Diesel Oxidation NO$_x$ Adsorption Catalysts

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for the degree of Doctor of Philosophy

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To everyone who has supported me during the course of this thesis
“Countries can attain a certain level of emission reductions on their own, but they can do much more if they collaborate with each other, in particular with certain specific sectors.”

Christiana Figueres
UN Climate Chief
2015
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Worldwide usage of diesel engines has been rising rapidly and, accordingly, more stringent emission standards are introduced to lower the concentrations of diesel exhaust pollutants.

NO\textsubscript{x} abatement is crucial, especially in diesel engines where controlling NO\textsubscript{x} is extremely difficult as oxygen is always in excess. The title and objective of this thesis arises from a novel approach, the diesel oxidation NO\textsubscript{x} adsorption catalyst (DONAC), where NO\textsubscript{x} is to be stored by a diesel oxidation catalyst (DOC).

Supported platinum catalysts are the most used technology for diesel oxidation catalysts. Hence, the investigation of the oxidation properties of supported platinum catalysts and particularly, how these properties are affected by the support material, is of great importance. This work addresses not only the effect of the support, platinum loading, preparation method, calcination conditions and platinum precursor, but also the effect of the titania phase composition (anatase or anatase-rutile). A series of supported platinum catalysts including Pt/TiO\textsubscript{2}, Pt/SiO\textsubscript{2}, Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/TiO\textsubscript{2}-SiO\textsubscript{2} and Pt/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} were prepared by non-aqueous impregnation and chemical vapour impregnation. In order to determine the effect of the support on the structural and electronic properties of the supported platinum catalysts detailed characterisation including XRD, BET, CO chemisorption, NH\textsubscript{3}-TPD, H\textsubscript{2}-TPR, TGA, DRIFTS, Raman, XPS, SEM, TEM and EDX was performed. Two relevant oxidation reactions, total oxidation of propane and oxidation of nitric oxide to nitrogen dioxide, were studied.

It is found that the activity of supported platinum catalysts is greatly affected by the support material, in general, their performance is enhanced by addition of SiO\textsubscript{2} to the TiO\textsubscript{2} support. The activity of the platinum catalysts depends strongly on oxidation state, with platinum in
metallic state being most active. However, it is not only the platinum oxidation state but a combination of several factors including metal dispersion, surface area, morphology and phase composition of the support that explains the variations in catalytic activity. Morphology and phase composition play an active role in the redox properties of the support and its interaction with supported metal particles. The high propane oxidation activity of Pt supported on anatase TiO$_2$ is attributed to highly reactive oxygen species within the support.

DeNO$_x$ technologies based on the concept of NO$_x$ storage have proven to be effective, however further studies are needed to succeed in finding an optimum NO$_x$ storage system. A series of metal (Cu, Fe and Pt) -exchanged zeolites with different compositions (SiO$_2$/Al$_2$O$_3$ = 5.1 – 50) and frameworks (Y, ZSM-5 and BETA) were prepared by two different exchange methods (WIE and CVI). The DOE method was applied to investigate the way in which preparation experimental variables affect the NO$_x$ storage capacity of Cu$^{II}$/ZSM-5 (30). Evaluation of NO$_x$ storage capacity, in the presence and absence of O$_2$, of metal-exchanged zeolites was carried out. In order to correlate the physicochemical properties of the metal-exchanged zeolites with their NO$_x$ storage performance, characterisation including XRD, BET, NH$_3$-TPD, H$_2$-TPR, DRIFTS, UV-Vis DRS, XPS, TEM and EDX was performed.

It is found that the NO$_x$ adsorption/desorption capacity and the stability of those adsorption species formed, is greatly affected by the nature of the exchanged metal and the structure and acidity of the zeolite support. Due to the intrinsic adsorption capacity of the parent zeolite, H$^+$-ZSM-5 (23), Cu$^{II}$/ZSM-5 (23) catalysts prepared by WIE and CVI exhibit high NO$_x$ storage capacities. The initial redox state, Cu$^{2+}$/Cu$^+$ and Fe$^{2+}$/Fe$^{3+}$ ratio, and bonding strength of the metal ions to the framework affect the reducibility of metal species and consequently the storage capacity.
The preparation method is found to be crucial in controlling metal loading, nature and distribution of active species and crystallites size. The statistical approach allowed for a significant enhancement in the storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) and, in particular, the amount of NO\textsubscript{x} desorbed at high temperature. Temperature is found to have the greatest effect on the NO\textsubscript{x} storage capacity. In addition, its influence is dependent on the copper precursor concentration.

Among the zeolite based catalysts studied, potential candidates for application under real working conditions, those that exhibit greater NO\textsubscript{x} desorption at high temperatures (T > 200 °C) were found.
GLOSSARY

Å  Angstrom \(10^{-10}\) meters

AQ IMP  Aqueous impregnation

a.u.  Arbitrary units

BET  Brunauer, Emmet and Teller

BETA  Zeolite BEA

cm  Centimetre

cm\(^{-1}\)  Reciprocal Centimetre

\(^{\circ}\)C  Degrees Celsius

CVI  Catalyst prepared by Chemical Vapour Impregnation

DRIFTS  Diffuse Reflectance Infrared Fourier Transform Spectroscopy

DOC  Diesel oxidation catalyst

DOE  Statistical design of experiments

DPF  Diesel particulate filter

EDX  X-ray energy dispersive spectroscopy

eV  Electron Volts

FID  Flame ionisation detector

FTIR  Fourier transform infrared spectroscopy

g  Gram

GC  Gas Chromatography

GHSV  Gas hourly space velocity

h  Hours

HC  Hydrocarbons

ICP-MS  Inductively Coupled Plasma Mass Spectroscopy

IWI  Catalyst prepared Incipient wetness impregnation

M  Molar

mg  Milligram \(10^{-3}\) g

mol  Moles

min  Minutes

MSI  Metal-support interaction

nm  Nanometre \(10^{-9}\) m

NSR  NO\(_x\) storage reduction catalyst

PM  Particulate matter

SCR  Selective catalytic reduction

SMSI  Strong metal support interaction
<table>
<thead>
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</tr>
</thead>
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<tr>
<td>SEM</td>
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<td>SiO$_2$/Al$_2$O$_3$</td>
<td>Molar ratio of SiO$_2$ to Al$_2$O$_3$ in a zeolite</td>
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<td>TCD</td>
<td>Thermal conductivity detector</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>TPR</td>
<td>Temperature programmed reduction</td>
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<td>TOF</td>
<td>Turnover frequency</td>
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<td>TWC</td>
<td>Three-way catalyst</td>
</tr>
<tr>
<td>NH$_3$-TPD</td>
<td>Temperature programmed ammonia desorption</td>
</tr>
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<td>Ultraviolet- Visible spectroscopy</td>
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</tr>
<tr>
<td>µmol</td>
<td>Micromoles ($10^{-6}$ moles)</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS

CHAPTER 1: Introduction -1-

1.1 Introduction -1-

1.2 Diesel exhaust emissions -6-
   1.2.1 Composition -7-
   1.2.2 Legislation -12-
   1.2.3 Aftertreatment -15-

1.3 Catalysts for diesel exhaust aftertreatment -22-
   1.3.1 Supported metal catalysts -22-
      1.3.1.1 Strong metal support interactions (SMSI) -23-
      1.3.2 Zeolite based catalysts -27-

1.4 References -32-

CHAPTER 2: Scope and objectives -38-

CHAPTER 3: Experimental -41-

3.1 Materials -41-

3.2 Catalyst Preparation -43-
   3.2.1 Supported platinum catalysts -43-
      3.2.1.1 Non aqueous impregnation (IMP) -45-
      3.2.1.2 Chemical vapour impregnation (CVI) -45-
      3.2.1.3 Aqueous impregnation (AQ IMP) -46-
      3.2.1.3 Incipient Wetness impregnation (IWI) -46-
3.2.2 Metal exchanged zeolites
   3.2.2.1 Wet ion exchange (WIE)  - 47-
   3.2.2.2 Chemical vapour impregnation (CVI)  - 47-
   3.2.2.3 Statistical design of experiments (DOE)  - 48-

3.3 Catalyst Testing  - 49-
   3.3.1 Propane oxidation  - 49-
      3.3.1.1 Reactor schematic  - 49-
      3.3.1.2 Sample delivery and temperature program  - 50-
      3.3.1.3 Data analysis & quantification  - 52-
   3.3.2 NOx storage  - 53-
      3.3.2.1 Reactor schematic  - 53-
      3.3.2.2 Data analysis & quantification  - 55-
   3.3.3 Oxidation of NO to NO2  - 57-
      3.3.3.1 Data analysis & quantification  - 58-

3.4 Catalyst Characterisation  - 59-
   3.4.1 X-ray powder diffraction (XRD)  - 59-
   3.4.2 X-ray photoelectron spectroscopy (XPS)  - 61-
   3.4.3 Brunauer Emmett Teller (BET) surface area analysis  - 62-
   3.4.4 Temperature programmed reduction (TPR)  - 65-
   3.4.5 NH3-Temperature programmed desorption (NH3-TPD)  - 67-
   3.4.6 CO Chemisorption  - 68-
   3.4.7 Thermogravimetric analysis  - 70-
   3.4.8 Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)  - 71-
   3.4.9 Diffuse reflectance UV-Vis spectroscopy  - 74-
   3.4.10 Raman spectroscopy  - 75-
   3.4.11 Scanning electron microscopy (SEM)  - 77-
   3.4.12 Transmission electron microscopy (TEM)  - 79-
   3.4.13 X-ray energy dispersive spectroscopy (EDX)  - 80-

3.5 References  - 82-
CHAPTER 4: Oxidation properties of supported platinum catalysts

4.1 Introduction

4.2 Total oxidation of propane
   4.2.1 The effect of the support
      4.2.1.1 Metal oxide supports
      4.2.1.2 Mixed metal oxide supports
      4.2.1.2 Discussion
   4.2.2 The effect of the transient temperature cycle
   4.2.3 The effect of the transient calcination conditions
   4.2.4 The effect of the preparation method
   4.2.5 The effect of the platinum precursor

4.3 Oxidation of nitric oxide to nitrogen dioxide
   4.3.1 The effect of the support
   4.3.2 In situ DRIFTS studies

4.4 Conclusions

4.5 References

CHAPTER 5: NOx storage on metal-exchanged zeolites

5.1 Introduction

5.2 NOx Adsorption-Desorption studies
5.3 Monometallic zeolitic systems

5.3.1 Wet ion exchange

5.3.1.1 Exchanged metal

5.3.1.2 Zeolite structure and aluminium content

5.3.2 Chemical vapour impregnation

5.3.2.1 Exchanged metal

5.3.2.2 Zeolite structure and aluminium content

5.4 Bimetallic and trimetallic zeolitic systems

5.5 High temperature NO\textsubscript{x} desorption from zeolite catalysts

5.6 Conclusions

5.7 References

CHAPTER 6: Optimising Cu\textsuperscript{II}/ZSM-5 (30)

for NO\textsubscript{x} storage

6.1 Introduction

6.2 Application of statistical design of experiments (DOE) to optimise NO\textsubscript{x} storage on Cu\textsuperscript{II}/ZSM-5 (30)

6.2.1 Wet ion exchange

6.2.2 Chemical vapour impregnation

6.3 Statistical analysis of NO\textsubscript{x} storage on Cu\textsuperscript{II}/ZSM-5 (30)

6.4 NO\textsubscript{x} storage under real working conditions
6.5 Conclusions

6.6 References

CHAPTER 7: Conclusions & Future Work

7.1 Conclusions

7.2 Recommended future work
   7.2.1 Oxidation properties of supported platinum catalysts
   7.2.2 Optimising NO\textsubscript{x} storage in metal exchanged in zeolites

7.3 References
Introduction

1.1 Introduction

Since legislation was established to control emissions from vehicles, heterogeneous catalysts have been used to reduce the concentration of the pollutants emitted.

The term catalysis was first introduced by Berzelius in 1836. A catalyst increases the rate of a chemical reaction without itself being consumed or changed in the process. Catalysis affects the kinetics of a reaction, not its thermodynamics.

![Diagram of energy level diagram associated with a catalytic reaction](image)

**Figure 1.1.** The simplified energy level diagram associated with a catalytic reaction.

Reproduced from reference \(^1\).

Catalysts do not and cannot change the thermodynamic equilibrium of a reaction. The overall change in free energy for the catalytic reaction equals that of the uncatalysed
reaction. Hence, the catalyst does not affect the equilibrium constant of the overall reaction. The catalyst provides an alternative reaction pathway that is, often, more complicated and includes several catalytic intermediates. However, the highest activation barrier in the catalysed pathway is still lower than that of the uncatalysed reaction. Hence, a catalyst offers an energetically favourable alternative to the uncatalysed reaction, thus enabling processes to be carried out under industrially feasible operating conditions.

Catalyst activity, selectivity and durability are the three most important characteristics of a catalyst. Activity refers to the extent to which the reaction is promoted by the presence of the catalyst. Selectivity determines which reactions are favoured in the presence of the catalyst, of the many reactions that could possibly occur. Durability is indispensable for commercial catalysts and refers to the absence of deactivation following use or aging of the catalyst.

Catalysts can be classified into three categories: homogeneous catalysts, heterogeneous catalysts and biocatalysts. In homogeneous catalysis, the catalyst is in the same phase as the reactants and products. In heterogeneous catalysis, the catalyst and the reactants are in different phases. Often, the catalyst is a solid and the reactants are gases or liquids. One important advantage of heterogeneous catalysis is that the catalyst is easy to separate and recover. In biocatalytic processes, natural catalysts are used. In most cases, the biocatalyst is an enzyme; a complex protein that catalyses reactions in living cells. The structure of enzymes offers a very shape-specific active site and therefore enzymes are highly specific catalysts.

A catalysed reaction comprises of five different steps: i) transport of the reactant(s) from the reaction medium (gas / liquid phase) to the catalyst surface, ii) chemisorption at the active centre, iii) reaction takes place to form the chemisorbed product(s), iv) desorption
of the product(s) and v) transport of the product(s) from the catalyst surface to the reaction medium.

![Diagram of reaction on a catalyst surface following the Langmuir-Hinshelwood model.](image)

**Figure 1.2.** Schematic of reaction on a catalyst surface that follows the Langmuir-Hinshelwood model. Taken from reference 2.

Adsorption is the first reactive step in the cycle of heterogeneous catalysis. The reaction mechanisms describe the adsorption and desorption of reactant(s) molecules at a catalytically active surface. For the reaction A + B → C, the Langmuir-Hinshelwood mechanism assumes that both reactants, A and B, are adsorbed on the catalyst surface before the reaction takes place. The so-called Eley-Rideal mechanism, describes the situation where only A is adsorbed on the catalyst surface and B from the reaction medium reacts with adsorbed molecules of A to form the product C. In the third mechanism, the Mars-Van-Krevelen mechanism, the surface itself participates actively in the reaction; one of the reactant forms a thin surface layer of metal-reactant on the catalytic surface and the other reactant reacts directly from the reaction medium with the chemically bonded atoms from the reactant surface. The Langmuir-Hinshelwood mechanism is the most common
situation in heterogeneous catalysis, partly because many reactants are activated by the adsorption on the catalyst surface.

The creation of a surface requires energy because bonds have to be broken. Thus, the total energy of the system increases, meaning that the surface free energy is always positive. The surface free energy is related to the cohesive energy of the solid and to the number of bonds between an atom and its nearest neighbours that have to be broken to create the surface. Because the surface is a region of high energy, thermodynamics dictates a tendency to minimise this energy. Minimization of the surface free energy is the driving force behind surface relaxation, surface reconstruction, sintering and adsorption.

![Diagram of a solid catalyst crystal surface](image)

**Figure 1.3.** Schematic representation of a solid catalyst crystal surface. Taken from reference 2.

The catalyst is, mostly, an inactive surface with a few very active sites. Catalytic surfaces are not uniform. As shown in Figure 1.3, metal crystal surfaces possess vacancies, terraces, steps and kinks. The surface free energy is related to the number of unsaturated bonds in the surface atom. Generally, low coordination surface atoms have the highest surface free energy, the highest reactivity and the strongest binding for the adsorbate (high heat of
adsorption). Hence, some catalytic reactions show dependence on the nature of the structure involved.

The interaction between catalysts and substrates, intermediates and products is of great importance and dictates catalyst performance. The catalyst/substrate interactions must be optimal, not too weak and not too strong. The active site follows Sabatier’s principle, is often not the energetically preferred site for adsorption, but that site which optimises the adsorption of reactants on the surface and desorption of products after reaction. Bulk parameters, such as particle size, shape and mechanical strength of the catalyst as well as, mass and heat transfer are crucial. Mass transport limitations decrease the rate of the reactant(s) adsorption and product(s) desorption. In addition, uneven heat transfer can lead to hotspots, sintering and runaway reactions. Ideally, the active sites should all be identical and isolated. However, industrial heterogeneous catalysts are often amorphous, multicomponent and multiphase solids that contain many types of active sites.

As already mentioned, the catalytic cycle consists of several elementary reactions or steps. The experimental reaction rate is not the average or the cumulative rate of these steps but the rate of the slowest step(s) in the cycle, also called the rate-determining step(s). The reaction rate depends on the heat of adsorption and follows a volcano plot. At the start of the reaction the heat of adsorption increases and as more reactants bind to the catalyst, the reaction rate also increases. When the heat of adsorption is too strong, desorption of the substrates (or products) is not feasible and the reaction rate starts to decrease.

A catalyst is not consumed during the reaction. While the catalyst may undergo changes during the catalytic cycle, it returns to its original form at the end of the cycle. Because the active site is regenerated, each site can participate in many consecutives cycles. As a result, only a small catalyst: substrate ratio is required and this ratio reflects the catalyst’s
efficiency, which is measured as turnover number (TON) or turnover frequency (TOF). In real applications, the catalytic system can lose or gain activity due to sensitivity to changes in acidity/basicity, temperature, pressure or phase composition. Moreover, with increasing conversion, products and by-products might bind to the catalyst and change the preferred reaction pathway. Processes including deactivation, sintering, inhibition and poisoning can cause a drop in catalytic performance.

1.2 Diesel exhaust emissions

In theory, the combustion reaction that takes place in engines (petrol or diesel) should completely oxidise the hydrocarbons (HC) present in the fuel to CO$_2$ and H$_2$O. Hence, the exhaust would be formed of N$_2$ and air. Unfortunately, this is not what happens under real working conditions. Fuel combustion involves many different reactions due to its complex composition. Not all the HC are oxidised and consequently, the exhaust emissions present a variety of compounds including partially combusted oxygenates and CO.

Popularity of diesel-powered cars has increased considerably since the early 1980s. The superior fuel economy and lower car tax in several countries makes diesel cars an attractive alternative to conventional petrol vehicles. Nowadays, around 50% of all new European cars have a diesel engine. Operation at low exhaust temperatures and high O$_2$ concentrations is characteristic of diesel engines. However, not only the operation mode is different in a diesel engine, exhaust emissions control and aftertreatment needs differ significantly from those applied in petrol powered vehicles.

Exhaust emissions vary with the equivalence ratio $\lambda$. The engine must operate in a very small window of fuel-air ratio because the chemical reactions that reduce NO$_x$ and oxidize
HC and CO are mixture dependent and mutually exclusive. As illustrated in Figure 1.4, while in a fuel rich environment, at $\lambda < 1$, the activity for reduction of NO\textsubscript{x} is high, in a lean environment, at $\lambda > 1$, the reverse occurs and the oxidation of CO and HC is feasible.

![Diagram](image)

**Figure 1.4.** The concentration of CO, NO and CH\textsubscript{4} emitted by a gasoline engine as a function of $\lambda$, the fuel-air ratio. Taken from reference \(^3\).

### 1.2.1 Composition

Diesel exhaust emissions present a truly complex composition. A large variety of compounds in different concentrations form the exhaust; including oxygen (O\textsubscript{2}), nitrogen (N\textsubscript{2}), water (H\textsubscript{2}O), carbon dioxide (CO\textsubscript{2}), carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO\textsubscript{x}), sulphur oxides (SO\textsubscript{x}) and particulate matter (PM). Among these, special attention has been paid to those present in higher concentration, which are related to air quality problems and exhibit adverse effects on the environment or human health.
Hydrocarbons (HC) and volatile organic compounds (VOC)

Diesel engine emissions are composed of a variety of organic compounds, ranging from C₂ to C_{12+4}^{5}. These compounds are attributed to unburnt HC, HC partial oxidation during combustion and pyrolysis and evaporation from the fuel tank.

The term VOC refers to volatile hydrocarbons, typically those with a boiling point below 100 °C.

Some of these compounds contribute to ozone depletion. Under atmospheric conditions, in the presence of sunlight, HCs react with NO_x to produce ozone-containing photochemical smog. Breathing problems and asthma are a direct consequence. Low levels of other secondary pollutants such as peroxyacetyl nitrate (PAN), which are lachrymators, are also formed through reaction of HCs with NO_x.

\[ \text{HC} + \text{NO}_x + \text{hv} \rightarrow \text{O}_3 + \text{other products} \quad \text{Equation 1.1} \]

Adverse effects on health are also attributed to the carcinogenic character of various of these HC \(^6\).

In extremely fuel-rich regions of the flame, HC polymerization is favoured over oxidation. As a result, polycyclic aromatic hydrocarbons (PAH) are formed. Limiting the emissions of these compounds is of great importance due to their carcinogenic and mutagenic character.

Carbon dioxide (CO₂)

CO₂ is the major product of the total oxidation of HCs. It is a nontoxic gas but represents one of the most important greenhouse gases and contributes towards acidification of oceans.
Restrictions on CO$_2$ emissions is then associated with finding alternatives to fossil-fuelled cars, for example electric or hydrogen cars.

Carbon monoxide (CO)

CO is the product of incomplete combustion. It is an intermediate in the oxidation of HCs to CO$_2$ and H$_2$O. Only when the temperature and the concentration of oxygen is sufficiently high will CO be oxidised to CO$_2$. Hence, poor mixing and insufficient oxygen concentrations lead to an increase in the CO levels emitted.

$$4 \text{C}_n\text{H}_m + (2n + m) \text{O}_2 \rightarrow 2m \text{H}_2\text{O} + 4n \text{CO}$$  \hspace{1cm} \text{Equation 1.2}

CO is an extremely toxic gas, which reduces the ability of blood to carry oxygen, causes headaches, respiratory problems and at high concentrations or long exposure, death.

Nitrogen oxides (NO$_x$)

Nitrogen oxides (NO$_x$) are a mixture containing mostly nitrogen monoxide, also called nitric oxide, (NO) and between 5 and 10 % of nitrogen dioxide (NO$_2$).

Nitric oxide (NO) is the principal nitrogen-containing by-product of combustion. NO is formed by three mechanisms: thermal, prompt and fuel NO$_x$ formation $^7$.

At high combustion temperatures, N$_2$ and O$_2$ react to establish an equilibrium with NO. The formation of NO by oxidation of atmospheric nitrogen can be expressed in terms of the overall reaction:

$$\text{N}_2 + \text{O}_2 \leftrightarrow 2 \text{NO}$$  \hspace{1cm} \text{Equation 1.3}

The reaction is highly endothermic $[\Delta H^0 (298 \text{ K}) = 90.4 \text{ kJ-mol}^{-1}]$. As a result, the equilibrium concentration of NO is high at high temperatures, typical of stoichiometric
combustion, and decreases rapidly away from that point. The direct reaction of N₂ with O₂ is too slow to account for significant NO formation. In 1947, Zeldovich et al. postulated a simple chain mechanism for thermal NO formation, where oxygen atoms produced in flames by dissociation of O₂ or by radical attack on O₂, react with nitrogen molecules to form NO.

\[
N₂ + O \leftrightarrow NO + N \quad \text{Equation 1.4}
\]

\[
N + O₂ \leftrightarrow NO + O \quad \text{Equation 1.5}
\]

Due to the high activation energy, the formation of NO by this mechanism is extremely temperature sensitive and proceeds at a slower rate than the oxidation of the fuel constituents. The production of atomic oxygen required for the first reaction represented in Equation 1.4, is also highly temperature sensitive.

NO can be formed from N₂ in air through a mechanism distinct from the thermal mechanism. Prompt NO is produced under low temperature, fuel-rich conditions and at short residence times. This mechanism was first postulated by Fenimore et al. in 1971. The NO formed is the result of the attack of a hydrocarbon free radical on N₂.

\[
HC + N₂ \rightarrow HCN + N \quad \text{Equation 1.6}
\]

Under certain fuel-rich conditions, the concentration of such hydrocarbon radicals is high enough that reactions with N₂ are important and this leads to significant NO formation. These reactions have relatively low activation energies and proceed at a rate comparable to that of the oxidation of the fuel.

Fuels contain organically bound nitrogen that is readily oxidised to NO during combustion. The contribution of fuel-nitrogen to NOₓ formation is most clearly shown when the

- 10 -
production of NO from N\textsubscript{2} is not feasible.

Although NO is thermodynamically unstable at room temperature, the concentration of NO is maintained when the gas rapidly expands during cool down. Consequently, significant amounts of NO\textsubscript{x} (up to 3500 ppm of NO with traces of NO\textsubscript{2}) are present in the exhaust effluent of diesel vehicles.

\[
2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2
\]  

Equation 1.7

During combustion, only NO is formed. However, as the NO cools, it can be oxidised to NO\textsubscript{2} as shown in Equation 1.7. The oxidation of NO to NO\textsubscript{2} is a third-order reaction, with the rate depending on the square of the NO concentration as in Equation 1.8.

\[
\frac{d\text{NO}_2}{dt} = k(P_{o_2})(P_{NO})^2
\]

Equation 1.8

NO\textsubscript{x} represent serious environmental hazards. Compounds resulting from the oxidation of NO\textsubscript{x} by ozone (O\textsubscript{3}), OH\textsuperscript{-} or HNO\textsubscript{2} radicals contribute to photochemical smog and acid rain.

\[
2 \text{NO} + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2
\]  

Equation 1.9

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3
\]

Equation 1.10

O\textsubscript{3} is also formed via photochemical dissociation of NO\textsubscript{2} followed by reaction of the atomic oxygen with O\textsubscript{2} (Equation 1.11). However, because of the low concentration of NO\textsubscript{2} in exhaust effluent, the contribution of this reaction to the total amount of O\textsubscript{3} present and ozone depletion is minimal.

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]  

Equation 1.11

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]  

Equation 1.12
Sulphur oxides (SO\textsubscript{x})

Sulphur is present naturally in petrol and diesel fuel. Sulphur dioxide (SO\textsubscript{2}) is formed during combustion. Other sulphur compounds, such as hydrogen sulfide (H\textsubscript{2}S), are also commonly encountered. SO\textsubscript{2} reacts to form acids, which are associated with acid rain and engine corrosion. Sulphur compounds can also contribute to formation of O\textsubscript{3} and particulate matter. Additionally, due to its catalyst-poisoning effects, sulphur needs to be removed from the fuel during the refining process.

Particulate matter (PM)

During combustion under fuel-rich conditions, reactive intermediates lead to formation of carbon that is not completely oxidised during lean conditions. As a result, surface material composed of agglomerated carbon particles is formed.

Emission of these particles directly concerns human health. Respiratory problems and cardiovascular diseases can be caused by inhalation of these particles, as small particles are able to pass deep into the lungs and even into the bloodstream.

1.2.2 Legislation

The consciousness of the adverse effects to environmental and human health caused by emissions from combustion sources has grown significantly worldwide. Several air pollutants are now continuously monitored and their emissions have been regulated in many countries, including carbon oxides (CO\textsubscript{x}), nitrogen oxides (NO\textsubscript{x}), particulate matter (PM), sulphur oxides (SO\textsubscript{x}) and volatile organic compounds (VOC).
Although the first European standard was introduced in 1970, fitting of catalytic converters on vehicles was not mandatory until 1993.

Table 1.1. EURO emissions standards limits expressed in g/km

<table>
<thead>
<tr>
<th>Limits g/km</th>
<th>CO</th>
<th>HC</th>
<th>HC + NOₓ</th>
<th>NOₓ</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 1 (1992)</td>
<td>2.72</td>
<td>2.2</td>
<td>0.97</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Euro 2 (1996)</td>
<td>2.72</td>
<td>1.0</td>
<td>0.97</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Euro 3 (2000)</td>
<td>2.3</td>
<td>0.20</td>
<td>0.5</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro 4 (2005)</td>
<td>0.64</td>
<td>0.10</td>
<td>0.56</td>
<td>0.25</td>
<td>0.025</td>
</tr>
<tr>
<td>Euro 5 (2009)</td>
<td>1.0</td>
<td>0.10</td>
<td>0.30</td>
<td>0.06</td>
<td>0.005</td>
</tr>
<tr>
<td>Euro 6 (2014)</td>
<td>0.5</td>
<td>0.10</td>
<td>0.23</td>
<td>0.18</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Euro Standards define the acceptable exhaust emissions limits of new vehicles sold in EU member states. Hence, every new car must pass all of those safety and environmental tests dictated by the legislation.

The Euro 1 standard was established in 1992 and imposes fitting of catalytic converters to reduce emissions (mainly CO). As presented in Table 1.1, emission limits have been progressively tightened since.

The latest standard, Euro 6, applies to all new prototype vehicles and manufactured cars from September 2014. This imposes a further, significant reduction in NOₓ emissions from diesel engines (55% reduction compared to Euro 5). The second stage of the Euro 6 introduces real driving emissions (RDE) tests. From September 2017, cars will be tested to ensure that they meet strict limits in a variety of on-road conditions.
Figure 1.5. EURO emissions standards NO\textsubscript{x} limits for diesel vehicles expressed in g/km

Horizon 2020\textsuperscript{9} is the eight framework programme (FP8) implemented by the European Commission in the 2014-2020 period to support and foster research in the European research area (ERA). The FP8 also defines the European environmental research and innovation policy\textsuperscript{10}, which addresses global challenges for sustainable development and environmental protection. The programme targets the establishment of future low emission vehicles with limits lower than Euro 6 and further improvement in fuel efficiency. The implementation of mandatory 2020 CO\textsubscript{2} emission targets for new passenger cars and light-commercial vehicles in the European Union is among the emission standards imposed and by 2021, all new cars must meet a 95 g CO\textsubscript{2}/km emission limit.
1.2.3 Aftertreatment

To meet increasingly stringent regulations, combustion strategies, aftertreatment components and fuel compositions have been under continuous investigation.

The process involved in the scale up of aftertreatment technologies, used to lower the emission levels of pollutants, from laboratory to commercial applications is complex. The main challenge is the optimisation of aftertreatment catalytic systems, reducing cost and complexity without sacrificing performance or stability.

Until now, research has focused primarily on investigating the applicability of three noble metals, Pt, Pd and Rh to exhaust aftertreatment technologies. These metals are promising candidates because they show sufficient activity, excellent thermal stability, inertness with respect to reactions with the support material and resistance to sulphur poisoning. Other noble metals such as Ru, Ir or Os have not been studied in the same detail because they form volatile oxides. Due to the high cost and limited availability of noble metals, many studies have tried to find an alternative catalyst using base metal oxides including oxides of Ni, Fe, Cu, Co, Mn or Cr. However, supported base metal oxides lack the intrinsic reactivity, durability and poisoning resistance required for automotive applications.

