within the washcoat to attach to hydroxyl sites within the porous structure. This may be due to the fact that the metal-organic complex is large and heavy and penetrating through the pores and depositing on their surface is a diffusional controlled process.

XRD analysis could not be used to determine palladium particle size primarily due to low catalyst loading. A representative TEM image is shown for the entrance region of catalyst 8 in Figure 5.6. The particle size in this region is expected to be the largest from all particles in all samples prepared. Most Pd particles have size around 4 to 5 nm. Note that the larger dark particles (ca 20 nm in size) are from the support particles (CeO₂). Particle sizes of the order of 5 nm are considered to be small enough for catalytic applications and lead to an increase in surface area. Typical palladium particle sizes using impregnation methods can achieve this order of magnitude (cf. Briot
and Primet, 1991) but due to the calcination procedure which takes place at high temperatures formation of bigger clusters and thus reduction of surface area may potentially take place (Hierso et al., 1998).
Figure 5.4: Palladium distribution profiles of catalysts 9, 11 and 12. (a) distribution along whole monolith length; (b) distribution along the first 10 mm.
5. Preparation of Axially Non-uniform Pd Catalytic Monoliths by Chemical Vapour Deposition

Figure 5.5: Radial palladium profile of catalyst 4.

Figure 5.6: TEM of upstream region of catalyst 8.
5.4.1.2 Effect of Sublimation Temperature

Increase of the sublimation temperature leads to an increase in precursor concentration at the monolith inlet for a fixed flowrate, process duration and deposition temperature. Thus the deposited amount of complex increases with increasing sublimation temperature for a fixed duration of the process (see Table 5.2).

Using the Clausius-Clapeyron equation derived for Pd(acac)_2 in Chapter 4, \( \ln P = -96 \times 10^3/RT + 29.26 \), the precursor concentration at a sublimation temperature of 100 °C is \( 5.9 \times 10^{-5} \) mol/m\(^3\) and at 110 °C is \( 1.29 \times 10^{-4} \) mol/m\(^3\). Precursor concentration thus increases by a factor of 2.2 and this is reflected on the total amount of palladium deposited, which is 2.5 times higher.

The mass of palladium flowing through the monolith substrate under a sublimation temperature of 100 °C, flowrate of 240 ml/min and duration of 2 hours is predicted using the Clausius-Clapeyron equation, and assuming saturation of the carrier gas, to be 180 µg. The mass of palladium deposited is approximately 49% of the amount passed through the monolith. At a sublimation temperature of 110 °C the amount of palladium that passed through the monolith is 379 µg. 59% of this amount was deposited in the form of the metal-organic precursor while the remainder was lost since it flowed through the monolith without depositing. The percentage of complex escaping deposition decreases with increasing concentration for a fixed deposition temperature, flowrate and time.

The distribution profiles of catalysts 4 and 5 are shown in Figure 5.7. The palladium amount at the entrance is shown to increase by a factor of 3 with a 10°C increase in sublimation temperature. This factor is higher than the factor by which the concentration of the complex increases with such a temperature rise (2.2). This is an indication of kinetic control prevailing at the entrance region. Furthermore kinetics of deposition are possibly higher than first order. It is worth noting that Moene et al. (1993) argue that if the metal-organic molecules does not dissociate upon adsorption and the whole molecule attaches to a free site (such as a hydroxyl group), first order kinetics would be observed. The higher than first order kinetic behaviour for our system may be due to a different deposition mechanism or alternatively to an autocatalytic effect. Arndt et al., (1995) demonstrated the existence of an autocatalytic mechanism by carrying out deposition on alumina supports where platinum particles had been previously deposited.
They observed deposition rates to be higher as compared to deposition on clean substrates.

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Tsub (°C)</th>
<th>Amount of Pd Deposited (µg)</th>
<th>Amount of Pd passed through monolith (µg)</th>
<th>Loss of palladium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 4</td>
<td>100</td>
<td>88</td>
<td>180</td>
<td>51</td>
</tr>
<tr>
<td>Catalyst 5</td>
<td>110</td>
<td>222</td>
<td>379</td>
<td>41</td>
</tr>
</tbody>
</table>

Table 5.2: Amounts of Pd deposited and passed through monolith at various sublimation temperatures, flowrate 240 ml/min, deposition temperature 130 °C and process duration 2 hours.

![Graph](image)

Figure 5.7: Palladium distribution profiles of catalysts 4 and 5.
5.4.1.3 Effect of Carrier Gas Flowrate

The amount of palladium complex and consequently the amount of palladium deposited onto the substrate increases with increasing flowrate in the MOCVD reactor (see Table 5.3). An increase in flowrate leads to an increase in sublimation rate assuming that the carrier gas is always saturated. Thus, more precursor complex passes through the monolithic substrate over a specific time, under a constant sublimation and deposition temperature. This results to a higher amount of precursor depositing. It must be reiterated that catalysts 1 and 3 were left to cool down inside the reactor after the carrier gas flow was stopped. Hence, additional deposition of palladium by diffusion may have taken place.

Using the Clausius-Clapeyron equation for Pd(acac)$_2$, the total amount of palladium that passed through the monolith, for a specific temperature, flowrate and process duration, can be predicted. From Table 5.3 it is evident that for catalysts 1 and 3, less palladium was expected to pass through the monolith than actually deposited. This is attributed to the cooling procedure employed, as mentioned previously. For catalyst 2, which was allowed to cool outside the reactor, the amount of palladium predicted to flow through the monolith is 32% greater than the amount actually deposited. Evidently palladium precursor flowed through without depositing.

The palladium deposition profile increases in amplitude and shifts down the monolith length with increasing flowrate, as shown in Figure 5.8. This shift can be explained by considering the hydrodynamic entrance effect. Namely, the flow developing length in the entrance region increases with flowrate. In this region, due to the high mass transfer coefficients, kinetic control is expected to prevail, specially at low temperatures. Beyond this region, mass transfer coefficient decreases and the controlling phenomenon is postulated to be external mass transport. A transition region exists between them. The developing length for flowrates 80 - 200 ml/min and 400 K is calculated to be in the range 0.5 - 1.5 mm (Kays and Crawford, 1980). This is smaller than the shift of palladium distribution observed in Figure 5.8. Therefore it is possible that not only the kinetic control but also the transition region contribute to this shift.
5. Preparation of Axially Non-uniform Pd Catalytic Monoliths by Chemical Vapour Deposition

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Flowrate (ml/min)</th>
<th>Amount of Pd Deposited (µg)</th>
<th>Amount of Pd passed through monolith (µg)</th>
<th>Loss of palladium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 1</td>
<td>80</td>
<td>206</td>
<td>198</td>
<td>-4.04</td>
</tr>
<tr>
<td>Catalyst 2</td>
<td>160</td>
<td>267</td>
<td>395</td>
<td>32.4</td>
</tr>
<tr>
<td>Catalyst 3</td>
<td>200</td>
<td>584</td>
<td>494</td>
<td>-18.2</td>
</tr>
</tbody>
</table>

Table 5.3: Amounts of Pd deposited and passed through monolith at various flowrates and sublimation temperature 110 °C, deposition temperature 140 °C and process duration 3 hours.

![Pd/Al_2O_3 Weight Ratio vs Monolith Length](image)

Figure 5.8: Palladium distribution profiles of catalysts 1, 2 and 3.
5.4.1.4 Effect of Deposition Temperature

The mass deposited increases with deposition temperature as shown in Table 5.4. For all samples (6, 7, 8) the total amount of palladium which flowed through the monolith is the same because sublimation temperature, flowrate and duration are kept constant. The higher deposition temperature increases both deposition rate constant (applicable to kinetic control regions) and mass transfer coefficient, applicable to mass transfer control regions. Therefore the palladium amount that is lost decreases with increasing temperature. Catalyst 8 was used for TEM analysis and thus its loading could not be obtained. It is expected though to be higher than that of catalysts 6 and 7. Figure 5.9 shows the palladium distributions for the three catalysts. The increase in palladium amount at the entrance of the monolith as temperature increases can only be explained if kinetic control in this region prevails. If we assume that mass transfer controls we should obtain an increase in inlet palladium loading from one sample to another by no more than 3% assuming a T^{1.75} dependence of mass transfer coefficient on temperature (Perry and Chilton, 1984). The distribution profile extends further downstream as deposition temperature increases. This may be attributed to higher deposition rates in the transition region due to faster deposition kinetics or most probably due to an autocatalytic effect as discussed previously. It is observed for most profiles that there is very little amount of palladium depositing after the first centimetre. This is the region of mass transfer control and deposition is slow, due to the low diffusivity of the relatively heavy Pd(acac)$_2$ molecules.
### Table 5.4: Amounts of Pd deposited and passed through monolith at various deposition temperatures, flowrate 160 ml/min, sublimation temperature 120 °C and process duration 4 hours.

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Tdep (°C)</th>
<th>Amount of Pd Deposited (μg)</th>
<th>Amount of Pd passed through monolith (μg)</th>
<th>Loss of palladium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 6</td>
<td>138</td>
<td>338</td>
<td>1108</td>
<td>69</td>
</tr>
<tr>
<td>Catalyst 7</td>
<td>145</td>
<td>608</td>
<td>1108</td>
<td>45</td>
</tr>
<tr>
<td>Catalyst 8</td>
<td>150</td>
<td>-</td>
<td>1108</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 5.9: Palladium distribution profiles of catalysts 6, 7 and 8.**
5.4.1.5 Effect of Deposition Time

The amount of palladium passing through the monolith is a linear function of time since sublimation rate is kept constant. However, as shown in Table 5.5, increase of deposited palladium with time is nonlinear. Pd(acac)\(_2\) molecules attach to active sites on the support. As time progresses the number of active sites available decreases and this should slow down deposition rates and result to the non-linear behaviour and higher palladium losses observed.

In Figure 5.10, deposition profiles for the three catalyst (9, 2, 10) are shown. The profile of catalysts 2 and 10 extend further downstream and may be due to the autocatalytic effect mentioned earlier. It is worth pointing out that if the areas under the curves in Figure 5.10 are compared to the corresponding amounts of palladium deposited in Table 5.5 the dependency with time is different. Since values in Table 5.5 correspond to overall loading while Figure 5.10 to palladium deposited on the surface of the washcoat, the difference is indicative of radial non-uniform deposition within the washcoat which is indeed observed experimentally (see Figure 5.5).

The above results show that the catalyst deposition profile can be manipulated by various operating parameters such as, temperature of sublimation, temperature of deposition, flowrate and time. Another parameter that can also affect the profile is the total pressure in the system but has not been investigated in this work. Pressure will affect both precursor concentration in the carrier gas and its bulk diffusivity.

CVD is a viable catalyst preparation method cost wise. A typical precursor used for preparing palladium catalyst by impregnation is Pd(NO\(_3\))\(_2\).2H\(_2\)O. The price is £28/g and has a palladium content of 40%. This is comparable to Pd(acac)\(_2\), £21/g, and palladium content of 33%. The amount of precursor which does not deposit on the monolith can potentially be captured at the reactor exit by placing a glass container which will allow the precursor to condense. The solid can then be re-utilised.
Table 5.5: Amounts of Pd deposited and passed through monolith at various process duration times, flowrate 160 ml/min, sublimation temperature 110 °C and deposition temperature 140 °C.

