Materials for High-Temperature Catalytic Combustion

Anders Ersson

KTH-Kungliga Tekniska Högskolan
Department of Chemical Engineering and Technology
Chemical Technology

Stockholm 2003

PhD Thesis
TRITA-KET R176
ISSN 1104-3466
ISRN KTH/KET/R—176--SE
ISBN 91-7283-482-X

To family and friends

***Front cover**: Grossular from Herräng, Uppland, Sweden, a naturally occurring member of the garnet group (Photo and collection Anders Zetterqvist).*

Abstract

Catalytic combustion is an environmentally friendly technique to combust fuels in e.g. gas turbines. Introducing a catalyst into the combustion chamber of a gas turbine allows combustion outside the normal flammability limits. Hence, the adiabatic flame temperature may be lowered below the threshold temperature for thermal NO_X formation while maintaining a stable combustion. However, several challenges are connected to the application of catalytic combustion in gas turbines. The first part of this thesis reviews the use of catalytic combustion in gas turbines. The influence of the fuel has been studied and compared over different catalyst materials.

The material section is divided into two parts. The first concerns bimetallic palladium catalysts. These catalysts showed a more stable activity compared to their pure palladium counterparts for methane combustion. This was verified both by using an annular reactor at ambient pressure and a pilot-scale reactor at elevated pressures and flows closely resembling the ones found in a gas turbine combustor.

The second part concerns high-temperature materials, which may be used either as active or washcoat materials. A novel group of materials for catalysis, i.e. garnets, has been synthesised and tested in combustion of methane, a low-heating value gas and diesel fuel. The garnets showed some interesting abilities especially for combustion of low-heating value, LHV, gas. Two other materials were also studied, i.e. spinels and hexaaluminates, both showed very promising thermal stability and the substituted hexaaluminates also showed a good catalytic activity.

Finally, deactivation of the catalyst materials was studied. In this part the sulphur poisoning of palladium, platinum and the above-mentioned complex metal oxides has been studied for combustion of a LHV gas. Platinum and surprisingly the garnet were least deactivated. Palladium was severely affected for methane combustion while the other washcoat materials were most affected for carbon monoxide and hydrogen.

Keywords: *catalytic combustion, catalyst materials, palladium, platinum, bimetallic, garnet, spinel, hexaaluminate, deactivation, sulphur, poisoning, diesel, methane, hydrocarbons*

Sammanfattning

Katalytisk förbränning är ett miljövänligt allternativ till konventionell förbränning i t.ex. gasturbiner. Genom att introducera en katalysator i förbränningsrummet kan man upprätthålla en stabil förbränning utanför de normala flamgränserna. Temperaturen kan därmed sänkas och bildandet av termisk NO_X undvikas. I den första delen av avhandlingen ges en kort översikt av katalytisk förbränning i gasturbiner. Vidare följer en undersökning av hur olika bränslen inverkar på den katalytiska förbränningen över olika katalysatormaterial.

Materialsektionen av avhandlingen består av två delar. Den första berör bimetalliska palladiumkatalysatorer. Dessa visade sig ha en mer stabil aktivitet för förbränning av metan jämfört med rena palladiumkatalysatorer. Vilket också verifierades både i labskala i en annulär reaktor vid atmosfärstryck och i pilotskala vid tryck och gashastigheter jämförbara med förhållandena i en verklig gasturbin.

Den andra delen berör högtemperaturmaterial, vilka antingen kan användas aktiva katalysatormaterial eller utgöra washcoat. En för katalys ny grupp material, granater, testades för förbränning av metan, lågvärmevärdesgas (lvv-gas) och en syntetisk diesel. Granaterna uppvisade intressanta egenskaper speciellt för förbränning av lvv-gasen. Vidare har två andra materialgrupper, hexaaluminater och spineller, studerats. Båda uppvisade en mycket lovande termisk stabilitet. De substituerade hexaaluminater visade också en god katalytisk aktivitet.

Avslutningsvis har deaktivering av katalysatormaterialen studerats. Här har bland annat svavelförgiftning av palladium, platina och de ovan nämnda komplexa metalloxiderna studerats för förbränning av lvv-gas. Platina och överraskande nog också granatmaterialet blev minst förgiftade. För palladium påverkades metanförbränningen negativt medan förbränningen av kolmonoxid och vätgas påverkades negativt över de övriga metalloxiderna.

Nyckelord: *katalytisk förbränning, katalysatormaterial, palladium, platina, bimetaller, granat, spinell, hexaaluminat, deaktivering, svavel, förgiftning, diesel, metan, kolväten*

PUBLICATIONS REFERRED TO IN THIS THESIS

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

I. Johansson, E. M., Papadias, D., Thevenin, P. O., Ersson, A. G., Gabrielsson, R., Menon, P. G., Björnbom, P. H., Järås, S. G. (1999), **Catalytic Combustion for Gas Turbine Applications**, in J. J. Spivey (Ed.) Catalysis – A Specialist Periodical Report, **14**, Royal Society of Chemistry, Cambridge, pp. 183-235.

II. Ersson, A. G., Kušar, H. M., Järås, S. G. (2003), **Catalytic combustion of diesel fuel**, submitted to Appl. Catal. A.

III. Ersson, A., Kušar, H., Carroni, R., Griffin T., Järås, S. (2003), **Catalytic combustion of methane over bimetallic catalysts a comparison between a novel annular and a high-pressure reactor**, accepted for publication in Catal. Today.

IV. Ersson, A. G., Johansson, E. M., Järås, S. G. (1998), **Techniques for Preparation of Manganese-Substituted Lanthanum Hexaaluminates**, B. Delmon et al (Eds.) Studies in Surface Science and Catalysis, **118,** Elsevier, Amsterdam, pp. 601-608.

V. Ersson, A. G., Kušar, H. M., Järås, S. G. (2003), **Catalytic combustion over novel garnet-based catalysts**, submitted to Appl. Catal. B.

VI. Thevenin, P. O., Ersson, A. G., Kušar, H. M. J., Menon, P.G., Järås, S. G. (2001), **Deactivation of High Temperature Combustion Catalysts**, Appl. Catal. A, **212**, 189-197.

VII. Kušar, H. M. J., Ersson, A. G., Thevenin, P. O., Järås, S. G. (2001), **Sulfur Poisoning in Catalytic Combustion of Gasified Waste**, in J.J. Spivey, B.H. Davis (Eds.) Studies in Surface Science and Catalysis, **139**, Elsevier, Amsterdam, pp. 463-470.

OTHER PUBLICATIONS

Other publications and conference papers on catalytic combustion and environmental catalysis not included in this thesis.

Papers

1. Johansson, E. M., Danielsson, K. M. J., Ersson, A. G., Järås, S. G. (1998), **Development of hexaaluminate catalysts for combustion of gasified biomass in gas turbines**, ASME Paper 98-GT-338, 1998.

2. Johansson, E. M., Danielsson, K. M. J., Ersson, A. G., Järås, S. G. (2002), **Development of hexaaluminate catalysts for combustion of gasified biomass in gas turbines**, J. Eng. Gas Turbine Pow., **124**, 235-238.

3. Kušar, H. M. J., Ersson, A. G., Järås, S. G. (2003), **Catalytic combustion of Gasified Waste**, accepted for publ. in Appl. Catal. B.

Conference contributions:

Oral presentations:

4. Thevenin, P. O., Ersson, A. G., Järås, S. G. (1998), **Catalytic Combustion of Ethanol and Diesel for Mobile Gas Turbine Applications**, Oral presentation/book of abstracts, 2nd World Congress on Environmental Catalysis, Miami Beach, USA.

5. Ersson, A. G., Thevenin, P. O., Menon, P. G., Järås, S. G. (1999), **The Influence of Preparation Techniques on the Catalytic Combustion of Diesel over Manganese Substituted Lanthanum Hexaaluminates**, Oral presentation/book of abstracts, EuropaCat IV, Rimini, Italy.

6. Ersson, A. G., Thevenin, P. O., Järås, S. G. (1999), **Novel High-Temperature Stable Catalyst Materials for Catalytic Gas Turbine Combustors**, Oral presentation/book of abstracts, 4th International Workshop on Catalytic Combustion, San Diego, USA.

7. Kušar, H. M. J., Ersson, A. G., Thevenin, P. O., Järås, S. G. (2000), **Catalytic Combustion of Gasified Industrial Waste**, Oral presentation/book of abstracts, 16th Canadian Symposium on Catalysis, Banff, Canada.

8. Ersson, A. G., Kušar, H. M. J., Carroni, R., Griffin, T., Järås, S. G. (2002), **Catalytic combustion of methane over palladium - a comparison between a novel annular and a high-pressure reactor**, Oral presentation/book of abstracts, 5th International Symposium on Catalytic Combustion, Seoul, Korea.

9. Jayasuriya, J., Fredriksson, J., Fransson, T., Ersson, A., Järås, S. (2003), **Catalytic Combustion Developments for Ultra Low Emission Gas Turbine Combustion,** accepted for oral presentation, 7th International Conference on Energy for a Clean Environment, Lisbon, Portugal.

Poster presentations:

10. Ersson, A. G., Johansson, E. M., Järås, S. G. (1998), **Catalytic Combustion of Diesel and Kerosene Fuels**, Poster presentation/book of abstracts, 8th Nordic Symposium on Catalysis, Oslo, Norway

11. Ersson, A. G., Johansson, E. M., Järås, S. G. (1998), **Techniques for Preparation of Manganese-Substituted Lanthanum Hexaaluminates**, Poster presentation/book of abstracts, 7th International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium.

12. Thevenin, P. O, Ersson, A. G., Menon, P. G., Järås, S. G. (1999), **Effect of Water Content in the Fuel for Catalytic Combustion of Ethanol Over Hexaaluminate Catalyst,** Poster presentation/book of abstracts, EuropaCat IV, Rimini, Italy.

13. Ersson, A. G., Kušar, H. M. J., Järås, S. G. (2000), **Catalytic Combustion of Diesel Fuels**, Poster presentation/book of abstracts, 9th Nordic Symposium on Catalysis, Lidingö, Sweden.

14. Kušar, H. M. J., Ersson, A. G., Järås, S. G. (2000), **Formation of Fuel-NO_X in Catalytic Combustion of Gasified Industrial Waste**, Poster presentation/book of abstracts, 9th Nordic Symposium on Catalysis, Lidingö, Sweden.

15. Ersson, A. G., Kušar, H. M. J., Thevenin, P. O., Järås, S. G. (2000), **Catalytic combustion of C1 to C6 hydrocarbons**, Poster presentation/book of abstracts, 16th Canadian Symposium on Catalysis, Banff, Canada.

16. Kušar, H. M. J., Ersson, A. G., Berg, M., Järås, S. G. (2001), **Catalytic Combustion of Gasified Low Heating Value Gas: Pilot scale tests using real gasified industrial waste,** Poster presentation/book of abstracts, 3rd International Conference on Environmental Catalysis, Tokyo, Japan.

17. Ersson, A. G., Kušar, H. M. J., Berg, M., Järås, S. G. (2001), **Catalytic combustion of diesel: A comparison between lab- and pilot scale tests**, Poster presentation/book of abstracts, 3rd International Conference on Environmental Catalysis, Tokyo, Japan.

18. Ersson, A. G., Kušar, H. M. J., Menon, P. G., Järås, S. G. (2001), **The Influence of Catalyst Materials on the Catalytic Combustion of C1 to C7 hydrocarbons,** Poster presentation/book of abstracts, Europacat V, Limerick.

19. Kušar, H. M. J., Ersson, A. G., Menon, P. G., Järås, S. G (2001), **NO_X formation from fuel bound nitrogen in catalytic combustion of low heating value fuels**, Poster presentation, Europacat V, Limerick.

20. Ersson, A. G., Kušar, H. M. J., Eriksson, S., Järås, S. G. (2002), **Catalytic combustion of methane over nano-sized bimetallic catalysts**, Poster presentation/book of abstracts, 5th International Symposium on Catalytic Combustion, Seoul, Korea.

21. Kušar, H. M. J., Eriksson, S., Ersson, A. G., Boutonnet, M., Järås, S. G. (2002), **Catalytic combustion of waste over bimetallic catalysts,** 10th Nordic Symposium on Catalysis, Helsingör, Denmark**.**

22. Ersson, A., Vosecký, M., Kušar, H., Carrera, A., Järås, S. (2003), **Selective catalytic oxidation of NH_3 in gasified biomass**, submitted to EuropaCat VI, Innsbruck, Austria.

23. Fakhrai, R., Carrera, A., Vosecký, M., Fransson, T., Ersson, A., Järås, S. (2003), **A New Experimental Investigation of Catalytic Conversion of NH_3 to N_2 In The Context of Pilot Scale Catalytic Combustion of Biomass for Gas Turbine Application**, submitted to EuropaCat VI, Innsbruck, Austria.

24. Jayasuriya, J., Fredriksson, J., Fransson, T., Ersson, A,. Järås, S. (2003), **High Pressure Catalytic Combustion of Methane – An Experimental Investigation of Pd-based Catalysts under Modern Gas Turbine Operating Conditions,** submitted to EuropaCat VI, Innsbruck, Austria.

Table of contents

- 1 - INTRODUCTION

Since the dawn of civilisation man has used fire to generate heat and light. In the beginning the heat was just used for heating and cooking. During the 18th century the invention of the steam engine made it for the first time possible to convert thermal energy of the fuel into useful work, something that earlier was produced mainly from hydropower. The invention of the steam engine is one of the reasons for the industrial revolution that shaped the world that we see today. During the last part of the 19th and the early part of the 20th century several other engines were developed, e.g. the Otto engine, the diesel engine, the steam turbine and the gas turbine. All of which are based on thermal combustion of fuels. The demand for energy has risen sharply during the 20th century; although power sources such as nuclear power have been developed during this period, the main contribution to the world's power demand still comes from combustion of fuels.

The use of combustion is not without problems. The combustion process generates a multitude of emissions of which many are harmful or even lethal to the environment. Some of them are formed when the combustion process is not complete, e.g. carbon monoxide (CO), unburned hydrocarbons (UHC), soot, dioxins etc. However even if the combustion process is fine-tuned some of the emissions are still formed such as nitrogen oxides (NO_X), sulphur oxides (SO_X) and carbon dioxide (CO_2). Especially CO_2 has drawn much attention in recent years as it is a greenhouse gas and contributes to global warming. CO_2 is very hard to avoid, as it is the main product in any form of combustion of hydrocarbon fuels. NO_X can be formed directly from the nitrogen and oxygen in the air if the temperature is high enough, i.e. above 1500 °C.

Introducing a catalytically active surface at which the fuel can react with the air makes it possible to move the combustion outside the normal limits of the air:fuel ratios. By for example using a much higher air to fuel ratio, the adiabatic flame temperature may be lowered below the threshold temperature for NO_X formation at the same time keeping the combustion stable, i.e. yielding very low emissions of NO_X as well as CO, UHC etc.

Catalytic combustion also tends to decrease thermo-acoustic variations, which is a problem in conventional lean-burn combustors. However, even though catalytic combustion has a number of advantages the commercialisation has taken a long time. This is due to a number of demands on the catalytic combustor that have to be met. Natural gas is the primary fuel for stationary gas turbines. Hence, the catalysts have to be very active in order to ignite the methane in the fuel at the compressor outlet temperature. The catalysts also have to withstand the high temperatures achieved in the combustion process as well as to retain their integrity after being submitted to large thermal variations.

1.1 The scope of this work

The scope of this thesis has been to study catalyst materials for combustion catalysts. The main focus has been on the use of high-temperature materials as active phase and/or support materials. The thesis is divided into three main parts.

The first part (paper I) deals with basic considerations in catalytic combustion. It describes the phenomenological background and the advantages and disadvantages with catalytic combustion in gas turbines.

The second part (papers II-V) focuses on different materials for use in combustion catalysts. In paper III, bimetallic materials for use as ignition catalysts are studied and papers II, IV, V consider the preparation and activity of a number of different complex metal oxide materials, which all are aimed for use in the higher temperature range. The fuels considered in these papers vary from methane to a synthetic diesel blend, i.e. n-heptane and toluene.

The third part (papers VI and VII) considers the deactivation of the catalysts. Paper VI deals with the basic considerations of deactivation in high-temperature catalytic combustion processes. The last paper, VII, deals with sulphur poisoning of various complex metal oxides as well as supported palladium and platinum catalysts.

- 2 - COMBUSTION

Combustion has been the primary source of energy since the beginning of civilisation. The first signs of humanoids using combustion in the form of fire have been found in Swartkrans, South Africa and at Chesowanja, in Kenya. These findings are dated back as long as 1.4 to 1.5 million years [James 1989, Goudsblom 1992]. However these findings are disputed. The earliest undisputed finds of the use of fire dates back 240,000 years and comes from Terra Amata, an ancient beach location on the French Riviera [Benditt 1989].

Even though the human society has developed remarkably since the first fires were lit by our ancestors, still today more than 90 % of the world's energy production comes from combustion sources. New energy sources, like nuclear fission, have been developed, but are only responsible for a fraction of the energy produced. All prognoses point at combustion remaining the main source of energy for the foreseeable future. However, during the last century several new combustion technologies have emerged, i.e. internal combustion engines such as the Otto and Diesel engines and the gas turbine, improving the efficiency as well as decreasing the emission levels. The combustion process in itself has proven elusive to the scientific community. For a long time the phlogiston theory founded by Georg Ernst Stahl was predominant, i.e. that the fuels contained phlogiston, a compound that was lost during combustion. This was the prevailing theory during the 18th century. At the end of the 18th century Antoine Lavoisier proposed the oxidation process. However, it is not until recently with the help of novel spectroscopic techniques like laser-induced fluorescence and advanced computer models that a more in-depth knowledge of the combustion process has been gained. Today it is known that combustion is a very complex process involving large numbers of different radicals and other short-lived species. For fuels like diesel or gasoline hundreds of reactions take place at the high temperatures involved in the combustion process.

Although the use of fire is commonly acknowledged as one of the founding pillars of civilisation it is also connected with many hazards. Uncontrolled fire has always been a major problem, but even a well-controlled combustion process is a source of some of the most poisonous compounds known to man, e.g. dioxins etc. The high temperatures and complex chemistry involved in the combustion processes yield emissions of reaction products ranging from small molecules like carbon monoxide and nitrogen oxides up to large particles of soot built up of thousands of polyaromatic hydrocarbons.

2.1 Emissions

The emissions have been divided into two different types, first emissions that are formed due to incomplete oxidation of the fuel and second those connected to the combustion process it self. To the later category belong the formation of NO_X, and CO_2, to the former different emissions of hydrocarbons and CO.

2.1.1 Nitrogen oxides

One of the major contaminants produced from combustion sources is the nitrogen oxides or NO_X. These emissions are damaging both for the environment and for humans. The nitrogen oxides are dangerous for humans if inhaled in as low concentrations as 0.05 ppm [Pitchon & Fritz 1997]. Furthermore NO_X is invoked in the acidification of water and soils as it is transformed into nitric acid. NO_X is also involved in the formation of ground-level ozone via a reaction involving hydrocarbons and sunlight. The ground-level ozone is dangerous for both animals and plants and is responsible for huge damages on crops and forests.

Nitrogen oxides are formed during combustion via four different routes. The first three involve the nitrogen in the combustion air, while the last one involves nitrogen bound in the fuel.

2.1.1.1 Thermal NO_X

Thermal NO_X is formed from the nitrogen and oxygen in the combustion air via a radical mechanism first proposed by Zeldovich (1946).

$$O + N_2 \leftrightarrow NO + N \qquad (1)$$

$$N + O_2 \leftrightarrow NO + O \qquad (2)$$

Reactions (1) and (2) were the steps originally proposed by Zeldovich, later another reaction, (3), was added comprising the extended Zeldovich mechanism [Lavoie et al 1970].

$$N + OH \leftrightarrow NO + H \qquad (3)$$

The production rate is almost linearly dependent on residence time. Moreover the formation rate increases rapidly with flame temperature as is shown in Figure 1. In gas turbines the formation of thermal NO_X becomes important at firing temperatures above 1500 °C.

