Mixed Metal Oxide - Noble Metal Catalysts for Total Oxidation of Volatile Organic Compounds and Carbon Monoxide

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ABSTRACT

CO, volatile organic compounds, and polyaromatics are ubiquitous air pollutants that give rise to deleterious health and environmental effects. Such compounds are emitted, for instance, by the combustion of wood, particularly from small-scale heating appliances. Total catalytic oxidation is considered to be an effective approach in controlling these emissions, however, some problems remain such as the non-availability of catalysts with low-cost, high activity and stability in prevailing conditions. Hence, this thesis aims at the development of oxidation catalysts and improved understanding of their behaviour.

The catalytic activity was evaluated for the oxidation of a mixture of CO, naphthalene (or ethylene), and methane in presence of carbon dioxide, water, oxygen and nitrogen. Various characterisation techniques, including Temperature-Programmed Reduction and Oxidation, BET-Surface Area Analysis, X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, Raman Spectroscopy and Scanning and Transmission Electron Microscopy were used.

In the first part of this thesis, catalysts based on metal oxides (MnOₓ, CuO) and/or a low amount of noble metals (Pt, Pd) supported on alumina washcoat were selected. It was shown that Pt and Pd possessed a superior catalytic activity to that of CuO and MnOₓ for the oxidation of CO, C₁₀H₈ and C₂H₄, while for the oxidation of CH₄, CuO was largely more active than noble metals, and MnOₓ as active as Pd and Pt. Some mixed metal oxide-noble metal catalysts showed decreased activity compared to that of noble metals, however, a higher noble metal loading or a successive impregnation with noble metals led to positive synergetic effects for oxidation.

Deactivation of the catalysts by thermal damage and sulphur poisoning is addressed in the second part of the dissertation. An alumina washcoat was found to be well anchored to the metallic support after thermal treatment at 900°C due to the growth of alumina whiskers. The sintering of the washcoat was accelerated after high temperature treatments in the presence of metal catalysts. In addition, alumina was found to react with CuO, particularly in presence of noble metals at 900°C, to form inactive CuAl₂O₄. However, MnOₓ catalyst benefits from the more active Mn₃O₄ phase at high temperature, which makes it a suitable active catalyst for the difficult oxidation of CH₄. Pt sintering was delayed when mixed with CuO, thus giving more thermally resistant catalyst. The mixed metal oxide-noble metal catalysts showed higher activity after pre-sulphation of the catalysts with 1000 ppm SO₂ in air at 600°C or during activity measurement in presence of 20 ppm SO₂ in the gas mixture, compared to single component catalysts. In some cases, the activities of the mixed catalysts were promoted by pre-sulphation due to the presence of sulphate species.

Thermal stabilisation of the catalytic components and the alumina by promotion of La in the washcoat is discussed in the third section. The stabilising effect of La at high temperature is also compared to that of Ce added in the catalysts for other purposes. Due to its better dispersion, La contributed to the thermal stabilisation of the alumina washcoat and its active components to a higher extent than Ce did. La provided a better dispersion and a higher saturation of metal oxides in the alumina support, and at the same time stabilised the activity of the catalysts by preventing undesirable solid-phase reactions between metal oxide and alumina. In addition, La was found to enhance the dispersion and the oxygen mobility of CeO₂. Cu-Ce interactions were found to promote substantially the CO oxidation due to an increase of the stability and reducibility of Cu species. Synergetic effects were also found between Ce and La in the washcoat of CuO-Pt catalyst, which facilitated the formation of reduced Pt and CeO₂, thus enhancing significantly the catalytic activity compared to that of a Pt only catalyst.

The last part was an attempt to demonstrate the potential of a catalyst equipped with a pre-heating device in a full-scale wood-fired boiler for minimising the high emissions during the start-up phase. During the first ten minutes of the burning cycle a significant reduction of CO and hydrocarbons were achieved.

Keywords: wood combustion, catalysts, total oxidation, manganese, copper, platinum, palladium, lanthanum, cerium, CO, VOC, methane, deactivation, thermal stability, sulphur dioxide.
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The work presented in this thesis is based on the following publications, referred to in the text using the following assigned Roman numerals:


OTHER DISSEMINATIONS

Some other publications, reports and conferences papers not included in this thesis.


CONTENTS

CHAPTER 1. INTRODUCTION
  1.1 Background
    1.1.1 The Power of Biomass .......................... 1
    1.1.2 Emissions from Small-Scale Combustion of Wood .... 2
    1.1.3 Environmental Targets and Legislation ............ 4
    1.1.4 Actions to Reduce the Emissions .................. 4
    1.1.5 Catalytic Oxidation ............................ 6
  1.2 Scope of the Thesis .................................. 7

CHAPTER 2. CATALYSTS FOR TOTAL OXIDATION
  2.1 Noble Metal Catalysts
    2.1.1 General ........................................ 9
    2.1.2 Results and Discussion .......................... 11
  2.2 Metal Oxide Catalysts
    2.2.1 General ........................................ 13
    2.2.2 Results and Discussion
      Choice of the metal oxides .......................... 15
      Manganese oxides catalysts ......................... 16
      Copper oxide catalysts ................................ 22
  2.3 Combination of Metal Oxides and Noble Metals
    2.3.1 General .......................................... 25
    2.3.2 Results and Discussion
      Effects of metal oxides on noble metals .............. 26
      Effects of noble metals on metal oxides ................ 31
      Combination of Pt and MnOx .......................... 34
  2.4 Concluding Remarks .................................. 39

CHAPTER 3. CATALYST DEACTIVATION
  3.1 Thermal Deactivation
    3.1.1 General ......................................... 41
    3.1.2 Results and Discussion
      Adherence of washcoat onto metallic monoliths ........ 43
      Characterisation of thermally-treated catalysts .... 45
      Effects of metals in the washcoat .................... 48
      Catalytic activity of thermally-treated catalysts .... 50
3.2 Sulphur Poisoning

3.2.1 General

3.2.2 Results and Discussion

3.2.2.1 Pre-sulphation of the catalysts

3.2.2.2 Sulphur poisoning on stream

3.3 Concluding Remarks

CHAPTER 4. ADDITIVES: LANTHANUM AND CERIUM

4.1 Stabilisers

4.2 Lanthanum

4.2.1 Preparation Method

4.2.2 Effect of the Loading

4.2.3 Effect of Steam

4.2.4 Mechanism of Stabilisation

4.2.5 Additional Effects of Lanthanum

4.3 Cerium in Catalysis

4.3.1 Oxygen Storage Capacity

4.3.2 Noble Metal-Ceria Interactions

4.3.3 Metal Oxide-Ceria Interactions

4.3.4 Additional Effects of Ceria

4.3.5 Deactivation of Ceria

4.3.6 Ceria Promoters

4.3.7 Synergetic Effect between La and Ce

4.4 Results and Discussion

4.4.1 Characteristics of the La- and/or Ce- Doped Washcoat

4.4.2 Effects of La on the Stability of Manganese Oxides Catalysts

4.4.3 Effects of La on the Reducibility of Copper Oxide Catalysts

4.4.4 Effects of La on the Stability of Copper Oxide Catalysts

4.4.5 Synergetic Effects in CuO-Ce and CuO-La-Ce

4.4.6 Synergetic Effects in CuO-Pt-La-Ce

4.5 Concluding Remarks

CHAPTER 5. FIELD APPLICATION

CHAPTER 6. CONCLUSIONS

REFERENCES

APPENDICES: PAPER I TO VI
1

INTRODUCTION

1.1 Background

Coal, oil and natural gas now account for more than 85% of the world’s industrial generation of energy and constitute the main driving force in all industrialised countries [Herzog et al., 2000]. Primarily as a result of burning fossil fuels, the concentration of CO$_2$ in the atmosphere has risen by almost one third, from 280 to 370 ppm, since the beginning of the industrial age, 150 years ago. There are risks for a long term climate change due to the increase of CO$_2$ in the atmosphere, because gases that reflect the infrared radiation from the earth are believed to contribute to surface warming, thereby seriously affecting the conditions of life on earth [Degobert, 1995].

CO$_2$, produced by combustion of biofuels is naturally recycled and consumed in photosynthesis. This means that there is no increase of CO$_2$ in the atmosphere when burning biomass for production of energy.

Efforts to develop ways of producing and using renewable and domestic resources such as biomass for heat and power generation are currently supported by various national and international programs. Governments of developed countries are searching for ways to reduce the emissions, especially CO$_2$, produced by combustion of traditional fuels, whereas developing countries face pressures to build energy systems that supply heat and power to rural areas.

1.1.1 The Power of Biomass

The total energy content of biomass reserves equals the proven oil, coal and gas reserves combined; markedly, 90% of this biomass energy is held in trees. There are indications that bioenergy is catching on as a feasible energy alternative. For example, 15% of the world’s energy requirements are met with biomass fuels; 35% in the developing countries and 3% in the industrialised countries [Kendall et al., 1997].

In Europe, and especially in the Nordic countries and the Alps regions, biofuels are easily available from agricultural and forestry products. In Sweden, a large supply of bioenergy is potentially available. Indeed, approximately 200 TWh could be utilised for production of energy while only 93 TWH is now being consumed of the total Swedish energy supply of 582 TWh [Löfgren, 1998a; Swedish National Energy Administration, 2000]. The
utilisation of bioenergy in Northern Europe has increased appreciably under the last 30 years, particularly after the oil crisis in the beginning of the 70’s. During the 80’s there was inexpensive electricity on the market, and electricity became a popular heating alternative. However, environmental concerns led to a renaissance of the idea of using biomass for energy production during the 90’s.

Due to the high cost for transportation of bulky fuels, large amounts of biofuels are used in residential small-scale heating appliances. In Sweden, the consumption of biofuels in small-scale wood appliances for house heating is around 12 TWh which is approximately 22% of the total energy utilisation for heating single family homes.

Approximately 600 000 boilers, out of a total of 747 000, are thought to be capable of burning wood for home heating in Sweden. Wood is burned regularly in 270 000 of these. Furthermore, there are 965 000 local wood appliances (for example stoves, tiled-stoves) of which 298 000 are used for heating [Askensten, 2000]. In total, more than one third of Swedish homes are able to use wood for heating.

Besides the zero CO₂ net-contribution of wood combustion, there are other advantages of using wood as fuel in Northern Europe. It is a cheap domestic fuel and many people have free access to it. The oil or electricity costs of a Swedish home can be lowered significantly by using wood [Krögerström, 1994]. Using biomass limits the dependence on foreign energy sources, such as coal and petroleum and the risks of sudden increase in their prices. Biomass contains less impurities, as sulphur and heavy metals compared to petroleum and coal. It differs from hydroelectric power, nuclear plants and transportation of fossil fuels with a low environmental impact risk profile.

Although biomass is CO₂-neutral, its combustion is a serious environmental problem. Harmful emissions are present in the flue gases, largely caused by incomplete combustion, particularly in small-scale combustion appliances, mainly in the range up to 100 kW. Indeed, combustion in small-scale appliances is unstable; the inhomogeneous fuel, lack of a proper control system and irregular fuelling are some of the causes that lead to increased emissions relative to larger installations.

1.1.2 Emissions from Small-Scale Combustion of Wood

In some areas wood combustion is regarded as the main contributor to air quality problems. The harmful emissions from combustion of wood consist mainly of Volatile Organic Compounds (VOC), tars including Polycyclic Organic Matter (POM), carbon monoxide (CO) and particulates. VOC refers to the organic compounds which are present in the atmosphere as gases, but under normal temperatures and pressure may also be liquids or solids. Polyaromatic hydrocarbons (PAH) constitute a sublevel to POM and include
all compounds with more than two aromatic rings composed only of carbon and hydrogen with boiling points around 200°C or higher. Under certain conditions there is also a significant emission of nitrogen oxides (NO\textsubscript{x}) due to high concentrations of nitrogen in the fuel and high excess of air.

In Sweden, the emission of VOC from electricity and heat production is 146 000 tons/year (29% of the total amount of VOC in Sweden) and the dominant part (94%; 136 000 tons/year) comes from the small-scale combustion of biofuels [Swedish Environmental Protection Agency, 1992], as seen in Figure 1. In addition, small-scale combustion units contribute to about 50% of the emissions of PAH although it represents only 5% of the total fuel energy [Köthnerg, 2000].

During the initial stage of a wood burning cycle, termed cold-start phase, 60% of the total emissions are released as a result of high volatilisation and low combustion temperature in the fired bed [Axell \textit{et al.}, 1997; Pettersson, 2000]. In the final stage of the combustion cycle, when only a small amount of fuel remains, the excess air ratio increases and the combustion temperature decreases. This is because the heat generation is lower than the heat conveyed by the air. This leads to a higher emission of CO, however, the level of unburned hydrocarbons (HCs) is relatively low, because at this stage the fuel is almost fully devolatilised.

![Figure 1. Distribution of VOC emissions between various sources in Sweden (left) and VOC from electricity and heat production (right) [Swedish Environmental Protection Agency, 1992].](image_url)

These emissions can give rise to deleterious health effects such as cancer, weakened immune defence, allergic reactions as well as odour problems. Also, such emissions may lead to local and global environmental impacts, such as ground level photochemical ozone formation, acidification, stratospheric ozone depletion and greenhouse effect [Erngren & Annerberg, 1993].
1.1.3 Environmental Targets and Legislation

The efficient removal of emissions that contribute to atmospheric pollution is an environmental issue of paramount importance. Increased environmental awareness coupled with European governmental regulations make it necessary to reduce such emissions.

At the European level, emissions of VOC and nitrogen oxides, which are involved in the formation of ground level ozone and photochemical smog, must be reduced by 75% if harmful ground-level ozone and photochemical oxidants levels are to be avoided.

The Swedish government has proposed national environmentally quality objectives. One objective is that by 2020 the emission of carcinogenic substances in urban areas should not exceed the low-risk levels for the protection of human health. This means that levels of benzene and ethene should be lower than $1 \mu g/m^3$ as an annual mean value. By 2020 the concentrations of particulates in the air must not exceed levels that may damage human health, cultural values and materials. This means that levels of inhalable particulates, are less than $15 \mu g/m^3$ as an annual mean value (health). Another objective set by Parliament is a 50% reduction in total emissions of VOC by the year 2010 as compared with 1995 levels (to 219 000 tonnes) [Swedish Environmental Protection Agency, 2001].

Concerning wood combustion in Sweden, regulations from the 80's are among the strongest in Europe. According to National Board of Housing, Building and Planning regulations all new wood-burning units installed in urban areas must be “environmentally approved”, from 1st January 1999. However, the Swedish Environmental Protection Agency proposes that the regulation must also be applied outside urban areas. Environmentally approved wood boilers are allowed to emit a maximum of 30 mg tars/MJ energy produced, and 40 mg/MJ for wood fired-stoves (except open fireplaces which are not included). The regulation is applied on installations that are used on a regular basis, therefore some local heating appliances, used only occasionally, are not included [Krögerström, 1994].

1.1.4 Actions to Reduce the Emissions

There are two principal approaches for decreasing emission from combustion: optimisation of the combustion process and cleaning of flue gases.

To achieve efficient combustion several conditions must be met. Oxygen must be brought in a sufficient amount and must be mixed properly with the fuel. Also, there is an optimum combustion temperature, i.e. 900–1000°C which is based on the conversion of unburned compounds and the formation
of fuel NOx. Finally, the residence time has to be long enough for complete reactions.

The high emission levels are largely due to existing out-of-date units. The average age of wood-fired boilers in Sweden is thought to be 20-25 years. Many existing boilers are of an old type constructed according to the natural draught burning principle with a chamber cooled by water. In these boilers, the combustion temperature is low, which leads to low efficiency, not more than 70%, and higher emission levels than in modern units (Table 1). Efficiency and low emission levels may be improved by fitting supplementary equipment to old boilers or by replacing them with new “environmentally approved” wood-burning boilers. The proportion of units meeting the emission standards set in the National Board of Housing, Building and Planning regulations (so called “environmentally approved units”) varies in Sweden, but it is estimated to be around 17% [Askensten, 2000]. Modern boilers are in theory very efficient with a well-designed ceramic insulated combustion chamber. However, these boilers are generally constructed for a higher output power than the immediate need. Indeed if the size of the combustion chamber is too small, the surfaces of the walls are too large in relation to the volume, leading to a great heat loss through the walls and short gas and particle residence times. Normally, to avoid over-heating of the surroundings, the amount of oxygen is decreased manually to minimise combustion, and this leads to high emission levels.

In order to optimise the utilisation of the boilers, they may be equipped with a hot water storage tank [Krögerström, 1994]. This technique gives a substantial improvement even in combination with traditional boilers. A storage tank allows the boiler to work at full load for shorter periods since the boiler is then being used at its full design capacity. Hot water is then stored in a tank and is available for the whole day. It results in much cleaner flue gases and more efficient boilers (Table 1). For example, the emissions of VOC and tar from traditional boilers equipped with a storage tank are reduced by around 60-70%. Also, this implies wood and time savings as the fuel is added only once or twice a day during wintertime. On the basis of surveys, it is estimated that approximately 30% of existing wood-burning boilers in Sweden are equipped with a hot water storage tank. By the 1st of January 2005, in urban areas all existing wood boilers will have to install a hot water storage tank, or equivalent equipment. A further requirement is that heat storage equipment should be large enough to store the heat generated by a full load of wood inserted in the unit [Köthnig, 2000].

The use of a proper fuel of a relatively small size, low moisture and ash content and of homogeneous composition may also contribute to improved and more even combustion. Pellets for instance have a high potential energy and boilers with pellets burners have low emissions (Table 1).
In some appliances, it is also possible to feed the fuel automatically. This can provide a more stable and efficient combustion, because the temperature, mixing, and residence time are better balanced. Moreover, starting and finishing phases are also decreased due to a more even combustion.

The supply of air that feeds the combustion can also be optimised. A too large supply of air may result in low residence time and low combustion temperature and at the same time, oxygen must be supplied in a sufficient amount to oxidise the products from the pyrolysis. The addition of air and its mixing with gases may be provided by using fans. A further improvement is the use of a sensor (lambda sond) to control the air supply, similar to that used in automotive exhaust systems, thus decreasing emissions during the starting and finishing phases.

Table 1. Comparison of the emissions from different burning units determined for a house with an annual consumption of ca 25 000 kWh [Löfgren, 1998b].

<table>
<thead>
<tr>
<th>Burning units</th>
<th>Emissions (kg/year)</th>
<th>VOC</th>
<th>Tars</th>
<th>Particulates</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional oil boiler</td>
<td>2</td>
<td>ca. 0</td>
<td>3</td>
<td>7</td>
<td>8</td>
<td>10 000</td>
<td></td>
</tr>
<tr>
<td>Traditional wood boiler</td>
<td>720</td>
<td>270</td>
<td>200</td>
<td>5</td>
<td>9</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Traditional wood boiler with hot water storage tank</td>
<td>225</td>
<td>45</td>
<td>8</td>
<td>5</td>
<td>11</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Modern wood boiler with hot water storage tank</td>
<td>28</td>
<td>0.5</td>
<td>2</td>
<td>5</td>
<td>13</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pellets burner</td>
<td>4</td>
<td>0.5</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

1.1.5 Catalytic Oxidation

Optimised combustion techniques can lead to emissions below the limits discussed above, however the costs engendered are sometimes prohibitive. In addition, it is likely that the emission legislation will be more stringent in the near future, since the current limits lead to unacceptable emissions from a health point of view [Viktorin, 1993]. An alternative or supplementary solution is to incorporate a catalytic system to oxidise the unburned compounds to CO₂ and water at moderate temperatures. However, the integration of a catalyst should be considered as a final step in the design of wood burning appliances, because the main objective is to achieve high combustion efficiency.

By using a catalyst the oxidation reactions in the flue gas can proceed although the temperature is lower and the residence time shorter than needed for homogeneous oxidation. It may be possible to install catalysts in traditional installations, but further studies are needed to evaluate this possibility. In addition, the utilisation of a catalytic system lowers the formation of NOₓ and
the material costs for boiler construction because catalytic oxidation is carried out at low temperature. The use of a properly designed and constructed catalytic system would also reduce the deposition of soot on the walls of the flue duct and hence limit the risk of fire.

Catalysts intended for abatement of emissions from wood combustion are found among those which are being developed for other applications such as oxidation in lean-burn engines and removal of industrial solvents, mainly based on noble metals. Catalysts are already used in American, Norwegian and Austrian wood stoves. High conversion of unburned compounds over the catalyst and thus very low emissions for wood-fired boilers equipped with such catalysts have already been demonstrated [Carnö et al., 1996; Berg, 2001]. Nevertheless, the implementation of catalysts in the hostile environment of small-scale wood burning appliances (which can include harsh treatment by user) poses some special problems and challenges, such as:

- Varying temperature conditions (thermal deactivation of the catalyst),
- Ash and particulates deposition on the catalytic surface (mechanical and chemical deactivation),
- Catalyst inefficiency during the cold start-up phase.
- Requirement for a low-cost catalytic system,

1.2 Scope of the Thesis

The present study was part of the activities within the framework of the EC FAIR-CT95–0682 project (1996-1998) “Abatement of emissions from small-scale combustion of biofuels” [Berg & Berge, 1999]. The work at the Royal Institute of Technology was focused on the development of total oxidation catalysts. In parallel with and as a continuation of this work, but outside the scope of this thesis, field tests were performed in collaboration with boiler manufacturers.

The objective of the work, presented here, is the development of catalysts for total oxidation of VOC, CO and CH₄, with particular emphasis on the utilisation of low-cost and environment-friendly raw materials, resistant to thermal and sulphur deactivation and high durability. Monolithic catalysts based on a mixture of metal oxides and noble metals supported on alumina are of particular interest here. Also, improving the understanding of the structural and chemical properties of the catalysts by various characterisation techniques has been attempted using Temperature-Programmed Reduction and Oxidation (TPR and TPO), BET-Surface Area Analysis, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy and Scanning and Transmission Electron Microscopy (SEM and TEM).
The present thesis consists of 6 papers and a main section where the results have been restructured in 4 chapters: “Catalysts for Total Oxidation”, “Catalyst Deactivation”, “Additives: Lanthanum and Cerium” and “Field Application”. Besides the results from the papers, a few additional experimental results are also included in the main section. The details concerning the preparation methods, characterisation techniques, reaction conditions and apparatus are described in the papers. It should be noted that the composition of the synthetic gas mixture used for catalytic activity measurements was chosen to represent some of the most essential compounds emitted from wood combustion. A mixture containing CO (ca 2500 ppm), naphthalene (ca 50 ppm), methane (ca 200 ppm), CO2 (12%), H2O (12%), O2 (10%) and N2 (balance, 66%) was chosen and denoted gas mixture 1. Naphthalene has been replaced in some of the activity measurements by the same amount of ethylene. In that case, the mixture was denoted gas mixture 2.

Paper I describes the influence of the Pt content (0.01 to 1mol%/alumina) and the calcination temperature (500°C and 800°C) on the reduction behaviour of mixed MnOx-Pt/alumina catalysts and on its activity for the oxidation of CO, C10H8 and CH4 in comparison with single component catalysts, i.e., Pt and MnOx catalysts.

Papers II and III discuss other combinations of metal oxides and noble metals. More specifically MnOx and CuO mixed with low amounts of Pt and Pd are investigated with emphasis on the thermal and sulphur resistance of mixed catalysts compared to metal oxide or noble metal catalysts.

Paper IV presents the development of a well-adhered washcoat deposited on a metallic support upon high temperature treatments and discusses the influence of the amount of washcoat as well as the content of MnOx on the oxidation of CO, C10H8 and CH4. Finally, the possibility of minimising the cold-start emissions in a commercial wood boiler by pre-heating a full-scale catalyst based on MnOx-Pt/Al2O3 supported on a metallic monolith is demonstrated.

Paper V focuses on the interactions between metal oxides (MnOx, CuO) and alumina doped with lanthanum. The stabilisation of the washcoat by lanthanum is examined, and more particularly the inhibition of undesirable solid-phase reactions between the active phases and the support during thermal treatment at high temperatures.

Paper VI deals with the promoting effect of Ce and/or La in alumina-supported CuO, Pt and mixed CuO-Pt catalysts. The study investigates the synergism between Cu-Ce and Pt-Ce.
2

CATALYSTS FOR TOTAL OXIDATION

Comparison of different studies concerning the active components in catalysts is usually very difficult because of the divergence in concentrations, supports, preparation techniques, catalyst history and test conditions. The aim of this study is to select catalysts suitable for total oxidation in our reaction medium while at the same time providing high activity and stability at low cost.

2.1 Noble Metal Catalysts

2.1.1 General

Noble metals are well-known oxidation catalysts with high activities, and are widely used for controlling exhaust gas emissions such as VOC, HCs and CO. Apart from the higher specific activities, noble metals are preferred because they are less liable to sulphur poisoning than metal oxide catalysts [Shelef et al., 1978]. Pt and Pd catalysts are the most commonly used for total oxidation [Kummer, 1980]. Pd was less used than Pt until the early 1990s partly because it is more sensitive to lead and sulphur compounds usually present in car exhaust gases. However, sharp decreases in lead levels in fuel led to increased interest in Pd-supported catalysts. The oxides of Pt and Pd formed during reaction cycles are not as volatile in contrast to RuO₂, OsO₄ or Ir₂O₃ which are also poisonous [Cotton & Wilkinson, 1988]. Other noble metals, such as Ag and Au, are not appropriate for high temperature and high space velocity applications. Also, the required use of Rh compared to Pt in TWCs far exceeds the natural ratio occurring in mines. In addition Rh₂O₃ is known to react with alumina [Yao et al., 1980; Shelef & Graham, 1994].

Information concerning the activities of Pt and Pd catalysts varies in the literature. Pt catalysts are well known to be the most active for the combustion of HCs containing more than one carbon atom whereas Pd is the most active catalyst for CO and CH₄ oxidation [Kummer, 1980; Satterfield, 1991; Kang et al., 1994; Burch & Hayes, 1995]. However, Ball & Stack reported that Pt had higher activity than Pd for both the oxidation of HCs and CO [Ball & Stack, 1991].

Oxidation over noble metals is generally considered to be a structure-sensitive reaction [Briot & Auroux, 1990; Briot & Primet, 1991; Hicks et al., 1990a; Baldwin & Burch, 1990], albeit there are some controversy in literature [Chin & Resasco, 1999]. It is an accepted view that whenever the surface
reaction involves the scissions of a C-C bond, structure-sensitivity is to be expected [Gandhi & Shelef, 1987]. Oxidation of saturated hydrocarbons, especially those of short chain length, does not proceed readily on noble metal catalysts with very high dispersion, but rather on larger crystallites of Pt [Gandhi & Shelef, 1987; Otto, 1989; Briot & Auroux, 1990] or Pd [Hicks et al., 1990a; Hicks et al., 1990b; Briot & Primet, 1991; Carstens et al., 1998]. In general, the specific catalytic activity per noble metal surface atom for emission control is larger for the metallic crystallites than for the dispersed metal oxides [Yu Yao, 1984]. However, for Pd, the high thermal stability of the dispersed oxide in particular when CeO₂ is present [Yu Yao, 1984; Groppi et al., 1999] makes it attractive for the oxidation of CO and olefinic or aromatic hydrocarbons. The turnover frequency (TOF) of the Pd for CH₄ oxidation has been reported to increase with the size of the Pd-particles [Hicks et al., 1990a; Chin & Resasco, 1999]. In addition, the activity is strongly influenced by the interaction between Pd and the support [Sekizawa et al., 1993]. Two kinds of Pd oxide has been postulated: dispersed Pd oxide on alumina and Pd oxide deposited on metallic Pd with the latter being very active [Hicks et al., 1990a; Carstens et al., 1998; Chin & Resasco, 1999]. The degree of Pd-oxidation depends on the Pd particle size with small particles being oxidised easily [Hicks et al., 1990a; Chin & Resasco, 1999], while for Pt the formation of dispersed or crystalline phases depends more on the support composition and the method of preparation [Hicks et al., 1990a]. At high temperatures (> 500°C) the activity of supported Pd catalyst for CH₄ oxidation might be due to the ability of the Pd oxide to chemisorb oxygen [Farrauto et al., 1992]. Pd as metal does not chemisorb oxygen above 650°C and is thus inactive toward CH₄ oxidation [Farrauto et al., 1992]. However, CH₄ can dissociatively adsorb on metallic Pd [Solymosi et al., 1994].

Pd was said to be more resistant to thermal sintering in an oxidising environment than Pt [Hegedus et al., 1979; Spivey & Butt, 1992; Heck & Farrauto, 1995]. Indeed, Pt does not penetrate into the alumina support but volatilise under oxidising conditions [Gandhi & Shelef, 1987]. This volatility of Pt when dispersed as an oxide on alumina under oxidising conditions results in a growth of the Pt crystallites. When Pt oxide is completely dispersed, it starts to decompose in oxygen at about 475°C [Kummer, 1986], while larger crystallites of Pt oxide may remained oxidised up to 700°C [Hicks et al., 1990a; Cotton & Wilkinson, 1988]. Pd, however, can be dispersed as oxides on Al₂O₃ at higher temperature (750-850°C) than does Pt [Kummer, 1986]. This interaction between PdO and Al₂O₃ gives considerable activity to Pd-Al₂O₃ catalysts in an oxidising atmosphere.