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \quad \text{Equation 1.13} \\
\text{CO} + \text{NO} & \rightarrow \frac{1}{2} \text{N}_2 + \text{CO}_2 \quad \text{Equation 1.14} \\
\text{C}_x\text{H}_y + n \text{O}_2 & \rightarrow x \text{CO}_2 + \frac{y}{2} \text{H}_2\text{O} \quad \text{Equation 1.15} \\
\text{C}_x\text{H}_y + m \text{NO} & \rightarrow \frac{m}{2} \text{N}_2 + \frac{y}{2} \text{H}_2\text{O} + x \text{CO}_2 \quad \text{Equation 1.16}
\end{align*}
\]

The first catalytic system for converting HC, CO and NO\textsubscript{x} employed, was a dual-bed converter. Three way catalysts (TWC) were introduced to respond to stricter NO\textsubscript{x} standards and resolve the limitations of dual-bed converters. The term TWC refers to a catalyst that
simultaneously catalyses the three types of reactions represented in the equations above (1.13-1.16): CO oxidation, HC oxidation and NO\textsubscript{x} reduction.

Although significantly improved, TWC are still the primary catalytic exhaust aftertreatment in use today. Since their introduction, the cost and performance of TWC have been greatly enhanced.

During the development of TWC formulations, cerium compounds were incorporated. \(\text{CeO}_2\) exhibits interesting redox and storage properties\textsuperscript{13 14 15 16 17 18 19 20}. \(\text{CeO}_2\) is used as an \(\text{O}_2\) trap: \(\text{O}_2\) is adsorbed under lean conditions (excess of \(\text{O}_2\)) and released under rich conditions (excess of fuel). Hence, the composition of the exhaust is buffered around the stoichiometric point, which enhances the conversion of HC, CO and especially \(\text{NO}_x\). The reactions involved in oxygen storage are shown in Equations 1.17 and 1.18:

\[
\text{Equation 1.17} \quad 2 \ \text{CeO}_2 + \ \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \ \text{CO}_2
\]

\[
\text{Equation 1.18} \quad \text{Ce}_2\text{O}_3 + \ \frac{1}{2} \ \text{O}_2 \rightarrow 2 \ \text{CeO}_2
\]

In traditional stoichiometric gasoline engines, the combustion mixture always contains sufficient oxygen to just combine with the fuel. In contrast, oxygen is always in excess in diesel engines. While an oxidising atmosphere should be advantageous for the oxidation of HCs and CO, it makes controlling \(\text{NO}_x\) emissions extremely difficult. Consequently, those TWC which exhibit high performance in gasoline engines are not as efficient in diesel engines. Although nitric oxide is thermodynamically unstable (\(\Delta H_t = +90 \text{ kJ/mol}\)), under lean conditions it is not possible to achieve its catalytic dissociation to \(\text{O}_2\) and \(\text{N}_2\). Hence, \(\text{NO}_x\) can only be converted to \(\text{N}_2\) by reaction with a reductant.
In order to address the challenges posed by the use of diesel engines, new aftertreatment components are required. Typically a diesel catalytic converter comprises of an oxidation catalyst, a particulate filter and a module for NO\textsubscript{x} abatement such as NSR or SCR \textsuperscript{12,21}.

Diesel oxidation catalyst (DOC)

One of the most effective and economically viable methods to reduce HC and CO emissions is total catalytic oxidation to carbon dioxide and water.

In 1989, Volkswagen launched the Umwelt\textsubscript{diesel} Golf fitted with a monolithic Pt oxidation catalyst. This was the first commercial application of DOC and was present in all Euro 3 and later vehicles. Since then, Pt based catalysts are the most frequently used aftertreatment technology for oxidation of HC and CO. Efforts were focused upon optimising catalytic systems with highly dispersed platinum and stability to thermal sintering. In addition, Pd was found to possess higher resistance to sulphur poisoning.

Frequently, two or more metals, typically Pt/Pd and Pt/Rh, are used in combination in DOCs. Bimetallic catalyst systems show significant improvement in activity, thermal stability and resistance against sintering.

While the excess of oxygen contributes positively to the oxidation reaction, the fuel efficient nature of diesel engines is associated with a lower temperature of operation compared to gasoline engines. When the engine starts, the temperature is low (120-150 °C in urban conditions) but a large percentage of total HC emissions are produced during the cold start period. Hence, it is important to improve the low-temperature oxidation activity of these catalysts. An alternative to this is the use of storage components, such as zeolites, to adsorb HC at low temperatures and desorbed them at high temperatures, by which point the Pt based catalyst is sufficiently active to oxidise these compounds.
Although oxidation catalysts were introduced first to control HC and CO emissions, their application is also extended to control NO\textsubscript{x}.

Lean NO\textsubscript{x} trapping or NO\textsubscript{x} storage reduction (NSR)

While NO\textsubscript{x} emissions can be limited by decreasing the flame temperature/burn duration, retarding the ignition/injection time and through exhaust gas recirculation, the use of catalysts is necessary for its abatement whilst maintaining the engine power output.

NSR catalysts comprise of: i) a storage component, typically alkali or alkaline earth metals oxides (BaO) ii) precious metals that catalyse the oxidation/reduction reactions (Pt) and iii) support metal oxides (Al\textsubscript{2}O\textsubscript{3}). Pt/BaO/Al\textsubscript{2}O\textsubscript{3} is the most typical NSR catalyst \textsuperscript{22}.

NSR systems are based on a mixed lean/rich operation mode, working under cyclic operations with periodic changes. The following steps describe the NSR reaction mechanism:

Under lean conditions:

i) NO is oxidised to NO\textsubscript{2} over Pt

\[
2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \quad \text{Equation 1.19}
\]

ii) NO\textsubscript{x} (NO and NO\textsubscript{2}) is adsorbed on the storage component (BaO) in the form of nitrite or nitrate species

\[
\text{NO}_2 + \text{BaCO}_3 \rightarrow \text{BaNO}_3 + \text{CO}_2 \quad \text{Equation 1.20}
\]

Switch to rich conditions:

iii) Evolution of reducing agents, such as H\textsubscript{2}, CO or hydrocarbons from the rich exhaust mixture
iv) NO\textsubscript{x} is desorbed from the storage component (BaO)

\[ 2 \text{BaNO}_3 \rightarrow 2 \text{BaO} + 2 \text{NO} + \text{O}_2 \]  
Equation 1.21

\[ \text{BaO} + \text{CO}_2 \rightarrow \text{BaCO}_3 \]  
Equation 1.22

v) Pt catalyses the reduction of NO\textsubscript{x} to N\textsubscript{2}

The NO oxidation step is crucial in the overall NSR mechanism. The storage component is more effective where NO\textsubscript{x} is adsorbed as NO\textsubscript{2}, since NO is more weakly adsorbed than NO\textsubscript{2}. Hence the rate of oxidation of NO to NO\textsubscript{2} determines the performance of a NO\textsubscript{x} storage catalyst and the temperature at which the NO\textsubscript{x}, adsorbed in the form of nitrites or nitrates, is destabilised and desorbed.

The following mechanism was proposed by Bhatia et al.\textsuperscript{23} to describe the mechanism involved in the oxidation of NO based on reversible adsorption of NO, O\textsubscript{2} and NO\textsubscript{2}:

\[ \text{NO} + \text{Pt} \leftrightarrow \text{NO-Pt} \]  
Equation 1.23

\[ \text{O}_2 + 2 \text{Pt} \leftrightarrow 2 \text{O-Pt} \]  
Equation 1.24

\[ \text{NO-Pt} + \text{O-Pt} \leftrightarrow \text{NO}_2\text{-Pt} + \text{Pt} \]  
Equation 1.25

\[ \text{NO}_2\text{-Pt} \leftrightarrow \text{NO}_2 + \text{Pt} \]  
Equation 1.26

O\textsubscript{2} adsorption was found to be the rate-determining step.

Frequently, NO\textsubscript{x} storage catalysts have two supported layers. The first layer consists of Pt and a storage component, such as BaO. Another precious metal, often Rh, is incorporated into the top layer. While Pt catalyses the oxidation of NO, Rh catalyses the reduction of NO\textsubscript{x} to N\textsubscript{2} under rich conditions. Hence, the NO\textsubscript{x} desorbed from the storage component has to pass through the Rh layer.
One of the main problems with NSR catalysts is that deactivation occurs in the presence of sulphur compounds. When SO$_2$ is present in the exhaust, Pt catalyses the oxidation reaction, forming SO$_3$. Subsequently, SO$_3$ reacts with the basic element of the storage component to form MSO$_4$. As sulphates are thermodynamically more stable than nitrates, MSO$_4$ accumulates over the surface of the storage component, decreasing its NO$_x$ storage capacity. In order to decompose the sulphates formed and recover the storage capacity, the catalyst must be exposed to higher temperatures than those used to desorb NO$_x$.

**Selective catalytic reduction (SCR)**

During selective catalytic reduction (SCR) the reduction is selective to NO$_x$. Thus, reduction of NO$_x$ (Equation 1.27) successfully competes with the reduction of O$_2$ (Equation 1.28), even when O$_2$ is in a large excess. HC- and Urea-SCR are the main technologies used.

$$\text{HC} + \text{NO}_x \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2 \quad \text{Equation 1.27}$$

$$\text{HC} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad \text{Equation 1.28}$$

At high temperatures HC oxidation is favoured, resulting in a decrease in NO$_x$ reduction. This is because the enthalpy associated with HC oxidation is greater than that of NO$_x$ reduction. As a consequence, NO$_x$ reduction can only occur in a restricted temperature range. Conversion in this narrow window can be improved by increasing the concentration of HC in the gas mixture, however this has a higher cost.

HC-SCR catalysts explored include those containing Pt$^{24}$, Cu, Ir and also Ag$^{25, 26, 27, 28}$. Catalyst formulations containing zeolites can provide enhanced NO$_x$ reduction activity due to their ability to maintain a high concentration of hydrocarbons within the catalyst$^{29, 30, 31}$.
NH$_3$ is used as a reductant for experimental convenience. Indeed, urea may readily decompose into NH$_3$ in the Urea-SCR catalytic system. NH$_3$-SCR is very selective to reduction of NO$_x$. However, this technology presents several disadvantages associated with the use of NH$_3$ as reductant as NH$_3$ is expensive, difficult to transport and is itself a pollutant.

Pt based catalysts present high performance at relatively low temperatures but V based catalysts are more commonly used at temperatures typical of heavy-duty diesel engines. Metal-exchanged zeolites, especially those containing Fe, Co, Cu and Ce, represent a group of promising SCR catalysts due to their significant performance.

It should be considered that at high temperatures, NO can also be formed through oxidation of NH$_3$. Hence total NO$_x$ conversion is decreased considerably. V based catalysts exhibit good selectivity for NO$_x$ reduction, with only small amounts of N$_2$O formed.

Diesel particulate filter (DPF)

The function of the DPF is to efficiently filter mass PM emissions. Diesel PM filtration generally involves the processes of diffusion and interception, coupled with thermophoresis and electrophoresis.

The most successful and frequently used DPF are porous ceramic wall-flow filters made of cordierite, silicon carbide or aluminium titanate. In these systems, the exhaust gas passes through whilst PM is trapped in the filter.

As the PM accumulates in the filter the backpressure increases, which results in a decrease in engine performance. Hence, in order to maintain optimal filter performance, the PM collected on the filter must be regularly removed. Regeneration of the filter occurs through a passive or active regeneration, in which the PM collected on the filter is oxidised via
reactions with O₂, NO₂ or HC. While the temperature of the engine is not high enough to oxidise the PM, NO is oxidised to NO₂ over the Pt oxidising catalyst. Subsequently, the NO₂ oxidises PM to produce NO, CO₂ and H₂O.

\[ 5 \text{NO}_2 + 2 \text{CH} \rightarrow 5 \text{NO} + 2 \text{CO}_2 + \text{H}_2\text{O} \]  

Equation 1.29

1.3 Catalysts for emissions abatement

With vehicle emission regulations becoming more stringent, highly active, low cost catalysts are required. Hence, development of active catalysts that are chemically and thermally stable and resistant to sintering and poisoning is addressed in many studies.  

1.3.1 Supported metal catalysts

Supported metal catalysts consist of small metal particles dispersed over a support. Supported metal catalysts, where the metal is a precious metal such as Pt, Pd or Rh, are among the most important components of catalytic exhaust removal technologies.  

When designing new catalysts, the active phase, typically metal particles, is as important as the support. The active phase is the catalytically active site where the principal or rate-determining step of the reaction occurs. Among the different roles of a support, the most relevant are: dispersing the active phase of the catalyst, increasing metal surface area and improving the catalytic performance through interactions with the metal through a metal support interaction (MSI). The MSI plays a crucial role in catalysis as it not only affects the catalytic activity and selectivity but also the thermal stability of the catalyst. Hence, MSI studies provide very valuable information.
MSI is a synergistic relationship. While the support improves the dispersion of metal particles and suppresses sintering, the metal particle can also enhance the redox properties and oxygen storage capacity of the support. The extent of the metal support interaction depends on various factors including the metal loading, the nature of the support and the preparation method.

Metal support interactions have been one of the main challenges since the early exhaust aftertreatment catalysts and persist today. How to most effectively support the active phase, and enhance the MSI is therefore a key consideration.

1.3.1.1 Strong metal support interactions (SMSI)

The term strong metal support interaction (SMSI) was first introduced by Tauster et al. in 1978 to explain the significant decrease in the chemisorption capacity of group VIII noble metals supported on TiO$_2$ after reduction at high temperatures, above 500 °C. The study showed that while reduction at 200 °C gives rise to well dispersed metal particles with the capacity to adsorb H$_2$ and CO, reduction at higher temperatures suppresses the adsorption almost completely. Characterisation studies confirmed that the metal dispersion was not decreased by metal agglomeration at higher reduction temperatures. Hence, the effect was explained as a chemical interaction between the noble metal and the support via metal bonding or formation of intermetallic compounds.

Ten months later, Horsley et al. developed a molecular orbital model to study the SMSI of Pt supported on TiO$_2$. The study suggested that suppression of H$_2$ chemisorption was caused by insertion of Pt atoms into surface oxygen ion vacancies in the support through a chemical bonding.
In 1981, Tauster et al. published an investigation of the metal-support interaction between group VIII metals and different transition metal oxides and its influence on Fischer-Tropsch synthesis. In this study, the unusual chemisorption properties of catalysts that exhibit SMSI were associated with superior activity and selectivity. The metal-support interaction was explained based on electron transfer from cations present within the support, such as Ti$^{3+}$ or Nb$^{4+}$, to the metal particle.

Since SMSIs were found to directly affect catalytic activity, multiple studies focus on understanding these interactions in further detail. SMSI were explained in terms of electronic and geometric effects. The first is based on charge transfer between the metal and the support. While Ti$^{4+}$ ions in TiO$_2$ have a d$^0$ configuration, reduced TiO$_2$ present Ti$^{3+}$ ions which present a d$^1$ configuration. The electron gained is transferred from the support to the metal particle, resulting in a strong metal support interaction. Encapsulation of the particle by the support is evidence of a geometric effect. Several studies provided evidence of both theories: reporting changes in the chemical nature of surface metal atoms and formation of a thin layer of reduced oxide covering the metal particle, which results in suppression of H$_2$ chemisorption performance. However, the degree to which the metal-support interaction involves electron transfer or involves changes in electronic properties induced by metal particle size and shape caused by heat treatments is not completely clear.

Since then, the controversial nature of SMSI has been investigated. In 1999, the effects of the support on the morphology and electronic properties of supported metal particles were reviewed. The effect of the support on the activity of supported metal catalysts was found to be caused by i) charge of the metal particle, ii) changes in metal particle shape and crystallographic structure and iii) presence of active sites at the metal-support interface.
Although several studies have reported cases in which catalytic activity is enhanced by a SMSI\textsuperscript{68,19}, occasionally, SMSI is also found to have a detrimental effect on the catalytic activity\textsuperscript{69}. Liotta \textit{et al.} found that the C\textsubscript{3}H\textsubscript{6}-SCR activity of supported platinum catalysts decreased when pretreated in H\textsubscript{2} at high temperatures (T > 800 °C). In this case, structural and electronic modifications were induced by SMSI and catalysts reduced at higher temperatures exhibited a decrease in the exposed metal surface area.

Evidence of SMSI between Pt and TiO\textsubscript{2} under oxidising atmospheres has also been reported\textsuperscript{70}. In this case, XPS and Ar\textsuperscript{+} sputtering analysis suggested that Pt\textsuperscript{0} can thermally diffuse into TiO\textsubscript{2} and be oxidised to Pt\textsuperscript{2+} to substitute for lattice Ti\textsuperscript{4+} or form interstitial ions.

The SMSI extent has been found to be dependent on the phase composition\textsuperscript{71} and crystal size of the support\textsuperscript{72}. Hence, Pd/TiO\textsubscript{2} catalysts exposed to H\textsubscript{2} exhibit SMSI for anatase TiO\textsubscript{2} but not for rutile TiO\textsubscript{2}. In addition, stronger metal support interactions were associated with smaller TiO\textsubscript{2} crystal sizes.

More recently, in 2013, Tingting \textit{et al.}\textsuperscript{51} published a review of the interactions between precious metals and supports in catalysts with application in automotive exhaust aftertreatment. The review covers literature which focuses on understanding and optimising SMSI between precious metals and Al\textsubscript{2}O\textsubscript{3} or Ce\textsubscript{2}O\textsubscript{3} based supports to avoid the deactivation caused by sintering.
Several authors found evidence of inhibition of sintering through a SMSI\textsuperscript{73, 74}. Recent studies showed stabilisation of small Ag and Pt particles supported Ceria through strong metal-support bonding. Precious metals can also improve the oxygen storage capacity of the support\textsuperscript{75, 76, 77, 78}. Various investigations have reported examples where Pt, Pd and Rh supported particles enhance the reduction of surface oxygen in CeO\textsubscript{2} and CeO\textsubscript{2}-ZrO\textsubscript{2} supports.
1.3.2 Zeolite based catalysts

The term zeolite derives from Greek and means “stone that boils”. In 1756, Baron von Cronstedt gave this name to minerals, found in rocks of volcanic origin, which released water and appeared to boil when heated rapidly.

Zeolites are microporous crystalline aluminosilicates with the following formula:

\[ \text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]z\text{H}_2\text{O} \]

where

- \( M \) is an exchangeable cation with valency \( n \) and \( y \) may vary from 2 to \( \infty \).

Zeolites exhibit high surface areas, typically of the order of 300 – 700 m\(^2\)/g, with more than 98% of the total surface area corresponding to highly accessible internal surfaces.

Structurally, zeolites are composed of TO\(_4\) tetrahedra (T = Si or Al) connected through their oxygen atoms which form a three-dimensional network containing channels and cavities of molecular dimensions. Hence, the basic building unit of zeolites is the tetrahedron in which each oxygen atom is coordinated to two T atoms.

![Zeolite structures including: a) sodalite cage b) zeolite A and c) zeolite Y.](image)

*Figure 1.7.* Zeolite structures including: a) sodalite cage b) zeolite A and c) zeolite Y.

Taken from reference 79.

The secondary building unit (SBU) of zeolites are non-chiral and can contain up to 16 T atoms. A unit cell always contains the same number of SBUs, however, different
combinations of SBUs within the zeolite framework are, rarely, encountered. The building block of zeolites is the zeolite cage; large polyhedral building blocks which are stacked to form the structure. The extended structure of the zeolite can be tailored such that the cavities and channels are of specific sizes. The sodalite cage, illustrated in Figure 1.6 a), is the structural element of faujasite. The sodalite cage has the structure of a truncated cuboctahedra and is made up of 4-rings and 6-rings.

When Si\(^{4+}\) is isomorphously replaced by Al\(^{3+}\), a negative charge is generated in the lattice. A cation compensates this negative charge and, in the case of charge compensating protons, generates Brønsted acid sites. The maximum number of protonic sites is proportional to the number of framework Al atoms. From a structural point of view, the Brønsted acid site in a zeolite is represented by a resonance hybrid of structures I and II. Structure I is a fully bridged oxygen with a weakly bonded proton and structure II is a silanol group with a weak Lewis acid interaction of the hydroxyl oxygen with an Al\(^{80}\).

These positively charged cations, required to balance the structure’s charge, are exchangeable by ion exchange methods. Hence, the number and density of protons can be adjusted through post synthesis treatments, including dealumination and ion exchange. The level of exchange varies with the Si/Al ratio. An increase in the Si/Al ratio (decrease in
aluminium content), is associated with a decrease in the concentration of acid sites as well as an increase in the acid strength and proton activity coefficients.

The acid strength of the Brønsted acid sites can also be controlled through isomorphous substitution of Si$^{4+}$ for a trivalent cation other than Al$^{3+}$. Substitution can be achieved by either synthesis or postsynthesis methods. To evenly distribute the metal species within the channel, channel dimensions must be large enough for the hydrated/hydrolysed metal ions to freely diffuse through them. Tetrahedral structures are stable for cations with $0.414 > \rho < 0.225$ ($\rho = r_M/r_O$, where $r_M$ and $r_O$ are the ratios of the cation and the oxygen ion respectively). Other requirements for a true substitution imply some flexibility of the heteroelements to accept the tetrahedral coordination and an oxidation state compatible with the overall framework charge.

The thermal and chemical stability of zeolites depends on their composition. Whereas zeolites with low silica content exhibit a decomposition temperature of 700 °C, are unstable in acid solutions, hydrophilic and tend to have structures with 4, 6 and 8 member rings; high-silica zeolites are more thermally stable (up to 1300 °C), stable in acid solutions, hydrophobic and tend to form 5 member rings.

As with the hydrophilicity, the polarity of a given zeolite can be controlled by changing the framework Si/Al ratio and number of silanol groups. Hence zeolites can be prepared with a wide range of surface polarities which makes them selective adsorbents for polar or non-polar molecules.

Zeolites have a natural or synthetic origin. At least 50 natural and 200 synthetic zeolite structure types have been recognised. These differ in the size, shape and connectivity of their channels, usually being from 8 to 30 rings.
Figure 1.9 Framework and channel view for a FAU, MFI and BEA structural type zeolite.
Zeolite structures are designated by a 3 letter code according to the Commission of the International Zeolite Association (IZA). Most zeolites can be classified in three groups:

i) Small pore zeolites with eight membered-ring pore apertures and channel diameters of 0.30-0.45 nm

ii) Medium pore zeolites with ten membered-ring apertures and channel diameters of 0.45-0.60 nm

iii) Large pore zeolites with 12 membered-ring apertures and channel diameters of 0.6-0.8 nm

Due to their structure and well defined, regular pore distribution, zeolites offer shape selectivity control as molecular sieves. This property is used in applications to discriminate reactants and products based on size and shape.

The tuneable textural properties and acidity characteristic of zeolites means that they play a crucial role in adsorption, catalysis and ion-exchange applications. Zeolites are one of the most important groups of industrial heterogeneous catalysts with applications in a large variety of reactions, from acid to base and redox catalysts. Zeolites are widely used in oil refining and petrochemistry but also in environmental catalysis and the synthesis of chemicals.

XRD, SEM, MAS NMR and IR spectroscopy are the techniques most frequently used for characterisation of zeolites. XRD allows determination of the zeolite structure and purity. The size and morphology of zeolite crystallites can be analysed by SEM. NMR provides information regarding the framework Si/Al ratio and coordination environment.

Framework properties, including Si/Al ratios and the nature of acid sites are obtained using IR spectroscopy.
1.4 References

Chapter 1

Introduction

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82. INTERNATIONAL ZEOLITE DATABASE http://www.iza-structure.org/databases/.


Scope and objectives

Nitrogen oxides (NO\textsubscript{x}) are major polluters of the atmosphere, with a direct harmful effect upon the environment and human health. NO\textsubscript{x} are a major source of acid rain, photochemical smog and ozone depletion. NO\textsubscript{x} contributes to the acidification and eutrophication of soil and water, leading to changes in species diversity. Accordingly, more stringent emission standards have been introduced to lower the concentrations of these pollutants.

NO\textsubscript{x} abatement is crucial, especially in diesel engines where controlling NO\textsubscript{x} is extremely difficult as oxygen is always in excess. The title and objective of this thesis addresses a novel approach; the diesel oxidation NO\textsubscript{x} adsorption catalyst (DONAC), where NO\textsubscript{x} is to be stored by the diesel oxidation catalyst (DOC).

DONAC provides an alternative to current approaches for NO\textsubscript{x} abatement and requires an adsorption catalyst which stores NO\textsubscript{x} at low temperatures (T < 250 °C) and releases it at higher temperatures, when NO\textsubscript{x} is reduced in the SCR system.

Enhancing the performance of oxidation catalysts is important in order to improve NO\textsubscript{x} storage capacities, as the oxidation of NO to NO\textsubscript{2} is an essential first step in the storage mechanism. Hence, Chapter 4 is dedicated to investigating the oxidation properties of supported platinum catalysts and particularly, how these properties are affected by the support material. The total oxidation of propane and oxidation of NO to NO\textsubscript{2} under lean conditions are the two reactions studied. In order to determine the effect of the support on
the structural and electronic properties of Pt catalysts and correlate these with oxidation performance, full characterisation is performed.

The overall aim is to find an optimal zeolite-based system for NO$_x$ storage. The zeolite composition and structure are likely to affect the storage capacity of the zeolite-based system. The Si/Al ratio influences the number of adsorption sites but also the affinity for H$_2$O, surface acidity and the stability of the zeolite, factors that have an impact on the storage capacity. The internal channels, their geometry and the extent to which they are interconnected determines which gas-phase components reach the active sites. Hence, the zeolite channels need to be large enough to allow diffusion of NO and NO$_2$, but small enough to exclude hydrocarbon molecules that block the adsorption sites. The inclusion of metals on the parent zeolite not only increases the number of adsorption sites but can also change the reactivity of the zeolite-based catalyst and promote its deactivation through dealumination.

The purpose is, then, to study the adsorption, storage and release of NO$_x$ by metal-exchanged zeolites under synthetic diesel exhaust gas, as a function of the temperature. A range of zeolites with different compositions and structures were used in order to correlate the NO$_x$ storage capacity with the physical and chemical characteristic of the parent zeolites. In addition, the effect of modifying the parent zeolites through post synthesis treatments, heat treatments and ion-exchange, was also examined.

Chapter 5 covers the initial screening of metal-exchanged zeolites for NO$_x$ storage under different conditions and a study of the effect of the Si/Al ratio, internal channels and inclusion of base and precious metals.

The catalyst preparation method has a significant effect on the NO$_x$ storage capacity of metal exchanged zeolites. Chapter 6 adopts the statistical design of experiments (DOE)
method to enhance the adsorption/desorption properties of the Cu$^{II}$/ZSM-5 (30) catalyst system. In this chapter, experimental design is used to generate a set of data to evaluate the influence which the experimental variables used for catalyst preparation has upon NO$_x$ storage performance. Furthermore, in order to correlate the physicochemical properties of the metal exchanged zeolites with their NO$_x$ storage performance, characterisation studies are performed.
Experimental

3.1 Materials

Unless specified, reagents were used as received.

- Propane (5000 ± 5 % ppm C₃H₈ /He, BOC gases)
- Nitric oxide (1000 ± 10 % ppm NO /He, BOC gases)
- Nitric oxide (5000 ± 1 % ppm NO /N₂, BOC gases)
- Oxygen (99.999% BOC gases)
- Helium (99.999% BOC gases)
- Nitrogen (99.999% BOC gases)
- Iron (III) Acetylacetonate, Fe(C₅H₉O₂)₃ (98%, Sigma Aldrich)
- Copper (II) Acetylacetonate, Cu(acac)₂ (98%, Sigma Aldrich)
- Platinum (II) Acetylacetonate, Pt(acac)₂ (48 wt. % Pt, Alfa Aesar)
- Iron (III) Chloride Hexahydrate, FeCl₃·6H₂O (98 %, Sigma Aldrich)
- Iron (II) Sulfate Heptahydrate, F(SO₄)·7H₂O (99 %, Sigma Aldrich)
- Copper (II) Acetate, Cu(CH₃COO)₂ (98%, Sigma Aldrich)
- Platinum (IV) nitrate, Pt(NO₃)₄ (15 wt. % Pt, Alfa Aesar)
- Chloroplatinic acid hydrate, H₂Cl₆Pt·xH₂O (99%, Sigma Aldrich)
- Zeolite Y (H⁺ form, SiO₂:Al₂O₃ = 5.1, 30, Alfa Aesar)
- ZSM-5 (NH₄⁺ form, SiO₂:Al₂O₃ = 23, 30, 50, Alfa Aesar)
- Zeolite BETA (NH₄⁺ form, SiO₂:Al₂O₃ = 38, Alfa Aesar)
- Titanium Dioxide, TiO₂ (P25, Degussa)
- Titanium Dioxide, TiO₂ (Anatase, 99.7%, Sigma Aldrich)
- Titanium Dioxide, TiO₂ (Rutile, 99.8%, Alfa Aesar)
- Silicon Dioxide, SiO₂, (Aerocat, Degussa)
- Aluminium oxide, γ-Al₂O₃ (Anhydrous, Merck)
- TiO₂ (A-R), (Anatase (80%), Rutile (20 %), Commercial support)
- TiO₂-SiO₂ (A-R) 5 % mol Si, (Anatase (80%), Rutile (20 %), Commercial support)
- TiO₂-SiO₂ (A-R) 16 % mol Si, (Anatase (80%), Rutile (20 %), Commercial support)
- TiO₂ (A) (Anatase, Commercial support)
- TiO₂-SiO₂ (A-R) 10 % mol Si, (Anatase, Commercial support)
- Al₂O₃-SiO₂ 10 % mol Si, (Commercial support)
- Toluene (Laboratory reagent grade, 99 %, Fisher)
- Ammonium hydroxide 35 %, NH₄(OH) (Analytical reagent grade, Fisher)
3.2 Catalyst Preparation

3.2.1 Supported platinum catalysts

A series of metal oxides (TiO\(_2\), SiO\(_2\) and Al\(_2\)O\(_3\)) and mixed metal oxides (TiO\(_2\)-SiO\(_2\) and Al\(_2\)O\(_3\)-SiO\(_2\)) included in the materials list, were used as supports.

Supported platinum catalysts were prepared by the different impregnation techniques described below. In all cases, the impregnation procedure was followed by a drying step at 110 °C for 16 h and a heat treatment at 400 °C (10 °C/min, 5 h) under different atmospheres (static air, flowing air, flowing helium and flowing 5 % H\(_2\)/Ar).

The calcination temperature used when preparing supported platinum catalysts influences both the dispersion and oxidation state of Pt\(^1\). It is known that increasing the calcination temperature above 400 °C results in an increase in the concentration of metallic platinum\(^2\). In addition, when using TiO\(_2\) supports, phase transformation occurs at high temperature. The anatase-rutile transformation results in a decrease in BET surface area, which is known to have a detrimental effect on the performance of the supported metal catalysts.