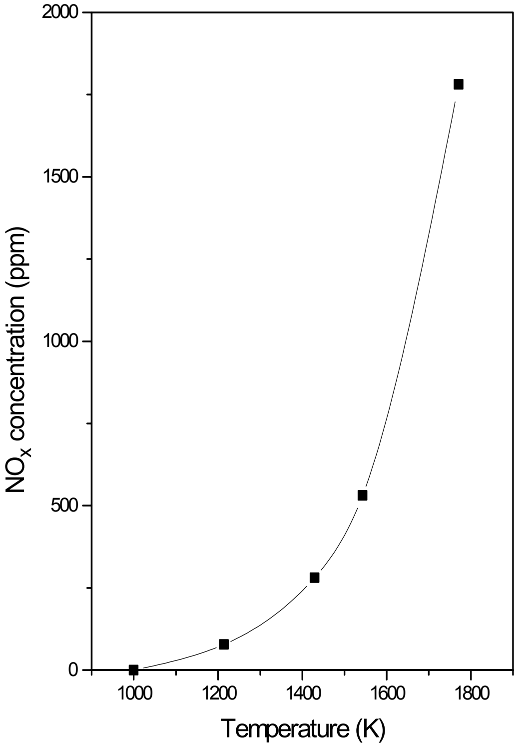

Figure 1. *The formation of thermal NO_X vs. temperature*

2.1.1.2 *Prompt NO_X*

Prompt NO_X is formed from reactions between hydrocarbon radicals and nitrogen molecules forming hydrogen cyanide, which is further oxidised into NO. The formation only takes place in hydrocarbon-containing flames. Most prompt NO_X is formed in rich flames. Prompt NO_X formation may occur at much lower temperatures than the formation of thermal NO_X. The prominent reaction for forming prompt NO_X is:

$$HC + N_2 \rightarrow HCN + N \qquad (4)$$

The N radical can then react further:

$$N + OH \rightarrow H + NO \qquad (5)$$

The formation of prompt NO_X cannot be avoided by lowering the combustion temperature, as is the case for the thermal NO_X, as the formation temperature is much lower than for the thermal NO_X, hence the only way to circumvent its formation is by lowering the amounts of hydrocarbon radicals formed.

2.1.1.3 *Nitrous oxide*

The third way of forming NO_X in flames is via nitrous oxide, N_2O, as an intermediate, which is then oxidised further to NO_X. The first step of the reaction involves a third body, M:

$$N_2 + O + M \rightarrow N_2O + M \qquad (6)$$

The reaction has long been overlooked, the reason for it is that it usually gives an insignificant contribution to the total NO_X in flames. However, in some applications, such as lean premixed combustion in gas turbines where the lean conditions suppress the CH formation and thereby the prompt NO_X formation and the temperature is lower than the threshold temperature for thermal NO_X formation it could be the main contributor to NO_X. The third-body nature of the reaction implies that the high temperature is not as important for the formation and also that the reaction is promoted by higher pressure, which is the case in gas turbine combustors.

2.1.1.4 Fuel NO$_X$

All living organisms contain various amounts of nitrogen, bound to various molecules, like amines etc. When the previously living matter is converted into fuels, either as biomass or during formation of coal or oil some of the nitrogen content will be kept. Except for natural gas, which usually contains insignificant amounts of fuel-bound nitrogen (however a large amount of molecular nitrogen is present), most fuels contains some nitrogen bound to the fuel. As the fuel is being burnt the nitrogen-containing molecules will thermally decompose into low molecular weight compounds and radicals. These radicals will then be oxidised into NO$_X$. The nitrogen contents will almost inevitably be oxidised to nitrogen oxide, as the oxidation process of the nitrogen-containing molecules is very fast, i.e. in the same time-scale as the main chain-branching reactions of the combustion.

2.1.2 Carbon monoxide

Carbon monoxide is well known for its toxicity, as it forms strong bonds to the hemoglobin molecules in the blood. Even in low amounts CO may affect people with heart and lung problems by lowering the uptake of oxygen in the blood. Much of the CO is formed from incomplete combustion of the fuel and high levels of CO are found at part load conditions when the temperature of the combustor is relatively low. If fuel-rich zones are present in the combustor large amounts of CO will be produced. Even at fuel-lean conditions large amounts of CO could be produced due to incomplete combustion. Lefebvre (1983) presents three reasons for CO formation in gas turbines:

1. Inadequate burning rate in the primary zone due to high air/fuel ratio and/or insufficient residence time.
2. Inadequate mixing of the fuel and the air, which produces fuel-rich regions as well as fuel-lean regions, which yields inadequate burning rates.
3. Quenching of the post-flame products by entrainment with the liner wall-cooling air.

As CO is relatively resistant to oxidation this process often sets the lower limit for the residence time and temperature that are needed for complete combustion of the fuel.

2.1.3 Hydrocarbons

In some cases hydrocarbons may survive the combustion zone and be emitted with the flue gases. These hydrocarbons are generally called unburned hydrocarbons, UHC, although the term is somewhat misleading as not only fuel components but also products of thermal degradation are included in the term. Usually inadequate combustion is the reason for these emissions. This could be due to inadequate burning rates, cooling effects of the cooling air or quenching of the reaction at the combustor walls. Emissions of UHC may be poisonous depending on the hydrocarbon involved. Hydrocarbons may also interact with nitrogen oxides and sunlight in order to form ground-level ozone. Some hydrocarbons like methane also have a high global warming potential, see section 2.1.5.

2.1.4 Soot

As early as 1775 Sir Percivall Pott discovered the connection between soot and scrotal cancers among chimneysweepers [Encyclopædia Britannica 2003]. Since then emissions of soot have been regarded as a major health problem. Although large particles of soot are easily visible the main danger is the small particles. These particles easily enter the lungs of humans and can cause cancer and other damage. Moreover, there are several other problems connected to the formation of soot, especially in gas turbines. Soot formed in the combustion chamber enhances the radiation energy emitted to the walls and thereby increases the thermal degradation of the liner. Soot could also be deposited at the walls and when such deposits break loose, due to vibrations etc, major damage may be done to the delicate turbine blades. Moreover, for military aircraft soot emissions may be detected from the ground, which is highly undesirable.

Soot is mainly composed of carbon, ~90 %, and hydrogen, ~10 % and has a graphite-like structure. Soot is formed via a number of steps starting with the formation of the first aromatic ring, which is often considered as the rate-limiting step. The aromatic rings are then reacted to large polyaromatic hydrocarbons, PAH. These PAH then react and form larger 3D structures, i.e. soot particles. The soot particles can collide and stick together and form even larger particles, this process is called coagulation. Further growth is governed by surface growth, i.e. the reaction between acetylene molecules and the surface. Finally the soot particles may form large clusters via so-called agglomeration. The formation of soot is most common in diffusion flames but may also occur in premixed flames. In the former case the choice of fuel is very important while in the latter case the fuel has only a minor influence on the soot formation [Glassman 1996, Haynes 1991].

2.1.5 Greenhouse gases

The increase in temperature at ground level due to the so-called greenhouse effect has during the last decade emerged as one of the most challenging environmental problems. The greenhouse effect is based on the fact that certain gases released to the atmosphere will reflect radiation back to earth and thereby trap heat at the earth's surface. The most well-known greenhouse gas is carbon dioxide, however a number of other gases may act as greenhouse gases. For combustion the most important besides CO_2 is methane, CH_4, and nitrous oxide, N_2O. The different gases have different impacts, in order to access the impact global warming potentials, GWP, have been established for these compounds. The GWP are usually given for a 100 years time horizon and are given with CO_2 as the reference gas, i.e. CO_2 has the value 1. Methane has a GWP of 21 and nitrous oxide has 310, making even small releases of such gases important.

Carbon dioxide is impossible to circumvent in combustion of hydrocarbon fuels, as it is one of the main reaction products. However, the amount of CO_2 released to the atmosphere may be lowered either through making the combustion process more efficient or through capturing of CO_2 from the flue gas. In the latter case the captured CO_2 may be stored either in geological formations such as old oil or gas wells or even deposited at large depths in the oceans. A third way to decrease the emissions of CO_2 to the atmosphere is to use renewable fuels like biomass, i.e. biological materials for which the re-growth of forests/fields will consume similar amounts of CO_2 as were released in the combustion process.

- 3 - GAS TURBINE

In this chapter a brief overview of the gas turbine is given. To understand the application of catalytic combustion in gas turbines it is very important to have some basic knowledge of gas turbines and the conditions prevailing in a combustion chamber.

Gas turbines consist of three main parts, a compressor, a combustion chamber or combustor and a turbine, see Figure 2. Work may be extracted from the turbine either directly, e.g. for propulsion or pumping etc., or via a generator as electricity. In jet engines only a small part of the work is extracted in the turbine and the rest of the thrust is used for propulsion of the plane. For more in-depth information of gas turbines see elsewhere [Lefebvre 1983, Cohen et al 1996].

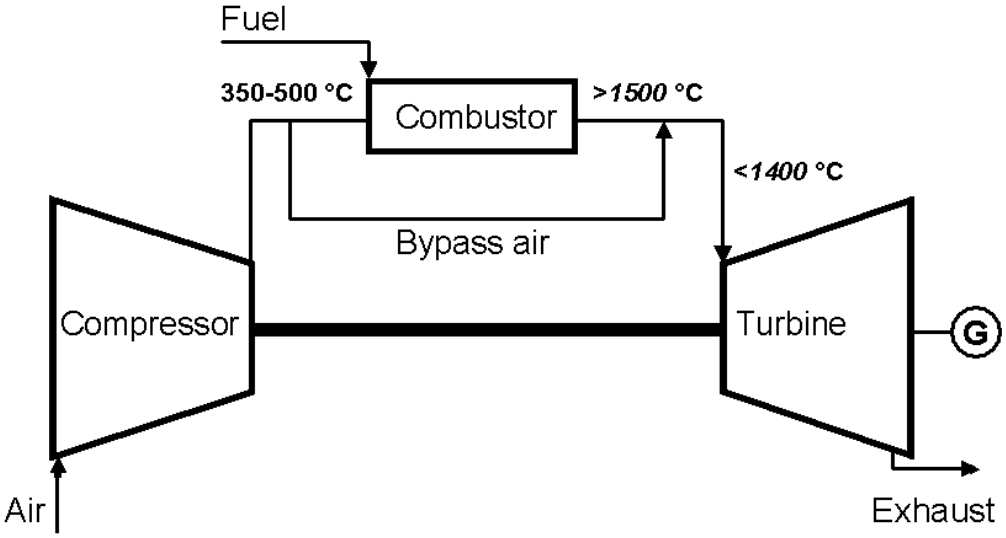

Figure 2. *A schematic of a conventional gas turbine*

The work cycle of a normal gas turbine follows the Brayton cycle, which is shown in Figure 3. First the air is compressed in the compressor increasing the pressure as well as the temperature of the gas. The fuel is combusted in the combustor at almost constant pressure and is then expanded in the turbine and released to the ambient air. In the ideal Brayton cycle the following steps are included: *A-B* isentropic compression, *B-C* constant pressure heat addition, *C-D* isentropic expansion and *D-A* constant pressure heat rejection.

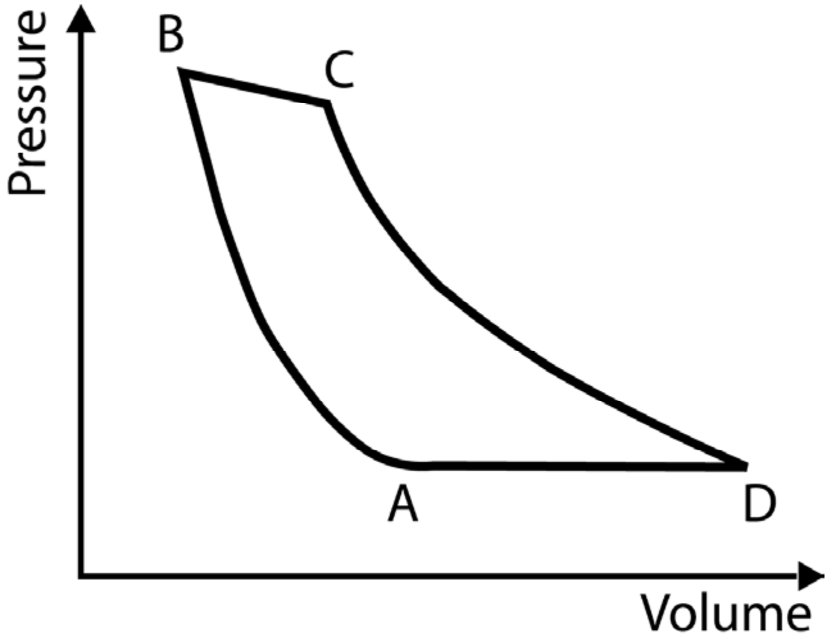

Figure 3. *A pV diagram showing the Brayton cycle for a normal gas turbine*

3.1 Gas turbine parts

In the following sections the parts of the gas turbine are described briefly. The gas turbine combustion chamber is described in a little more detail, as it is important to understand the working of a normal flame combustor before going into the specifics of the catalytic combustor.

3.1.1 Compressor

There are two types of compressors in gas turbines, centrifugal and axial flow compressors. The centrifugal compressor is the simplest and least expensive, however low pressure ratios limit its use to small industrial gas turbines. Most gas turbines today utilise axial flow compressors that allow high pressure-ratios. The axial flow compressor consists of a number of blades mounted around an axis. Each set of blades is called a compressor stage and modern compressor designs yield a compression ratio of about 1.4 to 1 in each stage.

3.1.2 Turbine

The turbine is similar to the axial flow compressor, however the flow is reversed. The blades in the inlet section of the turbine are subjected to very high temperatures as well as large centrifugal forces. The blades have to be carefully designed, using high temperature alloys; in some cases the blades consist of a single crystal to minimize stresses. Higher turbine inlet temperatures result in higher efficiencies and it is therefore of great interest to increase the working temperature of the turbine. However, this puts high demands on the material in the turbine blades. Advanced cooling systems have been designed to cool the blades and thereby allow higher inlet temperatures. This is mostly used in larger stationary gas turbines. Attempts to use high-temperature materials like ceramics have also been made, although most ceramic materials have proven to be too fragile for real applications.

3.1.3 Combustion chamber – combustor

The combustor is the "heart" in a gas turbine; it is where the chemical energy, stored in the fuel, is converted into thermal energy, which is later converted into work in the turbine. The combustor has to sustain the combustion process at the gas velocities and pressures delivered from the compressor. This is obtained by some kind of flame stabilization either by a physical flame holder and/or by designing of the flow field so that a recirculating zone is created, which can maintain the flame.

Three types of combustors are commonly used, the tubular or can type, the annular type and the tubo-annular or can-annular type. Most catalytic designs use the tubular type combustor. This consists of a cylindrical liner mounted concentrically in a cylindrical casing. This type is the simplest and is used mainly in industrial stationary turbines.

Lefebvre (1983) has listed a number of basic requirements for a gas turbine combustor.

1. High combustion efficiency (usually >99 %)
2. Reliable and smooth ignition
3. Wide stability limits
4. Freedom from pressure pulsation etc.
5. Low pressure loss
6. A tailored outlet temperature distribution, pattern factor, to minimise wears on blades etc.
7. Low emissions
8. Designed for minimum cost and ease of maintenance
9. Size and shape compatible with engine envelope
10. Durability
11. Multifuel capability

3.1.4 Low emission combustors

There are a number of different combustion strategies that aim at achieving low emissions of especially NO_X. The most common and maybe most successful so far is the lean-premixed combustion, LP. In LP combustors the fuel and air is premixed before the combustion zone at a ratio close to the lean flammability limit. Hence, the adiabatic flame temperature may be lowered so that only minor amounts of thermal NO_X will be formed, i.e. as low as 10 ppm NO_X could be achieved using advanced LP burners. The major drawback is that the combustion process will be very sensitive and instabilities may easily occur. Such instabilities may give rise to thermo-acoustics which can damaged the turbine.

Another type of low-NO_X burner is the rich-quench-lean burner, RQL. In the RQL the combustor is divided into two parts. In the first part a fuel-rich mixture is burnt after which the combustion process is stopped, i.e. quenched, and the hot combustion gas is then diluted with air to a very lean mixture and burnt in the second, lean part of the combustor. The main drawback with the RQL-burner is its complexity. The combustion process has to be stopped at exactly the right point and the hot gases have to be mixed with excess air before the reaction starts again, all this with a minimum of pressure drop.

Addition of water or steam to the combustion gases may also significantly lower the formation of NO_X. However, this is connected to major changes in the gas turbine designs both regarding the water of the steam handling systems as well as the increase in mass throughput from the injected steam. Recently advanced cycles using large amounts of steam have been proposed to increase the efficiency in gas turbines by combining some of the features of the steam turbines. These wet cycles are however still far from commercialisation.

3.1.5 Exhaust after treatment

There are a number of techniques to clean the exhaust from gas turbines. For NO_X the most common ones are selective catalytic reduction, SCR and selective non-catalytic reduction, SNCR. In both methods the formed NO_X are selectively reduced using a reducing agent, e.g. ammonia or urea. SCR is usually preferred if low NO_X levels are to be achieved. Both processes calls for good process control in order to avoid ammonia slip. If ultra-low NO_X emissions are to be reached processes like the so called SCONOX process have to be used. However, these processes are very costly.

3.2 Gas turbine fuels

Gas turbine fuels can be divided into two groups – i.e. fuels for aviation turbines and fuels for ground-based gas turbines. In the first group liquid fuels such as jet fuel or kerosene are the totally dominating fuels. In the second group the fuel is more dependent on the application. For large-scale power production natural gas is usually considered as the main fuel - however diesel or other fuels may be used as auxiliary fuel. For smaller gas turbines the situation is more complex, liquid fuels are usually used for mobile applications, while natural gas, naphtha or other liquid fuels may be used in smaller stationary gas turbines, depending on availability and price. The use of different fuels affects the combustion process very much, and this is true also for catalytic combustion as will be described in section

4.4. For more information about gas turbine fuels see for example Bartok & Sarofim (1991) and Schobert (1990).

3.2.1 Natural gas – methane

Natural gas is the most abundant fuel for stationary gas turbines for energy production. The natural gas is composed mainly of methane, however the composition differs greatly between different gas fields and even within a gas field there may be considerable well-to-well differences. Natural gas from the well always contains other hydrocarbons than methane such as ethane, propane etc. as well as nitrogen and carbon dioxide. Usually the gas also contains minor amounts of H_2S and nitrogen-containing species. Norway, Russia and the US are large producers of natural gas. It will most likely become one of the primary sources of energy in the near future. Moreover, changing from other fossil fuels to natural gas will decrease the emissions of the greenhouse gas CO_2 to the atmosphere.

3.2.2 Non-methane fuels

Even though natural gas or methane is the most widely used fuel for large-scale power producing gas turbines other fuels are important as well. These fuels may either be used as auxiliary fuel, e.g. diesel or heating oils in natural gas-fired turbines, or as main fuels, e.g. syngas from coal or biomass gasification. For smaller-scale power production, e.g. in distributed power production, a larger variety of fuels is considered depending on the availability and purpose of the turbine. For mobile application liquid fuels such as diesel and kerosene are totally dominating.

3.2.2.1 Gaseous hydrocarbons

The C1 to C4 hydrocarbons are gaseous at ambient conditions and are usually found as part of the natural gas or produced in the refineries. Propane or LPG is a widely used fuel in certain parts of the world where propane is abundant, e.g. in Canada and the US. Propane and butane are both liquefied at fairly low pressures and the storage and handling are therefore easier than for the gaseous methane and ethane.

3.2.2.2 *Diesel/Kerosene/Jet fuel*

Jet fuel and other liquid fuels are important fuels for gas turbines. Jet engines are the most common gas turbines and are totally dominated by liquid fuel. However, also other gas turbines use liquid fuel either as primary or secondary fuel. For stationary gas turbines diesel and/or heavier fractions are usually considered. In Table 1 are some properties for common gas turbine fuels listed.

Table 1. *The properties of different liquid gas turbine fuels*

Fuel	Boiling point range	Number of carbons	Type
0-GT	< 60 °C		Naphta
Jet B	60-260 °C		
1-GT / Jet A	160-260 °C	10-16	Kerosene
2-GT	230-340 °C	12-16	Diesel
3-GT/4-GT	> 230 °C		Heavy oils

3.2.2.3 *Renewable fuels*

As the threat of the global warming has been taken more and more seriously, large efforts have been made to use carbon dioxide-neutral fuels. One such fuel is biomass, which is a mixture of various fuels such as forest residues, spills from the pulp and paper industry, wood, straw and various energy crops [Johansson 1998].

Another group of fuels that is considered as renewable is waste. As the waste is burnt the energy content is utilised and the amount of waste that has to be deposited in landfills is decreased drastically.

One of the main features of all these fuels is that they are highly heterogeneous regarding the chemical compositions as well as physical properties. For biomass the type as well as the place of growth will affect the composition and large variations of especially the minor elements will occur. For wastes the origin is even more important. However, most of the renewable fuels are considered low-heating value fuels. A composition of a typical gasified biomass/waste is shown in Table 2.

Table 2. *The composition of a typical gasified biomass or waste [Johansson 1998]. A similar gas was used in paper V*

Gas component	Amount [%]
N_2	44.3
O_2	0.0
H_2	10.2
CO	14.7
CO_2	13.8
CH_4	4.6
C_2H_4	1.0
H_2O	11.2
NH_3	0.0165
H_2S	0.005

- 4 - CATALYTIC COMBUSTION

Catalytic combustion or catalytic deep oxidation may be divided into two types according to the temperatures involved. Low-temperature catalytic combustion is carried out at temperatures from room temperature up to around 300 °C to 400 °C. Typical for this type of catalytic combustion is that the fuel or, which is often the case, the pollutant is present in minor amounts, i.e. <5000 ppm, and therefore the temperature increase from the reaction will be limited. Low-temperature catalytic combustion is most commonly used for abatement of volatile hydrocarbons, VOC. For this purpose a high reactivity of the catalyst is crucial as usually very large amounts of gas have to be treated and heating will be costly. This type of applications will not be further discussed in this thesis.