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Time (h)</th>
<th>Amount of Pd Deposited (µg)</th>
<th>Amount of Pd passed through monolith (µg)</th>
<th>Loss of palladium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 9</td>
<td>2</td>
<td>192</td>
<td>263</td>
<td>27</td>
</tr>
<tr>
<td>Catalyst 2</td>
<td>3</td>
<td>267</td>
<td>395</td>
<td>33</td>
</tr>
<tr>
<td>Catalyst 10</td>
<td>4</td>
<td>328</td>
<td>527</td>
<td>38</td>
</tr>
</tbody>
</table>

Figure 5.10: Palladium deposition profiles of catalysts 2, 9 and 10.
6. Catalytic Combustion of Methane over Non-uniform Pd Catalytic Monoliths

6.1 Introduction

Environmental problems associated with conventional flame combustion are due to the high temperatures present (above 1500 °C). Such temperatures can be reduced by catalytic combustion to ca. 1300 °C in which thermal NOx formation is negligible. Reduction of thermal NOx is especially important in gas turbine applications where almost all the NOx formed is thermal NOx (Kolackowski, 1995). As one goal for natural gas fuelled turbines is better reliability while decreasing emissions further, problems such as catalyst durability need to be resolved. It has been well established that catalyst lifetime can be extended if wall temperature gradients, and consequently thermal stresses, can be alleviated (Thiart et al., 1993; Viljoen et al, 1995; Groppi et al., 1996).

The most common materials used in catalysts for catalytic combustion are noble metals or metal oxides on a suitable support (Zwinkels et al., 1993; Cybulski and Moulijn, 1994; Trimm, 1995; Eguchi and Arai, 1996). Supported noble metals are very active catalysts for total oxidation of hydrocarbons. For complete oxidation of methane to carbon dioxide and water, the superiority of palladium as a low temperature catalyst has been well known for years and extensive work has been carried out by Baldwin et al. (1990a; 1990b), Briot and Primet (1991), Mouaddib et al. (1992), Farrauto et al. (1992) and Burch et al. (1994; 1995), concerning the reaction mechanism. At present, mixed oxides (for example, Mn-substituted hexaaluminates) such as those developed by Arai and Machida, (1991), are reported as promising materials due to their excellent thermal stabilities. However, the catalytic activity of hexaaluminates is generally relatively low. Thus there is room for improving durability by avoiding thermal stresses for low temperature catalysts.

Non-uniform catalysts are known to offer better performance as opposed to uniform distribution (Oh et al., 1982; Psyllos and Philipoppoulos, 1993a and 1993b; Gavriilidis et al., 1993; Tronci et al., 1999). It has been shown theoretically that catalysts with higher activity at the monolith inlet as compared to the outlet alleviate wall temperature gradients under methane combustion conditions (Chapter 3). High reaction rates exist at the entrance, shifting the light-off position further towards the entrance.
Inlet wall temperature is much higher than in the case of a monolith reactor with uniform catalyst distribution. Maximum wall temperatures remain at similar levels and hence overall temperature gradients along the monolith wall are reduced significantly. This can be advantageous for minimising thermal stresses.

In this work, experimental results on the effect of axially non-uniform catalyst distributions on wall temperature profiles for methane combustion are presented. Conversions and wall temperature profiles achieved by non-uniform catalysts are compared to uniform catalysts prepared by impregnation. Axially non-uniform palladium catalysts have been prepared using metal-organic chemical vapour deposition. It is a simple method which allows to prepare such catalysts cheaply, involving only two preparation stages. Finally, experimental wall temperature profiles are compared with a mathematical model formulated to predict such profiles.

6.2 Experimental

6.2.1 Catalyst Preparation

6.2.1.1 Non-Uniform Catalyst Preparation

Catalysts with non-uniform distribution of palladium along the monolith length were prepared by metal-organic chemical vapour deposition (MOCVD). The monolith support (supplied by Johnson Matthey) was cordierite (2\(\text{MgO}.2\text{Al}_2\text{O}_3.5\text{SiO}_2\)) with \(\gamma\)-alumina washcoat. It had dimensions 8 x 8 x 50 mm (without corner channels as shown in Figure 6.1) and an average weight of 1.7 x 10\(^{-3}\) kg. The square channels had 1.2 mm hydraulic diameter. The cell density was 400 cells/inch\(^2\) and the open frontal area taking into account the washcoat thickness was 69 %. From a scanning electron micrograph the average thickness of the washcoat at the side of the channel was determined to be 200\(\mu\)m. Prior to every experiment, each monolith was heated in a furnace for 48 hours at 100 °C to remove any contaminants.

The deposition of palladium was performed by placing 50 mg of the precursor Pd(acac)\(_2\), supplied by Fluka with 33 % palladium content and 97 % purity, on quartz wool positioned 230 mm inside a quartz reactor (I.D. 10 mm and length 600 mm) from the inlet of the gas carrier stream (Figure 6.2). The quartz wool was supported by two
small indents in the tube. Glass beads of 1 mm in diameter and $0.6 \times 10^{-3}$ kg in total were placed on quartz wool 20 mm above the precursor again supported by two small indents in the tube. This arrangement was found to improve radial uniformity of the catalyst in the monolith. The sample was weighed and hung in the reactor tube by cotton thread 20 mm above the glass beads. The small gap between the monolith external walls and the quartz tube (ca. 1 mm each side) was plugged at the bottom end of the monolith in order to assist in achieving radial uniformity. The quartz tube was heated by a vertical resistance furnace (Carbolite CST 10/70) and the monolith was positioned at the centre of the uniform temperature zone (50 mm).

The deposition of the metal-organic precursor onto the substrate was carried out by heating the precursor and monolith in a helium environment (99.999 % purity, BOC CP grade). The sublimation and deposition temperatures were measured by thermocouples and varied from 100-120 °C and 130-150 °C respectively. Helium flowrates ranged from 80-240 ml/min and the duration of the deposition process varied from 2-4 hours.

At the end of the deposition stage the carrier gas flowrate and furnace were shut-down and the monolith was removed immediately and allowed to cool down to room temperature away from the precursor to avoid any further deposition. The monolith was placed back into the reactor, from which the precursor and glass beads had been removed, and was heated to 30 °C in a hydrogen flow of 80ml/min for 2 hours. This reduction process was necessary to obtain metallic palladium particles. After each experiment the reactor was cleaned using aqua regia and subsequently dried using compressed air and left overnight at room temperature.

To determine the overall amount of palladium present on each monolith, analyses were carried out by Atomic Absorption Spectroscopy (AAS) using a Philips PU9100 atomic absorption spectrophotometer, working at a wavelength of 248 nm. The distribution profile of two samples (which were considered to be typical of the other non-uniform distributions) was determined by Electron Probe X-ray Microanalysis (EPMA), using a JEOL 8600 at 20 keV.
6. Catalytic Combustion of Methane over Non-uniform Pd Catalytic Monoliths

6.2.1.2 Uniform Catalysts

Uniform catalysts were prepared by dissolving a weighed amount of precursor (Pd(acac)$_2$) in acetone. The entire monolith was submerged in the solution and in order to avoid the level of acetone from reducing significantly due to evaporation more acetone was added. The solution was stirred continuously while acetone was added until the solution colour became clearer. At this point a pipette was used to distribute the remaining solution along the monolith walls. The measuring cylinder was rinsed with acetone and the solution was again distributed with the pipette. The monolith was then placed in a furnace for 6 hours at 70°C. After it was allowed to cool, it was placed in a quartz reactor and heated to 30°C in a 80ml/min flow of hydrogen to reduce the metal-organic complex to metallic palladium. AAS was used to determine the catalyst loading. Distribution profiles of these catalysts were considered to be uniform as compared to MOCVD catalytic monoliths since the characteristic darker end of the non-uniform catalysts was not present, whereas a uniform colour was observed. As palladium loadings of catalysts prepared by MOCVD were low, preparation of equivalent uniform catalysts was limited to the two highest loadings achieved by MOCVD.

![Figure 6.1: Typical dimensions of a catalytic monolith.](image-url)

---

8 mm

8 mm

50 mm
Figure 6.2: Chemical vapour deposition set-up.
6.2.2 Catalyst Testing

Fresh catalysts were tested in a catalytic combustion set-up (Figure 6.3) operating at atmospheric pressure. Each catalyst was placed centrally in a quartz tube of length, 700 mm, and internal diameter, 10 mm. The tube was well insulated from the middle (where the monolith was positioned) up to the exit using Microtherm Super G quilt of thickness, 6 mm. The reactor was mounted centrally in a horizontal Carbolite CST 10/70 furnace. The gases used were 2.55 % CH₄/Air and additional air (purity 99.999 %) all from B.O.C.. The flow of each gas was controlled to give a total flowrate of 160 ml/min. The combusting mixture consisted of 2 % methane in air and was passed through a mixer prior to the reactor. The mixer consisted of a stainless steel tube of 50 mm O.D. and 350 mm length filled with glass beads 5 mm in diameter. Inlet and product gases were analysed by a flame ionization detector, AAL Model 523 FID Hydrocarbon Analyser. Outlet concentrations were continuously collected by the Schlumberger 359571A Impulse Data software. Data were obtained at various temperatures by progressively increasing the reactor temperature and for each increment fuel conversion was allowed to reach steady state. Once either 50 % fuel conversion was reached or bulk temperature exceeded 600 °C the reactor was shut down.

Channelling or by-passing of the gas between the catalyst and the inside wall of the reactor was minimised by placing a quartz wool ring around the upstream part of the monolith so as to direct the flow through the monolith.

To obtain wall temperature profiles a 1 mm diameter thermocouple was placed in the central channel of the catalytic monolith as shown in Figure 6.4. The end of the channel was sealed using ceramic cement to avoid contact with the gas. The thermocouple had a tight fit inside the channel and thus monitored wall temperatures. It should be noted that in order to avoid damaging the monolith structure, the thermocouple was pushed down the monolith channel until there was significant resistance. The initial position of the thermocouple tip was on the whole approximately 45-48 mm from the monolith entrance and was known at all times. For determination of axial wall temperature profiles the temperature at the initial position of the thermocouple was brought in the range 460 - 480 °C. When steady state was achieved the thermocouple was moved upstream by a pulling device (shown in Appendix 6) with precision 1 mm and at a rate of 1 mm per 5 s. The bulk gas temperature was determined once the thermocouple was pulled out of the monolith channel.
Figure 6.3: Catalytic combustion set-up
6.3 Results and Discussion

6.3.1 Catalytic Monoliths

Six non-uniform catalytic Pd/$\gamma$-Al$_2$O$_3$/cordierite monoliths were prepared utilising chemical vapour deposition as described previously. The specific operating conditions employed in the preparation are shown in Table 6.1. Uniform catalysts A2, D2 were prepared by impregnation are also included. Catalyst loading is based on the total mass of monolith. The weight ratio of Pd to $\gamma$-Al$_2$O$_3$ along the monolith for catalyst A and D, as determined by EPMA, is shown in Figure 6.5. It should be noted that if no palladium is detected on a specific location along the monolith then no symbol is shown on the graph.

It is observed that a large amount of palladium is concentrated towards the monolith entrance. Comparing catalysts A and D it is seen that the sample with the highest total loading (catalyst A) has also the highest inlet palladium loading. By visual inspection it was established that the inlet portion of the monolith with high Pd/Al$_2$O$_3$
ratio was black and it changed to cream a few millimetres downstream, where palladium amount was significantly reduced. Similar colour changes were also observed along the rest of the non-uniform monoliths. The six monoliths had a total amount of Pd ranging from 33 to 583 µg which corresponded to total loadings of 0.003 - 0.036 wt%.