Pt was found to have higher sulphur resistance than Pd [Hegedus et al., 1979; Deng et al., 1993; Kang et al., 1994] and a quicker recovery once sulphur was removed from the gas stream [Monroe et al., 1991; Beck & Sommers, 1995]. Pt is more active for the oxidation of SO₂ to SO₃ [Kummer, 1980; Ball & Stack,
1991; Heck & Farrauto, 1995], which is regarded as the first step for the formation of sulphate on the catalytic surface. However, the influence of sulphur on the oxidation of HCs was said to be insignificant on both Pt and Pd, especially at high temperatures [Musialik-Piotrowska et al., 1987; Beck & Sommers, 1995].

2.1.2 Results and Discussion [Paper III]

The Pd catalyst was slightly more active than the Pt (0.1 mol%) catalyst for the oxidation of CO, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4}, as seen in Figure 2. The activity loss above 500\degree C of the Pd catalyst for the oxidation of CH\textsubscript{4} with increasing temperature, termed “v” shape, is attributed to the decomposition of PdO to Pd metal, which is less active for the oxidation of CH\textsubscript{4} [Farrauto et al., 1992; Sekizawa et al., 1993; Chin & Resasco, 1999; Forzatti & Groppi, 1999].

![Figure 2. CO, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4} conversion for Al\textsubscript{2}O\textsubscript{3}-supported Pt and Pd (0.1 mol%/Al\textsubscript{2}O\textsubscript{3}), calcined at 800\degree C for 4 h in air. Gas mixture 1.](image)

When C\textsubscript{10}H\textsubscript{8} was replaced by C\textsubscript{2}H\textsubscript{4} in the gas mixture and with an amount of H\textsubscript{2}O of 4\% instead of 12\%, a peculiar C\textsubscript{2}H\textsubscript{4} conversion for Pd was observed as can be seen in Figure 3 [Ferrandon & Björnbom, 1998]. Namely, the conversion of C\textsubscript{2}H\textsubscript{4} occurred readily together with CO until CO was completely converted, above that temperature the oxidation of C\textsubscript{2}H\textsubscript{4} was slowed. This behaviour of C\textsubscript{2}H\textsubscript{4} was seen on the Pd catalyst but not on other catalysts such as Pt or metal oxides. When CO was removed from the gas mixture, the oxidation of C\textsubscript{2}H\textsubscript{4} occurred much slower, suggesting that the presence of CO has a positive effect on the oxidation of C\textsubscript{2}H\textsubscript{4} for a Pd catalyst. Similarly, the presence of CO in the gas mixture had a beneficial effect on the oxidation of CH\textsubscript{4} (Figure 3). Indeed, the temperature required for 50\% conversion of CH\textsubscript{4} was lowered by around 140\degree C, in the presence of CO. In all tests where both CO and CH\textsubscript{4} were present, i.e., experiments 1, 4 and 7 (Table 2), the conversion of CH\textsubscript{4} followed the “v” shape, while in the absence of CO,
no such behaviour was observed. An improvement for the oxidation of C$_{10}$H$_8$ was also seen in presence of CO (Table 2, tests 4 and 5), however, the effect was not as great as for C$_2$H$_4$ and CH$_4$.

![Figure 3. Conversion of the combustibles for a Pd/Al$_2$O$_3$ (0.1 mol%/Al$_2$O$_3$) ing a s mixture 2 (a) and without CO (b). 4% instead of 12% H$_2$O.]

At this stage it is difficult to draw conclusions about the role of CO on the Pd catalyst. However, Carstens et al. have reported that oxidation of Pd under reaction conditions with 3% CH$_4$ formed large PdO crystallites while in the absence of CH$_4$ amorphous PdO was formed, the former being more active for CH$_4$ oxidation [Carstens et al., 1998]. It is probable that the presence of 2500 ppm CO in our reaction medium induces a similar change at the PdO surface.

Table 2. Temperature (°C) for 50% conversion of the combustibles in different mixtures for a Pd/Al$_2$O$_3$ (0.1 mol%/Al$_2$O$_3$). 4% instead of 12% H$_2$O.

<table>
<thead>
<tr>
<th>Tests No.</th>
<th>Combustibles</th>
<th>T$_{50%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO, C$_{10}$H$_8$, C$_2$H$_4$, CH$_4$</td>
<td>181</td>
</tr>
<tr>
<td>2</td>
<td>- , C$_2$H$_4$, CH$_4$</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>CO, C$_2$H$_4$, -</td>
<td>192</td>
</tr>
<tr>
<td>4</td>
<td>CO, C$_{10}$H$_8$, CH$_4$</td>
<td>216</td>
</tr>
<tr>
<td>5</td>
<td>- , C$_{10}$H$_8$, CH$_4$</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>CO, C$_{10}$H$_8$, -</td>
<td>225</td>
</tr>
<tr>
<td>7</td>
<td>CO, - , CH$_4$</td>
<td>184</td>
</tr>
</tbody>
</table>

Some important results from Section 2.1:

The oxidation activity of the Al$_2$O$_3$-supported catalysts (0.1 mol%) is as follows:

- CO, C$_{10}$H$_8$, C$_2$H$_4$: Pd>Pt  
- C$_2$H$_4$: Pt>Pd

C$_{10}$H$_8$, C$_2$H$_4$ and CH$_4$ oxidation on Pd/Al$_2$O$_3$ are enhanced in presence of CO in the gas mixture.
2.2 Metal Oxide Catalysts

2.2.1 General

The high cost of precious metals, their limited availability and their sensitivity to high temperatures have long motivated the search for substitute catalysts. Metal oxides are an alternative to noble metals as catalysts for total oxidation. They have sufficient activity, although they are less active than noble metals at low temperatures. However, at high temperatures the activities are similar. Some metal oxides deteriorate when exposed alternately to oxidising/ reducing atmospheres [Satterfied, 1991]. They may also react with Al₂O₃ to form metal aluminates, MeAl₂O₄, of low activity [Taylor, 1984; Zwinkels et al., 1993; Bolt et al., 1998]. However, some combinations of oxides may have high catalytic performance and high thermal stability as compared to single components. Such catalysts include Cu-Mn [Puckhaber et al., 1989; Agarwal & Spivey, 1992; Wang et al., 1999; Mehandjiev et al., 2000], Cu-Cr [Yu Yao, 1975; Heyes et al., 1982b; Severino et al., 1986; Laine et al., 1987; Terlecki-Baričević et al., 1989; Laine et al., 1991; Stegenga et al., 1991; López Agudo et al., 1992; Kapteijn et al., 1993; Chien et al., 1995; Vass & Georgescu, 1996], Cu-V [Ahlström & Odenbrand, 1990], Ag-Mn [Mehandjiev et al., 1998], Ag-Co [Haruta & Sano, 1983; Watanabe et al., 1996; Luo et al., 1998], Ag-Co [Haruta & Sano, 1983; Luo et al., 1998], Cr-Co [Prasad et al., 1980; Vass & Georgescu, 1996] and Co-Zn [Klissurski & Uzunova, 1993].

Metal oxides are also more susceptible to poisoning by sulphur compounds than noble metals [Ball & Stack, 1991]. However, reports in literature claim some metal oxides have good sulphur poisoning resistance. For some applications, the higher overall loading of metal oxides in the catalysts makes them more tolerant to poisons than noble metals, since some compounds even at low concentrations may quickly poison the limited number of noble metal oxidation sites present [Hegedus et al., 1979]. It has been shown that oxides of Co could act both as catalysts for total oxidation of CO and at the same time they can act as sorbents for sulphur [Pope et al., 1976]. Zarkov and Mehandjiev [Zarkov & Mehandjiev, 1993] found that CoAl₂O₄ is stable towards SO₂ and has activity for CO oxidation similar to that of Pt catalysts. A catalyst containing mostly CuO on Al₂O₃ was found to have high activity for the oxidation of CO and HCs and high sulphur and lead poisoning resistance [Peiyan et al., 1987]. Terlecki-Baričević et al. [Terlecki-Baričević et al., 1989] reported that copper chromite was sulphur resistant because only SOₓ chemisorption occurs, rather than formation of sulphates [Farrauto & Wedding, 1974]. In an investigation of CH₄ and CO oxidation over metal oxides, Yu Yao [Yu Yao, 1975] studied CuO, CuCr₂O₄, Co₃O₄, Fe₂O₃, MnO₂,
SnO$_2$ and ZrO$_2$ and reported that CuO and CuCr$_2$O$_4$ had the highest activity and best sulphur tolerance.

The most active single metal oxide catalysts for complete oxidation for a variety of oxidation reactions are oxides of Ag, V, Cr, Mn, Fe, Co, Ni and Cu [Dmuchovsky et al., 1965; Moro-Oka et al., 1967; Shelef et al., 1968; Heyes et al., 1982a; Spivey, 1989; McCarty et al., 1997; Tahir & Koh, 1997]. However, vanadia is known to convert sulphur into sulphur oxides [Dunn et al., 1998], which can pose a problem when using Al$_2$O$_3$ as a support, since it may react and form sulphate. Chromium is toxic and thereby should be avoided. Among the oxides mentioned in the literature, a few seems particularly promising as follows.

CoO$_x$ is known to be an effective catalyst for total oxidation reactions [Pope et al., 1976; Boreskov, 1982; Sinha & Shankar, 1993; Zarkov & Mehandjiev, 1993; Luo et al., 1998; Ji et al., 2000].

CuO is also a well-known component of oxidation catalysts [Yu Yao, 1975; Kummer, 1980; Severino et al., 1986; Huang & Yu, 1991; Boon et al., 1992; Cordi et al., 1997; Park et al., 1998b], and has been considered as a substitute for noble metal catalysts in emission control applications due to its high activity, tolerance to sulphur [Yu Yao, 1975; Peiyan et al., 1987] and refractory nature [Prasad et al., 1984]. CuO-based catalysts show similar activity to noble metal catalysts for CO oxidation [Kummer, 1980; Larsson et al., 1996] and exhibit the greatest ability amongst Co$_3$O$_4$, MnO$_2$ and Pt to maintain oxidative capacity of butanal under the sulphating effect of mercaptan [Heyes et al., 1982a]. Also, CuO/TiO$_2$ was found to be more active than oxides of Co, Mn and Fe for both CO and toluene oxidation [Larsson et al., 1996].

Among the transition metal oxides, Mn oxides are recognised as being very active for total oxidation of CO and HCs [Kummer, 1980; van de Kleut, 1994; Kalantar Neyestanaki, 1995; Baldi et al., 1998; Lahousse et al., 1998; Tsyrulnikov et al., 1998; Parida & Samal, 1999; Zaki et al., 1999] and they are considered to be environment-friendly materials [Reidies, 1986]. Mn oxides assume a wide range of simple and mixed compositions with Mn atoms in different oxidation states such as $\beta$-MnO$_2$, $\gamma$-MnO$_2$, Mn$_3$O$_8$, $\alpha$-Mn$_2$O$_3$, $\gamma$-Mn$_2$O$_3$ and $\alpha$-Mn$_3$O$_4$, which can, according to Zener [Zener, 1951], establish the necessary electron-mobile environment for optimal surface redox catalysts. Also Mn oxides, compared with other metal oxides for example CuO, present a lower volatility at high temperatures in presence of steam [van de Kleut, 1994] and react to a lower extent with Al$_2$O$_3$ to form spinel aluminate, MnAl$_2$O$_4$, of low activity [Strohmeier & Hercules, 1984]. According to the phase diagrams, Mn oxides react with Al$_2$O$_3$ to form MnAl$_2$O$_4$ only from 1000°C upwards [Ranganathan et al., 1962], while from 800°C upwards, CuO reacts more readily with Al$_2$O$_3$ to form CuAl$_2$O$_4$ [Misra & Chaklader, 1963]. Commercial catalysts based on oxides of Mn are available and used in self-cleaning oven walls [Nishino et al., 1981; Tsyrulnikov et al., 1998].
2.2.2 Results and Discussion

Choice of the metal oxides

Al₂O₃-supported oxides of Cu, Mn, Fe, Co and Ni (prepared by incipient wetness technique and calcined at 800°C for 4 h in air) were compared for their ability to oxidise CO, C₁₀H₈ and CH₄ in the gas mixture, as seen in Figures 4a, 4b and 4c respectively.

Oxides of Cu and Mn seem to be the most active oxidation catalysts in our reaction medium. For the oxidation of CO and CH₄, CuO had a better activity compared to MnOₓ, while for C₁₀H₈, the opposite was observed. Grisel & Nieuwenhuys, also found that CuO was more active than MnOₓ for the oxidation of CO and CH₄ [Grisel & Nieuwenhuys, 2001]. Similar results were also found for unsupported metal oxides [Yu Yao, 1975; Boreskov, 1982].

The activities of oxides of Co and Ni supported on Al₂O₃ were very low, certainly due to the reaction with Al₂O₃ to form spinel at 500°C [Bolt et al., 1999]. It was reported that CoAl₂O₄ has activity for CO oxidation similar to that of Pt catalysts [Zarkov & Mehandjiev, 1993]. On the other hand, it is reported that spinel, such as cobalt and nickel aluminates, has low activity, in agreement with our present results [Garbowski et al., 1990; Schmieg & Belton, 1995; Ji et al., 2000].

Accordingly, further studies have focused on oxides of Mn and Cu.

![Figure 4a](image_url)

Figure 4a. CO conversion for Al₂O₃-supported oxides of Cu, Mn, Fe, Co and Ni (Metal: 10 mol%/Al₂O₃), calcined at 800°C for 4 h in air. Gas mixture 1.
Figure 4b. C<sub>10</sub>H<sub>8</sub> conversion for Al<sub>2</sub>O<sub>3</sub>-supported oxides of Cu, Mn, Fe, Co and Ni (Metal: 10 mol%/Al<sub>2</sub>O<sub>3</sub>), calcined at 800°C for 4 h in air. Gas mixture 1.

Figure 4c. CH<sub>4</sub> conversion for Al<sub>2</sub>O<sub>3</sub>-supported oxides of Cu, Mn, Fe, Co and Ni (Metal: 10 mol%/Al<sub>2</sub>O<sub>3</sub>), calcined at 800°C for 4 h in air. Gas mixture 1.

**Manganese oxides catalysts**

In the following section, the effects of the calcination temperature and the type of Al<sub>2</sub>O<sub>3</sub> support on the oxidation activity of MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> were investigated. Furthermore, the influence of the amount of washcoat that contained MnO<sub>x</sub> as well as the influence of MnO<sub>x</sub> concentration was studied.

**Calcination temperature [Papers I, II, III]**

As mentioned earlier, MnO<sub>x</sub> is known to have many oxidation states, redox reactions are thus of great importance. When heated in air, MnO<sub>x</sub> undergo phase transitions; according to literature data, between 500-600°C MnO<sub>2</sub> is converted into Mn<sub>2</sub>O<sub>3</sub> and above 890°C into Mn<sub>3</sub>O<sub>4</sub> [Reidies, 1986].

Figure 5 presents the results from the activity measurements at 50% conversion, performed in gas mixture 1, on MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (10 mol%/Al<sub>2</sub>O<sub>3</sub>)
catalysts calcined at different temperatures between 500°C and 900°C. The preparation method used for these catalysts was the deposition-precipitation technique, as described in Paper I.

A calcination temperature of 500°C results in the formation of a more active MnOₓ for the oxidation of CO and C₁₀H₈, compared to those calcined at 650°C or 800°C, provided that the catalysts were not exposed to higher temperature than that of the calcination. CH₄ oxidation occurs at a higher temperature than that of the calcination, consequently the activities were equal for catalysts calcined at 500°C and 650°C (Figure 5). According to characterisation using temperature-programmed reduction (TPR) (Table 3), Raman spectroscopy (Figure 6) and X-ray diffraction (XRD) (not shown here), Mn₂O₃ was prevalent in catalysts calcined between 500°C and 800°C, and this in line with literature data [Reidies, 1986].

After treatment at higher temperature, viz. 900°C for 60 h in air with 12% steam [Papers II, III], most of the MnOₓ catalysts were activated for the oxidation of CO and C₁₀H₈ and only slightly deactivated for the oxidation of CH₄, compared to the catalysts calcined at 800°C (Figure 5). The enhancement in activity of the hydrothermally treated MnOₓ catalyst for the oxidation of C₁₀H₈ and CO was probably due to the appearance of a new more active MnOₓ phase, Mn₃O₄ formed during the treatment at 900°C as observed in the characterisation using Raman (Figure 6) [Paper II]. It should be noted that this enhancement is obtained despite the much lower BET-surface area of MnOₓ/Al₂O₃ treated at 900°C (59 m²/g). Similar improvements have also been discussed by Tsyrulnikov et al. [Tsyrulnikov et al., 1991; Tsyrulnikov et al., 1998], who observed an increase in catalytic activity of MnOₓ with a lower average valence state for the oxidation of butane, benzene, and particularly, CO. They attributed the increase of activity to the formation of Mn₃O₄.2 which has a defective structure similar to the structure of Mn₃O₄ spinel.

Therefore it may be concluded that for the oxidation of all the compounds studied here the activity of alumina-supported Mn₃O₄ is superior to that of Mn₂O₃.

Table 3. TPR and BET data of MnOₓ/Al₂O₃ (Mn: 10 mol%/Al₂O₃) calcined at various treatments.

<table>
<thead>
<tr>
<th>Calcination treatments</th>
<th>TPR data</th>
<th>BET-surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/Mn ratio</td>
<td>Predominant species</td>
</tr>
<tr>
<td>500°C, 4 h, air</td>
<td>1.60</td>
<td>Mn₂O₃</td>
</tr>
<tr>
<td>800°C, 4 h, air</td>
<td>1.60</td>
<td>Mn₂O₃</td>
</tr>
</tbody>
</table>
Figure 5. Temperature for 50% conversion of CO, C_{10}H_8 and CH_4 for MnO_x/Al_2O_3 (Mn: 10 mol%/Al_2O_3) calcined at 500°C, 650°C, 800°C for 4 h in air and at 900°C for 60 h in air with 12% steam. Gas mixture 1.

Figure 6. Raman spectra of MnO_x/Al_2O_3 (Mn: 10 mol%/Al_2O_3) calcined at 800°C for 4 h in air (F) and after thermal treatment at 900°C for 60 h in air with 12% steam (A).

Influence of the support

Minimising the undesirable interactions between the active components and the washcoat is a prerequisite for practical applications of the catalysts. MnO_x was supported on either γ-Al_2O_3 or α-Al_2O_3 and tested for the oxidation of a mixture containing CO, C_2H_4 and CH_4.

α-Al_2O_3 was prepared by calcining γ-Al_2O_3 at 1200°C for 4 h, which gave a BET-surface area of 5 m^2/g, compared to γ-Al_2O_3 which has a surface area between 150-250 m^2/g (Table 4). α-Al_2O_3 has a hexagonal close-packed structure that cannot accommodate foreign ions to be in a defective spinel structure such as γ-Al_2O_3, thus the former may interact to a lesser extent with the catalytic components. α-Al_2O_3 is the most thermodynamically stable Al_2O_3, hence encapsulation of the active phases during high-temperature treatment
and thus loss of activity could be avoided, since final phase transformation has already occurred.

The results from the activity measurements, carried out in gas mixture 2, at 50% conversion are presented in Figures 7a, 7b and 7c. Both the oxidations of CO and C2H4 occurred at lower temperature on MnOx/\(\alpha\)-Al2O3, while for the oxidation of CH4, MnOx/\(\gamma\)-Al2O3 led to a higher activity. Remarkably, after a calcination temperature of 1000°C, MnOx/\(\alpha\)-Al2O3 shows a significant increase in activity for the oxidation of CH4 (Figure 7c).

XRD measurements on samples deposited on \(\alpha\)-Al2O3 demonstrated the presence of Mn3O4 already at a calcination temperature of 600°C (Table 4), whereas on samples deposited on \(\gamma\)-Al2O3, no Mn3O4 was found at a calcination temperature lower than 900°C, as shown previously (Table 3). Thereby, the early transformation into Mn3O4 results in a higher activity of the catalysts deposited on \(\alpha\)-Al2O3, compared to \(\gamma\)-Al2O3. The change in oxidation state of MnOx with temperature differs on the two supports, probably due to a higher dispersion of MnOx on \(\gamma\)-Al2O3 that is maintained on the larger surface area and more amorphous support. Because a large dispersion of active components is required for the oxidation of CH4, \(\gamma\)-Al2O3 seems to be the appropriate support for MnOx catalysts.

Table 4. Characteristics of the MnOx supported on \(\alpha\)-Al2O3 and \(\gamma\)-Al2O3 (Mn: 10 mol%/Al2O3) calcined at various temperatures for 4 h in air.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>BET data (m²/g)</th>
<th>XRD data</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-Al2O3</td>
<td>(\alpha)-Al2O3</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>243</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>229</td>
<td>Mn2O3/Mn3O4</td>
</tr>
<tr>
<td>700</td>
<td>201</td>
<td>Mn2O3/Mn3O4</td>
</tr>
<tr>
<td>800</td>
<td>178</td>
<td>Mn3O4</td>
</tr>
<tr>
<td>900</td>
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<td>Mn2O3/Mn3O4</td>
</tr>
<tr>
<td>1000</td>
<td>-</td>
<td>Mn3O4</td>
</tr>
</tbody>
</table>
Figure 7a. Temperature for 50% CO conversion for MnO$_x$ deposited on γ-Al$_2$O$_3$ and α-Al$_2$O$_3$ (Mn: 10 mol%/Al$_2$O$_3$), treated at various temperatures for 4 h in air. Gas mixture 2.

Figure 7b. Temperature for 50% C$_2$H$_4$ conversion for MnO$_x$ deposited on γ-Al$_2$O$_3$ and α-Al$_2$O$_3$ (Mn: 10 mol%/Al$_2$O$_3$), treated at various temperatures for 4 h in air. Gas mixture 2.

Figure 7c. Temperature for 50% CH$_4$ conversion for MnO$_x$ deposited on γ-Al$_2$O$_3$ and α-Al$_2$O$_3$ (Mn: 10 mol%/Al$_2$O$_3$), treated at various temperatures for 4 h in air. Gas mixture 2.
Concentration of active components [Paper IV]

The influence of the amount of washcoat (up to 20 wt% / catalyst weight), as well as the influence of the concentration of MnOx in it (Mn: 5 to 20 mol% / Al2O3) on the activity of catalysts calcined at 800°C for 4 h were studied. The results are presented in Figures 8 and 9.

For the catalysts containing the same total amount of Mn but different amount of washcoat (Figure 8), a high concentration of MnOx in the washcoat, i.e. low amount of washcoat, favoured the oxidation of CO and C10H8, whereas a lower concentration of MnOx in the washcoat, i.e. a high amount of washcoat, gave higher activity for the oxidation of CH4. Because the reaction of CO and C10H8 are fast reactions, an increase dispersion of Mn would increase the internal diffusion and thereby limit the reaction.

In the catalysts, which had the same amount of washcoat (Figure 9), an increased total amount of MnOx resulted in an increase in activity for the oxidation of the three combustibles.

Figure 8. Temperature for 50% conversion of CO, C10H8 and CH4 for MnOx/Al2O3 with different amounts of washcoat, but the same total amount of Mn (ca 3.4 x 10^-4 mol) calcined at 800°C for 4 h in air. Gas mixture 1.

Figure 9. Temperature for 50% conversion of CO, C10H8 and CH4 for MnOx/Al2O3 with different amounts of Mn, but the same total amount of washcoat (20 wt%) calcined at 800°C for 4 h in air. Gas mixture 1.
Copper oxide catalysts [Paper V]

According to reports in the literature, CuO/Al₂O₃ is present under various species that differ in activity towards oxidation of CO and HCs [Marion et al., 1991; Park & Ledford, 1998b]. Therefore it was important to identify the Cu species present in our catalyst samples.

TPR is a very useful method that gives information about the species produced during calcination, especially through analysis of the reduction temperature [Hurst et al., 1982], and it further shows the influence of the support on the metal oxides [Gentry & Walsh, 1982; Solcova et al., 1993].

Dumas et al. [Dumas et al., 1989] showed that H₂ TPR of CuO/Al₂O₃ exhibits different reduction peaks. One corresponds to the reduction at 200-220°C of the surface Cu species for Cu loading under saturation of Al₂O₃, i.e. < 6.4 - 8 mol% Cu / 100 m²/g Al₂O₃ [Friedman et al., 1978]. According to several authors [Wolberg & Roth, 1969; Lo Jacono & Schiavello, 1976; Friedman et al., 1978; Strohmeier et al., 1985], these species, in strong interaction with Al₂O₃, would consist of Cu²⁺ ions, forming on the surface of the Al₂O₃, a structure related to that of a spinel compound. Also, Garbowski and Primet [Garbowski & Primet, 1991] reported that Cu²⁺ ions may be anchored by the hydroxyl groups of Al₂O₃. It is believed that a “surface spinel” compound is an unusual structure (different to bulk spinel compounds), occupying tetragonal distorted octahedral sites (>90%) with only a small fraction located in the tetrahedral sites [Freeman & Friedman, 1978; Friedman et al., 1978]. Two surface Cu species can be distinguished by ESR and magnetic susceptibility: isolated and interacting or clustered ions [Berger & Roth, 1967; Centi et al., 1995; Park & Ledford, 1998b]. As the Cu loading increases, the ratio between the isolated and the interacting species decreased, however Centi et al. reported the latter to be predominant even at very low loading [Centi et al., 1995].

To understand the nature of the Cu species occurring in this study, some TPR experiments on CuO/Al₂O₃ (1.6 to 8 mol% Cu / 100 m²/g Al₂O₃), were conducted. At 1.6 mol% Cu, the TPR profile showed a single peak at 250°C which appeared at a lower temperature with increasing amounts of Cu (Figure 10). It can be seen that above 4.8 mol% Cu, a second peak appeared at 250°C and grew with increasing content of Cu, which also corresponded to the detection of CuO by XRD analyses (data not shown here). Furthermore, the colour of the samples changed from green to grey with an increasing amount of Cu, indicating the progressive formation of CuO. It is known that with higher Cu loading, segregation of CuO appears. Reduction of bulk CuO appears at a higher temperature (ca. 300-350°C) than the reduction of surface Cu²⁺ [Dumas et al., 1989; Marion et al., 1991], since surface ions are more reactive towards hydrogen [Marion et al., 1991]. Moreover, on a large CuO aggregate, H₂ first reduces the surface, generating a skin of metallic copper on the top of CuO. This may in turn reduce the H₂-diffusion rate to the bulk CuO,
hence longer time and consequently temperatures are required to completely reduce the aggregate. It can be observed (Figure 10) that with a higher concentration of Cu, the temperature for reduction of the 2nd step increased indicating that the larger the particle size, the higher is the reduction temperature which tended to be close to that of the bulk CuO. These observations would be helpful concerning the activities in the next sections of this thesis.

Figure 10. TPR profiles of CuO/Al₂O₃ (1.6 to 8 mol% Cu / 100 m²/g Al₂O₃) calcined at 300°C for 4 h. TPR of bulk CuO is also shown. TPR experimental conditions: 40 ml/min, 5% H₂ in Ar.

Some important results from Section 2.2:

 risking oxidation activity of the Al₂O₃-supported oxide catalysts (10 mol%) is as follows:

\[\text{CO, CH}_4: \quad \text{Cu} > \text{Mn} > \text{Fe} > \text{Co} = \text{Ni}\]
\[\text{C}_{10}\text{H}_8: \quad \text{Mn} > \text{Cu} = \text{Fe} > \text{Co} = \text{Ni}\]

\(\text{Fe} \quad \text{Between 500°C and 800°C Al}_2\text{O}_3\)-supported MnOₓ is in the form of Mn₂O₃, while above 900°C as Mn₃O₄ which is more active for the oxidation of CO, C₁₀H₈ and CH₄.

\(\text{Fe} \quad \text{The oxidation activity of the } \gamma \text{ or } \alpha\text{-Al}_2\text{O}_3\text{-supported MnO}_x\text{ catalysts (Mn: 10 mol%/Al}_2\text{O}_3\text{) calcined at different temperature is as follows:}\)
\[\text{CO, C}_2\text{H}_4: \quad \text{MnO}_x/\alpha\text{-Al}_2\text{O}_3 > \text{MnO}_x/\gamma\text{-Al}_2\text{O}_3 \quad (500-1000°C)\]
\[\text{CH}_4: \quad \text{MnO}_x/\gamma\text{-Al}_2\text{O}_3 > \text{MnO}_x/\alpha\text{-Al}_2\text{O}_3 \quad (500-950°C)\]
\[\text{CH}_4: \quad \text{MnO}_x/\alpha\text{-Al}_2\text{O}_3 > \text{MnO}_x/\gamma\text{-Al}_2\text{O}_3 \quad (950-1000°C)\]
The oxidation activity of the Al₂O₃-supported MnOₓ catalysts depends on both the amount of washcoat and the Mn content in the washcoat.

For the same total amount of Mn in the washcoat a low amount of washcoat is preferred for the oxidation of CO and C₁₀H₈, conversely to CH₄. For the same amount of washcoat, an increased amount of Mn enhances the oxidation of all combustibles studied here.