The second type of catalytic combustion is high-temperature catalytic combustion; in this case the fuel is combusted over the catalyst mainly to produce heat either for direct use or for transformation to electricity or mechanical work, for example in a gas turbine. In these applications large amounts, >10000 ppm, of fuel are used. Typically the maximum temperatures exceed 1000 °C for these applications, this implies a number of problems for the catalyst. In this thesis the focus will be on the application in gas turbines.

4.1 Introduction

The reaction occurring in total oxidation over a catalytic surface is very different from the reactions taking place in gas phase combustion, even though the final products are the same, i.e. carbon dioxide and water. While gas phase combustion occurs via a large number of radical reactions at high temperatures, its catalytic counterpart occurs via surface or near-surface reactions at as low temperatures as room temperature depending on the fuel and catalyst chosen. The exact reaction pathways for the catalytic oxidation of hydrocarbons are not known and the reaction mechanism may differ between different catalyst materials and fuels. However most results points towards the breaking of the first C-H bond being the rate-limiting step. As soon as this first step has taken place the following steps occur rapidly. However, not only the reaction kinetics can be rate limiting, other processes such as transport to the surface of the catalyst as well as the diffusion of the reactants and products through the porous framework of the catalyst may also be limiting.

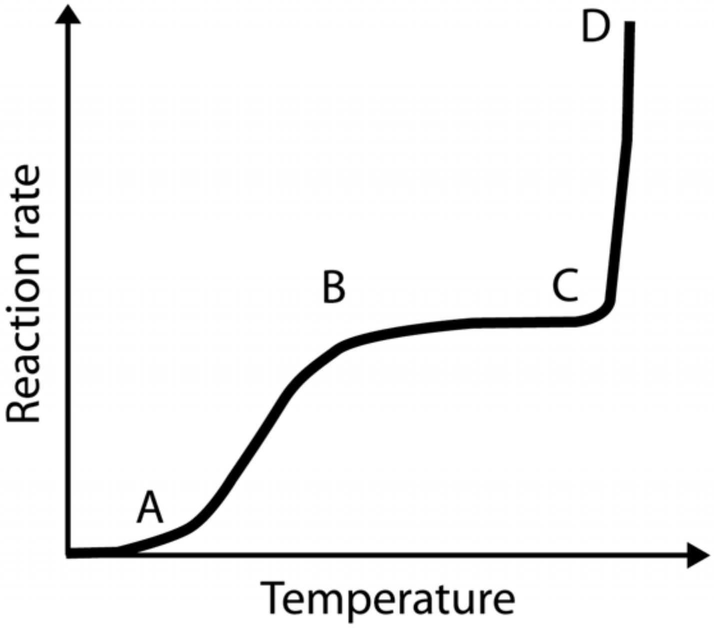

Figure 4. *The different regions of a combustion catalyst, ignition (A), kinetic control (A-B), mass transfer control (B-C) and homogeneous reactions (C-D)*

A schematic of the different regions is shown in Figure 4 [Zwinkels et al 1993]. At low temperatures the kinetics is rate limiting and the reaction rate increases with temperature (A to B). As the reaction rate increases, at a certain point the diffusing reactants will not reach the surface at the same rate as they are consumed and transport will be rate limiting. The diffusion is only slightly dependent on the temperature and therefore the reaction rate is almost constant over the temperature range (B to C). If the temperature is increased even further at a certain point a temperature will be reached when gas phase reactions start to occur and finally the gas phase will ignite. The reaction rate will then increase rapidly (C to D).

4.2 Catalytic combustion in gas turbines (Paper I)

Pfefferle first proposed catalytic combustion for gas turbine applications in the early 70s. Catalytic combustion could offer a number of advantages compared to conventional combustion. Most of these advantages are connected to the catalyst's ability to combust even minute amounts of hydrocarbons without any stability problems. This opens for stable operation of the combustor outside the normal flammability limits. Hence, the flame temperature may be lowered without the unwanted instabilities that occur in conventional lean premixed combustors and the formation of thermal NO_X may be avoided. Moreover, emissions of HC, CO and soot may be kept to a minimum. When applying catalytic combustion to a gas turbine it is very important to understand the special requirements for any catalysts used in a gas turbine combustion chamber.

4.2.1 Requirements

If catalytic combustion is to be commercially viable the catalytic combustion chamber has to meet a number of demands that usually are placed on conventional combustion chambers of modern gas turbines. Recently Carroni et al (2002) have reviewed these demands, see Table 3. All these, or at least most of them, have to be met before the catalytic combustion chamber may be a competitor to conventional low-emission combustors.

Table 3 *Requirements for a catalytic combustion chamber in gas turbines.*

Type:	Requirement:
Inlet temperature	350-450 °C
Exit temperature	1500 °C
Pressure	8-30 bar
Pressure drop	<3 %
Mixedness	80-85 %
Ambient conditions variations	-25 - +40 °C
Working life	>8000 h
Poisons	Sulphur and others
Thermal shocks	>500 °C/s
Multifuel capability	Natural gas / Liquid fuels
Size restrictions	Typically 300 mm length 180 mm diameter

The first demand is also maybe the most problematic one. The fuel-air mixture has to be ignited at a fairly low temperature, which especially in the case of methane has proven very difficult. Although catalysts have been known to ignite even methane at low temperatures these high-activity materials are very susceptible to the high temperatures that will result after igniting the gas. Most studies have therefore focused on conventional materials such as palladium. However the ignition temperature will then usually end up in the 500 °C to 600 °C range. In order to solve this problem the gas has to be preheated either via a heat exchanger or directly using preburners. The heat exchanger will be a major redesign of the gas turbine and is not suitable in most cases. The preburners are a viable engineering solution, however they are likely to contribute to the NO_X production.

The second criterion is also of major importance as the outlet temperature of the combustion chamber corresponds to the maximum temperature of the catalyst if total conversion is achieved within the catalyst. The temperature of 1500 °C is well outside the working range for all conventional catalyst materials, especially if one takes into account the operating time of the catalyst. However the total amount of fuel does not have to be combusted over the catalyst to achieve the benefits of catalytic combustion. As the fuel-air mixture is preheated by the catalytic combustion a stable homogeneous combustion may be achieved after the catalytic zone. This has made it possible to solve the high-temperature problems using different engineering solutions, which will be described more in detail in the subsequent section.

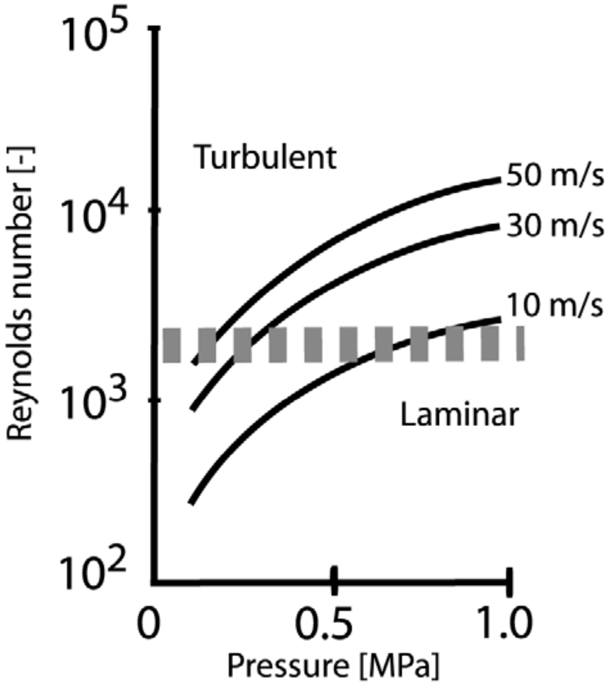

Figure 5. *The Reynolds number, and flow regimes for different gas velocities and pressures in a channel of a 200 cpsi monolith, adopted from Mandai & Gora (1995).*

The difference between the catalytic combustion in gas turbines compared to other applications is the high pressures and flow velocities involved. Only few experimental studies of the influence of pressure have been presented in the literature and therefore the influence of pressure is hard to assess. However, if the flow in the catalyst channels is turbulent the influence of pressure should be limited. The flow regimes at different gas velocities and pressures are shown in Figure 5. The increase in pressure is still important from another aspect, as elevated pressure increases the probability of homogeneous ignition of the air-fuel mixture within the catalyst segments. This has to be avoided, as this would rapidly increase the temperature to the adiabatic flame temperature.

The pressure drop over the combustion chamber including the mixing section is around 3 % for a conventional combustion chamber. This may not be exceeded. This implies some mixing problems, as the mixing will give rise to a pressure drop. Thus perfect mixing might not be achieved. It also implies that hotspots may occur where higher fuel concentrations are present. The mixedness for a conventional lean premixed combustion chamber is usually around 80 to 85 %, which may lead to variations in adiabatic flame temperature of 150 °C. Also most gas turbines are working in places with variations in ambient temperature, for example a gas turbine placed in the north of Sweden may easily have an inlet temperature of the air to the compressor of between –40 °C in winter time and +30 °C in summer time, with subsequent temperature differences in the inlet temperature to the catalyst as a result.

The lifetime requirements would be the same as for the service interval of a conventional combustion chamber, i.e. >8000 h. This puts great demands on the materials used. It is also important for the reliability of the combustor that the catalytic activity stays stable over the operating time, i.e. is resistant towards poisoning, thermal shocks and other forms of thermal degradation. These phenomena will be covered in more detail in Section 6.

4.2.2 System configurations

In order to come to terms with some of the catalyst stability problems in the catalytic combustor a number of different engineering solutions have been proposed. These solutions have mainly been aimed at lowering the temperatures of the catalyst materials and thereby increasing the lifetime of the catalyst. Typically four different types of combustors have been proposed, see Figure 6:

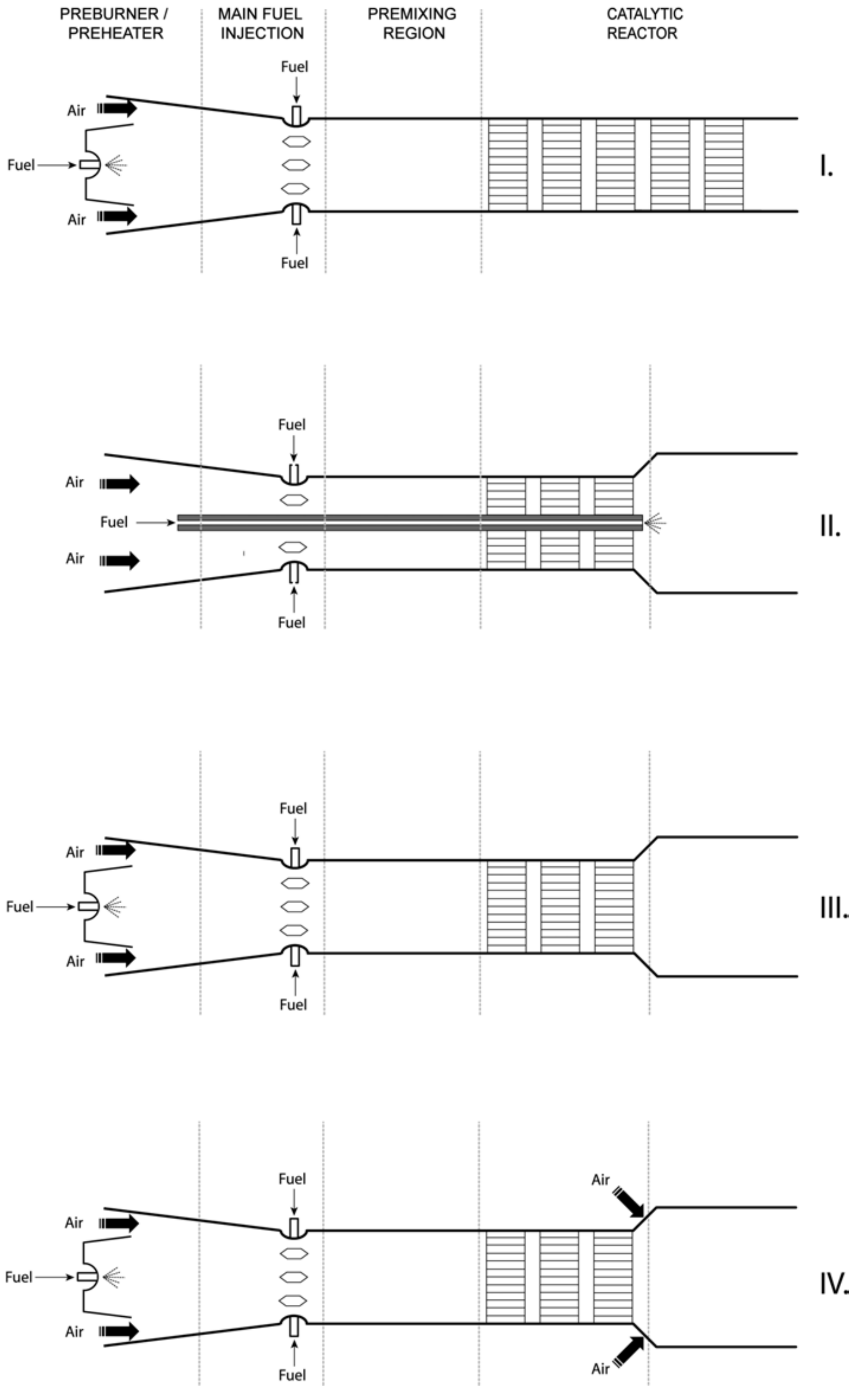

Figure 6. *The four different types of catalytic combustion systems described above. Fully catalytic, I; secondary fuel, II; passive channels, III; secondary air, IV*

1. Fully catalytic: in this design the total amount of fuel is passed over the catalyst segments. This implies that the last segment will see a temperature in the same range as the inlet temperature to the turbine section, i.e. around 1300 °C. The advantage of this type of combustor is its simplicity as no secondary fuel or air has to be mixed in and no flame has to be anchored. However, the very high temperatures in the final segments as well as the difficulty of controlling the heat releases in the first segments will probably make this design difficult for most gas turbine applications. Although for micro-turbines and other applications using a low turbine inlet temperature it still could be a viable solution.
2. Hybrid combustor with secondary fuel: in this design not all of the fuel is allowed to pass over the catalyst segments but some of the fuel is mixed in after the last catalyst segment and is burnt in a homogeneous combustion zone downstream the catalysts. Toshiba has proposed this design in collaboration with Tokyo Electric Power Company. The design is supposed to keep the temperature of the catalyst segments below 1000 °C. The catalyst will work as a preheater increasing the temperature to a level where ultra-lean combustion may take place. Hence, the flame limits could be extended to air-fuel mixtures yielding temperatures well below the ones needed for the formation of thermal NO_X.
3. Passive channels: this design is built on similar ideas as the former design, but instead of mixing in fuel after the last segments only a part of the fuel is burnt over the catalyst. This is achieved by a selective coating of the catalyst channels, i.e. leaving a number of channels uncoated. This has a number of advantages, first there will be no need for a secondary mixing zone after the last catalyst segment and the unreacted gas in the passive channels will heat exchange with the active channels and thereby limit the temperature of the catalyst. However, there will always be a risk of homogeneous reactions taking place in the uncoated channels. An ignition of the

gas in the passive channels will be disastrous, as the temperature in the catalyst segments will reach the turbine inlet temperature.

4. Secondary air: all the above-mentioned designs are based on the lean-premixed combustor design. However, RQL or rich-quench-lean has long been proposed for use in normal flame combustors in order to achieve ultra-low emissions. The last design could be said to be the catalytic equivalent to an RQL combustor. In this design the whole amount of fuel is passed over the catalyst and is allowed to react, the amount of air is modulated so that the temperature increase is within the limits of what the catalyst may endure. After the catalyst segments secondary air is mixed in and the last part of the temperature increase is achieved in a homogeneous combustion zone. The catalyst performs a partial oxidation of the fuel, which will both preheat the gas as well as "upgrade" the fuel by producing more hydrogen and other easily combustible components.

4.2.3 Special gas turbine applications

As mentioned above the introduction of a catalyst stabilises the combustion in a gas turbine combustor. This ability has made catalytic combustion suitable for a number of special gas turbine cycles such as the HAT cycle or wet cycle where large amounts of steam are present in the combustion gas; this normally implies combustion instabilities in a conventional flame combustor [Dalili 2003]. However the large amounts of steam present also affect the catalysts. Palladium catalysts are severely deactivated as formation of Pd-OH occurs. In other materials such as the common washcoat material alumina, steam increases the rate of sintering.

4.3 Other applications

Even if catalytic combustion in gas turbines has received much attention during the last decades other applications have emerged [Saint-Just & der Kinderen 1996]. Some of them have also been commercialised. Most of these applications are for heating or drying purposes. Several types of catalytic industrial burners have been designed [Saracco et al 1999]. The catalytic burners have several advantages over conventional burners:

- Low emissions
- Safety – possible to use in explosive atmospheres
- Performance – efficiency, homogeneity, high modulation radiative power.

Despite the advantages several things are hindering the introduction of catalytic burners, especially the lack of strict enough emission standards but also the lack of high-temperature stable catalyst materials etc. Most of these industrial catalytic burners are aimed for drying applications.

Catalytic burners for household appliances have also been developed and a camping stove was introduced in the end of the 90s. Several projects aiming for the development of a catalytic cooking stove have been performed by e.g. Gastec in Holland and Gaz de France. The main challenges for developers is the long working life, i.e. >5000 h compared to the 300 h for the camping stove and the high power density, i.e. 200 kW/m^2.

4.4 Influence of fuel

Although natural gas is at present the fuel most commonly considered for catalytic gas turbines, a number of other fuels may be considered. As mentioned earlier diesel fuel as well as different renewable fuels, such as gasified biomass or waste, are or will be important gas turbine fuels. The fuels react very differently over the catalysts and it is therefore of great importance to carefully design the catalyst set-up for the fuel.

4.4.1 Single hydrocarbons

It is generally known that methane, which is a very stable molecule, is one of the most difficult hydrocarbons to oxidise over a catalyst. For methane palladium-based catalysts is the catalyst of choice, see section 5.1.1. Catalytic combustion of methane has also been studied over a number of other catalysts both noble metals as well as metal oxides.

For non-methane the literature is much more sparse, especially for the concentrations of interest for gas turbine applications. Most of the literature deals with oxidation of minor amounts of various hydrocarbons in flue gases from different processes [Spivey 1987]. Generally the ease of oxidation increases with the length of the hydrocarbon chain, this is well in accordance with the hypothesis that the breaking of the first carbon-hydrogen bond is the rate-limiting step [O'Malley & Hodnett 1999]. This has been shown by several authors. A typical example of this is shown in Figure 7. In this study a number of hydrocarbons ranging from methane (C1) to n-heptane (C7) have been combusted over three different catalysts, i.e. one palladium-based, another platinum-based and a manganese-substituted lanthanum hexaaluminate. The test conditions were similar to those described in paper II.

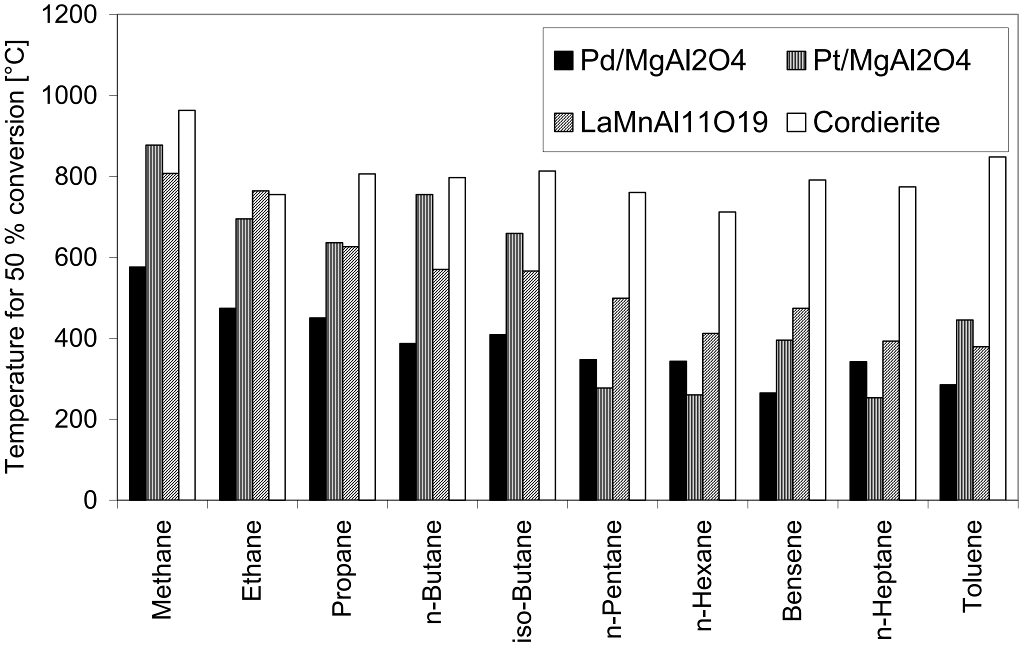

Figure 7. *Temperatures for 50 % conversion of C1 to C7 hydrocarbons over 5 weight % Pd on* $MgAl_2O_4$*, 5 weight % Pt on* $MgAl_2O_4$*,* $LaMnAl_{11}O_{19}$ *and cordierite, i.e. uncoated monolith*

As can be seen in Figure 7 there is a great influence of the type of hydrocarbon on the temperature for 50 % conversion, $T_{50\%}$. There is also a difference between the two noble metal catalysts. For methane and the gaseous hydrocarbons, i.e. ethane, propane and butane, the palladium-based catalyst showed a significantly higher activity. However for liquid paraffins platinum showed the superior activity. The latter is well in accordance with results reported by other authors [Prasad et al 1984]. For the aromatic hydrocarbons used in the study, i.e. benzene and toluene, palladium turned out to be the most active catalyst, which is in contrast to data reported earlier in literature [Prasad et al 1984]. Toluene showed a slightly higher $T_{50\%}$ than benzene, which is well in accordance with literature data [Kim 2002].