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Tsub (°C)</th>
<th>Tdep (°C)</th>
<th>He flowrate (ml/min)</th>
<th>Deposition time (h)</th>
<th>Pd mass deposited (µg)</th>
<th>Catalyst loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110</td>
<td>140</td>
<td>200</td>
<td>3</td>
<td>583</td>
<td>0.036</td>
</tr>
<tr>
<td>B</td>
<td>110</td>
<td>140</td>
<td>160</td>
<td>3</td>
<td>266</td>
<td>0.016</td>
</tr>
<tr>
<td>C</td>
<td>110</td>
<td>140</td>
<td>160</td>
<td>2</td>
<td>192</td>
<td>0.011</td>
</tr>
<tr>
<td>D</td>
<td>120</td>
<td>150</td>
<td>160</td>
<td>2</td>
<td>318</td>
<td>0.018</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>130</td>
<td>160</td>
<td>2</td>
<td>64</td>
<td>0.004</td>
</tr>
<tr>
<td>F</td>
<td>110</td>
<td>130</td>
<td>80</td>
<td>4</td>
<td>33</td>
<td>0.003</td>
</tr>
<tr>
<td>A2 (imp)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>556</td>
<td>0.033</td>
</tr>
<tr>
<td>D2 (imp)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>312</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Table 6.1: Conditions employed for the preparation of catalysts and their loadings.

![Graph showing catalyst distribution profiles for samples A and D.](image)

Figure 6.5: Catalyst distribution profiles for samples A and D.
6.3.2 Wall Temperature Profiles

Reaction experiments are divided into two groups depending on the inlet bulk gas temperature used during methane combustion (see Table 6.2). Group 1, where catalysts A, B and C are used, have inlet bulk temperatures ranging from 456-458 °C. Group 2, where catalysts D, E and F are employed, have inlet bulk temperatures ranging from 469-474 °C. It must be noted that wall outlet temperatures quoted in Table 6.2 are in fact measured a few millimetres before the end due to the presence of the sealant (see Figure 6.4). Wall temperature profiles determined in these experiments are given in Figure 6.6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total Amount of Palladium (µg)</th>
<th>Inlet Bulk Temperature (°C)</th>
<th>Wall Temperature at Monolith Inlet (°C)</th>
<th>Wall Temperature at Monolith Outlet (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>583</td>
<td>456</td>
<td>474</td>
<td>467</td>
</tr>
<tr>
<td>B</td>
<td>266</td>
<td>458</td>
<td>468</td>
<td>465</td>
</tr>
<tr>
<td>C</td>
<td>192</td>
<td>456</td>
<td>462</td>
<td>460</td>
</tr>
<tr>
<td>Group 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>318</td>
<td>474</td>
<td>484</td>
<td>482</td>
</tr>
<tr>
<td>E</td>
<td>64</td>
<td>472</td>
<td>476</td>
<td>474</td>
</tr>
<tr>
<td>F</td>
<td>33</td>
<td>469</td>
<td>471</td>
<td>472</td>
</tr>
</tbody>
</table>

Table 6.2: Temperatures observed during catalytic combustion experiments for non-uniform catalysts.

In group 1, catalyst A has the highest total amount of palladium (583 µg) and the highest inlet palladium loading. With an inlet bulk gas temperature of 456 °C the inlet wall temperature achieved is 18 °C higher. The wall then experiences a decline in temperature along its length, approximately 7 °C. The highly exponential nature of the distribution of the active material leads to significantly lower reaction rates further down the monolith. Heat transferred from the wall to the bulk leads to cooling of the wall as little or no heat is being produced to compensate for this loss towards the monolith end.
Catalyst B has approximately half the palladium amount of catalyst A (266 μg). With an inlet bulk temperature of 458 °C it achieves an inlet wall temperature 10 °C higher. This is approximately half the temperature difference experienced by catalyst A. Catalyst B has a lower total palladium amount and hence lower inlet palladium loading, since the metal is concentrated to the monolith entrance. The difference between inlet and outlet wall temperatures due to the limited heat production at the monolith end is 3 °C. Catalyst C has approximately one-third the palladium amount of catalyst A (192 μg). With an inlet bulk temperature of 456 °C the inlet wall temperature achieved is 6 °C higher. This is one-third the temperature difference catalyst A experiences. The wall temperature remains approximately constant up to 20 mm down the monolith. Subsequently, a 2 °C decline in temperature is experienced by the wall.

In group 2, catalyst D has a total palladium amount of 318 μg and with an inlet bulk temperature of 474 °C exhibits a wall inlet temperature 10 °C higher. Wall temperature declines to approximately 480 °C before it rises again to reach 482 °C at the exit. This minimum is unexpected and may be due to structural damage caused by the thermocouple. Catalyst E has significantly less amount of palladium than catalyst D (64 μg) yet light-off is seen to be experienced again at the monolith inlet. With a bulk temperature of 472 °C a wall inlet temperature 4 °C higher is experienced by the catalyst. The temperature decreases by 2 °C along the monolith to reach 474 °C at the outlet. Finally catalyst F has approximately half the amount of palladium of catalyst E. The loading is very low and with an inlet bulk temperature of 469 °C an inlet wall temperature of 2 °C higher is achieved. The wall temperature continues to increase until it reaches a maximum approximately 25 mm down the monolith (473 °C). The outlet wall temperature observed is 1 °C higher than the inlet one. For this monolith there is only a small amount of palladium at the entrance and thus heat generated by reaction exotherm is lower and more evenly distributed as compared to strongly non-uniform catalyst. The temperature profile is qualitatively between those observed for strongly non-uniform catalytic monoliths and uniform ones (see Figure 6.7). It is worth noting that in Figure 6.6 no sharp temperature gradients at the ends of the monolith are observed which would be indicative of significant radiation losses. This is due to the low temperatures employed in these experiments.

The results presented demonstrate that non-uniform catalyst distributions affect the wall temperature profile. When a large amount of active material is located at the
monolith entrance, heat generation in this section can be so large that a significant
difference between inlet bulk and wall temperature can develop. The heat produced at
the wall is transferred by conduction to the bulk fluid. The ratio of heat generated to
heat removed depends on the amount of catalyst and thus varies along each monolith as
well as among different catalysts. For the highly non-uniform distribution A, heat
generation decreases rapidly along the monolith giving rise to decreasing temperature
profiles. The difference between inlet and outlet wall temperature becomes smaller as
catalyst loading and inlet heat generation decrease and the trend eventually reverses i.e.
Tout > Tin for catalyst F.
Figure 6.6: Axial wall temperature profiles for non-uniform catalytic monoliths.
6.3.2.1 Comparison of Non-uniform Catalysts with Uniform Catalysts

In order to compare performance of non-uniform with uniform distributions, two catalytic monoliths (A2, D2) were prepared by impregnation as described previously, having similar total loadings with the non-uniform distributions A and D (see Table 6.3).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total Amount of Palladium (µg)</th>
<th>Inlet Bulk Temperature (°C)</th>
<th>Wall Temperature at Monolith Inlet (°C)</th>
<th>Wall Temperature at Monolith Outlet (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>583</td>
<td>456</td>
<td>474</td>
<td>467</td>
</tr>
<tr>
<td>A2</td>
<td>557</td>
<td>452</td>
<td>453</td>
<td>469</td>
</tr>
<tr>
<td>D</td>
<td>318</td>
<td>474</td>
<td>484</td>
<td>482</td>
</tr>
<tr>
<td>D2</td>
<td>312</td>
<td>468</td>
<td>469</td>
<td>488</td>
</tr>
</tbody>
</table>

Table 6.3: Temperatures observed during catalytic combustion experiments for uniform and non-uniform catalysts.

Figure 6.7 shows axial wall temperature profiles for the two pairs, A-A2 and D-D2. Wall temperature gradients experienced by uniform catalysts are higher than those of non-uniform ones with equivalent palladium loadings. Inlet wall temperatures of uniform distributions are approximately the same as inlet bulk temperatures as shown in Table 6.3. While catalyst A achieves an overall wall temperature difference of 7 °C, with the inlet temperature being higher than the outlet, the uniform catalyst (A2) experiences an overall wall temperature difference of 16 °C with the inlet temperature being lower than the outlet. The temperature difference between inlet bulk temperature and inlet wall temperature for the non-uniform catalyst is 18 °C and 1 °C for the uniform. In Figure 6.7, catalyst D shows an overall wall temperature difference of 2 °C (again the wall temperature at the inlet is greater than the outlet), while the corresponding uniform catalyst (D2) exhibits a difference of 19 °C. The temperature difference between the bulk and the inlet wall is 10 °C for the non-uniform catalyst and 1 °C for the uniform.

The non-uniform catalysts show smaller temperature gradients as compared to the uniform ones but at the expense of lower outlet wall temperatures. If this is
undesirable, non-uniform catalysts should have less sharp exponential distribution thus allowing more palladium to be present at the monolith end.

The above results illustrate that catalysts with non-uniform distribution of the active material achieve high reaction rates in the entrance of the monolith. Large heat generation in that region ultimately results to decreasing temperature profiles. In addition, light-off is obtained at the monolith entrance. In contrast, in uniform catalysts heat generation is also more uniform along the monolith. Therefore, increasing temperature profiles are observed while light-off is shifted in the monolith interior. Temperature gradients may thus be alleviated with suitable exponential distributions but care must be exercised to avoid highly exponential distributions as this leads to insufficient reaction rates at the monolith end.
Figure 6.7: Axial wall temperature profiles for non-uniform A, D and uniform A2, D2 catalytic monoliths.
6.3.2.2 Comparison of Experimental and Simulated Wall Temperature Profiles

The model used to compare theoretical data with experimental is similar to that given in Chapter 3. It is two-dimensional and considers heat losses from the monolith sides due to radiation. Reaction rate constant is a function of the axial co-ordinate, $z$, and temperature, $T$.

$$K_c(z,T) = k_e^0 m(z) \exp\left[\left(-\frac{E}{RT}\right)\left(\frac{1}{T} - \frac{1}{T'}\right)\right]$$

(6.1)

where $k_e^0$ is catalyst activity at a reference temperature, $T'$, per unit catalyst weight and

$$m(z) = \left[C \exp\left(-\frac{z}{\zeta}\right)\right]$$

(6.2)

is the palladium amount (kg Pd) as a function of monolith location. The constant $\zeta$ is calculated based on the EPMA determined palladium distribution while the constant, $C$, by utilising the expression

$$\frac{1}{L_0} \int_0^L m(z) dz = m_0$$

(6.3)

where $m_0$ is the total mass determined by AAS. The Thiele modulus for a first order reaction is expressed as, $\varphi = L_w \sqrt{K_c/D_{eff}}$, where $L_w$ is washcoat thickness.

At the wall the rate of diffusion from the bulk to the surface is equal to the rate of catalytic reaction,

$$D_f \rho \frac{\partial m_f}{\partial r} = -\eta K_c L_w \rho m_f$$

(6.4)

while the rate of heat dissipation to the fluid is equal to the rate of energy generation due to reaction, conduction in the solid and radiation. The steady state energy balance at the wall is thus,

$$k_f \frac{\partial T_r}{\partial r} = -\Delta H_r \eta K_c L_w \rho \frac{m_f}{RMM_f} + \frac{(1-e)}{e} \frac{d}{dz} \left[ \left(k_t + k_r \right) \frac{\partial T_w}{\partial z} \right]$$

(6.5)

The boundary condition at the wall inlet ($z = 0$) is,

$$k_t \frac{\partial T_w}{\partial z} = \varepsilon \sigma (T_w^4 - T_w^4)$$

(6.6)
and at the wall outlet ($z = L$) is,

$$-k_1 \frac{\partial T_w}{\partial z} = \varepsilon \sigma (T_w^4 - T_\infty^4) \tag{6.7}$$

where $\varepsilon$ is the emissivity, $\sigma$ is Stefan Boltzmann's constant and $T_\infty$ is the temperature of the environment.