The Al₂O₃ washcoat can accommodate a Cu concentration between 3.2 and 4.8 mol% Cu / 100 m² Al₂O₃. Under this saturation value, Cu species are in the form of surface Cu²⁺ species. Above this saturation value, CuO crystallites are formed.
2.3 Combination of Metal Oxides and Noble Metals

2.3.1 General

As a single component, base metal oxide catalyst cannot rival a precious metal catalyst, hence improvement in their activities has been attempted by combining base metal oxide catalysts and small amounts of noble metals. Mixtures of noble metal and metal oxide merit more attention as catalysts for total oxidation, since both components have different good properties by themselves. Namely, noble metals have moderate oxygen affinity and its release proceeds smoothly [Haruta & Sano, 1983]. So the activity of noble metals may be further increased by combining them with other elements, such as metal oxides, which modify the mobility of oxygen. The role of metal oxides is also to diminish the CO inhibition which is typical of Pt catalysts at low temperatures [Mergler et al., 1996]. On the other hand, Pt helps metal oxides with multioxidation states to accelerate the oxygen transfer from the gas phase to the catalyst [Ménézo et al., 1993]. Pt and Pd can also be incorporated in catalytic systems containing metal oxides in order to increase the selectivity towards CO₂ [Ménézo et al., 1993; Khairulin et al., 1997]. Some studies reported the particular performance of Pt and Pd mixed with metal oxides when pre-reduced [Mergler et al., 1996; Törncrona et al., 1997; Holmgren et al., 1999]. However, in the conditions studied here, with an excess of oxygen, pre-reducing treatment would not be useful for long-term use of the catalysts.

A famous example of synergism is shown by a Au - Fe oxides composite catalysts developed by Haruta et al. for low-temperature oxidation of CO [Haruta et al., 1993]. Au/MnOₓ has also been regarded as a promising catalyst for such reaction with relatively high durability [Gardner et al., 1991]. Grisel & Nieuwenhuys studied the effect of various combinations of metal oxides with Au for the oxidation of CO and concluded that the activities were related to the average particle size whereas the identity of the metal oxides was less important [Grisel & Nieuwenhuys, 2001]. They found also that the oxidation of CH₄ occurred more swiftly on Au/MnOₓ/Al₂O₃ compared to single component catalysts. They concluded that both CO and CH₄ were adsorbed at Au/MnOₓ interface, while the role of MnOₓ was to dissociate O₂ and supply oxygen since Au itself is not active in O-O bond scission.

Another example is a catalyst containing Mn₂O₃ and Pd that showed higher activity for the oxidation of CO than a Pd catalyst and other combinations such as Pd/Fe₂O₃ and Pd/Co₃O₄ catalysts [Tsuji & Imamura, 1993; Imamura et al., 1995]. Imamura et al. attributed the increase of CO oxidation, for unsupported Pd/Mn₂O₃, to an adsorption of CO onto oxidised Pd in contact with Mn₂O₃, and then oxidation of CO into CO₂ which migrates and desorbs from Mn₂O₃ [Imamura et al., 1995]. Also, addition of CoOₓ to Pd causes a
significant decrease in the temperature for oxidation of CO and C₃H₈ under stoichiometric conditions [Skoglundh et al., 1996]. It was observed that CoOₓ could be reduced and oxidised and that the redox Co sites are active for oxidation [Skoglundh et al., 1996; Törncrona et al., 1997]. Some authors also noted that doping of Pd with oxides of Co or Cr decreases the amount of bonded sulphate and thus restrains the poisoning effect on these catalysts [Khairulin et al., 1997].

Mixtures of metal oxides with Pd were reported to be highly active for the oxidation of CH₄. Particularly oxides of Ni have been reported to decrease the Pd particles size and, by stabilising the PdO phase, enhance its activity [Ishihara et al., 1993; Kalantar Neyestanaki & Lindfors, 1998; Widjaja et al., 1999].

The doping of Pt with Al, Cr, Cu, Mn and Co has been reported to result in catalysts with high activity for the oxidation of CO and stability with respect to SO₂ poisoning [Osmanov, 1986]. Compared with unpromoted Pt, promotion with pre-oxidised CoOₓ enhances the low-temperature activity for both CO and C₃H₆ in lean conditions [Törncrona et al., 1997]. Mergler et al. discussed a number of models which could account for the observed improvement in CO oxidation in stoichiometric or rich conditions over a CoOₓ-Pt catalyst [Mergler et al., 1997]. One is based on the reaction between weakly bound O on CoOₓ and CO on Pt at the Co-Pt interface.

2.3.2 Results and Discussion

Combinations of MnOₓ or CuO and Pt or Pd supported on Al₂O₃ were studied in this thesis. Their activities were compared to single component catalysts to identify any synergetic effects, as found for other combinations in the literature reports.

Effects of metal oxides on noble metals [Paper II, III, VI]

Table 5 and Figures 11 and 12 present the results from the activity measurements carried out with the gas mixture 1, while Table 6 and Figure 13 present the results from activity tests performed with the gas mixture 2 (see Section 1.2).

Addition of MnOₓ (10 mol%/Al₂O₃) to the noble metals (up to 0.1 mol%), particularly Pd, decreased the activity of the corresponding noble metals for the oxidation of CO and C₁₀H₈ (Table 5).

Increasing the amount of Pt (0.5 mol%), as seen in Figure 11 and Table 6, dampened the negative effect of mixing Pt and MnOₓ. Indeed, the temperature difference for 50% CO conversion between Pt and MnOₓ-Pt was 80°C at 0.05 mol% Pt, 45°C at 0.1mol% Pt, and only 10°C at 0.5 mol% Pt. In
addition, as seen in Figure 11, MnO\textsubscript{x}-Pt (10-0.5) had a higher activity than Pt catalyst at low conversion levels. For the oxidation of CH\textsubscript{4}, the mixed MnO\textsubscript{x}-Pt and MnO\textsubscript{x}-Pd catalysts had an activity similar to that of the MnO\textsubscript{x} catalyst (Table 5 and Figure 12).

The activity of the mixed CuO-Pt (10-0.1) catalyst was similar, but very slightly decreased, compared to Pt catalyst for the oxidation of CO and C\textsubscript{10}H\textsubscript{8}, and similar to the CuO catalyst for the oxidation of CH\textsubscript{4}, as can be seen in Table 5.

A similar behaviour was observed for mixed CuO-Pd for the oxidation of CO, C\textsubscript{10}H\textsubscript{8} (=Pd) and CH\textsubscript{4} (= CuO). A clear synergetic effect between CuO and Pt was observed for the CuO-Pt catalyst for CO and C\textsubscript{2}H\textsubscript{4} at increased amount Pt (0.5 mol%), as seen in Table 6 and Figure 13.

**Table 5.** Temperature for 50% conversion of CO, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4} for Al\textsubscript{2}O\textsubscript{3}-supported MnO\textsubscript{x}, CuO, Pd, Pt and mixed catalysts calcined at 800°C for 4 h. Mn, Cu, Pt and Pd mol%/Al\textsubscript{2}O\textsubscript{3} are indicated in parentheses. Gas mixture 1.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO</th>
<th>C\textsubscript{10}H\textsubscript{8}</th>
<th>CH\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO\textsubscript{x} (10)</td>
<td>425</td>
<td>365</td>
<td>645</td>
</tr>
<tr>
<td>CuO (10)</td>
<td>344</td>
<td>420</td>
<td>590</td>
</tr>
<tr>
<td>Pt (0.05)</td>
<td>265</td>
<td>270</td>
<td>690</td>
</tr>
<tr>
<td>Pt (0.1)</td>
<td>245</td>
<td>250</td>
<td>640</td>
</tr>
<tr>
<td>Pd (0.1)</td>
<td>217</td>
<td>220</td>
<td>640</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-Pt (10-0.05)</td>
<td>345</td>
<td>335</td>
<td>640</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-Pt (10-0.1)</td>
<td>290</td>
<td>290</td>
<td>640</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-Pd (10-0.1)</td>
<td>290</td>
<td>290</td>
<td>640</td>
</tr>
<tr>
<td>CuO-Pt (10-0.1)</td>
<td>255</td>
<td>265</td>
<td>593</td>
</tr>
<tr>
<td>CuO-Pd (10-0.1)</td>
<td>220</td>
<td>229</td>
<td>595</td>
</tr>
</tbody>
</table>

**Table 6.** Temperature for 50% conversion of CO, C\textsubscript{2}H\textsubscript{4} and CH\textsubscript{4} for Al\textsubscript{2}O\textsubscript{3}-supported MnO\textsubscript{x}, CuO, Pt and mixed catalysts calcined at 800°C for 4 h. Mn, Cu: 10; Pt: 0.5 mol%/Al\textsubscript{2}O\textsubscript{3}. Gas mixture 2.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO</th>
<th>C\textsubscript{2}H\textsubscript{4}</th>
<th>CH\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO\textsubscript{x}</td>
<td>406</td>
<td>450</td>
<td>619</td>
</tr>
<tr>
<td>CuO</td>
<td>327</td>
<td>471</td>
<td>578</td>
</tr>
<tr>
<td>Pt</td>
<td>200</td>
<td>206</td>
<td>629</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-Pt</td>
<td>210</td>
<td>218</td>
<td>620</td>
</tr>
<tr>
<td>CuO-Pt</td>
<td>175</td>
<td>182</td>
<td>576</td>
</tr>
</tbody>
</table>

It should be noted that in the concentrations used in this study, Pt and Pd possess a superior catalytic activity to that of CuO and MnO\textsubscript{x} for the oxidation of CO, C\textsubscript{10}H\textsubscript{8} and C\textsubscript{2}H\textsubscript{4}, while for the oxidation of CH\textsubscript{4}, CuO is largely more active than Pt and Pd, while MnO\textsubscript{x} is as active as Pd and Pt.
Figure 11. CO conversion for Al₂O₃-supported MnOₓ, Pt and mixed MnOₓ-Pt catalysts calcined at 800°C for 4 h in air. Mn and Pt mol% / Al₂O₃ are indicated in parentheses. Gas mixture 1.

Figure 12. CH₄ conversion for Al₂O₃-supported CuO, MnOₓ, Pd, mixed CuO-Pd and MnOₓ-Pd catalysts calcined at 800°C for 4 h in air. Mn, Cu and Pd mol% / Al₂O₃ are indicated in parentheses. Gas mixture 1.

Figure 13. CO conversion for Al₂O₃-supported CuO, Pt and mixed CuO-Pt catalysts calcined at 800°C for 4 h. Cu: 10; Pt: 0.5 mol% / Al₂O₃. Gas mixture 2.
The different effects of metal oxides on noble metals can explain the differences in the activity behaviour of the mixed metal oxide-noble metal catalysts, with either MnOx or CuO, compared to the activity of the noble metals. SEM analyses were conducted on some of the samples. Back-scattered electron (BSE) detection, based on composition contrast was used to distinguish the heavy platinum (white spots) from the lighter components in the washcoat (darker background). It revealed a better dispersion and smaller size of Pt particles in CuO-Pt (Figure 14b), compared to Pt alone (Figure 14a), whereas in MnOx-Pt catalyst (Figure 14c), Pt seemed to disappear in the washcoat. Encapsulation of the noble metals by the metal oxides could explain a lower activity of MnOx-Pt and MnOx-Pd catalysts relative to the noble metal catalysts, as observed by SEM measurements. With increasing amounts of noble metal but similar amounts of metal oxides, the effect of the encapsulating phenomenon is dampened. The encapsulating effect is also stronger from MnOx than for CuO. The effect is more obvious on mixed-Pd than on mixed-Pt catalysts. The fact that the oxidation of CH4 is inhibited at low conversion on mixed CuO-Pd compared to that of Pd may be due to encapsulation of Pd that is covered, since at low conversion the reaction occurs on the surface. Since the oxidation of CH4 requires large numbers of active sites, the effect of the encapsulation phenomenon prevails, hence the activity of the mixed catalysts is similar to that of metal oxides.

Figure 14: SEM micrographs of Pt/Al2O3 (a), CuO-Pt/Al2O3 (b) and MnOx-Pt/Al2O3 (c) calcined at 800°C for 4 h in air. Mn, Cu: 10; Pt: 0.5 mol%/Al2O3. White spots correspond to Pt particles.
There are maybe also other effects than mechanical encapsulation of the noble metals by metal oxides.

Hurst et al., 1982 have studied the interaction between noble metal and metal oxide by TPR and reported the inclusion of small amounts of noble metals in the lattice of metal oxides [Hurst et al., 1982]. They observed also that at high noble metal loading, a metal oxide lattice is less able to tolerate noble metal ions and phase separation occurs, producing a noble metal-rich phase that can result in a shoulder in the TPR profile. TPR experiments performed on MnO\textsubscript{x}-Pt with two different loadings of Pt (0.1 and 1 mol%/Al\textsubscript{2}O\textsubscript{3}) indicated the formation at 1 mol% Pt of a low-temperature peak in the reduction profile, as seen in Figure 15. This confirms the formation of a mixed Pt-MnO\textsubscript{x} phase at a low Pt loading and a Pt-rich phase at a higher Pt loading. This is also in agreement with the activity tests which show that at low Pt loadings due to strong interactions between metal oxides and Pt, the mixed MnO\textsubscript{x}-Pt catalysts are less active than Pt catalysts, while at higher Pt loadings, the activity of the mixed catalysts are approaching the activities of Pt catalysts.

![Figure 15. TPR profiles of Al\textsubscript{2}O\textsubscript{3}-supported MnO\textsubscript{x}-Pt calcined at 800°C for 4 h. Mn, 10; Pt 0.1 and 1 mol%/Al\textsubscript{2}O\textsubscript{3}. TPR experimental conditions: 17 ml/min, 10% H\textsubscript{2} in Ar.](image)

Another reason for the decrease in activity when a noble metal is mixed with a less electronegative cation has been discussed by several authors. Sugaya et al. found that the oxidation of Pt is favoured by the addition of basic MgO\textsubscript{x} and that PtO\textsubscript{x} is less active than Pt metal for the oxidation of some alkanes [Yu Yao, 1980; Sugaya et al., 1994]. However, due to the small amounts of noble metals, it is difficult to characterise them, therefore we cannot conclude on this last point.
Effects of noble metals on metal oxides [Papers I, II, III]

In the previous sub-section, metal oxides were found to affect the activity of noble metals. Here some contradictory effects are presented, i.e. noble metals, Pd or Pt, are shown to affect the reduction behaviour of oxides of Mn and Cu, as well as their oxidation state.

The reduction behaviour of CuO and MnO\textsubscript{x} was studied by means of TPR. Mn and Cu-based samples containing noble metals, and more particularly Pd showed lower reduction peak temperatures compared to MnO\textsubscript{x} or CuO alone, as seen in Figures 16a and 16b. The effect of noble metals on the reduction temperature of metal oxides has been reported [Gentry et al., 1981; Hurst et al., 1982] with Pd having a stronger effect than Pt. The presence of group VIII metals promotes the reduction of metal oxide. Gentry et al. [Gentry et al., 1981] studied the effect of various amounts of Pt and Pd on the reduction of unsupported CuO. They proposed the following mechanism: Hydrogen is dissociatively adsorbed on metal islands of Pd and Pt and transferred by a spillover process to CuO, which then is easily reduced. According to Gentry et al., Pd has a stronger effect on the reduction of CuO relative to Pt due to the ability of Pd\textsuperscript{2+} to substitute Cu\textsuperscript{2+} within the CuO lattice without phase separation.

Figure 16. TPR profiles of Al\textsubscript{2}O\textsubscript{3}-supported MnO\textsubscript{x}, MnO\textsubscript{x}-Pt and MnO\textsubscript{x}-Pd, (a); CuO, CuO-Pt and CuO-Pd, (b). All samples calcined at 800°C for 4 h. Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al\textsubscript{2}O\textsubscript{3}. TPR experimental conditions: 17 ml/min, 10% H\textsubscript{2} in Ar.
When increasing the amount of noble metals, the reducibility of MnO$_x$ was enhanced as seen in Figure 17. For the mixed MnO$_x$-Pt catalysts, the reduction rate was high and resulted in narrow single peaks at lower temperatures than for MnO$_x$ alone.

The presence of noble metals not only affected the reducibility of metal oxides but also the oxidation state that is fixed during preparation of the catalysts. This was determined according to the hydrogen consumed during TPR measurements carried out on MnO$_x$/Al$_2$O$_3$ and mixed MnO$_x$-Pt/Al$_2$O$_3$. The amount of hydrogen consumed remained constant for all the catalysts calcined at 800°C and gave a O/Mn molar ratio close to 1.6, which corresponds to the level of Mn$_2$O$_3$ present. When the catalysts were calcined at 500°C, the ratio was also 1.6 for the Mn sample but increased with increasing amount of Pt and reached 1.95, which corresponded to the presence of MnO$_2$, when the Pt amount was 1 mol% /Al$_2$O$_3$. This increase of the O/Mn ratio in the presence of 1 mol% Pt and this could not be attributed to an oxygen increase caused by Pt oxide, since its reduction causes low hydrogen consumption. Thus, Pt at high concentration increased the oxidation state of MnO$_x$.

![Graph](image)

Figure 17. TPR profiles of Al$_2$O$_3$-supported MnO$_x$ and mixed MnO$_x$-Pt with different concentrations of Pt calcined at 800°C for 4 h. Mn: 10; Pt: 0.01 to 0.5 mol% /Al$_2$O$_3$. TPR experimental conditions: 50 ml/min, 10% H$_2$ in Ar.

With TPR it is somehow difficult to evaluate the proportions of different oxides, since the hydrogen consumption during TPR gives the total oxidation
Moreover, in the presence of noble metals, the reduction steps particular to each oxidation state of MnO\(_x\) are not so well defined. Therefore, the use of a more accurate technique was necessary. Raman spectroscopy was conducted on reference compounds (Figure 18a) and on MnO\(_x\) alone and mixed with noble metals after different thermal treatments (Figure 18b). When comparing the composition of the catalysts calcined at 800°C (F), an increase in oxidation state can be observed in the presence of noble metals, i.e. towards MnO\(_2\), while MnO\(_x\) alone contains mostly Mn\(_2\)O\(_3\). A similar tendency towards higher oxidation state of MnO\(_x\) in the presence of noble metals was observed after thermal treatments at 900°C for 60 h in air with 12% steam (A), especially for MnO\(_x\)-Pd. Indeed, the addition of noble metals decreased the amount of Mn\(_3\)O\(_4\) (Figure 18b). This is in agreement with the activity measurements of thermally treated catalysts. Whereas, on MnO\(_x\) alone, the formation of Mn\(_3\)O\(_4\) induced a significant increase in activity, as seen in Figure 19, it could not be observed on MnO\(_x\)-Pd (10-0.1) catalyst, since the latter contained a lower amount of Mn\(_3\)O\(_4\). However, for a lower amount of Pt (0.05) in MnO\(_x\)-Pt, the boost of activity could be observed (Figure 20), because a lower amount of noble metals influences the oxidation state of MnO\(_x\) to a lower extent. The possible reason for an increase of oxidation state of MnO\(_x\) in the presence of noble metals, is an activation of oxygen in the gas phase during calcination that adsorbs preferentially on noble metals and is spilled over MnO\(_x\).

Figure 18. Raman spectra of bulk MnO\(_2\), Mn\(_2\)O\(_3\), Mn\(_3\)O\(_4\) and MnO reference compounds (a), Al\(_2\)O\(_3\) supported MnO\(_x\), mixed MnO\(_x\)-Pt and MnO\(_x\)-Pd samples calcined at 800°C for 4 h in air (F) and after thermal treatment at 900°C for 60 h in air with 12% steam (A). Mn: 10; Pt, Pd: 0.1 mol%/Al\(_2\)O\(_3\).
Figure 19. \(\text{C}_{10}\text{H}_8\) conversion for \(\text{Al}_2\text{O}_3\)-supported \(\text{MnO}_x\) and mixed \(\text{MnO}_x\)-Pd calcined at \(800^\circ\text{C}\) for 4 h in air (F) and after thermal treatments at \(900^\circ\text{C}\) for 60 h in air with 12\% steam. \(\text{Mn}: 10; \text{Pd}: 0.1\text{ mol\%}/\text{Al}_2\text{O}_3\). Gas mixture 1.

Figure 20. \(\text{C}_{10}\text{H}_8\) conversion for \(\text{Al}_2\text{O}_3\)-supported \(\text{MnO}_x\), Pt and mixed \(\text{MnO}_x\)-Pt calcined at \(800^\circ\text{C}\) for 4 h in air (F) and after thermal treatments at \(900^\circ\text{C}\) for 60 h in air with 12\% steam (A). \(\text{Mn}: 10; \text{Pt}: 0.05\text{ mol\%}/\text{Al}_2\text{O}_3\). Gas mixture 1.

**Combination of Pt and \(\text{MnO}_x\)**

Among the combinations of metal oxide and noble metal, our interest has been focused on the mixture of \(\text{MnO}_x\) and Pt. Some results concerning the deposition method of Pt and its concentration into \(\text{MnO}_x\)-Pt/\(\text{Al}_2\text{O}_3\), as well as the effect of the calcination temperature on the activity of the mixed \(\text{MnO}_x\)-Pt/\(\text{Al}_2\text{O}_3\) catalysts are presented here.

**Impregnation method of Pt on \(\text{MnO}_x/\text{Al}_2\text{O}_3\)**

Two methods of impregnation of Pt into \(\text{MnO}_x\)-Pt (\(\text{Mn}, 10; \text{Pt}, 0.1\text{ mol\%}/\text{Al}_2\text{O}_3\)) catalysts were investigated. The aim is to see if there is a
possibility to avoid encapsulation of Pt by MnOₓ and if one method tends to stabilise Pt against thermal damages. The first consisted of mixing the Pt precursor in the aqueous slurry together with Mn salt, Al₂O₃ and urea [Paper IV] before precipitating the active components. The second method was carried out by impregnating the Pt precursor after Mn has been deposited onto Al₂O₃ and calcined at 500°C for 4 h. Thus, the first method was denoted as co-impregnation (CI) and the second as successive impregnation (SI). In both cases, the catalysts were finally calcined at 800°C for 4 h.

As seen in Figure 21 and in Table 7, the SI method used for the mixed catalysts calcined at 800°C for 4 h resulted in a higher activity for both CO and C₂H₄ oxidation, while for CH₄, there was no difference (not shown here). This was probably due to the inhibition of the encapsulation of Pt into MnOₓ by employing the SI technique, conversely to the CI one.

Interestingly, it can be seen that MnOₓ-Pt (SI) had a larger activity for the oxidation of CO and C₂H₄ compared to the Pt catalyst (Figure 21). Thus not only the encapsulation of the noble metals was avoided, but the activity was enhanced, probably due to the synergetic effect of metal oxides that provided oxygen and noble metals that adsorbed CO or C₂H₄, while the reaction occurred at the interface, as discussed in the introduction of this chapter.

However, after thermal treatments at either 900°C or 1000°C, the activity seemed to be better stabilised when using the CI method, as seen in Figure 22 and Table 7.

It can be concluded that encapsulation of Pt by MnOₓ may lower the activity of fresh Pt catalyst, but at higher temperatures the CI method may result in a slightly more thermally stable catalyst.

![Figure 21. Conversion of CO for MnOₓ-Pt/Al₂O₃, prepared by co-impregnation (CI) or successive impregnation (SI) calcined at 800°C for 4 h in air. Pt/Al₂O₃ calcined at 800°C for 4 h in air is also added. Mn: 10; Pt: 0.1 mol%/Al₂O₃. Gas mixture 2.](image-url)
Figure 22. Conversion of CO for MnO\textsubscript{x}-Pt/Al\textsubscript{2}O\textsubscript{3}, prepared by co-impregnation (CI) or successive impregnation (SI) calcined at 900°C (70 h) and 1000°C (4 h) in air. Gas mixture 2.

Table 7. Temperature for 50% conversion of C\textsubscript{2}H\textsubscript{4} for mixed MnO\textsubscript{x}-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts calcined under various treatments in air. Mn: 10; Pt: 0.1 mol%Al\textsubscript{2}O\textsubscript{3}. Gas mixture 2.

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Calcination treatments</th>
<th>800°C, 4h</th>
<th>900°C, 70h</th>
<th>1000°C, 4h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-impregnation</td>
<td>253</td>
<td>267</td>
<td>285</td>
<td></td>
</tr>
<tr>
<td>Successive-impregnation</td>
<td>194</td>
<td>262</td>
<td>279</td>
<td></td>
</tr>
</tbody>
</table>

Effect of the amount of Pt on MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts [Paper I]

Figures 23a and 23b show the conversion of CO and C\textsubscript{10}H\textsubscript{8}, respectively, for combined MnO\textsubscript{x}-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts with varying amounts of Pt, calcined at 800°C.

It clearly shows that the higher the concentration of Pt, the higher the activity. Even very low amounts of Pt, such as 0.05 mol% of the washcoat amount, had effects on the activity for oxidation of CO and C\textsubscript{10}H\textsubscript{8}. Compared to the catalyst with only MnO\textsubscript{x}, the temperature for 50% conversion was decreased by 90°C for CO and by 25°C for C\textsubscript{10}H\textsubscript{8} oxidation, respectively.

The activity for CH\textsubscript{4} oxidation was not as affected by the addition of Pt at low concentrations (not shown here). This is consistent with the fact that metal oxides and noble metals have similar activities at high temperatures. Namely the temperatures for 50% CH\textsubscript{4} conversion for MnO\textsubscript{x} and MnO\textsubscript{x}-Pt, with an amount of Pt up to 0.5 mol%, were similar and equal to ca 640°C. An amount of 1 mol% Pt was necessary to enhance the activity to T\textsubscript{50%} = 612°C. Thus, the superiority of Pt to MnO\textsubscript{x} seemed to be less pronounced for CH\textsubscript{4} oxidation than for oxidation of the other compounds.
Figure 23a. CO conversion for Al₂O₃-supported MnOₓ and MnOₓ-Pt calcined at 800°C for 4 h in air. Mn: 10; Pt: 0.01 to 1 mol%/Al₂O₃. Gas mixture 1.

Figure 23b. C₁₀H₈ conversion for Al₂O₃-supported MnOₓ and MnOₓ-Pt calcined at 800°C for 4 h in air. Mn: 10; Pt: 0.01 to 1 mol%/Al₂O₃. Gas mixture 1.

Calcination temperature of MnOₓ-Pt/Al₂O₃ [Paper I]

The influence of the calcination temperature on MnOₓ-Pt/Al₂O₃ catalysts with various concentrations of Pt in it was studied. The results are presented in Figure 24 and Table 8.

With increasing Pt content in the mixed catalysts, from 0.05 to 0.5 mol%, the activities for CO and C₁₀H₈ oxidation of the catalysts calcined at 800°C gained over those calcined at 500°C, as seen in Figure 24 for CO. A possible explanation is that higher calcination temperatures may result in the migration of “trapped” Pt to the surface, increasing the activity of the mixed catalysts calcined at 800°C relative to those calcined at 500°C. However, when the concentration of Pt was 0.01 or 1 mol% the mixed catalysts calcined at 500°C were more active.

MnOₓ as well as Pt alone catalysts were more active when calcined at 500°C instead of 800°C as seen in Figure 24 for MnOₓ catalysts and in Table 8 for Pt
catalysts for the oxidation of CO and C_{10}H_{8}. For the oxidation of CH_{4}, Pt calcined at 500°C has higher activity compared to that calcined at 800°C, however for MnO_{x}, the temperatures for oxidation are similar for both calcination. Thus it may be assumed that the higher activity for the mixed catalysts exposed to the higher temperature is due to some favourable synergetic effects.

Table 8. Temperature for 50% conversion of CO, C_{10}H_{8} and CH_{4} for Pt/Al_{2}O_{3} (0.05 mol%/Al_{2}O_{3}) calcined at various temperatures for 4 h in air. Gas mixture 1.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>T_{50%} (°C)</th>
<th>CO</th>
<th>C_{10}H_{8}</th>
<th>CH_{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>226</td>
<td>241</td>
<td>665</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>265</td>
<td>270</td>
<td>686</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 24. Temperature for 50% conversion of CO and CH_{4} for MnO_{x}/Al_{2}O_{3} and MnO_{x}-Pt/Al_{2}O_{3} calcined at 500°C and 800°C for 4 h in air. Mn: 10; Pt: 0.01 to 1 mol%/Al_{2}O_{3}. Gas mixture 1.](image)

Some important results from Section 2.3:

When 0.1 mol% Pt or Pd is mixed with metal oxides (Mn, Cu: 10 mol%/Al_{2}O_{3}), it results in either an alteration (with MnO_{x}) or a similarity (with CuO) of the activity of the noble metal catalysts for the oxidation at CO and C_{10}H_{8}. The order of activity of the catalysts, calcined at 800°C, is as follows:

\[
\text{Pd} = \text{CuO-Pd} > \text{Pt} = \text{CuO-Pt} > \text{MnO}_{x}-\text{Pd} > \text{MnO}_{x}-\text{Pt}
\]

At higher noble metal concentration (Pt: 0.5 mol%/Al_{2}O_{3}) the effect is dampened:

\[
\text{MnO}_{x}-\text{Pt} = \text{Pt} > \text{MnO}_{x}
\]

and for CuO-Pt catalysts there is a synergetic effect:

\[
\text{CuO-Pt} > \text{Pt} > \text{CuO}
\]

For the oxidation of CH_{4}, the mixed catalysts have a similar activity to that of the metal oxides:

\[
\text{CH}_{4}: \quad \text{CuO} = \text{CuO-Pd} = \text{CuO-Pt} > \text{Pd} = \text{MnO}_{x}-\text{Pd} = \text{MnO}_{x}-\text{Pt} = \text{MnO}_{x} = \text{Pt}
\]
The presence of noble metals in the mixed catalysts induces an increase of reducibility for CuO and MnOx and a higher oxidation state of MnOx.