4.4.2 *Hydrocarbon mixtures (Paper II)*

As was mentioned in section 3.2 most of the hydrocarbon fuels used consist of mixtures of different hydrocarbons. For example diesel contains a wide variety of hydrocarbons. Usually diesel contains between 5 % and 20 % aromatics. In order to study the catalytic combustion of diesel a synthetic diesel fuel was used, comprised of 20 mol % toluene and 80 mol % n-heptane. The catalytic combustion over a number of palladium, platinum and metal oxide catalysts was studied. Judging from the results presented above for the pure components the catalyst of choice should be a platinum-based catalyst as it has a superior activity for n-heptane combustion. However, as can be seen in Figure 8 the palladium catalyst is the most active one, having a $T_{50\%}$ more than 50 °C lower than the platinum catalyst. The presence of toluene seems to inhibit the oxidation of n-heptane over the platinum catalyst. This effect, and similar, have been reported by several authors [van de Beld et al 1995, Gangwal et al 1988, Ordóñez et al 2002, Papaefthimiou et al 1997]. The explanation could be that the toluene molecule adsorbs strongly onto the platinum surface thereby blocking the access for the more readily reacting n-heptane molecules [Ordóñez et al 2002]. This clearly illustrates the difficulty of transferring single component data to mixtures.

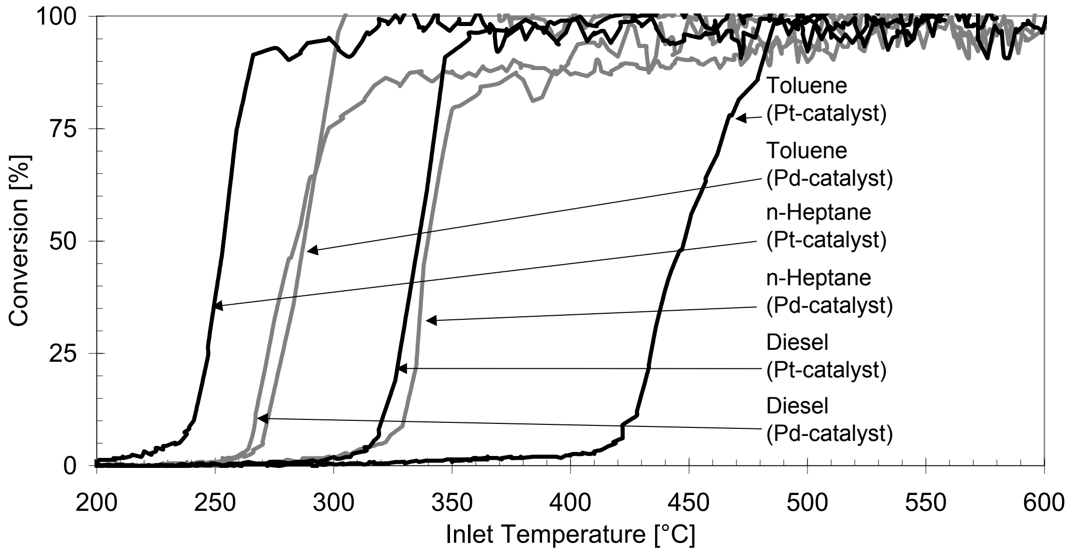

Figure 8. *The conversion of n-heptane, toluene and a mixture of 80 mol % n-heptane and 20 mol % toluene, i.e. a synthetic diesel blend, over Pd-impregnated* $MgAl_2O_4$ *and Pt-impregnated* $MgAl_2O_4$

- 5 - CATALYST MATERIALS

Finding suitable materials for use in catalytic combustion has proven to be a very demanding task. Several review papers have been published dealing with materials for high-temperature catalytic combustion [Zwinkels et al 1993, McCarty et al 1999, Choudhary et al 2002]. There is no single material that could fulfil all the demands on the catalysts in a catalytic combustion chamber and, as was described earlier in section 4.2.2, staging of the catalysts has been proposed to overcome this problem. For a staged combustor three different temperature zones with different demands on the catalyst materials can be found:

1. *The low-temperature catalyst*: This first catalyst segments would preferably ignite the fuel at the compressor outlet temperature, which usually is between 350-550 °C depending on the gas turbine. These catalyst segments have to be highly active and resistant to poisoning etc at low temperatures. This implies the use of highly dispersed noble metals.
2. *The mid-temperature catalyst*: This catalyst segments have to be active in the temperature range between 500 to 1000 °C, depending on the inlet temperature. As accurate temperature control over the whole width of operation parameters will be difficult to achieve the catalyst will have to be designed to withstand higher temperatures. This together with the long time of operation will imply the use of a high-temperature material such as hexaaluminate.
3. *The high-temperature catalyst*: The last catalyst segments have to be extremely stable. However, a high catalytic activity or a large surface area is not necessary since, at the high temperatures regareded, the surface reaction will be very fast and the overall reaction rate will be mass-transfer limited.

For a fully catalytic design, all of these catalysts have to be present in the combustion chamber. For the hybrid concepts, only the first and the second types are needed.

In gas turbines minimising the pressure-drop is of paramount importance, as any pressure drop will directly influence the efficiency. Hence, any catalyst introduced in the combustion chamber has to disturb the flow as little as possible. The use of monolithic catalysts is inevitably needed to fulfil the low pressure-drop at the high flow velocities and pressure present. The monolith acts as support for the washcoat and makes up for the geometrical surface area of the catalyst. A washcoat is applied onto the monolith. The washcoat is usually a material with a large surface area, which may be catalytically active in itself, or act as a support onto which the active phase is dispersed. The nature of the monoliths is discussed in section 5.3. Some of the materials used as active phase and washcoat are described below, see also paper I for more information.

5.1 Noble metals

Noble metals are considered to be the most active of all metals in oxidation reactions. The noble metals are the platinum-group metals, i.e. Pt, Pd, Rh, Ru, Ir and Os as well as gold and silver. Gélin & Primet (2002) recently reviewed the use of noble metals as methane oxidation catalysts. Most widely used in catalytic combustion are palladium and platinum due to their comparatively larger abundance, lower volatility and higher activity than most of the other noble metals. The low volatility is of special importance due to the long operating life of the combustion catalysts in a gas turbine, see section 6. In order to achieve a large exposed metal surface, the noble metals have to be deposited onto some washcoat material in order to keep the metal particles dispersed.

5.1.1 Palladium

Palladium is one of the most active catalysts for the oxidation of methane in excess of oxygen. This, together with its relative abundance and thermal stability has made palladium the prime choice for catalytic combustion. However, in spite of its obvious advantages palladium has a number of drawbacks. Dispersed palladium particles are usually found in the form of palladium oxide at normal temperatures and pressures. However, as the temperature increases the PdO will decompose into metallic palladium.

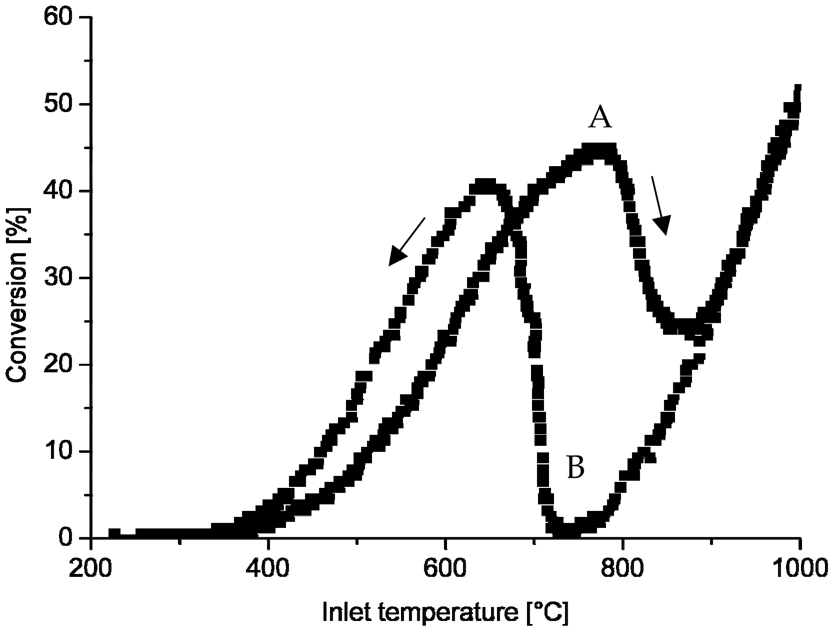

Figure 9. *A typical conversion curve for methane oxidation over a Pd-based catalyst, i.e. 5% Pd on Al_2O_3. Note the hysteresis between the heating cycle and the cooling cycle. A shows the decomposition temperature and B the reformation temperature of the PdO*

This transformation will take place at temperatures around 700-800 °C depending on support material, atmosphere etc. The transformation results in a characteristic conversion curve, as the catalytic activity of metallic palladium is lower than for palladium oxide at the transformation temperature. This is illustrated in Figure 9, which shows oxidation of methane over a palladium on alumina catalyst. Moreover, a hysteresis is present as palladium oxide is reformed at a lower temperature than the decomposition temperature. Temperature-programmed oxidation, TPO, shows that the decomposition of PdO progresses in three different steps, i.e. occurs at three different temperatures, cf. Figure 14. Groppi et al have suggested that PdO is present as two different species where the first species is transformed into the second species [Groppi et al 2000, Groppi et al 2001]. The third peak in the TPO found at high temperatures is supposed to be PdO in close contact with the support. The nature of the two first PdO species is still a matter of discussion. High-temperature XRD has ruled out the possibility of different crystal phases. A hypothesis is that the first species, which also shows the highest activity, could be PdO in close contact with metallic Pd, as many authors suggest the combustion of methane to be a dual-site mechanism involving one reduced site, e.g. metallic Pd, for the dissociation of the methane molecule.

The PdO-Pd transformation has been suggested as a “chemical thermostat” in a gas turbine combustor to avoid overheating the catalyst. This could be achieved by keeping the temperature at A in Figure 9, any increase in temperature will result in a decrease in activity and hence a lower temperature. However, the reality seems to be more complex as can be seen in Figures 10-11, which shows the conversion of methane vs. time on stream at 5 bar with gas velocities and methane concentrations close to real gas turbine conditions. As can be seen every increase in inlet temperature for the fresh catalyst is followed by a large increase in conversion, however this increase is followed by a rapid decline in conversion. For the aged catalyst the peaks are gone but the conversion is lower. An explanation for this could be the above-mentioned different PdO species as the temperatures measured are below the PdO-Pd transformation temperature. Another possible explanation is water inhibition. Water, which is formed in the combustion process, is a well known poison for the PdO catalyst. The water from the reaction forms PdOH which is much less active and hence the decrease in activity [Burch et al 1996, Ciuparu et al 2002]. The support could also affect the conversion as can be seen from Table 5. Palladium was impregnated on three materials, i.e. spinel (cf. section 5.2.1), hexaaluminate (cf. section 5.2.2) and garnet (5.2.3) and the catalytic activity was evaluated for a number of fuels. The order of activity of the Pd catalysts for methane seemed to correlate to the surface area of the support. However, supporting the Pd on an active support as $LaMnAl_{11}O_{19}$ gave a beneficial effect for low-heating value gas, i.e. a mixture of H_2, CO and CH_4, as well as for n-heptane. For the synthetic diesel and toluene similar activities were found for all three catalysts.

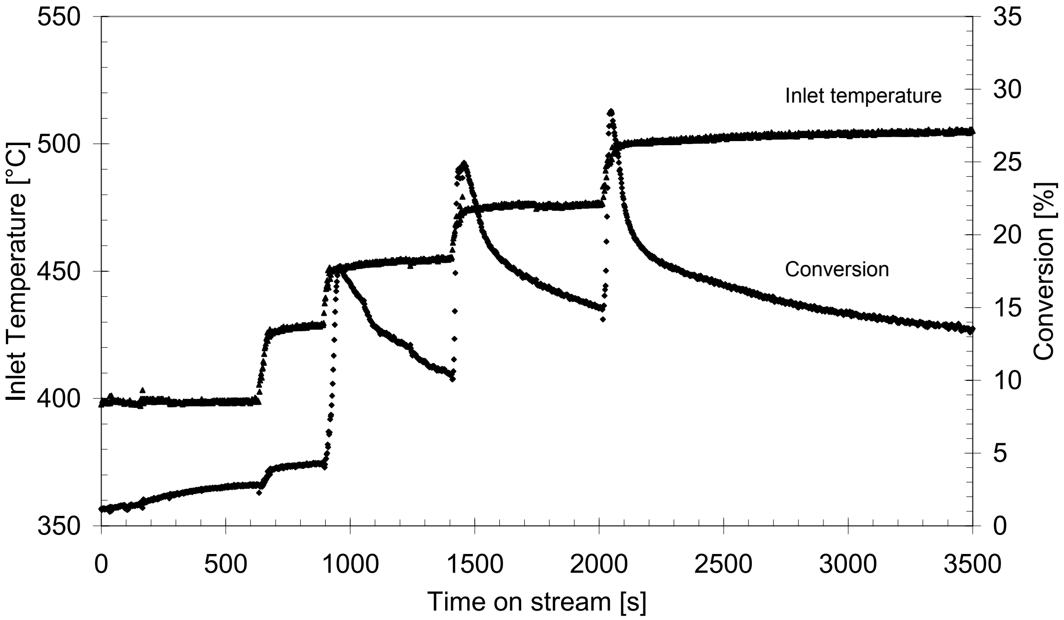

Figure 10. *Catalytic combustion of methane over Pd/alumina catalyst in a pilot-scale reactor at 5 bar and a gas velocity of 15 m/s showing the first cycle*

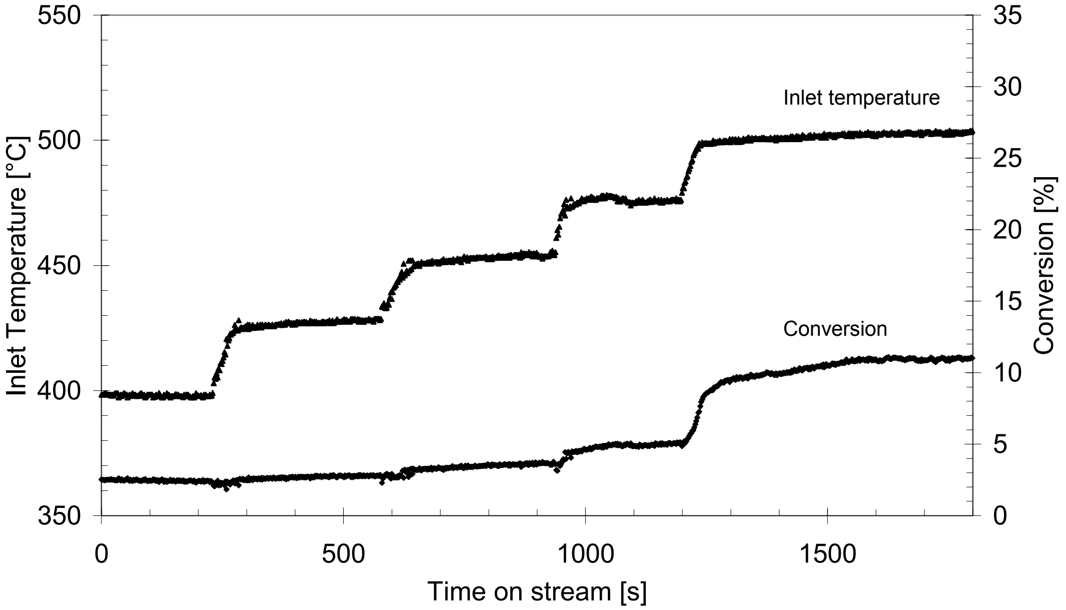

Figure 11. *Catalytic combustion of methane over Pd/alumina catalyst in a pilot-scale reactor at 5 bar and a gas velocity of 15 m/s, after three cycles*

5.1.2 *Other noble metals*

Even if palladium is the prime choice for methane combustion, and thereby the most widely studied catalyst material for gas turbine applications, most other precious metals also show good oxidation abilities. The use of other platinum-group metals is limited by their high-temperature stability, abundance etc. Regarding the former Pd is the least volatile followed by Ir, Pt and Ru. For the latter palladium and platinum are the most abundant followed by Rh, Ir and Ru, however the prices do not always reflect the abundance.

Platinum has been widely studied for low-temperature catalytic oxidation of VOC. As was shown in section 4.4.1 platinum has superior oxidation activity for higher alkanes. Platinum has also proven to be less sensitive to sulphur poisoning than palladium.

Of the precious metals not included in the platinum group, gold has emerged as a very potent oxidation catalyst during the last decade.

In order to be active, however, the gold must be highly dispersed, which limits its use to low temperatures to avoid sintering. Silver has also shown activity for total oxidation [Kundakovic & Flytzani 1999]. Sintering and volatilisation most likely limit the use of silver catalysts at high temperatures.

5.1.3 *Bimetallic catalysts (Paper III)*

As is shown in Figures 10-11 there may be significant problems with the stability of palladium-based catalysts. In order to improve the performance of the palladium-based catalysts another metal can be mixed with the palladium, forming a bi-metallic catalyst. The addition of noble metals such as Pt, Rh, and Ru etc. as co-metals has been studied for many applications including both hydrogenation and oxidation reactions. Several authors have found an enhancement of the catalytic activity for addition of platinum as the co-metal together with palladium [Skoglundh 1991, Narui 1999]. Ryu et al. (1999) have found that the addition of ruthenium could improve the sulphur resistance of palladium. Rhodium, which is an important co-metal in three-way catalysts, has been tested in oxidation reactions by a number of authors but the results have not been conclusive. Some authors have found a beneficial effect [Rassoul 2001, Tochihara 1999] while others have found no effect at all [Ryu 1999].

In paper III the influence of platinum and rhodium as co-metals with palladium has been examined for methane combustion using two different reactors, i.e. an annular and a pilot-scale pressurized reactor. The lab-scale tests were conducted with co-metal:palladium molar ratios of 2:1, 1:1 and 1:2.

The addition of platinum resulted in an increase in activity for the 2:1 and 1:1 ratios for the ignition of the catalysts, cf. Figure 12. The increase was especially pronounced at higher temperatures, i.e. above the transition temperature for PdO to Pd. TPO studies, cf. Figure 14, revealed that the addition of platinum shifted the decomposition peak to much lower temperatures even for low platinum additions, i.e. 2:1. For the 1:2 catalysts the activity dropped and the catalyst behaviour was more “platinum like”. This was also seen in the TPO experiment where no traces of peaks appeared for the 1:2 catalyst. During extinction the pure palladium catalyst showed a higher activity than for the Pt:Pd catalysts; this is also illustrated by the shallow dip in the TPO coming from the re-formation of the PdO. The re-formation is also shifted towards lower temperatures by the addition of platinum.

The addition of rhodium showed a decrease in activity as can be seen in Figure 13; this corresponds well with the TPO results shown in Figure 14. The TPO reveals a much lower peak connected to the main decomposition of PdO occurring at the same temperature as for the pure palladium catalyst.