The values of the various parameters used in the calculations are shown in Table 6.4. The constant $k_c^0$ was chosen in order to give a monolith temperature in the range of those observed experimentally. The activation energy, 95.65 kJ/mol was obtained from Baldwin and Burch (1990a).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel (CH$_4$) molar fraction at catalyst inlet, $Y$</td>
<td>0.02</td>
</tr>
<tr>
<td>Inlet bulk temperature, $T^0$</td>
<td>474°C for Catalyst D</td>
</tr>
<tr>
<td></td>
<td>468°C for Catalyst D2</td>
</tr>
<tr>
<td>Pressure, $P$</td>
<td>$1.015 \times 10^5$ N/m$^2$</td>
</tr>
<tr>
<td>Inlet gas velocity (referred to the cross section immediately upstream the catalyst inlet), $u^0$</td>
<td>0.1068 m/s</td>
</tr>
<tr>
<td>Open frontal area, $\varepsilon$</td>
<td>0.69</td>
</tr>
<tr>
<td>Radius of channel, $R$</td>
<td>$6 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Channel length, $L$</td>
<td>0.05 m</td>
</tr>
<tr>
<td>Washcoat Thickness, $L_w$</td>
<td>$200 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Hydraulic diameter, $d_{eq}$</td>
<td>$12 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Inlet amount of catalyst, $C$ (see equation 6.2 )</td>
<td>$7.94 \times 10^{-6}$ kg/m for Catalyst D</td>
</tr>
<tr>
<td>$Z$-intercept of distribution profile at axial axis, $\zeta$ (see equation 6.2)</td>
<td>$1.36 \times 10^{-3}$ m for Catalyst D</td>
</tr>
<tr>
<td>Total mass of palladium (in a channel), $m_0$</td>
<td>$9.9375 \times 10^{-9}$ kg Catalyst D</td>
</tr>
<tr>
<td></td>
<td>$9.75 \times 10^{-9}$ kg Catalyst D2</td>
</tr>
<tr>
<td>Reaction rate coefficient, $k_c^0$, at 350 °C</td>
<td>$52 \times 10^3$ kg$^{-1}$Pd. s$^{-1}$</td>
</tr>
<tr>
<td>Activation energy, $E_a$</td>
<td>95.65 KJ/mol</td>
</tr>
<tr>
<td>Reaction enthalpy, $\Delta H_r$</td>
<td>$-802$ kJ/mol</td>
</tr>
</tbody>
</table>

Table 6.4: Operating conditions, monolith characteristics and physicochemical parameters used in the simulations.
The actual and theoretical (i.e. employed in the simulations) normalised distribution profile of non-uniform catalyst D are shown in Figure 6.8. It should be noted that the differences arise from the fact that the set of PDEs are solved using 11 grid points in the axial direction (for central finite difference method). In the radial direction, 10 grid points were found to be sufficient (for orthogonal collocation method).

As Hayes et al. (1996) state, it is difficult to be precise in modelling radiation phenomena as the environment radiation temperature is unknown as well as the emissivity of the monolith. In order to obtain reasonable matches between theory and experiment the emissivity in this work was set equal to 0.5 and the environment temperature was set as being equal to the inlet bulk gas temperature.

The model shows good qualitative and reasonable quantitative agreement with the experimental wall temperatures as shown in Figure 6.9 and Table 6.5. The greatest difference between the experimental and theoretical profiles is observed by catalyst D2. The inlet wall temperature is overpredicted by 3.2% while the wall temperature at 35 mm down the monolith length is overpredicted by 1.2%. The model predicts the increasing trend of the temperature profile for catalyst D2. In the case of the non-uniform catalyst D it underpredicted the actual inlet wall temperature by 0.8% while the temperature 35 mm down the monolith length was underpredicted by 0.6%. The model predicts a flat profile along the monolith length while experimentally a decrease in temperature is observed.

Agreement between model and experiment is deemed satisfactory especially if one considers that many variables were obtained from literature. The reaction kinetics ($k_c^0$, $E_a$, reaction order) are expected to have a strong influence in the temperature profiles since they affect the heat generation term. Therefore the model can be improved by determining experimentally intrinsic kinetics for the catalyst used in this work.
Figure 6.8: Normalised actual and theoretical distribution profile of catalyst D.

Figure 6.9: Comparison between theoretical and experimental wall temperature profiles.
Table 6.5: Comparison between observed and predicted values of the reactor wall temperatures.

<table>
<thead>
<tr>
<th>CATALYST SAMPLE</th>
<th>TEMPERATURE at inlet (°C)</th>
<th>TEMPERATURE at 35 mm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OBSERVED</td>
<td>PREDICTED</td>
</tr>
<tr>
<td>D</td>
<td>484</td>
<td>480</td>
</tr>
<tr>
<td>D2</td>
<td>469</td>
<td>484</td>
</tr>
</tbody>
</table>

6.3.3 Methane Conversion

So far the emphasis of the discussion was placed on axial wall temperature profiles which can affect thermal stresses. However, apart from durability the catalysts must achieve sufficient fuel conversion. Outlet conversion of methane is shown with respect to inlet bulk temperature in Figure 6.10 for non-uniform catalysts A - F. Overall activity of the catalysts is low due to the low palladium loading. Evidently the higher the total amount of palladium the lower the inlet bulk temperature required to achieve 50% conversion. Catalyst A achieved 50% conversion at 480°C while catalyst E, which has approximately nine times less amount of palladium, requires a temperature above 600°C to achieve the same conversion.

Figure 6.10: Methane conversion for catalysts A - F activated in 2% methane in air under atmospheric conditions.
An important comparison is between uniform and non-uniform monoliths with the same total catalyst loading. This is shown in Figure 6.11 for the pairs A-A2, D-D2. Non-uniform distributions achieve higher conversions for the same inlet bulk temperature even though reaction rates are low towards the end of the monolith as there is little catalyst present. For non-uniform catalyst A inlet bulk temperatures of 369 - 480 °C are required to achieve 10 - 50 % conversion while for uniform catalyst A2, temperatures of 383 - 499 °C are required to achieve the same conversions. More specifically at a bulk temperature of 475 °C the uniform catalyst achieves conversion of 40 % while the non-uniform catalyst of 47 %. The non-uniform catalyst thus improves fuel conversion by 17.5 %. Catalyst D achieves a fuel conversion of 10 - 50 % with inlet bulk temperatures of 378 - 490 °C while the uniform catalyst D2 requires temperatures of 396 - 508°C for the same conversions. More specifically at the temperature of 475 °C the uniform catalyst achieves conversion of 37 % while the non-uniform catalyst 44 %. The non-uniform catalyst improves fuel conversion by 15.9 %. The above results illustrate that non-uniform catalysts can also achieve significant improvements in conversion. This indicates that high reaction rates in the entrance region more than compensate for low reaction rates towards the end of the monolith.
Figure 6.11: Conversion of methane by non-uniform catalysts A and D and uniform catalysts A2 and D2.
7. Conclusions and Future Work

7.1 Conclusions

The performance of axially non-uniform palladium catalytic monoliths was investigated both theoretically and experimentally and assessed based on their application in gas turbine combustors. Chemical vapour deposition as a method for preparing such catalysts was in addition examined The following conclusions from these investigations were made.

From Chapter 3, based on the theoretical investigation of the catalyst performance,

I. Exponentially decreasing catalyst distribution profiles with adequate amount of catalyst towards the monolith end were found to be favourable for alleviating temperature gradients under steady state conditions. Outlet wall temperatures remained at the same level as those achieved by uniform catalyst with the same total loading. Inlet wall temperatures though were considerably higher in the case of non-uniform catalysts and this led to the reduction of temperature gradients.

II. As long as there is sufficient catalyst downstream to sustain reactions non-uniform distributions can achieve slightly improved fuel conversion as high reaction rates are initiated further upstream at the monolith entrance. In addition, higher bulk outlet temperatures can be achieved as compared to the uniform case even though outlet wall temperatures are at the same level. This indicated that it may be possible to reduce the monolith length without an adverse effect to a downstream homogeneous reaction section.

III. For two out of the three transient conditions simulated i.e. start-up and fuel-disturbance, axial temperature gradients are kept sufficiently low for the non-uniform distribution considered (distribution 3). However this is at the expense of large temporal gradients particularly for the case of fuel disruption. From the above it is concluded that non-uniform distributions can achieve lower thermal stresses under steady state operation but care should be exercised during transient conditions.
7. Conclusions and Future Work

From the investigation of the sublimation, deposition and reduction of palladium (II) acetylacetonate in Chapter 4,

I. The temperature range for clean sublimation of palladium (II) acetylacetonate was determined to be 100-160 °C. This metal-organic precursor requires to be sublimed in the presence of an inert carrier gas such as helium and in the absence of high temperatures and hydrogen. At a sublimation temperature of 190 °C the complex was found to decompose and carbon contamination was high. In the presence of even 1 % hydrogen in helium the precursor complex reduced to the palladium metal even at room temperature. The Clausius-Clapeyron equation presented in this work is indicative of the low vapour pressure of this metal-organic complex.

II. For catalyst preparation it was found that two stages should be utilised. First, the deposition of palladium (II) acetylacetonate in helium and second, its reduction to palladium metal. The temperature range for clean deposition (that is without decomposition of the precursor) was determined to be 100-150 °C. An increase in deposition temperature encouraged more precursor to deposit up to 140°C from whereon a further increase in temperature led to a limited increase in amount deposited. Thus at the upper limit of the temperature range investigated, mass transfer controls the deposition process. Reduction of the complex can effectively be carried out in pure hydrogen atmosphere even at room temperature.

III. The presence of hydroxyl groups was determined to be important for deposition. Substrates such as γ-alumina were found to be suitable for CVD of palladium (II) acetylacetonate whereas substrates such as α-alumina and Fecralloy failed to encourage any deposition.

From the preparation of axially non-uniform Pd catalytic monoliths, using CVD in Chapter 5, it was concluded that,

I. Sublimation and deposition of Pd(acac)₂ on γ-Al₂O₃/cordierite is a viable method for preparing palladium non-uniform catalytic monoliths. The axial distribution is influenced by the hydrodynamic entry length, the presence of autocatalytic effects and the existence of mass transfer control, kinetic control and transition regions within each monolith. Radial non-uniformity within the
washcoat was also observed. Palladium particles obtained are small which is desirable for good catalytic activity.

The performance of catalysts prepared was evaluated in Chapter 6,

I. Wall temperatures in general decreased from inlet to outlet of the monolith and the extent of this was dependent on the amount of catalyst at the inlet. For high palladium loading, heat generation in the entrance was significantly more than the outlet thus leading to the higher inlet temperatures. Experiments performed with uniform catalysts with the same total loading showed that for these catalyst, wall temperature increased from inlet to outlet. In addition, they showed larger temperature gradients as compared to non-uniform catalysts, which can be beneficial for the alleviation of thermal stresses. The mathematical model showed good qualitative and satisfactory quantitative agreement with experimental wall temperatures.