![Figure 3.1. TG curve of the platinum (II) acetylacetonate precursor in air](image)
Thermogravimetric analysis of the platinum (II) acetylacetonate precursor, presented in Figure 3.1, shows that decomposition occurs in the 200 - 300 °C window.

Raman spectra of fresh and calcined TiO$_2$ (A-R) support are shown in Fig. 3.2. Two different calcination temperatures, 200 °C and 400 °C, were used to investigate whether a phase transformation of TiO$_2$ from anatase to rutile occurs at these temperatures. The analysis revealed that TiO$_2$ (A-R) presents a biphasic anatase - rutile structure and that the calcination temperatures studied do not change the phase structure, confirming that the anatase to rutile transformation has an onset temperature of over 600 °C at ambient pressure, as has been reported before by Hanaor et al.$^3$. Hence, the calcination temperature was set to 400 °C, allowing complete decomposition of the platinum precursor.
3.2.1.1 Non-aqueous impregnation (IMP)

Catalysts of 0.5 wt. %, 1 wt. % and 1.5 wt. % Pt were prepared by impregnating the as-received support (≈ 2 g) with a solution of Pt(acac)$_2$ in toluene (0.0403 g in 100 mL). The suspensions were stirred for 24 h at room temperature (ca. 25 °C). Toluene was removed by a rotatory evaporator.

3.2.1.2 Chemical vapour impregnation (CVI)

Catalysts of 1 wt. % Pt were prepared by CVI. The as-received support (≈ 2 g) was added to the desired mass of Pt(acac)$_2$ (0.0403 g). Following physical mixing of the metal precursor and support, the dry mixture was transferred to a Schlenk flask and heated to sublimation-deposition temperature (145 °C) under continuous vacuum (ca. 10$^{-3}$ mbar) for 1 hour. The sample was then allowed to cool to ambient temperature. This process is illustrated in Figure 3.3.

Figure 3.3. Schematic representation of the CVI preparation method
3.2.1.3 Aqueous impregnation (AQ IMP)

Catalysts of 1 wt. % Pt were prepared by impregnating the as-received support ($\approx$ 2 g) with a solution of Pt(NO$_3$)$_4$ in deionized H$_2$O (0.1241 g in 100 mL). The suspensions were stirred for 24 h at room temperature ($ca$. 25 °C). Water was removed by a rotatory evaporator.

3.2.1.4 Incipient Wetness impregnation (IWI)

Catalysts of 1 wt. % Pt were prepared by IWI. Prior to impregnation, the pore volume of the support was determined by adding the solvent dropwise until no loose material was observed. The desired mass of Pt(NO$_3$)$_4$ (0.1241 g) was dissolved in an amount of deionized H$_2$O corresponding to the pore volume of the support ($\approx$ 2 mL). The Pt precursor solution was added dropwise to the support during mixing until a paste was formed.

To ensure homogeneous impregnation of the Pt precursor onto the support, a modified IWI method was used. In this case, the desired mass of Pt(NO$_3$)$_4$ (0.1241 g) was dissolved in a limited volume of deionized H$_2$O ($\approx$ 4 mL).

3.2.2 Metal exchanged zeolites

A series of zeolites with different framework type (Y, ZSM-5 and BETA) and acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1 - 50$), included in the materials list, were used as supports. Commercial zeolites were purchased from Alfa Aesar. Prior to exchange, those in the ammonium form were activated via conversion to their acid form. The NH$_4^+$ was transformed to the H$^+$ form by calcination for 5 h at 550 °C (20 °C/min) in flowing air.
Metal exchanged zeolites were prepared by the different exchange techniques described below. In all cases, the exchange procedure was followed by a drying step at 110 °C for 16 hours and calcination for 3 hours at 550 °C (20 °C/min) in static air.

3.2.2.1 Wet ion exchange (WIE)

Various metal containing zeolite catalysts were prepared by wet ion exchange using an aqueous solution of copper (II) acetate, iron (III) chloride, iron (II) sulphate and chloroplatinic acid.

The stepwise procedure was as follows; a 50 mM aqueous solution of the metal precursor (1.853 g of Cu(CH$_3$COO)$_2$ in 200 mL of deionised H$_2$O, for Cu$^{II}$ containing zeolites; and 2.758 g of FeCl$_3$·6H$_2$O in 200 mL of deionised H$_2$O, for Fe$^{III}$ containing zeolites) was placed in contact with the zeolite support in the H$^+$ form ($\approx$ 2 g) at 25 °C under vigorous stirring during either 24 or 48 h. Pt$^{IV}$ containing zeolites were prepared by WIE with an aqueous solution of 0.5 mM H$_2$PtCl$_6$ following the same procedure. Fe$^{II}$ containing zeolites were also prepared in a similar way, under a N$_2$ atmosphere.

The solid phase was then separated from the aqueous metal solution by vacuum filtration. The solid was washed thoroughly with deionized H$_2$O.

3.2.2.2 Chemical vapour impregnation (CVI)

1 wt. % Cu, Fe and Pt monometallic exchanged zeolites were prepared by CVI. Prior to exchange, a known mass of the zeolite in the H$^+$ form (typically 3.5 g) was heat treated at 150 °C for 2 h under continuous vacuum. Subsequently, the dried zeolite support ($\approx$ 2 g) was added to the desired mass of metal acetylacetonate (0.0824 g of Cu(acac)$_2$, 0.1265 g of Fe(acac)$_3$ and 0.0403 g of Pt(acac)$_2$. Following physical mixing of the metal precursor and zeolite, the dry mixture was transferred to a Schlenk flask and heated to sublimation-
deposition temperature (150 °C) under continuous vacuum (ca. $10^{-3}$ mbar) for 2 hours. The sample was then allowed to cool to ambient temperature.

Bi- and tri- metallic exchanged zeolites were prepared by CVI following the same procedure. In this case, the dried zeolite support ($\approx 2$ g) was added to the desired mass of each metal acetylacetonate and physically mixed.

**3.2.2.3 Statistical design of experiments (DOE)**

The most significant parameters that affect the WIE and CVI methods were screened based on a fractional factorial design.

Cu$^{II}$/ZSM-5 (30) catalysts were prepared by the same WIE procedure described, using copper (II) acetate as the precursor. The aqueous copper solution concentration, washing volume, solution temperature, time and pH were adjusted based on the DOE matrix described in Table 6.2 in Chapter 6. Experiments at high temperature (90 °C) were performed under reflux conditions. The initial pH of the aqueous copper solution was monitored with a pH meter and adjusted to the desired value by dropwise addition of NH$_4$(OH) 35%.

Cu$^{II}$/ZSM-5 (30) catalysts were also prepared by the same CVI procedure described, using copper (II) acetylacetonate as precursor. The copper loading, impregnation temperature and time were adjusted based on the DOE matrix described in Table 6.7 in Chapter 6.
3.3 Catalyst Testing

3.3.1 Propane oxidation

3.3.1.1 Reactor schematic

Catalytic testing for the total oxidation of propane under flow conditions was carried out in the custom built reactor shown in Figure 3.4.

![Figure 3.4. Schematic representation of the propane oxidation reactor](image)

The catalytic total oxidation of propane was carried out in a stainless steel reactor tube (0.5 cm i.d.) heated using a tubular Carbolite furnace at atmospheric pressure. For each experiment, the catalyst was packed to a constant volume to give a gas hourly space velocity (GHSV) of 50,000 h\(^{-1}\). A typical catalyst bed consisted of ca. 30 mg of powdered catalyst (0.06 mL) sandwiched between two quartz wool layers. The reactor feed contained 5000 ppm propane in synthetic air (20% O\(_2\), He as balance gas) with a total flow rate of 50 mL/min. The volumetric ratio used for the catalytic combustion of propane was C\(_3\)H\(_8\):O\(_2\)=1:50. The gas flow was adjusted by mass flow controllers. Temperature heating
tapes were used to keep the reactor lines heated and ensure that the feed stayed in the gas phase. The reactants and products were analysed by an online Varian 3800 gas chromatograph with a thermal conductivity (TCD) and flame ionisation detector (FID). Two chromatographic columns were employed: Hayesep Q (to separate CO$_2$ and hydrocarbons) and MolSieve 13X (to separate CO and O$_2$). The experiments were performed in a temperature programmed way between 100 °C and 500 °C at intervals of 50 °C, and the reaction temperature was measured by a thermocouple placed within the catalyst bed. Analyses were made at each temperature until a steady-state was attained, three analyses were taken and data averaged.

3.3.1.2 Sample delivery and temperature program

Analytes were separated and analysed using a Varian 3800 GC with FID and TCD detectors. The reaction gas was injected into the GC using a six-port valve (V1) heated to 210 °C, and He was used as the carried gas.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>V1 (Sample injection)</th>
<th>V2 (Bypass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fill (-)   Inject (+)</td>
<td>Series (+) Bypass (-)</td>
</tr>
<tr>
<td>Initial</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>0.01</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>1.32</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Hydrocarbons and CO$_2$ were separated in the HayeSep Q column (80-100 mesh, 1.8 m). CO and O$_2$ were separated in the MolSieve 13X column (80-100 mesh, 2 m). Because CO$_2$ binds irreversibly to the MolSieve column causing deactivation, a second six-port valve (V2) is necessary to bypass this column after CO and O$_2$ are eluted (1.32 min after the
analysis starts). The valve sequence parameters for the sample delivery program used are described in Table 3.1.

An effective separation and elution of the analytes was achieved with the column oven temperature program described in Table 3.2.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature °C</th>
<th>Rate °C/min</th>
<th>Hold min</th>
<th>Total min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>50</td>
<td>-</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>68</td>
<td>2.0</td>
<td>3.50</td>
<td>12.50</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>70.0</td>
<td>2.50</td>
<td>17.17</td>
</tr>
</tbody>
</table>

Analytes were identified by comparing their retention times with those of commercial standards. O₂, CO₂ and CO were detected in the TCD channel and C₃H₈ in the FID channel. The TCD is a universal detector generally used for detection of inorganic compounds. The current signal is generated based on the difference in thermal conductivity between the sample gas and the reference carrier gas. The FID is the industry standard detector used for analysis of HC concentrations. The current signal is generated based on the detection of ions formed during combustion of HC in a hydrogen flame. The response is proportional to the concentration of HCs.

The overall chromatogram obtained from both channels presents three peaks at ca. 0.9 min (O₂), 1.6 min (CO₂) and 14.1 min (C₃H₈). Other selective oxidation products, such as C₃H₆, were not detected, indicating that propane is completely oxidised by the catalyst to form CO₂ and H₂O.
3.3.1.3 Data analysis & quantification

Quantitative analysis was performed by quantifying reactants consumed and products formed.

Propane conversion (%) was determined from propane consumption with the difference between the propane inlet and outlet concentration using the following equation:

$$\left( \frac{C_3H_8_{IN} - C_3H_8_{OUT}}{C_3H_8_{IN}} \right) \cdot 100$$

$C_3H_8_{IN}$ was calculated with the peak area counts prior to light off, when conversion is zero and the outlet propane concentration is equal to the inlet propane concentration. $C_3H_8_{OUT}$ corresponds to the average peak area counts obtained at each temperature.

The GC was calibrated for CO$_2$ analysis by injecting known amounts of CO$_2$. The response factor (RF = peak area / analyte concentration) was obtained from the calibration plot that correlates the analyte concentration with the peak area.

Conversion (%) was also calculated from products formed, with the average peak area counts obtained for propane and CO$_2$ at each temperature:

$$\left( \frac{\text{Products}_{OUT}}{C_3H_8_{OUT} + \text{Products}_{OUT}} \right) \cdot 100 = \left( \frac{CO_2}{\frac{3}{C_3H_8} + \frac{CO_2}{3}} \right) \cdot 100$$

While for conversions below 10 %, conversion was obtained with conversion from products, for conversions greater or equal to 10 %, conversion was determined from the consumption of propane.

Blank experiments conducted in an empty reactor tube showed negligible activity over the temperature range used in this study. Quantification of the error associated with the testing
methodology was obtained by measuring the standard deviation for propane conversion when the same catalyst was tested three times. Results give an error of ± 4 % conversion. Carbon balances were in the range 100 ± 10%.

3.3.2 NO\textsubscript{x} storage

3.3.2.1 Reactor schematic

The NO\textsubscript{x} adsorption/desorption experiments were carried out under atmospheric pressure in the fixed-bed flow reactor shown in Figure 3.4.

![Figure 3.4. Schematic representation of the NO\textsubscript{x} reactor](image)

The catalyst (ca. 300 mg, 0.4 mL), or hereafter also called adsorbent, in the form of pellets (20-40 mesh size) was sandwiched between two quartz wool layers in a stainless steel tube (1 cm \textit{i.d.}). The reactor tube was fitted in a tubular furnace that controlled the temperature of the catalyst bed. The temperature in the catalyst bed was monitored with a thermocouple. Temperature heating tapes were used to keep the reactor lines heated and ensure that the feed stayed in the gas phase, therefore avoiding condensation. The gas mixture, which
varied during the experiment, was fed from cylinders using mass flow controllers. The total gas flow was 200 mL/min which corresponded to a gas hourly space velocity (GHSV) of 35,000 h⁻¹. The effluent composition was analysed continuously by a FT-IR spectrometer (Gasmet DX-4000) equipped with a 0.4 L heated cell, to ensure the sample stays in gaseous phase. Concentration results in ppm were measured using the Calcmet™ software with internal calibration. Prior to NO adsorption, the sample was pretreated at 500 °C in a flow of He and then cooled to 30 °C. Subsequently, the He flow was switched to a model flue gas for NOₓ adsorption at 30 °C. For experiments in the absence of O₂, the model flue gas contained 1000 ppm NO balanced in He. For experiments in the presence of O₂, the model flue gas contained 1000 ppm NO in 7.5 % O₂, balanced in He. The volumetric ratio used for NOₓ adsorption in the presence of O₂ was NO:O₂=1:75. The adsorbent was first bypassed to control the inlet NOₓ concentration. After saturation of the catalyst, identified by the NO concentration regaining the inlet value, the adsorbent was again bypassed to allow flushing of the lines with He. Temperature programme desorption (TPD) was then conducted with a flow of 100 % He. After a purging period at constant temperature to remove the reversibly adsorbed NOₓ species, the adsorbent was heated at 10 °C/min up to 500 °C.

NOₓ storage experiments under real working conditions were performed in the same reactor using a more complicated gas mixture. The gas mixture, which varied during the experiment, was fed from cylinders using mass flow controllers. Water vapour was added into the feed with a controlled evaporator mixer. The total gas flow was 200 mL/min which corresponded to a gas hourly space velocity (GHSV) of 30,000 h⁻¹. Prior to storage, the sample was heated up to 500 °C (10 °C/min) and then cooled to 80 °C in a gas mixture containing 10 v. % O₂, 5 v. % H₂O and 5 v. % CO₂ balanced in N₂. Subsequently, the sample was exposed to a model flue gas during storage at 80 °C and TPD up to 500 °C.
(10 °C/min). The model flue gas contained 10 v. % O\textsubscript{2}, 5 v. % H\textsubscript{2}O, 5 v. % CO\textsubscript{2}, 200 ppm NO, 200 ppm CO and 500 ppm C\textsubscript{3}H\textsubscript{8} balanced in N\textsubscript{2}.

### 3.3.2.2 Data analysis & quantification

Quantitative analysis of NO\textsubscript{x} during the adsorption-desorption processes was carried out by continuously monitoring the effluent gas composition using a FTIR spectrometer.

Identification of IR active species is possible because each molecule possesses a unique IR absorption spectrum. The IR spectrum is the result of vibrational excitation caused by the interaction of a molecule with infrared radiation. All different vibrations, rotations and their combinations result in absorption bands of specific wavelengths in the IR region.

Quantification of the IR spectra is possible using the Beer-Lambert law, which establishes a direct relationship between the infrared radiation absorbance presented by an analyte and its concentration:

\[
\log \left( \frac{I_0}{I} \right) = \log(A) = \log \left( \frac{1}{T} \right) = \varepsilon \cdot L \cdot C
\]

Where: \( I_0 \) = intensity of the incident IR radiation (before sample IR absorption), \( I \) = intensity of the transmitting IR radiation (after sample IR absorption), \( A \) = absorbance, \( T \) = transmittance, \( \varepsilon \) = absorptivity, \( L \) = optical path length and \( C \) = sample concentration

Quantitative analysis of multiple components is possible because the infrared radiation absorption at each wavelength is directly proportional to the concentration of absorbing molecules.

The Calcmet\textsuperscript{TM} software calculates the concentration of each molecule by comparing the sample IR spectrum with reference IR spectra. This is feasible because the software possesses a reference library with the IR spectrum of each single gas molecule at specific
concentrations. Hence, to obtain reliable results, the analysis library must have the IR spectra of all those molecules present in the sample in the concentration range studied.

Prior to sample analysis, the spectrometer cell was flushed until signal stabilisation and a background was acquired using flowing He, which does not absorb infrared radiation. Sample analysis was then carried out in a continuous measurement mode at specific time intervals. Short time intervals of 2 seconds are required because adsorption/desorption processes occur rapidly. IR spectra were acquired and measured automatically at those time intervals specified. Quantification of the spectra gives the evolution of the concentration (expressed as ppm or v. %) of each molecule present in the sample with time. The error associated with quantification of the spectra using the library reference spectra was found to be 2.6 %. This value was determined by measuring the standard deviation of the NO\textsubscript{x} concentration obtained from the FITR spectrum acquired for 12 different gas samples with same the NO\textsubscript{x} concentration.

The representation of the overall concentration profile was obtained by plotting the results in Origin\textsuperscript{®} 9.1 analysis and graphing software. Total areas for adsorption and desorption peaks were calculated using the integration tool. NO\textsubscript{x} adsorption/desorption capacities, expressed in mgNO\textsubscript{x}/g\textsubscript{catalyst}, were calculated by integration of the NO adsorption/desorption curves and correlation with the response factor. The response factor was obtained by correlating integrated areas with known amounts of NO. It should be noted that the results obtained are an estimation of time on-line analysis. The spectrometer cell volume is 0.4 L, therefore using a 200 mL/min gas flow it takes approximately 2 minutes to fill the cell with the reaction gas. Hence, when using time intervals below 2 minutes, quantification of NO\textsubscript{x} concentrations is likely underestimated due to dilution by residual feed gas in the cell.
NO conversion (%) was determined from NO consumption with the difference between the NO inlet and outlet concentrations using the following equation:

\[
\left(\frac{\text{NO}_{\text{IN}} - \text{NO}_{\text{OUT}}}{\text{NO}_{\text{IN}}}\right) \cdot 100
\]

\(\text{NO}_{\text{IN}}\) is equal to the inlet NO concentration when conversion is zero. Thus, \(\text{NO}_{\text{IN}}\) corresponds to the concentration of NO before storage, when the catalyst bed is bypassed. \(\text{NO}_{\text{OUT}}\) corresponds to the steady state concentration obtained at the end of the storage period. Nitrogen balances were in the range 100 ± 8 %.

### 3.3.3 Oxidation of NO to NO\(_2\)

NO oxidation experiments were performed in the same reactor shown in Figure 3.4. For each experiment, the catalyst was packed to a constant volume to give a gas hourly space velocity (GHSV) of 50,000 h\(^{-1}\). The bed contained \(\text{ca. 30 mg}\) of powdered catalyst (0.24 mL) sandwiched between two quartz wool layers. The reactor feed contained 1000 ppm NO in 7.5 % O\(_2\), He as balance gas with a total flow rate of 200 mL/min. The volumetric ratio used for the catalytic combustion of propane was NO:O\(_2\)=1:75. The gas flow was adjusted by mass flow controllers. Temperature heating tapes were used to keep the reactor lines heated and ensure that the feed stayed in the gas phase. The experiments were performed in a temperature programmed way between 100 °C and 500 °C at intervals of 50 °C. The reaction temperature was measured by a thermocouple placed within the catalyst bed. Analyses were made at each temperature until a steady-state in activity was attained. The effluent gas composition was analysed continuously by a FT-IR spectrometer (Gasmet DX-4000) equipped with a 0.4 L heated cell, to ensure the sample stayed in the gas phase. Concentration results in ppm were determined using the Calcmet™ software with internal calibration.
3.3.3.1 Data analysis

NO conversion (%) was determined from NO consumption with the difference between the NO inlet and outlet concentrations using the following equation:

$$\left( \frac{NO_{IN} - NO_{OUT}}{NO_{IN}} \right) \cdot 100$$

$NO_{IN}$ is equal to the inlet NO concentration when conversion is zero. Thus, $NO_{IN}$ corresponds to the concentration of NO at 25 °C when the catalyst bed is bypassed. $NO_{OUT}$ corresponds to the steady state concentration obtained at each temperature. Nitrogen balances were in the range 100 ± 8%.
3.4 Catalyst characterisation

Characterisation of the catalysts prepared and tested over the course of this thesis was performed using a series of analytical techniques. The background theory and experimental procedure followed for each characterisation technique is here explained.

3.4.1 X-Ray Powder Diffraction (XRD)

XRD is a powerful and frequently used characterisation technique for crystal structure analysis of solid materials. It is a bulk technique, used for identification and quantification of crystalline phases and estimation of crystallite sizes.

X-rays are electromagnetic radiation with wavelengths in the region of $10^{-10}$ m (1 Å). X-Rays are generated in a vacuum tube when high energy electrons, released by the cathode (a tungsten filament), collide with the atoms and nuclei of the anode or metal target (typically copper). When electrons have enough energy, the metal target’s inner orbital electrons are dislodged and electrons from higher energy levels fill the vacancies. As a result, X-rays of specific wavelength are emitted. Generated X-rays are filtered, collimated and concentrated to produce monochromatic radiation, which is directed towards the sample.

Crystalline materials are formed by repetition of ordered arrangements of atoms. X-ray wavelengths are about the same order as molecular bond lengths (1 Å). Hence, XRD techniques require long-range order. Interaction of the indecent X-Rays with the sample results in a constructive interference when Bragg’s law is complied. Hence, X-ray diffraction is dictated by the Bragg equation $^4$:
\[ n\lambda = 2 \ d \ \sin \ \theta \]
where:

- \( n \) is the order of reflection, an integer number (\( n = 1, 2, 3 \ldots \))
- \( \lambda \) is the incident X-ray wavelength
- \( d \) is the distance between two lattice planes
- \( \theta \) is the angle of incidence

The diffracted X-Rays are detected, processed and counted with a movable detector that scans the radiation intensity as a function of the angle \( 2\theta \).

Each crystalline material possesses a unique characteristic X-Ray pattern used as a “fingerprint”. Thus, identification of crystalline phases present in a sample is possible through comparison with a database of XRD patterns. Structure determination is achieved by conversion of the diffraction peaks to d-spacings.

It is possible to calculate the crystallite size of a given phase using the diffraction peak’s width via the Debye-Scherrer equation \(^5\):

\[ \beta_k = \frac{k \lambda}{d_{hkl} \ \cos \theta} \]
where:

- \( \beta_k \) is the peak with \( \beta_k = \beta_{\text{obs}} - \beta_{\text{std}} \)
- \( \beta_{\text{obs}} \) is the overall peak with
- \( \beta_{\text{std}} \) is the instrument line broadening component
- \( k \) is the Scherrer constant, a shape factor
- \( \lambda \) is the incident X-ray wavelength
- \( d_{hkl} \) is the crystalline size
- \( \theta \) is the peak position

The main limitation of this technique is that samples require sufficient long range order to observe clear diffraction peaks and that its application is restricted to compounds with
particle sizes of greater than 4 nm. The rotation of the ground/powdered sample maximises the chance that particles are orientated such that a certain crystal plane is at the $\theta$ right angle defined by the Bragg's law, contributing to the diffraction pattern.

Powder X-ray diffraction patterns were obtained on a PANalytical X’Pert Pro diffractometer using Cu Kα ray source operating at 40 kV and 40 mA. The signal was recorded for 2θ comprised between 10° and 80° with a step of 0.02°. The XRD patterns were analysed following the JCPDS database.

### 3.4.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a frequently used characterisation technique for qualitative and quantitative analysis of the elements present on a sample’s surface and determination of the metal oxidation state of surface species.

This technique is based upon the photoelectric effect. The sample atoms are irradiated with monochromatic X-ray radiation. If the energy of the incident photon ($h\nu$) is equal to or greater than the binding energy ($E_b$) of a core or valance electron, this electron is ejected with kinetic energy ($E_k$) given by the following equation:

$$E_k = h\nu - E_b - \varphi$$

where:

- $E_k$ is the ejected electron’s kinetic energy
- $h$ is the Plank’s constant
- $\nu$ is the frequency of the incident radiation
- $E_b$ is the binding energy of the electron with respect to the Fermi level of the sample
- $\varphi$ is the work function of the spectrometer
XPS spectra are typically a representation of the intensity of the photoelectrons generated against the binding energy. Analysis of the composition of the sample is based on the fact that each atom possesses a set of characteristic binding energies. XPS spectra also contain information about the chemical environments of the different elements because the energy levels of the core electrons are dependent on the oxidation state of the atom. Generally, an increase in oxidation state is associated with an increase in binding energy. Hence, a metal in its oxide form will give a XPS peak shifted towards higher binding energies with respect to that peak corresponding to the metallic form.

The main limitation of this technique is that it is surface sensitive, as XPS has a probing depth of between 1.5 and 6 nm, depending on the photoelectron’s kinetic energy.

X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a Kratos Axis Ultra DKD photoelectron spectrometer equipped with a monochromatic Al source (1486.6 eV). All spectra were obtained with a pass energy of 40 eV for high resolution scans and 160 eV for survey spectra over an analysis area of 700 x 300 µm. All binding energies were normalized with respect to the C (1s) peak of surface adventitious carbon (284.7 eV). Qualitative and quantitative interpretation of the data was carried out using CasaXPS software.

3.4.3 Brunauer Emmett Teller (BET) surface area analysis

Nitrogen adsorption at 77 K is the most frequently used technique for pore analysis and surface area determination. Physisorption of nitrogen is a phenomenon similar to liquefaction or condensation. At low temperature, N₂ forms a monolayer that is only dependant on the N₂ molecule size (0.16 nm²). After the sample surface has been cleaned
under vacuum, it is dosed with the adsorbate gas (typically N₂) at different pressures. The adsorption isotherm is a representation of the volume of adsorbed nitrogen against the relative pressure.

The isotherm shape depends on the pore structure of the sample. Four different types of adsorption isotherm are represented in Figure 3.5. The BET isotherm is based on either the type II or III isotherm. The type I shows a monolayer (Langmuir isotherm). The type II isotherm shows how the adsorbate covers the surface gradually until a monolayer is formed and that as the pressure increases further, multilayer growth occurs. Type IV shows first a monolayer, followed by filling the mesopores. The black dot in isotherms I, II and IV indicates the formation of monolayer (point B).

![Figure 3.5. Nitrogen adsorption isotherm types. Taken from Reference 8.](image)

Brunauer Emmet and Teller developed the BET method for determination of surface area considering multilayer adsorption, which was not addressed by the Langmuir isotherm. The BET linearised equation is:

\[
\frac{V}{V_m} = \frac{p}{p^0} \frac{1}{1 - \frac{p}{p^0}}
\]
\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_0}
\]

where:

- \(P\) is the equilibrium pressure
- \(P_0\) is the saturation pressure
- \(V\) is the volume adsorbed
- \(V_m\) is the volume required to cover the surface in a monolayer
- \(C\) is a constant

A plot of \(\frac{P}{V(P_0 - P)}\) versus \(\frac{P}{P_0}\) gives a straight line, with intercept equal to \(\frac{1}{V_m C}\) and gradient equal to \(\frac{(C-1)}{V_m C}\).

The surface area of a sample is then calculated with the following equation:

\[
S = \frac{V_m}{22414} \cdot (N_A \cdot S \cdot 10^{-8})
\]

where:

- \(V_m\) is the volume required to cover the surface in a monolayer
- \(N_A\) is the Avagadro’s number (6.022 x 10^{23})
- \(S\) is the cross section area of N\(_2\) (0.162 nm\(^2\))

The BET surface areas of mesoporous materials (metal oxides) were measured on a Micromeritics Gemini 2360 analyser, coupled with a Micromeritics FlowPrep 060. Before \(N_2\) adsorption at 77 K, the samples were cleaned with \(N_2\) at 120 °C for 45 minutes. Analysis was performed through a five-point BET method using adsorption data in the standard pressure range 0.05-0.35 \(P/P_0\).

Analysis of the surface area and pore volume of microporous materials (zeolites) was performed on an Autosorb-1 Quantachrome instrument. Before \(N_2\) adsorption at 77 K, the samples were cleaned with \(N_2\) at 200 °C for 12 hours under vacuum. Analysis was performed through an 80-point BET method using adsorption data in the linear region of
the isotherm, corresponding to a standard pressure range $0.0003-0.05 \ P/P_0$. A Monte Carlo based model was used in determining pore volumes.

### 3.4.4 Temperature programmed reduction (TPR)

TPR is a characterisation technique used to obtain qualitative and quantitative analysis of the reducible species present in a sample.

The sample is exposed to a reducing atmosphere (typically $\text{H}_2$ balanced in an inert gas) whilst it is heated according to a programmed linear temperature ramp. If reducible species are present in the sample, then reduction will take place at a determined temperature through consumption of $\text{H}_2$. As a result, a reduction peak is obtained. Occasionally, negative peaks are observed due to release of $\text{H}_2$ stored in the sample. Generally, the consumption of $\text{H}_2$ is monitored using a TCD. TPR curves are the representation of the TCD signal versus temperature. It is a powerful technique when studying interactions between the metal and support as the reduction profile of a metal oxide is affected by the support via a MSI $^6$.

Temperature programmed reduction (TPR) was carried out using a TPDRO 1100 series analyser. Samples ($\approx 20 \ \text{mg}$ of reducible material) were pre-treated at $110 \ ^\circ\text{C}$ ($20 \ ^\circ\text{C/min}$) for 1 hour in a flow of Argon ($20 \ \text{mL/min}$). Subsequently, $\text{H}_2$-TPR was conducted by heating the sample to $800 \ ^\circ\text{C}$ ($10 \ ^\circ\text{C/min}$), with a 5 minutes hold at the $T_{\text{max}}$, in a flow of 10% $\text{H}_2$/Argon. Hydrogen uptake was monitored using a TCD.
A calibration curve was obtained by quantification of the amount of H$_2$ consumed during reduction of known masses of CuO. CuO is reduced to Cu metallic at 350 °C in a single step:

$$\text{CuO} + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}_2\text{O}$$ \hspace{1cm} \text{Equation 3.1}

The amount of H$_2$ consumed is directly proportional to the amount of CuO, with a stoichiometry of 1:1. The area under the H$_2$-TPR curve was integrated using Origin®9.1.

Figure 3.6 shows the linear regression plot and equation that correlates the area under the TPR curve with the amount of H$_2$ consumed during reduction.
3.4.5 NH$_3$-Temperature programmed desorption (NH$_3$-TPD)

TPD techniques are based on the desorption of a probe molecule, previously adsorbed on the sample surface, when it is heated accordingly to a programmed linear temperature ramp. Generally, the adsorption/desorption are monitored using a TCD. TPD curves are the representation of the TCD signal versus temperature. Qualitative and quantitative analysis of the data provides information regarding the adsorption energy, interaction between adsorbates and the extent of adsorbate coverage.