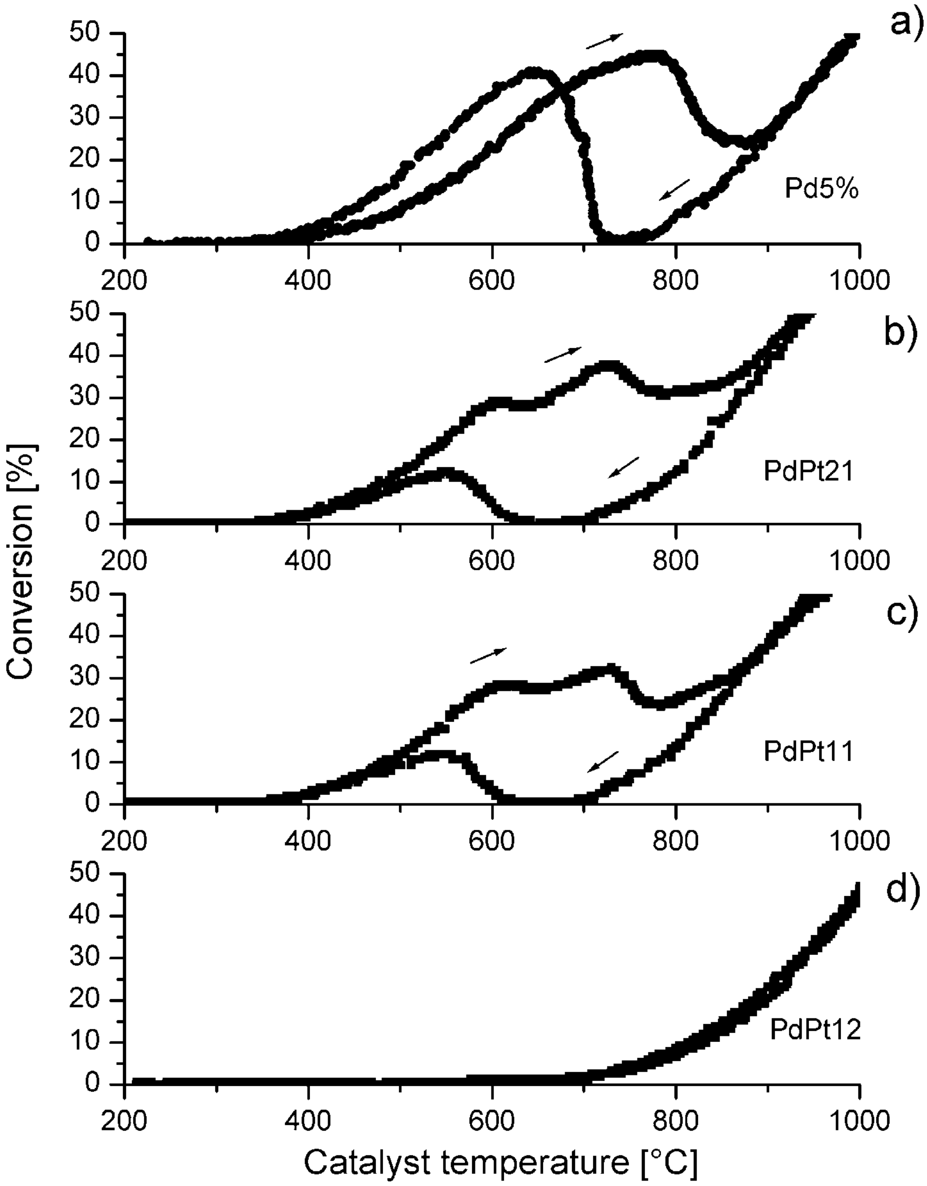

Figure 12. *The combustion of methane over Pd:Pt bimetallic catalysts. Pure Pd shown as a reference a), Pd:Pt ratio of 2:1 b), 1:1 c) and 1:2 d) using an annular reactor and 1.5 vol. % methane in air*

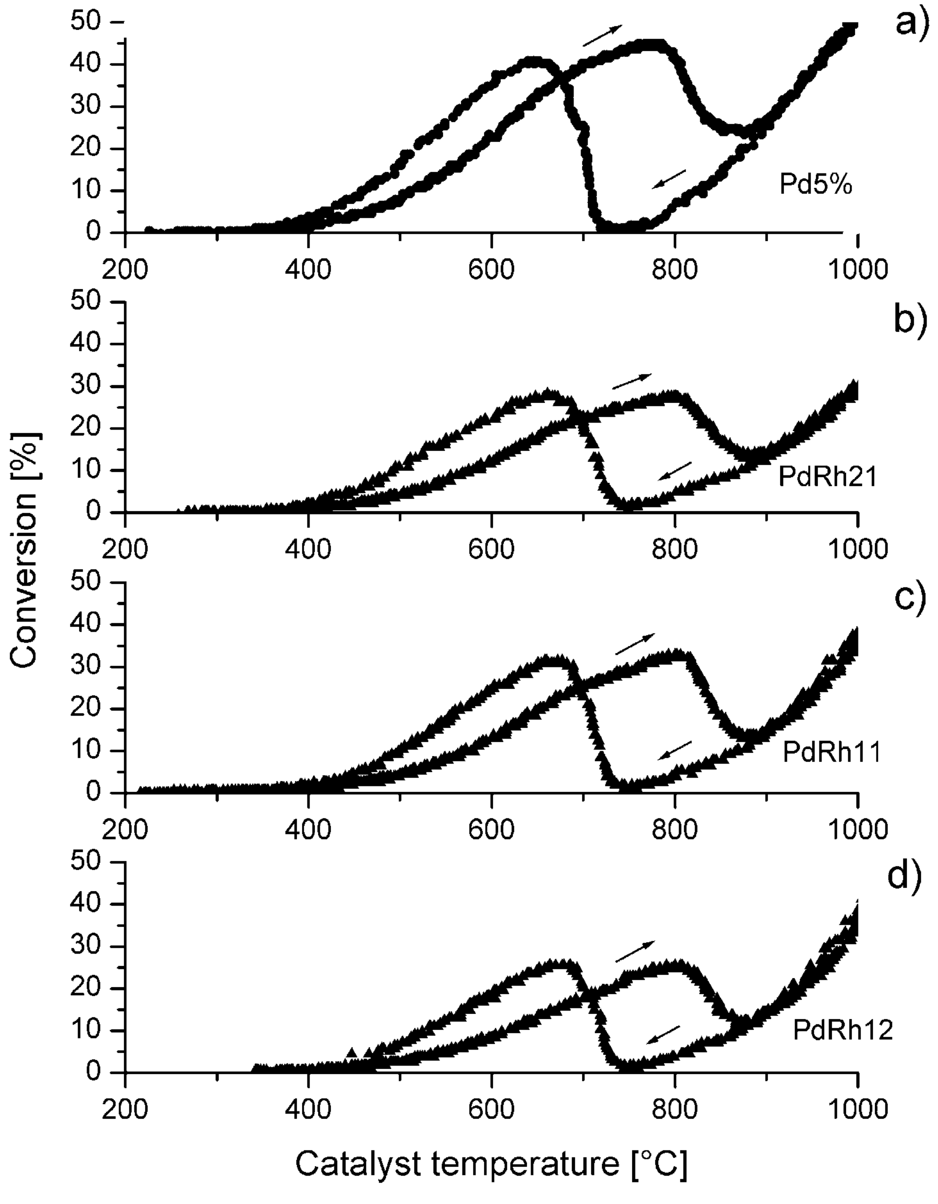

Figure 13. *The combustion of methane over Pd:Rh bimetallic catalysts. Pure Pd shown as a reference a), Pd:Rh ratio of 2:1 b), 1:1 c) and 1:2 d) using an annular reactor and 1.5 vol. % methane in air*

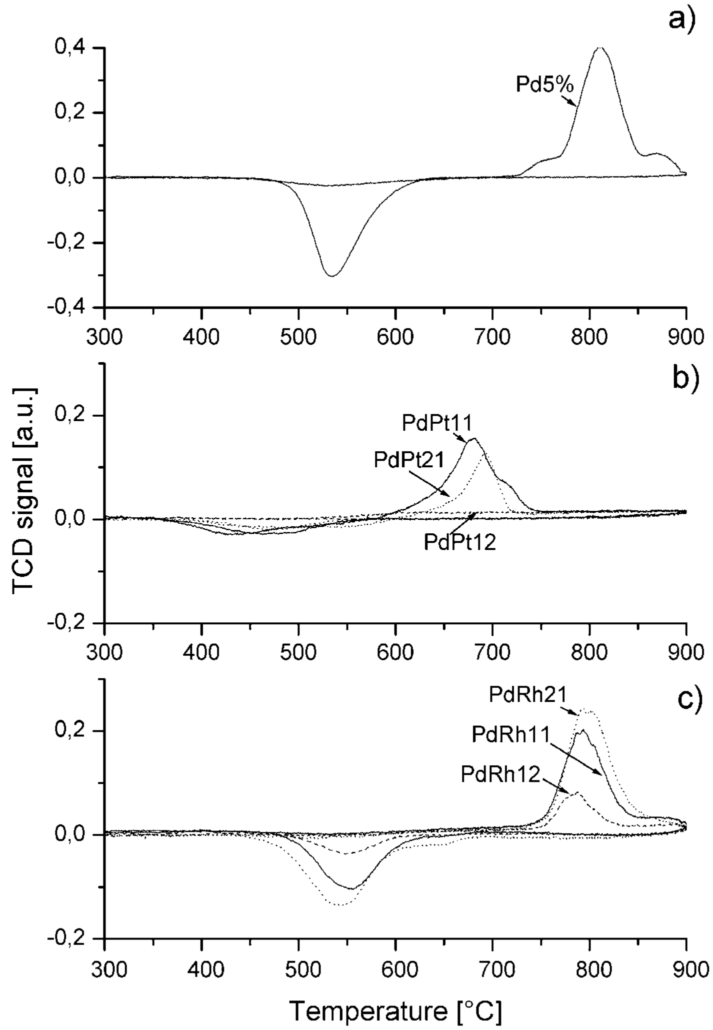

Figure 14. *Temperature programmed oxidation of the bi-metallic catalysts. Note the distinct shift in temperature for the PdO decomposition peak for Pd:Pt compared to pure Pd*

The conversion at constant temperature of methane over Pd:Pt and Pd:Rh are shown in Figure 15 and Figure 16, respectively. The addition of a second metal, both Pt and Rh, to Pd had a positive influence on the stability of the activity. However, the overall activity was significantly lower for the Pd:Rh catalyst compared to the Pd catalysts. The Pd:Pt catalyst showed an activity that was lower than the initial activity of the pure Pd catalysts, however the activity remained stable and thereby surpassing the activity of the pure Pd as its activity decayed with time. Similar beneficial effects were found in the 5 bar tests, for which the activity instabilities were much lower for the fresh catalyst. Moreover, the activity of the "aged" catalyst was higher for the Pd:Pt catalyst compared to the pure palladium catalyst.

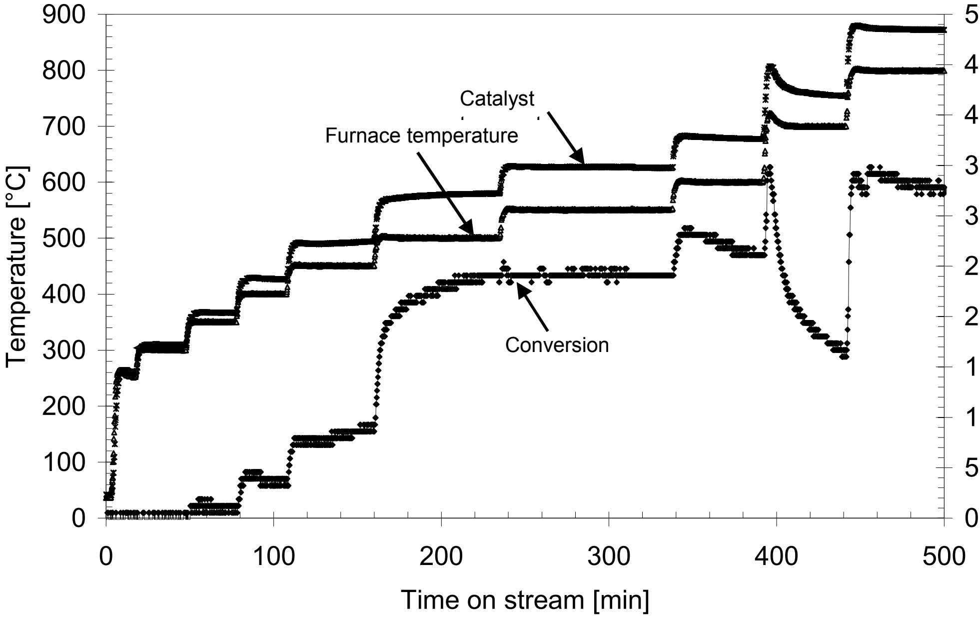

Figure 15. *Conversion at constant temperature of CH_4 over Pd:Pt (1:1 mole ratio) for 1.5 vol. % methane in air in an annular reactor*

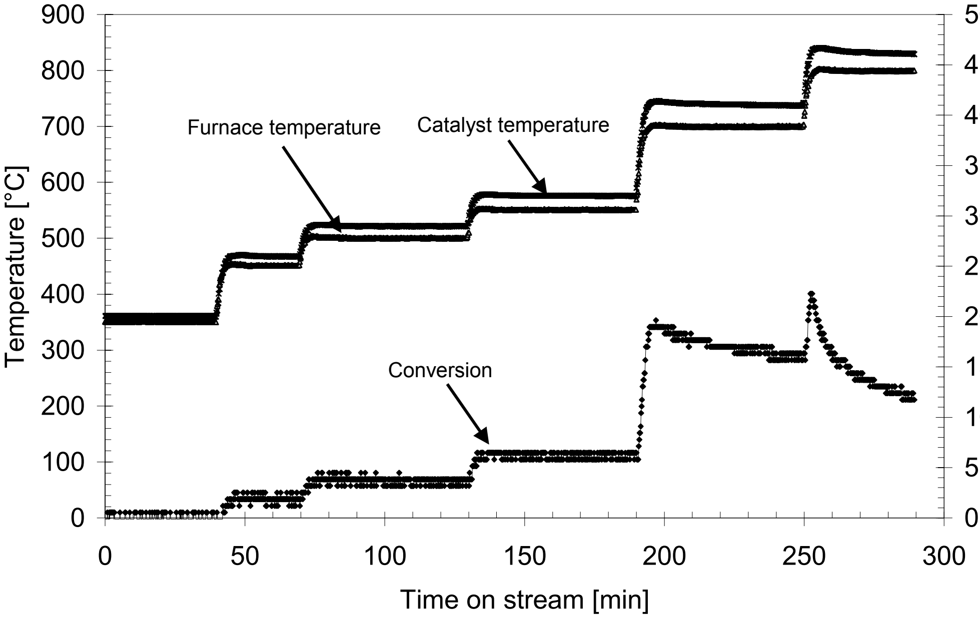

Figure 16. *Conversion at constant temperature of CH_4 over Pd:Rh (1:1 mole ratio) for 1.5 vol. % methane in air in an annular reactor*

5.2 Metal oxide materials

As mentioned earlier the use of noble metals is restricted to the low and mid-temperature part of the combustor. Other, more stable catalysts have to be used as the temperature increases. Higher temperatures increase the reaction rate, which means that the use of a catalyst material with lower activity such as metal oxides is possible. The use of single metal oxides in catalytic combustion has been surveyed by McCarthy et al (1997). The order of reactivity for methane oxidation over single metal oxides supported on $LaAlO_3$ was found to be $PdO > RuO_2 > CoO_4 > CuO > NiO > Mn_2O_3 > Cr_2O_3$. Most of the single metal oxides sinter readily at temperatures above 1000 °C and have to be supported on some kind of washcoat material to maintain a good dispersion. Common washcoat materials such as alumina, zirconia and silica are all limited to working temperatures around 1000 °C. To overcome the stability problems complex oxides may be used; three of these high-temperature stable materials, i.e. spinels, hexaaluminates and garnets, will be described below.

5.2.1 Spinels (Paper II)

Spinels are a group of complex metal oxides with the general formula AB_2X_4 where X usually is oxygen and the B site has octahedral coordination and the A site has either tetrahedral (normal spinel) or octahedral and tetrahedral (inverse spinel) coordination [Müller 1993]. This yields a versatility of possible substitutions into the crystal lattice that may be used to improve the thermal stability as well as the catalytic activity of the material. Several authors have studied catalytic reactions over spinels [Marti et al 1994, Thormälen et al 2001, Xanthopoulou 1999]. Several spinel materials have found use in catalysis as support materials, e.g. in steam reforming. The thermal stability of some spinels, e.g. $MgAl_2O_4$, has been shown to be very good, surface areas of 43 m^2/g after calcination at 1100 °C have been reported in literature [Marti et al 1994]. Large surface areas were also reported for sol-gel prepared $MgAl_2O_4$, i.e. 10 m^2/g, after calcination at 1200 °C for 16 h in 10 % steam [Zwinkels et al 1998]. However, the formation of spinel compounds may also be a problem, supported metal oxides or metals form inactive spinel phases due to solid state reactions between the support and the active phase; this is a problem in many high-temperature catalytic processes, e.g. catalytic cracking etc.

Table 4. *The surface area of the materials in papers II and V after consecutive calcination at 1000 °C (4 h in air), 1200 °C (4 h in air) and 1400 °C (10 h in 15 % steam.)*

Material	Surface area [m²/g]		
	1000 °C	1200 °C	1400 °C
Hexaaluminates:			
$LaAl_{11}O_{19}$	89.3	50.7	9.7
$LaMnAl_{11}O_{19}$	63.5	24.9	10.7
Spinels:			
$MgAl_2O_4$	85.3	32.9	7.5
$MgMn_{0,25}Al_{1,75}O_4$	11.2	9.4	8.1
Garnets:			
$Y_3Al_5O_{12}$	34.3	7.6	3.0
$Y_3Mn_{0,1}Al_{4,9}O_{12}$	71.8	7.5	1.3

In paper II, two different spinels, $MgAl_2O_4$ and $MgMn_{0,25}Al_{1,75}O_4$ were prepared using the co-precipitation technique described in section 5.4.2. The surface areas of the spinel materials are shown in Table 4. The surface area of $MgAl_2O_4$ proved to be comparable to that of the hexaaluminates. For the Mn-substituted spinel the surface area was initially low but the decrease in surface area was very low after the consecutive calcinations at 1200 °C and 1400 °C. The fact that the final crystal phase was present already at 1000 °C for $MgMn_{0,25}Al_{1,75}O_4$ could explain this behaviour, as much of the surface area loss could be attributed to the crystallisation of the material. The incorporation of manganese ions into the crystal lattice seems both to lower the temperature at which the crystallisation takes place as well as render a single-phase material. This could be due to an increased mobility within the crystal lattice connected to stresses occurring due to the incorporation of the Mn^{3+} ion. Similar effects have been found for the hexaaluminates.

Even though the surface areas of the spinels are in the same range as those of the hexaaluminates, the catalytic activity is lower as can be seen in Table 5 and Figure 17. The catalytic activity for the Mn-substituted spinel is much lower than for its hexaaluminate counterpart. In the spinel lattice the manganese ion is fixed as Mn^{3+}, hence the much lower activity for methane combustion of the substituted spinel compared to the hexaaluminate where the Mn ions could be either 2+ or 3+.

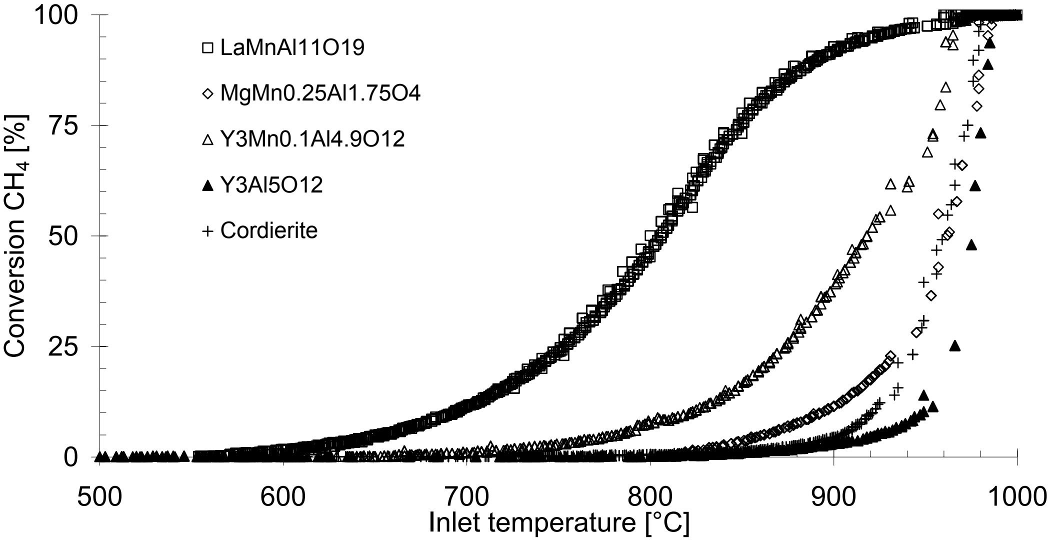

Figure 17. *The conversion of methane vs. inlet temperature to the catalyst for the spinel,* $MgMn_{0.25}Al_{1.75}O_4$*, the garnets,* $Y_3Al_5O_{12}$ *and* $Y_3Mn_{0.1}Al_{4.9}O_{12}$*, and the hexaaluminate,* $LaMnAl_{11}O_{19}$*.and uncoated monolith (cordierite)*

Table 5. *The surface areas and catalytic activities for the catalysts in papers II and V*

Catalyst	Surface area	Temperature for 50 % conversion [°C]						
	[m^2/g]	LHV gas			Methane	n-Heptane	Toluene	Diesel
		H2	CO	CH4				
Pd/$MgAl_2O_4$	32.9	225	225	740	580	340	290	290
Pd/$LaMnAl_{11}O_{19}$	24.9	210	210	545	600	315	280	280
Pd/$Y_3Al_5O_{12}$	7.6	240	240	715	690	350	280	290
Pt/$MgAl_2O_4$	32.9	340	340	740	880	255	445	340
$MgAl_2O_4$	32.9	-	-	-	-	-	-	-
$MgMn_{0,25}Al_{1,75}O_4$	9.4	510	630	750	960	520	640	610
$LaMnAl_{11}O_{19}$	24.9	600	610	725	810	390	380	380
$Y_3Al_5O_{12}$	7.6	460	460	755	975	780	795	760
$Y_3Mn_{0,1}Al_{4,9}O_{12}$	7.5	630	740	740	920	740	690	770

5.2.2 Hexaaluminates (Paper IV)

The hexaaluminates were first proposed as combustion catalysts in the late 80s by Arai et al (1989). Since then, this group of materials has drawn much attention for their high thermal stability and catalytic activity and several reviews have been published covering the hexaaluminates [Groppi et al 1997, Ramesh et al 1997]. Hexaaluminates are a group of materials with the general formula $AB_xAl_{11-x}O_{19-\alpha}$, where the *A* ion is a rare earth or an alkaline earth metal, e.g. La or Ba, and the *B* ion is a transition metal of similar size as the aluminium ion.