II. Even though the non-uniform monoliths exhibited slightly lower outlet wall temperatures they achieved higher conversions, approximately 15 %, greater than the uniform ones. The trends of the wall temperature profiles were captured satisfactorily with a two-dimensional mathematical model. Overall performance was found to be improved for the non-uniform catalysts.

7.2 Future Work

The mathematical model formulated can be linked to a thermal stress model such as those developed by Viljoen et al. (1995). This will allow direct deduction of material failure with various catalyst distribution. The model can also be improved by modelling the washcoat layer two dimensionally in order to determine whether certain non-uniform distribution lead to radial temperature gradients within the washcoat layer. Implementing heat losses at the monolith ends due to radiation requires the use of valid data obtained from industry as these cannot be found in literature. For achieving better prediction of experimental wall temperature profiles, intrinsic kinetics for the catalysts used should be obtained experimentally.
Investigation of sublimation and deposition of Pd(acac)$_2$ and the subsequent preparation of catalysts under reduced pressure may be useful as pressure is an important parameter which can affect the morphology of catalyst. Modelling of the MOCVD reactor may also prove useful in order to understand better the principles behind the various effects of operating variables.
Nomenclature

a  constant
b  constant
c  constant
C  concentration of precursor molecules  molecules/m³
C₀  concentration of precursor molecules at gas-solid interface  molecules/m²
Cₚ  heat capacity at constant pressure per unit mass  J/kg K
D  diffusion coefficient  m²/s
D₉  molecular diffusivity  m²/s
Dₑff  effective diffusivity  m²/s
Dₖ  Knudsen diffusivity  m²/s
dₑq  equivalent diameter  m
Eₐ  activation energy  J/mol
e  open frontal area
G  constant
K  sublimation rate  kg/s
Kₑ  intrinsic rate constant  s⁻¹
Kᵣ  reaction rate coefficient  kgₚd⁻¹ s⁻¹
kₑ  thermal conductivity  W/m K
kᵣ  equivalent conductivity due to radiation  W/m K
k  constant
Lₑ  channel length  m
L  position along y-axis where precursor concentration becomes negligible  m
Lₙ  washcoat thickness  m
m  mass of precursor  kg
Mᵢ  molar mass  kg/mol
mᵣ  mass fraction of fuel  kgₚd
m  mass of palladium  kgₚd
m₀  total mass of palladium  kgₚd
n  number of molecules per gas-solid interfacial area  molecules/m²
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
<td>molecules/mol</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$P_0$</td>
<td>vapour pressure of $\text{Pd(acac}_2$</td>
<td>Pa</td>
</tr>
<tr>
<td>$R$</td>
<td>channel radius</td>
<td>m</td>
</tr>
<tr>
<td>$R_g$</td>
<td>ideal gas constant</td>
<td>J/mol.K</td>
</tr>
<tr>
<td>$\text{RMM}$</td>
<td>relative molecular mass</td>
<td>g/mol</td>
</tr>
<tr>
<td>$r$</td>
<td>radial coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$r_p$</td>
<td>pore radius</td>
<td>m</td>
</tr>
<tr>
<td>$S_R$</td>
<td>sublimation rate</td>
<td>molecules/m².s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$u$</td>
<td>axial velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$v$</td>
<td>radial velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$Y$</td>
<td>molar fraction</td>
<td></td>
</tr>
<tr>
<td>$y$</td>
<td>vertical axis in TGA</td>
<td>m</td>
</tr>
<tr>
<td>$z$</td>
<td>axial coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$Z$</td>
<td>frequency of collision</td>
<td>s⁻¹</td>
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</table>

### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>active catalyst layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_r$</td>
<td>heat of reaction</td>
<td>J/mol</td>
</tr>
<tr>
<td>$\Delta H_{\text{sub}}$</td>
<td>enthalpy of sublimation</td>
<td>J/mol</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>emissivity</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>catalyst void fraction</td>
<td></td>
</tr>
<tr>
<td>$\zeta$</td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>effectiveness factor</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>mean free path</td>
<td>m</td>
</tr>
<tr>
<td>$\mu$</td>
<td>viscosity</td>
<td>Pa.s</td>
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<tr>
<td>$\mu$</td>
<td>reduced mass</td>
<td>kg</td>
</tr>
<tr>
<td>$v$</td>
<td>average velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$\xi$</td>
<td>constant</td>
<td></td>
</tr>
</tbody>
</table>
Nomenclature

\( \rho \)
\begin{align*}
\rho & \quad \text{density} \\
\sigma & \quad \text{Stefan Boltzmann constant} \\
\sigma & \quad \text{collision diameter} \\
\tau_p & \quad \text{tortuosity factor} \\
\phi & \quad \text{Thiele Modulus} \\
\chi & \quad \text{channel aspect ratio}
\end{align*}

Subscripts and Superscripts
\begin{align*}
0 & \quad \text{inlet conditions} \\
f & \quad \text{fuel conditions} \\
m & \quad \text{mean} \\
w & \quad \text{wall conditions} \\
\infty & \quad \text{environment} \\
1 & \quad \text{Pd(acac)}_2 \\
2 & \quad \text{carrier gas} \\
T & \quad \text{total}
\end{align*}
References


References


References


References


Gozum, J. E., Pollina, D. M., Jensen, J. A. and Girolami, G. A., “Tailored-organometallics as precursors for the chemical vapor deposition of high purity
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Handelsblatt Newspaper, Nr.23, 52, 2nd February 2000.


References


References


References

Stambler, I., “‘Cool’ catalytic combustor design limits NOx to less than 0.5 ppm”, *Gas Turbine World*, May-June, 1993.


To validate the isothermality assumption in the model, the Prater number, $\beta$, for the extreme case of the highest washcoat thickness of distribution profile 4 was calculated. The values of the parameters used are given in Table A.1.

$$\beta = \left(\frac{-\Delta H}{D_{\text{eff}}C_s^s}\right) \frac{\lambda_{\text{eff}}}{T_s^s} = 2.5 \times 10^{-6} \quad (A.1)$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wall Inlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy of reaction, $\Delta H$, kJ/kmol</td>
<td>802</td>
</tr>
<tr>
<td>Effective diffusivity, $D_{\text{eff}}$, m²/s</td>
<td>$7.17 \times 10^{-7}$</td>
</tr>
<tr>
<td>Fuel concentration at the solid surface, $C_s^s$, kmol/m³</td>
<td>$1.88 \times 10^{-3}$</td>
</tr>
<tr>
<td>Effective thermal conductivity, $\lambda_{\text{eff}}$, W/m. k (Froment and Bischoff, 1990)</td>
<td>0.4</td>
</tr>
<tr>
<td>Temperature at surface of wall, $T_s^s$</td>
<td>1085</td>
</tr>
</tbody>
</table>

*Table A.1: Parameter values used to calculate the Prater number.*
Both steady state and transient models formulated are given below.

#STEADY STATE MODEL OF A CATALYTIC MONOLITH REACTOR WITH CYLINDRICAL CHANNELS

DECLARE

TYPE
Mass_fraction = 0.009 : -1E30 : 1E20
Notype = 0.9 : -1E30 : 1E30
NonNegative = 0.42 : -1E10 : 1E30
Ratio = 1 : -1E10 : 1E30
Temperature = 800 : 1 : 1E30
Velocity = 7.75 : -1E30 : 1E30
Velocity_r = 0 : -1E30 : 1E30
Velocity_z = 8 : -1E30 : 1E30
Velocity_radial = 0 : -1E30 : 1E30
Velocity_radial_r = 0 : -1E30 : 1E30
Velocity_radial_z = 0 : -1E30 : 1E30
Pressure = 10.15E5 : -1E20 : 1E10
Diffusivity_mol = 9.8E-6 : -1E20 : 1E10
Diffusivity_mol_Kn = 4.9E-6 : -1E20 : 1E30
Diffusivity_ther = 5.3E-2 : -1E20 : 1E30
Diffusivity_eff = 5.7E-7 : -1E20 : 1E30
Diffusivity_ther_w = 2 : -1E20 : 1E30
Diffusivity_rad = -7.1E-21 : -1E20 : 1E30
Viscosity = 7.2E-5 : -1E20 : 1E30
Reaction_coeff = 200 : -1E20 : 1E30
Density = 4.8 : -1E10 : 1E30
Activity = 1.9E-5 : -1E30 : 1E30
HCapacity = 1112 : -1E30 : 1E30

END #Declare

#Model is based on a single cylindrical channel of the catalytic monolith

MODEL CatalyticMonolith

PARAMETER

#System dependent parameters
Y_CH4, Y_AIR, P, T_const AS REAL

#Geometrical parameters
ReactorRadius, ReactorLength, e, tp, ep, rp, deg, s AS REAL

#Physical properties
Cpf, RhoS, MWf, MWa AS REAL

#Reaction
A, GC, React_enth AS REAL

DISTRIBUTION_DOMAIN

Axial AS ( 0 : ReactorLength )
Radial AS ( 0 : ReactorRadius )

VARIABLE

mf AS DISTRIBUTION(Axial,Radial) OF Mass_fraction
Temp AS DISTRIBUTION(Axial,Radial) OF Temperature
mf_inlet AS DISTRIBUTION(Axial) OF Mass_fraction
Temp_inlet AS DISTRIBUTION(Axial) OF Temperature
Df AS DISTRIBUTION(Axial,Radial) OF Diffusivity_mol
Dk AS DISTRIBUTION(Axial) OF Diffusivity_ther
Deff AS DISTRIBUTION(Axial) OF Diffusivity_eff
kg AS DISTRIBUTION(Axial,Radial) OF Diffusivity_ther
kg_inlet AS DISTRIBUTION(Axial) OF Diffusivity_ther
RhoG AS DISTRIBUTION(Axial,Radial) OF Density

END #Model

#ALL UNITS ARE IN S.I.
BOUNDARY

# Inlet conditions (z = 0)
Temp(0,0:ReactorRadius|-) = Temp_inlet ;
PARTIAL(Temp(0,ReactorRadius),Axial) = 0 ;
mf(0,0:ReactorRadius|-) = mf_inlet ;
U(0,0:ReactorRadius|-) = U_ref ;
V(0,0:ReactorRadius) = 0 ;
Pr(0,0:ReactorRadius) = P_inlet ;

# Outlet conditions (z = L)
PARTIAL(Temp(ReactorLength,0:ReactorRadius),Axial) = 0 ;
PARTIAL(mf(ReactorLength,0:ReactorRadius|-),Axial) = 0 ;
PARTIAL(U(ReactorLength,0:ReactorRadius|-),Axial) = 0 ;
V(ReactorLength,0:ReactorRadius) = 0 ;

# Symmetry conditions at the channel axis (r = 0)
PARTIAL(Temp(0|+:ReactorLength|-,0),Radial) = 0 ;
PARTIAL(mf(0|+:ReactorLength|-,0),Radial) = 0 ;
PARTIAL(U(0|+:ReactorLength|-,0),Radial) = 0 ;
V(0|+:ReactorLength|-,0) = 0 ;
PARTIAL(P(0|+:ReactorLength,0),Radial) = 0 ;

# Mass fraction Conditions at catalytic walls (r = R)
Df(0|+:ReactorLength,ReactorRadius) * RhoG(0|+:ReactorLength,ReactorRadius) *
PARTIAL(mf(0|+:ReactorLength,ReactorRadius),Radial)
= - Eta(0|+:ReactorLength) * Kc(0|+:ReactorLength) *
Delta(0|+:ReactorLength)
* RhoG(0|+:ReactorLength,ReactorRadius) * mf(0|+:ReactorLength,ReactorRadius) ;