When Pt is successively impregnated (SI) in the preparation of the mixed MnOx-Pt catalysts calcined at 800°C, it results in synergetic effect for the oxidation of CO and C2H4:

\[
\text{MnOx-Pt (SI) > Pt > MnOx-Pt (CI) (800°C, 4 h)}
\]

At higher calcination temperature the co-impregnation method (CI) is catching on:

\[
\begin{align*}
\text{MnOx-Pt (SI) = MnOx-Pt (CI) (900°C 70 h)} \\
\text{MnOx-Pt (CI) > MnOx-Pt (SI) (1000°C, 4 h)}
\end{align*}
\]

## 2.4 Concluding Remarks

In our reaction medium, the activity of 0.1 mol% Pd/Al2O3 was found to be superior to that of the same amount of Pt for the oxidation of CO, C10H8 and CH4, whereas the opposite was observed for the oxidation of C2H4. When CO (2500 ppm) is present in the synthetic gas mixture, it was found to enhance appreciably the activity of the Pd/Al2O3 catalyst for the oxidation of the other combustibles, i.e. C2H4, C10H8 and CH4.

Al2O3-supported MnOx and CuO (Mn, Cu: 10 mol%/Al2O3) were selected, among the oxides of Fe, Co and Ni, as high active catalysts for the oxidation of all the combustibles studied here. It was found that a calcination temperature of 900°C on MnOx/Al2O3 results in an increase in the oxidation state of MnOx towards Mn3O4, yielding, despite a surface area loss, a more active catalyst.

Pt and Pd possess superior catalytic activity relative to CuO and MnOx for the oxidation of CO, C10H8 and C2H4, however, for the oxidation of CH4, CuO is largely more active than Pt and Pd, while MnOx is as active as Pd and Pt.

In mixed catalysts, MnOx tends to form a mixed phase with Pt at low noble metal loadings that encapsulate noble metals, hence inhibiting activity. The encapsulation is avoided by using a successive impregnation of Pt which in addition leads to enhanced catalytic activities for mixed MnOx-Pt compared to that of Pt. Furthermore, the inhibiting effect is dampened by using a higher amount of Pt, i.e. 0.5 mol%.

Mixed CuO-Pt and CuO-Pd catalysts (Cu: 10; Pt, Pd: 0.1 mol%) preserve the individual activities of each active components for the respective combustible. In addition, at higher Pt loading (0.5 mol%), there is a synergetic effect between CuO and Pt which yields a higher conversion of CO and C2H4, relative to single component catalysts.

All mixed metal oxide-noble metal catalysts benefit from the presence of the metal oxides for the oxidation of CH4.

The synergetic catalytic effects between metal oxides and noble metals can be related to the increase of reducibility of the metal oxides in the presence of
noble metals which may enhance the oxygen transfer from the gas phase to the noble metals.
The practical application of a particular catalyst depends not only on its activity but also on its thermal stability and resistance to poisons. Increasing the lifetime of catalysts for the removal of VOC is one of the biggest challenges of catalyst development today. The deactivation of catalysts falls into four general categories: chemical, fouling, mechanical and thermal [Carol et al., 1989]. In this chapter, thermal treatments in the presence of steam, presulphation and sulphur poisoning on stream are discussed.

3.1 Thermal Deactivation

3.1.1 General

The thermal degradation of supported catalysts in wood boilers is caused not only by high temperature but also by sudden temperature changes. Usually the maximum temperature within a flue duct is around 700°C, however, peaks at higher temperatures have also been registered [Berg, 2001]. Moreover, the sintering of catalysts could be accelerated due to the oxidising [Wanke & Flynn, 1975] and steam-containing atmosphere [Wanke et al., 1987] in wood boilers as well as in many industrial applications [Brey & Krieger, 1949; Aldcroft et al., 1968].

Thermal deactivation, in contrast to other types of deactivation, is a more serious problem as it is irreversible. Thermal deactivation of the catalysts may result in thermal damage of the monolith substrate, washcoat and the active phases as well, as the formation of compounds of lower or negligible activities by reactions of the active material with the support [Trimm, 1991].

Monolith substrates may be made of either metallic or ceramic materials. Metallic monoliths present some advantages over ceramic monoliths, such as lower heat capacities and greater thermal shock resistance. Metallic monoliths are used in pre-heated catalytic converters for minimising the cold-start phase. Any flow maldistribution concentrates the thermal ageing to certain areas of the monolith. Compared with the ceramic monolith, the metallic monolith, with its higher thermal conductivity, suffers less from thermal ageing [Twigg & Webster, 1998]. The lower heat resistance of metallic supports compared with that of ceramic supports does not have to be a limitation in wood boiler
applications since the maximum temperatures in the flue gas duct can be kept below 900°C. Nevertheless, metallic monoliths present some disadvantages. For example, the deposition of washcoats on metallic monoliths is not as well developed as for ceramic monoliths. The non-porous nature of the metal foil, coupled with the mismatch in the thermal expansion between the foil and the ceramic washcoat, contributes to a washcoat adhesion problem during thermal cycling.

Many important industrial processes are based on high-surface-area (150-200 m²/g) γ-Al₂O₃-supported catalysts. γ-Al₂O₃ loses surface area by two processes: sintering and phase transformation to α-Al₂O₃ at about 1000-1150°C, depending on the starting material [Trimm, 1991]. α-Al₂O₃ is the most thermodynamically stable phase with a surface area of ca 2 m²/g [Trimm, 1991]. Sintering is the redistribution of material in the solid state in order to decrease the surface energy. With a high temperature, and in the presence of water vapour, the surface defects become very mobile and reactive, allowing interactions between Al₂O₃ particles (hydrogen bonded hydroxyl groups for instance), and by subsequent water elimination, a “neck” is formed [Johnson, 1990]. This process can continue, resulting in a low surface area Al₂O₃ and finally its transformation into the α form. Sintering occurs before the phase transformation due to very different kinetic rates between both processes [Schaper et al., 1985; Burtin et al., 1987b]. Moreover, when γ-Al₂O₃ is transformed to the α state this is accompanied by a decrease in the mechanical strength of the catalyst [Shkrabina et al., 1995].

Because the transformation of the metastable α-phase is irreversible, loss of activity is permanent. Such morphological changes in a catalyst support are accompanied by a loss of activity occasioned by an encapsulation of the active component, known as the “earthquake phenomena” [Tucci, 1982]. Moreover, thermal sintering of the Al₂O₃ washcoat causes loss of the metal surface area (crystallite sintering) due to macroscopic movements of the substrate during phase transformation of the Al₂O₃ [Dalla Betta et al., 1976; Chu & Ruckenstein, 1978; Miyoshi et al., 1989].

On the other hand, it has been observed that metals such as Pt [Kozlov et al., 1973; Vereschagin et al., 1982; Burtin et al., 1987a], as well as oxides of metals such as Mn, Fe, Ni, Mo, Co, V and Cu [Fink, 1968; Bye & Simpkin, 1974; Gauguin et al., 1975; Young et al., 1980; Vereschagin et al., 1982; Peiyan et al., 1995; Ozawa et al., 1996a], accelerated the phase transformation of Al₂O₃ into the stable α form. Fink proposed that the impurities act as mineralisers, destroying the metastable Al-O-Al bond in γ- or θ-Al₂O₃ [Fink, 1968]. This can be explained by cation migration of some transition metals, which occurs at temperatures of ca 1000°C at rates of 100-1000 times faster than those of Al₂O₃ [McCarty et al., 1999]. In addition, metal oxides generally have a stronger effect on sintering than noble metals, because of their higher concentration.
3.1.2 Results and Discussion

In this part, the effects of thermal treatments on i) the adherence of washcoat onto metallic substrate, ii) the properties of the active components, and iii) the influence of active phases on the Al₂O₃-phase transformation are discussed. Finally the activity of mixed noble metal-metal oxide and single component catalysts are presented.

Adherence of washcoat onto metallic monoliths [Paper IV]

The effect of hydrothermal treatment at 900°C for 270 h in air with 10% steam on the adherence of the washcoat onto a Fecralloy metallic substrate (Emitec GmbH, Germany) was studied using SEM. To obtain a better adherence of the washcoat onto the substrate, the latter was first subjected to a special treatment in our laboratory. This led to the migration of Al₂O₃ to the surface, formed by the oxidation of bulk aluminium, thus providing a textured whisker structure, as seen in Figure 25a. The mean size of the whiskers formed, which completely covered the metal surface, varied between 1 and 2 µm. The advantage associated with the Al₂O₃ film is its compatibility with Al₂O₃-containing washcoat, which substantially eases application and ensures its adhesion to the substrate. Also, the Al₂O₃ layer completely covered the metal surface, thus rendering the alloy highly oxidation-resistant.

Figure 25 a. SEM micrographs of the alumina whiskers on bare metal. Side view (left) and view from above (right).
SEM pictures revealed the presence of cracks in the washcoat after calcination at 800°C for 4 h, probably due to the mismatch in the thermal expansion between the metal foil and the washcoat (not shown here). Figure 25b shows a layer of washcoat deposited on the Al₂O₃ whiskers from the metallic surface. The whiskers act as anchors for the washcoat when deposited onto the substrate. Figure 25c shows the layer of washcoat deposited on the metallic substrate after hydrothermal treatment at 900°C for 270 h in air with 10% steam. It can be seen that the whiskers become bigger when exposed to higher temperature, thus well-adhered washcoat onto the metallic support can be achieved through the growth of the Al₂O₃ whiskers.

Figure 25 b. SEM micrographs of the alumina washcoat deposited on metal (left) and enlargement of a section (right), after calcination at 800°C for 4 h in air.

Figure 25 c. Same as Figure 25b after hydrothermal treatment at 900°C for 270 h in air with 10% steam.
Characterisation of thermally-treated catalysts [Paper II]

The present study concerns characterisation, by Raman, TPR and XPS, of active components (MnO$_x$ or CuO mixed with Pt or Pd) supported on γ-Al$_2$O$_3$ after a hydrothermal treatment at 900°C for 60 h in air with 12% steam. The aim is to observe any interaction metal-supports.

Manganese oxides-containing catalysts

The TPR profiles of the fresh and hydrothermally treated samples of MnO$_x$ alone and mixed with Pt or Pd are shown in Figure 26. After hydrothermal treatment the reduction profile of the MnO$_x$ sample is shifted to higher temperatures and the peaks are less well defined than for the fresh sample. For the mixed MnO$_x$-Pt sample the range of reduction temperature is almost the same as for the fresh sample. The H$_2$/Mn ratios for all the samples are equal to ca 0.5, thus MnO$_x$ can be composed of either mainly Mn$_2$O$_3$ or a mixture of oxides that lead to the same hydrogen consumption, and hence it is difficult to comment on the valency of MnO$_x$ in this system.

Mn/Al ratios, as determined by XPS, are strongly increased after thermal treatment as seen in Table 9. These results are in conformity with an increased surface MnO$_x$ concentration which is probably due to the decrease in surface area and/or to an increased metal oxide particle size due to sintering. The B.E. of the principal Mn 2p$_{3/2}$ peak for all the samples containing MnO$_x$ alone and mixed with noble metals were between 642.6-642.8 and 642.7-642.9 eV for fresh and aged samples, respectively (Table 9). References samples from literature are also shown in this table. There is respectively a complete and large overlapping of the Mn 2p$_{3/2}$ peak position domain between MnO$_2$ and Mn$_2$O$_3$ on the one hand and Mn$_2$O$_3$ and Mn$_3$O$_4$ on the other hand [Wagner et al., 1979]. Therefore, determination of the MnO$_x$ oxidation-state on the basis of the Mn 2p$_{3/2}$ peak position is difficult. There was no indication that MnAl$_2$O$_4$ existed in our samples. It has been reported that the formation of MnAl$_2$O$_4$ occurs only when samples are calcined in reducing atmosphere, because of the instability of Mn$^{2+}$ ions in air at temperatures above 150°C [Lo Jacono & Schiavello, 1976; Strohmeier & Hercules, 1984].

On the other hand, the use of Raman Spectroscopy could reveal some discrepancies between the composition of the fresh and treated samples. Mn$_2$O$_3$ and Mn$_3$O$_4$ were found in samples calcined at 800°C for 4 h and after thermal treatments at 900°C, respectively (see Section 2.2.2, Figure 6).
Figure 26. TPR profiles of Al₂O₃-supported MnOₓ, MnOₓ-Pt and MnOₓ-Pd, calcined at 800°C for 4 h in air (thin line) and after thermal treatment at 900°C for 60 h in air with 12% steam (thick line). Mn: 10; Pt, Pd: 0.1 mol%/Al₂O₃. TPR experimental conditions: 17 ml/min, 10% H₂/Ar.

Table 9. Data from XPS analyses for Al₂O₃-supported MnOₓ, mixed MnOₓ-Pt and MnOₓ-Pd calcined at 800°C for 4 h (F) and after thermal treatment at 900°C for 60 h in air with 12% steam (A). Mn: 10; Pt, Pd: 0.1 mol%/Al₂O₃. Binding energies of reference compounds are included.

<table>
<thead>
<tr>
<th>Catalysts and reference compounds</th>
<th>Mn2p3/2 binding energies (eV) a</th>
<th>Atomic ratio Mn/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnOₓ/Al₂O₃</td>
<td>642.6 642.9</td>
<td>0.084 0.26</td>
</tr>
<tr>
<td>MnOₓ-Pt/Al₂O₃</td>
<td>642.8 642.7</td>
<td>0.10 0.35</td>
</tr>
<tr>
<td>MnOₓ-Pd/Al₂O₃</td>
<td>642.8 642.8</td>
<td>0.10 0.29</td>
</tr>
<tr>
<td>MnO₂</td>
<td>641.7 [Baltanás et al., 1987]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>642.1 [Strohmeier &amp; Hercules, 1984]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>642.2 [Wagner et al., 1979; Baltanás et al., 1987]</td>
<td></td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>641.4 [Strohmeier &amp; Hercules, 1984]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>641.5 [Di Castro &amp; Polzonetti, 1989]</td>
<td></td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>640.9 [Strohmeier &amp; Hercules, 1984]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>641.1 [Di Castro &amp; Polzonetti, 1989]</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>640.1 [Baltanás et al., 1987]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>640.6 [Di Castro &amp; Polzonetti, 1989]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>641.2 [Strohmeier &amp; Hercules, 1984]</td>
<td></td>
</tr>
<tr>
<td>MnAl₂O₄</td>
<td>641.1 [Strohmeier &amp; Hercules, 1984]</td>
<td></td>
</tr>
</tbody>
</table>

a All B.E.’s (eV) referenced to C1s=284.6 eV
Copper oxide-containing catalysts

The TPR profiles of the fresh and hydrothermally treated samples of CuO alone and mixed with Pt or Pd are shown in Figure 27b. Reference compounds of bulk CuO and bulk copper aluminate, i.e. CuAl$_2$O$_4$, are included for comparison (Figure 27a).

The profiles of the treated samples show two separate peaks with the first one at a lower temperature and the second peak at a higher temperature than the single peak in the fresh samples. The temperature of the first reduction peak for both mixed samples is lower than for the CuO/Al$_2$O$_3$ alone. A similar effect of Pd on the reduction behaviour of CuO was observed for the fresh sample (Figure 16b). TPR suggested the presence of CuAl$_2$O$_4$ in the samples by comparison with the reduction profile of a reference CuAl$_2$O$_4$ compound (Figure 27a). It is known that bulk copper aluminate (60% tetrahedral and 40% octahedral Cu$^{2+}$) can only be formed at high calcination temperatures, i.e. above ca 800°C [Misra & Chaklader, 1963; Wolberg & Roth, 1969; Friedman et al., 1978], and is reduced at temperatures of approximately 500°C [Dumas et al., 1989; Marion et al., 1991]. The formation of the copper aluminate seems to be increased when noble metals are present in the catalysts.

Figure 27. TPR profiles of bulk CuO and CuAl$_2$O$_4$ reference compounds (a), Al$_2$O$_3$-supported CuO, CuO-Pt and CuO-Pd calcined at 800°C for 4 h in air (thin line) and after treatment at 900°C for 60 h in air with 12% steam (thick line) (b). Cu: 10; Pt, Pd: 0.1 mol%/Al$_2$O$_3$. TPR experimental conditions: 40 ml/min, 5% H$_2$/Ar (a) and 17 ml/min, 10% H$_2$/Ar (b).
Effects of metals in the washcoat [Paper III, IV, V]

Tables 10 and 11 show the results from characterisation studies using BET and XRD concerning the effects of metal oxides (CuO or MnOx) and noble metals (Pt or Pd) on the properties of washcoat.

The presence of the active components in the washcoat increased the sintering, as seen by a decrease of the BET-surface area, transformation of γ- to α-Al2O3 phases at lower temperatures, increase of the Al2O3 particle size, and reactions of the active phases, notably CuO, with Al2O3, especially after thermal treatment at 900°C for 60 h in air with 12% steam Table 10 [Paper III] and for 300 h in air with 10% steam, Table 11 and Figure 28 [Paper V].

The effects of metal oxides, particularly Cu, are stronger than those of noble metals, and this can be seen in both Tables and in Figure 28, with a higher formation of α-Al2O3 and spinel compound CuAl2O4. The effect of Pd in mixed catalysts on the loss of surface area is also stronger than that of Pt, as seen after a treatment for a longer period of time, i.e., 300 h (Table 11).

Table 10. Surface area of catalysts after hydrothermal treatment at 900°C for 60 h in air with 12% steam. Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al2O3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>115</td>
</tr>
<tr>
<td>Pt/Al2O3</td>
<td>111</td>
</tr>
<tr>
<td>Pd/Al2O3</td>
<td>110</td>
</tr>
<tr>
<td>MnOx/Al2O3</td>
<td>59</td>
</tr>
<tr>
<td>CuO/Al2O3</td>
<td>39</td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>15</td>
</tr>
<tr>
<td>MnOx-Pd/Al2O3</td>
<td>18</td>
</tr>
<tr>
<td>CuO-Pt/Al2O3</td>
<td>10</td>
</tr>
<tr>
<td>CuO-Pd/Al2O3</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 11. Surface area, α-Al2O3 content and α-Al2O3 particle size in the catalysts determined on samples calcined at 800°C for 4 h in air (F) and hydrothermally treated at 900°C for 300 h in air with 10% steam (A). Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al2O3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET data</th>
<th>XRD data on α-Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>surface area (m²/g)</td>
<td>%a</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>A</td>
</tr>
<tr>
<td>Al2O3</td>
<td>169</td>
<td>97</td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>156</td>
<td>27</td>
</tr>
<tr>
<td>MnOx-Pd/Al2O3</td>
<td>149</td>
<td>10</td>
</tr>
<tr>
<td>CuO-Pt/Al2O3</td>
<td>133</td>
<td>15</td>
</tr>
<tr>
<td>CuO-Pd/Al2O3</td>
<td>131</td>
<td>7</td>
</tr>
</tbody>
</table>

a Determined from the intensity of the peak 2θ = 35.2
b Determined by Scherrer’s formula at 2θ = 35.2
In general terms, the role of foreign ions can be explained. Thermal reorganisation involves diffusion via defects and vacancies [Trimm, 1991]. The presence of both MnO_x and CuO accelerated the sintering, with CuO having a stronger effect than MnO_x. In both studies, after calcination at 800°C, Cu^{2+} was found to be present on Cu-containing samples and Mn_2O_3 was present in the Mn-containing samples. After ageing at 900°C, Cu^{2+} (copper aluminate) and Mn_3O_4 were found on Cu and Mn-containing catalysts, respectively, as discussed previously. The size of the ionic radius and the charge also play an important role in the mobility of the ion into the Al_2O_3. A larger charge and ionic radius hampers the mobility [Burtin et al., 1987a; Miyoshi et al., 1989; Church et al., 1993]. The ionic radii of these metal ions are 0.72 Å and 0.66 Å for Cu(II) and Mn(III), respectively [Weast & Astle, 1979]. According to the model described by Burtin et al., which takes in account charge and ionic radius, it seems that Cu(II) has a more pronounced effect as an accelerator than Mn(III). Also Tijburg suggested that growth of copper aluminate observed during treatment at high temperature results in a disordered Al_2O_3 layer at the interface with copper aluminate, where α-Al_2O_3 can nucleate more easily [Tijburg, 1989]. That could explain the higher mobility of Cu in the Al_2O_3 structure compared to Mn, leading to the higher level of Al_2O_3 sintering.

![Figure 28. XRD patterns of Al_2O_3, MnO_x-Pt, MnO_x-Pd, CuO-Pt and CuO-Pd deposited on Al_2O_3 after hydrothermal treatment at 900°C for 300 h in air with 10% steam. Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al_2O_3. α: α-Al_2O_3, s: CuAl_2O_4.](image)

The effect of metals on washcoat properties depends not only on the type of active phases but also on their concentration. For instance with increasing concentrations of Mn in the washcoat, a decrease in BET-surface area was observed after thermal treatment, as can be seen in Figure 29 [Paper IV].
Catalytic activity of thermally-treated catalysts [Paper III]

Mixtures of MnOₓ or CuO and Pt or Pd subjected to thermal treatments at 900°C for 60 h in air with 12% steam were tested for the catalytic oxidation of CO, C₁₀H₈ and CH₄ in the gas mixture 1. Comparisons were made with single component catalysts.

After the treatment, the MnOₓ catalyst shows higher activity than the fresh catalyst for the oxidation of C₁₀H₈ and CO and almost no change in activity for the oxidation of CH₄, as seen in Table 12. This enhancement, discussed in Section 2.2.2, correlates with the change in MnOₓ oxidation state towards Mn₃O₄.

For the treated CuO catalyst, the temperatures for 50% conversion of CO and CH₄ were increased by 60°C and 130°C, respectively, whereas the oxidation of C₁₀H₈ was almost not affected. In the thermally treated catalysts, the formation of CuAl₂O₄, as mentioned in the characterisation study, could have contributed to decreased activity. Indeed Cu in CuAl₂O₄ cannot change oxidation state, but remains as Cu(II). Thus Cu cannot be an active redox centre for oxidation of VOC’s, which generally proceed via the Mars-van Krevelen type mechanism (i.e. redox mechanism) [Spivey, 1989].

After hydrothermal treatment of the Pd catalyst, the oxidation of CO and C₁₀H₈ was only slightly decreased, and the oxidation of CH₄ was decreased to a higher extent, as seen in Table 12. The Pt catalyst showed a larger decrease in activity for the oxidation of CO and C₁₀H₈ than the Pd catalyst, as can be seen in Table 12, while the Pt catalyst showed less decrease in activity for the oxidation of CH₄.

The treated and mixed MnOₓ-Pt catalyst showed a slight deactivation for all components, shown in Table 12. It can also be seen that the thermal deactivation, i.e. ΔT, of the mixed MnOₓ-Pt catalyst was lower than for the Pt
catalyst. After hydrothermal treatment, the Pt catalyst was still slightly more active than the mixed MnO\(_x\)-Pt catalysts for the oxidation of CO and C\(_{10}\)H\(_8\) oxidation, but the opposite was observed for CH\(_4\).

The hydrothermally treated mixed CuO-Pt catalyst had a higher activity than the treated Pt catalyst for the oxidation of all the combustibles studied here, as seen in Figure 30 and Table 12. It seems that there was a stabilising effect between CuO and Pt which made the mixed CuO-Pt catalyst more resistant to thermal deactivation than CuO or Pt catalysts alone, despite the lower surface area of the mixed catalyst compared to the single-component catalysts (Table 10).

The treated mixed MnO\(_x\)-Pd and CuO-Pd catalysts showed a higher decrease in activity than the treated Pd catalyst for the oxidation of CO and C\(_{10}\)H\(_8\). However, for the oxidation of CH\(_4\), the activities of the treated mixed MnO\(_x\)-Pd and CuO-Pd catalysts were better than the activity of the treated Pd catalyst.

As discussed in Section 2.3.2, the mixed MnO\(_x\)-Pd catalyst benefited from the presence of the new active Mn\(_3\)O\(_4\) phase, which was formed during the thermal treatment, to a lesser extent than MnO\(_x\) catalyst. Therefore, MnO\(_x\)-Pd catalyst had a lower activity than the treated MnO\(_x\) catalyst for the oxidation of C\(_{10}\)H\(_8\) and CH\(_4\).

Table 12. Temperature for 50% conversion of CO, C\(_{10}\)H\(_8\) and CH\(_4\) for Al\(_2\)O\(_3\)-supported MnO\(_x\), CuO, Pd, Pt and mixed catalysts calcined at 800\(^\circ\)C for 4 h (F) and after treatment at 900\(^\circ\)C for 60 h in air with 12% steam (A). Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al\(_2\)O\(_3\). Gas mixture 1.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO</th>
<th></th>
<th></th>
<th>C(_{10})H(_8)</th>
<th></th>
<th></th>
<th>CH(_4)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>A</td>
<td>(\Delta T)</td>
<td>F</td>
<td>A</td>
<td>(\Delta T)</td>
<td>F</td>
<td>A</td>
<td>(\Delta T)</td>
</tr>
<tr>
<td>MnO(_x)/Al(_2)O(_3)</td>
<td>425</td>
<td>360</td>
<td>-65</td>
<td>365</td>
<td>315</td>
<td>-50</td>
<td>645</td>
<td>655</td>
<td>10</td>
</tr>
<tr>
<td>CuO/Al(_2)O(_3)</td>
<td>344</td>
<td>407</td>
<td>63</td>
<td>420</td>
<td>430</td>
<td>10</td>
<td>590</td>
<td>720</td>
<td>130</td>
</tr>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>245</td>
<td>287</td>
<td>42</td>
<td>250</td>
<td>284</td>
<td>34</td>
<td>640</td>
<td>720</td>
<td>80</td>
</tr>
<tr>
<td>Pd/Al(_2)O(_3)</td>
<td>217</td>
<td>230</td>
<td>13</td>
<td>220</td>
<td>237</td>
<td>17</td>
<td>640</td>
<td>745</td>
<td>105</td>
</tr>
<tr>
<td>MnO(_x)-Pt/Al(_2)O(_3)</td>
<td>290</td>
<td>317</td>
<td>27</td>
<td>290</td>
<td>310</td>
<td>20</td>
<td>640</td>
<td>690</td>
<td>50</td>
</tr>
<tr>
<td>MnO(_x)-Pd/Al(_2)O(_3)</td>
<td>290</td>
<td>340</td>
<td>50</td>
<td>290</td>
<td>332</td>
<td>42</td>
<td>640</td>
<td>715</td>
<td>75</td>
</tr>
<tr>
<td>CuO-Pt/Al(_2)O(_3)</td>
<td>255</td>
<td>270</td>
<td>15</td>
<td>265</td>
<td>275</td>
<td>10</td>
<td>593</td>
<td>705</td>
<td>112</td>
</tr>
<tr>
<td>CuO-Pd/Al(_2)O(_3)</td>
<td>220</td>
<td>330</td>
<td>110</td>
<td>229</td>
<td>365</td>
<td>136</td>
<td>595</td>
<td>695</td>
<td>100</td>
</tr>
</tbody>
</table>

\(\Delta T = T_{50\%}(A) - T_{50\%}(F)\)
Optimisation of thermally-stable MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts [Paper IV]

As discussed previously, a high amount of metal oxides may accelerate the sintering of the Al\textsubscript{2}O\textsubscript{3} support. On the other hand, MnO\textsubscript{x} has interesting properties when subjected to high temperatures, i.e., phase transformation towards a more active state. Therefore it seems to be important to optimise the amount of washcoat and the concentration of MnO\textsubscript{x} to obtain the maximum activity after ageing.

Thus, the influence of the amount of washcoat (up to 20 wt%/catalyst weight), as well as the influence of the concentration of MnO\textsubscript{x} (Mn: 5 to 20 mol%/Al\textsubscript{2}O\textsubscript{3}) on the activity of catalysts after hydrothermal treatment were studied.

Figure 30. CO conversion for Al\textsubscript{2}O\textsubscript{3}-supported Pt, CuO and mixed CuO-Pt calcined at 800°C for 4 h (F) and after hydrothermal treatment at 900°C for 60 h in air with 12% steam (A). Cu: 10; Pt: 0.1 mol%/Al\textsubscript{2}O\textsubscript{3}. Gas mixture 1.

Figure 31. Temperature for 50% conversion of CO, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4} for MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} with different amounts of washcoat, but the same total amount of Mn (ca 3.4 10\textsuperscript{-4} mol) calcined at 900°C for 270 h in air with 10% steam. Gas mixture 1.
After hydrothermal treatment, the catalyst with a concentration of MnOₓ of 10 mol%/Al₂O₃ seems to be optimum (Figures 31 and 32), showing a high activity due to the presence of the new Mn₃O₄ phase and stability, i.e. relatively high surface area (Figure 29).