NH$_3$-TPD is a useful technique used to determine the acidity of a sample. The probe molecule, NH$_3$, is adsorbed onto the surface based on its interaction with acidic surface species. The desorption of NH$_3$ at different temperatures, during the TPD, is dictated by the strength of the bond between adsorbate and substrate. Thus, the NH$_3$-TPD curve represents the distribution of weak and strong acid sites (low and high temperature desorption respectively). The acid density and adsorption capacity of a sample can be calculated via quantification of the amount of NH$_3$ desorbed.

NH$_3$-TPD was carried out using a CHEMBET TPR/TPD chemisorption Analyser, Quantachrome Instruments fitted with a TCD. The samples were first pre-treated 130 °C (15 °C /min) for 1 hour in a flow of He (30 mL/min). Subsequently, NH$_3$ adsorption was carried out by exposing the sample to pure NH$_3$ until surface saturation (ca. 15 minutes). The adsorption temperature was set to 30 °C, unless another adsorption temperature is specified. Weakly adsorbed NH$_3$ was removed by flushing with He at 100 °C for 1 hour. TPD to 900 °C (15 °C/min) was then conducted in a flow of He (30 mL/min) to desorb chemisorbed ammonia. NH$_3$ desorption was monitored using a TCD, current 180 mV, attenuation 1.
A calibration curve was obtained by injecting known volumes (and therefore known mol) of pure NH$_3$ directly into the TCD sampling loop. By integrating the corresponding area under the TCD curve a calibration factor for NH$_3$ was determined.

Figure 3.7 NH$_3$-TPD calibration curve

Figure 3.7 shows the linear regression plot and equation that correlates the area under the TPD curve with the amount of NH$_3$ injected. Quantification of the acid site density of the samples was calculated with the area under the curve obtained by integration in Origin® 9.1.

3.4.6 CO Chemisorption

Characterisation techniques based on chemisorption are commonly used in catalysis to determine physicochemical properties of the samples.

Chemisorption is characterised by an interaction between the adsorbate and the sample surface through a chemical bond formation. When the interaction is relatively weak, only
physisorption occurs. Chemisorption is usually associated with an activation energy ($E_a = 60 - 100 \text{ kJ/mol}$) and takes place at temperatures above the critical temperature of the adsorbate. Chemisorption involves formation of a monolayer of the adsorbate on the surface through a chemical bond with localised active sites. However, further physical adsorption on top of the chemisorbed layer forming a multilayer and diffusion of the chemisorbed species into the bulk of the material should also be taken into consideration.

Assuming formation of a monolayer, the number of active sites can be determined by quantifying the amount of adsorbate chemisorbed (chemisorbed gas). For quantification purposes, the stoichiometry of the chemisorption, which indicates the number of metal atoms that are bonded to one molecule of adsorbate, is essential to obtain accurate results.

CO and H$_2$ chemisorption techniques are often used in catalysis to determine the surface area, particle size and dispersion of exposed active sites (exposed active metal atoms on the surface of the support).

The active surface area (ASA) represents the surface area of active sites present in the sample surface given as m$^2$/g:

$$\text{ASA} = \frac{N_m \cdot S \cdot A_m}{166}$$

where:

- $N_m$ is the number of gas molecules adsorbed
- $S$ is the adsorption stoichiometry
- $A_m$ is the cross sectional area of the active surface metal atom

For a specific metal particle shape, the average crystallite size is calculated as:

$$\text{Average crystallite size} = \frac{100 \cdot N \cdot f}{\text{ASA} \cdot p}$$

where:
N is the mass of the active metal

f is the shape correlation factor (6 for spherical particles)

ASA is the active surface area

ρ is the active metal density

The metal dispersion represents the amount of active metal atoms exposed and available to catalyse the surface reaction, given as percentage of the total metal loading:

\[
D = \frac{N_m \cdot S \cdot M}{100 \cdot x}
\]

where:

D is the metal dispersion

N_m is the number of gas molecules adsorbed

S is the adsorption stoichiometry

M is the molecular weight of the active metal

x is the total metal loading of the sample (expresses as wt. %)

CO chemisorption was performed using a Quantachrome ChemBET TPR/TPD chemisorption analyser. Prior to chemisorption of CO at 30 °C, samples were treated under pure H_2 (30 mL/min) at 200 °C for 2 hours. The platinum dispersion was calculated from the total CO uptake, based on the assumption of a 1:1 stoichiometry of CO adsorbed: surface platinum atoms.

3.4.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis determines the weight loss of a material as a function of temperature in a controlled atmosphere. This technique is used to identify the temperature at which chemical changes occur including redox reactions, decompositions, phase
transformations and desorption of adsorbed species. TGA curves are the representation of the weight loss, given as a percentage of the initial sample weight, versus temperature.

TGA analysis was conducted using a TGA/DSC Setaram instrument. Approximately 20 mg of the sample was placed in an Al crucible. After stabilisation, TGA was conducted in air (40 mL/min) by heating the sample from 30 °C to 800 °C (10 °C/min).

3.4.8 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Infrared (IR) spectroscopy is a characterisation technique which is used for chemical analysis and determination of molecular structure.

It is a vibrational spectroscopy technique. The sample is irradiated with infrared radiation, which exhibits wavenumbers in the region of 400 – 5000 cm\(^{-1}\). Molecular vibrations occur in the IR region. Hence, IR-active molecules absorb IR radiation at energies which correspond to the frequency of a mode of vibration, the molecule will then vibrate undergoing transition to a higher energy vibrational state. The dipole moment of the molecular bond has to change during vibration in order to be IR active. Some vibrations are infrared inactive such as the stretching vibrations of completely symmetrical double and triple bonds. The frequency at which a bond vibrates is dependent upon the bond strength and mass of atoms bonded, and is therefore characteristic of a particular bond. Specific functional groups in chemical compounds have characteristic absorption frequencies. Hence, IR spectroscopy provides qualitative and quantitative information about the different functional groups present in a sample.

An IR spectrum represents the transmission of the IR radiation through the sample at each wavelength. For each wavelength, the transmittance is calculated by dividing the intensity
of IR radiation that has passed through the sample by the intensity of the incident IR radiation. Usually, results are shown as an absorption spectrum, which graphically represents the amount of IR absorbed by the sample at each specific wavelength.

![Diagram of diffuse reflectance](image)

**Figure 3.8** An illustration of diffuse reflectance

Fourier Transform Infrared (FTIR) is a non-dispersive IR spectroscopy. This method overcomes the limitation of dispersive instruments; the scanning process is sped up by measuring all of the IR frequencies simultaneously. A parallel, polychromatic radiation is directed from the IR source to an interferometer. The interferometer produces a unique type of signal with all of infrared frequencies. A spectrum with all of the individual frequencies is obtained from the digitised interferogram by performing a Fourier Transform. This is applied by a computer, utilising a Fast Fourier Transform (FFT) algorithm.

Diffuse reflection Fourier Transform Infrared (DRIFT) spectroscopy measures the IR radiation reflected as a combination of internal and external reflections. It is used to maximise the interaction between IR radiation and the sample, which is crucial to obtain IR spectra of solids.

*In situ* DRIFTS studies are generally used to understand chemisorption on supported metal catalysts and to identify adsorbed species and intermediates, which are crucial in
elucidating the mechanisms involved in catalytic reactions. DRIFTS is also used to investigate Brønsted acidity of catalysts such as zeolites, associated with changes in the near IR region (4000 – 3000 cm\(^{-1}\)) \(^{10}\).

When applying chemisorption techniques, some considerations should be addressed, including the determination of physisorption or chemisorption, the nature of the chemical bond and the formation of multilayers of the adsorbate. Spectroscopic studies such as FTIR are used to identify the bonding geometry of adsorbate molecules with the active metal. The adsorbate molecule adopts a range of bonding geometries with coordination to one (linear), two (bridging) or three metal atoms (bridging three fold).

DRIFT spectra were collected on a Bruker Tensor 27 spectrometer fitted with a liquid N\(_2\)-cooled Mercury Cadmium Telluride (MCT) detector. Samples were housed within a Praying Mantis high temperature diffuse reflection environmental reaction chamber (HVC-DRP-4) in situ cell fitted with zinc selenide windows. Background scans were taken using finely ground KBr. Prior to analysis, samples were ground to a fine powder in an Agate pestle and mortar. For in situ heat treatments a Harrick ATC heater was used in heating the sample cell according to a predefined heating program which was controlled via Watlow EZ-Zone software. The gas flow was adjusted by mass flow controllers. Scans were collected across the range 4000 cm\(^{-1}\) to 600 cm\(^{-1}\), 4 cm\(^{-1}\) frequency, 64 scans.

CO-DRIFTS studies were performed as follows. Prior to CO exposure, the sample was reduced in 10% H\(_2\)/N\(_2\) (30 mL/min) at 300\(^\circ\)C (10 \(^\circ\)C/min) for 2 hours and subsequently cooled to 30 \(^\circ\)C in N\(_2\). The sample was then exposed to a flow of 100 % CO (30 mL/min) at 30 \(^\circ\)C. Successive experiments were carried out to collect information about CO adsorption on the catalyst surface. Scans were taken at 1 minute intervals across the range 4000 cm\(^{-1}\) to 500 cm\(^{-1}\), 4 cm\(^{-1}\) frequency, 64 scans.
The oxidation of NO to NO$_2$ was studied using DRIFTS as follows. For experiments using NO, CaF$_2$ windows were used on the \textit{in situ} cell. The sample was exposed to 5000 ppm NO/N$_2$ (27 mL/min) and O$_2$ (3 mL/min). The sample cell was heated from 100 °C to 500 °C at intervals of 50 °C. Successive experiments were carried out to collect time resolved information about the NO oxidation. At each temperature, 15 scans were taken at 1 minute intervals across the range 4000 cm$^{-1}$ to 500 cm$^{-1}$, 4 cm$^{-1}$ frequency, 64 scans.

\subsection*{3.4.9 Diffuse Reflectance UV-Vis Spectroscopy (UV-Vis DRS)}

UV-Vis spectroscopy is a characterisation technique used for qualitative and quantitative analysis of chromophores present in a sample.

Ultraviolet-Visible radiation exhibits wavelengths in the region of 200 – 900 nm. The promotion of valence electrons to higher energy levels occurs in the UV-Vis region. Valence electrons are generally found in single (σ), double or triple (π) and non-bonding orbitals. When a sample is irradiated with UV-Vis radiation, photons of a specific energy are absorbed and employed in exciting valence electrons to higher energy states. The electronic transition usually involves the promotion of an electron from a HOMO to a LUMO orbital. The energy needed to promote electrons between orbitals depends on the bonding system and atoms involved. Hence, the wavelength at which an absorption band is observed provides information as to ionic charge, local environments and electronic bonding, all of which effects the transition energy$^{13}$.

The electronic transitions are determined by selection rules. The spin selection rule ($\Delta S = 0$) states that changes in spin multiplicity are forbidden. The Laporte selection rule states that a change in the symmetry of the complex is needed for a transition to occur.
Mathematical treatments of the energy levels of orbital systems suggest that while some electronic transitions are statistically probable, other transitions have a probability of zero and are said to be “forbidden” but they frequently occur giving weak absorption bands. Some particularly useful forbidden transitions are $d \rightarrow d$ absorptions in transition metals.

UV Vis spectra were collected using a Varian 4000 UV-Vis spectrophotometer. Prior to analysis, samples were ground to a fine powder in an Agate pestle and mortar. Background scans were taken using a high purity PTFE disc. Scans were collected across the wavelength range 200-800 nm, at a scan rate of 150 nm min$^{-1}$, with a UV – visible changeover wavelength of 350 nm.

3.4.10 Raman Spectroscopy

Raman spectroscopy is a powerful and frequently used characterisation technique used for chemical analysis and determination of molecular structure.

It is a vibrational spectroscopy based on the Raman scattering phenomena produced by interaction of a sample with incident electromagnetic radiation. Raman scattering is associated with absorption of radiation energy which corresponds to vibrational and rotational modes of molecular bonds. Selection rules dictate which molecules are Raman active and thus, which rotations and vibrations are permitted. In order to be Raman active, a molecule must possess changeable polarizability and lack centres of symmetry.

When the kinetic energy of the scattered photon is equal to the energy of the incident radiation, elastic scattering occurs and is termed Rayleigh. If the kinetic energy of the scattered photon is different to the energy of the incident radiation, elastic scattering occurs
and it is termed anti-Stokes or Stokes depending on whether the scattered photon gains or loses kinetic energy respectively.

![Diagram of molecular energy states](image)

**Figure 3.9** Representation of excitation and relaxation of the molecular energy states during Raman scattering

The Raman spectrum represents the intensity of the scattered radiation at each wavelength. It is formed of a primary band corresponding to Rayleigh and two symmetric secondary bands corresponding to Raman Stokes and Anti-Stokes. Each material exhibits a characteristic set of bands located at specific wavelengths that provide information about the chemical bonds and molecular structure.

To maximise the scattering, high intensity monochromatic radiation is required. Hence, lasers are the most common source of incident radiation.

Raman spectra were obtained using a Renishaw inVia Raman microscope equipped with a Stellar-REN 3B argon ion laser ($\lambda = 514$ nm) operated at a power of 20 mW.
3.4.11 Scanning Electron Microscopy (SEM)

Electron microscopy is a powerful characterisation technique frequently used to determine the topology, morphology and composition of a sample. It is generally used to determine the size and shape of supported metal particles.

It is based on the interaction of an electron beam with the sample. Electrons have characteristic wavelengths in the range of atomic radius (< 1 Å) and thus, it is possible to obtain images with atomic detail.

![Representation of the interaction between the primary electron beam and the sample in an electron microscope](image)

**Figure 3.10** Representation of the interaction between the primary electron beam and the sample in an electron microscope

When the primary electron beam, with energy between 100 and 400 eV, hits the sample several processes can occur. These interactions are illustrated in Figure 3.10.

- The electrons can pass through the sample without losing energy or losing energy as result of consecutive inelastic collisions.
- Emission of secondary electrons occurs via electron excitation by collisions with the electron beam. Most of the secondary electrons emitted correspond to
conduction band electrons, which have their last energy loss process in the surface region.

- If orientations are favourable, electrons are diffracted by particles present in the sample. Detection of diffracted electrons is used to obtain dark-field images and crystallographic information.

- Electrons can be scattered by collisions with atoms present in the sample. Backscattering is associated with elastic scattering, which involves changes in the trajectory of the incident electrons without significant change in their kinetic energy. Backscattering is dependent on the atomic number (Z), as heavier atoms have a higher probability of producing an elastic collision because of their greater cross-sectional area. Hence, detection of backscattered electrons provides information about the distribution of different elements in a sample.

- Auger electrons and X-Rays are emitted as a result of relaxation of ionised core atoms.

- Electrons can excite characteristic vibrations in the sample.

- Interaction of the sample with the electrons can produce the emission of photons in the UV to IR range. This emission is usually associated with recombination of electron-hole pairs in the sample.

Electron microscopes usually operate under high vacuum to prevent electron scattering. The electron beam is generated from a field emission gun (FEG) formed of a very fine single crystal of tungsten. A series of fine apertures and lenses focus the beam to a fine point and direct it onto the sample, producing different types of emissions.

Scanning electron microscopy (SEM) is based on the detection of either secondary and backscattered electrons as a function of the position of the beam. The 3D images obtained
represent the topology, morphology and composition of the sample in the area irradiated.
SEM has a probing depth of between 3 and 10 nm.

Scanning electron microscopy images were obtained using a Carl Zeiss EVO 40 operated at 25 kV. All samples were mounted on carbon Leit adhesive discs. Images were collected using backscattered and secondary electron detectors. For EDX (X-ray energy dispersive spectroscopy) analysis, high probe currents (up to 25 nA) were required to allow sufficient generation of X-rays. The data was collected using an Oxford EDX analyser coupled to the EVO 40 SEM.

3.4.12 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is based on the detection of transmitted and diffracted electrons. Bright field images represent a 2D projection of the transmitted electrons, which depends on the mass distribution; the density and thickness of the sample. Dark field images represent the diffracted electrons, which have a slightly different angle than that of the transmitted beam. Contrast in the images is caused by attenuation of the electron beam, dependent on the density and thickness of the sample, and also by diffraction and interference\textsuperscript{6}. TEM instruments operate in a similar way to an optical microscope, with electromagnetic lenses and an electron beam instead of optical lenses and light. Typically, a TEM instrument has superior magnification and resolution to a SEM instrument.

TEM is widely used in catalysis to determine the dispersion, particle size and morphology of supported particles and to investigate metal support interactions\textsuperscript{14}.

Scanning Transmission Electron Microscopy (STEM) combines both TEM and SEM operation modes. It is possible to select specific regions of the sample that are irradiated
with the primary electron beam and obtain either bright or dark field images. Dark field images are obtained based on the electrons that are diffracted by the metal particles and thus, images of supported metal particles with improved contrast are obtained.

High resolution TEM (HRTEM) analyses were conducted on a JEOL-2100 JEM electron microscope at an accelerating voltage of 300 kV. The catalysts for TEM observation were dispersed in ethanol and dropped onto a copper mesh with a carbon micro-grid. STEM-EDX imaging experiments were performed on the same instrument.

3.4.13 X-Ray Energy Dispersive Spectroscopy (EDX)

Usually, SEM and TEM instruments are coupled with EDX analysis, which provides information as to the elemental composition of a sample.

Upon interaction of the electron beam with the sample, if the incident electron has enough energy it will eject a bound electron from an orbital of the atom. The core electron vacancy generated, is filled with an electron from a higher energy level and a X-ray photon with energy equal to the energy gain is emitted. The emitted X-rays are detected with an energy-dispersive X-ray detector that is located in a fixed position with respect to the sample. The detector consists of a liquid nitrogen cooled semiconductor crystal (typically Si(Li)). The X-ray is converted into a photoelectron with kinetic energy equal to

\[ E_k = E_{\text{X-ray}} - E_b \]

where \( E_b \) is the binding energy of the photoelectron emitted. This photoelectron utilises its kinetic energy in creating electron-hole pairs (3.8 eV per pair). The current detected is proportional to the number of electron-hole pairs formed. The EDX spectrum represents the intensity of the signal detected as a function of the wavelength of the X-rays generated. Each atomic element has a characteristic wavelength
or set of wavelengths attributed to the energy difference between core electrons and higher energy electrons. Hence, EDX allows qualitative and quantitative analysis of the different elements present in the sample.

The area of the discrete regions analysed is limited by the microscope’s resolution.
3.5 References

4.1 Introduction

Diesel oxidation catalysts (DOC) are used in exhaust aftertreatment to cut pollutants emitted from diesel engines. DOCs generally consist of a monolith honeycomb matrix coated with the active phase, contained in a stainless steel canister. As its name indicates, an oxidation catalyst will promote the oxidation of compounds of a reducing character. The DOC is designed to oxidise carbon monoxide, gas phase hydrocarbons and the soluble organic fraction (SOF) of diesel particulate matter to CO$_2$ and H$_2$O. Generally, the DOC is combined with a diesel particulate filter and either a NO$_x$ storage catalyst (NSC) or a selective catalytic reduction (SCR) catalyst and is positioned upstream of the other units. The title and objective of this thesis arises from a novel approach, the diesel oxidation NO$_x$ adsorption catalyst (DONAC), where NO$_x$ is to be stored by the DOC.

Platinum-based diesel oxidation catalysts are the most used technology and much of the DOCs development has focussed on decreasing the light-off temperature in order to improve the oxidation activity, principally during cold starts.

The aim of this chapter is to investigate the oxidation properties of supported platinum catalysts and particularly, how these properties are affected by the support material. Two oxidation reactions were studied:

- Total oxidation of propane \( \text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O} \) \hspace{1cm} \text{Equation 4.1}
- Oxidation of nitric oxide to nitrogen dioxide \( 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \) \hspace{1cm} \text{Equation 4.2}
4.2 Total oxidation of propane

4.2.1 The effect of the support

Propane is not the most representative hydrocarbon (HC) of the diesel engines exhaust composition. Despite this, total oxidation of propane was investigated because short chain alkanes are recognised as some of the most difficult VOCs to oxidise and thus, it is expected that a catalyst which promotes the oxidation of propane at low temperatures will also perform well under real conditions.

The catalytic activity of supported metal catalysts is governed by a complex mix of different factors including dispersion, morphology, reducibility, electronic structure and mechanical and chemical properties. The properties of supported catalysts are known to be affected by the support in many catalytic reactions and consequently, the interaction between the active phase and the support becomes crucial in understanding the catalytic behaviour and in catalyst design.

Although Al₂O₃ has been extensively used as a support, it is of great interest to investigate other metal oxides as potential supports for HC oxidation catalysts. Specifically, mixed metal oxide supports show exclusive and interesting effects on catalyst performance.

Many studies have investigated platinum catalysts for the total oxidation of VOCs. Nevertheless, a degree of uncertainty persists in determining whether the reaction is structure sensitive and in the true nature of the active site.

The aim of this study is to rationalise the effect of a series of mixed TiO₂ and Al₂O₃ based supports on propane combustion in an oxidising atmosphere over platinum catalysts.
4.2.1.1 Metal oxide supports

In this section, commercial metal oxide supports - TiO$_2$, SiO$_2$, and γ-Al$_2$O$_3$ - were used to prepare supported platinum catalysts by non-aqueous impregnation for total oxidation of propane under an oxidizing atmosphere.

Alumina (Al$_2$O$_3$) is extensively used as a support for commercial diesel oxidation catalysts $^{20}$. This is due to a favourable combination of its properties including: surface area, pore volume, pore size distribution, Lewis acidity, thermal and mechanical stability, interaction with Pt group metals and low manufacturing cost. However, its high reactivity with SO$_x$ results in performance degradation by sulphur poisoning $^{21}$ $^{22}$ $^{23}$ $^{24}$.

Titania (TiO$_2$) is a reducible support that exhibits a strong metal-support interaction (SMSI) with Pt group metals and is broadly used in heterogeneous catalysis due to its tuneable surface area and pore distribution. Additional desirable physical properties include: Lewis acidity, redox properties, thermal stability and mechanical strength $^{25}$. TiO$_2$ also presents high corrosion resistance and sulphur tolerance, leading to superior catalytic activity and durability in an oxidising atmosphere $^{26}$ $^{27}$ $^{28}$.

Silica (SiO$_2$) is an irreducible support with high surface area. Compared with alumina, possesses lower thermal stability. It is assumed to be relatively inert and presents high resistance to sulphur poisoning, however supported platinum particles suffer from sintering due to weak metal-support interactions $^{29}$.

Among the different roles of supports, the most relevant are: dispersing the active phase of the catalyst, increasing metal surface area and improving the catalytic performance through interactions between the metal and support. The morphology, surface area, pore volume and pore size distribution of the support material plays an important role in enhancing
catalyst stability and performance. The BET surface area and density of the supports used in this section are listed in Table 4.1. SiO₂ exhibits the highest surface area at 222 m²/g, which is 1.7 and 4.1 times greater than those of Al₂O₃ and TiO₂ respectively. Of the three supports, TiO₂ P25 is the least dense (0.16 g/mL).

Table 4.1. Surface area measured by N₂ physisorption and density of the commercial supports and supported platinum catalysts

<table>
<thead>
<tr>
<th>Catalyst support</th>
<th>Surface area BET (m²/g)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ P25</td>
<td>54</td>
<td>0.16</td>
</tr>
<tr>
<td>2 wt. % Pt/TiO₂ P25</td>
<td>51</td>
<td>0.49</td>
</tr>
<tr>
<td>SiO₂</td>
<td>222</td>
<td>0.25</td>
</tr>
<tr>
<td>2 wt. % Pt/SiO₂</td>
<td>181</td>
<td>0.15</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>130</td>
<td>1.18</td>
</tr>
<tr>
<td>2 wt. % Pt/Al₂O₃</td>
<td>118</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The catalytic activities of supported platinum catalysts (2 wt. % Pt) for the total oxidation of propane were evaluated and the results are shown in Figure 4.1. 2% wt. % Pt/SiO₂ is the least active, requiring a relatively high temperature before any activity is observed (350 ºC) and failing to achieve 100 % propane conversion, even at 500 ºC. TiO₂ P25 and γ-Al₂O₃ based catalysts exhibit similar behaviour, with 100 % propane conversion to CO₂ at 450 ºC and T₅₀ values of 350 ºC (± 4 ºC).
These trends differ from those obtained in previous studies. Yazawa et al. \(^{30}\) reported that 5 wt. % platinum supported on SiO\(_2\) is more active for propane oxidation (\(T_{50} \approx 307 \, ^{\circ}\)C) than that supported on Al\(_2\)O\(_3\) (\(T_{50} \approx 397 \, ^{\circ}\)C). In addition, Avila et al. \(^{16}\) reported that 0.5 wt. % platinum supported on TiO\(_2\) is more active (\(T_{50} \approx 327 \, ^{\circ}\)C) than that supported on Al\(_2\)O\(_3\) (\(T_{50} \approx 395 \, ^{\circ}\)C). This could be ascribed to differing testing conditions as Yazawa et al. and Avila et al. used O\(_2\)/C\(_3\)H\(_8\) ratios of 2.5 and 12.4 respectively. Additionally, the catalysts used in the work of Yazawa et al. were reduced in a N\(_2\)/H\(_2\) atmosphere at 550 \(^{\circ}\)C before catalytic testing. The oxygen concentration was therefore much lower than that used in the present work (O\(_2\)/C\(_3\)H\(_8\) = 50). This is significant, as it has been reported that
the catalytic activity of platinum supported upon metal oxides varies with the reaction mixture composition. Indeed, work carried out by Men et al. demonstrated that propane conversion on supported platinum catalysts is suppressed in an excess of oxygen, with chemisorbed O$_2$ acting as an inhibitor for the reaction at full coverage. The O$_2$/C$_3$H$_8$ ratio used in the work presented in this thesis is equal to 50, which is much higher that the stoichiometric ratio of 5. In this way oxygen is in excess, which is representative of the real working conditions in a diesel engine.

The temperatures for 10 % ($T_{10}$) and 50 % ($T_{50}$) propane conversion over supported platinum catalysts containing 1 and 2 wt. % Pt are reported in Figure 4.2.

![Figure 4.2. Temperature in degrees Celsius for 10 % propane conversion ($T_{10}$) and 50 % propane conversion ($T_{50}$) over supported platinum catalysts](image)

Based on a lower $T_{50}$ value, the most active catalyst at 1 wt. % Pt is Pt/TiO$_2$, with the overall order of activity found to be thus:

$$
Pt/TiO_2 > Pt/Al_2O_3 > Pt/SiO_2
$$
For catalysts containing 2 wt. % Pt, both Pt/TiO$_2$ and Pt/Al$_2$O$_3$ present comparable T$_{50}$ values of 347 °C and 352 °C respectively. These are ca. 115 °C lower than the T$_{50}$ observed for Pt/SiO$_2$ (465 °C), obeying the following order of catalytic activity:

\[ \text{Pt/TiO}_2 \approx \text{Pt/Al}_2\text{O}_3 > \text{Pt/SiO}_2 \]

Given that propane oxidation is a highly exothermic reaction and that mass transfer limitations are negligible at low temperatures, it is probably more telling to compare the T$_{10}$ values, which obey a similar sequence.

Increasing support surface area does not necessarily correlate with increasing catalyst activity. For the Pt catalysts represented in Figures 4.1 and 4.2, Pt/TiO$_2$ P25 shows superior catalytic performance to Pt/SiO$_2$ catalysts, despite SiO$_2$ having a higher surface area.

Compared to the bare supports, surface areas decreased after impregnation of platinum, as shown in Table 4.1. Depositing 2 wt. % Pt onto TiO$_2$ P25, SiO$_2$ and γ-Al$_2$O$_3$ results in a decrease in the BET surface area of 6 %, 19 % and 9 % respectively.

In order to determine the platinum particle size and dispersion on these supports, detailed electron microscopy studies were performed. Figure 4.3 shows representative micrographs obtained from Scanning Electron Microscopy (SEM) using a Backscattered detector (BSD). In these images, the platinum particles display bright contrast.

Relatively well dispersed platinum particles with spherical-oblong morphology and a mean diameter of 200 nm (0.2 μm) are observed on the TiO$_2$ P25 support. Figure 4.3 b) shows spherical platinum particles of 50-100 nm supported on the SiO$_2$ support; and also larger clusters of platinum (2 and 4.5 μm) indicating sintering. Platinum is poorly dispersed on the surface of γ-Al$_2$O$_3$, with isolated spherical platinum particles (mean diameter of 60 nm) found in certain regions.
Figure 4.3. Selected scanning electron microscopy (SEM) images (BSD detector) of

a) 1 wt. % Pt/TiO$_2$ P25 b) 1 wt. % Pt/SiO$_2$ and c) 1 wt. % Pt/Al$_2$O$_3$

The surface state of the supported platinum catalysts and oxidation state of the platinum was investigated by X-ray photoelectron spectroscopy (XPS). Figure 4.4 shows the Pt 4f region in the XPS spectra of the calcined catalysts. After correcting the C 1s value to 284.7 eV, each spectrum can be fitted with pairs of Gaussian-Lorentzian curves of equal half-widths, an intensity ratio of $\frac{3}{4}$ and a separation of 3.3 eV. For 1 wt. % Pt/TiO$_2$ and
1 wt. % Pt/SiO$_2$ (Figures 4.4 a and b), spectra are fitted with a pair of signals at 72.3 eV (Pt 4f$_{7/2}$) and 75.6 eV (Pt 4f$_{5/2}$), attributed to platinum (II) oxide (PtO). On the Pt/Al$_2$O$_3$ catalyst (Figure 4.4 c), analysis of the XPS spectra is difficult due to the intense Al 2p signal which overlaps with the Pt 4f region. However, spectral deconvolution in (c) reveals the presence of two possible platinum environments; the signal of Pt 4f$_{7/2}$ at 71.6 eV is assigned to metallic platinum and that at 74.3 eV to platinum (IV) oxide (PtO$_2$).