# Temperature Conditions at catalytic walls (r = R)
( kg(0|+:ReactorLength|-,ReactorRadius) *
PARTIAL(Temp(0|+:ReactorLength|-,ReactorRadius),Radial) )
= (- ( React_enth * Eta(0|+:ReactorLength|-)
* Kc(0|+:ReactorLength) ) *
Delta(0|+:ReactorLength) * RhoG(0|+:ReactorLength|-,ReactorRadius) *
( mf(0|+:ReactorLength|-,ReactorRadius) / MWf ))
+ ((1 - e)/e) * (deg/4) *
PARTIAL((kt(0|+:ReactorLength|-) + kr(0|+:ReactorLength|-)) *
PARTIAL(Temp(0|+:ReactorLength|-,ReactorRadius)
,Axial), Axial) ;

U(ReactorLength,ReactorRadius) = 0 ;
V(0|+:ReactorLength|-,ReactorRadius) = 0 ;

EQUATION

# GAS PHASE MATERIAL BALANCE

FOR z := 0|+ TO ReactorLength|- DO
FOR r := 0|+ TO ReactorRadius|- DO
r * RhoG(z,r) * U(z,r) * PARTIAL( mf(z,r) ,Axial)
= ((r * RhoG(z,r) * V(z,r) * PARTIAL( mf(z,r) ,Radial))
+ ( (PARTIAL(r * Df(z,r) * RhoG(z,r) * (PARTIAL( mf(z,r),
Radial)), Radial)) + (r * PARTIAL(Df(z,r) * RhoG(z,r) * (PARTIAL(mf(z,r), Axial))

-----------------------------------------------------------------------------------------------
-----------------------------------------------------------------------------------------------
# GAS PHASE ENERGY BALANCE

FOR z := 0 TO ReactorLength DO
FOR r := 0 TO ReactorRadius DO
   Cpf * RhoG(z,r) * U(z,r) * PARTIAL(Temp(z,r), Axial)
   = (( - Cpf * RhoG(z,r) * V(z,r) * PARTIAL(Temp(z,r), Radial))
      + (U(z,r) * PARTIAL(Pr(z,r), Axial))
      + V(z,r) * PARTIAL(Pr(z,r), Radial));
END
END

# CONTINUITY EQUATION

FOR z := 0 TO ReactorLength DO
FOR r := 0 TO ReactorRadius DO
   (PARTIAL((RhoG(z,r) * U(z,r)), Axial))
   + (1/r) * (PARTIAL((RhoG(z,r) * V(z,r) * r), Radial)) = 0;
END
END

# MOMENTUM BALANCE IN AXIAL DIRECTION

FOR z := 0 TO ReactorLength DO
FOR r := 0 TO ReactorRadius DO
   r * U(z,r) * RhoG(z,r) * PARTIAL(U(z,r), Axial)
   = - r * PARTIAL(Pr(z,r), Axial)
      + ( - r * V(z,r) * RhoG(z,r) * PARTIAL(U(z,r), Radial))
      + PARTIAL(r * Mi(z,r) * PARTIAL(U(z,r), Radial), Radial)
      + PARTIAL(Mi(z,r) * r * V_z(z,r), Radial)
      - r * PARTIAL((2/3) * Mi(z,r) * (PARTIAL(U(z,r), Axial) + V_r(z,r)), Axial)
      + r * PARTIAL(2 * Mi(z,r) * PARTIAL(U(z,r), Axial), Axial));
END
END

# MOMENTUM BALANCE IN RADIAL DIRECTION

FOR z := 0 TO ReactorLength DO
FOR r := 0 TO ReactorRadius DO
   r * U(z,r) * RhoG(z,r) * PARTIAL(V(z,r), Axial)
   = ( - r * V(z,r) * RhoG(z,r) * PARTIAL(V(z,r), Radial))
      + ( - r * Mi(z,r) * PARTIAL(V(z,r), Radial), Radial)
      + r * PARTIAL(Mi(z,r) * PARTIAL(V(z,r), Axial), Axial)
      + r * PARTIAL(Mi(z,r) * PARTIAL(V(z,r), Axial), Axial)
      - PARTIAL((2/3) * Mi(z,r) * r * (V_r(z,r)
      + U_z(z,r), Radial));
END
END

# PARTIAL U(z,r) WITH RESPECT TO RADIUS

FOR z := 0 TO ReactorLength DO
FOR r := 0 TO ReactorRadius DO
   U_r(z,r) = PARTIAL(U(z,r), Radial);
END
END

# PARTIAL U(z,r) WITH RESPECT TO AXIS
FOR z := 0 TO ReactorLength DO
  FOR r := 0 TO ReactorRadius DO
    U_z(z,r) = PARTIAL(U(z,r),Axial);
  END
END

#PARTIAL V(z,r) WITH RESPECT TO AXIS
#======================================
FOR z := 0 TO ReactorLength DO
  FOR r := 0 TO ReactorRadius DO
    V_z(z,r) = PARTIAL(V(z,r),Axial);
  END
END

#PARTIAL V(z,r) WITH RESPECT TO RADIUS
#=====================================
FOR z := 0 TO ReactorLength DO
  FOR r := 0 TO ReactorRadius DO
    V_r(z,r) = (1/r) * PARTIAL(r * V(z,r),Radial);
  END
END

V_r(0:ReactorLength,0) = 0;

#REACTION
#================
Kc(0:ReactorLength) = Kc_inlet * EXP(Dummy * (-A/GC) * (1/Temperature(0:ReactorLength,ReactorRadius) - 1/Temperature_inlet));

#THERMAL CONDUCTIVITY OF WALL
#==============================
kt(0:ReactorLength) = 0.9558 - (2.09E-4 * Temperature(0:ReactorLength,ReactorRadius));

#HEAT CAPACITY OF WALL
#======================
Cpw(0:ReactorLength) = 948 + (0.227 * Temperature(0:ReactorLength,ReactorRadius));

#CONDUCTIVITY TERM DUE TO RADIATION FROM WALL
#============================================
kr(0:ReactorLength) = (16/3) * s * 1E-8 * ReactorRadius * (Temperature(0:ReactorLength,ReactorRadius))^3 * PSI;

#EFFECTIVENESS FACTOR
#====================
Eta(0:ReactorLength) * PHI(0:ReactorLength) = TANH(PHI(0:ReactorLength));

(Phi(0:ReactorLength)^2) * Deff(0:ReactorLength) = (Delta^2) * Kc(0:ReactorLength);

#BULK DIFFUSION COEFFICIENT
#==========================
FOR \( z := 0 \) TO ReactorLength DO
FOR \( r := 0 \) TO ReactorRadius DO
\[ D_f(z, r) = 9.9 \times 10^{-5} \times \left( \frac{(\text{Temp}(z, r)^{1.75})}{P} \right) ; \]
END
END

## KNUDSEN DIFFUSION COEFFICIENT

\[ D_k(0: \text{ReactorLength}) = D_k_{\text{inlet}} \times \left( \frac{\text{Temp}(0: \text{ReactorLength}, \text{ReactorRadius})}{\text{Temp}_{\text{inlet}}} \right)^{0.5} ; \]

## EFFECTIVE DIFFUSIVITY

\[ \frac{1}{D_{\text{eff}}(0: \text{ReactorLength})} = \left( \frac{1}{D_f(0: \text{ReactorLength}, \text{ReactorRadius})} + \frac{1}{D_k(0: \text{ReactorLength})} \right) \times \left( \frac{\text{tp}}{\text{ep}} \right) ; \]

## THERMAL DIFFUSION COEFFICIENT

FOR \( z := 0 \) TO ReactorLength DO
FOR \( r := 0 \) TO ReactorRadius DO
\[ k_g(z, r) = 1.679 \times 10^{-2} + (5.073 \times 10^{-5} \times \text{Temp}(z, r)) ; \]
END
END

## DENSITY

FOR \( z := 0 \) TO ReactorLength DO
FOR \( r := 0 \) TO ReactorRadius DO
\[ \rho_G(z, r) = \frac{\left( P \times \left( \left( Y_{\text{CH}_4} \times MW_f \right) + (Y_{\text{AIR}} \times MW_a) \right) \right)}{(GC \times \text{Temp}(z, r))}/1000 ; \]
END
END

## VISCOSITY

FOR \( z := 0 \) TO ReactorLength DO
FOR \( r := 0 \) TO ReactorRadius DO
\[ \mu(z, r) = (5.55 \times 10^{-11} \times \text{Temp}(z, r)^2) + 8.523 \times 10^{-8} \times \text{Temp}(z, r) - 1.865 \times 10^{-5} ; \]
END
END
\[ \mu(\text{ReactorLength}, 0: \text{ReactorRadius}) = 0 ; \]

## DELTA

FOR \( z := 0 \) TO ReactorLength DO
\[ \Delta(z) = 20 \times 10^{-6} ; \]
END

\$\text{Dummy} = 1 ;$

END # model catalytic monolith

PROCESS SS
UNIT
SS AS CatalyticMonolith
# MONITOR
# CMS.$Temp(*);

SET
WITHIN SS DO
  Axial := [CFDM, 2, 20];
  Radial := [OCFEM, 3, 3];
END

WITHIN SS DO
  ReactorRadius := 6E-4;
  ReactorLength := 0.1;
  Y_CH4 := 0.02;
  Y_AIR := 0.98;
  R := 10.15E5;
  T_const := 723;
  Cpf := 1080;
  RhoS := 1710;
  MWf := 16.03;
  MWa := 28.84;
  React_enth e := -802E6;
  e := 0.68;
  A := 90.1652E3;
  GC := 8.314;
  ep := 0.5;
  tp := 3;
  R := 100;  # 1E-6cm
  deq := 12E-4;
  s := 5.66932;  # Stefan-Boltzmann Constant
END

ASSIGN
WITHIN SS DO
  # inlet conditions
  U_ref := 7.75;
  Dk_inlet := (97 * rp * 1E-10 * ep * (SQRT(T_const/16)));
  Df_inlet := ((1.013E-2 * (T_const)^1.75) * ((1/MWf) + (1/MWa))^0.5)/
              ((P * ( (24.42)^(-1/3) ) +  (20.1)^(-1/3) ))^2);
  kg_inlet := 1.679E-2 + (5.073E-5 * T_const);
  RhoG_inlet := ((P * (Y_CH4 * MWf) + (Y_AIR * MWa)))/(GC * T_const)/1000;
  Temp_inlet := 450 + 273;
  mf_inlet := (Y_CH4 * MWf)/((Y_CH4 * MWf) + (Y_AIR * MWa));
  Kc_inlet := 200;  # 209;
  Ml_inlet := (5.55E-11 * T_const^2) + (8.523E-8 * T_const)- 1.865E-5;
  P_inlet := 10.15E5;
  Delta_inlet := 40E-6;
  PSI := 1 + ((ReactorLength/deq)^3)/4 - (( (ReactorLength/deq) ^2 ) *
             (SQRT( ( (ReactorLength/deq)^2 ) + 1 )))^4) +
        ((SQRT(((ReactorLength/deq)^2) + 1))/8) -
        (9/8 * (ReactorLength/deq)) *
        LOG((ReactorLength/deq) +
        (SQRT(((ReactorLength/deq)^2) + 1)));
  Dummy := TIME;
END

PRESET
RESTORE "SS"

SOLUTIONPARAMETERS
  gPLOT := OFF;
  gRMS := ON;
  ReportingInterval := 1;