![Graph](image)

Figure 32. Temperature for 50% conversion of CO, C₁₀H₈ and CH₄ for MnOₓ/Al₂O₃ with different amounts of Mn, but the same total amount of washcoat (20 wt%) calcined at 900°C for 270 h in air with 10% steam. Gas mixture 1.

**Some important results from Section 3.1:**

- After hydrothermal treatment at 900°C, Al₂O₃ whiskers grew from the metallic substrate thus yielding to well-adhered washcoat.
- Hydrothermal treatment at 900°C on catalysts induces a surface enrichment of Mn and Cu and the formation of CuAl₂O₄.
- Metals increase the sintering of alumina, i.e.:
  - increase the α-Al₂O₃ particle size,
  - lower the temperature for γ-Al₂O₃ → α-Al₂O₃ transformation, which is accompanied by a decrease of surface area.
- The sequence of activity of the hydrothermally treated catalysts (900°C, 60 h in air with 12% steam), with an amount of noble metal of 0.1 mol%, for the oxidation of the combustibles is as follows:
  - CO: Pd > CuO-Pt > Pt > MnOₓ-Pt > CuO-Pd > MnOₓ-Pd > MnOₓ > CuO
  - C₁₀H₈: Pd > CuO-Pt > Pt > MnOₓ-Pt > MnOₓ > MnOₓ-Pd > CuO-Pd > CuO
  - CH₄: MnOₓ > MnOₓ-Pt = CuO-Pd > CuO-Pt > MnOₓ-Pd = CuO = Pt > Pd
- An amount of 10 mol% Mn/Al₂O₃ in MnOₓ/Al₂O₃ hydrotreated at high temperature was found to be the optimum for the oxidation of CO, C₁₀H₈ and CH₄.
3.2 Sulphur Poisoning

3.2.1 General

Sulphur poisoning is a serious cause for deactivation of catalysts. Usually the sulphur level in the flue gases from wood combustion is in the range of 20 to 200 ppm, mainly in the form of SO$_2$. It is extremely difficult to simulate the way in which the catalysts are subjected to poisons in realistic conditions. Indeed, both fuel composition and operating conditions affect the poisoning process. Wood containing bark or residues from agriculture contain higher amount of inorganic materials [Linsmeyer & Hofbauer, 1994]. Sulphur poisoning is less of a problem at higher operating temperatures, approximately 600-800°C, and regeneration of poisoned catalysts is possible with similarly elevated temperatures [Yao et al., 1981; Ball & Stack, 1991; Deng et al., 1993; Beck & Sommers, 1995]. On the other hand, higher operating temperatures have additional energy penalties, and risk of deactivation by sintering of active components or washcoat, as discussed previously.

Under oxidising conditions there are several basic means by which sulphur poisoning of catalysts occurs. The first occurs at temperatures above 300-350°C and involves the conversion of SO$_2$ to SO$_3$, which then reacts directly with the catalytic components or the washcoat. If Al$_2$O$_3$ is present, the compound formed will be Al$_2$(SO$_4$)$_3$, a large volume, low density material that blocks active sites [Heck & Farrauto, 1995]. The second mechanism is the chemisorption of SO$_2$ or SO$_3$ onto catalytic sites at lower temperatures, which prevents those sites from further catalytic action by either inaccessibility of active surface sites due to geometric blockage or changes in the structure of the catalytic surface.

The sulphur species that accumulate on catalysts tend to be sulphates or sulphite species [Zwinkels, 1994]. Sulphur deactivates both noble metals and metal oxides, but apparently through different mechanisms. On noble metals, the sulphur retained on the catalyst is desorbed at elevated temperatures. On metal oxides, however, the sulphur is incorporated within the catalyst or support as a sulphate or stable adsorbates (H$_2$SO$_4$ or SO$_3$) and the SO$_3$ remains bonded to the surface even at temperatures at which the sulphate decomposes [Sultanov et al., 1987]. Metal oxides are therefore more susceptible to poisoning by sulphur compared to noble metal catalysts [Shelef et al., 1978].

In most cases sulphur components in the gas stream have been shown to decrease the activity of catalysts. However, a chemisorbed species can also have electronic effects on the surrounding catalytic surface that maybe beneficial, in which case it is termed a promoter [Satterfield, 1991]. SO$_2$ has been reported to have a promoting effect on Pt/γ-Al$_2$O$_3$ catalyst for the oxidation of propane [Yao et al., 1981; Monroe et al., 1991; Hubbard et al., 1993;
Ishikawa et al., 1994; Marecot et al., 1994; Sugaya et al., 1994]. Burch et al. noticed that there is both a transient effect which causes a temporary sharp increase in activity and a more-lasting effect which may be associated with accumulation of sulphate species on the alumina support [Burch et al., 1998].

The reason for the enhancing effect was suggested to be the promotion of the dissociative adsorption of propane on the Pt, which is the rate determining step in C-H bond activation. Wilson et al. proposed that pre-adsorption of oxygen reacts with SO₂ to yield co-adsorbed sulphate species on Pt that lead to the initial dissociative adsorption of propane by abstraction of H by SOₓ, which then forms an intermediate that is more easily oxidised [Wilson et al., 1996]. Burch et al. suggested also that the oxidation of SO₂ to SO₃ by Pt causes the removal of surface oxygen thus facilitating the adsorption of propane [Burch et al., 1998]. The promotional effect of SO₂ onto Pt is usually lower for hydrocarbons higher than propane, since the activation of the C-H bond in these molecules would be less susceptible to additives [Burch & Hayes, 1995].

Wilson et al. also reported that the reaction is not only support-mediated as the enhancement is also observed on a Pt(111) surface in the complete absence of a support phase [Wilson et al., 1996]. In addition, early work carried out by Yao et al. demonstrated that the extent of the promotional effect of SO₂ was directly related to the Pt dispersion onto the support [Yao et al., 1981].

However, some studies show that the support may affect the promotion by SO₂. Sugaya et al. [Sugaya et al., 1994] claimed that increased acidity of the catalysts led to increased activity for propane oxidation, because the role of the acidic support is to prevent the oxidation of Pt into less active Pt oxides. However, Hubbard et al. observed that alumina-supported Pt is promoted while silica-supported Pt was not promoted by SO₂ and concluded that the changes in the acid-strength does not account for the activity of a Pt catalyst for propane oxidation [Hubbard et al., 1993]. Apart from the possibility of discrepancies between the morphological effects of the Pt deposited on the two different supports, the alumina may also contribute to the promotion by SO₂. Sulphate is much more stable on alumina than on silica and the probability to find a sulphate species adjacent to a Pt-particle is more likely on the former. Also, Pt is known to catalyse the formation of SO₂ to SO₃ which will proceed at a Pt particle and SO₃ can react with alumina to form Al₂(SO₄)₃ and this reaction is further catalysed by Pt. The role of the support would also be to provide sulphate species that are more stable on the alumina than on Pt at high temperatures. Thus the promoting effect could be due to the presence of both sulphate on, or adjacent to, a Pt particle. The phenomenon is unique for Pt catalysts since it forms relatively unstable bonds to sulphur oxides.

Conversely, the effect of SO₂ onto Pd is inhibitory since PdO can react strongly with SO₂ and the surface Pd sulphate is inactive for the C-H bond breaking [Hubbard et al., 1995; Burch & Hayes, 1995].
3.2.2 Results and Discussion

In this part, two types of sulphur poisoning are presented. The first one consists in treating the catalysts in a SO\(_2\)-containing stream prior to any activity measurements or characterisation studies, while the second one consists on introducing a small amount of SO\(_2\) in the feed gas during the activity measurements.

Pre-sulphation of the catalysts [Paper II, III]

Catalysts based on a combination of metal oxides and noble metals, calcined at 800°C for 4 h in air, were subjected to SO\(_2\) treatments with 1000 ppm SO\(_2\) (2 l/min) in air at 600°C for 16 h.

Characterisation [Paper II]

Characterisation using TPR and XPS was carried out on fresh and sulphur-treated samples of MnO\(_x\) and CuO.

The reduction profile of sulphur-treated samples of MnO\(_x\) has changed drastically compared to that of fresh samples; most of the species are reduced at much higher temperatures at around 480-560°C, as seen in Table 13 and Figure 33. There is an increase in the reduction temperature and in the hydrogen consumption for all the sulphur-treated samples compared to the fresh ones, which is probably due to the reduction of formed sulphate, MnSO\(_4\). The reduction temperature for the mixed samples is lower than for the MnO\(_x\) alone. A similar effect of Pt and Pd on the reduction behaviour of MnO\(_x\) was observed for the fresh samples, with Pd having stronger influence than Pt. As in the fresh samples, noble metals seem to catalyse the reduction, in this case of manganese sulphate. Table 13 shows a larger increase in the hydrogen consumption when MnO\(_x\) is mixed with noble metals and this can be attributed to a higher amount of sulphate which formation is catalysed by noble metals.

XPS measurements were conducted on Mn-containing samples which revealed the presence of adsorbed sulphate species, as seen by the B.E. of S 2p which is about 169.4 eV for all the samples (Table 13) [Briggs & Seah, 1983]. We cannot discriminate between Mn and Al bonded species. The increasing uptake of sulphur by MnO\(_x\) with the addition of noble metal, which is suggested by the increasing ratios S/Al and S/Mn, was also confirmed by TPR.
Table 13. Maximum reduction temperature, Tm, and H₂/Mn ratio from TPR experiments, S 2p binding energies (B.E.), S/Al and S/Mn ratios, determined by XPS, on pre-sulphated samples. Mn: 10; Pt, Pd: 0.1 mol%/Al₂O₃.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tm (°C)</th>
<th>H₂/Mn</th>
<th>S 2p B.E. (eV)</th>
<th>S/Al</th>
<th>S/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnOₓ/Al₂O₃</td>
<td>562</td>
<td>1.33</td>
<td>169.4</td>
<td>0.015</td>
<td>0.106</td>
</tr>
<tr>
<td>MnOₓ-Pt/Al₂O₃</td>
<td>501, 522</td>
<td>1.55</td>
<td>169.5</td>
<td>0.013</td>
<td>0.13</td>
</tr>
<tr>
<td>MnOₓ-Pd/Al₂O₃</td>
<td>482</td>
<td>1.43</td>
<td>169.4</td>
<td>0.028</td>
<td>0.20</td>
</tr>
</tbody>
</table>

a TPR conditions: 10% H₂ in Ar, 17 ml/min, 5°C/min
b All B.E.’s (eV) referenced to Al₂p=74.6 eV

Figure 33. TPR profiles of Al₂O₃-supported MnOₓ and CuO calcined at 800°C for 4 h in air, before (thin line) and after pre-sulphation (thick line). Mn, Cu: 10 mol%/Al₂O₃.

TPR experimental conditions: 17 ml/min, 10% H₂/Ar.

All the samples of CuO alone (and mixed with noble metals, not shown) treated by sulphur show one main peak occurring at slightly higher temperatures than for the fresh ones, and a “hill” in the range 350-700°C (Figure 33). The small increase in the reduction temperature of the CuO samples is probably due to the treatment at 600°C for 16 h which has induced stronger interaction with the support and causes the reduction to occur at higher temperatures. The hill observed at 350-700°C probably corresponds to reduction of the sulphate. The change in the TPR profile for Cu-containing samples is nevertheless very small compared to that of Mn-containing samples. Thus this indicates the larger stability of manganese sulphate.
compared to copper sulphate. Namely, it is known that CuSO$_4$ has a lower decomposition temperature than MnSO$_4$ [Ostroff & Sanderson, 1959].

**Catalytic activity [Paper III]**

Table 14 and Figure 34 present the results from the activity measurements performed after the pre-sulphation performed with 1000 ppm SO$_2$ (2 l/min) in air at 600°C for 16 h.

For the MnO$_x$ catalyst, the activity for the oxidation of C$_{10}$H$_8$ and CH$_4$ was almost the same before and after sulphur treatment, whereas the oxidation of CO was more inhibited, as seen in Figure 34 and Table 14.

![Figure 34. CO, C$_{10}$H$_8$ and CH$_4$ conversion for MnO$_x$/Al$_2$O$_3$ calcined at 800°C for 4 h in air, before (F) and after the pre-sulphation (S). Mn: 10 mol%/Al$_2$O$_3$. Gas mixture 1.](image)

The activity of the CuO catalyst was affected for the oxidation of CO in a similar way by the sulphur treatment as the MnO$_x$ catalyst, but with a lesser deactivation, as is shown in Table 14. However, there was an appreciable promoting effect for the oxidation of C$_{10}$H$_8$.

The specific impediment in the oxidation of CO, which affected both MnO$_x$ and CuO catalysts by sulphur treatment, could be attributed to an inhibiting effect of SO$_2$ on the adsorption sites of CO, whereas the adsorption sites of HCs were not affected to the same extent [Farrauto & Wedding, 1973; Yu Yao, 1975]. Farrauto and Wedding attributed this difference to a fast poisoning of the carbonyl sites (responsible for CO oxidation) and a slow poisoning of the carbonate sites (responsible for the HC oxidation) and that SO$_2$ selectively adsorbs on the carbonyl sites at low temperatures and on carbonate sites at higher temperatures.
Table 14. Temperature for 50% conversion of CO, C_{10}H_{8} and CH_{4} for Al_{2}O_{3}-supported MnO_{x}, CuO, Pd, Pt and mixed catalysts, calcined at 800°C for 4 h in air, before (F) and after the pre-sulphation (S). Mn, Cu, Pt and Pd mol%/Al_{2}O_{3} are indicated in parentheses. Gas mixture 1.

| Samples | CO | | | | C_{10}H_{8} | | | CH_{4} | |
|---------|----|---|---|---|---|---|---|---|
|         | F  | S  | ∆T| F  | S  | ∆T| F  | S  | ∆T|
| MnO_{x} (10) | 425 | 535 | 110| 365 | 375 | 10| 645 | 666 | 21|
| CuO (10) | 344 | 395 | 51| 420 | 382 | -38| 590 | 628 | 38|
| Pt (0.1) | 245 | 276 | 31| 250 | 277 | 17| 640 | 655 | 15|
| Pd (0.1) | 217 | 242 | 25| 221 | 248 | 27| 640 | 681 | 41|
| MnO_{x}-Pt (10-0.05) | 344 | 317 | -27| 334 | 317 | -17| 640 | 665 | 25|
| MnO_{x}-Pt (10-0.1) | 290 | 300 | 10| 291 | 300 | 9| 638 | 654 | 16|
| MnO_{x}-Pd (10-0.1) | 290 | 274 | -16| 290 | 282 | -8| 641 | 681 | 40|
| CuO-Pt (10-0.1) | 254 | 273 | 19| 264 | 278 | 14| 593 | 630 | 37|
| CuO-Pd (10-0.1) | 220 | 216 | -4| 230 | 219 | -11| 595 | 630 | 35|

As seen in Table 14, the noble metals Pt and Pd seem to be more sulphur-resistant than the transition metal oxides, in agreement with reports in the literature [Shelef et al., 1978; Kummer, 1980]. The sulphur deactivation of the Pt catalyst slightly affected the oxidation of all the combustibles (Table 14). The Pd catalyst had a higher sulphur sensitivity than the Pt catalyst which also is in agreement with literature data [Hegedus et al., 1979; Deng et al., 1993; Kang et al., 1994].

Several different effects were observed on the mixed catalysts. After exposure to SO_{2}, the activities of the mixed MnO_{x}-Pt (10-0.05) and MnO_{x}-Pd (10-0.1) catalysts were enhanced for the oxidation of C_{10}H_{8} and CO, and almost no deactivation was observed with a higher amount of Pt (0.1) in the catalyst. The conversion of CH_{4} was slightly decreased for MnO_{x}-Pd and both mixed MnO_{x}-Pt catalysts. However, the activity of the mixed MnO_{x}-Pd catalyst for the oxidation of CO and C_{10}H_{8} remained slightly lower than the activity of the Pd catalyst after sulphur treatment. The extent of the decrease in activity for the oxidation of CH_{4} was the same for both Pd and mixed MnO_{x}-Pd catalysts, which is seen with 40°C increase of the temperature for 50% conversion.

The mixed CuO_{x}-Pt catalyst was slightly deactivated by the sulphur treatment. It is deactivated to the same extent as the Pt catalyst for the oxidation of CO and C_{10}H_{8} and also to the same extent as the CuO catalyst for the oxidation of CH_{4}. The CuO-Pd catalyst showed an interesting behaviour. After sulphur treatment, the activity was slightly enhanced for the oxidation of CO and C_{10}H_{8}, and decreased for the oxidation of CH_{4}. However, the activity of the sulphur treated mixed CuO-Pd catalyst for the oxidation of all the combustibles studied here was better than the activity of the Pd catalyst.
A reason for the promotional effect by sulphur treatment in the activity of the mixed MnO\textsubscript{x}-Pt (Pt: 0.05 mol%/Al\textsubscript{2}O\textsubscript{3}) catalyst for the oxidation of C\textsubscript{10}H\textsubscript{8} can be attributed to formation of sulphate species, that activates C-H bond, as mentioned in the introduction part of this section [Sekizawa et al., 1993; Burch et al., 1998; Zaki et al., 1999]. This effect was not observed at higher Pt concentration and this may reflect a difference in Pt dispersion or interaction with manganese or aluminium sulphate that may change the effect of SO\textsubscript{2} [Burch et al., 1998]. On mixed catalysts containing Pd, there are also some promoting effect in contradiction with the literature concerning Pd only catalysts [Hubbard et al., 1995]. Because metal oxides readily react with SO\textsubscript{2} to form stable sulphate, metal oxides can serve as a sink and prevent the formation of strongly adsorbed sulphate on the active Pd catalyst. In addition, compared to the metal oxide catalysts, the sulphate species in the Pt or Pd catalysts are not as stable, thus metal oxides provide sulphate species that are stable at higher temperatures.

**Sulphur poisoning on stream**

The behaviour of pre-sulphated catalysts may differ from that of catalysts subjected to SO\textsubscript{2} on stream. Table 15 compares results from activity tests without and with the presence of 20 ppm SO\textsubscript{2} in the gas mixture 2. For the Pt catalyst, in presence of 20 ppm SO\textsubscript{2}, the conversion of CO and C\textsubscript{2}H\textsubscript{4} is slightly hampered whereas CH\textsubscript{4} was unaffected. For the mixed MnO\textsubscript{x}-Pt, only the temperature for CH\textsubscript{4} oxidation was increased during the test in the presence of 20 ppm SO\textsubscript{2}, whereas the oxidation of CO and C\textsubscript{2}H\textsubscript{4} was similar to that in the absence of SO\textsubscript{2}. The oxidation of all the combustibles on the CuO-Pt catalyst was hampered. However, the CuO-Pt catalyst was more active for all the combustibles studied here than Pt or MnO\textsubscript{x}-Pt catalysts both in the absence and in the presence of 20 ppm SO\textsubscript{2}.

Interestingly, it can be seen that the activity of a Pd catalyst in the presence of 20 ppm SO\textsubscript{2} differed greatly from that of a Pt catalyst. The oxidation was enhanced for C\textsubscript{2}H\textsubscript{4}, while the oxidations of CO and CH\textsubscript{4} were inhibited (Figure 35). This enhancement correlated with reduced CO conversion, which allowed the oxidation of C\textsubscript{2}H\textsubscript{4} to occur readily, as discussed in Section 2.1.2 (Figure 3). Mixed catalysts with Pd were, despite a negative effect by SO\textsubscript{2}, more active for the oxidation of some combustibles and more sulphur resistant than the Pd catalyst.
Table 15. Temperature for 50% conversion of CO, C2H4 and CH4 for Al2O3-supported Pd, Pt and mixed catalysts, calcined at 800°C for 4 h in air, without (a) and with 20 ppm SO2 in the gas stream (b). Mn, Cu: 10; Pt, Pd: 0.1 mol%/Al2O3. Gas mixture 2.

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th></th>
<th></th>
<th>C2H4</th>
<th></th>
<th></th>
<th>CH4</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>ΔT</td>
<td>a</td>
<td>b</td>
<td>ΔT</td>
<td>a</td>
<td>b</td>
<td>ΔT</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Pt /Al2O3</td>
<td>208</td>
<td>244</td>
<td>36</td>
<td>225</td>
<td>251</td>
<td>26</td>
<td>634</td>
<td>634</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>296</td>
<td>296</td>
<td>0</td>
<td>306</td>
<td>306</td>
<td>0</td>
<td>631</td>
<td>678</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO-Pt/Al2O3</td>
<td>204</td>
<td>226</td>
<td>22</td>
<td>215</td>
<td>236</td>
<td>21</td>
<td>583</td>
<td>624</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/Al2O3</td>
<td>180</td>
<td>214</td>
<td>34</td>
<td>275</td>
<td>222</td>
<td>-53</td>
<td>640</td>
<td>670</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnOx-Pd/Al2O3</td>
<td>189</td>
<td>194</td>
<td>5</td>
<td>290</td>
<td>290</td>
<td>0</td>
<td>628</td>
<td>682</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO-Pd/Al2O3</td>
<td>184</td>
<td>203</td>
<td>19</td>
<td>202</td>
<td>218</td>
<td>16</td>
<td>594</td>
<td>653</td>
<td>59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ΔT = T50%(b) – T50%(a)

Figure 35. Conversion of CO and C₂H₄ for a Pd (0.1 mol%/Al₂O₃) catalyst, calcined at 800°C for 4 h in air, without (a) and with 20 ppm SO₂ (b). Gas mixture 2.

Some important results from Section 3.2:

The sequence of activity of the sulphur treated catalysts (1000 ppm SO₂ in air at 600°C for 16 h), with an amount of noble metal of 0.1 mol%, for the oxidation of the combustibles is as follows:

CO: CuO-Pd > Pd > CuO-Pt = Pt > MnOₓ-Pd > MnOₓ-Pt > MnOₓ > CuOₓ

C₁₀H₈: CuO-Pd > Pd > CuO-Pt = Pt > MnOₓ-Pd > MnOₓ-Pt > CuO > MnOₓ

CH₄: CuO-Pd > CuO-Pt = CuO > MnOₓ = MnOₓ-Pt = Pt > MnOₓ-Pd = Pd

The sequence of activity of catalysts in presence of 20 ppm SO₂, with an amount of noble metal of 0.1 mol%, for the oxidation of the combustibles is as follows:

CO: MnOₓ-Pd > CuO-Pd > Pd > CuO-Pt > Pt > MnOₓ-Pt

C₁₀H₈: CuO-Pd = Pd > CuO-Pt > Pt > MnOₓ-Pd > MnOₓ-Pt

CH₄: CuO-Pt > Pt > CuO-Pd > Pd > MnOₓ-Pt > MnOₓ-Pd
3.3. Concluding Remarks

The effect of the hydrothermal treatment at 900°C on the adherence of the washcoat onto a metallic substrate was studied using SEM. It revealed a well-anchored washcoat onto the metallic support due to the growth of the alumina whiskers during the treatment.

The sintering of the washcoat, viz. decrease of the BET-surface area, transformation of $\gamma$- to $\alpha$-$\text{Al}_2\text{O}_3$ phases at lower temperatures and increase of the $\text{Al}_2\text{O}_3$ particle size, is accelerated after high temperature treatments in the presence of metal catalysts. This effect is more pronounced in the presence of Cu and Pd, compared to Mn and Pt, respectively, and increases with an increasing metal loading.

In addition, alumina was found to react with CuO, particularly in the presence of noble metals at 900°C, to form inactive CuAl$_2$O$_4$. However, MnO$_x$ catalyst benefits from the more active Mn$_3$O$_4$ phase at high temperature and an optimum loading of 10 mol% Mn/Al$_2$O$_3$ was found for the oxidation of all combustibles.

Pt sintering was delayed when mixed with CuO, thus giving more thermal resistant catalyst. The mixed MnO$_x$-Pd and CuO-Pd catalysts were less active than Pd catalyst for the oxidation of CO and C$_{10}$H$_8$ however the opposite was observed for CH$_4$. After a thermal treatment at 900°C for 60 h in air with 12% steam, Pd and CuO-Pt were found to be the most active for CO and C$_{10}$H$_8$ oxidation, while for CH$_4$, MnO$_x$ had the highest activity.

Pre-sulphating the catalysts with 1000 ppm SO$_2$ (2 l/min) in air at 600°C for 16 h results in the formation of sulphate on MnO$_x$-containing catalysts to a higher extent than on CuO-containing catalysts, and particularly in the presence of the noble metals. The oxidation of CO was largely inhibited by the pre-sulphation of the MnO$_x$ and CuO catalysts while the oxidation of C$_{10}$H$_8$ and CH$_4$ was less inhibited with the MnO$_x$ catalyst, and the oxidation of C$_{10}$H$_8$ substantially improved with the CuO catalyst. Sulphur treatment was found to enhance the activity of some mixed catalysts while noble metal catalysts were not promoted by sulphation. CuO-Pd/Al$_2$O$_3$ catalyst was found to be the most active catalyst after pre-sulphation treatment for the oxidation of all combustibles.

20 ppm SO$_2$ in the synthetic gas mixture results in a significant enhancement of the catalytic activity of Pd/Al$_2$O$_3$ catalyst for the oxidation of C$_2$H$_4$. However, the mixed catalysts were more active than the noble metal catalysts. Namely, in presence of 20 ppm SO$_2$ in the feed, MnO$_x$-Pd was found the most active for the oxidation of CO, CuO-Pd and Pd for the oxidation of C$_2$H$_4$ and CuO-Pt for the oxidation of CH$_4$.
4

ADDITIVES: LANTHANUM AND CERIUM

In order to cope with thermal damage, a catalyst and all its components may be exposed to during elevated temperature and thermal fluctuations, the promotion by a stabiliser seems necessary. Furthermore it is important to develop low-temperature active catalysts, as this is one of the most promising ways to minimise the cold-start period.

4.1 Stabilisers

The addition of a stabiliser may inhibit the sintering effects. The transition aluminas are found to be stabilised by: Be$^{2+}$, Cr$^{3+}$, Sc$^{3+}$ [Vereschagin et al., 1982], K$^+$, Cs$^+$, Na$^+$ [Miyoshi et al., 1989], Yb$^{3+}$, Y$^{3+}$ [Ozawa et al., 1990b], Cr$^{6+}$ [Bye & Simpkin, 1974; Tsuchida et al., 1983], Th$^{4+}$ [Vereschagin et al., 1982; Burtin et al., 1987a], Sm$^{3+}$, Gd$^{3+}$, Dy$^{3+}$ [Kato et al., 1989; Ozawa et al., 1990b], Mg$^{2+}$ [Gauguin et al., 1975; Schaper et al., 1982; Miyoshi et al., 1989], Si$^{4+}$ [Gauguin et al., 1975; Church et al., 1993; Huuska & Maunula, 1993; Ismagilov et al., 1995], Ca$^{2+}$ [Vereschagin et al., 1982; Burtin et al., 1987a; Miyoshi et al., 1989], Sr$^{2+}$ [Vereschagin et al., 1982; Miyoshi et al., 1989; Mizukami et al., 1991; Church et al., 1993], Nd$^{3+}$ [Oudet et al., 1988; Kato et al., 1989; Ozawa et al., 1990b], Pr$^{3+}$ [Oudet et al., 1988; Kato et al., 1989; Church et al., 1993], Ba$^{2+}$ [Miyoshi et al., 1989; Mizukami et al., 1991; Church et al., 1993], and Zr$^{4+}$ [Schaper et al., 1982; Burtin et al., 1987a; Mizukami et al., 1991]. There is a body of literature on studies concerning the stabilisation by La$^{3+}$ [Schaper et al., 1982; Sauvion & Ducros, 1985; Burtin et al., 1987a; Oudet et al., 1988; Kato et al., 1989; Miyoshi et al., 1989; Ozawa et al., 1990a; Ozawa et al., 1990b; Mizukami et al., 1991; Church et al., 1993; Ismagilov et al., 1995; Groppi et al., 2000] and Ce$^{4+}$ [Gauguin et al., 1975; Vereschagin et al., 1982; Sauvion & Ducros, 1985; Kato et al., 1989; Ozawa et al., 1990b; Ismagilov et al., 1995]. Some contradictory effects have been found with: Na$^+$ [Gauguin et al., 1975], Mg$^{2+}$ [Vereschagin et al., 1982; Burtin et al., 1987a], Sr$^{2+}$ [Mizukami et al., 1991], Ba$^{2+}$ [Mizukami et al., 1991; Huuska & Maunula, 1993], Yb$^{3+}$ [Kato et al., 1989], Cr$^{3+}$ [Tsuchida et al., 1983], Y$^{3+}$ [Vereschagin et al., 1982; Kato et al., 1989], and La$^{3+}$ [Vereschagin et al., 1982; Huuska & Maunula, 1993]. Discrepancies may be attributed to a non-optimised loading of stabiliser for the temperature of the treatment. Substitution of stabilisers in the surface of Al$_2$O$_3$ may be beneficial in several ways. Johnson suggests that stabilising elements slow phase transformations by replacing surface hydroxyls and as a result, slow the formation of Al-O-Al.
bridges [Johnson, 1990]. Silica has been found to interact with surface hydroxyls on Al₂O₃ and this is assumed to reduce sintering. Also the foreign ion may occupy a vacancy in the Al₂O₃ lattice, thereby reducing diffusion [Schaper et al., 1985]. The fact that foreign ion reacts with a host lattice to form a new compound that stabilises Al₂O₃ is however certain [Young et al., 1980; Beguin et al., 1991]. Some authors noted a relationship between stabilisation and the radius and/or the charge of the added cation and attributed this to a reduction in mobility with increase in cation size and larger charge [Wakao & Hibino, 1962; Burtin et al., 1987a; Miyoshi et al., 1989; Mizukami et al., 1991; Church et al., 1993]. A stabiliser must remain at the surface in order to decrease the rate of surface diffusion. Large ions are therefore required to prevent dissolution into the bulk. It is also preferable that the additive may form a compound with the Al₂O₃ surface. Based on these considerations, the lanthanides are a logical choice.