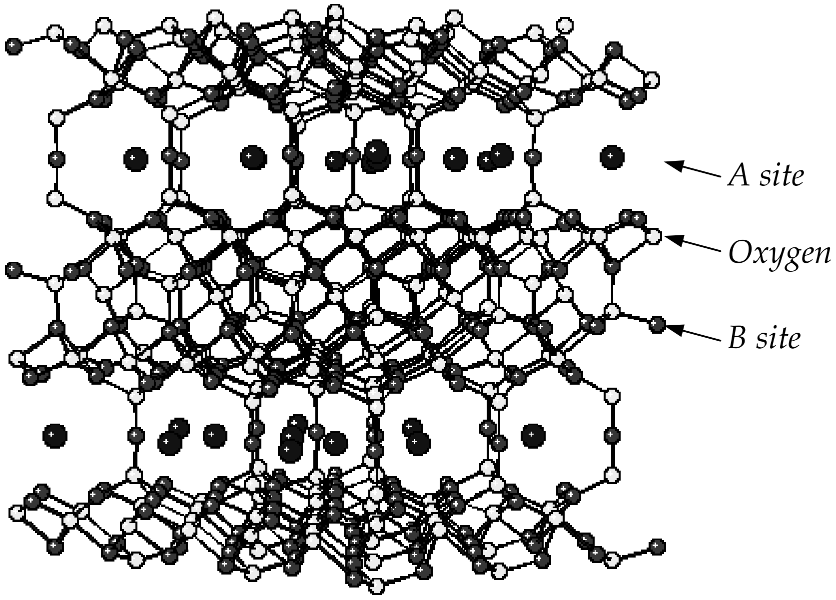

Figure 18. *The hexaaluminate structure, clearly showing the layered structure with the mirror planes in which the A ions is situated dividing the spinel blocks.*

The crystal structure of the hexaaluminate has been studied by several authors [Inoue et al 1996, Inoue et al 1996, Iyi et al 1989, Machida et al 1995]. The hexaaluminates form crystals with a high aspect ratio, i.e. flake-like crystals. There are two types of structures depending on the type of *A* ion, the magnetoplumbite and the β-alumina structures. For both structures the main components are two blocks with a spinel-like structure, i.e. similar to Al_2O_3. A mirror plane, in which the large *A* ions are situated, divides these two blocks, cf. Figure 18.

This mirror plane lowers the diffusion of ions along the *c*-axis, i.e. perpendicular to the mirror plane, and thereby lowers the crystal growth along the same axis. This gives rise to the high aspect-ratio crystals mentioned above. This crystal form is thermodynamically unfavourable and the crystal growth is therefore hindered, yielding a material that sinters very slowly [Arai et al 1989]. Due to their ability to withstand sintering, as well as the versatility of possible substitutions, the hexaaluminates have drawn much attention as candidates for the high-temperature part in the catalytic combustor.

The surface area of the hexaaluminates is affected by the preparation method as well as the choice of *A* and *B* ions. The effect of the former is shown in paper IV where three types of preparation techniques are compared, i.e. two co-precipitation techniques and a sol-gel technique. This is further discussed in section 5.4. The effect of the latter has been studied by several authors, both on the surface area as well as the catalytic activity. Generally the choice of *B* ion is more important for the catalytic activity than the *A* ion. The effects of substitution of different metal ions into the *A* and *B* positions in the hexaaluminate structure, on the surface area and the catalytic activity for methane combustion, are summarized in Table 6. Mn, Fe and Cu show the highest activities for substituted hexaaluminates. Groppi et al (2001) found that presence of Mg^{2+} could enhance the catalytic activity by stabilising the Mn ions at a high oxidation state.

Table 6. *Influence of the substitution of A and B ions into the $ABAl_{11}O_{19}$ on the surface area and catalytic combustion of methane, i.e. temperatures for 10 % and 90 % conversion*

A ion	B ion	Surface area [g/m²]	$T_{10\%}$ [°C]	$T_{90\%}$ [°C]	Ref
Ba	Al	15.3	710	730	(Machida 1989)
Ba	Al	10	675	780	(Artizzu, 1998)
Ba	Al	14.5	710	845	(Yan 1998)
Ba	Cr	15.7	700	770	(Machida 1989)
Ba	Mn	13.7	540	740	(Machida 1989)
Ba	Mn	16.3	600	775	(Yan 1998)
Ba	Mn	2.0	745	-	(Yan 1998)
Ba	$Mn_{0,5}Co_{0,5}$	14.3	585	740	(Yan 1998)
Ba	Fe	11.1	560	780	(Machida 1989)
Ba	Fe	5-7	600	850	(Groppi 1997)
Ba	Fe	14.1	514	634	(Naoufal 1998)
Ba	Co	15.2	690	720	(Machida 1989)
Ba	Co	13.9	660	815	(Yan 1998)
Ba	Ni	11.1	710	770	(Machida 1989)
Ba	Cu	11	510	740	(Artizzu, 1998)
Sr	Mn	20.8	550	770	(Inoue 1996)
$Sr_{0,6}Ce_{0,4}$	Mn	10.7	-	-	(Inoue 1996)
$Sr_{0,6}Pr_{0,4}$	Mn	14.9	520	770	(Inoue 1996)
$Sr_{0,6}Nd_{0,4}$	Mn	18.6	500	770	(Inoue 1996)
$Sr_{0,6}Sm_{0,4}$	Mn	15.3	520	780	(Inoue 1996)
$Sr_{0,6}Gd_{0,4}$	Mn	16.8	540	780	(Inoue 1996)
Pr	Mn	12.5	520	810	(Inoue 1996)
Nd	Mn	11.1	520	770	(Inoue 1996)
Sm	Mn	6.3	570	870	(Inoue 1996)
Gd	Mn	6.6	-	-	(Inoue 1996)
Thermal	-	-	810	860	(Machida 1989)

The high catalytic activity of especially the Mn-substituted hexaaluminates is due to the ability of the manganese ion to change its valence states, i.e. between Mn^{3+} and Mn^{2+}. The catalytic activity of a Mn-substituted hexaaluminate is therefore much higher than that of corresponding Mn-substituted spinel as can be seen in Table 5 and Figure 17. The activity of the substituted hexaaluminates is however much lower for methane combustion than for palladium-based catalysts. The activity of the hexaaluminates for combustion of larger hydrocarbons, e.g. toluene or n-heptane, more closely resembles the ones of palladium and platinum, cf. Figure 7. This is also valid for the toluene/n-heptane mixture used for simulating diesel fuel, cf. Figure 19. Interesting to note is the behaviour of the palladium-impregnated hexaaluminate which shows a higher activity compared to the impregnated spinel. Such enhanced catalytic activity has been described for methane combustion by several authors [Sekizawa et al 1996, Sohn 2002].

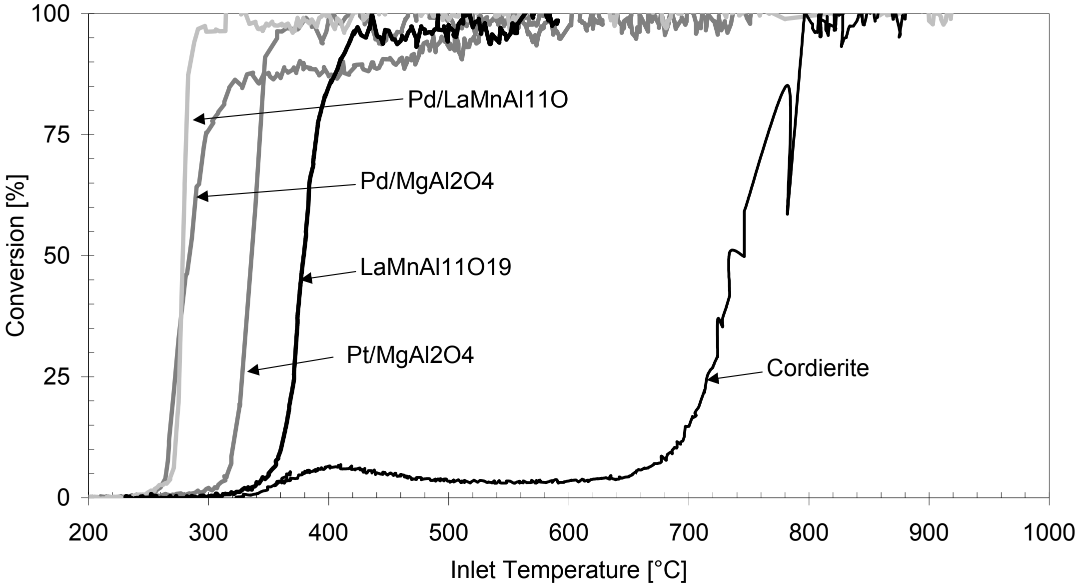

Figure 19. *Catalytic combustion of 80 mol % n-heptane and 20 mol % toluene over 5 % Pd on* $MgAl_2O_4$*, 5 % Pd on* $LaMnAl_{11}O_{19}$*, 5 % Pt on* $MgAl_2O_4$*,* $LaMnAl_{11}O_{19}$ *and cordierite (uncoated monolith)*

5.2.3 *Garnet (Paper V)*

The structure of the garnets is even more complex than those of spinels and hexaaluminates. There are three different sites that can be substituted. The general formula is $A_3B_2C_3O_{12}$ where the *A* site is a dodecahedral site, the *B* site is an octahedral and the *C* site is a tetrahedral site. In nature the garnets are orthosilicates and found in rocks that have undergone high-temperature modification. Garnets, or materials with garnet structure, have found a wide variety of applications ranging from laser crystals to magnetic materials and thermal barrier coatings. However, very few attempts to use garnets as catalytic materials have been reported in literature to this date [Haralambous et al 1991, Tsagaroyannis et al 1996]. The purpose of paper V was to investigate the thermal stability and catalytic activity of garnet-based materials. The thermal stability of the garnet materials proved to be good, however not as good as the above-mentioned hexaaluminate. It must here be stressed that this study just concerned a limited number of garnet compositions and it is therefore likely that more thermally stable material may be synthesised using a different composition or preparation technique. All the tested garnet powders were prepared using a co-precipitation technique similar to the one described in section 5.4.2. An yttrium aluminium garnet, $Y_3A_5O_{12}$ (YAG), and a manganese-substituted garnet, $Y_3Mn_{0.1}Al_{4.9}O_{12}$ (YMAG), were prepared. The thermal stability of the garnet materials was evaluated by consecutive calcinations at 1000 °C (4 h), 1200 °C (4 h) and 1400 °C (4 h and 15 % steam). The surface areas of the garnets are shown in Table 4. The surface areas were lower than for the spinels and the hexaaluminates.

The catalytic activity was tested in five different combustion reactions, i.e. methane, n-heptane, toluene, synthetic diesel mixture and a low-heating value gas, and is summarised in Table 5. The activity of the garnet materials was generally low. Resembling the substituted spinel, the manganese substitution only increased the catalytic activity slightly, as can be seen for methane in Figure 17. For the low-heating value gas, however, the YAG showed a remarkably high activity as can be seen in Figure 20. The YAG also showed a comparably low selectivity for oxidising NH_3 into NO_X at temperatures between 450 °C and 550 °C, i.e. 50 % selectivity to NO_X for a conversion of 50 % of the NH_3.

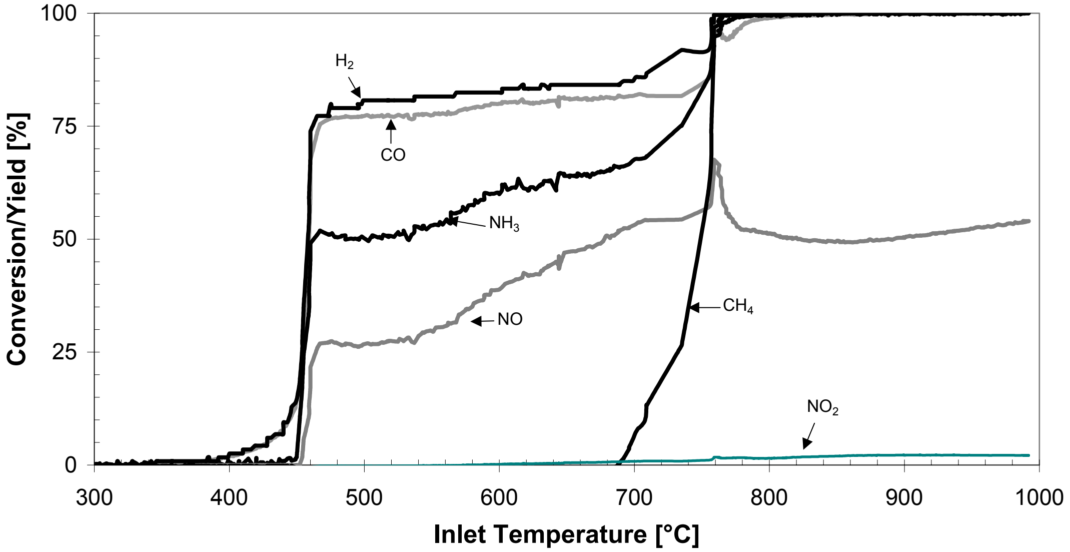

Figure 20. *The conversion of gasified waste, a LHV gas containing* H_2*, CO and* CH_4 *as the main fuel components and minor amount of* NH_3*, over* $Y_3Al_5O_{12}$ *catalyst*

5.3 Support materials

As was mentioned above, the support has to make up for the geometrical shape of the catalyst. The supports used for gas turbine applications are usually honeycombs or monoliths. These consist of parallel channels with normally a square cross section. The size of the channels may vary but is usually in the range of 1 to 10 mm in cross section. The two main forms of monoliths are ceramic and metallic.

5.3.1 Ceramic supports

The ceramic supports are usually produced by extrusion of a ceramic paste. The most common material is cordierite, an aluminium silicate. Cordierite, $Mg_2Al_4Si_5O_{18}$, has excellent thermal properties including thermal shock resistance, for use at temperatures below 1250 °C. Even if the melting point is much higher this temperature is limiting as cordierite becomes soft at higher temperatures and the monoliths are easily deformed. The silica content is also a problem as silica can diffuse to the surface and effectively poison the catalyst.

Other materials such as alumina and mullite, also an aluminium silicate, and zirconia have been used in ceramic supports. However, for most of these materials the thermal shock resistance, see section 6, problematic. The same is true for hexaaluminates, which have been used as support material.

5.3.2 *Metallic supports*

The metallic substrates usually consist of rolled corrugated metal sheets, stashed corrugated metal sheets or alternating corrugated and flat metal sheets, usually consisting of FeCrAlloy. The metal monolith is much less susceptible to thermal shocks than its ceramic counterparts. The walls may also be made thinner, which decreases the pressure-drop and the thermal conductivity is higher, which may be beneficial for the ignition as heat may be conducted from the reaction zone towards the inlet of the catalyst. However, for most metals the use is limited to temperatures below 1000 °C.

5.4 Preparation methods (Paper IV)

Catalyst preparation is a complex field. It spans from the preparation and extrusion of the monoliths to the impregnation of small metal nano-clusters on the washcoat materials. The field of catalyst preparation has recently been reviewed by Campanati et al (2003). In this section some aspects on the preparation of the above-mentioned metal oxide catalysts are discussed.

5.4.1 *Solid-state methods*

Solid-state methods are the most simple preparation techniques for preparing complex metal oxides. The method is based on the solid-state reactions between different solid compounds. Basically compounds containing the different metals included in the metal oxide are mixed, e.g. milled, and heated to a temperature at which solid-state reactions may take place. The metal-containing compounds can be metal oxides, nitrates etc. The difficulty in achieving mixing on an atomic scale usually yields low surface-area materials and in some cases pure crystal phases may be hard to achieve. However, the easy preparation has made it a widely used method for preparation of ceramic materials, especially for dense materials.

5.4.2 Co-precipitation

The co-precipitation technique utilises the fact that metal ions may form insoluble metal salts. Soluble metal salts, e.g. nitrates, are dissolved in a solvent. The solution is then added to some precipitating agent. The method often yields a very homogeneous material and high surface areas may be achieved. A good example of co-precipitation is the preparation of hexaaluminates using metal nitrates as the precursor salt. The carbonate method has been described in detail by Groppi et al (1994). The metal nitrates in stochiometric amounts are dissolved in water. The aqueous solution is then slowly added to an aqueous solution of ammonium carbonate under vigorous stirring. The pH is kept constant at 8.5. A precipitate is formed immediately, which is composed of aluminium hydroxide and metal carbonates and hydroxycarbonates. The precipitate is then washed and dried before the final calcination that converts it into the hexaaluminate phase.

The carbonate route has proven to be a very successful preparation technique for complex metal oxides with large surface areas. In the scope of the work included in this thesis magnesium spinels, paper II, and yttrium garnets, paper V, both pure and substituted have been prepared using the carbonate route. Clean crystal phases and comparably large surface areas have been achieved in all cases.

5.4.3 Sol-gel

The sol-gel methods incorporate a number of different preparation techniques with the common feature that they all form a gel at some stage. Alkoxides are commonly used as precursor materials [Brinker 1990]. An alkoxide is composed of a metal to which a number of alkoxy groups are attached. The alkoxy groups may then be hydrolysed and form a polymeric network. For hexaaluminates two different strategies may be used. Either all the metal components are present in the form of alkoxides or some of the metals are added in the form of water-soluble metal salts dissolved in the added water. The latter strategy was used for the preparation in paper IV.

Several parameters may be varied during the preparation, e.g. the amount of water [Woo et al 1998], addition of a modifier, and drying technique

[Mizushima & Hori 1994]. Depending on the drying method a xerogel or an aerogel may be formed. The xerogel is formed if conventional drying is used and in this case the porous system of the precursor gel is collapsed. In the aerogel, which is formed after supercritical drying, the features of the precursor gel are kept. This results in a much more porous material with a high surface area, as can be seen in Figure 21. By using different modifiers such as acetylacetone (Acac) or acetic acid, the rate of hydrolysis may be changed, this in turn will change the morphology of the resulting gel and thereby the morphology of the final precursor powder. This can be used to tailor the morphology of the metal oxide powders. The effects of Acac on cerium isopropoxide have been described by Sanchez et al (1992). Low additions of Acac, e.g. an Acac/Ce molar ratio of 0.15, would give a combination between a polymeric network and a precipitate, a so-called closo structure. At Acac/Ce ratio of 0.5 a branched polymeric network is formed and at a ratio of 1, molecular clusters are formed.

In paper IV manganese-substituted lanthanum hexaaluminates were prepared using two different co-precipitation techniques, i.e. precipitation as hydroxides and carbonates, and sol-gel techniques. Different amounts of Acac were added to the aluminium isopropoxide ranging from Acac/Al=1 to 0. The study showed that the pore size distribution and surface area could be controlled by the choice of synthesis method, which influenced both the initially, after calcination at 600 °C, and final, after calcination at 1200 °C, specific surface area strongly, cf. Figure 21. Materials with an initially high fraction of small pores below 50 Å, i.e. xerogels, lost a large part of the small pores upon calcination at temperatures at and above 1000 °C. On the other hand, hexaaluminate powders with an initial pore size distribution with a large fraction of pores between 80 and 600 Å, such as the carbonate and the aerogels, could preserve these pores and consequently retain higher specific surface areas. The small pores seemed to collapse more readily than the larger pores after high temperature calcination. Hence, material with sharp small pore size distributions should be avoided and materials with broad pore size distributions in the 80 to 600 Å range should be favoured, if high surface areas at and above 1200 °C are desired.