SCHEDULE
SEQUENCE
  SAVE "SS"
  WHILE SS.Dummy < 1 DO
    RESET
    SS.Dummy := OLD(SS.Dummy) + 0.1;
  END
END

SAVE "SSI"

END  # Process Simulation
#TRANSIENT MODEL OF A CATALYTIC MONOLITH REACTOR WITH CYLINDRICAL CHANNELS

---

DECLARE

TYPE

Mass_fraction = 0.009 : -1E30 : 1E20
Notype = 0.9 : -1E30 : 1E30
NonNegative = 0.42 : -1E10 : 1E30
Ratio = 1 : -1E10 : 1E30
Temperature = 800 : 1 : 1E30
Velocity = 7.75 : -1E30 : 1E30
Velocity_r = 0 : -1E30 : 1E30
Velocity_z = 8 : -1E30 : 1E30
Velocity_radial = 0 : -1E30 : 1E30
Velocity_radial_r = 0 : -1E30 : 1E30
Velocity_radial_z = 0 : -1E30 : 1E30
Pressure = 10.15E5 : -1E20 : 1E10
Diffusivity_mol = 9.8E-6 : -1E20 : 1E10
Diffusivity_mol_Kn = 4.9E-6 : -1E20 : 1E30
Diffusivity_ther = 5.3E-2 : -1E20 : 1E30
Diffusivity_eff = 5.7E-7 : -1E20 : 1E30
Diffusivity_ther_w = 2 : -1E20 : 1E30
Diffusivity_rad = -7.1E-21 : -1E20 : 1E30
Viscosity = 7.2E-5 : -1E20 : 1E30
Reaction_coeff = 200 : -1E20 : 1E30
Density = 4.8 : -1E10 : 1E30
Activity = 1.9E-5 : -1E30 : 1E30
HCapacity = 1112 : -1E30 : 1E30

END #Declare

#ALL UNITS ARE IN S.I.

#MODEL CatalyticMonolith

PARAMETER

# System dependent parameters
Y_CH4, Y_AIR, P, T_const, m_0, m_in, md_0, KSI_m AS REAL

# Geometrical parameters
ReactorRadius, ReactorLength, e, tp, ep, rp, deq, s AS REAL

# Physical properties
Cpf, RhoS, MWf, MWa AS REAL

# Reaction
A, GC, React_enth AS REAL

DISTRIBUTION_DOMAIN

Axial AS ( 0 : ReactorLength )
Radial AS ( 0 : ReactorRadius )

VARIABLE

C AS Notype
mf AS DISTRIBUTION(Axial,Radial) OF Mass_fraction
Temp AS DISTRIBUTION(Axial,Radial) OF Temperature
mf_inlet AS Mass_fraction
Temp_inlet AS Temperature
N AS DISTRIBUTION(Axial) OF Notype
O AS DISTRIBUTION(Axial) OF Notype
mf_bulk AS DISTRIBUTION(Axial) OF Mass_fraction
M AS DISTRIBUTION(Axial) OF Mass_fraction
Q AS DISTRIBUTION(Axial) OF Mass_fraction
Df AS DISTRIBUTION(Axial,Radial) OF Diffusivity_mol
Df_inlet AS Diffusivity_mol
DK AS DISTRIBUTION(Axial) OF Diffusivity_mol_Kn
DK_inlet AS Diffusivity_mol_Kn
Deff AS DISTRIBUTION(Axial) OF Diffusivity_eff
kg AS DISTRIBUTION(Axial,Radial) OF Diffusivity_ther
kg_inlet AS Diffusivity_ther
BOUNDARY

#Inlet Conditions (z= 0)
Temp(0,0:ReactorRadius|-) = Temp_inlet ;
PARTIAL(Temp(0,ReactorRadius), Axial) = 0 ;
mf(0,0:ReactorRadius|-) = mf_inlet ;
U(0,0:ReactorRadius|-) = U_ref ;
V(0,0:ReactorRadius) = 0 ;
Pr(0,0:ReactorRadius) = P_inlet ;

#Outlet Conditions (z= L)
PARTIAL(Temp(ReactorLength,0:ReactorRadius), Axial) = 0 ;
PARTIAL(mf(ReactorLength,0:ReactorRadius|-, Axial) = 0 ;
PARTIAL(U(ReactorLength,0:ReactorRadius|-, Axial) = 0 ;
V(ReactorLength,0:ReactorRadius) = 0 ;

#Symmetry Conditions at the channel axis (r= 0)
PARTIAL(Temp(0|+:ReactorLength|-0), Radial) = 0 ;
PARTIAL(U(0|+:ReactorLength|-0), Radial) = 0 ;
V(0|+:ReactorLength|-0) = 0 ;
PARTIAL(Pr(0|+:ReactorLength,0), Radial) = 0 ;

#Mass_fraction Conditions at Catalytic Walls (r= R)
Df(0:ReactorLength,ReactorRadius) * RhoG(0:ReactorLength,ReactorRadius) *
PARTIAL(mf(0:ReactorLength,ReactorRadius), Radial) = - Eta(0:ReactorLength) * Kc(0:ReactorLength) *
Delta(0:ReactorLength) * RhoG(0:ReactorLength,ReactorRadius) * mf(0:ReactorLength,ReactorRadius) ;

#Temperature Conditions at Catalytic Walls (r= R)
{(1 - e)/e} * (deg/4) * Cpw(0|+:ReactorLength|-) * RhoS *
**Temp(0|+:ReactorLength|-,ReactorRadius)
= - ( kg(0|+:ReactorLength|-,ReactorRadius) * 
PARTIAL(Temp(0|+:ReactorLength|-,ReactorRadius), Radial)
- ( React_enth * Eta(0|+:ReactorLength|-) * 1E3 *
Kc(0|+:ReactorLength|-) * 
Delta(0|+:ReactorLength|-) * RhoG(0|+:ReactorLength|-,ReactorRadius) * 
{ mf(0|+:ReactorLength|-,ReactorRadius) / MWf })
+ ((1 - e)/e) * (deg/4) *
PARTIAL((kt(0|+:ReactorLength|-) + kr(0|+:ReactorLength|-))
* PARTIAL(Temp(0|+:ReactorLength|-,ReactorRadius), Axial), Axial) ;

#Velocity Conditions at the Catalytic Walls (r= R)
U(0:ReactorLength,ReactorRadius) = 0 ;
V(0|+:ReactorLength|-,ReactorRadius) = 0 ;

EQUATION

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
# GAS PHASE MATERIAL BALANCE
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0|+ TO ReactorLength|- DO
FOR r := 0|+ TO ReactorRadius| - DO
  r * RhoG(z,r) * U(z,r) * PARTIAL( mf(z,r) ,Axial) =
  ((r * RhoG(z,r) * V(z,r) * PARTIAL( mf(z,r), Radial)) +
   (PARTIAL(r * Df(z,r) * RhoG(z,r) * (PARTIAL( mf(z,r),
     Radial)), Radial)) + (r * PARTIAL(Df(z,r) * RhoG(z,r) * (PARTIAL(mf(z,r),
     Axial)) Axial)) )
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
# GAS PHASE ENERGY BALANCE
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0|+ TO ReactorLength| - DO
  FOR r := 0|+ TO ReactorRadius| - DO
    Cpf * RhoG(z,r) * U(z,r) * PARTIAL(Temp(z,r) ,Axial) =
    (( - Cpf * RhoG(z,r) * V(z,r) * PARTIAL( Temp(z,r) ,Radial)) +
     ((1/r) * ( PARTIAL( r * kg(z,r) * (PARTIAL( Temp(z,r), Radial)), Radial)) + ( PARTIAL(kg(z,r) * (PARTIAL(Temp(z,r), Axial)) , Axial)) +
      (U(z,r) * PARTIAL(Pr(z,r), Axial)) +
      V(z,r) * PARTIAL(Pr(z,r),Radial) )
  END
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = ==
# CONTINUITY EQUATION
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0|+ TO ReactorLength| - DO
  FOR r := 0|+ TO ReactorRadius| - DO
    (PARTIAL((RhoG(z,r) * U(z,r)), Axial)) +
     (1/r) * (PARTIAL((RhoG(z,r) * V(z,r) * r), Radial)) = 0
  END
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = :
# MOMENTUM BALANCE IN AXIAL DIRECTION
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0|+ TO ReactorLength| DO
  FOR r := 0|+ TO ReactorRadius| DO
    r * U(z,r) * RhoG(z,r) * PARTIAL(U(z,r) ,Axial) =
    - r * PARTIAL(Pr(z,r),Axial) +
      ( - r * V(z,r) * RhoG(z,r) * PARTIAL(U(z,r), Radial) +
        PARTIAL(r * Mi(z,r) * PARTIAL( U(z,r) ,Radial) ,Radial)
        - r * PARTIAL(2/3) * Mi(z,r) * (PARTIAL (U(z,r),Axial) + V_r(z,r)) ,Axial)
      + r * PARTIAL(2 * Mi(z,r) * PARTIAL(U(z,r),Axial),Axial)
  END
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = :
# MOMENTUM BALANCE IN RADIAL DIRECTION
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0|+ TO ReactorLength| DO
  FOR r := 0|+ TO ReactorRadius| DO
    r * U(z,r) * RhoG(z,r) * PARTIAL(V(z,r) ,Axial) =
    - r * PARTIAL(Pr(z,r),Radial) +
      ( - r * V(z,r) * RhoG(z,r) * PARTIAL(V(z,r) ,Radial) +
        r * PARTIAL(Mi(z,r) * V_r(z,r)) ,Radial)
      + r * PARTIAL(V(z,r) ,Axial)
      + PARTIAL((2/3) * Mi(z,r) * (PARTIAL (V(z,r),Axial) + U_r(z,r)) ,Axial)
      + U_z(z,r),Radial)
  END
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = :
# PARTIAL U(z,r) WITH RESPECT TO RADIUS
#====================================================;
FOR z := 0 TO ReactorLength| DO
  FOR r := 0 TO ReactorRadius| DO
    U_r(z,r) = PARTIAL(U(z,r),Radial)
  END
END
# PARTIAL U(z,r) WITH RESPECT TO AXIS

FOR z := 0 TO ReactorLength DO
    FOR r := 0 TO ReactorRadius DO
        U_z(z,r) = PARTIAL(U(z,r),Axial);
    END
END

# PARTIAL V(z,r) WITH RESPECT TO AXIS

FOR z := 0 TO ReactorLength DO
    FOR r := 0 TO ReactorRadius DO
        V_z(z,r) = PARTIAL(V(z,r),Axial);
    END
END

# PARTIAL V(z,r) WITH RESPECT TO RADIUS

FOR z := 0 TO ReactorLength DO
    FOR r := 0 TO ReactorRadius DO
        V_r(z,r) = (1/r) * PARTIAL(r * V(z,r),Radial);
    END
END

V_r(0:ReactorLength,0) = 0;

# REACTION

Kc(0:ReactorLength) = Kc_inlet * EXP((-A/GC) * (1/Temp(0:ReactorLength,ReactorRadius) - 1/Temp_inlet));

# THERMAL CONDUCTIVITY OF WALL

kt(0:ReactorLength) = 0.9558 - (2.09E-4 * Temp(0:ReactorLength,ReactorRadius));

# HEAT CAPACITY OF WALL

Cpw(0:ReactorLength) = 948 + (0.227 * Temp(0:ReactorLength,ReactorRadius));