Quantitative analysis of the supported platinum catalysts obtained from the Pt 4f region of XPS spectra is presented in Table 4.2. A higher concentration of surface platinum species is observed for Pt/TiO$_2$ P25 (≈ 11 wt %) and Pt/Al$_2$O$_3$ (≈ 6 wt %) than with Pt/SiO$_2$ (≈ 3 wt. %). This could be attributed to heterogeneous dispersion of the platinum on SiO$_2$. Note that in all cases the surface content of platinum exceeds total theoretical loading (1 wt % Pt), indicating a platinum concentration gradient between the surface and bulk of the catalyst.
Table 4.2. Quantitative analysis of the supported platinum catalysts obtained from the XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt(^0)</th>
<th>Pt(^{2+})</th>
<th>Pt(^{4+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At. %</td>
<td>Wt. %</td>
<td>Conc. %</td>
<td>Conc. %</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO(_2) P25</td>
<td>10.6</td>
<td>11.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1 wt. % Pt/SiO(_2)</td>
<td>2.3</td>
<td>3.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1 wt. % Pt/Al(_2)O(_3)</td>
<td>4.8</td>
<td>6.3</td>
<td>53</td>
<td>0</td>
</tr>
</tbody>
</table>

Whilst platinum oxide (PtO) is exclusively observed on the Pt/TiO\(_2\) and Pt/SiO\(_2\) catalysts, platinum was found to exist as both (+4) oxide (with \(\approx 47\%\) PtO\(_2\)) and metallic state (with \(\approx 53\%\) Pt\(^0\)) on the Pt/Al\(_2\)O\(_3\) catalyst. However, as mentioned before, the spectral deconvolution and quantification for Pt/Al\(_2\)O\(_3\) should be considered carefully as the Al 2p signal overlaps with the Pt 4f region and could lead to false interpretation.

Based on the results presented, it is possible that the inferior catalytic activity observed in Figures 4.1 and 4.2 for Pt/SiO\(_2\) catalysts is due to the sintering of PtO particles and the lower concentration of platinum species at the catalyst surface. These results are in agreement with previous studies which showed that the catalytic activity of DOCs is affected by platinum sintering\(^{32, 33}\).
4.2.1.2 Mixed metal oxide supports

It has been shown in the previous section that, at equal loading, platinum supported on TiO$_2$ presents comparable catalytic activity for propane oxidation to an Al$_2$O$_3$ supported catalyst. As mentioned previously, TiO$_2$ shows high tolerance to sulphur poisoning. As this is an important requirement of DOCs, novel TiO$_2$-based mixed oxide supports were investigated.

To improve catalytic activity whilst also increasing mechanical strength, thermal stability, surface area and modulating surface acidity, titania and alumina can be modified through addition of other metal oxides. Using a combination of different metal oxides results in a novel category of supports with superior performance, through combining the characteristics intrinsic to each constituent metal oxide and interactions between oxide phases.

Three groups of commercially available mixed-oxide supports were used: (i) anatase + 20% rutile TiO$_2$ – (SiO$_2$), (ii) anatase-only TiO$_2$ – (SiO$_2$) and (iii) $\gamma$ Al$_2$O$_3$-SiO$_2$ mixed oxide supports. Limited information about the physicochemical properties of these commercial supports was provided by the supplier, therefore full characterisation was performed.

A summary of the physicochemical properties of the six different supports used in this section are shown in Table 4.3. Anatase-rutile TiO$_2$ based supports are found to be denser than anatase-only TiO$_2$ based supports, which are denser than the Al$_2$O$_3$-SiO$_2$ support.
### Table 4.3. Physicochemical properties of the supports

<table>
<thead>
<tr>
<th>Support</th>
<th>Surface area [a] (m²/g)</th>
<th>Density (g/mL)</th>
<th>Particle size [b] D (0.50) μm</th>
<th>Acidity [c] μmol NH₃/g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anatase + 20 % Rutile TiO₂ based supports</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ (A-R)</td>
<td>52</td>
<td>0.76</td>
<td>30.07</td>
<td>1666</td>
</tr>
<tr>
<td>TiO₂-SiO₂ (5 mol % Si, A-R)</td>
<td>84</td>
<td>0.68</td>
<td>30.88</td>
<td>1330</td>
</tr>
<tr>
<td>TiO₂-SiO₂ (16 mol % Si, A-R)</td>
<td>72</td>
<td>0.60</td>
<td>47.51</td>
<td>613</td>
</tr>
<tr>
<td><strong>Anatase TiO₂ based supports</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ (A)</td>
<td>80</td>
<td>0.58</td>
<td>1.62</td>
<td>934</td>
</tr>
<tr>
<td>TiO₂-SiO₂ (10 mol % Si, A)</td>
<td>107</td>
<td>0.51</td>
<td>1.41</td>
<td>1142</td>
</tr>
<tr>
<td><strong>γ-Al₂O₃ based supports</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃-SiO₂ (10 mol % Si)</td>
<td>197</td>
<td>0.4</td>
<td>X</td>
<td>1813</td>
</tr>
</tbody>
</table>

[a] Surface area measured by N₂ physisorption, density  
[b] Particle size distribution determined by light scattering analysis  
[c] Acidity measured by NH₃-TPD

The BET surface area of the anatase-rutile titania support (TiO₂ A-R) is ≈ 50 m²/g. Comparable with that of TiO₂ P25, this increases by up to 38 % with increasing SiO₂ content (72 m²/g). The supports with anatase as the only crystalline phase (TiO₂ A) present higher surface area. Additionally, the Al₂O₃-SiO₂ support exhibits the highest surface area of 197 m²/g, which is 2.7 and 1.8 times larger than TiO₂-SiO₂ (16 mol % Si, A-R) and TiO₂-SiO₂ (10 mol % Si, A) respectively.

The acidity of the supports was probed using temperature-programmed desorption of NH₃ preadsorbed at 100 °C. The NH₃-TPD curves are shown in Figure 4.5. Generally, the profile presents a broad desorption corresponding to several overlapping desorption events between 200 and 800 °C. This is comparable with those obtained in recent publications ¹⁵
The peaks represent different acid sites strengths, with desorption occurring in two regions: low temperature region ($T < 400 \, ^\circ C$) being attributed to desorption of NH$_3$ from weak acid sites and high temperature region ($T > 400 \, ^\circ C$) being assigned to desorption of NH$_3$ from strong Brønsted and Lewis acid sites. Weak acid sites are generally associated with terminal hydroxyl (-OH) groups and presence of Si-O-Ti in the support.

![NH$_3$-TPD profiles of the supports](image)

**Figure 4.5.** NH$_3$-TPD profiles of the supports:

a) TiO$_2$ (A-R), b) TiO$_2$-SiO$_2$ (5 mol % Si, A-R), c) TiO$_2$-SiO$_2$ (16 mol % Si, A-R),
d) TiO$_2$ (A), e) TiO$_2$-SiO$_2$ (10 mol % Si, A) and f) Al$_2$O$_3$-SiO$_2$ (10 mol % Al)

All supports present comparable acidic sites strength with a broad desorption peak centred near 350 $^\circ$C assigned to weak acid sites on the surface, and several shoulder peaks at higher temperatures (at $\approx$ 500 and 625 $^\circ$C). The total number of acid sites per g of support was quantified from the total amount of NH$_3$ desorbed from the surface using the response factor calculated using the NH$_3$ calibration presented in Chapter 3, Figure 3.8. The results...
reported in Table 4.3 are given as total acid site density (μmol NH₃/g support). The total acid site density of TiO₂ (A) is about 44% lower than that of TiO₂ (A-R). Furthermore, while the acid site density of the anatase-rutile titania (TiO₂ A-R) based mixed oxide supports decreases with increasing SiO₂ content (Table 4.3), acidity increases upon addition of SiO₂ to the anatase-only titania support (TiO₂ A) (Table 4.3). Of the supports analysed, Al₂O₃-SiO₂ is the most acidic. The acidity trends obtained for the TiO₂ A-R supports are inconsistent with those obtained in previous studies, which showed that the Brønsted acidity of TiO₂-based supports increases with increasing SiO₂ content.

Contrarily, other investigations demonstrated that in mixed TiO₂-SiO₂ oxides, both the density and strength of acid sites decreases with increasing SiO₂ content. These studies showed that the molecularly dispersed titanium cations on the silica surface act as redox sites rather than acid sites for methanol oxidation, increasing the oxidising potential.

The source of the acidity of TiO₂-SiO₂ mixed oxides is debated. Tanabe et al. proposed that new Brønsted acid sites could be created by a charge imbalance at Ti-O-Si interfaces in the SiO₂. Work by Notari et al. showed that high purity TiO₂-SiO₂ mixed oxides do not contain Brønsted acid sites. These results were opposite to studies by Bonelli et al. and Junling et al., who demonstrated the presence of Brønsted acid sites on TiO₂-SiO₂ with high titania loadings and also found that isolates Ti⁴⁺ cations on TiO₂-SiO₂ have strong Lewis acidity. Differences in synthesis conditions and thermal treatments could be responsible for the variation in the reported acidity of TiO₂-SiO₂ mixed oxides.

Further studies using Hammett indicators and IR spectra of adsorbed pyridine would be beneficial in understanding in more detail the nature of acid sites (Lewis and Brønsted) on the surface of these supports. In addition, to complete the study of the acidic and basic
properties of the supports and catalysts, CO$_2$-TPD experiments to measure the surface basicity should be performed.

![Figure 4.6. Powder X-Ray diffraction patterns of the supports:](image)

Figure 4.6. Powder X-Ray diffraction patterns of the supports:

a) TiO$_2$ (A-R), b) TiO$_2$-SiO$_2$ (5 mol % Si, A-R), c) TiO$_2$-SiO$_2$ (16 mol % Si, A-R),

d) TiO$_2$ (A), e) TiO$_2$-SiO$_2$ (10 mol % Si, A) and f) Al$_2$O$_3$-SiO$_2$ (10 mol % Al)

The X-Ray Diffraction (XRD) patterns of the supports are shown in Figure 4.6. As expected, anatase and rutile crystalline phases are present in the TiO$_2$ (A-R) based supports and only anatase is found in the TiO$_2$ (A) based supports. The main anatase (101) peak appears at 2$\theta$ of 25°, and that corresponding to rutile (110) appears at 27.4°. No SiO$_2$ diffraction peaks are observed, which indicates that the silica exists in an amorphous phase. In pure SiO$_2$, the amorphous structure has a characteristic wide peak at 2$\theta$ of around 23°. The relative proportions of the crystalline titania phases in the biphase supports, calculated following the JCPDS database, are approximately 80 % anatase and 20 % rutile, concordant with the
phase composition of the widely used TiO\textsubscript{2} P25\cite{46}. In the case of the Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} support, the XRD pattern exhibits the characteristic peaks of $\gamma$-Al\textsubscript{2}O\textsubscript{3}, which is formed from well-ordered boehmite with diffraction peaks at $2\theta$ of 37°, 39°, 45° and 66°.

The different titania phase composition (anatase- only and biphase anatase-rutile structure) of the supports was confirmed by Raman Spectroscopy, Figure 4.7. The characteristic peaks of the anatase phase are observed at 400, 520 and 650 cm\textsuperscript{-1}, the peak at 450 and the shoulder at 610 cm\textsuperscript{-1} are attributed to the rutile phase.

![Figure 4.7. Raman spectra of the supports](image)

Figure 4.8 shows representative scanning electron microscopy (SEM) images of the as-received supports. Significant variation in morphology is observed: anatase-rutile TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} supports are mainly formed by interconnected spheres, whilst anatase- only TiO\textsubscript{2} supports present a more compact aspect with large aggregates forming a “cloud-like” shape.

Particle size distribution of the supports measured by light scattering are shown in Table 4.3. These confirm the difference in metal oxide particle size between anatase-rutile and anatase- only supports, with D (0.5) = 40 μm for TiO\textsubscript{2} (A-R) and D (0.5) = 1.5 μm for TiO\textsubscript{2} (A).
Figure 4.8. Selected scanning electron microscopy (SEM) images (SE1 detector) of the supports

- a) TiO$_2$ (A-R), b) TiO$_2$-SiO$_2$ (5 mol % Si, A-R), c) TiO$_2$-SiO$_2$ (16 mol % Si, A-R),
- d) Al$_2$O$_3$-SiO$_2$ (10 mol % Al), e) TiO$_2$ (A) and f) TiO$_2$-SiO$_2$ (10 mol % Si, A)

Figure 4.9 shows the XPS spectra in the O 1s region of the as-received supports. The spectrum of anatase-rutile, TiO$_2$ (A-R), contains one peak appearing at 529.9 eV, which is typical for TiO$_2$ molecules. Spectra of TiO$_2$-SiO$_2$ supports show two peaks; one appearing at $\approx$ 530 eV, typical of TiO$_2$, and another peak at $\approx$ 532 eV, typical of SiO$_2$. The relative heights indicate that, as expected, the SiO$_2$ peak intensity increases with the SiO$_2$ content.
of the support. Notice that the spectrum for the anatase- only TiO\(_2\) (A) support indicates the presence of a shoulder centred at \(\approx 532\) eV, this peak can be assigned to SiO\(_2\) but also to the surface adsorbed hydroxyl group (Ti-OH)\(^{48,49}\).

**Figure 4.9.** XPS spectra in the O 1S binding energy region of the fresh supports:

a) TiO\(_2\) (A-R), b) TiO\(_2\)-SiO\(_2\) (5 mol % Si, A-R), c) TiO\(_2\)-SiO\(_2\) (16 mol % Si, A-R),

d) TiO\(_2\) (A), e) TiO\(_2\)-SiO\(_2\) (10 mol % Si, A)

Figure 4.10 shows the XPS spectra in the O 1s and Si 2p region of the titania supports: TiO\(_2\) P25, TiO\(_2\) (A-R) and TiO\(_2\) (A). Whilst only one oxygen environment, associated with the TiO\(_2\), is found for the anatase-rutile support, two different oxygen environments are present for the anatase- only titania and commercial TiO\(_2\) P25 supports. These results suggest the presence of a small amount of SiO\(_2\) in TiO\(_2\) P25 and TiO\(_2\) (A) and correlate with the XPS spectra in the Si 2p binding energy region.
Figure 4.10. XPS spectra in the O 1S and Si 2p binding energy region of the titania supports:

a) TiO$_2$ (A-R)   b) TiO$_2$ (A)   c) TiO$_2$P25

Quantitative analysis of the supports obtained from the XPS spectra is presented in Table 4.4. The surface silicon composition correlates with the theoretical loading provided by the support supplier. Note that in the case of the TiO$_2$ (A) support, the surface silicon represents approximately 2.5 wt. % of the total composition. This is similar to that of the TiO$_2$ P25, which presents 2 wt % silicon.

Table 4.4. Quantitative analysis of the supported platinum catalysts obtained from the XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Wt. %</td>
<td>At %</td>
<td>Wt. %</td>
</tr>
<tr>
<td>TiO$_2$ (A-R)</td>
<td>32.01</td>
<td>58.49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$ (5 % mol Si, A-R)</td>
<td>24.30</td>
<td>47.41</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$ (16 % mol Si, A-R)</td>
<td>14.41</td>
<td>30.80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$ (A)</td>
<td>28.58</td>
<td>53.90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$ (10 % mol Si, A)</td>
<td>19.93</td>
<td>47.33</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al$_2$O$_3$-SiO$_2$ (10 mol % Si)</td>
<td>0</td>
<td>0</td>
<td>0.72</td>
<td>7.20</td>
</tr>
</tbody>
</table>
Signals in the W 4d region are observed for the anatase- only TiO$_2$-SiO$_2$ (10 % mol Si, A) support, Appendix A. This result is exclusive to this support. TEM imaging coupled with EDX confirms the presence of tungsten in this support, with quantitative analysis showing that tungsten accounts 7 wt. % of the support composition.

Thermogravimetric (TG) analyses of the supports are presented in Figure 4.11. TG curves show a weight loss below 100 °C, corresponding to a broad endothermic peak assigned to desorption of surface water. The weight loss is lower than 1 % for the anatase-rutile based supports, whilst TiO$_2$ (A) and TiO$_2$-SiO$_2$ (10 % mol Si, A) show a weight loss of 4 % and 6 % respectively. This indicates that anatase-based supports may be more hydrophilic. A discrete increase in weight of $\approx 2$ % at temperatures above 650 °C is observed for all the
supports, very likely due to solid-state transformations of anatase to rutile. *In situ* XRD analysis should be performed to support these observations.

The effect of these mixed metal oxide supports on propane oxidation over platinum catalysts under oxidising atmosphere was studied.

Many studies \(^{12, 50, 51}\) have confirmed that metal oxide supports present negligible intrinsic activity for propane oxidation and that, although the metal-support interaction plays a crucial role in the performance, the active phase is the noble metal. Therefore, catalytic tests were performed using the supported platinum catalysts but not the blank supports.

![Graph showing propane conversion vs temperature](image)

**Figure 4.12.** Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h\(^{-1}\), \(C_3H_8:O_2 = 1:50\)

Catalysts prepared by non-aqueous impregnation and calcined at 400 °C in static air
Figure 4.12 shows the platinum catalysts to be active for the total oxidation of propane to CO\(_2\) and H\(_2\)O. Propane conversion as a function of reaction temperature varied with the nature of the support material. For the 1 wt. % platinum catalysts supported on anatase-rutile TiO\(_2\) based supports, the propane oxidation activity increases in the sequence: Pt/TiO\(_2\) (A-R) < Pt/TiO\(_2\)-SiO\(_2\) (5 mol % Si, A-R) < Pt/TiO\(_2\)-SiO\(_2\) (16 mol % Si, A-R). Therefore, the catalytic activity is found to be promoted by the SiO\(_2\) content of the support.

The Pt/TiO\(_2\) (A-R) system (T\(_{50}\) = 357 °C) presents comparable catalytic activity to platinum supported on commercial TiO\(_2\) P25 (T\(_{50}\) = 379 °C), it has been shown that catalytic activity is enhanced through using a combination of titania and silica as the support for platinum catalysts. This enhancement of activity is not the result of the additive effect of Pt/TiO\(_2\) and Pt/SiO\(_2\), since the activity of Pt/SiO\(_2\) catalysts for propane oxidation is very low, indeed they are almost inactive at 350 °C. This suggests that there is a synergistic effect between TiO\(_2\) and SiO\(_2\) for the catalytic oxidation of propane over supported platinum catalysts.

In order to understand the interaction of TiO\(_2\) with SiO\(_2\) in further detail, a new support was prepared by physical mixing of the TiO\(_2\) (A-R) and the TiO\(_2\) (A-R)-SiO\(_2\) support resulting in a MIX support with ca. 12 mol % of Si. Total oxidation of propane results for the platinum catalyst prepared using this MIX support (grey curve) and using the chemically prepared TiO\(_2\)-SiO\(_2\) supports are presented in Figure 4.13. Although platinum supported on the TiO\(_2\)+TiO\(_2\)-SiO\(_2\) MIX support presents favourable performance to that supported on pure TiO\(_2\) (A-R), the catalyst prepared using the chemically mixed TiO\(_2\)-SiO\(_2\) support is still more active than either. This suggests that the enhancement in activity is the result of a synergistic effect and interaction between TiO\(_2\) and SiO\(_2\) which forms during the chemical preparation of the mixed metal oxides supports.
Stability tests over the most representative catalysts were performed at low conversion such that the reaction was kinetically controlled. Figure 4.14 shows the conversion of propane as a function of reaction time over 1 wt. % Pt/TiO$_2$ (A-R) at 350 °C and 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R) at 250 °C. After 10 hours, the rate of propane conversion reaches a steady state and no deactivation was observed during ca. 50 h on line.
It should be noted that in Figure 4.14, 1 wt. % Pt/TiO$_2$ (A-R) shows higher propane conversion than 1 wt. % Pt/TiO$_2$-SiO$_2$ (A-R), whilst the opposite was shown in Figure 4.13. This is because the time on-line curve for 1 wt. % Pt/TiO$_2$ (A-R) was carried out at a higher temperature of 350 °C, as this catalyst showed negligible propane conversion at 250 °C in Figure 4.13. Although up to 10 hours were required to reach a steady state for both catalysts, they present different activity profiles. At steady state, 1 wt. % Pt/TiO$_2$ (A-R) showed ca. 68 % propane conversion (at 350 °C, Figure 4.14). This differs significantly from the 42 % propane conversion which was observed at the same temperature in the light off curve in Figure 4.13. On the other hand, the degree of propane conversion observed at steady state...
over 1 wt. % Pt/TiO$_2$-SiO$_2$ (A-R) (at 250 °C) is consistent with Figure 4.12, at ca. 20 %. Stability tests at the same temperature for each of the catalysts should be performed.

Reaction rates and turnover frequency (TOF) of propane oxidation were calculated from the conversion-time curves. Turnover frequencies for the platinum catalysts were calculated by dividing the reaction rate ($\mu$mol$_{\text{propane}}$ / (g$_{\text{catalyst}}$·s)) by propane uptake ($\mu$mol$_{\text{propane}}$/ g$_{\text{catalyst}}$). The turnover frequency of 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R) at 250 °C is 77.12 mol$_{\text{C}_3\text{H}_8}$·mol$_{\text{Pt}}^{-1}$·h$^{-1}$.

**Figure 4.15.** Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h$^{-1}$, C$_3$H$_8$·O$_2$ = 1:50

Catalysts prepared by non-aqueous impregnation and calcined at 400 °C in static air

Light-off curves for propane oxidation over the anatase-only TiO$_2$ based platinum catalysts are shown in Figure 4.15.
In contrast to the results previously presented for mixed phase TiO$_2$ (A-R) catalysts, the introduction of 10 % mol of SiO$_2$ into TiO$_2$ (A) does not result in a major change in catalytic activity. In fact, catalytic activity is comparable to that of the most active TiO$_2$ (A-R) catalysts studied (1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R)).

It is worthwhile to compare the activity of platinum supported on different titania supports (with no SiO$_2$ content). As presented in Figure 4.16, 1 wt. % Pt/TiO$_2$ (A) (pink curve) showed excellent activity for the total oxidation of propane. This was much higher than that of 1 wt. % Pt/TiO$_2$ (A-R) (red curve) and similar to that of the most active catalyst studied in the previous section, 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R). TiO$_2$ (A) exhibits a higher surface area, 1.5 times that of TiO$_2$ (A-R), and it is well known that a higher support surface area favours the reaction, improving the dispersion of platinum and the extent of reactant adsorption. In order to determine the degree which the support crystalline phase composition and surface area affects the reaction, 1 wt. % Pt catalysts were prepared using commercially available 100 % anatase TiO$_2$ (55 m$^2$/g surface area) and 100 % rutile TiO$_2$ (2 m$^2$/g surface area). Propane oxidation results over these catalysts are shown in Figure 4.16. As reported previously in the literature $^{19}$, the activity of Pt/TiO$_2$ (100 % anatase) is comparable with the activity of Pt/TiO$_2$ (100 % rutile) at low conversions and slightly higher at conversions over 20 %, which implies that the observed significant enhancement of Pt activity in TiO$_2$ (A) is not, to a great extent, due to the crystalline phase and surface area of the titania support. The pore structure of the support is equally important because the distribution of the pores may affect conversion by impeding diffusion of reactants and products throughout the porous medium. Accordingly, studies to analyse the pore size distribution of the bare supports and the platinum catalysts would be needed.
The performance of the platinum catalysts for total oxidation of propane improves considerably with the addition of SiO\textsubscript{2} to the TiO\textsubscript{2} (A-R) support. The same effect is found with the addition of SiO\textsubscript{2} to Al\textsubscript{2}O\textsubscript{3}, as shown in Figure 4.17. 1 wt. % Pt/Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (violet curve) is much more active than 1 wt. % Pt/Al\textsubscript{2}O\textsubscript{3} (black curve), with up to 50 \% higher conversion of propane, and presents similar activity to the 1 wt. % Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (5 \% mol Si, A-R) catalyst (Figure 4.12).
A summary of the catalytic activity, where $T_{10}$ and $T_{50}$ are the reaction temperatures at which 10% and 50% propane conversion was achieved, is presented in Figure 4.18. Of the supported 1 wt. % platinum catalysts studied, the propane oxidation activity follows the sequence:

$$
\text{Pt/TiO}_2 \text{ (A-R)} < \text{Pt/TiO}_2\text{-SiO}_2 \text{ (5%, A-R)} \approx \text{Pt/Al}_2\text{O}_3\text{-SiO}_2 \text{ (10%) < Pt/TiO}_2 \text{ (A)}
$$

$$
< \text{Pt/TiO}_2\text{-SiO}_2 \text{ (16%, A-R)} \approx \text{Pt/TiO}_2\text{-SiO}_2 \text{ (10%, A-R)}
$$

Figure 4.17. Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h$^{-1}$, $C_3H_8$:O$_2$ = 1:50

Catalysts prepared by non-aqueous impregnation and calcined at 400°C in static air.
The catalytic activity is found to increase considerably with increasing SiO\(_2\) content in the TiO\(_2\) (A-R) support, the shift of the T\(_{50}\) towards lower temperatures exceeds 70 °C when the SiO\(_2\) content reaches 16 % mol. Platinum supported on anatase-only TiO\(_2\) is more active than that supported on biphase anatase-rutile TiO\(_2\) with T\(_{50}\) shifted 65 °C towards lower temperatures. Platinum supported on SiO\(_2\)-Al\(_2\)O\(_3\) presents similar activity to the 1 wt. % Pt/TiO\(_2\)-SiO\(_2\) (5 % mol Si, A-R) catalyst, with T\(_{50}\) shifted towards lower temperatures by 55 °C when compared with the TiO\(_2\) (A-R) catalyst. These differences in conversion temperatures (50 – 70 °C) are significant and represent a major energy saving as, under real conditions, DOCs require the heating of great amounts of air to function.

**Figure 4.18.** Temperature in degrees Celsius for 10 % propane conversion (T\(_{10}\)) and 50 % propane conversion (T\(_{50}\)) over supported platinum catalysts (1 wt. % Pt) prepared by non-aqueous impregnation and calcined at 400 °C in static air

These results agree with those obtained in previous studies\(^9\)\(^{52}\), where catalytic activity for propane oxidation under an oxidising atmosphere was found to increase considerably with
an increase in SiO$_2$ content of TiO$_2$ based supports. Kobayashi et al. reported a $T_{50}$ of 250 °C when 2 wt. % of platinum was supported on TiO$_2$-SiO$_2$ (20 % mol Si). Yazawa et al. reported a $T_{50}$ of 257 °C when 2 wt. % of platinum was supported on SiO$_2$-Al$_2$O$_3$ (13 % mol Al).

![Figure 4.19](image)

**Figure 4.19.** Total oxidation of propane over supported platinum catalysts with reaction error bars

Reaction conditions: Flow reactor, GHSV = 50,000 h$^{-1}$, C$_3$H$_8$:O$_2$ = 1:50

Catalysts prepared by non-aqueous impregnation and calcined at 400 °C in static air

To quantify the error associated with the testing methodology, two catalysts (1 wt.% Pt/TiO$_2$ (A-R) and 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R)) were tested twice, with the standard error shown in Figure 4.19. Whilst the testing error (Figure 4.19) is negligible, the errors associated with the preparation of the platinum catalysts are considerable, as shown in Figure 4.20. Although catalytic activity always follows the same trend, increasing with the SiO$_2$ content of the support, Figure 4.20 shows the error bars.
obtained by testing the same catalyst prepared in different batches under the same conditions. Reproducibility of catalyst performance was difficult, especially in the case of platinum supported on TiO$_2$ (A-R) which showed an error in propane conversion of up to 60 % depending on the temperature.

![Graph](image.png)

**Figure 4.20.** Total oxidation of propane over supported platinum catalysts, preparation error bars

Reaction conditions: Flow reactor, GHSV = 50,000 h$^{-1}$, C$_3$H$_8$:O$_2$ = 1:50

Catalysts prepared by non-aqueous impregnation and calcined at 400 ºC in static air

The effect of Pt loading on catalyst performance was investigated. Figure 4.21 compares the performance of supported platinum catalysts of various platinum loadings (0.5, 1 and 1.5 wt %). As expected, the catalytic activity for total oxidation of propane is, in general, enhanced with increasing platinum loading. This is the case for all the catalysts except
Pt/TiO$_2$ (A). An increase in the platinum content from 1 wt. % to 1.5 wt. % does not have a significant effect in the catalytic activity when supported on anatase-only TiO$_2$, and even decreases slightly. This could be due to sintering of platinum particles at higher loadings.

![Temperature in degrees Celsius for 10% propane conversion ($T_{10}$) and 50% propane conversion ($T_{50}$) over supported platinum catalysts (different platinum loadings) prepared by non-aqueous impregnation and calcined at 400 $\degree$C in static air.]

**Figure 4.21.** Temperature in degrees Celsius for 10% propane conversion ($T_{10}$) and 50% propane conversion ($T_{50}$) over supported platinum catalysts (different platinum loadings) prepared by non-aqueous impregnation and calcined at 400 $\degree$C in static air.

Many studies have focused on identifying differences on the oxidation properties of platinum catalysts and correlate these with the catalytic activity for propane oxidation. In order to understand how the support varies the activity of the catalyst, the effect of the TiO$_2$ and TiO$_2$-SiO$_2$ mixed supports on the structural and electronic properties of platinum was studied.
As listed in Table 4.5, and, compared to the bare supports surface areas decrease after the impregnation of platinum. This is in agreement with the literature \cite{16,32,53}. Deposition of 1 wt. % Pt on the TiO\textsubscript{2} (A-R) and TiO\textsubscript{2} (A) based supports results in 1-6 % reduction of the BET surface area.

**Table 4.5.** Physicochemical properties of the supported platinum catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m\textsuperscript{2}/g)\textsuperscript{[a]}</th>
<th>Density (g/mL)</th>
<th>Pt Av. Crystallite size (Å)\textsuperscript{[b]}</th>
<th>Pt Dispersion (%)\textsuperscript{[b]}</th>
<th>Pt surface area (m\textsuperscript{2}/g)\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2} (A-R)</td>
<td>50</td>
<td>0.55</td>
<td>24</td>
<td>47</td>
<td>1.2</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}–SiO\textsubscript{2} (5 % mol Si, A-R)</td>
<td>83</td>
<td>0.45</td>
<td>69</td>
<td>16</td>
<td>0.4</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}–SiO\textsubscript{2} (16 % mol Si, A-R)</td>
<td>71</td>
<td>0.40</td>
<td>n.d</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2} (A)</td>
<td>75</td>
<td>0.55</td>
<td>46</td>
<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}–SiO\textsubscript{2} (10 % mol Si, A)</td>
<td>96</td>
<td>0.45</td>
<td>94</td>
<td>12</td>
<td>0.3</td>
</tr>
<tr>
<td>1 wt. % Pt/Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} (10 mol % Si)</td>
<td>222</td>
<td>0.25</td>
<td>17</td>
<td>66</td>
<td>1.6</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Surface area measured by N\textsubscript{2} physisorption, density

\textsuperscript{[b]} CO chemisorption. Pretreatment: 300°\textdegree C, 2 h, H\textsubscript{2}. CO chemisorption performed at room temperature using 77 µL pulses of CO. Sample mass used ca. 500 mg

Based on the CO Chemisorption data in Table 4.5, higher contents of SiO\textsubscript{2} in the support (shown to lead to more active catalysts) give rise to larger Pt particles and a lower degree of dispersion. An adsorption stoichiometry of Pt/CO = 1 was assumed. The least active
catalyst, 1 wt. % Pt/TiO₂ (A-R), displays the highest dispersion (≈ 47 %) and the smallest crystallite size among the TiO₂-SiO₂ based catalysts. It is worth pointing out that these results are inconsistent with those obtained from microscopy and should be considered carefully for the following reasons; whilst platinum supported on TiO₂ presents the typical CO uptake, platinum on supports containing SiO₂ present a “u-shaped” CO uptake indicating possible reduction of the catalyst by the CO, Appendix B. Calculations based in the “u-shaped” CO uptake can therefore lead to incorrect dispersion values.