4.2 Lanthanum

La appears to be one of the best additives for inhibiting the sintering of high surface-area Al₂O₃ [Burtin et al., 1987a; Church et al., 1993; Peiyan et al., 1995], especially when active species are deposited on it [Shkrabina et al., 1995; Ozawa et al., 1996b].

The stabilisation of Al₂O₃ appears to be a rather complex process and is dependent upon several factors such as preparation method, La loading, temperature and presence of water.

4.2.1 Preparation Method

A good dispersion of La throughout the Al₂O₃ depends on the methods used to insert the La. Mizukami et al., reported that the sol-gel aluminas show higher surface areas between 550 and 1000°C than the corresponding precipitated ones, although the differences between the two procedures are not existent at calcination temperatures of 1000°C and above [Mizukami et al., 1991]. Also, compared with incipient wetness impregnation and deposition-precipitation, the specific adsorption of a La(EDTA)⁻ complex on Al₂O₃ has been found to result in supports that were more homogeneously covered with La and thereby require lower loading of La to stabilise Al₂O₃ at 1050°C [Tijburg et al., 1991].

4.2.2 Effect of the Loading

Depending on the preparation method and on the treatment conditions used, the optimum concentration of La to be added into the Al₂O₃ may vary
[Schaper et al., 1983; Oudet et al., 1987; Beguin et al., 1991; Tijburg et al., 1991]. Usually, a low La content is sufficient to preserve the Al₂O₃ against thermal sintering at temperatures below 1050°C [Beguin et al., 1991]. A higher temperature or the presence of steam usually requires a higher loading of La [Beguin et al., 1991]. However, the amount of La necessary to ensure such a stabilising effect depends also on the properties of the starting Al₂O₃ material [Mizukami et al., 1991] and also the deposition method of La. Therefore many studies in the literature may lead to some discrepancies as follows.

For ageing at temperatures of 1000°C, an amount of 1 and 2 mol% La₂O₃ was found to be best [Schaper et al., 1983; Matsuda et al., 1984; Kato et al., 1989]. At 1100°C, an amount of 2 mol% La₂O₃ [Ozawa et al., 1990b] was found to have a better retarding effect on sintering than 1 mol% [Schaper et al., 1983] or 5 mol% [Church et al., 1993]. However, after an ageing at 1200°C a higher amount (5.6 mol% La₂O₃) was found to give the highest surface area [Matsuda et al., 1984; Kato et al., 1989] whereas an optimum amount of 0.5-1 mol% La₂O₃ was also reported [Miyoshi et al., 1989; Ozawa et al., 1990a].

There is an optimum of La content in the Al₂O₃ washcoat that is shifted to higher loadings as the calcination temperature increases. An excess of La loading decreases the surface area of Al₂O₃ due to the solid state reaction of La with Al₂O₃ and formation of the perovskite structure LaAlO₃ [Matsuda et al., 1984; Kato et al., 1989; Miyoshi et al., 1989; Beguin et al., 1991], that is able for instance to include Pd in the crystal lattice and therefore impedes the catalytic activity [Matsuda et al., 1984].

### 4.2.3 Effect of Steam

La is particularly adapted for atmosphere which contains water [Schaper et al., 1984; Beguin et al., 1991]. Beguin et al. investigated response to ageing of low and high loaded La-Al₂O₃ samples (2.65 and 11wt%La/Al₂O₃) at 1050°C and 1220°C in 20% humidity-containing atmosphere which corresponds to the content of water during the combustion of natural gas [Beguin et al., 1991]. Schaper et al. also aged samples of γ-Al₂O₃ promoted with 0-5 mol% La₂O₃ under 12 bar partial steam pressure at 840°C for 40 h [Schaper et al., 1984]. In both studies, the influence of water in the sintering test performed at high temperature becomes less pronounced as the amount of La introduced increases. Such behaviour was connected with the increase in the amounts of the LaAlO₃ perovskite phase found in both studies which lacks hydroxyl groups, in contrast to Al₂O₃, and as such cannot so readily react with water.
4.2.4 Mechanism of Stabilisation

The main role of La is to stabilise Al₂O₃ against thermal damages. The mechanism of stabilisation by La is not yet fully established. The role of La, according to Schaper et al. is to decrease the rate of surface diffusion that prevents sintering and loss of surface area [Schaper et al., 1985].

According to Ozawa et al., at low La loadings and low temperatures, La³⁺ substitutes in the Al₂O₃ lattice and hinders both bulk and surface diffusion [Ozawa et al., 1990]. There is a concentration limit, termed saturation value, to which the Al₂O₃ support can accommodate dispersed La in the form of a two-dimensional overlayer invisible by XRD. Bettman et al. and Scheitauer et al. concluded, by Auger electron spectroscopy and CO₂ chemisorption, and by Raman spectroscopy, respectively, a saturation value equal to 8-9 µmol La/m² [Bettman et al., 1989; Scheitauer et al., 1998]. However Xie et al. and Yang and Swartz used XRD methods and found ca 17-18 µmol La/m² [Yang & Swartz, 1984; Xie et al., 1984]. Haack et al. found a value between 35 and 61 µmol La/m² by XPS measurements [Haack et al., 1992a]. The exaggerated values found may be due to the low detection limit of the XRD since small invisible crystallites may be formed. Also, Haack et al. calcined their samples at higher temperatures. Matsuda et al. found that below a ratio of La/Al=1, La is in dispersed phase for samples calcined at 800°C [Matsuda et al., 1984]. Compared to the other studies, Matsuda et al. used the co-precipitation method (against incipient wetness technique with lanthanum nitrate) that allows a better homogeneity, and thus a higher saturation value.

Bettman et al. have demonstrated that above this critical concentration La would only form crystalline oxides which in general at calcination temperatures below 800°C, exist as La₂O₃, whereas at higher temperatures LaAlO₃ could be observed. Indeed at higher temperatures or higher La concentration the formation of LaAlO₃ phase has been reported [Schaper et al., 1983; Schaper et al., 1984; Ledford et al., 1987; Oudet et al., 1988; Bettman et al., 1989; Béguin et al., 1991; Haack et al., 1992a; Haack et al., 1992b]. LaAlO₃ has a perovskite structure involving only octahedral aluminium and according to Béguin et al. [Béguin et al., 1991], a strongly bound surface layer is formed which protects tetrahedral aluminium in the underlying Al₂O₃ against transformation.

However, work by Haack et al. [Haack et al., 1992b] shows that after thermal treatment at 1500°C for low La/Al ratios (<0.1), the predominant La-containing phase is lanthanum-β-alumina (La₂O₃.11Al₂O₃) as previously claimed by Matsuda et al. [Matsuda et al., 1984]. These authors attributed the ability of added La to retard sintering as a consequence of lanthanum-β-alumina and not LaAlO₃ formation, because at low concentration the formation of LaAlO₃ is unlikely [Haack et al., 1992b]. However, Béguin et al.
claimed that the loss of stabilisation is associated with the solid reaction of \( \text{LaAlO}_3 \) and \( \text{Al}_2\text{O}_3 \) to form lanthanum-\( \beta \)-alumina [Béguin et al., 1991]. The formation of lanthanum-\( \beta \)-alumina requires both a sufficiently low La concentration and a high calcination temperature. Dexpert-Ghys et al. [Dexpert-Ghys et al., 1976] reported that the lanthanum-\( \beta \)-alumina phase exists over the composition range \( \text{La} / \text{Al} = 1/11 \) to 1/14. They synthesised lanthanum-\( \beta \)-alumina by firing \( \text{La}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) powder. Ropp and Caroll [Ropp & Caroll, 1980] have observed that lanthanum-\( \beta \)-alumina is formed via \( \text{LaAlO}_3 \) at temperatures above 1400°C by firing \( \text{La}_2\text{O}_3-\text{Al}_2\text{O}_3 \) (8.3-91.7) mixture for 24 h. The formation rate of lanthanum-\( \beta \)-alumina is extremely slow below 1500°C. However, in some studies, formation of lanthanum-\( \beta \)-alumina at a lower temperature, i.e. 1000°C, could be observed [Matsuda et al., 1984; Kato et al., 1989]. This formation may result from the difference in the preparation method, i.e. co-precipitation compared to mixing of two oxides by Ropp and Caroll. The co-precipitation method gave a larger surface area for the two oxides, which resulted in the formation of lanthanum-\( \beta \)-alumina at the relatively low temperature.

Thus it is clear that La has a positive effect on the stabilisation of \( \text{Al}_2\text{O}_3 \) at high temperatures. Nevertheless the mechanism of the stabilising effect is unclear, because the dispersed La phase, the perovskite \( \text{LaAlO}_3 \) and the lanthanum-\( \beta \)-alumina were all found to be responsible for the stabilisation.

### 4.2.5 Additional Effects of Lanthanum

Besides the thermal stabilisation effect on the support, La has been proven to be very effective for increasing the dispersion and stabilising the particle size of Pt [Yang & Swartz, 1984; Drozdov et al., 1986; Oudet et al., 1987; Oudet et al., 1989; Härkönen et al., 1991] and Pd [Matsuda et al., 1984; Chou et al., 1995]. Oudet et al. reported that the presence of La strongly modifies the morphological aspect of the \( \text{Al}_2\text{O}_3 \) support, which appears poorly crystallised and composed of particles of undefined shape [Oudet et al., 1989]. This provides an increased number of nucleation sites for metals during the first steps of deposition, leading to an enhancement of the initial repartition and dispersion of the metallic phase on the doped samples. Xie et al. suggested that the promotion by La changes the surface property of the support and the interface energy between Ni and the support causes the crystallite of Ni to become smaller [Xie et al., 1982]. It is certain that the role of La is also to decrease the movements of the washcoat and thus restrain the coalescence or encapsulation of the metal particles. La has also been reported to be effective against the undesirable reactions between \( \text{Al}_2\text{O}_3 \) and \( \text{CuO} \) that lead to copper aluminate [Tijburg, 1989].
The durability of Pd catalyst modified by La for the oxidation of CH₄ has been shown by several authors [Matsuda et al., 1984; Kato et al., 1989; Chou et al., 1995]. A 4 h test performed at 860°C for the combustion of CH₄ showed that the activity of a Pd/Al₂O₃ with 6% La₂O₃ could be retained. TPO studies demonstrated that the retardation in Pd sintering resulted from an increase in the bond strength Pd-O [Chou et al., 1995]. Kato et al. studied the durability of combustion catalysts using a mixture containing 3 vol% CH₄ at the inlet temperature of 500°C and at about 1200°C in the catalyst bed temperature after CH₄ combustion. The CH₄ conversion was above 99.5% for the Pd/La₂O₃-Al₂O₃ (La/Al = 5/95) during 1000 h, while it decrease from 99.3 to 90% for the Pd/Al₂O₃ only after 250 h [Kato et al., 1989].

4.3 Cerium in Catalysis

It is an ambitious task to define the role of ceria (CeO₂) in catalysis, particularly for abatement of pollutants, since many effects have been attributed to CeO₂. The different applications and roles of Ce have been reviewed by several authors [Kummer, 1986; Trovarelli, 1996; Kašpar et al., 1999]. Ceria is already used in three-way catalysts [Kim, 1982; Kummer, 1986; Gandhi & Shelef, 1987], diesel oxidation catalysts [Farrauto & Voss, 1996] and combustion catalysts [Groppi et al., 1999]. Its use in catalysts was implemented in the beginning of the 1980s following the use of FeO and NiO as oxygen storage components [Funabiki et al., 1991].

4.3.1 Oxygen Storage Capacity (OSC)

The most crucial role of ceria is its ability to exchange oxygen with the environment. Ceria is a non-stoichiometric compound [Yao & Yu Yao, 1984; Harrisson et al., 1988] which exhibits two valences, Ce(+III) and Ce(+IV), with low redox potential. The oxygen storage on the catalyst is simply described as a cyclic reduction and oxidation of CeO₂. The process of oxygen storage and transport in ceria can be described by the defect mechanism and there are two types of defects: intrinsic and extrinsic [Cho, 1991; Mogensen et al., 2000].

The former is due to the oxygen anion vacancies created upon the reduction of ceria according to the redox process involving ceria:

\[ \text{CeO}_2 + \delta R \rightleftharpoons \text{CeO}_{2-\delta} + \delta \text{RO} + \delta \text{V}_o \]

where R is a reductant, RO is a gaseous product, and Vo is an oxygen anion vacancy which may be charged singly or doubly [Cho, 1991].

The extrinsic defects are due to the oxygen anion vacancies created by the charge compensation effect of foreign cations, which have a valence, lower
than that of the host Ce ions they substitute. For example, the doping reaction of ceria with bi- or tri-valent cations can be written as:

$$2MO + Ce_{Ce} \rightarrow 2M_{Ce} + CeO_2 + 2V_o$$

$$2M_{2}O_3 + 3Ce_{Ce} \rightarrow 4M_{Ce} + 3CeO_2 + 2V_o$$

where M is the bi- or tri-valent cation, Ce_{Ce} is the Ce cation on the Ce site of the ceria lattice, M_{Ce} is the foreign cation on the Ce cation site [Cho, 1991]. Trivalent dopants generally produce a higher ionic conductivity, i.e. oxygen mobility, than divalent ones [Cho, 1991]. Both of these vacancies were believed to provide a practical way to increase the OSC of CeO₂.

4.3.2 Noble metal-Ceria Interactions

In TWC catalysts the air/fuel ratio in TWC oscillates around the stoichiometric value, due to the lag between the oxygen sensor and the carburettor. Hence, CeO₂ dominates in the oxidative atmosphere, while in reducing atmosphere Ce₂O₃ becomes predominant. Thus according to a cyclic rich-lean composition fluctuation in the automotive exhaust gas, the cerium oxide can either provide oxygen for the oxidation of CO and HC, for instance, or remove oxygen from the gas phase for the reduction of NOₓ to N₂ [Gandhi et al., 1976]. The formation of lattice oxygen vacancies in CeO₂, which plays an important part in the oxidation of CO [Jin et al., 1987; Sanchez & Gasquez, 1987] is associated with the reduction of Ce(+IV) to Ce(+III) [Yao & Yu Yao 1984]. The interaction of CeO₂ with precious metals (Pt, Pd and Rh) and its effect on catalytic activity has been intensively studied [Yao & Yu Yao, 1984; Crucq et al., 1991]. CeO₂ itself does not have good O₂ adsorption. Yao and Yu Yao found no OSC on CeO₂ alone at 300°C and very little at 400°C. This is consistent with the fact that surface capping oxygen (SCO) in CeO₂ which contributes to catalytic reactions [Funabiki et al., 1997] cannot be reduced below 300-350°C [Yao & Yu Yao, 1984; Harrison et al., 1988]. However, when it coexists with noble metals, the total amount of O₂ is greatly increased even at 300°C [Yao & Yu Yao, 1984] and the presence of Pt, Pd or Rh lowers the temperature of the surface CeO₂ reduction [Yao & Yu Yao, 1984; Harrison et al., 1988; Bernal et al., 1993; Serre et al., 1993; Bouly et al., 1995; Funabiki et al., 1997]. Yu Yao also showed that Pd, Pt and Rh metals promote the reduction of Ce⁴⁺ to Ce³⁺ and thus facilitate the charge transfer from metal to Ce, which results in the higher oxidation states of the metals and hence increases the oxygen storage capacity of CeO₂ [Yu Yao, 1984].
There is significant evidence that oxygen storage property in noble metal catalysts is correlated with the degree of interaction between a group VIII metal and CeO$_2$ [Nunan et al., 1992; Funabiki et al., 1997]. Noble metals/CeO$_2$ catalysts have been found to have considerable activity at very low temperatures after certain pre-treatments. The noble metals in the order of Rh, Pd, Pt helped to enhance the O$_2$ uptake and maintain the SCO after thermal ageing due to intimate contact with noble metals [Funabiki et al., 1997]. Yu Yao observed an improved activity after a reduction in CO at 300°C for the oxidation of CO and HC with either Pt, Pd or Rh supported on CeO$_2$ [Yu Yao, 1984]. Kubsh et al. observed higher activity of Pt/Rh/CeO$_2$ catalysts after reduction at 500°C [Kubsh et al., 1991]. Nunan et al. observed an improved low-temperature activity of Pt/CeO$_2$ for both oxidation of CO and HC and reduction of NO$_x$, after a reductive pre-treatment in a rich synthetic exhaust gas mixture at 450°C [Nunan et al., 1992]. The same observation has been made with other reducing agents: H$_2$ at 200°C [Holmgren et al., 1999], 300°C [Diwell et al., 1991], 500°C [Kubsh et al., 1991] and CO at 490°C [Serre et al., 1993b]. The high activity is discussed in terms of reduction of CeO$_2$ in the vicinity of Pt particles [Nunan et al., 1992; Serre et al., 1993b; Holmgren et al., 1999] and that decreasing CeO$_2$ crystallite size leads to higher Pt/Ce interaction and hence greater activity [Nunan et al., 1991].

Unfortunately, without any pre-reducing treatment and in lean conditions CeO$_2$ is reported to convert Pt and Pd metals into an oxidised and less active state for the oxidation of alkanes [Yu Yao, 1980; Kummer, 1986; Gandhi & Shelef, 1987; Shyu & Otto, 1989]. However, for the oxidation of CH$_4$, the promotion of Pd by CeO$_2$ may be beneficial. According to several authors, CeO$_2$ retards the thermal decomposition of PdO and promotes Pd oxidation through Pd-Ce interactions [Shyu et al., 1988b; Ishihara et al., 1993; Hu et al., 1996; Groppi et al., 1999; Ciuparu et al., 2000]. However, some authors also reported negative effects of CeO$_2$ onto Pd for oxidation of CH$_4$ [Hicks et al., 1990c; Ahlström-Silversand & Odenbrand, 1997].

### 4.3.3 Metal Oxide-Ceria Interactions

Previous studies of Ce promoters have focused primarily on its effects on the structure and activity of noble metal catalysts. Studies of the promoter effect on supported transition metal oxide catalysts have been limited. However, in some studies CeO$_2$ has been examined as a promoter for oxidation reactions. The catalytic activity of CeO$_2$ for the oxidation of CO is reported to be enhanced in the presence of Zr [De Leitenburg et al., 1996; Terribile et al., 1999], Ag [Luo et al., 1998] Mn [Imamura et al., 1996; Terribile et al., 1999] and Mn-Cu [Agarwal & Spivey, 1982; Terribile et al., 1999]. Cu catalysts prepared on CeO$_2$/Al$_2$O$_3$ supports are particularly effective for
oxidation reactions of CO and CH₄ [Peiyan et al., 1987; Peiyan et al., 1995; Liu & Flytzani-Stephanopoulos, 1995a; Luo et al., 1997; Xavier et al., 1998; Martínez-Arias et al., 1998; Terribile et al., 1999; Larsson & Andersson, 2000; Radwan et al., 2001] compared to any other base metal catalysts found in the literature and to a 0.5 wt% Pt catalyst [Liu & Flytzani-Stephanopoulos, 1995c]. Oxidation of CO at room temperature has been reported to occur on CuO deposited on pure CeO₂ [Liu & Flytzani-Stephanopoulos, 1995a]. In addition to an enhanced activity, the CuO/Ce(La)O₂/Al₂O₃ catalyst also showed a much better resistance to water vapour than other Cu catalysts [Liu & Flytzani-Stephanopoulos, 1995a; Xavier et al., 1998]. What makes doped CeO₂ more active is the increase of oxygen mobility, which is the result of introduction of defect sites by addition of dopants into CeO₂ lattice (extrinsic defects). The reason for this behaviour can be found in the efficiency of the Ce(IV)-Ce(III) redox couple, which is strongly enhanced in solid solutions due to the introduction of the smaller cation into the fluorite lattice of CeO₂. This generates defects throughout the matter which in turn, brings about an increase in oxygen mobility and diffusion in the lattice [Pijolat et al., 1995; Lamonier et al., 1996]. Thus this increases the total amount of oxygen that can be reversibly exchanged between the solid and the surrounding atmosphere, and affects the kinetics of the redox processes by lowering the activation energy for “hopping” of oxygen, which in turns results in a higher oxygen storage capacity. The synergetic effect between Cu and Ce, that leads to an increase in activity, has also been attributed to the presence of reduced Cu [Liu & Flytzani-Stephanopoulos, 1995b] particularly active for the oxidation of CO [Jernigan & Somorjai, 1994], and an increase of CO adsorption on CuO-CeO₂ compared to CuO or CeO₂ alone [Luo et al., 1997].

4.3.4 Additional Effects of Ceria

One of the main functions of CeO₂ in TWC catalysts is to promote the water-gas shift reaction [Gandhi et al., 1976; Schlatter & Mitchell, 1980; Kim, 1982; Herz & Sell, 1985; Harrison et al., 1988]:

\[ CO + H₂O \rightarrow CO₂ + H₂ \]

and the steam reforming reaction [Diwell et al., 1991]:

\[ C₃H₈ + 3H₂O \rightarrow 3CO + 7H₂ \]

Ce which is included in the catalysts for automotive emission control for other purposes than stabilisation of the washcoat has also been claimed to be an effective stabiliser to a small extent [Rogemond et al., 1997], but less than
other rare earth oxides such as La [Harrison et al., 1988; Kato et al., 1989; Ozawa et al., 1990; Church et al., 1993; Ismagilov et al., 1995; Shkrabina et al., 1995; Ahlström-Silversand & Odenbrand, 1997; Groppi et al., 1999].

CeO₂ is also used to improve the dispersion of noble metals, Pt [Yao, 1984; Drozdov et al., 1986; Gandhi & Shelef, 1987; Diwell et al., 1991; Gonzales-Velasco et al., 1993], Pd [Duplan & Praliaud, 1991], and Rh [Yu Yao, 1980]. The addition of ceria leads to an increase of the resistance to sintering of precious metals [Sanchez & Gazquez, 1987; Diwell et al., 1991]. The deactivation of Rh, which is a crucial component of TWC particularly with regard to CO and to NO to N₂ conversion, is thought to be due to a strong Rh-Al₂O₃ interaction, which fixes Rh in a high oxidation state and may inhibit the redox capability of Rh under transient conditions. This effect can be retarded by the incorporation of CeO₂ into the catalyst [Harrison et al., 1988].

However, some studies have shown negative effects using Ce in combination with noble metals, as follows. It was reported that the addition of CeO₂ in Pt (0.02 wt% Pt) catalysts decreased the dispersion and increased the particle size with increasing Ce content, whereas for Pd (0.05 wt%), the content of Ce did not affect the dispersion. However, CeO₂ did not keep either Pt or Pd in a highly dispersed state during exposure at 900°C [Summers & Ausen, 1979]. These results are consistent with those of Hicks et al. who studied the thermal stability of Pd in a range of temperature from 500°C to 900°C [Hicks et al., 1990c] and found that with high loadings of Pd (2.5 wt%), CeO₂ did not alter the thermal stability of the Pd, whereas at lower loadings (0.2 wt%) and temperatures above 600°C, the stability of Pd is greatly reduced by CeO₂ [Hicks et al., 1990c]. It was concluded that CeO₂ might preferentially cover sites on Al₂O₃ that bond tightly to oxidised Pd at high temperatures, and thereby promote the agglomeration of the oxidised Pd.

However, on Cu/Al₂O₃ catalysts the promotion by CeO₂ was reported to stabilise Cu against sintering, by decreasing the particle size and the formation of copper aluminate due to Cu-Ce interactions [Fernández-García et al., 1997].

Besides these effects, Ce in catalysts has been reported to reduce the inhibition effect of CO, and makes the oxygen partial-pressure dependence less pronounced [Yu Yao, 1984; Oh & Eickel, 1988].

4.3.5 Deactivation of Ceria

The deactivation of the oxygen storage capacity is a large problem. The deactivation has been found to be mainly due to thermal sintering. Indeed, the increasing restrictions for the automotive emissions led to the development of so-called closed-coupled catalysts (CCC). These catalysts, being manifold mounted, experience high temperatures (1000-1100°C), and thus require extremely high thermal resistance [Cuif et al., 1998; Kašpar et al., 1999].
Thermal ageing of CeO$_2$ resulted in a significant decrease in the surface capping oxygen (SCO), but caused no change in bulk oxygen [Funabiki et al., 1997]. The suppression of the redox capacity of CeO$_2$ in aged catalysts is associated with the crystallisation of CeO$_2$ [Engler et al., 1989; Nunan et al., 1991; Zhang et al., 1995; Funabiki et al., 1997; Rogemond et al., 1997], decrease of surface area [Yao & Yu Yao, 1984; Funabiki & Yamada, 1988; Kašpar et al., 1999], loss of metal-CeO$_2$ interactions [Nunan et al., 1992; Bouly et al., 1995; Schmieg & Belton, 1995] and formation of CeAlO$_3$ that fixes Ce in one oxidation state [Geller & Raccah, 1970].

Other deactivation mechanisms have been suggested such as CeO$_2$ poisoning by P [Smedler et al., 1993], and S to form sulphate [Harrison et al., 1988; Trimm, 1991; Boaro et al., 2000] thus inhibiting the water-gas shift reaction [Schlatter & Mitchell, 1980; Su & Rotschild, 1986].

4.3.6 Ceria Promoters

Structural doping of CeO$_2$ may provide an efficient route to stabilise and to enhance the oxygen storage and hence catalytic activity.

The effects of doping with foreign cations, at relatively low concentrations, on the thermal stability of CeO$_2$ has been extensively investigated by Pijolat et al. [Pijolat et al., 1995]. These authors tried to rationalise the ability of foreign cations to stabilise CeO$_2$ against sintering by developing a complete set of equations based on the diffusion of Ce vacancies as the limiting step in the sintering process. Among the different cations investigated (Th$^{4+}$, Zr$^{4+}$, Si$^{4+}$, La$^{3+}$, Y$^{3+}$, Sc$^{3+}$, Al$^{3+}$, Ca$^{2+}$ and Mg$^{2+}$), those with ionic radii smaller than that of Ce$^{4+}$ effectively stabilised the CeO$_2$ against sintering [Pijolat et al., 1995]. As a general trend, an increase in the amount of added cation decreased sintering. Thermal stabilisation of a CeO$_2$ surface area was observed also in mixed oxides prepared by co-precipitation method [Kubsch et al., 1991]. Conversely, all the dopants whose radii are larger than that of Ce$^{4+}$, e.g. La, Nd and Y significantly stabilised CeO$_2$. The discrepancy between the results found by the studies was due to the preparation method, according to Kaspar et al., because Pijolat et al. used the incipient wetness method that gave large particle diameter, thus only the small cations had the ability to migrate into CeO$_2$ lattice and form a solid solution.

Numerous studies concern mixed CeO$_2$-ZrO$_2$ systems which were already employed in the 4th generation TWCs, in close coupled catalysts by the mid-1990s [Heck & Farrauto, 1995; De Leintenburg et al., 1996; Nunan et al., 1996; Cuif et al., 1997; Fornasiero et al., 2000]. Ce-Zr solutions were reported to be effective catalysts for the total oxidation of CH$_4$ [Zamar et al., 1995]. The improved OSC is due to the higher lability of oxygen atoms compared to pure CeO$_2$. Some oxygen atoms are located at long distances from the Zr atoms, providing higher mobility. Abundant literature is available on the study of
interactions between CeO\textsubscript{2}–ZrO\textsubscript{2} and Pt or Rh [Nunan et al., 1991; Trovarelli, 1996]. The addition of 10\% Zr has been found to enhance significantly the O\textsubscript{2} uptake of Pt/CeO\textsubscript{2} catalysts [Funabiki et al., 1997]. In the fuel-rich conditions, the role of ZrO\textsubscript{2} which is to strongly enhance the reducibility of CeO\textsubscript{2} with or without noble metals, led to an enhanced NO removal at lower temperatures [Fornasiero et al., 1995]. In addition, the presence of ZrO\textsubscript{2} facilitates removal of sulphate species under reductive atmospheres, thus restoring most of the OSC of Rh/CeO\textsubscript{2}–ZrO\textsubscript{2} catalyst compared to Rh/CeO\textsubscript{2} after sulphur poisoning [Boaro et al., 2000]. Also, higher thermal stabilities were reported [Balducci et al., 1995; Nunan et al., 1996; Permana et al., 1997; Cuif et al., 1998]. For instance, Pd/CeO\textsubscript{2}–ZrO\textsubscript{2} catalyst showed higher oxygen storage characteristics after 1050\textdegree C ageing than Pd/CeO\textsubscript{2} catalyst [Cuif et al., 1998].