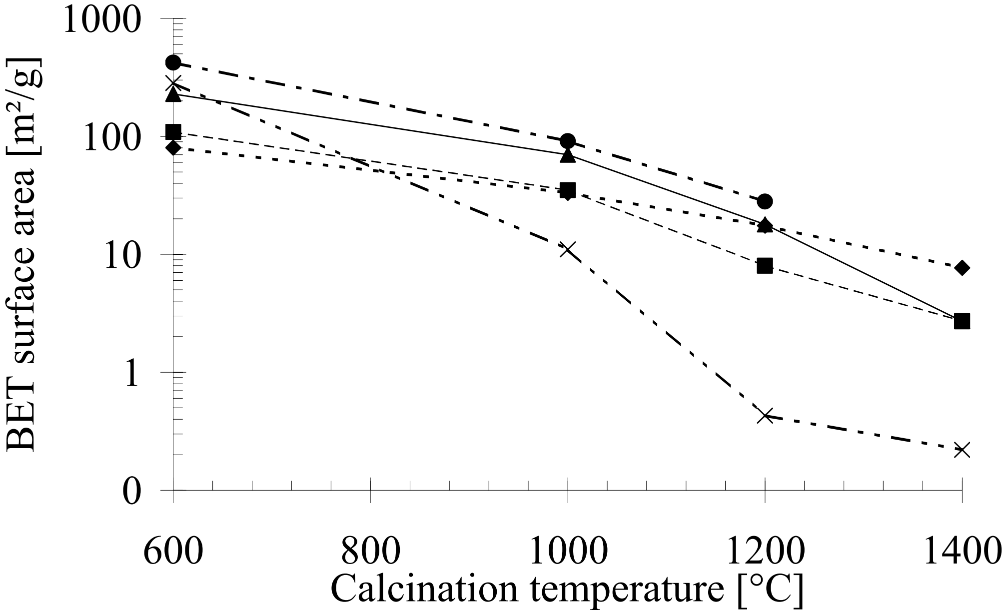

Figure 21. *The BET surface areas of LaMnAl$_{11}$O$_{19}$ after consecutive calcinations at 600 °C, 1000 °C, 1200 °C and 1400 °C prepared by co-precipitation as hydroxides (■) and carbonates (▲) and sol-gel techniques: xerogel with Acac/Al=0 (◆), xerogel with Acac/Al=0.5 × and aerogel with Acac/Al=0.5* ●

5.4.3.1 Microemulsion

In the microemulsion technique the precipitation of the metal oxide takes place inside the micelles of a microemulsion containing water and oil phases and a tenside. The small droplets act as small micro reactors and due to the small size the mixing at the microscopic scale is very good, yielding a well-mixed phase, usually leading to a lower crystallisation temperature. The size of the micelles also decides the sizes of the particles. The method may be used both for preparing noble metal particles, either single metal or bimetallic, or metal oxides. The use of the microemulsion technique has proven to be very valuable in the preparation of hexaaluminates, as the hexaaluminate phase is formed at a much lower temperature compared to conventional techniques, i.e. 1050 °C compared to 1250-1350 °C for Ba-hexaaluminate. As the hexaaluminate phase is formed the sintering of the material is retarded and thereby a high surface area may be kept even at high temperatures, i.e. 100-160 m²/g after calcination at 1300°C [Zarur & Ying 2000, Zarur et al 2000].

- 6 - DEACTIVATION (PAPER VI)

Even though the definition of a catalyst is a material that is not consumed in the process, most catalysts will eventually have to be exchanged due to a diminished catalytic activity. This is due to deactivation of the catalyst material itself. For some catalytic applications this process may take years and for others a rapid deactivation may take place and the catalyst has to be exchanged continuously. The deactivation of the catalyst has to be taken into account when a catalytic process is designed and knowledge about deactivation is of paramount importance for a successful operation of any catalytic process. This is especially true in catalytic combustion where the lifespan of the catalytic combustor has to be at least 8000 h as described earlier. Deactivation has been reviewed in several papers [Farrauto & Bartholomew 1997, Trimm 1997, Forzatti & Lietti 1999]. Combustion catalysts are susceptible to a wide variety of deactivation phenomena, some of the most common are:

- Poisoning
- Sintering
- Vaporisation
- Phase transformation
- Thermal shock

Of these modes of deactivation the first is dependent on the composition of the fuel, while the rest are caused by high temperatures. The poisoning and sintering will be further discussed in the subsequent sections.

Vaporisation or volatilisation of the catalyst material may present a problem especially at high temperatures and high gas-flow rates. Moreover some metals can react with compounds in the gas stream and form more volatile compounds, e.g. platinum halides. Volatilisation might also play a major role in the sintering of the materials as will be discussed further in section 6.1.

At the high temperatures found in a gas turbine combustor the atoms within the crystal lattice of the catalysts materials may start to migrate. This may give rise to sintering or, if the catalyst is composed of two or more materials, to a reaction between the different materials, which in many cases will give rise to a strong deactivation of the catalyst. An example of this is shown in Figure 22, where a $LaMnAl_{11}O_{19}$ coated monolith has been calcined at 1000 °C and 1200 °C for 4 h, respectively. The latter is completely deactivated. The EDS analysis shows that Si and Mg have diffused into the washcoat from the monolith beneath probably forming silicates on the surface.

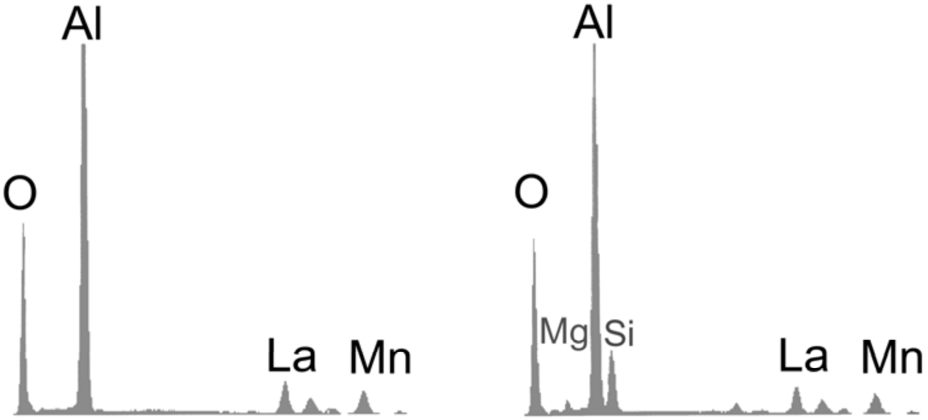

Figure 22. *Energy dispersive X-ray spectra of* $LaMnAl_{11}O_{19}$*-coated cordierite monoliths, after calcination at 1000 °C (left) and 1200 °C (right)*

Poisoning, sintering, volatilisation and phase transformation are common to many catalytic processes especially the ones working at high temperatures. However, thermal shock is uncommon in other applications than in gas turbines. Thermal shock occurs when a rapid change in temperature is induced on any material. In gas turbines this may take place if the fuel supply is stopped; the temperature will then rapidly decrease to the compressor outlet temperature, as the incoming air will cool the catalyst. This is the case if the turbine trips and has to be shut down. The temperature change may in this case be several hundreds of degrees in a fraction of a second. For most ceramic materials such large variations in temperature will induce catastrophic failure. The parameter that is supposed to govern this behaviour is the thermal expansion, i.e. a low thermal expansion material is less susceptible to thermal shocks than one with high thermal expansion. A good resistance to thermal shocks is more important for larger structures, hence it is more important for the materials in the monoliths to have a low thermal expansion than for the washcoat material. However, if there is a mismatch between the thermal expansion of the washcoat and the support, the thermal cycling may induce fractures.

6.1 Sintering

Although the oxidation of hydrocarbons over the catalyst will be limited by mass transfer to the catalyst surface at high temperatures, several studies have shown the importance of a large surface area material for ignition of the fuel. Hence, sintering of the catalyst materials is a very important mode of deactivation for a catalyst used in a gas turbine combustor.

The processes behind the sintering of ceramic materials as well as supported metals have been widely studied and reviewed [Kingery et al 1976, Forzzati & Lietti 1999] The sintering usually requires high temperatures and is in some cases enhanced by the presence of steam. High temperatures and steam are both always found in a gas turbine combustor. Sintering may affect the activity of the catalysts in two ways. First, the catalyst surface will diminish and secondly the sintering may lead to encapsulation of active material into the washcoat [Heck & Farrauto 1995].

6.2 Poisoning (Paper VII)

Poisoning is a classic mode of deactivation in catalytic applications and has been studied extensively for e.g. car exhaust catalysts [Gandhi & Shelef 1991, Shelef et al 1978]. In poisoning a substance binds to or reacts with the active sites of the catalyst and thereby blocks the sites for the intended reaction. The poisoning may either be reversible, i.e. the activity is restored when the poison is no longer present in the feed, or irreversible, which is a lasting deactivation even if the poison in the feed is removed [Forzatti & Lietti 1999].

Table 7. *The sulphur contents of some common fuels [Irwin 1998]*

Fuel	Sulphur content
Natural gas	< 1 ppm
Gasified biomass/Waste	20-200 ppm
Diesel:	
Conventional diesel	400 ppm
Environmental diesel	< 10 ppm
Jet fuel:	
JP-A	< 0.3 wt %
JP-1	< 0.2 wt %
JP-4/JP-8	< 0.4 wt %
Gasoline	< 0.07 wt %
Fuel oil:	
Kerosene (Fuel oil #1)	< 0.5 wt %
Fuel oil #2	< 0.32 wt %
Fuel oil #6	< 2 wt %

Sulphur is one of the most well-known catalyst poisons and is found in varying amounts in most common fuels as shown in Table 7. Sulphur is a very potent poison and it has been shown that as low concentrations as 1 ppm sulphur could poison a catalyst [Lampert et al 1997]. Sulphur poisons a catalyst in several different ways, e.g. either by forming sulphates, which bind to the active sites and thereby block access to them or by forming sulphides and thereby lowering their activity. The former is the most common type of sulphur poisoning in oxidising environment, e.g. in a catalytic combustor, where most of the sulphur components are oxidised into SO_2 or SO_3. The stability of the formed sulphates depends on the temperature and the metal onto which the sulphates bond. Transition metals usually form more stable sulphates than noble metals such as palladium or platinum. If the temperature is high enough the surface sulphates will eventually decompose. Hence, the irreversible deactivation is lower at high temperatures. The nature of the support is also important. Alumina forms sulphates more readily than for example silica and this greatly affects the poisoning of supported palladium catalysts

[Hoyos et al 1993]. The formation of surface sulphates and sulphite could even affect the surface area of the catalyst [Yu & Shaw 1998].

In paper VII, the sulphur poisoning of palladium and platinum supported on a magnesium aluminium spinel, $MgAl_2O_4$ (denoted MAS in Figures 23-25) a manganese-substituted lanthanum hexaaluminate, $LaMnAl_{11}O_{19}$ (denoted LMA in Figures 23-25), and an yttrium aluminium garnet, $Y_3Al_5O_{12}$ (denoted YAG in Figures 23-25), was investigated for the combustion of gasified waste, i.e. a fuel mixture of CO, H_2 and CH_4. The results are shown in Figure 23-25. For the noble metal-based catalysts the addition of sulphur only slightly affected the conversion of H_2 and CO, which occurred at temperatures below 300 °C. This is true for conversions up to 90 % for the palladium-based catalysts; to achieve 100 % conversion a significantly higher temperature was needed for the poisoned catalysts. For methane the palladium-based catalysts were severely deactivated, while the platinum-based catalysts retained their activity. However, the platinum catalysts had a much lower initial activity compared to their palladium counterparts. For the washcoat materials a severe deactivation could be seen for the $MgAl_2O_4$ and $LaMnAl_{11}O_{19}$ for both H_2 and CO. The activity of the $Y_3Al_5O_{12}$ increased, however from a very low level. For methane the activity of the washcoat materials remained unchanged. The deactivation behaviour can be related to the formation of surface sulphates/sulphites. It has been shown that the formation of such compounds is much less pronounced on platinum than on palladium [Meeyoo et al. 1998]. Some studies have even shown that the presence of sulphur may enhance the activity for certain reactions [Skoglundh et al 2001, Burch et al 1998]. The deactivation of the palladium catalysts is due to the formation of palladium sulphates/sulphite, which is stable up to about 650 °C. These species are known to inhibit the oxidation of CH_4 over palladium. Studies of exhaust catalysts have also shown that the oxidation of CO could remain unchanged while the conversion of CH_4 drops. Mowery et al (1999) suggest that the apparent insensitivity for CO conversion could be due to a too large catalyst volume. As CO, as well as H_2, is relatively easy to oxidise most of the reactions take place in the inlet section of the catalyst. The catalyst volume for complete conversion will then increase and if the catalysts volume is too large the deactivation effect will not be noted.

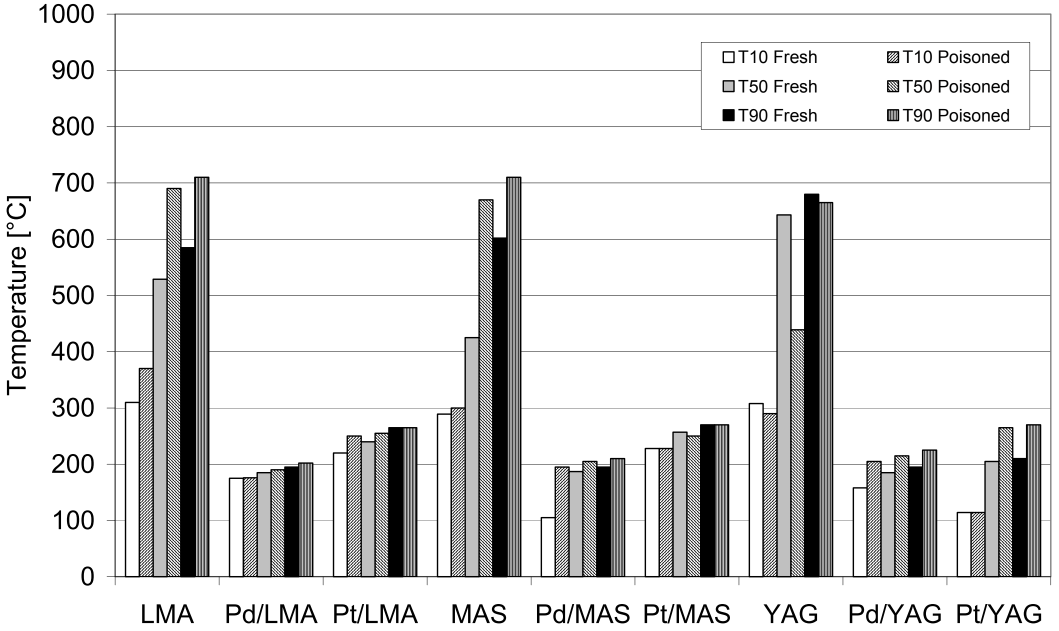

Figure 23. *The influence of 25 ppm sulphur in the form of* SO_2 *on the combustion of the hydrogen component in gasified waste*

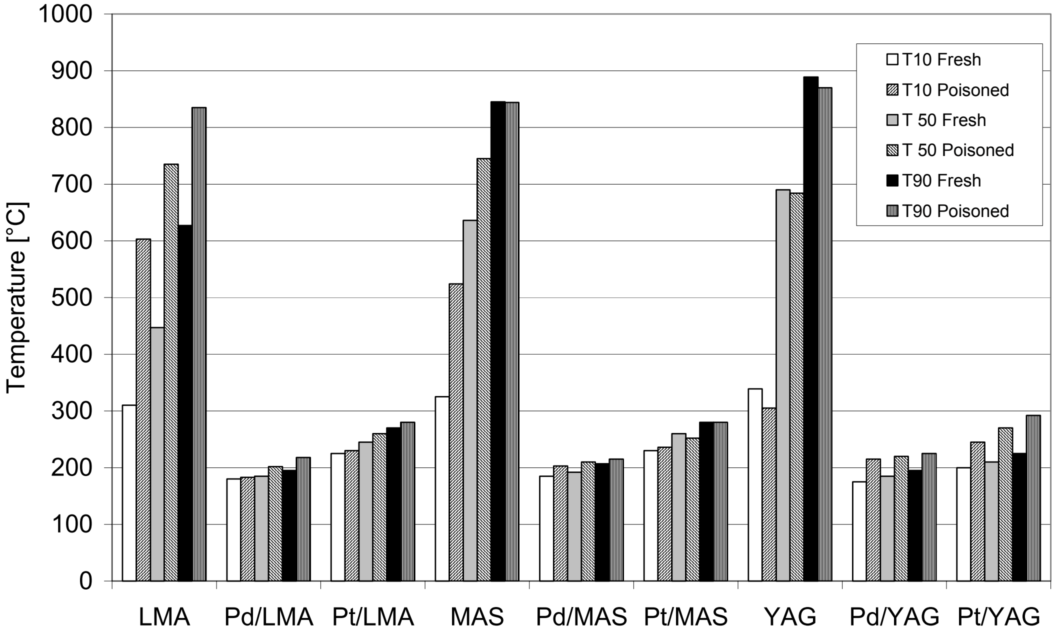

Figure 24. *The influence of 25 ppm sulphur in the form of* SO_2 *on the combustion of the carbon monoxide component in gasified waste*

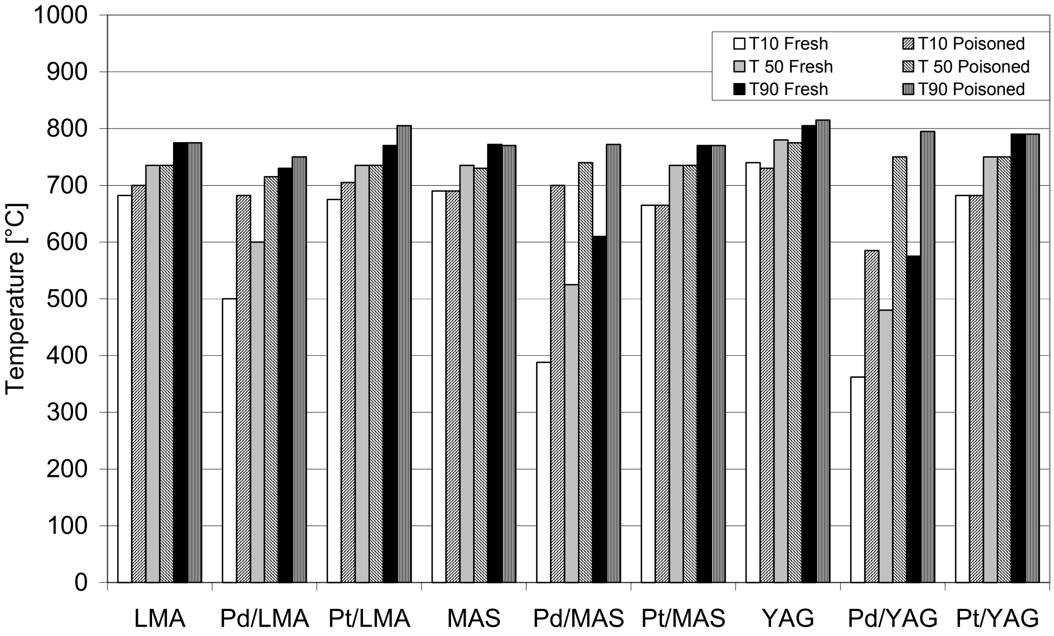

Figure 25. *The influence of 25 ppm sulphur in the form of SO_2 on the combustion of the methane component in gasified waste*

The metal oxide-based catalysts, i.e. the nonimpregnated washcoats, also form metal sulphates and sulphites with SO_2 [Khairulin et al 1997, Rosso et al 2001]. These compounds are generally less stable at the high temperature which is required for CH_4 combustion, and hence the ignition of CH_4 was not affected by the SO_2. However the ignition temperatures of H_2 and CO are well within the stability range of the metal sulphates, and hence their ignition are affected. In the case of $Y_3Al_5O_{12}$ the effect was an improvement of the catalytic activity; however small, this could probably be contributed to the increased acidity of the catalysts, as has been described for alumina catalysts.

- 7 - CONCLUSIONS

High-temperature catalytic combustion has proven to be a viable technique to lower the formation of NO_X in gas turbine combustors while maintaining a stable combustion with low emissions of carbon monoxide, hydrocarbons and soot. However close to commercialisation the technique still has a number of unsolved issues. Most of these are related to the catalysts and especially the materials. The very long expected lifetimes of the catalysts, at least 8000 h, together with the harsh conditions in the combustor require very stable catalyst materials. Moreover, the use of natural gas with methane as the main component puts great demand on the catalytic activity of the catalyst. At the same time if all the fuel is converted within the catalyst, the high-energy contents of the fuel/air mixture may increase the temperature well above 1200 °C. These temperatures will easily deactivate most catalysts.

The aim of this thesis has been to investigate materials for use in catalytic combustion, which could meet the requirements for stability as well as activity. To find a single material that could live up to both the high activity needed for the ignition segment and the thermal stability needed in the final segments of a catalytic combustor is almost impossible.