FTIR spectra of the 1 wt. % Pt/TiO₂ (A-R) and 1 wt. % Pt/TiO₂-SiO₂ (16 % mol Si, A-R) are shown in Figure 4.22. The bands centred at 1620 cm⁻¹ and 3350 cm⁻¹ correspond to the bending and stretching vibrational modes of the hydroxyl groups, characteristic of surface-adsorbed water. The sharp peaks at 3700 cm⁻¹ and 3750 cm⁻¹ are characteristic of Ti-OH and Si-OH coordination vacancies. Several weak peaks associated with vibrational modes of TiO₂ are observed in the region between 500 and 800 cm⁻¹. For the TiO₂ (A-R) spectrum, the band observed at 925 cm⁻¹ is associated with the stretching and bending vibration modes of the Ti-O-Ti bonds. For the TiO₂-SiO₂ spectrum, the band observed at 970 cm⁻¹ is associated with Si-O-Ti vibration and the two strong bands at 1100 cm⁻¹ and 860 cm⁻¹ are associated with asymmetric and symmetric Si-O-Si stretching vibrations. The FTIR spectrum of 1 wt. % Pt/TiO₂-SiO₂ shows the hydroxyl species specific to pure TiO₂ and SiO₂, indicating that the addition of SiO₂ to TiO₂ does not alter the type of hydroxyl sites significantly.
Figure 4.22. DRIFT spectra of the supported Pt catalysts

Figure 4.23 shows the IR spectra of CO chemisorbed onto the surface of these catalysts. The band in the region of 2150-2200 cm\(^{-1}\) is assigned to gaseous CO. Three overlapping bands at 2030, 2050 and 2080 cm\(^{-1}\) are observed with both catalysts, and can be assigned to linear CO adsorbed on platinum (Pt\(^{0}\)) terrace and step sites and on partially oxidised platinum (Pt\(^{δ+}\)) sites\(^{56}\)\(^{32}\)\(^{57}\)\(^{58}\). Although the analysis is only qualitative, it is possible to compare the relative intensity of the bands. The relative intensity of the band for CO associated with oxidised platinum sites (2080 cm\(^{-1}\)) is higher on 1 wt. % Pt/TiO\(_2\) (A-R), indicating that platinum species on this support are more electron-deficient. The broad band at 1840 cm\(^{-1}\) is attributed to bridging CO adsorbed on Pt\(^{0}\) particles\(^{53}\), for which the relative intensity is much lower for 1 wt. % Pt/TiO\(_2\)-SiO\(_2\) than on 1 wt.% Pt/TiO\(_2\) (A-R).
From the DRIFTS results it can be concluded that CO chemisorption occurs in both catalysts studied and that more reducible Pt$^{\delta+}$ species are found on the Pt/TiO$_2$ (A-R) catalyst. This correlates with the results obtained for the CO chemisorption pulse studies, which showed that PtO is the predominant species on the TiO$_2$ (A-R) support, with Pt$^{2+}$ not completely reduced by H$_2$ during the pretreatment. This platinum may be reduced by CO during the first pulses.
The surface state of the catalysts was investigated by XPS. Figure 4.24 shows the Pt 4f region of XPS spectra of the supported platinum catalysts.

![Figure 4.24. XPS spectra in the Pt 4f binding energy region of the 1 wt. % platinum catalysts](image)

- d) Pt/TiO\(_2\) (A), e) Pt/TiO\(_2\)-SiO\(_2\) (10 mol % Si, A) and f) Pt/ SiO\(_2\)-Al\(_2\)O\(_3\) (10 % mol Si)

The spectra can be fitted with two or three pairs of overlapping Gaussian-Lorentzian curves. The Pt 4f7/2 and Pt 4f5/2 lines appearing at 71.4 eV and 74.7 eV are attributed to metallic platinum (Pt\(^0\)). The second pair appearing at 72.9 eV and 76.3 eV is assigned to platinum (II) oxide (PtO) and the third pair appearing at 74.6 eV and 77.9 eV is assigned to platinum (IV) oxide (PtO\(_2\)). In the figure, the relative heights indicate that metallic platinum is favoured, in general, with increasing SiO\(_2\) content and that platinum oxide is predominant in both titania materials, TiO\(_2\) (A) and TiO\(_2\) (A-R). These results agree with...
those obtained in previous work\textsuperscript{9}, which showed that the oxidation-resistance of platinum is significantly enhanced by addition of SiO\textsubscript{2} to the TiO\textsubscript{2} support.

Table 4.6. Quantitative analysis of the supported platinum catalysts obtained from the XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt\textsuperscript{0}</th>
<th>Pt\textsuperscript{2+}</th>
<th>Pt\textsuperscript{4+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Wt. %</td>
<td>Conc. %</td>
<td>Conc. %</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2} (A-R)</td>
<td>0.42</td>
<td>3.07</td>
<td>26.70</td>
<td>73.30</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (5 % mol Si, A-R)</td>
<td>0.26</td>
<td>2.03</td>
<td>42.09</td>
<td>57.90</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (16 % mol Si, A-R)</td>
<td>0.23</td>
<td>1.93</td>
<td>67.49</td>
<td>32.52</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2} (A)</td>
<td>0.18</td>
<td>1.36</td>
<td>30.03</td>
<td>69.97</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (10 % mol Si, A)</td>
<td>0.22</td>
<td>1.82</td>
<td>22.65</td>
<td>77.35</td>
</tr>
<tr>
<td>1 wt. % Pt/Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (10 mol % Si)</td>
<td>0.01</td>
<td>0.13</td>
<td>45.83</td>
<td>32.29</td>
</tr>
</tbody>
</table>

Nevertheless, XPS analysis (not shown here) reveals that metallic platinum is the predominant species in all the 1.5 wt. % supported platinum catalysts.

Characteristic X-ray diffraction planes of platinum appear at 2\(\theta\) of 39\(\degree\) (111), 46\(\degree\) (200) and 67\(\degree\) (220)\textsuperscript{59}. However, as reported in previous studies\textsuperscript{53}, the absence of diffraction lines corresponding to platinum within the XRDs of the supported platinum catalysts in Appendix C, indicates that the relatively low loading of platinum is highly dispersed, with a small average particle size. Therefore, it was not possible to calculate the average size of platinum particles from XRD using the Debye-Scherrer equation.
To confirm the high dispersion of Pt over the support surface, the size and crystalline structure of the catalysts was analysed using microscopy imaging experiments coupled with EDX analysis. Many areas of the samples were analysed, and representative images are shown in Figure 4.25.

Selected SEM micrographs of the supported platinum catalysts are presented in Figure 4.25 and Figure 4.26. Whereas the BET surface area of Pt catalysts is comparable with that of the bare supports, the morphology and particle size distribution of 1 wt. % Pt/TiO$_2$ (A-R), but not that of 1 wt. % Pt/TiO$_2$ (A), changes following impregnation of platinum and calcination. For 1 wt. % Pt/TiO$_2$ (A-R), irregular agglomerates with a large window size range of 2 - 120 μm are formed.

**Figure 4.25** SEM images of the TiO$_2$ (A-R) support

a), c) before impregnation and b), d) after impregnation and calcination
The presence of large particles (2-6 μm) with bright contrast, corresponding to PtO, heterogeneously distributed over this support is confirmed by Energy-dispersive X-ray spectroscopy (EDX) in Figure 4.26. The large oblong platinum-containing clusters observed over this support are completely absent over the TiO₂-SiO₂ supports.

Figure 4.26 Selected SEM images and an EDX map and line scan of the 1 wt. % Pt/TiO₂ (A-R) catalyst

Figures 4.27 and 4.28 show high-resolution transmission electron microscopy (HRTEM) images of 1 wt. % Pt/TiO₂ (A-R) and 1 wt. % Pt/TiO₂-SiO₂ (16 % mol Si, A-R) following calcination at 400 °C in static air. On the TiO₂-SiO₂ (A-R) support, figure 4.28, small segregated Pt particles (dark coloured spherical particles) with a particle size of ≈ 2-5 nm are observed. On the other hand, platinum particles are rarely observed on the surface of the TiO₂ (A-R) support in figure 4.27, though some with a particle size of ca. 10 nm are identified by STEM images and EDX analysis.
Figure 4.27. Selected HRTEM and STEM images and an EDX line scan of the 1 wt. % Pt/TiO$_2$ (A-R) catalyst
Figure 4.28. Representative HRTEM and STEM and EDX map scan of the 1 wt. % Pt/TiO₂-SiO₂ (16 % mol Si, A-R) catalyst.
In such Z-contrast images, due to the higher atomic mass of Pt compared with Ti, Si and O, the metallic particles can be clearly identified as they display a high degree of contrast against the support. Although the STEM images do not allow clear discrimination between Pt and PtO particles, imaging coupled with EDX analysis provides complementary information to identify the metallic and oxide particles.

Titania consists of aggregated primary particles formed of aggregates. Aggregates of 30 μm and 1.5 μm are observed for the anatase and anatase-rutile phases respectively, whilst the primary particles have a mean diameter of ca. 20 nm. As shown in Figure 4.27, the lattice spacing measurements confirm the presence of anatase ((101), d = 0.35 nm) and rutile ((101), d = 0.25 nm, (110), d = 0.32 nm) \(^{60,61}\), in accordance with XRD and Raman results in Figures 4.6 and 4.7.

After analysing multiple areas on 1 wt. % Pt/TiO\(_2\)-SiO\(_2\) (5 % mol Si, A-R) and 1 wt. % Pt/TiO\(_2\)-SiO\(_2\) (16 % mol Si, A-R), the resulting particle size distribution is presented in Figure 4.29. The majority of the distribution falls into the 1.5 - 3.5 nm size range and some minor extent particles with a lower population in the 0 - 1 nm and 4 - 7 nm ranges.

TEM images indicate that the platinum dispersion increases and particle size decreases notably with the addition of SiO\(_2\) to the support. This data contrasts with the particle size obtained from the CO Chemisorption experiments in Table 4.5, in which the addition of SiO\(_2\) to the TiO\(_2\) support tends to decrease the dispersion of platinum particles.

This correlates with previous work that concluded that using a mixed metal oxide support, such as TiO\(_2\)-SiO\(_2\) improves the dispersion of platinum and other metal/metal oxides by enhancing the interaction between the nanoparticles and the support \(^{59,62,63,64}\).
Figure 4.29. Selected HRTEM and STEM images and platinum particle size distribution

a) 1 wt. % Pt/TiO₂-SiO₂ (5 mol % Si, A-R) and b) 1 wt. % Pt/TiO₂-SiO₂ (16 mol % Si, A-R)

Representative HRTEM and STEM images from 1 wt. % Pt/TiO₂ (A) are shown in Figure 4.30. In this sample, some particles with size of 4 - 8 nm are observed. The dispersion of the platinum is somewhat enhanced when supported on anatase-only titania instead of anatase-rutile titania.

HRTEM images in Figure 4.31 show the presence of numerous dark spherical particles smaller than 1 nm which could be attributed to platinum particles. This supposition cannot be confirmed by STEM as the particles do not show high image contrast against the support. This is potentially due to the small particle size.
Figure 4.30. Selected HRTEM and STEM images of the 1 wt. % Pt/TiO$_2$ (A) catalyst

Figure 4.31. Selected HRTEM images of the 1 wt. % Pt/TiO$_2$-SiO$_2$ (10 % mol Si, A-R) catalyst
Figure 4.32 shows that the platinum is evenly distributed on the SiO$_2$-Al$_2$O$_3$ support with a particle size range of 1 - 3 nm.

**Figure 4.32.** Selected HRTEM and STEM images, EDX map scan and platinum particle size distribution of the 1 wt. % Pt/SiO$_2$-Al$_2$O$_3$ (10 % mol Si)
Quantitative analysis obtained from different techniques; XPS and microscopy coupled with EDX, is presented in Table 4.7.

**Table 4.7. Quantitative analysis of the supported platinum catalysts obtained from the XPS spectra and from the SEM and TEM imaging coupled with EDX**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ti wt. %</th>
<th>Al wt. %</th>
<th>Si wt. %</th>
<th>O wt. %</th>
<th>Pt wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Pt/TiO$_2$ (A-R)</td>
<td>XPS</td>
<td>55.46</td>
<td>0</td>
<td>0</td>
<td>41.51</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>50.04</td>
<td>0</td>
<td>0</td>
<td>49.28</td>
</tr>
<tr>
<td></td>
<td>TEM-EDX</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO$_2$-SiO$_2$ (5 % mol Si, A-R)</td>
<td>XPS</td>
<td>46.52</td>
<td>0</td>
<td>6.97</td>
<td>44.48</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>TEM-EDX</td>
<td>XPS</td>
<td>56.01</td>
<td>0</td>
<td>2.68</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R)</td>
<td>XPS</td>
<td>30.60</td>
<td>0</td>
<td>18.27</td>
<td>49.20</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>48.90</td>
<td>0</td>
<td>8.19</td>
<td>41.98</td>
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<tr>
<td></td>
<td>TEM-EDX</td>
<td>50.20</td>
<td>0</td>
<td>7.16</td>
<td>41.67</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO$_2$ (A)</td>
<td>XPS</td>
<td>52.80</td>
<td>0</td>
<td>2.32</td>
<td>43.52</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>58.87</td>
<td>0</td>
<td>0.32</td>
<td>39.69</td>
</tr>
<tr>
<td></td>
<td>TEM-EDX</td>
<td>54.28</td>
<td>0</td>
<td>4.12</td>
<td>40.95</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO$_2$-SiO$_2$ (10 % mol Si, A)</td>
<td>XPS</td>
<td>39.98</td>
<td>0</td>
<td>11.67</td>
<td>46.53</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>TEM-EDX</td>
<td>45.94</td>
<td>0</td>
<td>10.49</td>
<td>42.62</td>
</tr>
<tr>
<td>1 wt. % Pt/Al$_2$O$_3$-SiO$_2$ (10 mol % Si)</td>
<td>XPS</td>
<td>0</td>
<td>12.50</td>
<td>37.29</td>
<td>50.08</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>TEM-EDX</td>
<td>0</td>
<td>39.04</td>
<td>11.74</td>
<td>48.08</td>
</tr>
</tbody>
</table>

Variations in the silicon concentration calculated by techniques which differ by analysis depth suggest a non-homogeneity of the anatase-rutile based supports’ composition. Whilst the surface silicon concentration measured by XPS (~10 nm penetration) correlates with the loading provided by the support supplier, the silicon content decreases considerably when measured by EDX (~1 - 2 μm penetration). This indicates the presence of a silicon gradient with a higher concentration of SiO$_2$ at the surface. On the other hand, the silicon concentration remains constant at different depths for the anatase- only based catalysts,
which present a different morphology and have a higher surface area, demonstrating a homogeneous composition of the support.

The heterogeneity of the composition becomes even more relevant for the Al$_2$O$_3$-SiO$_2$ support, which presents a concentration gradient for both SiO$_2$ and Al$_2$O$_3$ phases. For this support the silicon concentration is three times higher at the catalyst surface than at 2 $\mu$m depth, and the aluminium concentration is three times lower at the catalyst surface than at 2 $\mu$m depth.

In cases, a higher concentration of platinum species is found on the surface of the catalysts, exceeding the theoretical loading of $\approx$ 1 wt %. Whilst the bulk-sensitive analysis (EDX) shows platinum loadings similar to the theoretical values when platinum is supported on the mixed metal oxides; TiO$_2$-SiO$_2$ and Al$_2$O$_3$-SiO$_2$, the loading is lower on anatase-only and anatase-rutile TiO$_2$. This could be attributed to the poor dispersion of the platinum on the titania supports, as observed in Figure 4.27 for TiO$_2$ (A-R) and 4.30 for TiO$_2$ (A). As mentioned previously (Figure 4.24), quantitative results obtained from the XPS data for 1 wt. % Pt/Al$_2$O$_3$-SiO$_2$ should be considered carefully because the intense Al 2p signal overlaps with that of the Pt 4f.

Although these techniques can give a general idea about catalyst composition, elemental analysis via a different technique such as ICP-MS would be necessary in order to obtain a more representative quantification of the elements present within the supports and catalysts.
4.2.1.3 Discussion

Based on detailed characterisation studies, it has been possible to propose a model to describe the structural and electronic properties of the catalysts.

In general, the shape of the platinum particles is spherical. Platinum dispersion is enhanced with the addition of SiO$_2$ to both titania; anatase and anatase-rutile. Meanwhile, small nanoparticles (2-5 nm) are highly dispersed on the TiO$_2$-SiO$_2$ supports, whilst large, poorly dispersed platinum particles ($\approx$ 10 nm) are found on SiO$_2$-free supports. Increasing the SiO$_2$ content of TiO$_2$ supports increases surface area and it is well known that an increment of the support surface area improves the dispersion of nanoparticles.

Although it is observed that the more active SiO$_2$-containing catalysts have smaller platinum particles, the presence of silica also modifies the electronic properties of the supported platinum catalysts. Electronic properties depend on the Pt-support interactions and have been shown to have a significant influence towards increasing catalytic activity for hydrocarbon combustion.

The oxidation state of platinum varies with the support material. For the anatase-rutile TiO$_2$ based supports, the presence of metallic platinum becomes more favourable with increasing SiO$_2$ content; such that platinum is predominantly present in metallic state on TiO$_2$-SiO$_2$ (16 % mol Si, A-R) and exists as platinum oxide on TiO$_2$ (A-R). This tendency was consistent with previous studies$^{9,10,30,52}$. Changes in catalytic activity upon varying of support materials comes from the chemical modification of supported platinum catalysts, with the oxidation resistance of the noble metal being improved by more acidic/electrophilic supports, i.e. with the SiO$_2$ content.
As illustrated in Figure 4.33, there is a clear relationship between the platinum oxidation state and propane conversion. A decrease in the Pt$^{2+}$/Pt$^{0}$ ratio corresponds to a significant improvement in catalytic activity.

![Figure 4.33](image-url)  
**Figure 4.33.** Activity of the supported platinum catalysts for total oxidation of propane at 300 °C as a function of the Pt$^{2+}$/Pt$^{0}$ ratio

However, based on the results obtained here, there is not a clear relationship between the platinum oxidation resistance and support acidity. NH$_3$ TPD experiments show the opposite to previous studies 30, as the total acidity of the anatase-rutile titania based mixed oxide supports decreases with the SiO$_2$ content. Garetto et al. 65 reported that the superior activity shown by platinum supported on acidic zeolites for propane combustion was due to the
increase in the density of adsorbed propane molecules rather than acid strength of the support materials. Hence, propane uptake on the supported catalysts should be measured.

Yazawa et al. \(^{52}\) reported that the catalytic activity of supported platinum catalysts for low temperature propane combustion varied not only with the acid strength of support materials but also with the platinum dispersion, thus, the turnover frequency increased with increasing support acidity and with a decrease in platinum dispersion. They concluded that variation in catalytic activity with platinum dispersion is linked to the oxidation state of platinum, since large platinum particles are less readily oxidised than small ones\(^{52}\). These results are contrary to those obtained in this thesis, where catalytic activity is enhanced with the SiO\(_2\) content of the support, which it is linked not only to an improvement in the oxidation resistance but also the dispersion of the platinum nanoparticles.

In the case of the anatase- only based supports, the presence of metallic Pt\(^0\) does not increase with the SiO\(_2\) content and platinum is predominantly present as the oxide (PtO) on both TiO\(_2\) (A) and TiO\(_2\)-SiO\(_2\) (10 % mol Si, A). The platinum loading, dispersion and oxidation state are comparable in both of these supports but platinum supported on TiO\(_2\) (A) is much more active than that supported on TiO\(_2\) (A-R). Surface area, morphology and phase composition differ between these two supports.

Although it is well known that anatase TiO\(_2\) possesses a higher surface area than rutile TiO\(_2\) and that an increase in the surface area of the support improves nanoparticle dispersion, it has already been proven, via experiments using commercial titania and rutile supports, that the significant enhancement of the activity is not, to a great extent, due to these factors. Figure 4.34 shows a fair relationship between the surface area of the support and propane conversion under the conditions studied. However, as shown in the TEM micrographs in
Figure 4.30, the dispersion of platinum on TiO$_2$ (A) is poor and comparable with that obtained for platinum on TiO$_2$ (A-R), figure 4.26 and 4.27.

Figure 4.34. The activity of supported platinum catalysts for the total oxidation of propane at 300 °C as a function of BET surface area.

In conclusion, the potential influence of the anatase-only TiO$_2$ support on the catalytic activity of supported platinum catalysts for propane oxidation remains unclear.
4.2.2 The effect of the transient temperature cycle

Results for stability tests over the most representative catalysts have already been shown in Figure 4.14 of this chapter. To help investigate the light-off characteristics of a catalyst under more realistic conditions, which simulate changes in engine load, experiments with a transient temperature cycle were carried out. The main objective is to demonstrate that even with a constant exhaust composition, activation or deactivation phenomena can be observed.

Propane oxidation reactions using different temperature cycles, consisting of both upwards and downwards ramps, were performed. Platinum catalysts tested under a transient temperature cycle exhibit hysteresis behaviour, indicating that the catalytic activity during the cool-down exceeds the activity of the first heat-up cycle.

![Figure 4.35. Temperature in degrees Celsius for 10% propane conversion ($T_{10}$) and 50% propane conversion ($T_{50}$) during hysteresis: Heat-up, cool-down and heat-up cycles. Supported platinum catalysts (1 wt. % Pt) prepared by non-aqueous impregnation and calcined at 400 °C in static air.](image)
Figure 4.35 shows the $T_{10}$ and $T_{50}$ temperatures for 1 wt. % platinum supported on commercial TiO$_2$ P25, SiO$_2$ and Al$_2$O$_3$ during up – down - up temperature cycles. Whilst the $T_{50}$ temperature decreases by 65 ºC and 35 ºC for the TiO$_2$ and Al$_2$O$_3$ catalysts respectively upon cycling back up, no variation in the $T_{10}$ and $T_{50}$ is observed for the SiO$_2$ catalyst.

**Figure 4.36.** Total oxidation of propane over supported platinum catalysts

Hysteresis: Heat-up (solid line) and cool-down (dashed line) light-off curves

Reaction conditions: Flow reactor, GHSV = 50,000 h$^{-1}$, C$_3$H$_8$:O$_2$ = 1:50

Catalysts prepared by non-aqueous impregnation and calcined at 400 ºC in static air
Figure 4.36 shows propane conversion as a function of temperature in an experiment where the temperature was ramped from 100 °C up to 500 °C, back to 100 °C and up to 500 °C again. In accordance with the results in Figure 4.35, the conversion of propane is higher during the negative ramp than during the first positive ramp. If the cycle is repeated, the conversion closely follows that of the first negative ramp.

Repeated temperature cycling significantly improves catalytic activity of 1 wt. % Pt/TiO$_2$ (A-R). Initially, 5 % propane conversion was observed at 350 °C. This increased to 70 % after the second and third cycles at 500 °C. This can be explained by a self-activation of the catalyst under reaction conditions.

Compared to the transient temperature cycle Figure 4.14, if the catalyst is operated at the same temperature (350 °C) for a longer time, a steady state is observed that corresponds to the higher conversion during the hysteresis cycle.

The $T_{10}$ and $T_{50}$ temperatures observed for different supported platinum catalysts during up-down-up temperature hysteresis are illustrated in Figure 4.37. The catalytic activity enhancement is of great importance for 1 wt.% Pt/TiO$_2$ (A-R) catalyst, with a decrease in $T_{50}$ of 86 °C but is not as significant for the platinum supported on TiO$_2$ (A) or any of SiO$_2$ – containing catalysts, with a decrease in $T_{50}$ of only 10 °C.
A similar phenomenon was reported in previous studies for CO oxidation on platinum \(^\text{66, 67}\), showing hysteresis behaviour with a higher degree of conversion during cool down than during heat up.
There are several physical and chemical effects which can cause regular hysteresis: (i) thermal inertia of the catalyst, (ii) multiple steady states due to the exothermic reaction and (iii) surface inhibition. The most likely explanation for the observed hysteresis behaviour in this study is an *in situ* reduction of the surface platinum.

Catalysts were analysed by XPS following temperature cycling experiments. Quantitative analysis of the Pt 4f binding energy region for these catalysts is presented in Table 4.8. The variation in the oxidation state of platinum can also explain the changes in activity during hysteresis cycles.

As illustrated in Figure 4.38, platinum in the metallic state is the predominant species after the first heat-up cycle, thus enhancing propane conversion. Whilst the Pt$^{2+}$/Pt$^{0}$ ratio in 1 wt. % Pt/TiO$_2$ (A-R) decreases considerably after the first propane oxidation reaction, from 2.8 to 0.24, the decrease is subtle for 1 wt. % Pt/TiO$_2$-SiO$_2$ (A-R), from 0.48 to 0.21.

*Figure 4.38.* XPS spectra in the Pt 4f binding energy region of the 1 wt. % platinum catalysts:

- Pt/TiO$_2$ (A-R): a) Fresh  
  b) After Propane oxidation

- Pt/TiO$_2$-SiO$_2$ (16 mol % Si, A-R): c) Fresh  
  d) After Propane oxidation
It is thus proposed that at high temperatures, platinum is reduced by propane despite the large excess of oxygen in the gas feed. The metallic platinum is not oxidised back to its original state at lower temperatures, indicating that the new platinum species formed is stable.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;4+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A-R)</td>
<td>Fresh</td>
<td>0.42</td>
<td>3.07</td>
<td>26.70</td>
</tr>
<tr>
<td></td>
<td>After Propane ox.</td>
<td>0.15</td>
<td>1.34</td>
<td>80.68</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (16 % mol Si, A-R)</td>
<td>Fresh</td>
<td>0.23</td>
<td>1.93</td>
<td>67.49</td>
</tr>
<tr>
<td></td>
<td>After Propane ox.</td>
<td>0.16</td>
<td>1.42</td>
<td>82.66</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A)</td>
<td>Fresh</td>
<td>0.18</td>
<td>1.36</td>
<td>30.03</td>
</tr>
<tr>
<td></td>
<td>After Propane ox.</td>
<td>0.17</td>
<td>1.29</td>
<td>12.23</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (10 % mol Si, A)</td>
<td>Fresh</td>
<td>0.22</td>
<td>1.82</td>
<td>22.65</td>
</tr>
<tr>
<td></td>
<td>After Propane ox.</td>
<td>0.14</td>
<td>1.14</td>
<td>100</td>
</tr>
<tr>
<td>1 wt. % Pt/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (10 mol % Si)</td>
<td>Fresh</td>
<td>0.01</td>
<td>0.13</td>
<td>45.83</td>
</tr>
</tbody>
</table>

The difference in the Pt<sup>2+</sup>/Pt<sup>0</sup> ratio before and after reaction and, therefore, the performance, is greater when the platinum is supported on TiO<sub>2</sub> (A-R) than when supported on TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides. These results also explain the enhancement in activity observed for 1 wt. % Pt/TiO<sub>2</sub> (A-R) during the time on-line experiment in Figure 4.14. The 62 % increase in propane conversion after 10 hours at 350 °C is potentially due to the in situ reduction of PtO to Pt<sup>0</sup>. 
Again, the anatase based catalysts do not follow the same trends, with no clear correlation between the catalytic performance and oxidation state of platinum. The concentration of metallic platinum decreases after the first heat-up cycle, from 30 to 12 %, but even then, the catalytic activity remains high.

These differences can be explained in terms of the redox properties and the reducibility of the platinum when supported on different materials.

### 4.2.3 The effect of the calcination conditions

The study and determination of the optimal conditions for catalyst preparation, pretreatment and activation is of great importance. The preparation of high surface area solid catalysts requires an oxidation or reduction step at elevated temperatures following metal impregnation. This is required to remove the precursor and obtain well dispersed metal nanoparticles. Calcination conditions influence the texture, specific surface area and morphology of the final catalyst and subsequently influence the catalytic performance. While calcination conditions have already been discussed in the experimental chapter, the effect of a range of calcination atmospheres on the catalysts and their performance was investigated.

In order to investigate the effect of the calcination atmosphere, each catalyst was calcined at 400 °C for 5 hours under: static air, flowing air and flowing helium. These catalysts were tested for propane oxidation.

Figures 4.39 and 4.40 show the effect of the calcination atmosphere on propane conversion.
Figure 4.39. Temperature in degrees Celsius for 10 % propane conversion ($T_{10}$) and 50 % propane conversion ($T_{50}$) over supported platinum catalysts (1 wt. % Pt) prepared by non-aqueous impregnation, calcined at 400 °C in static and flowing air.

Figure 4.40. Temperature in degrees Celsius for 10 % propane conversion ($T_{10}$) and 50 % propane conversion ($T_{50}$) over supported platinum catalysts (1.5 wt. % Pt) prepared by non-aqueous impregnation, calcined at 400 °C in static air and helium.
It can be observed in Figure 4.39 that the catalysts calcined under flowing air present lower activity than those calcined under static air. This effect is more noticeable for the platinum supported on TiO$_2$ (A-R), with $T_{50}$ shifted $\approx 26 \, ^\circ C$ towards higher temperatures.

The effect of using an inert atmosphere during the heat-treatment is illustrated in Figure 4.40. The catalysts calcined under helium presents enhanced performance compared with the catalyst calcined under static or flowing air. Again this effect is more apparent for the platinum supported on TiO$_2$ (A-R), with $T_{50}$ shifted $\approx 16 \, ^\circ C$ towards lower temperatures.

With consideration of the obtained results, it can be concluded that whilst the changes are subtle, the performance of the catalysts is, in general, affected by the calcination atmosphere. Catalytic activity follows the order: helium $>$ static air $>$ flowing air.

Quantitative analysis of the supported platinum catalysts obtained from the XPS spectra, Pt 4f region, is presented in Table 4.9. Although it has been reported previously that the composition of the calcination atmosphere can affect the final oxidation state and surface metal centres, no clear change in the Pt$^{2+}$/Pt$^0$ ratio is observed in Table 4.9 when comparing the different calcination atmospheres. Whilst for the 1 wt. % Pt catalysts, metallic platinum becomes more favourable with increasing SiO$_2$ content of the support; for the 1.5 wt % Pt catalysts, metallic platinum is the predominant species independent of the support.

It is found that the calcination atmospheres studied have no significant effect upon the oxidation state of the platinum. The differences in performance for propane oxidation are therefore likely related to the nature of the support.

The oxidation activity of the 1 wt. % Pt catalysts depends strongly on oxidation state, with metallic platinum being the most active. To extend the understanding of the effect of the
platinum oxidation state on the catalytic activity for hydrocarbon oxidation, the effect of a reductive pretreatment on catalytic performance was studied.