4.3.7 Synergetic Effect between La and Ce

The initial studies concerning the use of solid solution CeO\textsubscript{2}–ZrO\textsubscript{2} to enhance OSC have stimulated interest on investigating the effects of other doping agents, for example La. The addition of La to CeO\textsubscript{2} has been suggested to have several positive effects.

It is known that rare earths have high solubility in fluorite oxides [Kim, 1982] and dissolution of La\textsuperscript{3+} ions into CeO\textsubscript{2} lattice to form La\textsubscript{2}O\textsubscript{2}–CeO\textsubscript{2} solid solution has been reported by several authors [Miyoshi et al., 1989; Miki et al., 1990; Bernal et al., 1997; Groppi et al., 1999]. This leads to an improvement of CeO\textsubscript{2} dispersion [Graham et al., 1993], a decrease of CeO\textsubscript{2} crystallite growth [Pijolat et al., 1995; Groppi et al., 1999] and an inhibiting effect of sintering of CeO\textsubscript{2} with or without Pt/Rh at high temperatures in oxidising environments [Miyoshi et al., 1989; Kubsh et al., 1991; Ozawa et al., 1991]. XPS measurements carried out on La/CeO\textsubscript{2} indicated that stabilisation of surface area with this tri-valent dopant is a surface La\textsuperscript{3+} enrichment that impedes CeO\textsubscript{2} crystallite growth under oxidising conditions [Kubsh et al., 1991; Harrison et al., 1996].

Also, inhibition of the formation of CeAlO\textsubscript{3} could be achieved by incorporating La\textsuperscript{3+} [Graham et al., 1993]. La\textsuperscript{3+} has to be deposited before CeO\textsubscript{2} is added because surface segregation of La\textsuperscript{3+} onto CeO\textsubscript{2}, impedes the reducibility of CeO\textsubscript{2}, apparently due to an effective blocking of the reducible-oxides surfaces [Kubsh et al., 1991].

However, in the presence of La the reducibility of CeO\textsubscript{2} is reported to increase [Miyoshi et al., 1989; Bernal et al., 1997; Groppi et al., 1999] and the degree of oxidation of CeO\textsubscript{2} to be decreased [Talo et al., 1995; Harrison et al., 1996]. Thus La accelerates the diffusion of oxygen from the bulk to surface and the total amount of O\textsubscript{2} adsorbed is much larger than that in undoped CeO\textsubscript{2} [Miyoshi et al., 1989; Cho, 1991; Logan & Shelef, 1994; Bernal et al., 1997].

Many studies have reported the impact of La on TWC performance. Combination of La and Ce have been found to improve the light-off
performance of the Pt-Rh/CeO$_2$/La$_2$O$_3$/Al$_2$O$_3$ catalysts for abatements of CO, NO and HC at low temperatures [Miyoshi et al., 1989; Miki et al., 1990; Nunan et al., 1992]. Miki et al. [Miki et al., 1990] found that the oxygen storage capacity of CeO$_2$ was increased in presence of La$_2$O$_3$ but only in the presence of noble metals, due to the greater potential of precious metals over Ce to activate hydrogen and oxygen in the gas phase by adsorbing them on the surfaces. However, at high temperatures, the diffusion rates of both the lattice oxygen and oxygen vacancies in CeO$_2$ are facilitated leading to the enhanced activities with hydrogen and oxygen in the gas phase without the aid of the precious metals [Miki et al., 1990]. The maximum increase in the oxygen storage capacity is reached when the amount of La in CeO$_2$ is 25% [Miki et al., 1990]. However, Kubsh et al. observed a decreased TWC catalytic activity in the presence of La. The discrepancy in the results may be due to the preparation methods used and the fact that in the other studies Al$_2$O$_3$ was used, whereas Kubsh et al. studied the addition of La on Pt-Rh/CeO$_2$ catalysts [Kubsh et al., 1991].

4.4 Results and Discussion

According to reports in the literature, many studies concern the interaction between La and Al$_2$O$_3$, but little information is available on the interaction of La with the active phases in the washcoat, particularly for metal oxides.

The utilisation of CeO$_2$ in catalysis other than TWC catalysts seems to be very promising. However, the oxygen storage capacity of CeO$_2$ is insufficient to meet future requirements [Cuif et al., 1998]. Therefore, it seems important to develop catalytic systems that can stabilise CeO$_2$ against thermal damages and can be utilised in oxidising conditions. Only a few studies concern the promotion of Ce in metal oxide catalysts and almost none deal with a combination of metal oxide and noble metals.

The following studies aims to tackle some of these problems.

4.4.1 Characteristics of the La- and/or Ce- Doped Washcoat

[Paper VI]

The addition of either 3 mol% La, 3 mol% Ce, or a mixture of 1.5 mol% La and 1.5 mol% Ce onto the Al$_2$O$_3$ was done by specific adsorption of a Me(EDTA)-(Me=La, Ce) complex on Al$_2$O$_3$ [Tijburg et al., 1991]. This method was originally applied only for the deposition of La. We could observe some differences between La- and Ce-modified washcoat by characterisation with XRD, BET, TPR, XPS and SEM.
XRD did not indicate any La-containing phase on all samples even after high-temperature treatments up to 1000°C and XPS measurements evidenced the formation of a dispersed “La” phase. Indeed, the La 3d$_{5/2}$ B.E. values for the samples containing La are equal to 835.5 eV (Table 16), which are substantially higher than the values observed for B.E. observed for La$_2$O$_3$, i.e. 833.2-833.8 eV, but they correspond to the values found for the dispersed "La" phase, i.e. 835.0-836.1 eV (Table 16). This La species gives a La XP line similar to that reported for La$_2$O$_3$, La(OH)$_3$ or LaAlO$_3$ which has two doublets [Haack et al., 1992; Siegmann et al., 1978]. However, La$_2$O$_3$ or LaAlO$_3$ would be formed at higher concentrations [Bettman et al., 1989; Haack et al., 1992]. According to Bettman et al., under saturation concentration, i.e. 8.5 µmol La/m$^2$, La is in a two-dimensional lanthanum aluminate [Bettman et al., 1989]. Therefore the La, present at less than 1.7 µmol La/m$^2$, was probably present as a dispersed phase. In addition the atomic ratios of La/Al determined for CuO-Pt/La-Al$_2$O$_3$ and CuO-Pt/La-CeAl$_2$O$_3$ samples were close to that of theoretical ratios, as seen in Table 16, thus a good dispersion was obtained.

No CeO$_2$ was detected on samples containing Ce when calcined below 900°C for 4 h, as observed by XRD and XPS in the Ce-Al$_2$O$_3$, La-Ce-Al$_2$O$_3$ samples, but only in samples without active phases, as seen by XRD in Table 17. Also TPR results, as seen in Figure 36, indicated the presence of three reducible species, i.e., at 100°C the removable oxygen anions on the bare amorphous alumina support in the presence of ceria [Yao & Yu Yao, 1984], at 200-500°C the surface capping oxygen anions attached to a surface Ce$^{4+}$ ion in octahedral co-ordination [Rosynek, 1977] and at 600°C the CeAlO$_3$ precursor that is reduced to CeAlO$_3$ [Shyu et al., 1998a], but no peak that corresponds to the reduction of bulk ceria, at usually 750-900°C, was detected. This is in agreement with Yao and Yu Yao who conducted TPR and chemisorption studies [Yao & Yu Yao, 1984] and Shyu et al. [Shyu et al., 1988a] who did not observe the formation of CeO$_2$ bulk below a concentration of Ce of ca. 2.5 µmol CeO$_2$/m$^2$ Al$_2$O$_3$, which is much higher than our values (1.7 µmol CeO$_2$/m$^2$ Al$_2$O$_3$ for 3 mol%Ce/Al$_2$O$_3$). These well-dispersed Ce species were reported to be CeAlO$_3$ precursors, in agreement with our results from TPR and XPS measurements [Shyu et al., 1988a]. Che et al. proposed that CeAlO$_3$ precursors were stabilised in the cation vacancies of the Al$_2$O$_3$ surface [Che et al., 1973].

However, in presence of Cu, already after pre-treatment at 800°C, some CeO$_2$ crystallites could be detected by XRD and also by XPS, as seen in Table 18, probably due to the sintering of CeO$_2$ accelerated by the addition of Cu [Park & Ledford, 1998a].
Table 16. Data from XPS analyses of samples calcined at 800°C for 4 h in air. Binding energies of reference compounds are included. La: 3; Ce: 3; La-Ce: 1.5-1.5; Cu: 10; Pt: 0.5 mol%/Al₂O₃.

<table>
<thead>
<tr>
<th>Samples</th>
<th>La 3d₅/₂ binding energies (eV)ᵃ</th>
<th>Surface atomic ratioᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref.</td>
<td>Exp.</td>
</tr>
<tr>
<td>CuO-Pt/La-Al₂O₃</td>
<td></td>
<td>835.5</td>
</tr>
<tr>
<td>CuO-Pt/Ce-Al₂O₃</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CuO-Pt/La-Ce-Al₂O₃</td>
<td></td>
<td>835.5</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>833.2</td>
<td>[Haack et al., 1992a]</td>
</tr>
<tr>
<td></td>
<td>833.5</td>
<td>[Ledford et al., 1989]</td>
</tr>
<tr>
<td></td>
<td>833.8</td>
<td>[Alvero et al., 1987]</td>
</tr>
<tr>
<td>LaAlO₃</td>
<td>833.8</td>
<td>[Haack et al., 1992a]</td>
</tr>
<tr>
<td></td>
<td>835.7</td>
<td>[Ledford et al., 1989]</td>
</tr>
<tr>
<td>La(OH)₃</td>
<td>834.8</td>
<td>[Alvero et al., 1987]</td>
</tr>
<tr>
<td>Dispersed “La”</td>
<td>835.0</td>
<td>[Haack et al., 1992a; Talo et al., 1995]</td>
</tr>
<tr>
<td></td>
<td>835.5</td>
<td>[Alvero et al., 1987]</td>
</tr>
<tr>
<td></td>
<td>836.1</td>
<td>[Ledford et al., 1989]</td>
</tr>
</tbody>
</table>

ᵃ All B.E.’s (eV) referenced to C1s=284.6 eV
ᵇ theoretical ratios are indicated in parentheses

Figure 36. TPR of Ce-Al₂O₃ and La-Ce-Al₂O₃ calcined at 800°C for 4 h in air. Ce: 3; La-Ce: 1.5-1.5 mol%/Al₂O₃. TPR experimental conditions: 5 ml/min, 5% H₂/Ar.

When La was added, a Ce-La solid solution could be detected by XRD as observed by a shift of the 2θ position of the diffraction peaks of La-Ce-Al₂O₃ to lower angles with respect to the position of the same peaks in Ce-Al₂O₃ (not shown here) [Paper VI]. The insertion of La into the CeO₂ lattice resulted into
the stabilisation of CeO₂, as seen by an increase of Ce dispersion (Table 16), and a lower formation of CeO₂ crystallites (Table 17). Although the amount of Ce in the La-Ce-Al₂O₃ sample was half of that in Ce-Al₂O₃, the intensity corresponding to the CeO₂ diffraction peak was much smaller when La is present, thus La appeared to stabilise CeO₂. Remarkably, dopants whose radii are larger than that of Ce⁴⁺, e.g. La, were reported to significantly stabilise CeO₂ [Kubsh et al., 1991]. These interactions between La and Ce also promote the reducibility of CeO₂, as observed by a increase by 40% of the H₂ consumption during TPR experiments in presence of La in Ce-doped alumina sample [Paper VI]. This is in agreement with literature and indicates that La increases the OSC of CeO₂ because when La³⁺ is partly substituted for Ce⁴⁺, the charge is compensated by the formation of oxygen vacancies which promote the diffusion of oxygen in the bulk [Miyoshi et al., 1989; Cho, 1991].

Table 17. BET-surface area of Al₂O₃ alone and modified after calcination in air at 800°C, 900°C and 1000°C (4 and 200 h). Weight % of corundum and peak intensities of CeO₂ crystallites (2θ = 28.546) determined by XRD are indicated in parentheses. La: 3; Ce: 3; La-Ce: 1.5-1.5 mol%/Al₂O₃.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET-surface area (m²/g)</th>
<th>XRD data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C 4 h</td>
<td>900°C 4 h</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>184</td>
<td>148</td>
</tr>
<tr>
<td>La-Al₂O₃</td>
<td>176</td>
<td>138</td>
</tr>
<tr>
<td>Ce-Al₂O₃</td>
<td>169</td>
<td>133</td>
</tr>
<tr>
<td>La-Ce-Al₂O₃</td>
<td>174</td>
<td>138</td>
</tr>
</tbody>
</table>

The results from the BET-surface area and XRD experiments obtained for washcoat with or without active phases are reported in Tables 17 and 18. It can be noted that La was a more effective inhibitor to washcoat sintering than Ce. Notably no copper aluminate was found in samples containing La, indicating an effective inhibition by La in the reaction between CuO and Al₂O₃. The superiority of La over Ce in the thermal stabilisation of washcoats has also been reported by other researchers [Kato et al., 1988; Ozawa et al., 1990; Church et al., 1993; Ismagilov et al., 1995; Shkrabina et al., 1995; Groppi et al., 1999]. Some authors maintained that La is inserted into the crystal lattice of Al₂O₃ with a spinel structure, while Ce remains on the surface in the form of CeO₂ [Church et al., 1993; Groppi et al., 1999]. This characteristic difference explains why the modification by La was more effective than that of Ce in improving the thermal stability of Al₂O₃. Also this higher dispersion of La led to a more efficient restraint of the undesirable reaction between Al₂O₃ and CuO, which forms bulk copper aluminate.
Table 18. BET-surface area of CuO deposited on Al₂O₃ alone and modified after calcination in air at 800°C, 900°C and 1000°C, for 4 h in air. Weight % of corundum, peak intensities of CeO₂ (2θ = 28.546) and CuAl₂O₄ (2θ = 36.858) crystallites determined by XRD are indicated in parentheses. La: 3; Ce: 3; La-Ce: 1.5-1.5; Cu: 10 mol% / Al₂O₃.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET-surface area (m²/g)</th>
<th>XRD data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C</td>
<td>900°C</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>148</td>
<td>94</td>
</tr>
<tr>
<td>CuO/La-Al₂O₃</td>
<td>143</td>
<td>112</td>
</tr>
<tr>
<td>CuO/Ce-Al₂O₃</td>
<td>144</td>
<td>107</td>
</tr>
<tr>
<td>CuO/La-Ce-Al₂O₃</td>
<td>140</td>
<td>108</td>
</tr>
</tbody>
</table>

4.4.2 Effects of La on the Stability of Manganese Oxides catalysts [Paper V]

The stabilising effect of La on MnOₓ catalysts in mixtures with small amounts of Pt or Pd was investigated by means of XPS, EDX, XRD and TPR after calcination at 800°C for 4 h in air and after thermal treatments in air with 10% steam at 900°C for 300 h. Catalytic activity was evaluated by oxidation of CO, C₁₀H₈ and CH₄ (gas mixture 1).

The dispersion of Mn was determined by XPS measurements (Table 19). It can be observed that the ratios Mn/Al measured for the fresh samples were higher than the theoretical one (0.05), due to a surface enrichment. In presence of La in the MnOₓ-Pt catalysts, the measured Mn/Al ratio was higher, as seen in Table 19. This indicates that La increased the dispersion of MnOₓ, or that Mn particles were smaller in the presence of La. This can be attributed to interactions between La and Mn during insertion of the Mn salt. Indeed, the La/Al atomic ratio increased following the deposition of Mn and calcination at 800°C for 4 h in air (0.024 for La-Al₂O₃ and 0.034 for MnOₓ-Pt/La-Al₂O₃), which suggests that La phases dissolved in the solution containing Mn salt.

However, after hydrothermal treatment at 900°C for 300 h, the samples deposited on Al₂O₃ alone become enriched in Mn at the surface as seen by an increasing Mn/Al ratio, whereas, for the MnOₓ-Pt/La-Al₂O₃ sample the Mn/Al ratio was similar to that of the fresh sample. EDX was also used to determine the atomic ratio of Mn/Al in the thermally treated samples. The Mn/Al ratio for the aged MnOₓ-Pt/La-Al₂O₃ sample (0.058) was close to the theoretical ratio (0.05), while it was higher in the undoped sample (0.07), as seen in Table 19. This could be explained by the fact that La stabilises the washcoat and the dispersion of the metal oxides and prevents coalescence of particles after hydrothermal treatment. The discrepancy between the two analytical methods is due to the lower analysis depth of XPS compared to EDX.
Table 19. Mn/Al atomic ratio determined by EDX (HRTEM) and by XPS for catalysts calcined at 800°C for 4 h in air (F) and hydrothermally treated at 900°C for 300 h in air with 10% steam (A). La: 3; Mn: 10; Pt: 0.1 mol%/Al2O3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS data</th>
<th>EDX data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>A</td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>0.078</td>
<td>0.15</td>
</tr>
<tr>
<td>MnOx-Pt/La-Al2O3</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*a 2-nm depth

*b 14-nm depth

XRD revealed no Mn phases before and after thermal treatment, probably because of small sized particles in the samples, thus a good dispersion of Mn was obtained. Neither was MnAl2O4 detected, in agreement with data in the literature [van de Kleut, 1994].

The TPR profiles of the samples containing manganese oxides (MnOx-Pt/Al2O3, MnOx-Pt/La-Al2O3, MnOx-Pd/Al2O3 and MnOx-Pd/La-Al2O3) were similar and not well defined, therefore these will not be discussed here. However the initial composition of the samples could be determined. The addition of La did not affect the oxidation state of MnOx/Al2O3, since Mn2O3 was found to be the predominant species in all the samples (doped and undoped) calcined at 800°C for 4 h in air, and Mn3O4 for all the thermally treated samples.

The results of the activity measurements performed for the mixed MnOx-noble metal catalysts in gas mixture 1 are given in Table 20. For the oxidation of CH4, the addition of La decreased the temperature for 50% conversion by ca. 20°C for both fresh MnOx-Pd and MnOx-Pt catalysts. This enhancement in activity for CH4 oxidation can be explained by a better dispersion of Mn in the presence of La, as determined by characterisation studies.

After hydrothermal treatment, the activities of the modified catalysts are larger than that of unmodified ones for the oxidation of all combustibles and more particularly for CH4, certainly due to the stabilisation effect of La on the washcoat and MnOx.

Table 20. Temperature (°C) for 50% conversion CO, C10H8 and CH4 for catalysts calcined at 800°C for 4 h in air (F) and hydrothermally treated at 900°C for 300 h in air with 10% steam (A). La: 3; Mn: 10; Pt, Pd: 0.1 mol%/Al2O3. Gas mixture 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CO</th>
<th>C10H8</th>
<th>CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>A</td>
<td>ΔT</td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>290</td>
<td>330</td>
<td>40</td>
</tr>
<tr>
<td>MnOx-Pt/La-Al2O3</td>
<td>288</td>
<td>327</td>
<td>39</td>
</tr>
<tr>
<td>MnOx-Pd/Al2O3</td>
<td>283</td>
<td>342</td>
<td>59</td>
</tr>
<tr>
<td>MnOx-Pd/La-Al2O3</td>
<td>287</td>
<td>310</td>
<td>23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>C10H8</th>
<th>ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>327</td>
<td>33</td>
</tr>
<tr>
<td>A</td>
<td>316</td>
<td>32</td>
</tr>
<tr>
<td>ΔT = T50%(A) – T50%(F)</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>MnOx-Pd/Al2O3</td>
<td>332</td>
<td>48</td>
</tr>
<tr>
<td>MnOx-Pd/La-Al2O3</td>
<td>314</td>
<td>27</td>
</tr>
<tr>
<td>MnOx-Pt/Al2O3</td>
<td>320</td>
<td>33</td>
</tr>
<tr>
<td>MnOx-Pt/La-Al2O3</td>
<td>316</td>
<td>32</td>
</tr>
</tbody>
</table>

MnOx-Pt/Al2O3               | 320     | 33      |
| MnOx-Pt/La-Al2O3            | 316     | 32      |
4.4.3 Effects of La on the Reducibility of Copper Oxide Catalysts [Paper V]

In chapter 2, Section 2.2.2, Cu species in CuO/Al₂O₃ catalysts with various amounts of Cu, were identified by means of TPR. The aim of the present study is to compare the influence of La on the formation of reducible Cu-species in CuO/La-Al₂O₃ samples calcined at 300°C for 4 h in air. Thus TPR experiments on CuO/La-Al₂O₃ (from 1.6 to 8 mol% Cu / 100 m²/g Al₂O₃) were performed (Figure 37).

The results show that, for each Cu content, the reduction of CuO on doped Al₂O₃ occurs at a higher temperature than that with Al₂O₃ alone. This could be a consequence of stronger interactions between Cu and Al₂O₃, [Gentry & Walsh, 1982] as the support could be less crystalline in the presence of La. Indeed, Solcova et al. [Solcova et al., 1993] found that more crystalline supports helped increase the reducibility of NiO due to weaker interactions between NiO and the support, as compared to that on an amorphous support [Mile et al., 1988; Kadkhodayan & Brenner, 1989].

In addition, the formation of CuO appeared at a Cu concentration of 4.8-6.4 mol% for the sample containing La, whereas in the case of Al₂O₃ alone, CuO was already detectable at a concentration of 3.2-4.8 mol%. This indicates that La increased the dispersion of Cu onto Al₂O₃, thus leading to a higher saturation value to Cu in Al₂O₃.

![Figure 37. TPR profiles of CuO/Al₂O₃ (1.6 to 8 mol% Cu/100 m²/g Al₂O₃) alone (thin line) and stabilised with La (thick line), calcined at 300°C for 4 h in air. TPR of bulk CuO is added. TPR experimental conditions: 40 ml/min, 5% H₂/Ar.](image-url)
4.4.4 Effects of La on the Stability of Copper Oxide Catalysts [Paper V]

The stabilising effect of La on Cu species in mixture with small amounts of Pt or Pd was investigated by means of TPR, XRD and XPS after calcination at 800°C for 4 h and after thermal treatments in air with 10% steam at 900°C for 300 h. Catalytic activity was evaluated by oxidation of CO, C10H8 and CH4.

On samples calcined at 800°C for 4 h, surface Cu²⁺ species were present in all samples (CuO-Pt/Al₂O₃, CuO-Pt/La-Al₂O₃, CuO-Pd/Al₂O₃ and CuO-Pd/La-Al₂O₃). Indeed the hydrogen consumption during TPR measurements indicated Cu²⁺ species while according to the analysis of the TPR reduction temperature no reduction peak that corresponds to bulk CuO was found, but only the reduction of surface Cu²⁺ species [Dumas et al., 1989], as discussed above and in Section 2.2.2 (Figure 10).

The sample containing La had a higher reduction peak temperature compared to that without La (Figure 38, CuO-Pt/Al₂O₃, CuO-Pt/La-Al₂O₃ samples only are shown). XPS measurements evidenced also the presence of Cu species different from bulk CuO (Table 21). Indeed the B.E. of the principal Cu 2p₃/₂ peak was lower than the values usually found for CuO, as seen in Table 21. Also the satellite intensity of Cu 2p₃/₂ to that of the main photoelectron line for all the samples calcined at 800°C for 4 h was smaller (ca 0.20) than those found for bulk CuO (0.45) and bulk CuAl₂O₄ (1.10) [Strohmeier et al., 1985]. Thus the Cu species present maybe surface Cu²⁺.

After hydrothermal treatment at 900°C for 300 h, copper aluminate, i.e. CuAl₂O₄, was detected by XRD analyses (Figure 39) and TPR measurements (Figure 38) on Cu-containing samples without La (CuO-PtAl₂O₃ and CuO-Pd/Al₂O₃), as seen by the peak observed at ca 400°C (see also Section 3.1.2, Figure 27a). According to the hydrogen consumption corresponding to the “CuAl₂O₄ peak”, ca. 64 and 81% of the initial CuO had reacted with Al₂O₃ to form bulk aluminate in both CuO-Pt and CuO-Pd, respectively. The hydrogen consumption in the second step for both CuO-Pt and CuO-Pd samples were proportionally related to the XRD intensities of CuAl₂O₄ in these samples. Hence, CuAl₂O₄ would seem to be the major species after hydrothermal treatment.

The presence of bulk spinel compound after hydrothermal treatment at 900°C was detected only in the Cu-containing undoped samples, but not in those containing La. In addition, in the hydrothermal treated samples, bulk CuO appeared on the unpromoted Cu-based catalysts, whereas, in the presence of La, the surface Cu²⁺ species were still present. This was clearly seen by the formation of a new reduction step during TPR analyses of
hydrothermally treated CuO-Pt/Al$_2$O$_3$, (Figure 38) and by the highest B.E. value obtained for the same sample from XPS analyses (Table 21).

Figure 38. TPR profiles of CuO-Pt deposited on Al$_2$O$_3$ alone and stabilised with La calcined at 800°C for 4 h (thin line) and after hydrothermal treatment at 900°C for 300 h in air with 10% steam (thick line). La: 3; Cu: 10; Pt: 0.1 mol%/Al$_2$O$_3$. TPR experimental conditions: 40 ml/min, 5% H$_2$/Ar.

Table 21. XPS data determined for catalysts calcined at 800°C for 4 h in air (F) and after hydrothermal treatment at 900°C for 300 h in air with 10% steam (A). Binding energies of reference compounds are included. La: 3; Cu: 10; Pt: 0.1 mol%/Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu 2p$_{3/2}$ binding energies (eV)$^a$</th>
<th>Surface composition Cu/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref. F</td>
<td>A</td>
</tr>
<tr>
<td>CuO-Pt/Al$_2$O$_3$</td>
<td>933.4(3.6)</td>
<td>933.6(3.7)</td>
</tr>
<tr>
<td>CuO-Pt/La-Al$_2$O$_3$</td>
<td>932.8(3.2)</td>
<td>933.2(3.4)</td>
</tr>
<tr>
<td>Bulk CuO</td>
<td>933.6 [Friedman et al., 1978; Strohmeier et al., 1985]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>933.7 [Ertl et al., 1980]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>933.9 [Wolberg et al., 1970; Park &amp; Ledford, 1998b]</td>
<td></td>
</tr>
<tr>
<td>Bulk CuAl$_2$O$_4$</td>
<td>934.5 [Strohmeier et al., 1985]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>934.6 [Friedman et al., 1978]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>934.8 [Wolberg et al., 1970]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>935.0 [Park &amp; Ledford, 1998b]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All B.E.’s (eV) referenced to C1s=284.6 eV. FWHM indicated in parentheses
Moreover, the ratio of the satellite intensities (relative to the main Cu 2p3/2 photoelectron line), determined by XPS, was ca. 0.42 (= bulk CuO) for the hydrothermally-treated CuO-Pt/Al2O3, while lower ratios were found for the fresh samples of CuO-Pt/Al2O3 and for the fresh and aged samples of CuO-Pt/La-Al2O3. This meant that bulk CuO was present only in the hydrothermally treated CuO-Pt/Al2O3, as confirmed by TPR. It is likely that the surface of the aged CuO-Pt/Al2O3 sample was covered by a layer of CuO, which could explain why bulk copper aluminate could not be detected by XPS.

Also, the presence of La in the samples was found to stabilise the surface composition, as observed by similar Cu/Al ratios before and after hydrothermal treatment at 900°C for 300 h in presence of La (Table 21).

Thus, it can be summarised that the role of La was to prevent coalescence of particles, by stabilising the washcoat and the dispersion of the metal oxides, and to restrain solid-phase reactions between alumina and metal oxides after hydrothermal treatment.

For the Cu-based catalysts, calcined at 800°C for 4 h, the presence of La did not influence the activity for the conversion of C10H8 and CO (Table 22). This is probably due to the fact that La affects the dispersion of metal oxides more than noble metals, the latter being the “active phases” for the oxidation of CO and C10H8 [Paper III]. Characterisation using XPS and TPR indicated the presence of surface Cu2+ species in all fresh samples (doped and undoped), thus no significant difference in activity between the doped and undoped catalysts could be observed. These isolated Cu2+ species, and not CuO clusters, were reported to be the active species for the oxidation of CH4 [Marion et al., 1991; Jiang et al., 1997]. The CuO-Pd (on Al2O3 and La-Al2O3) catalysts had the best activity for the oxidation of the combustibles studied here, followed by the CuO-Pt catalysts.
The activities of the catalysts containing La were better after hydrothermal treatment at 900°C for 300 h in air with 10% steam, particularly for the oxidation of CH$_4$ (Table 22). This is mainly due to the stabilisation effect of La on the washcoat against sintering. Also, the formation of copper aluminate in absence of La may have contributed to a decrease in activity, as discussed in Section 3.1.2 due to the fact that in CuAl$_2$O$_4$, the oxidation state of Cu is fixed to one valence. It could be also due to the formation of CuO crystallites that are less active than surface Cu$^{2+}$ for the oxidation of CH$_4$ [Marion et al., 1991]. The CuO-Pd/La-Al$_2$O$_3$ catalyst (Figure 40) remained the best catalyst for the oxidation of CO, C$_{10}$H$_8$ and CH$_4$ after hydrothermal treatment, and this was also true when compared to mixed catalysts with Mn (see Section 4.4.2).