The catalytic oxidation activity for the materials was investigated for a number of different hydrocarbons ranging from C1 to C7. The ignition temperature generally decreases with increasing chain length. For the gaseous hydrocarbons, i.e. methane, ethane, propane and butane the Pd-based catalysts were the most active. For alkanes with a chain length >4 carbons the Pt-based catalyst showed the highest activity, while for aromatic hydrocarbons the Pd was the most active. A fuel mixture consisting of 80 mol % n-heptane and 20 mol % toluene was used as a simulated diesel fuel. Even though n-heptane was the major component, the Pd catalysts showed a much higher activity compared to the Pt catalyst.

Palladium is the most used catalyst for methane oxidation and hence is commonly considered as an ignition catalyst. However, the high-pressure pilot scale tests conducted at conditions resembling that of a conventional combustor clearly illustrated the need for a more stable catalyst.

In order to stabilise the palladium a co-metal was added, i.e. Pt or Rh. In both cases the addition had a beneficial effect on the stability. However, while Rh significantly decreased the conversion compared with the pure palladium catalyst, Pt showed almost as high activity as for the palladium catalyst both in lab scale and pilot scale tests. Investigations using TPO showed that the decomposition temperature of the PdO was shifted towards a lower temperature with the addition of Pt while it remained constant for the Rh:Pd compared to pure Pd catalyst.

To achieve the long lifetime at the temperatures present in the combustor, high-temperature stable materials have to be used. In this thesis three material groups have been studied, i.e. spinels, hexaaluminates and garnets. The former two have already found their application in catalysis while garnet materials are new to catalysis. Two main properties were evaluated for these materials, the ability to retain the surface area and the catalytic activity. The spinel, $MgAl_2O_4$, and the hexaaluminate, $LaMnAl_{11}O_{19}$, showed the largest surface areas after calcinations at temperatures ≤ 1200 °C. The substituted spinel, as well as the garnets, showed slightly lower surface areas. The activity for these materials is lower than for noble metal-based catalysts especially for methane combustion. The $LaMnAl_{11}O_{19}$ was the most active of the complex metal oxides for all fuels except H_2 and CO in the LHV gas, where the garnet, $Y_3Al_5O_{12}$, with low activity for most other fuels, proved to be the most active.

The last part of the thesis deals with deactivation of catalysts. Besides the above-mentioned loss of surface area, i.e. sintering, poisoning could be a major problem. The poisoning effect of 25 ppm SO_2 in the gas was studied over the above-mentioned three metal oxide materials, both pure and impregnated with noble metals, i.e. Pd or Pt. The trend was that the activity of the Pt catalysts remained almost unchanged for all components. For the Pd catalysts the conversion of CH_4 was negatively affected by the sulphur addition. Negative effects were also seen for H_2 and CO conversions over the $MgAl_2O_4$ and $LaMnAl_{11}O_{19}$. For $Y_3Al_5O_{12}$ the activity seemed to increase with the addition of sulphur to the flow.

- 8 - ACKNOWLEDGEMENTS

First I would like to thank my supervisor Professor Sven Järås for his supervision and confidence in me.

I would like to thank all my colleagues, former and present, at Chemical Technology and Chemical Reaction Engineering. A special thanks to Magnus Callavik (formerly Johansson) for introducing me to the exciting subject of catalytic combustion and for his guidance. I am also greatly indebted to Henrik Kušar, not only for sharing office with me for several years, but also for his collaboration and friendship. I would also like to thank Philippe Thevenin for his collaboration (including all the late nights spent in the lab the day before leaving for conferences) as well as for all the fruitful discussions over a cold beer and of course for his friendship. I would also like to thank Dennis Papadias, Katarina Persson and Sara Eriksson, the other members of our catalytic combustion group and Jeevan Jayasuriya and all others at Heat and Power.

I would also like to thank the undergraduate students that I have had the opportunity to work with, Martin Vosecky, Erik Elm Svensson, Laura Furno-Sola, Mariam Hagphana and Henrik Anderson.

I would also like to give a special thanks to Christina Hörnell without whose linguistic skills this thesis would have been much worse. Moreover, I would like to thank Sara Lögdberg for her valuable comments on the thesis.

Furthermore, I would also like to thank Richard Carroni, Timothy Griffin and all the people at ALSTOM Power, Technology Center in Switzerland who made my four months stay perfect. A special thanks to Martin Holkedahl, for his hospitality and friendship during my stay in Switzerland.

I would further like to thank Govind Menon, Jesper Brandt, Rolf Gabrielsson, Robert Lundberg and Inga Groth for their help and interesting discussions.

Marcus Aldén, Fabian Mauss and all others involved in the Cecost soot project are also acknowledged.

Moreover, I would also like to thank the Centre for Combustion Science and Technology, CECOST, and the Swedish Energy Administration for their financial support, without which none of this would have been possible.

Last but not least I would like to thank all of my friends, family and especially my wonderful and understanding girlfriend for all their support during the years.

REFERENCES

Arai, H., Eguchi, K., Machida, M. (1989), Cation substituted layered hexaaluminates for a high-temperature combustion catalyst, MRS Int'l. Mtg. on Adv. Mats., Materials Research Soc., Vol. 2, pp. 65-74.

Arai, H., Machida, M. (1991), Recent progress in high-temperature catalytic combustion, Catal. Today, 10, 81-94.

Artizzu, P., Guilhaume, N., Garbowski, E., Brullé, Y., Primet, M. (1998), Catalytic combustion of methane on copper-substituted barium hexaaluminate, Catal. Letters, 51, 69-75.

Artizzu-Duart, P., Brullé, Y., Gaillard, F., Garbowski, E., Guilhaume, N., Primet, M. (1999), Catalytic combustion of methane over copper- and manganese-substituted barium hexaaluminates, Catal. Today, 54, 181-190.

W., Bartok, A. F., Sarofim (Eds) (1991), Fossil fuel combustion: a source book, Wiley, New York.

Benditt, J. (1989), Cold water on the fire: a recent survey casts doubt on evidence for early use of fire, Scientific American, May, 21-22.

van de Beld, L., van der Ven, M. C., Westerterp, K. R. (1995), A kinetic study of the complete oxidation of ethene, propane and their mixtures on a Pd/Al2O3 catalyst, Chem. Eng. Proc., 34, 469-478.

Brinker, C. J., Scherer, G. W. (1990), Sol-gel science: the physics and chemistry of sol-gel processing, Academic Press, San Diego.

Burch, R., Loader, P. K., Urbano, F. J. (1996), Some aspects of hydrocarbon activation on platinum group metal combustion catalysts, Catal. Today, 27, 243-248.

Burch, R., Halpin, E., Hayes, M., Ruth, K., Sullivan, J. A. (1998), The nature of activity enhancement for propane oxidation over supported Pt catalysts exposed to sulphur dioxide, Appl. Catal. B. 19, 199-207.

Campanati, M., Fornasari, G., Vaccari, A. (2003), Fundamentals in the preparation of heterogeneous catalysts, Catal. Today, 77, 299-314.

Carroni, R., Schmidt, V., Griffin, T. (2002), Catalytic combustion for power generation, Catal. Today, 75, 287-295.

Choudhary, T. V., Banerjee, S., Choudhary, V. R. (2002), Catalyst for combustion or methane and lower alkanes, Appl. Catal. A, 234, 1-23.

Ciuparu, D., Lyubovsky, M. R., Altman, E., Pfefferle, L. D., Datye, A. (2002), Catalytic combustion of methane over palladium-based catalysts, Catal. Rev., 44, 593-649.

Correa, S.M. (1992), A review of NOx formation under gas turbine combustion conditions, Combust. Sci. and Tech., 329-362.

Dalili F. (2003), Humidification in evaporative power cycles, PhD thesis, Kungl Tekniska Högskolan, Stockholm.

Encyclopædia Britannica (2003), “Cancer." Encyclopædia Britannica Online. 12 Mar, 2003 <http://search.eb.com/eb/article?eu=410257>.

Farrauto, R. J., Bartholomew, C. H. (1997), Fundamentals of industrial catalytic processes, Chapman & Hall, London, p. 265.

Feinmore, C.P. (1970), 13th Symp (int.) Combustion, Combust. Inst. Pittsburg, PA, pp. 373-380.

Forzatti, P., Lietti, L. (1999), Catalyst Deactivation, Catal. Today 52, 165-181.

Gandhi, H. S., Shelef, M. (1991), Effects of sulphur on noble metal automotive catalysts, Appl. Catal, 77, 175-186.

Gangwal, S. K., Mullins, M. E., Spivey, J. J., Caffrey, P. R., Tichenor, B.A. (1988), Kinetics and selectivity of deep catalytic oxidation of n-hexane and benzene, Appl. Catal., 231-247.

Gélin, P., Primet, M. (2002), Complete oxidation of methane at low temperature over noble metal based catalysts: a review, Appl. Catal. B, 39, 1-37.

Glasman, I. (1996), Combustion, Academic Press Inc, San Diego.

Goudsblom, J. (1992), Fire and Civilization, Penguin Books, London.

Groppi, G., Cristiani, C., Forzatti, P. (1994), Phase composition and mechanism of formation of Ba-β-alumina-type systems for catalytic combustion prepared by precipitation, J. Mat. Sci., 29, 3441-3450.

Groppi, G., Cristiani, C., Forzatti, P. (1997), Preparation and characterization of hexaaluminate materials for high-temperature catalytic combustion, in J. J. Spivey (Ed.) Catalysis – A Specialist Periodical Report, **13**, Royal Society of Chemistry, Cambridge, 85-113.

Groppi, G., Cristiani, C., Forzatti, P. (1997), $BaFe_xAl_{(12-x)}O_{19}$ system for high-temperature catalytic combustion: Physico-chemical characterization and catalytic activity, J. Catal., 168, 95-103.

Groppi, G., Cristiani, C., Lietti, L., Forzatti, P. (2000), Study of PdO/Pd transformation over alumina supported catalysts for natural gas combustion, in A. Corma et al (Eds.) Studies in Surface Science and Catalysis 130, Elsevier, Amsterdam, p. 3801.

Groppi, G., Artioli, G., Cristiani, C., Lietti, L., Forzatti, P. (2001), Decomposition/reformation processes and CH_4 combustion activity of PdO over Al_2O_3 supported catalysts for gas turbine applications, in E. Iglesia et al. (Eds.) Studies in Surface Science and Catalysis 136, Elsevier, Amsterdam, p. 345.

Groppi, G., Cristiani, C., Forzatti, P. (2001), Preparation, characterization and catalytic activity of pure and substituted La-hexaaluminate systems for high temperature catalytic combustion, Appl. Catal. B, 35, 137-148.

Haralambous, K. J., Loizos, Z., Spyrellis, N. (1991), Catalytic properties of some mixed transition-metal oxides, Mat. Let., 11(3-4), 133-141.

Haynes, B. S. (1991), Soot and hydrocarbons in combustion, in Bartok et al (Eds) Fossil fuel combustion: a source book, Wiley, New York, pp. 261-326.

Heck, M. R., Farrauto, R. J. (1995), Catalytic air pollution control – commercial technology, van Nostrand Reinhold, New York, p. 64.

Hoyos, L. J., Praliaud, H., Primet, M. (1993), Catalytic combustion of methane over palladium supported on alumina and silica in presence of hydrogen sulfide, Appl. Catal. A 98, 125-138.

Inoue, H., Sekizawa, K., Eguchi, K., Arai, H. (1996), Changes of crystalline phase and catalytic properties by cation substitution in mirror plane of hexaaluminate compounds, J. Solid State Chem 121, 190-196.

Inoue, H., Machida, M., Eguchi, K., Arai, H. (1996), Single-crystal X-ray structure analysis of Mn-substituted barium hexaaluminates as-grown and after reduction, J. Mater. Chem, 6, 455-458.

Irwin, R.J., Van Mouwerik, M., Stevens, L., Seese, M.D., Basham W. (1998), Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed on the Internet via the Nature Net portion of the Park Service Home Page (www.nps.gov).

Iyi, N., Takekawa, S., Kimura, S. (1989), Crystal chemistry of hexaaluminates: β-alumina and magnetoplumbite structures, J. Solid State Chem., 83, 8-19.

James, S. R. (1989), Hominid use of fire in the lower and middle Pleistocene. A review of the evidence, Current Anthropology, 30, 1-26.

Johansson, M. (1998), Catalytic combustion of gasified biomass for gas turbine applications, PhD thesis, Kungl Tekniska Högskolan, Stockholm.

Kundakovic L., Flytzani-Stephanopoulos, M. (1999), Deep oxidation of methane over zirconia supported Ag catalysts, App. Catal. A, 183, 35-51.

Khairulin, A., Béguin, B., Garbowski, E., Primet, M. J. (1997), Catalytic properties of chromium-palladium loaded alumina in the combustion of methane in the presence of hydrogen sulfide, Chem. Soc. Faraday Trans., 93, 2217-2224.

Kim, S. C. (2002), The catalytic oxidation of aromatic hydrocarbons over supported metal oxide, J. Haz. Mat., B91, 285-299.

Kingery, W. D., Bowen, H. K., Uhlmann, D. K. (1976), Introduction to Ceramics, Wiley, New York, p. 468.

Lampert, J. K., Kazi, M. S., Farrauto, R. J. (1997), Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles, Appl. Catal. B 14, 211-223.

Lavoie, G.A, Heywood, J. B., Keck, J. C. (1970), Experimental and theoretical study of nitric oxide formation in internal combustion engines, Comb. Sci. Tech., 1, 313-326.

Lefebvre, A.H. (1983), Gas Turbine Combustion, Hemisphere Publishing Corp., Bristol.

Machida, M., Eguchi, K., Arai, H. (1989), Catalytic properties of $BaMAl_{11}O_{19-\alpha}$ (M=Cr, Mn, Fe, Co, and Ni) for high-temperature catalytic combustion, J. Catal. 120, 377-386.

Machida, M., Sato, A., Kijima, T., Inoue, H., Eguchi, K., Arai, H. (1995), Catalytic properties and surface modification of hexaaluminate microcrystals for combustion catalyst, Catal. Today, 26, 239-245.

Marti, P. E., Maciejewski, M., Baiker, A. (1994), Methane combustion over $La_{0.8}Sr_{0.2}MnO_{3+x}$ supported on MAl_2O_4 (M=Mg, Ni and Co) spinels, Appl. Catal. B, 4, 225-235.

McCarty, J. G., Chang, Y.-F., Wong, V. L., Johansson, E. M. (1997), Kinetics of high temperature methane combustion by metal oxide catalysts, Symp. Catalytic Combustion, San Francisco, Am. Chem. Soc., Div. Petrol. Chem. , 42, 158-165.

McCarty, J. G., Gusman, M., Lowe, D. L., Hildebrand, D. L., Lau, K. N. (1999), Stability of supported metal and supported metal oxide combustion catalysts, Catal. Today, 45, 5-17.

Meeyoo, V., Trimm, D. L., Cant, N.W. (1998), The effect of sulfur containing pollutants on the oxidation activity of precious metals used in vehicle exhaust catalysts, Appl. Catal. B, 16, L101-L104.

Mizushima, Y., Hori, M. (1994), Preparation of barium hexa-aluminate aerogel, J. Mater. Res., 9, 2272-2276.

Mowery, D. L., Graboski, M. S., Ohno, T. R., McCormick, R. L. (1999), Deactivation of PdO-Al_2O_3 oxidation catalyst in lean-burn natural gas engine exhaust: aged catalyst characterization and studies of poisoning by H_2O and SO_2, Appl. Catal. B, 21, 157.

Müller, U. (1993), Inorganic Structural Chemistry, Wiley, Chichester.

Naoufal, D., Millet, J.-M., Grabowski, E. E., Brullé, Y., Primet, M. (1998), Synthesis, structure and catalytic properties of Fe-substituted barium hexaaluminates, Catal. Let., 54, 141-148.

O'Malley, A., Hodnett, B. K. (1999), The influence of volatile organic compound structure on conditions required for total oxidation, Catal. Today, 54, 31-38.

Papaefthimiou, P., Ioannides, T., Verykios, X. E. (1997), Combustion of non-halogenated volatile organic compounds over group VIII metal catalysts, Appl. Catal. B, 13, 175-184.

Pitchon, V., Fritz, A. (1997), The current state of research on automotive lean NO_x catalysis, Appl. Catal B, 13, 1-25.

Ramesh, K. S., Kingsley, J. J., Hubler, T. L., McCready, D. E., Cox, J. L. (1997), Catalytic combustion over hexaaluminates, in K.S. Ramesh et al (Eds) Catalyst materials for high-temperature processes, The Am. Cer. Soc., Westerville, pp. 51-69.

Rosso I., Garrone E., Geobaldo F., Onida B., Saracco G., Specchia V. (2001), Sulphur poisoning of $LaMn_{1-x}Mg_xO_3$ catalysts for natural gas combustion, Appl. Catal. B., 30, 61-73.

Saint-Just, J., der Kinderen, J. (1996), Catalytic combustion: from reaction mechanism to commercial applications, Catal. Today, 29, 387-395.

Sanchez, C., Ribot, F., Doeuff, S. (1992), Transition metal oxy polymers synthesized via sol-gel chemistry, in R. M. Laine (Ed.) Inorganic and Organometallic Polymers with Special Properties, Kluwer, Dordrecht, pp. 267-295.

Saracco, G., Cerri, I., Specchia, V., Accornero, R. (1999), Catalytic pre-mixed fibre burners, Chem. Eng. Sci., 54, 3599-3608.

Schobert, H. H. (1990), The chemistry of hydrocarbon fuels, Butterworth & Co, UK.

Sekizawa, K., Machida, M., Eguchi, K., Arai, H. (1993), Catalytic properties of Pd-supported hexaaluminate catalysts for high temperature catalytic combustion, J. Catal, 142, 655-663.

Sekizawa, K., Eguchi, K., Widjaja, H., Machida, M., Arai, H. (1996), Properties of Pd-supported catalysts for catalytic combustion, Catal. Today, 28, 245-250.

Shelef, M., Otto, K., Otto, N. C. (1978), Poisoning of automotive catalysts, Advances in catalysis, 27, 311-365.

Skoglundh, M., Ljungqvist, A., Petersson, M., Fridell, E., Cruise, N., Augustsson, O., Jobson, E. (2001), SO_2 promoted oxidation of ethyl acetate, ethanol and propane, Appl. Catal. B, 30, 315-328.

Sohn, J. M., Kang, S. K., Woo, S. I. (2002), Catalytic properties and characterization of Pd supported on hexaaluminate in high temperature combustion, J. Mol. Catal. A, 186, 135-144.

Spivey, J. J. (1987), Complete catalytic oxidation of volatile organics, Ind. Eng. Chem. Res., 26, 2165-2180.

Thormählen, P., Fridell, E., Cruise, N., Skoglundh, M., Palmqvist, A. (2001), The influence of CO_2 C_3H_6, NO, H_2, H_2O or SO_2 on the low-temperature oxidation of CO on a cobalt-aluminate spinel catalyst ($Co_{1.66}Al_{1.34}O_4$), Appl. Catal. B, 31, 1-12.

Trimm, D. L. (1997) Deactivation and regeneration, in G. Ertl et al (Eds) Handbook of heterogeneous catalysis, vol 3, Wiley-VCH, Weinheim, pp. 1263-1282.

Tsagaroyannis, J.; Haralambous, K.-J.; Loizos, Z.; Petroutsos, G.; Spyrellis, N. (1996), Gadolinium-iron ferrites: catalytic effect on the water-gas shift reaction, Mat. Let., 28, 393-400.

Woo, S. I., Kang, S. K., Sohn, J. M. (1998), Effect of water content in the precursor solution on the catalytic property and stability of $Sr_{0.8}La_{o.2}MnAl_{11}O_{19}$ high-temperature combustion catalyst, Appl. Catal. B, 18, 317-324.

Yan, L.-C., Thompson, L. T. (1998), Synthesis and characterization of aerogel-derived cation-substituted barium hexaaluminates, Appl. Catal. A, 171, 219-228.

Yu, T-C., Shaw H. (1998), The effect of sulfur poisoning on methane oxidation over palladium supported on γ-alumina catalysts, Appl. Catal. B, 18, 105-114.

Zarur, A. J., Hwu, H. H., Ying, J. Y. (2000), Reverse microemulsion-mediated synthesis and structural evolution of barium hexaaluminate nanoparticles, Langmuir, 16, 3042-3049.

Zarur, A. J., Ying, J. Y. (2000), Reverse microemulsion synthesis of nanostructured complex oxides for catalytic combustion, Nature, 403, 65-67.

Zeldovich, J. (1946), The oxidation of nitrogen in combustion and explosions, Acta Physiochimica URSS, 21, 577-628.

Zwinkels, M. F. M., Järås, S. G., Menon, P. G., Griffin, T. A. (1993), Catalytic materials for high-temperature combustion, Catal. Rev. –Sci. Eng., 35(3), 319-358.

Zwinkels, M. F. M., Druesne, S., Menon, G., Björnbom, E., Järås, S. G. (1998), Thermal stability of complex oxide combustion catalyst supports, Ind. Eng. Chem. Res., 37, 391-397.