**Table 4.9.** Quantitative analysis of the supported platinum catalysts, calcined under different atmospheres, obtained from the XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Wt %</td>
<td>Conc. %</td>
<td>Conc. %</td>
<td>Conc. %</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A-R)</td>
<td>Static air</td>
<td>0.42</td>
<td>3.07</td>
<td>26.70</td>
<td>73.30</td>
</tr>
<tr>
<td></td>
<td>Flowing air</td>
<td>0.42</td>
<td>3.02</td>
<td>30.72</td>
<td>69.27</td>
</tr>
<tr>
<td>1.5 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A-R)</td>
<td>Static air</td>
<td>0.55</td>
<td>4.02</td>
<td>81.59</td>
<td>18.41</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>0.65</td>
<td>4.67</td>
<td>77.09</td>
<td>22.91</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (5 % mol Si, A-R)</td>
<td>Static air</td>
<td>0.26</td>
<td>2.03</td>
<td>42.09</td>
<td>57.90</td>
</tr>
<tr>
<td></td>
<td>Flowing air</td>
<td>0.26</td>
<td>2.00</td>
<td>43.75</td>
<td>56.25</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (16 % mol Si, A-R)</td>
<td>Static air</td>
<td>0.23</td>
<td>1.93</td>
<td>67.49</td>
<td>32.52</td>
</tr>
<tr>
<td></td>
<td>Flowing air</td>
<td>0.24</td>
<td>2.02</td>
<td>63.01</td>
<td>36.98</td>
</tr>
<tr>
<td>1.5 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (16 % mol Si, A-R)</td>
<td>Static air</td>
<td>0.29</td>
<td>2.45</td>
<td>74.99</td>
<td>25.01</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>0.32</td>
<td>2.74</td>
<td>100</td>
<td>0.00</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A)</td>
<td>Static air</td>
<td>0.18</td>
<td>1.36</td>
<td>30.03</td>
<td>69.97</td>
</tr>
<tr>
<td></td>
<td>Flowing air</td>
<td>0.21</td>
<td>1.60</td>
<td>36.65</td>
<td>63.35</td>
</tr>
<tr>
<td>1.5 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A)</td>
<td>Static air</td>
<td>0.37</td>
<td>2.80</td>
<td>65.63</td>
<td>34.37</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>0.39</td>
<td>2.95</td>
<td>67.89</td>
<td>32.11</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (10 % mol Si, A)</td>
<td>Static air</td>
<td>0.22</td>
<td>1.82</td>
<td>22.65</td>
<td>77.35</td>
</tr>
<tr>
<td></td>
<td>Flowing air</td>
<td>0.22</td>
<td>1.80</td>
<td>17.41</td>
<td>82.59</td>
</tr>
</tbody>
</table>
Since it has been demonstrated that the catalytic activity of supported platinum varies with its oxidation state, reduction at elevated temperature could be beneficial in the synthesis of supported metal catalysts. However, heating a supported metal catalyst can cause morphological changes in the metal particles depending upon the particular metal-oxide system. When using titania as the support some considerations should be taken into account. As reported by Hanaor et al.\textsuperscript{68}, phase transformation of titania from anatase to rutile occurs at temperatures above 600 °C and ambient pressure. This leads to a decrease in the support’s surface area. In addition, the so-called strong-metal-support-interaction (SMSI) exhibited when metals in group 8-10 are supported on reducible metal oxides, such as TiO\textsubscript{2}, and reduced in hydrogen results in sintering, encapsulation, inter-diffusion and alloy formation that leads to important changes in catalytic activity and selectivity\textsuperscript{69}.

Figure 4.41 shows propane conversion as a function of temperature for the supported platinum catalysts following reduction under 5 % H\textsubscript{2}/Ar at 400 °C for 5 hours. In accordance with previous results, the conversion of propane is enhanced by the SiO\textsubscript{2} content of the TiO\textsubscript{2} (A-R) support.
Chapter 4  
Oxidation properties of supported platinum catalysts

**Figure 4.41** Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h\(^{-1}\), \(C_3H_8:O_2 = 1:50\)

Catalysts prepared by non-aqueous impregnation and reduced at 400 °C in 5 % H\(_2\)/Ar

From the \(T_{10}\) and \(T_{50}\) values shown in Figure 4.42, it can be concluded that reductive pretreatment has a significant effect upon the catalytic activity of only one catalyst, 1 wt. % Pt/TiO\(_2\) (A). For this catalyst, the catalytic activity decreases considerably with \(T_{50}\) shifted 37 °C towards higher temperatures. Whilst this catalyst presents high performance when calcined in an oxidising or inert atmosphere (Figure 4.40), its activity decreases when heat treated under a reducing atmosphere. Catalytic activity for propane oxidation is now similar for 1 wt.% Pt/TiO\(_2\) (A) and 1 wt.% Pt/TiO\(_2\) (A-R).
Quantitative analysis of the reduced platinum catalysts obtained from the XPS spectra is shown in Table 4.10, revealing that metallic platinum is the predominant species in all catalysts, accounting for approximately 60% of the total concentration for the TiO$_2$-SiO$_2$ based catalysts and 100% of platinum in the Al$_2$O$_3$-SiO$_2$ based catalyst. It should also be noted that a higher concentration of platinum species, 2.38 wt. %, is found on the surface of the 1 wt. % Pt/TiO$_2$ (A) catalyst after being reduced, overcoming the total loading of $\approx$ 1 wt %. This is also observed for the TiO$_2$ (A-R) based catalysts, independent of the calcination conditions.

Figure 4.42. Temperature in degrees Celsius for 10% propane conversion ($T_{10}$) and 50% propane conversion ($T_{50}$) over supported platinum catalysts (1 wt. % Pt) prepared by non-aqueous impregnation, calcined at 400 °C in static air and reduced at 400 °C in 5 % H$_2$/Ar
Table 4.10. XPS quantitative analysis and Pt 4f<sub>7/2</sub> core binding energies of the supported platinum catalysts reduced at 400 °C in 5 % H<sub>2</sub>/Ar methods (numbers in parentheses are the relative concentration of the platinum species)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Pt&lt;sup&gt;4+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Wt %</td>
<td>eV (%)</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A-R)</td>
<td>Static air 0.42</td>
<td>3.07</td>
<td>71.5 (26.7)</td>
</tr>
<tr>
<td></td>
<td>5 % H&lt;sub&gt;2&lt;/sub&gt;/Ar 0.39</td>
<td>2.87</td>
<td>70.8 (54.6)</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (16 % mol Si, A-R)</td>
<td>Static air 0.23</td>
<td>1.93</td>
<td>71.4 (67.5)</td>
</tr>
<tr>
<td></td>
<td>5 % H&lt;sub&gt;2&lt;/sub&gt;/Ar 0.16</td>
<td>1.39</td>
<td>71.6 (59.2)</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt; (A)</td>
<td>Static air 0.18</td>
<td>1.36</td>
<td>71.4 (30.0)</td>
</tr>
<tr>
<td></td>
<td>5 % H&lt;sub&gt;2&lt;/sub&gt;/Ar 0.31</td>
<td>2.38</td>
<td>71.5 (61.6)</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO&lt;sub&gt;2&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (10 % mol Si, A)</td>
<td>Static air 0.22</td>
<td>1.82</td>
<td>71.6 (22.7)</td>
</tr>
<tr>
<td></td>
<td>5 % H&lt;sub&gt;2&lt;/sub&gt;/Ar 0.14</td>
<td>1.20</td>
<td>71.6 (68.2)</td>
</tr>
<tr>
<td>1 wt. % Pt/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-SiO&lt;sub&gt;2&lt;/sub&gt; (10 mol % Si)</td>
<td>Static air 0.01</td>
<td>0.13</td>
<td>71.4 (45.8)</td>
</tr>
<tr>
<td></td>
<td>5 % H&lt;sub&gt;2&lt;/sub&gt;/Ar 0.01</td>
<td>0.03</td>
<td>71.8 (100)</td>
</tr>
</tbody>
</table>

Of particular interest is the shift towards a lower binding energy of the peak corresponding to metallic platinum for 1 wt. % Pt/TiO<sub>2</sub> (A-R) shown in Figure 4.43. Kobayashi et al. also reported that the peak corresponding to Pt<sup>0</sup> was shifted 0.6 eV towards lower binding energy when a Pt/TiO<sub>2</sub>-SiO<sub>2</sub> catalyst was pretreated in a reducing environment rather than in an oxidising one. This effect is only seen when platinum is supported on anatase-rutile and not on anatase- only TiO<sub>2</sub>. Once again, the differences in performance for propane oxidation are mainly related to the nature of the support. Titania interacts with platinum, modifying the electronic state of surface species.
Various studies have investigated the metal-support interaction in precious metal-TiO₂ and -Ce₂O₃ systems, using several characterisation techniques including TEM, XPS, FTIR and Raman. The Pt₀ peak shift towards lower binding energies in the XPS spectra in Figure 4.43 could be indicative of an SMSI effect. Electron transfer from TiO₂ to Pt forms electron rich (Pt)ₙ⁺ species, resulting in a local charge density change and surface core level shifts in the Pt 4f⁷/₂ and Pt 4f⁵/₂. However, several authors argued that the relation between activity and metal-support interaction is due to structural modification; a geometric effect, and proved by TEM analysis that the surface Pt is progressively covered/encapsulated by the reducible support when the catalyst is exposed to H₂ at high temperatures (T > 500 °C). In addition, Lewera et al. demonstrated that the observed binding energy shifts of core-level electrons were due to changes in the electronic
properties of platinum induced by not only charge transfer from the metal oxide but also changes in the lattice parameter due to alloy formation.

Encapsulation and electronic interactions might occur simultaneously but the electronic perturbation starts at lower reduction temperature than the geometric effect. Haerudin et al. found that reduction of titania begins at 200 °C and results in the formation of surface oxygen vacancies, Ti³⁺ ions and electrons. Hence, the reductive pretreatment at 400 °C performed in this study is likely to induce an electronic rather than geometric effect on the platinum.

In order to study the reducibility of the catalysts, temperature programmed reduction (TPR) experiments were performed using 10% H₂/Ar as the reducing agent. H₂-TPR profiles for the supported platinum catalysts are shown in Figure 4.44. In general, the profiles show a small peak below 100 °C and a series of weak overlapping uptake peaks in the temperature range 250 – 500 °C. Based on previous studies, the peak at ca. 80°C can be assigned to reduction of PtOₓ species to metallic platinum. The broad peak centred at 350 °C is attributed to the reduction of surface Ti⁴⁺ species to Ti³⁺ via H₂ spill-over. It should be noted that in Figure 4.44 d), the high temperature peak (Ti⁴⁺ - Ti³⁺) for 1 wt.% Pt/TiO₂ (A) is more intense and is shifted 50 °C towards lower temperatures.
Figure 4.44. H₂-TPR curves of the 1 wt. % platinum catalysts calcined at 400 °C in static air:

a) TiO₂ (A-R), b) TiO₂-SiO₂ (5 mol % Si, A-R), c) TiO₂-SiO₂ (16 mol % Si, A-R),
d) TiO₂ (A), e) TiO₂-SiO₂ (10 mol % Si, A) and f) Al₂O₃-SiO₂ (10 mol % Al)

H₂-TPR profiles of both TiO₂ (A) and TiO₂ (A-R) are presented in Figure 4.45. Reduction of bulk oxygen within TiO₂ has been reported to occur at temperatures of above 600 °C. Regarding the reducibility of the TiO₂ (A-R), no significant H₂ consumption peaks were detected. In contrast, the anatase-only TiO₂ (A) exhibits one intense reduction peak at 500 °C. This can be attributed to reduction of the surface capping oxygen in TiO₂. Such data is consistent with the general consideration that the temperature at which Ti⁴⁺ sites were reduced in 1 wt.% Pt/TiO₂ (A) (Figure 4.44 d) is 200 °C lower than that of bare TiO₂ (A) (Figure 4.45 b). Based on previous studies, these results provide information as to the influence of platinum on the reducibility of the supports, suggesting that platinum facilitates the reduction of oxygen species on the TiO₂ surface. Platinum catalyses the
surface reduction of the support by lowering the temperature at which dissociative adsorption of H$_2$ occurs $^{16}$.

The supports and catalysts’ total hydrogen consumption determined from the TPR profiles are presented in Table 4.11. The H$_2$ consumption for anatase titania on 1 wt. % Pt/TiO$_2$ (A) is 562 $\mu$mol H$_2$/g catalyst. This is 5 times greater than that obtained for anatase-rutile titania in 1 wt. % Pt/TiO$_2$ (A-R). These values were determined by calculating the theoretical amount of H$_2$ consumed in reducing the PtO (obtained from XPS quantitative analysis) to Pt$^0$, and subtracting this from the total H$_2$ consumption. The amount of H$_2$ consumed during the TPR of the anatase-rutile based supports is approximately 28 $\mu$mol H$_2$/g catalyst. This value is comparable with that obtained for

![Figure 4.45. H$_2$-TPR curves of the as received titania supports:](image)

- a) TiO$_2$ (A-R)  
- b) TiO$_2$ (A)
Pt/TiO$_2$ P25 in previous studies. In addition, the anatase support's hydrogen consumption is 322 μmol H$_2$/g catalyst.

**Table 4.11** Hydrogen consumption obtained from the H$_2$-TPR profiles of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total H$_2$ consumption</th>
<th>Support H$_2$ consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmol H$_2$/g catalyst</td>
<td>µmol H$_2$/g catalyst</td>
</tr>
<tr>
<td>TiO$_2$ (A-R)</td>
<td>Support 28</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>1 wt. % Pt 152</td>
<td>114</td>
</tr>
<tr>
<td>TiO$_2$-SiO (5 % mol Si, A-R)</td>
<td>Support 28</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>1 wt. % Pt 126</td>
<td>96</td>
</tr>
<tr>
<td>TiO$_2$-SiO (16 % mol Si, A-R)</td>
<td>Support 29</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>1 wt. % Pt 133</td>
<td>116</td>
</tr>
<tr>
<td>TiO$_2$ (A)</td>
<td>Support 322</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>1 wt. % Pt 598</td>
<td>562</td>
</tr>
<tr>
<td>TiO$_2$-SiO (10 % mol Si, A)</td>
<td>1 wt. % Pt 116</td>
<td>76</td>
</tr>
<tr>
<td>Al$_2$O$_3$-SiO$_2$ (10 mol % Si)</td>
<td>1 wt. % Pt 80</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 4.46 shows the TPR profiles for 1 wt. % Pt/TiO$_2$ following (a) calcination in static air (400 °C) and (b) reduction in 5 % H$_2$/Ar (400 °C). The peak at 300 °C is not present when the catalyst is heat-treated in a reducing atmosphere prior to the TPR experiment, indicating that this peak is, certainly, the result of a reduction reaction and not a thermal desorption. From these results and trends in Figure 4.42, it can be concluded that an increase in the concentration of surface capping oxygen species on the TiO$_2$ (A) support enhances the propane oxidation activity of 1 wt. % Pt/TiO$_2$ (A), as this catalyst shows much higher activity when calcined in static air than when reduced in 5 % H$_2$/Ar.
The superior performance of the anatase over the anatase-rutile based catalyst, 1 wt. % Pt/TiO₂ (A) vs. 1 wt. % Pt/TiO₂ (A-R), may result from the fact that TiO₂ (A) serves as a reservoir of oxygen in the oxidation reaction. A number of studies have reported the reduction behaviour of other reducible supports, such as CeO₂, and their use as a redox/oxygen storage components in three-way-catalysts (TWC) \textsuperscript{90,91,92,93,94,95,96,97,98}. In these materials, oxygen vacancy defects can be rapidly generated and eliminated, giving a high oxygen storage capacity (OSC). Activity depends on oxygen mobility and so called “weak” metal-oxygen bonds. A high concentration of surface oxygen with low binding energies on the catalyst surface has been reported to be required for catalyst activity. Oxygen species on the metal particles diffuse rapidly to the metal-support interface and result in the formation of the new active sites which are more active for the combustion.

**Figure 4.46.** H₂-TPR curves of the 1 wt. % platinum catalysts calcined in different atmospheres:

\[\text{Pt/TiO}_2 (A): \quad \text{a) Static air} \quad \text{b) 5 \% H}_2/\text{Ar}\]
reaction, preserving the catalyst surface from over-oxidation. Those platinum species which react readily with the lattice oxygen of the support, are responsible for the increased propane oxidation activity. The highly reactive oxygen species are thought to be responsible for the high hydrocarbon total-oxidation activity shown by platinum and palladium-based catalysts \(^1\), operating via a Mars-Van Krevelen type mechanism.

The reduction of CeO\(_2\) depends strongly on the ceria crystallite size, with the oxygen transfer and reduction enhanced by the grain boundaries and defects in small ceria particles \(^99\). In the same way the “cloud-shape” morphology, high surface area and small particle size of the TiO\(_2\) (A) studied, positively affects the reducibility and redox properties of TiO\(_2\). In studies by Gao et al. \(^41\), it was confirmed that highly dispersed surface titania species on silica exhibit completely different catalytic behaviour for methanol oxidation compared to bulk titania, due to redox products that are formed preferentially on the dispersed TiO\(_2\).

TPR data has proven to be useful in understanding the performance of oxidation catalysts and the relation between catalytic activity and the redox properties of the supported platinum catalysts. The oxidation properties of supported platinum catalysts mainly depend upon the inherent reducibility of the pure oxide support. The structure, morphology and crystallite size of titania plays an important role in facilitating oxygen transfer from the support to the platinum.

To complete the study of the supports’ redox properties, repeated TPR/O cycles, oxygen storage capacity and oxygen mobility experiments should be performed. In addition, propane oxidation tests over the bare supports would provide information as to what extent the metal oxide and mixed metal oxide supports, particularly TiO\(_2\) (A), contribute to catalyst performance.
4.2.4 The effect of the preparation method

It is widely recognised that specific preparation methods can allow control of the physicochemical properties of catalysts, therefore influencing their stability and catalytic activity.

From the results presented in this study and in agreement with previous work, it can be concluded that the dispersion of platinum particles over the support has a significant effect on catalyst properties and catalytic activity.

Since Forde *et al.* developed the chemical vapour impregnation (CVI), a simplified, facile, reproducible and easily controlled metal vapour deposition technique, it has been widely used within the group.

Supported platinum catalysts were prepared by chemical vapour impregnation using the same precursor, platinum (II) acetylacetonate.

Figure 4.47 shows propane conversion as a function of temperature for 1 wt. % Pt catalysts prepared by CVI and calcined at 400 °C for 5 hours in static air. Consistent with previous trends: propane conversion is clearly improved by increasing the support’s SiO₂ content and platinum exhibits better performance when supported on anatase-only TiO₂/TiO₂-SiO₂ than when supported on anatase-rutile TiO₂/TiO₂-SiO₂ respectively.

Of the supported 1 wt. % platinum catalysts studied, the propane oxidation activity follows the sequence:

\[
\text{Pt/TiO}_2 (\text{A-R}) < \text{Pt/Al}_2\text{O}_3-\text{SiO}_2 (10 \%) < \text{Pt/TiO}_2 (\text{A}) < \text{Pt/TiO}_2-\text{SiO}_2 (16 \%, \text{A-R}) < \text{Pt/TiO}_2-\text{SiO}_2 (10 \%, \text{A})
\]
Figure 4.47. Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h⁻¹, C₃H₈:O₂ = 1:50

Catalysts prepared by chemical vapour impregnation and calcined at 400 °C in static air

Figure 4.48 compares the T_{10} and T_{50} of supported platinum catalysts prepared by non-aqueous impregnation and chemical vapour impregnation. Catalyst activity is not generally enhanced with the chemical vapour impregnation preparation method, though the difference in T_{10} and T_{50} is within the error associated with reproducibility of the catalyst preparation shown in Figure 4.20.
Figure 4.48: Temperature in degrees Celsius for 10% propane conversion ($T_{10}$) and 50% propane conversion ($T_{50}$) over supported platinum catalysts (1 wt. % Pt) prepared by non-aqueous impregnation (IMP) and chemical vapour impregnation (CVI), calcined at 400 °C in static air.

To study the effect of the support on the structural and electronic properties of platinum catalysts prepared by CVI, XPS and TEM analysis were carried out.

From the deconvolution of the XPS curves in the Pt 4f binding energy region and quantitative analysis, the concentration of the surface platinum species, Pt$^0$ and PtO, was determined. Results are presented in Table 4.12. In accordance with the conclusions obtained for the catalysts prepared by non-aqueous impregnation, metallic platinum is favoured with increasing SiO$_2$ content and PtO is the predominant species for both TiO$_2$ (A) and TiO$_2$ (A-R) supports. The concentration of platinum species on the surface of the catalysts prepared by CVI is even higher than that of the catalysts prepared by non-aqueous impregnation, overcoming the total loading of 1 wt. %.
Table 4.12. XPS quantitative analysis and Pt 4f_{7/2} core binding energies of the supported platinum catalysts, prepared by CVI (numbers in parentheses are the relative concentration of the platinum species)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt⁰</th>
<th>Pt²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Pt/TiO₂ (A-R)</td>
<td>0.60</td>
<td>4.33</td>
<td>36.63</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO₂-SiO₂ (5 % mol Si, A-R)</td>
<td>0.37</td>
<td>2.86</td>
<td>49.67</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO₂-SiO₂ (16 % mol Si, A-R)</td>
<td>0.25</td>
<td>2.10</td>
<td>70.74</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO₂ (A)</td>
<td>0.19</td>
<td>1.51</td>
<td>36.66</td>
</tr>
<tr>
<td>1 wt. % Pt/TiO₂-SiO₂ (10 % mol Si, A)</td>
<td>0.24</td>
<td>1.98</td>
<td>24.69</td>
</tr>
<tr>
<td>1 wt. % Pt/Al₂O₃-SiO₂ (10 mol % Si)</td>
<td>1.46</td>
<td>12.93</td>
<td>49.02</td>
</tr>
</tbody>
</table>

Figures 4.49 and 4.50 show TEM micrographs of the supported platinum catalysts prepared by CVI. Platinum appears as dark particles in the HRTEM images and shows bright contrast in the STEM images. Although the number of images acquired was not sufficient to calculate accurate particle distributions, it can be concluded that increasing the SiO₂ content of the support enhances platinum dispersion.

Poorly dispersed platinum particles with a size of 5 – 10 nm are found on TiO₂ (A-R), Figure 4.49. a). This result diverges from that obtained by Forde et al.¹⁰⁰ who reported that when platinum was deposited onto TiO₂ P25 using CVI, a uniform distribution of metal nanoparticles with a reasonably narrow size distribution and mean particle size of 1.5 ± 0.3 nm was formed. It should be noted that the total platinum loading was higher than
that of the catalysts studied in the present thesis, 2.5 vs. 1 wt %, and that while in Forde’s work the prepared materials were reduced in 5 % H₂/Ar at 400 °C, the catalysts presented here were calcined in static air (at the same temperature). The higher platinum loading and reductive heat-treatment could explain the differences in dispersion of the metal nanoparticles between studies. On the other hand, well dispersed platinum particles, with mean particle size of 1.5 nm ± 0.1 nm and size range of 0 – 6 nm, are observed on the anatase-rutile TiO₂-SiO₂ support, Figure 4.49. b).

In agreement with the results obtained for supported platinum catalysts prepared by non-aqueous impregnation, some particles with mean size of 5 nm are detected on the TiO₂ (A), as shown in, Figure 4.49 c). No dark (HRTEM) or bright spots (STEM), attributed to platinum nanoparticles, appear in Figure 4.49 d) for platinum supported on the anatase-only TiO₂-SiO₂ support. Despite this, quantitative analysis by EDX confirms the presence of well dispersed platinum, accounting for 1 wt % of the total composition. It could be supposed then, that the platinum is homogeneously dispersed on the TiO₂-SiO₂ (A) support, mainly as PtO. Due to the small size, potentially subnanometric, and poor contrast it is not possible to observe the particles clearly at the resolution of the TEM instrument used.

Distinctively, the morphology in 1 wt. % Pt/Al₂O₃-SiO₂ prepared by CVI, shown in Figures 4.49 e) and f), varies from the equivalent catalyst prepared by non-aqueous impregnation (Figure 4.32). A large size window is characteristic of this support, with platinum particles and clusters in the range of 2 - 80 nm observed on the STEM micrographs in Figure 4.50. e) and f). For this support, the most distinctive feature is the appearance of large platinum crystallites with cubic morphology that were not found when the catalyst was prepared by impregnation.
Chapter 4                           Oxidation properties of supported platinum catalysts

Figure 4.49. Selected HRTEM of the supported platinum catalysts prepared by CVI
Figure 4.50. Selected STEM images of the supported platinum catalysts prepared by CVI
It can be concluded that, under the conditions studied, the oxidation properties of supported platinum catalysts are more greatly affected by the support material than by the preparation method. Previous studies reported that the change in catalytic activity with support materials comes from chemical modification of the catalysts’ properties, the oxidation resistance of the noble metal and also the dispersion, which is improved with support acidity/electrophilicity. Another factor is the hydrophobicity of the support. R. Armstrong (Cardiff Catalysis Institute, currently unpublished work) has shown that when preparing Cu/ZSM-5 catalysts by CVI, the hydrophobicity of the support plays an important role in enhancing dispersion and giving rise to smaller nanoparticles.

Meanwhile Al₂O₃ and TiO₂ P25 present a hydrophilic character caused by hydroxyl groups on the surface, amorphous SiO₂ possess a largely hydrophobic quality due to the absence of charged silanol groups on silica surfaces. Hence, increasing the SiO₂ content enhances the hydrophobic character of the support, the interaction with the hydrophobic precursor (platinum (II) acetylacetonate) and therefore, the platinum dispersion. Opposed to this, several studies showed that the addition of SiO₂ to TiO₂ films increases the acidity and also its hydrophilicity and photocatalytic activity.

Whilst Al₂O₃ and TiO₂ P25 present a hydrophilic character caused by hydroxyl groups on the surface, amorphous SiO₂ possess hydrophobic groups chemically bonded to the surface. Hence, increasing the SiO₂ content enhances the hydrophobic character of the support, the interaction with the hydrophobic precursor and therefore, the platinum dispersion. To measure the surface hydrophilicity/hydrophobicity of the support materials several suitable characterization methods could be used: surface adsorption, affinity coefficient and contact angle.
Despite some slight differences, the electronic and structural properties of the supported platinum catalysts are comparable for both preparation methods. This explains the limited difference in catalytic activity shown in Figure 4.48 for catalysts prepared by non-aqueous impregnation and CVI.

4.2.5 The effect of the platinum precursor

The two methods used to prepare the platinum catalysts studied in this thesis; non-aqueous impregnation and chemical vapour impregnation, require conditions and metal precursors that differ from those applied widely in industry. Using an aqueous solution is characteristic of the preparation methods commonly employed to produce supported metal catalysts.

In order to compare the performance of the catalysts presented here, with those prepared frequently in the catalysis industry, platinum was supported on TiO$_2$ (A-R) by aqueous-impregnation and incipient wetness impregnation using platinum (IV) nitrate as the precursor. Figure 4.51 shows propane conversion as a function of temperature for the supported platinum catalysts prepared by these methods and calcined at 400 °C for 5 hours in static air.
Chapter 4  
Oxidation properties of supported platinum catalysts

Figure 4.51. Total oxidation of propane over supported platinum catalysts

Reaction conditions: Flow reactor, GHSV = 50,000 h\(^{-1}\), \(C_3H_8\):\(O_2\) = 1:50

Catalysts prepared by aqueous impregnation (IMP) and incipient wetness impregnation (IWI)
using \(\text{Pt(NO}_3\text{)}_4\) as precursor and calcined at 400 \(^\circ\)C in static air

The performance of the Pt/TiO\(_2\) (A-R) catalysts is comparable for the three preparation methods.

The \(T_{10}\) and \(T_{50}\) of the Pt/TiO\(_2\) (A-R) catalyst prepared by different methods; aqueous and non-aqueous, are shown in Figure 4.52. Catalytic activity is equivalent across the group and differences in performance are within the error shown in Figure 4.20.
Chapter 4  Oxidation properties of supported platinum catalysts

Figure 4.52. Temperature in degrees Celsius for 10 % propane conversion ($T_{10}$) and 50 % propane conversion ($T_{50}$) over 1 wt. % Pt supported on TiO$_2$ (ANATASE-RUTILE) prepared by different methods and calcined at 400 ºC in static air

XPS was used to investigate the oxidation state of the surface platinum species and their relative populations. Spectra in the Pt 4f binding energy are shown in Figure 4.53. They are fitted with two pairs of Gaussian-Lorenzian curves with Pt 4f$_{7/2}$ binding energies between 71.8 and 72.0 eV and between 73.5 and 74.9 eV. The assignment of these is not completely clear. Based on XPS analysis of reference materials and previous studies$^{111, 112}$, bulk metallic platinum appears at 71.2 eV, platinum (II) oxide appears at 72.5 eV and platinum (IV) oxide at 74.5 eV. Hence, for the 1 wt. % Pt/TiO$_2$ (A-R) catalysts prepared by aqueous and incipient wetness impregnations, the XPS spectral lines are shifted by $\approx 0.6 – 1$ eV to binding energies between the characteristic values of metal and metal oxides. This shift is more pronounced for the aqueous impregnation than for the incipient wetness impregnation, where the volume of water during the preparation is drastically reduced, approximately equal to the pore volume of the support. The Pt 4f$_{7/2}$ binding energy of the first pair of curves is relatively high for Pt$^0$ and as explained previously, a strong platinum-titania interaction could lead to a shift towards lower binding energies. Accordingly, it has
been proposed that platinum is in an oxidised form and that the peak at 71.8 – 72.0 eV corresponds to PtO and that at 73.5 – 73.9 eV to PtO₂. This should be considered carefully, as previous studies have confirmed that platinum supported on titania at a pH of 5-7, contains both metallic platinum (70.8 eV) and PtO (72.2 eV) ¹¹³. In addition, various investigations ¹¹⁴ ¹¹⁵ have shown that variations in platinum particle size could also shift the binding energy and thus, the position of the lines. It was found that for platinum supported on TiO₂, SiO₂ and Al₂O₃, the Pt 4f₇/₂ line is shifted towards higher binding energies, which corresponds to a decrease in platinum particle size.

![Figure 4.53. XPS spectra in the Pt 4f binding energy region of the 1 wt. % Pt/TiO₂ (A-R) prepared by: a) Non-aqueous impregnation   b) Aqueous Impregnation   c) Incipient Wetness Impregnation](image)

Figure 4.53. XPS spectra in the Pt 4f binding energy region of the 1 wt. % Pt/TiO₂ (A-R) prepared by: a) Non-aqueous impregnation   b) Aqueous Impregnation   c) Incipient Wetness Impregnation
Binding energy values and platinum species concentrations for 1 wt. % Pt/TiO$_2$ (A-R) prepared by non-aqueous and aqueous methods are summarised in Table 4.13. Both PtO and PtO$_2$ are present for the catalyst prepared by the three aqueous preparation methods. Of these, the concentration of PtO is higher ($\approx 78\%$) when platinum is supported on TiO$_2$ (A) by IWI, a preparation method which keeps the volume of water to a minimum. This indicates that platinum species in a higher oxidation state are favoured when a high concentration of water is present during the preparation. Note that although the surface platinum concentration overcomes the total loading of 1 wt. %, it is lower than that of the same catalyst prepared by a non-aqueous method.