Table 22. Temperature (°C) for 50% conversion CO, C$_{10}$H$_8$ and CH$_4$ for catalysts calcined at 800°C for 4 h in air (F) and hydrothermally treated at 900°C for 300 h in air with 10% steam (A). La: 3; Cu: 10; Pt, Pd: 0.1 mol%/Al$_2$O$_3$. Gas mixture 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CO F</th>
<th>CO A</th>
<th>ΔT</th>
<th>C$_{10}$H$_8$ F</th>
<th>C$_{10}$H$_8$ A</th>
<th>ΔT</th>
<th>CH$_4$ F</th>
<th>CH$_4$ A</th>
<th>ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-Pt/Al$_2$O$_3$</td>
<td>266</td>
<td>284</td>
<td>18</td>
<td>271</td>
<td>289</td>
<td>18</td>
<td>602</td>
<td>724</td>
<td>122</td>
</tr>
<tr>
<td>CuO-Pt/La-Al$_2$O$_3$</td>
<td>266</td>
<td>276</td>
<td>10</td>
<td>273</td>
<td>281</td>
<td>8</td>
<td>599</td>
<td>686</td>
<td>87</td>
</tr>
<tr>
<td>CuO-Pd/Al$_2$O$_3$</td>
<td>216</td>
<td>392</td>
<td>176</td>
<td>221</td>
<td>406</td>
<td>185</td>
<td>578</td>
<td>748</td>
<td>170</td>
</tr>
<tr>
<td>CuO-Pd/La-Al$_2$O$_3$</td>
<td>214</td>
<td>259</td>
<td>45</td>
<td>221</td>
<td>268</td>
<td>47</td>
<td>577</td>
<td>652</td>
<td>75</td>
</tr>
</tbody>
</table>

ΔT=T$_{50}$(A)-T$_{50}$(F)

Figure 40. Conversion of CO and CH$_4$ over CuO-Pd catalysts deposited on Al$_2$O$_3$ alone and stabilised with La calcined at 800°C for 4 hours in air (F) and after hydrothermal treatment at 900°C for 300 hours in air with 10% steam (A). La: 3; Cu: 10; Pd: 0.1 mol%/Al$_2$O$_3$. Gas mixture 1.
4.4.5 Synergetic Effects in CuO-Ce and CuO-La-Ce [Paper VI]

In this study, the effects of Ce, La or both in Al₂O₃ support on CuO catalysts are presented. Characterisation techniques such as XRD, TPR, TPO and XPS have shed some light on the chemical and physical changes of the samples in the absence or presence of these additives. Catalytic activity was evaluated using a mixture containing CO, C₂H₄ and CH₄ (gas mixture 2).

XRD measurements determined the formation of a solid solution between Ce and Cu, as seen by a shift towards higher angles of the peak positions of CeO₂ in CuO/Ce-Al₂O₃ with respect to those of Ce-Al₂O₃ [Paper VI]. These interactions may be reached during the deposition of Cu that preferentially deposited on CeO₂, as observed from TEM studies by Fernandez-Garcia et al. [Fernández-García et al., 1997]. Namely, in the present work, hydrogen TPR on CuO/Ce-Al₂O₃ indicated the presence of two Cu species, whereas on CuO/Al₂O₃ only one was detected (Figure 41). The first species reduced at lower temperature corresponds to Cu²⁺ in interactions with Ce, whereas the second corresponds to Cu²⁺ deposited on Al₂O₃.

As seen by XPS means, the surface concentration of Ce was affected by the subsequent deposition of Cu, whereas the surface concentration of La was not, as seen by the atomic ratios Ce/Al and La/Al (Table 23). In addition, a higher fraction of Ce⁴⁺ in the presence of Cu was determined as calculated from the XPS measurements. Contacts between Cu and Ce resulted in the stabilisation of Cu, as seen by a lesser formation (Table 18) and a lower average particle size of bulk copper aluminate, i.e. CuAl₂O₄, in CuO/Ce-Al₂O₃ compared to CuO/Al₂O₃ after ageing at 1000°C for 4 h (Table 23). The stabilisation of CuO by CeO₂ can also be seen by the slower re-oxidation and lower oxygen
consumption of reduced Cu in the presence of CeO$_2$ during TPO after reduction of the samples up to 700°C (Table 23).

Table 23. XPS, XRD and TPO data. La: 3; Ce: 3; La-Ce: 1.5-1.5; Cu: 10 mol%/Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS data $^a$</th>
<th>XRD data</th>
<th>TPO data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La/Al</td>
<td>Ce/Al</td>
<td>% Ce$^{4+}$</td>
</tr>
<tr>
<td>La-Ce-Al$_2$O$_3$</td>
<td>0.012</td>
<td>0.011</td>
<td>6</td>
</tr>
<tr>
<td>CuO/Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuO/Ce-Al$_2$O$_3$</td>
<td>-</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>CuO/La-Ce-Al$_2$O$_3$</td>
<td>0.010</td>
<td>0.0059</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ determined on samples calcined at 800°C for 4h in air; % Ce$^{4+}$ obtained from u”” and v”” relative amounts in Ce 3d [Paper VI]

$^b$ determined by Scherrer’s formula at 2θ = 36.858°, samples calcined at 1000°C for 4 h in air.

$^c$ TPO experimental conditions: 42 ml/min, 5% O$_2$ in N$_2$, samples calcined at 800°C for 4 h in air and reduced in 5% H$_2$ in Ar up to 700°C.

n.d.: not determined.

The promotion of CeO$_2$ into CuO catalyst led to a decreased in the temperature for 50% conversion of CO by more than 80°C, as seen in Figure 42. No enhancement was seen for the oxidation of C$_2$H$_4$ and CH$_4$.

![Figure 42](image-url)

Figure 42. CO conversion on CuO catalysts deposited on Al$_2$O$_3$ alone and modified after calcination at 800°C for 4 h in air. La: 3; Ce: 3; La-Ce: 1.5-1.5; Cu: 10; Pt: 0.5 mol%/Al$_2$O$_3$. Gas mixture 2.

We showed that this enhancement is seen even without any steam in the feed, thus it cannot be attributed to the water-gas shift reaction, despite the fact that it has been reported that CuO enhances this reaction when deposited on pure CeO$_2$ [Li et al., 2000].

Some authors [Lamonier et al., 1996; Xavier et al., 1998] reported the creation of anionic vacancies due to the insertion of Cu$^{2+}$ into the CeO$_2$ lattice. The insertion of Cu into a CeO$_2$ lattice led to the creation of vacancies that increases the CuO reducibility, i.e., lowers the CuO reduction temperature, as seen by
Figure 41. This enhancement in oxygen mobility in Cu catalysts doped with CeO$_2$ favours a higher redox process, according to the Mars-van Krevelen type of mechanism, and significantly promotes the CO oxidation. Luo et al. claimed that the enhancement in CO oxidation was due to CO adsorption, which occurs only for Cu interacting with CeO$_2$ [Luo et al., 1997]. Despite the fact that in this study, B.E. determined from XPS and H$_2$ consumption from TPR experiments indicated the presence of mainly Cu$^{2+}$, an Auger peak that can be assigned to Cu$^+$ was also found in Cu catalyst containing only Ce as additive [Paper VI]. The stabilisation of reduced Cu, as Cu$^+$, was also clearer after reduction and re-oxidation during TPO of CuO/Ce-Al$_2$O$_3$ (Table 23). Liu et al. [Liu & Flytzani-Stephanopoulos, 1995a] also reported that CeO$_2$ enhanced the oxidation of CO on CuO catalysts. The authors attributed these results to the presence of small, dispersed Cu$^+$ clusters stabilised by interaction with the CeO$_2$ [Liu & Flytzani-Stephanopoulos, 1995b], and proposed a model according which Cu clusters provide surface sites for CO adsorption and the CeO$_2$ provides the oxygen source which is then transferred to CO. Furthermore, Jernigan and Somorjai compared the CO oxidation over CuO, Cu$_2$O and Cu, and concluded that the apparent activation energy increases with increasing CuO oxidation state [Jernigan & Somorjai, 1994]. Therefore, both effects (from Cu$^{2+}$ and Cu$^+$) maybe present in the CuO/Ce-Al$_2$O$_3$ catalyst. Inhibition of CO poisoning by the presence of CeO$_2$ is unlikely to be the cause of the enhancement due to the net oxidising conditions and of the high working temperature [Oh & Eickel, 1988].

The oxidation of C$_2$H$_4$ and CH$_4$ was, however, not boosted by the addition of CeO$_2$ in CuO/Al$_2$O$_3$ catalyst. It seems that the Cu-Ce system has a propensity to activate the oxidation of CO while oxidation of HCs are not affected [Park & Ledford, 1998a; Larsson & Andersson, 2000]. We demonstrated that this peculiar effect could not be attributed to the WGS reaction that involves only CO and no HCs, as discussed earlier. The slow step of alkane oxidation has been postulated to be the dissociative chemisorption of the alkane on the metal with the breakage of the weakest C-H bond [Cullis et al., 1970].

Despite the lower amount of Ce in CuO/La-Ce-Al$_2$O$_3$ compared to CuO/Ce-Al$_2$O$_3$, the CO oxidation is also favoured, probably because the presence of La promotes the effect of CeO$_2$ on CuO, as observed by an increase of CeO$_2$ reducibility during TPR experiments. Thus La and Ce do have a synergetic effect on the catalytic oxidation of CuO catalyst.
4.4.6 Synergetic Effects in CuO-Pt-La-Ce [Paper VI]

In this study, the effects of Ce, La or both in Al₂O₃ support on Pt and CuO-Pt catalysts are presented. Characterisation techniques such as XRD and XPS were used. Catalytic activity was evaluated using a mixture containing CO, C₂H₄ and CH₄ (gas mixture 2).

Characterisation studies and activity measurements confirmed the slight influence of the additives (La, Ce or both of them) on Pt alone catalysts. Markedly, the effect of the additives on Pt catalysts was much clearer when Cu was also present. Namely, in CuO-Pt/Al₂O₃ catalysts Ce induced a lower fraction of metallic Pt whereas mixed La-Ce brought about a higher fraction of metallic Pt and reduced Ce, compared to CuO-Pt/Al₂O₃ without additives, determined from XRD and XPS measurements.

Figure 43 shows the XRD profiles of all CuO-Pt samples calcined at 800°C for 4 h. Pt crystallites were detected in all CuO-Pt samples, as well as in all Pt catalysts (not shown here), despite the low concentration of Pt loading. No Pt oxides were detected, probably due to their high dispersion and/or too small a crystallite size to be made visible by XRD. Pt peak intensities were found to be the highest in the CuO-Pt/La-Ce-Al₂O₃ sample, followed by CuO-Pt/Al₂O₃ and the lowest in CuO-Pt/La-Al₂O₃ and CuO-Pt/Ce-Al₂O₃ samples. This indicates that the fraction of Pt in metallic form was the highest in CuO-Pt/La-Ce-Al₂O₃.

Concerning the XPS data, when comparing the relative amounts of Ce⁴⁺ in the CuO-Pt/Ce-Al₂O₃ (21%) and CuO-Pt/La-Ce-Al₂O₃ (13%), it could be observed that the presence of La lowers the Ce⁴⁺ fraction by 8% which is in agreement with the results reported by Talo et al. [Talo et al., 1995]. Moreover, it was observed that the addition of Pt in CuO/La-Ce-Al₂O₃ sample, when comparing CuO/La-Ce-Al₂O₃ (20%) and CuO-Pt/La-Ce-Al₂O₃ (13%), also
lowers the Ce\textsuperscript{4+} fraction, which suggests the presence of interactions between Pt and Ce.

In the present study, CuO-Pt/Ce-Al\textsubscript{2}O\textsubscript{3} and Pt/Ce-Al\textsubscript{2}O\textsubscript{3} catalysts had slightly lower activities than CuO-Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/Al\textsubscript{2}O\textsubscript{3} catalysts, respectively, as seen by the results in Table 24. Several authors reported that after pre-treatment of Pt/CeO\textsubscript{2}-containing catalysts in an oxidising atmosphere, the Pt at the interface with CeO\textsubscript{2} was partially oxidised thus leading to a worsened or similar activity compared to Pt/Al\textsubscript{2}O\textsubscript{3} catalyst [Yu Yao, 1980; Serre et al., 1993b].

However, when Ce was mixed with La in CuO-Pt/La-Ce-Al\textsubscript{2}O\textsubscript{3} catalyst, more reduced Ce and Pt were found, as determined by XPS and XRD, respectively, as discussed above, compared to CuO-Pt/Ce-Al\textsubscript{2}O\textsubscript{3} catalyst, as well as Pt-CeO\textsubscript{2} interactions were detected. These resulted in a very active CuO-Pt/La-Ce-Al\textsubscript{2}O\textsubscript{3} catalyst compared to CuO-Pt/Al\textsubscript{2}O\textsubscript{3}, CuO-Pt/Ce-Al\textsubscript{2}O\textsubscript{3} or any Pt catalysts for all combustibles, as seen in Table 24, particularly for the oxidation of C\textsubscript{2}H\textsubscript{4} presented also in Figure 44.

Table 24. Temperature (\degree C) for 50% conversion of the catalysts calcined at 800\degree C for 4 h in air. La: 3; Ce: 3; La-Ce: 1.5-1.5; Cu: 10; Pt: 0.5 mol%/Al\textsubscript{2}O\textsubscript{3}. Gas mixture 2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CO</th>
<th>C\textsubscript{2}H\textsubscript{4}</th>
<th>CH\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}</td>
<td>200</td>
<td>206</td>
<td>629</td>
</tr>
<tr>
<td>Pt/La-Al\textsubscript{2}O\textsubscript{3}</td>
<td>212</td>
<td>212</td>
<td>627</td>
</tr>
<tr>
<td>Pt/Ce-Al\textsubscript{2}O\textsubscript{3}</td>
<td>216</td>
<td>216</td>
<td>633</td>
</tr>
<tr>
<td>Pt/La-Ce-Al\textsubscript{2}O\textsubscript{3}</td>
<td>223</td>
<td>223</td>
<td>645</td>
</tr>
<tr>
<td>CuO-Pt/Al\textsubscript{2}O\textsubscript{3}</td>
<td>175</td>
<td>182</td>
<td>576</td>
</tr>
<tr>
<td>CuO-Pt/La-Al\textsubscript{2}O\textsubscript{3}</td>
<td>173</td>
<td>179</td>
<td>581</td>
</tr>
<tr>
<td>CuO-Pt/Ce-Al\textsubscript{2}O\textsubscript{3}</td>
<td>186</td>
<td>190</td>
<td>600</td>
</tr>
<tr>
<td>CuO-Pt/La-Ce-Al\textsubscript{2}O\textsubscript{3}</td>
<td>156</td>
<td>146</td>
<td>573</td>
</tr>
</tbody>
</table>

Pt/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts have been found to have considerable activity for CO oxidation at low temperatures under stoichiometric fuel-conditions, but this improvement was present only after a high-temperature reduction with H\textsubscript{2} [Diwel et al., 1991; Golunski et al., 1995; Holmgren et al., 1999], and CO [Serre et al., 1993b]. Serre et al. proposed that the high temperature was needed to reduce PtO\textsubscript{2} and PtO at the interface between Pt and CeO\textsubscript{2}, and that it was this reduced Pt in contact with Ce that was responsible for the high activity. Reduced Ce in the vicinity of reduced Pt atoms on the surface were also proposed by other authors to be the most active sites of the catalyst, especially for CO oxidation [Nunan et al., 1992; Holmgren et al., 1999]. Serre et al. [Serre et al., 1993a] gave two interpretations of the Pt-CeO\textsubscript{2} interactions: a C-O bond weakening when CO is adsorbed on Pt particles, thus a CO adsorbed near the Pt-CeO\textsubscript{2} interface will more easily insert an oxygen atom from CeO\textsubscript{2} into its structure, and will quickly desorb as CO\textsubscript{2}; a decrease of the Ce-O bond.
strength for CeO₂ localised near Pt. This interpretation is supported by results from Yu Yao [Yu Yao, 1984] who pointed a charge transfer from metal to CeO₂, leading to a small increase in the oxidation state of metal, indicating that Ce is also slightly reduced, leading to a decrease of the Ce-O bond strength [Yao, 1984]. Also, Golunski et al. proposed that the improvement might be due to strong metal-support interaction (SMSI) obtained during the high-temperature reduction, which could led to migration of CeO₂ to cover Pt thus diminishing the CO adsorption capacity of Pt [Golunski et al., 1995].

In this study, the promotion of Pt/CeO₂-Al₂O₃ catalyst with both Cu and La could improve significantly the oxidation for CO, C₂H₄ and CH₄ in oxidising atmosphere. Moreover this result was achieved without any prior reducing treatment of the samples, which is usually needed to improve the activity of Pt/CeO₂ catalysts [Diwell et al., 1991; Kubsh et al., 1991; Serre et al., 1993b; Holmgren et al., 1999]. This is an advantage since pre-reducing treatment would have only a short time effect on the activity of the catalysts, and hence be useless for total oxidation applications.

Interestingly, after calcination at 900°C, the synergetic effects are enhanced as seen by a decrease of the temperature for 50% conversion for CuO-Pt/Al₂O₃ and particularly for CuO-Pt/La-Ce-Al₂O₃, while the activity of Pt/Al₂O₃ is hampered, as seen in Figure 45. The activity of CuO-Pt/La-Al₂O₃ was similar before and after calcination at 900°C, thus the improvement cannot be provided by La alone. The enhancement in activity can be attributed to enrichment in Pt that migrated at the surface with a higher calcination temperature and hence the synergetic effects that were already observed for the CuO-Pt samples calcined at 800°C are emphasised.

Therefore the combined CuO-Pt/La-Ce-Al₂O₃ catalyst was concluded to have the highest activity and thermal stability of all the catalysts tested.
4.5 Concluding Remarks

Due to its dispersed form, La contributes to the thermal stabilisation of the alumina washcoat, thus allowing it to retain a high surface area and its amorphous structure under high temperature conditions. Indeed, to a higher extent than Ce, because Ce sinters and remains on the surface in the form of CeO₂. This La stabilisation of the alumina structure results in a better dispersion and higher saturation of metal oxides onto an alumina support, and at the same time stabilised the oxidation activity of catalysts by preventing the interaction of metal oxide with alumina to form inactive bulk spinel compounds such as CuAl₂O₄. After calcination at 800°C and after hydrothermal treatments at 900°C for 300 hours in 10% steam performed on a series of mixed catalysts doped and undoped with La, the CuO-Pd/La-Al₂O₃ catalyst was found to be very active for the oxidation of CO, C₁₀H₈ and CH₄.

Moreover, due to the formation of a La-Ce solid solution, the promotion of the Ce-doped washcoat by La stabilised CeO₂ and increased its dispersion, as well as enhanced the oxygen mobility of CeO₂.

In CuO/Ce-Al₂O₃, the formation of a Cu-Ce solid solution, which was detected by XRD and by TPR, led to a higher thermal stability of Cu by producing smaller amounts of CuAl₂O₄ and of lower particle size than on CuO/Al₂O₃ after thermal treatments at 1000°C. CeO₂ also promoted the formation of some reduced copper (Cu⁺) in catalysts calcined in air, and particularly after a redox cycle. In addition, this interaction brought down a significant increase in oxygen mobility that resulted in an increase of CuO.
reducibility. Thus, these two effects led to a substantial enhancement of CO oxidation.

In the mixed CuO-Pt/Al₂O₃ catalysts, the addition of Ce led to a decrease in the fraction of metallic Pt, thus decreasing the activity of the catalysts. However, this effect was countered by the addition of La, which facilitated the reduction of both Pt and CeO₂, thus enhancing greatly the catalytic activity.
To demonstrate the possibility of using a full-scale catalytic system, a metallic monolith equipped with a pre-heating device was inserted in a commercial 30 kW wood-fired boiler (model CTC V30, CTC Parca AB, Sweden), as seen in Figure 46 [Paper IV]. The catalyst prepared was based on an 100 cpsi metallic monolithic substrate, Fecralloy (Emitec GmbH), of the same kind as described in Paper IV, which contained a mixture of MnO$_x$ (Mn: 10 mol%/Al$_2$O$_3$) and Pt (0.5 mol%/Al$_2$O$_3$) deposited on Al$_2$O$_3$ stabilised with 3% La [Paper IV]. The shape of the catalyst was half a cylinder divided into 4 segments (Figure 46), each with a length of ca 50 mm, separated by approximately 10 mm in order to increase mass transfer within the catalyst sections as a result of increased turbulence at the inlet sections [Berg & Berge, 1999; Berg, 2001]. In these experiments, an electric hot air heater introduced through the ash pit door pre-heated the catalyst. The heater had to be switched off and the ash pit door closed before ignition of the fuel, at which point the catalyst started to cool down, as seen in Figure 47. The flue gas flow was approximately 100 Nm$^3$/h, corresponding to a space velocity of 32 000 h$^{-1}$.

Figure 46. Commercial boiler with the MnO$_x$-Pt/La-Al$_2$O$_3$ catalyst (reprinted with permission from Termiska Processer AB).
For experiments with and without preheating, the temperature and the emission of CO and total HC (THC) during the first 10 minutes after ignition of the first small batch of wood was measured. The results for the oxidation of CO and THC are presented in Figures 48a and 48b, respectively. The catalyst temperature during the start-up phase was above 250°C, therefore a good effect on the conversion of CO over the pre-heated catalysts could be expected when comparing with results obtained in laboratory [Paper IV]. Since the pre-heating of the catalyst was interrupted just before the fuel is ignited, the temperature of the pre-heated catalyst decreased during the first 3 minutes (Figure 48). After this period, the hot flue gases increased the temperature of the pre-heated catalyst and after 8 to 10 minutes no significant difference in temperature between the different experiments remained. It is, however, clear that the pre-heated catalyst results in lower emissions during the period from 1 up to 8 or 9 minutes, the latter part of the period being the time when the effect of pre-heating can no longer be seen on the temperature measurements. The reduction of CO during these 10 minutes with the pre-heated catalyst compared with the boiler operating without any catalyst is 67%. Higher conversion could be expected if the space-velocity is lowered or if the pre-heating of the catalyst is increased or not interrupted. Also lack of oxygen could contribute to insufficient oxidation. Other solutions could of course be chosen if the catalyst was installed in a commercial unit but this study is a first attempt to demonstrate the potential of this method. Another advantage with pre-heating the catalyst is that the deactivation may be reduced, especially for a boiler designed without any possibility to by-pass the catalyst during start-up, since the condensation of tars on the cold catalyst surface contributes significantly to deactivation.

Figure 47. Temperature measured downstream the MnO$_x$-Pt/La-Al$_2$O$_3$ catalyst calcined at 800°C for 4 h in air, with and without pre-heating. La: 3; Mn: 10; Pt: 0.5 mol%/Al$_2$O$_3$. 
Figure 48a. CO concentration measured downstream the MnOₓ-Pt/La-Al₂O₃ catalyst, calcined at 800°C for 4 h in air, with and without pre-heating. La: 3; Mn: 10; Pt: 0.5 mol%/Al₂O₃.

Figure 48b. Total hydrocarbons concentration measured downstream the MnOₓ-Pt/La-Al₂O₃ catalyst, calcined at 800°C for 4 h in air, with and without pre-heating. La: 3; Mn: 10; Pt: 0.5 mol%/Al₂O₃.
6

CONCLUSIONS

The general conclusion from this work is that the mixed metal oxide (CuO, MnO\textsubscript{x}) - noble metal (Pt, Pd) catalysts selected for this study are superior to single component catalysts, for complete oxidation of volatile organic compounds, carbon monoxide and methane.

The combined utilisation of characterisation techniques have shed some light on the properties of the catalytic components and the washcoat and allowed a better understanding of some catalytic phenomena.

In our reaction medium, the activity of 0.1 mol\% Pd/Al\textsubscript{2}O\textsubscript{3} is higher compared to that of the catalyst with the same amount of Pt for the oxidation of CO, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4}, whereas the opposite is observed for the oxidation of C\textsubscript{2}H\textsubscript{4}. CO enhances appreciably the activity of the Pd/Al\textsubscript{2}O\textsubscript{3} catalyst for the oxidation of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{10}H\textsubscript{8} and CH\textsubscript{4}.

Al\textsubscript{2}O\textsubscript{3}-supported MnO\textsubscript{x} and CuO (Mn, Cu: 10 mol\%/Al\textsubscript{2}O\textsubscript{3}) have been selected, among the oxides of Fe, Co and Ni, as high active catalysts for the oxidation of all the combustibles studied here.

Pt and Pd possess superior catalytic activity compared to CuO and MnO\textsubscript{x} for the oxidation of CO, C\textsubscript{10}H\textsubscript{8} and C\textsubscript{2}H\textsubscript{4}, however, for the oxidation of CH\textsubscript{4}, CuO is much more active than Pt and Pd, while MnO\textsubscript{x} is as active as the noble metals.

In mixed MnO\textsubscript{x}-Pt catalysts with low noble metal loading (Pt, Pd: 0.1 mol\%/Al\textsubscript{2}O\textsubscript{3}), MnO\textsubscript{x} tends to encapsulate the noble metal, hence hampering its activity. The encapsulation can be avoided by using a successive impregnation with Pt which, in addition, leads to improved catalytic activities for the mixed MnO\textsubscript{x}-Pt compared to that of Pt alone. Higher amount of Pt, i.e. 0.5 mol\%, also dampens the inhibiting effect.

Mixed CuO-Pt and CuO-Pd catalysts (Cu: 10; Pt, Pd: 0.1 mol\%/Al\textsubscript{2}O\textsubscript{3}) preserve the activities of the most active components in the catalysts for the oxidation of the combustible. At higher Pt loading (0.5 mol\%), a synergetic effect between CuO and Pt yields a higher conversion of CO and C\textsubscript{2}H\textsubscript{4}, relative to single component catalysts. All mixed metal oxide-noble metal catalysts benefit from the presence of the metal oxides which are active for the oxidation of CH\textsubscript{4}.
The synergetic effects between metal oxides and noble metals can be related to increased reducibility of the metal oxides in the presence of noble metals which may enhance the oxygen transfer from the gas phase to the noble metals.

An investigation concerning the effect of hydrothermal treatment at 900°C of the catalysts based on alumina-supported MnOₓ or CuO and/or Pt or Pd reveals that the presence of active components significantly accelerates the sintering of the washcoat support. In addition, at 900°C alumina reacts with CuO, particularly in the presence of noble metals, to form inactive bulk spinel CuAl₂O₄. However, MnOₓ catalyst benefits from the more active Mn₃O₄ phase obtained at high temperature which makes it suitable for the high temperature oxidation of CH₄. A loading of 10 mol% Mn/Al₂O₃ is a good compromise between conversion and extent of washcoat sintering. When mixed with CuO, the sintering of Pt is delayed thus giving more thermal resistant catalyst. After a thermal treatment at 900°C for 60 h in air with 12% steam, Pd and CuO-Pt are the most active for CO and C₁₀H₈ oxidation, while MnOₓ has the highest activity for CH₄ oxidation.

Further attempt to increase the thermal stability of the washcoat and the active components by promotion with La and/or Ce indicates that due to better dispersion, La is more efficient than Ce for stabilising the high-surface area and the amorphous structure of the alumina washcoat. In addition, La contributes to a better dispersion and a higher saturation of metal oxides in the alumina, and at the same time it stabilises the oxidation activity of the catalysts by preventing the solid-phase reactions between metal oxides and alumina. After calcination at 800°C and after hydrothermal treatments at 900°C for 300 hours in 10% steam, the CuO-Pd/La-Al₂O₃ catalyst was very active for oxidation of CO, C₁₀H₈ and CH₄.

After pre-sulphation of the catalysts (1000 ppm SO₂ for 16 h at 600°C) prior to activity tests or in the presence of SO₂ (20 ppm) in the synthetic gas stream, the mixed catalysts, particularly CuO-Pd/Al₂O₃ and CuO-Pt/Al₂O₃ catalysts, are more resistant to sulphur poisoning compared to single component catalysts.

CeO₂ provides a substantial enhancement of the low-temperature CO oxidation with CuO/Al₂O₃ catalysts due to beneficial Cu-Ce interaction. Moreover, in combination with La, the stabilisation and the dispersion of CeO₂ as well as its oxygen mobility are appreciably increased. Positive synergetic effect is observed also in CuO-Pt/La-Ce-Al₂O₃ catalyst that leads to enhanced catalytic activity and thermal stability compared to Pt alone catalyst.
Scanning Electron Microscope revealed a well-anchored washcoat onto the metallic support, which is employed for fast pre-heating of the catalysts, due to the growth of whiskers from the metallic substrate during a treatment at high temperature.

Experiments in a commercial wood-fired boiler with pre-heating of a catalyst with a metallic monolith have shown significant decrease of the emissions of CO and unburned hydrocarbons during the start-up phase.

The potential of highly active and thermally stable catalysts of low cost for total oxidation has been clearly demonstrated in this thesis. Application of stabilised washcoat supports could provide long-term and cost-effective utilisation of mixed metal oxides and noble metals catalysts for the removal of VOC, CO and CH₄, under high temperature conditions and sulphur-containing atmosphere.

Large numbers of catalysts, prepared in parallel to this study, have been subjected to ageing in wood-fired boilers. The results concerning the stability are encouraging, however, in wood-burning appliances due to the complexity of the flue gases composition, the diversity of the existing installations and the placement of the catalyst in them, it is still difficult to evaluate sufficiently well their lifetime.
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