# CONDUCTIVITY TERM DUE TO RADIATION FROM WALL

kr(0:ReactorLength) = (16/3) * s * 1E-8 * ReactorRadius * (Temp(0:ReactorLength,ReactorRadius))**3 * PSI;

# BULK TEMPERATURE

FOR z := 0 TO ReactorLength DO
    N(z) = INTEGRAL(x := 0:ReactorRadius;
                             Rhog(z,x) * U(z,x) * Temp(z,x) * r);
END

FOR z := 0 TO ReactorLength DO
    Temp_bulk(z) * O(z) = N(z);
END

FOR z := 0 TO ReactorLength DO
\[ \text{INTEGRAL} \left( r := 0:\text{ReactorRadius} ; \right. \\
\left. \text{RhoG}(z,r) \times \text{U}(z,r) \times r \right) = O(z) \]

---

**BULK MASS FRACTION**

FOR \( z := 0 \) TO \( \text{ReactorLength} \)
\[
\text{M}(z) = \text{INTEGRAL} \left( r := 0:\text{ReactorRadius} ; \\
\text{RhoG}(z,r) \times \text{U}(z,r) \times \text{mf}(z,r) \times r \right) ;
\]
END

FOR \( z := 0 \) TO \( \text{ReactorLength} \)
\[
\text{mf}\_\text{bulk}(z) \times \text{Q}(z) = \text{M}(z) ;
\]
END

FOR \( z := 0 \) TO \( \text{ReactorLength} \)
\[
\text{INTEGRAL} \left( r := 0:\text{ReactorRadius} ; \\
\text{RhoG}(z,r) \times \text{U}(z,r) \times r \right) = \text{Q}(z) ;
\]
END

---

**EFFECTIVENESS FACTOR**

\[
\text{Eta}(0:\text{ReactorLength}) \times \text{PHI}(0:\text{ReactorLength}) = \\
\text{TANH}(\text{PHI}(0:\text{ReactorLength})) ;
\]
\[
(\text{PHI}(0:\text{ReactorLength})^2) \times \text{Deff}(0:\text{ReactorLength}) = (\Delta)^2 \times \\
\text{Kc}(0:\text{ReactorLength}) ;
\]

---

**BULK DIFFUSION COEFFICIENT**

FOR \( z := 0 \) TO \( \text{ReactorLength} \)
FOR \( r := 0 \) TO \( \text{ReactorRadius} \)
\[
\text{Df}(z,r) = 9.9E-5 \times ((\text{Temp}(z,r)^{1.75})/\text{P}) ;
\]
END
END

---

**KNUDSEN DIFFUSION COEFFICIENT**

\[
\text{Dk}(0:\text{ReactorLength}) = \text{Dk}\_\text{inlet} \times \\
((\text{Temp}(0:\text{ReactorLength}, \text{ReactorRadius}) \\
/\text{Temp}\_\text{inlet})^{0.5}) ;
\]

---

**EFFECTIVE DIFFUSIVITY**

\[
1/\text{Deff}(0:\text{ReactorLength}) = (1/\text{Df}(0:\text{ReactorLength}, \text{ReactorRadius}) \\
+ 1/\text{Dk}(0:\text{ReactorLength})) \times (\text{tp}/\text{ep}) ;
\]

---

**THERMAL DIFFUSION COEFFICIENT**

FOR \( z := 0 \) TO \( \text{ReactorLength} \)
FOR \( r := 0 \) TO \( \text{ReactorRadius} \)
\[
\text{kg}(z,r) = 1.679E-2 + (5.073E-5 \times \text{Temp}(z,r)) ;
\]
END
END

---

**DENSITY**

---
FOR z := 0 TO ReactorLength DO
  FOR r := 0 TO ReactorRadius DO
    RhoG(z, r) = ((P * ((Y_CH4 * MWf) + (Y_AIR * MWa)) / (GC * Temp(z, r))) / 1000 ;
  END
END

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
# VISCOSITY
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0 TO ReactorLength - DO
  FOR r := 0 TO ReactorRadius DO
    Mi(z, r) = (5.55E-11 * Temp(z, r) * 2) + 8.523E-8 * Temp(z, r)
    - 1.865E-5 ;
  END
END
Mi(ReactorLength, 0:ReactorRadius) = 0 ;

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
# DELTA
# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
FOR z := 0 TO ReactorLength DO
  Delta(z) = C * (exp(-(z*100)/1.617))
  C * INTEGRAL( z := 0:ReactorLength ; (exp(-(z*100)/1.617)) )
  = 20E-6 * 0.1 ;
END

#$Dummy = 1 ;
END # model catalytic monolith

# = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
PROCESS US
UNIT US AS CatalyticMonolith
MONITOR US.Temp(*);
SET WITHIN USExp DO
  Axial := [CFDM , 2, 15] ;
  Radial := [OCFEM, 3, 2] ;
END WITHIN US DO
  ReactorRadius := 6E-4 ;
  ReactorLength := 0.1 ;
  Y_CH4 := 0.02 ;
  Y_AIR := 0.98 ;
  P := 10.15E5 ;
  T_const := 723 ;
  Cpf := 1080 ;
  RhoS := 1710 ;
  MWf := 16.03 ;
  MWa := 28.84 ;
  React_enth := -802E3 ;
  e := 0.68 ;
  A := 90.1652E3 ;
  GC := 8.314 ;
  ep := 0.5 ;
  tp := 3 ;
  rp := 100 ; #Angstrom
  deq := 12E-4 ;
  s := 5.66932 ; #Stefan-Boltzmann Constant
  m_0 := 205E-6 ;
  m_in := 1.25 ;
  md_0 := 1 ;
  KSI_m := 1 ;
END

ASSIGN WITHIN US DO
# inlet conditions

\[
\begin{align*}
U_{\text{ref}} & := 7.75; \\
D_{\text{k_inlet}} & := (97 \times \rho_p \times 1E-10 \times (\sqrt{T_{\text{const}}/(\text{MW}_{f})))); \\
D_{\text{f_inlet}} & := ((1.013E-2 \times (T_{\text{const}})^{1.75} \times ((1/\text{MW}_{f}) + (1/\text{MW}_{a}))^{0.5})/
\quad \text{US.}P \times (1^2/3) + ((20.1)^2/3)^2); \\
k_{\text{g_inlet}} & := 1.679E-2 + (5.073E-5 \times T_{\text{const}}); \\
RhoG_{\text{inlet}} & := ((P \times ((Y_{\text{CH4}} \times \text{MW}_{f}) + (Y_{\text{AIR}} \times \text{MW}_{a}))) / (\text{GC} \times T_{\text{const}})) / 1000; \\
\text{Temp}_{\text{inlet}} & := 450 + 273; \\
mf_{\text{inlet}} & := 0; \\
K_{\text{c_inlet}} & := 200; \\
M_{\text{i_inlet}} & := (5.55E-11 \times T_{\text{const}}^2) + (8.523E-8 \times T_{\text{const}}) - 1.865E-5; \\
P_{\text{inlet}} & := 10.15E5; \\
a_d & := (m_{\text{in}} - m_{\text{d_0}})/\text{KSI}_{m} - (1/3); \\
b & := -2 \times \text{KSI}_{m} \times (m_{\text{in}} - m_{\text{d_0}})/\text{KSI}_{m} - (1/3)); \\
\text{PSI} & := 1 + ((\text{ReactorLength}/\text{deq})^3/4 - ((\text{ReactorLength}/\text{deq})^2)^2) \times (
\text{SQRT}(((\text{ReactorLength}/\text{deq})^2 + 1))/4) + 
((\text{SQRT}(((\text{ReactorLength}/\text{deq})^2 + 1))/8 - 
(9/8 \times (\text{ReactorLength}/\text{deq})) \times 
\text{LOG}((\text{ReactorLength}/\text{deq}) + 
(SQRT(((\text{ReactorLength}/\text{deq})^2 + 1))))); \\
\text{Dummy} & := \text{TIME}; \\
\text{END} & : \text{TIME}; \\
\text{PRESET} & \text{RESTORE "US"}; \\
\text{INITIAL} & \text{US.}\text{Temp}(0|+:\text{US.}\text{ReactorLength}|-,\text{US.}\text{ReactorRadius}) = \text{US.}\text{Temp}_{\text{inlet}}; \\
\text{SOLUTIONPARAMETERS} & \text{gPLOT := ON;}; \\
\text{gRMS} & := \text{ON}; \\
\text{ReportingInterval} & := 1; \\
\text{SCHEDULE} & \text{Gradually change Dummy from 0 to 1} \\
\text{SEQUENCE} & \text{START-UP} \\
\text{RESET} & \text{US.}\text{mf}_{\text{inlet}} := (\text{US.}Y_{\text{CH4}} \times \text{US.}\text{MW}_{f})/ 
((\text{US.}Y_{\text{CH4}} \times \text{US.}\text{MW}_{f}) + (\text{US.}Y_{\text{AIR}} \times \text{US.}\text{MW}_{a})) ; \\
\text{END} & \text{CONTINUE FOR 30} \\
\text{LOAD DISRUPTION} & \text{RESET} \\
\text{US.}\text{mf}_{\text{inlet}} & := 0; \\
\text{END} & \text{CONTINUE FOR 3} \\
\text{RESET} & \text{US.}\text{mf}_{\text{inlet}} := (\text{US.}Y_{\text{CH4}} \times \text{US.}\text{MW}_{f})/ 
((\text{US.}Y_{\text{CH4}} \times \text{US.}\text{MW}_{f}) + (\text{US.}Y_{\text{AIR}} \times \text{US.}\text{MW}_{a})) ; \\
\text{END} & \text{CONTINUE FOR 30} \\
\text{SHUTDOWN} & \text{RESET} \\
\text{US.}\text{U}_{\text{ref}} & := 0; \\
\text{US.}\text{mf}_{\text{inlet}} & := 0; \\
\text{END} & \text{CONTINUE FOR 1000} \\
\text{END} & \text{END # Process Simulation}
A.3

The sublimation rate with respect to flow direction at a helium flowrate of 55 ml/min and temperature of 170°C is shown in Figure A.1.

Figure A.1: Effect of flow direction with respect to sample boat, on the sublimation rate of 50mg Pd(acac)$_2$ at 170°C and helium flowrate 55ml/min.
Appendix

A.4

The washcoat and cordierite wall thickness of a typical $\gamma$-Al$_2$O$_3$/cordierite monolith is shown in Figure A.2.

Figure A.2: Image of cordierite wall between two layers of washcoat of a typical $\gamma$-Al$_2$O$_3$/cordierite monolith.
A.5

The calibration curve of the atomic absorption spectroscope is shown in Figure A.3, while the raw data obtained are given in Table A.2.

![Calibration curve for atomic absorption spectroscope](image)

**Figure A.3:** Calibration curve for atomic absorption spectroscope.
<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Volume of Solution (ml)</th>
<th>Absorbance</th>
<th>Blank</th>
<th>Corrected Absorbance</th>
<th>Concentration of Palladium (µg/ml)</th>
<th>Mass of Palladium (µg)</th>
<th>Overall Mass of Catalytic Monolith (g)</th>
<th>Palladium Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 1</td>
<td>50</td>
<td>0.044</td>
<td>0.002</td>
<td>0.042</td>
<td>4.12</td>
<td>206</td>
<td>1.67</td>
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Table A.2: Atomic absorption raw data.
A.6

The thermocouple pulling device used in the catalytic combustion set-up is shown in Figure A.4.

Figure A.4: Thermocouple pulling device.