**Table 4.13.** XPS quantitative analysis and Pt 4f$_{7/2}$ core binding energies of the Pt/TiO$_2$ (A-R) catalyst prepared by different methods

(numbers in parentheses are the relative concentration of the platinum species)

<table>
<thead>
<tr>
<th>1 wt. % Pt/TiO$_2$ (A-R)</th>
<th>Pt</th>
<th>Pt$^0$</th>
<th>Pt$^{2+}$</th>
<th>Pt$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Wt %</td>
<td>eV (%)</td>
<td>eV (%)</td>
</tr>
<tr>
<td>CVI</td>
<td>0.60</td>
<td>4.33</td>
<td>71.6 (36.6)</td>
<td>72.6 (63.4)</td>
</tr>
<tr>
<td>NON AQ. IMP</td>
<td>0.42</td>
<td>3.07</td>
<td>71.5 (26.7)</td>
<td>73.0 (73.3)</td>
</tr>
<tr>
<td>AQ. IMP</td>
<td>0.24</td>
<td>1.82</td>
<td>0</td>
<td>71.8 (54.4)</td>
</tr>
<tr>
<td>IWI</td>
<td>0.32</td>
<td>2.39</td>
<td>0</td>
<td>72.0 (78.1)</td>
</tr>
<tr>
<td>IWI (modified)</td>
<td>0.38</td>
<td>2.83</td>
<td>0</td>
<td>72.1 (58.5)</td>
</tr>
</tbody>
</table>

HRTEM images in Figure 4.54. and 4.55 indicate that the size of the platinum particles decreases markedly when 1 wt. % Pt/TiO$_2$ (A-R) is prepared by aqueous and incipient wetness impregnation using Pt(NO$_3$)$_4$. 

- 168 -
Figure 4.54. Selected HRTEM images and particle size distribution of the Pt/TiO$_2$ (A-R) catalyst prepared by aqueous impregnation.
Figure 4.55. Selected HRTEM images and particle size distribution of 1 wt. % Pt/TiO$_2$ (A-R) prepared by incipient wetness impregnation.
From the particle size distribution, a mean platinum particle size of 1.1 ± 0.6 is obtained for both aqueous preparation methods, this differs considerably from the poorly dispersed, large platinum particles found when the same catalyst was prepared by aqueous impregnation or chemical vapour impregnation. Despite the small particle size, platinum is not highly dispersed over the support’s surface, but appears concentrated in certain regions of the titania.

Based on the results, it can be concluded that the metal precursor has a significant effect on the electronic and structural properties of platinum supported on TiO₂ (A-R), but not on the catalytic activity for propane oxidation under an oxidising atmosphere. It should be mentioned that not only the precursor but also the solvent was different, hence, this study compares platinum catalysts prepared via a non-ionic system, Pt(acac)₂ in toluene, with those prepared via an ionic system, Pt(NO₃)₄ in H₂O.

Platinum dispersion is enhanced when the catalyst is prepared in an aqueous environment, which gives rise to small nanoparticles. This could be explained in terms of the hydrophilicity of the system; as the hydrophilic platinum precursor will have a stronger interaction with the support due to the hydrophilic character of the titania. Besides, the binding energy of the Pt 4f⁷/₂ in the XPS spectrum for the catalysts prepared in an aqueous solution is shifted towards higher values, lying between the characteristic values of bulk metallic platinum and its oxides. There are two possible explanations for this shift: (i) a strong metal support interaction will result in charge transfer from the support, modifying its electronic surface species and thus, the binding energy position and (ii) nanoparticle size can also affect the position of the peaks. Despite differences in these properties of the catalysts, no significant variation in catalytic performance is observed, probably because platinum is in an oxidised state.
4.3 Oxidation of nitric oxide to nitrogen dioxide

4.3.1 The effect of the support

The oxidation of nitric oxide (NO) to nitrogen dioxide (NO₂) on supported platinum catalysts under lean-burn conditions plays an important role in Diesel exhaust aftertreatment technologies\textsuperscript{116 117 118 119 120}. The Diesel Particulate Filter (DPF) requires NO₂ for the oxidation of soot; Selective Catalytic Reduction (SCR) is promoted in a mixture of NO/NO₂ and the oxidation of NO is an essential first step of the storage mechanism for NOₓ storage catalysts.

It is known that the activity of platinum catalysts towards NO oxidation is strongly influenced by the support\textsuperscript{121 122 123}. Hence, the effect of the support on the oxidation of NO to NO₂ in the temperature range between 100 and 450 °C was assessed using the same platinum catalysts as tested for total the oxidation of propane. Conversion profiles for NO are presented in Figure 4.56. The main product for NO oxidation was NO₂ and formation of other nitrogen-containing products, such as N₂O, was negligible. As reported previously\textsuperscript{124 125}, the catalytic conversion of NO to NO₂ is kinetically-controlled at low temperatures (T < 350 °C) and operates under equilibrium control at higher temperatures (T > 350 °C).

After reaching thermodynamic equilibrium, the conversion of NO to NO₂ follows the thermodynamic equilibrium curve.

All the catalysts present the same conversion profile, with NO conversion and thus, the concentration of NO₂, reaching a maximum at 350 °C. Conversion then decreases at higher temperature, as the reaction is limited by the thermodynamic equilibrium.
The activities of the 1 wt. % Pt catalysts for NO oxidation are significantly dependent on the supports. For the supported platinum catalysts studied, the activity order is:

\[
1 \text{ wt. \% } \text{Pt/TiO}_2\text{-SiO}_2 (A) \quad < \quad 1 \text{ wt. \% } \text{Pt/Al}_2\text{O}_3\text{-SiO}_2 (10 \text{ \% mol Si}) \quad < \quad 1 \text{ wt. \% } \text{Pt/TiO}_2 (A-R) \\
< \quad 1 \text{ wt. \% } \text{Pt/TiO}_2 (A) \quad < \quad 2 \text{ wt. \% } \text{Pt/\gamma-Al}_2\text{O}_3 \quad \approx \quad 1 \text{ wt. \% } \text{Pt/TiO}_2\text{-SiO}_2 (16 \text{ \%, A-R})
\]
Figure 4.57 shows the degree of NO conversion observed over the supported platinum catalysts at 350 °C. 1 wt. % Pt/TiO₂-SiO₂ (16 % mol Si, A-R) (orange solid line in Figure 4.56) is the most active among the supported platinum catalysts studied with 48 % NO conversion to NO₂ shown at 350 °C. Its performance is comparable with that observed for a typical commercial oxidation catalyst, 2 wt. % Pt/Al₂O₃ (grey dashed line in Figure 4.56.) which presents 46 % conversion of NO to NO₂ at 350 °C.

In agreement with those results obtained for the total oxidation of propane, for the anatase-rutile based catalysts, catalytic activity for NO oxidation was promoted by addition of SiO₂ to the support. While 1 wt. % Pt/TiO₂ (A-R) gives 28 % conversion of NO to NO₂, 1 wt. % Pt/TiO₂-SiO₂ (16% mol Si, A-R) gives 48 % conversion. In fact, oxidation activity is almost doubled when the SiO₂ content of the support reaches 16 mol %.

Figure 4.57. NO conversion in % for oxidation of NO to NO₂ over supported platinum catalysts at 350 °C

Reaction conditions: Flow reactor, GHSV = 50,000 h⁻¹, NO:O₂ = 1:75
Contrary to earlier data for total oxidation of propane, addition of SiO$_2$ to the Al$_2$O$_3$ support does not result in an improvement in NO oxidation activity, with 1 wt. % Pt/Al$_2$O$_3$-SiO$_2$ (10 %) presenting 26 % conversion at 350 °C. This is equal to that obtained for silica-free 1 wt. % Pt/Al$_2$O$_3$.

Once again, those catalysts obtained from the impregnation of platinum on anatase-only based supports, Pt/TiO$_2$-(SiO$_2$) (A), perform differently for NO oxidation when compared with their analogous anatase-rutile based catalysts, Pt/TiO$_2$-(SiO$_2$) (A-R). 1 wt. % Pt/TiO$_2$ (A-R) gives 34 % NO conversion at 350 °C and 1 wt. % Pt/TiO$_2$ (A) gives only 28 % conversion. Hence, platinum supported on anatase-only supports is more active than that supported on biphase anatase-rutile TiO$_2$ containing supports, although the difference in activity is not as significant as that observed for the total oxidation of propane.

More interestingly, 1 wt. % Pt/TiO$_2$-SiO$_2$ (10% mol Si, A) presents the lowest oxidation activity among the catalysts studied, with 20 % NO conversion at 350 °C. Whilst addition of SiO$_2$ to the TiO$_2$ (A) support had no effect upon propane oxidation activity, this support modification led to a 41 % decrease in NO conversion at 350 °C.

Many investigations have ascribed the oxidation activity of supported platinum catalysts to the presence of metallic platinum\textsuperscript{122 126}, and it is well known that oxygen poisoning of the catalyst inhibits NO oxidation and that conversion drops considerably when platinum is oxidised\textsuperscript{123 127 128 129 130 131 132 133}. As illustrated in Figure 4.58, there is a linear relationship between oxidative NO conversion and the concentration of metallic platinum present in the catalyst at the beginning of the experiment. In general, an increase in the SiO$_2$ content of the support enhances the oxidation-resistance of platinum.
The structure sensitive nature of NO oxidation has been investigated in previous work. It has been reported that Pt particle size influences the rate of NO oxidation and that when the dispersion is decreased, giving larger particles, the conversion of NO to NO\(_2\) is promoted. This increase in activity with particle size is ascribed to the fact that small platinum particles are easier to oxidise than larger ones. Boubnov et al. studied structure-performance relationships for the catalytic oxidation of CO and NO over Pt/Al\(_2\)O\(_3\) catalysts. They found that CO oxidation is size sensitive, with optimal conversion shown with
platinum particles of 2-3 nm. Lower conversion was observed with particles either smaller or larger than this. For NO oxidation, conversion increases with particle size, indicating that particles larger than ca. 5 nm possess a greater population of active sites for NO oxidation.

Based on the results presented in this thesis it is not possible to reach a clear conclusion as to whether NO oxidation is a structure sensitive reaction, under the conditions studied. Figure 4.27 shows that 1 wt. % Pt/TiO$_2$ (A-R) contains poorly dispersed, large platinum particles, and Figures 4.28 and 4.29 show highly dispersed small nanoparticles (2-5 nm) on 1 wt. % Pt/TiO$_2$-SiO$_2$ (16% mol Si, A-R). Platinum dispersion is enhanced with the SiO$_2$ content of the support, as is NO conversion, potentially due to the high concentration of metallic platinum on this catalyst. Platinum supported on the anatase-based mixed support, 1 wt. % Pt/TiO$_2$-SiO$_2$ (10% mol Si, A), is an interesting case study. Its performance for NO oxidation is poor (green line in Figure 4.56), which could be explained in terms of the oxidation state of the platinum, which is shown in Figure 4.58 to predominately present as its oxidised form (PtO). In addition, TEM analysis shown in Figure 4.31 confirms the presence of small platinum nanoparticles; 1 nm and subnanometer, on the TiO$_2$-SiO$_2$ (10% mol Si, A) support. The smaller size of the nanoparticles could be leading to the low conversion of this catalyst for NO oxidation but not for total oxidation of propane. The NO/NO$_2$/O$_2$ mixture could be more effective in oxidising the catalyst than the O$_2$, as the formation of surface oxides from oxygen is kinetically limited. Hence, under the experimental conditions used for NO oxidation tests (0.1 % NO, 7.5 % O$_2$, He as balance) the small platinum particles are likely to be readily oxidised.

The existence of a strong relationship between the redox nature and activity of different platinum surface sites has been confirmed. The activity of a DOC changes during the NO
oxidation reaction; NO\textsubscript{2}, because of its highly oxidising nature, promotes the formation of platinum oxides which thereby decreases catalyst activity. The formation of surface platinum oxide is reversible, with PtO reduced to Pt\textsuperscript{0} above 350 \(^\circ\)C due to thermal decay and also by NO at low temperatures\textsuperscript{137}.

Initial studies to determine the performance of the most active catalyst, 1 wt. \% Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (16% mol Si, A-R), under real working conditions were carried out. Quantitative analysis obtained from XPS spectra of the catalyst before and after NO oxidation is presented Table 4.14. The concentration of metallic platinum does not decrease after reaction indicating that there is no irreversible formation of PtO during the NO oxidation reaction. Based on its performance in total oxidation of propane, it could be suggested that this catalyst will perform well under the transient temperature conditions characteristic of exhaust aftertreatment.

\textbf{Table 4.14.} Quantitative analysis of the supported platinum catalysts, before and after reaction, obtained from the XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt\textsuperscript{0}</th>
<th>Pt\textsuperscript{2+}</th>
<th>Pt\textsuperscript{4+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Pt/TiO\textsubscript{2}-SiO\textsubscript{2} (16 % mol Si, A-R)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.23</td>
<td>1.93</td>
<td>67.49</td>
<td>32.52</td>
</tr>
<tr>
<td>After NO ox.</td>
<td>0.15</td>
<td>1.29</td>
<td>71.26</td>
<td>28.74</td>
</tr>
</tbody>
</table>

In order to study the activity-loss of supported platinum catalysts under strong oxidising conditions and assess the structure sensitive nature of the reaction, hysteresis experiments with characterisation before and after reaction should be performed.
4.3.2 In situ DRIFTS studies

To identify reaction intermediates at the catalyst surface, an in-situ FTIR study of NO oxidation over the supported platinum catalysts was performed.

Diffuse reflectance infrared fourier transform (DRIFT) spectra of surface adsorbed species on Pt catalysts under NO + O$_2$, and their evolution with temperature from 30 °C to 450 °C, are shown in Figure 4.59. A baseline spectrum was acquired prior to introducing the reactant gas mixture, which contained 0.45 % NO and 10 % O$_2$, in N$_2$ as diluent.

The adsorbed species on all catalysts are mainly nitrates and nitrites. It is clearly shown in Figure 4.59 that adsorption of NO leads to formation of nitrite species (NO$_2^-$) which are further oxidised to form nitrate species (NO$_3^-$). These reactions occur simultaneously, and the intensity of these bands decreases considerably at temperatures above 300 °C. Although the work presented here is only qualitative, as quantitative analysis requires response factors based on normalized areas determined using chemisorption, it is possible to analyse and compare the data in terms of relative peaks intensities.

1 wt. % Pt/TiO$_2$ (A-R) shows chelating nitrate at 1580 cm$^{-1}$, and bridging nitrate at 1610 cm$^{-1}$. There is also a broad peak centred at 1490 cm$^{-1}$ due to linear nitrite. In addition, bridging nitrites appear at 1250 cm$^{-1}$ and 1290 cm$^{-1}$ respectively. The almost negligible peak at 1790-1810 cm$^{-1}$ can be attributed to linear and gaseous NO. Increasing the temperature to 400 °C results in a gradual decrease in the intensity of bands corresponding to nitrates (chelating and bridging) and nitrites (linear and bridging). At 200 °C, a low intensity band at 1550 cm$^{-1}$ is observed, which can be assigned to monodentate nitrate. This disappears at 400 °C. The spectrum of NO adsorbed on 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R) shows the peaks at 1580 cm$^{-1}$ and 1610 cm$^{-1}$
previously assigned to chelating and bridging nitrate. Increasing the temperature leads the bands to diminish, disappearing entirely at 300 °C.

![DRIFTS spectra](image)

**Figure 4.59** DRIFTS of NO adsorption at 30 - 450 °C on supported platinum catalysts under NO + O₂ (0.5 % NO, 10 % O₂, N₂ balance)

The DRIFT spectra for 1 wt. % Pt/TiO₂ (A) are similar to those obtained for the anatase-rutile based catalyst, 1 wt. % Pt/TiO₂ (A-R). Peaks previously assigned to nitrate (chelating, bridging and monodentate) and nitrite (bridging) are observed, as is a new spectral band at 1350-1360 cm⁻¹ which corresponds to free nitrate ion, NO₃⁻. The relative intensity of this NO₃⁻ peak increases with temperature, and is still present at 450 °C. This implies that at high temperatures, as reported previously with ceria based catalysts, the TiO₂ (A)
provides active oxygen for the oxidation of nitrites to nitrates and the transformation of different nitrate species from lower stability species to higher ones (from bidentate to monodentate and then to ionic nitrates). Hence, as discussed earlier in this chapter (Figure 4.46), anatase phase titania, TiO$_2$ (A), possesses highly reactive oxygen species that, in this case, promote the formation of ionic nitrate on the surface but not the oxidation of NO to NO$_2$.

In the case of 1 wt. % Pt/TiO$_2$-SiO$_2$ (10 % mol Si, A), DRIFT spectra are similar to those obtained for the anatase-rutile analogue, 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R). Distinctively, note that the peaks assigned to chelating and bridging nitrate (1580 cm$^{-1}$ and 1610 cm$^{-1}$) are still present at temperatures above 250 $^\circ$C. Also, a weak peak that corresponds to free nitrate ion, NO$_3^-$, is observed at high temperature.

The interpretation of DRIFTS data is not fully understood but the dramatic difference in the relative intensities is clear evidence that NO$_x$ adsorption is limited by the oxidation of NO to NO$_2$. A strong chemisorption of nitrates and nitrites, which disfavour desorption due to their high thermal stability, could be related with a decrease in activity for NO oxidation. In this way the high NO oxidation activity of 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R) correlates with the fact that nitrate and nitrite bands are much weaker and almost absent above 150 $^\circ$C.

Further DRIFTS experiments and the total uptake of NO$_x$ should be measured in order to find routes involved in the NO$_x$ adsorption and NO oxidation and therefore, propose a possible mechanism to explain the differences in the activity of these catalysts.
4.4 Conclusions

The oxidation properties of supported platinum catalysts and the effect of the support materials, in particular TiO$_2$-SiO$_2$ mixed metal oxides, were assessed.

It is found that the activity of supported platinum catalysts for total oxidation of propane and oxidation of NO to NO$_2$ is greatly affected by the support material. In general, their performance is enhanced by addition of SiO$_2$ to the TiO$_2$ support.

The order of activity for the supported 1 wt. % Pt catalysts, prepared by non-aqueous impregnation and calcined at 400 °C in static air, follows the sequence:

$\text{Pt/TiO}_2$ (A-R) $<$ $\text{Pt/TiO}_2$-SiO$_2$ (5 %, A-R) $\approx$ $\text{Pt/Al}_2\text{O}_3$-SiO$_2$ (10 %) $<$ $\text{Pt/TiO}_2$ (A)

$<$ $\text{Pt/TiO}_2$-SiO$_2$ (16 %, A-R) $\approx$ $\text{Pt/TiO}_2$-SiO$_2$ (10 %, A) for total oxidation of propane and

$\text{Pt/TiO}_2$-SiO$_2$ (10%, A) $<$ $\text{Pt/Al}_2\text{O}_3$-SiO$_2$ (10 %) $<$ $\text{Pt/TiO}_2$ (A-R) $<$ $\text{Pt/TiO}_2$ (A)

$<$ $\text{Pt/TiO}_2$-SiO$_2$ (5 %, A-R) $<$ $\text{Pt/TiO}_2$-SiO$_2$ (16 %, A-R) for oxidation of NO to NO$_2$

Among the oxidation platinum catalysts studied, 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R) is the most active. It is stable and gives high conversion for both oxidation reactions studied. Platinum is predominantly present in the metallic state and is highly dispersed over the support in the form of small (2-5 nm) spherical nanoparticles. No deactivation under steady and transient conditions is observed.

Evaluation of how the calcination atmosphere, preparation method and platinum precursor effect the catalytic activity was also performed. It can be concluded that these experimental
variables do not significantly affect catalytic activity and that it is the nature of the support used that led to variations in catalyst performance.

The activity of the platinum catalysts depends strongly on oxidation state, with platinum in metallic state being most active. However, it is not only the platinum oxidation state but the combination of several factors including metal dispersion, surface area, morphology and phase composition of the support that explains the variations in catalytic activity.

Addition of SiO$_2$ to TiO$_2$ supports results in an increase in support surface area and improved dispersion of platinum nanoparticles. Moreover, anatase-only TiO$_2$ presents a higher surface area than biphase anatase-rutile TiO$_2$ (A-R).

Platinum catalysts prepared using anatase-based supports, TiO$_2$-(SiO$_2$) (A), present high performance for total oxidation of propane but not for the oxidation of NO. These supports not only possess a high surface area but a “cloud shape” morphology with highly dispersed small TiO$_2$ crystallites. Morphology and phase composition play an active role in the redox properties of the support and its interaction with the metal particles.

It is widely recognised that platinum in metallic state is the most active species for the oxidation of hydrocarbons and NO with O$_2$. Results presented in this chapter show that there is a linear relationship between the oxidation state of platinum and catalytic activity for NO oxidation, with conversion clearly higher with an increasing presence of Pt$^0$. However, for the total oxidation of propane this relationship is not as unequivocal. While performance of anatase-rutile based catalysts, Pt/TiO$_2$-(SiO$_2$) (A-R), is enhanced with an increasing concentration of Pt$^0$, comparable activity is observed for anatase based catalysts, Pt/TiO$_2$-(SiO$_2$) (A), in which platinum exists predominantly as PtO.
Many studies have reported the structure sensitive nature of these oxidation reactions, with metal dispersion and particle size influencing conversion, as small platinum particles are more readily oxidised, thereby resulting in decreased catalyst performance. Contrarily, addition of SiO$_2$ to the TiO$_2$ support improves not only the platinum dispersion but also the metal oxidation resistance and thus small nanoparticles typical to the TiO$_2$-SiO$_2$ supports are less readily oxidised than those particles on the TiO$_2$ supports, which are generally larger. To assess the real effect of dispersion on catalytic activity, the oxidation activities of platinum catalysts which differ in metal dispersion and particle size, but are supported on the same metal oxide, should be evaluated.

Metal-support interactions are of great importance to understand the observed differences in catalytic activity. Through these interactions the support modifies the electronic and structural properties of the metal, creating unique active sites at the metal-support interface and even performing as an active participant in the reaction. Many examples covered during this chapter have demonstrated the relevance of such metal-support interactions. The most remarkable of these is that the extraordinary activity of 1 wt. % Pt/TiO$_2$(A) is attributed to highly reactive oxygen species within the titania support, which promote the total oxidation of propane but not the oxidation of NO to NO$_2$.

Completion of this work will require further characterisation studies to fully understand the catalytic systems, and stability tests under realistic conditions for those promising catalysts found.
4.5 References


Chapter 4  Oxidation properties of supported platinum catalysts


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Chapter 4  Oxidation properties of supported platinum catalysts


**NO\textsubscript{x} storage on metal-exchanged zeolites**

5

5.1 Introduction

Nitrogen oxides NO\textsubscript{x} (NO + NO\textsubscript{2}) which are present in exhaust emissions are a major pollutant of the atmosphere, with a direct harmful effect upon the environment and human health. NO\textsubscript{x} are a major source of acid rain, photochemical smog and ozone depletion. Accordingly, more stringent emission standards have been introduced to lower the concentrations of these pollutants.

NO\textsubscript{x} abatement is crucial, especially in diesel engines where controlling NO\textsubscript{x} is extremely difficult as oxygen is always in excess. There are two ways of converting NO\textsubscript{x} to N\textsubscript{2} under lean conditions\textsuperscript{1} (i) NO\textsubscript{x} storage-reduction (NSR), where the engine is operated in a mixed lean/rich operation mode and (ii) selective catalytic reduction (SCR) with ammonia (NH\textsubscript{3}) or hydrocarbons (HC), where reduction of NO\textsubscript{x} is achieved even in large excess of oxygen.

As introduced earlier in this thesis, the objective of this chapter is to find an adsorption catalyst that stores NO\textsubscript{x} at low temperature (T < 250 °C) and releases it at high temperatures. Investigations of NO\textsubscript{x} adsorption-desorption on metal-exchanged zeolites have been reported in a large number of publications\textsuperscript{2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24}, however, further studies are needed to succeed in finding a catalytic system sufficiently active, selective and stable. The overall aim is to find an optimum zeolite-based system for NO\textsubscript{x} storage. Preparation and evaluation of a variety of metal-exchanged zeolites with different compositions and structures was performed to study the effect of the silicon/aluminium ratio, internal channels and inclusion of base and precious metals.
5.2 NO$_x$ adsorption-desorption studies

The first part of this study was the designing, construction and commissioning of a flow reactor to evaluate NO$_x$ storage over different catalytic systems. A detailed description of the experimental procedure is given in Chapter 3, Section 3.3.2.1. In summary, quantitative analysis of NO$_x$ adsorption-desorption processes was carried out by continuously monitoring the effluent gas composition using a FTIR spectrometer.

Nitrogen oxides (NO$_x$) are a mixture containing mostly nitrogen monoxide (NO) and between 5 and 10 % of nitrogen dioxide (NO$_2$). Hence, 1000 ppm of NO balanced in Helium (He) was used as a model flue gas and He (100 %) was used as the purge gas.

Figure 5.1. Typical concentration profile over the zeolite-based catalysts during pretreatment

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, He
Chapter 5 \textit{NO$_x$ storage on metal-exchanged zeolites}

The microporous structure of the zeolites makes them adsorbents with a high affinity for water. Before adsorption-desorption experiments, zeolites catalysts were pretreated to remove water and other species from the surface. The pretreatment profile for Cu/ZSM-5 (30) is shown in Figure 5.1. Analysis of the gas effluent shows that desorption of H$_2$O, CO$_2$ and CO occurs up to 500 °C during pretreatment in He. H$_2$O presents two desorption peaks: at room temperature and 100 °C, corresponding to free and surface adsorbed water. CO$_2$ desorption occurs at room temperature, 250 °C and 400 °C. CO desorption is also observed at temperatures above 250 °C.

The storage capacity of zeolite-based systems was investigated using 0.1 % NO (1000 ppm) in He. The combined adsorption-desorption profile for Cu/ZSM-5 (30) is shown in Figure 5.2. The first 15 minutes correspond to the adsorption of NO at 30 °C. Initially, the concentration of NO decreases considerably, indicating that NO is being adsorbed by the catalyst. The NO concentration then slowly increases, tending towards the NO inlet concentration of $\approx$ 1000 ppm. After 10 minutes the catalyst becomes saturated, with the NO concentration reaching steady state. During the storage period CO$_2$ is desorbed. This has been reported in previous studies and corresponds to decomposition of carbonates, which are unstable in the presence of NO/O$_2$.

After 15 minutes of adsorption, the catalyst bed is bypassed and the gas feed is switched to He (100 %) so the FTIR cell is flushed until an NO concentration of 0 ppm is observed. NO is desorbed at 30 °C (15 minutes) in He followed by a temperature programmed desorption (TPD) from 30 °C to 500 °C (10 °C min$^{-1}$). NO, H$_2$O, CO$_2$ and a low concentration of CO are detected during the desorption. It should be noted that even if a zeolite catalyst has been pretreated to remove surface H$_2$O, it rehydrates during the storage process as the gas feed is not completely dry. NO$_x$ is desorbed as NO, N$_2$O is not detected
and trace amounts of NO$_2$ are identified. NO desorption peaks at 30 °C and 100 °C correspond to physisorption and weak chemisorption of NO at the surface.

![Temperature in °C (dashed line) (---) H$_2$O v. % (---) CO$_2$ v. % (---) CO ppm (---) N$_2$O ppm (---) NO ppm (---) NO$_2$ ppm](image)

**Figure 5.2.** Typical concentration profile over the zeolite-based catalysts during NO adsorption at 30 °C and TPD with He up to 500 °C.

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO in He

Since the inlet concentration of NO is quantified, the amount of adsorbed/desorbed NO$_x$ can be quantified by integration of the area under the corresponding curves and correlation with the response factor. Figure 5.3 shows the same adsorption-desorption experiment, for Cu/ZSM-5 (30), including only the NO$_x$ profiles and the integrated areas.
Temperature in °C (dashed line) --- N$_2$O ppm (---) NO ppm (----) NO$_2$ ppm

**Figure 5.3.** Typical NO$_x$ concentration profile over the zeolite-based catalysts during NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO in He

Results are expressed as mg of NO$_x$ (NO, NO$_2$ or NO$_3$) per g of catalyst. The standard deviation, calculated by repeating the same adsorption/desorption experiment three times, is found to be ± 0.1 mg/g.

It was not possible to obtain an accurate nitrogen balance. The shaded regions in Figure 5.3 represent total adsorbed and desorbed NO. Both areas should be equal or, if as reported previously in the literature, irreversible adsorption occurs: NO desorbed should be less than NO adsorbed. Contrarily, the total amount of NO desorbed (3.7 mg NO$_x$/g catalyst)
Chapter 5

NO\textsubscript{x} storage on metal-exchanged zeolites

exceeds the total amount of NO adsorbed (2.6 mg NO\textsubscript{x}/g catalyst). This can be explained according to the following two points:

i) The amount of NO calculated from the area under the desorption peak at 30 °C is the result of physisorbed NO but also residual NO that is confined in the reactor tube. Nevertheless, adsorption/desorption experiments performed over a blank adsorbent bed confirm that the residual NO only accounts for a maximum of 0.15 mg NO\textsubscript{x}/g catalyst, this amount is much lower than the difference between NO adsorbed and desorbed obtained (1.1 mg NO\textsubscript{x}/g catalyst).

ii) The key limitation to consider is that the total amount of NO adsorbed is underestimated. The FTIR cell volume is 0.4 L and the gas flow used is 200 mL/min, thus, a few minutes are needed to reach a constant NO concentration. NO\textsubscript{x} adsorption occurs rapidly and is hindered by the volume of NO already present in the FTIR cell.

Based on these considerations, while NO\textsubscript{x} adsorption results are valid in comparing the adsorption capacity of different catalysts, the quantification is not completely accurate, as adsorption values are underestimated. On the other hand, the total amount of NO\textsubscript{x} desorbed is considered to be precise as the cell is flushed with He prior to desorption.

Due to the nature of the FTIR detector, analysis of N\textsubscript{2} is not possible. However, reduction of NO\textsubscript{x} to N\textsubscript{2} under these conditions is unlikely.

No NO\textsubscript{x} desorption is observed above 100 °C. It is widely known that NO is more weakly adsorbed on zeolites than NO\textsubscript{2} and that the oxidation of NO to NO\textsubscript{2} is necessary to improve storage capacity
\textsuperscript{10, 15, 25, 26}. Oxidation of NO to NO\textsubscript{2} under the oxygen- free gas feed conditions studied does not occur. Hence, the storage capacities of the zeolite-based
systems were also evaluated in the presence of excess oxygen: 0.1 % NO, 7.5 % O\textsubscript{2} balanced in He. The combined adsorption-desorption profile for Cu/ZSM-5 (30) is shown in Figure 5.4.

After pretreatment at 500 °C under He, the zeolite-based catalyst is exposed to the gas mixture of model flue and oxygen (0.1 % NO, 7.5 % O\textsubscript{2} balanced in He) at 30 °C for 30 minutes. Concordant with the adsorption profile in the absence of oxygen (Figure 5.3), the concentration of NO decreases considerably early in the adsorption period, indicating that NO is being adsorbed by the catalyst. After 5 minutes of adsorption the NO concentration begins to gradually increase. In contrast to the profile obtained in the absence of oxygen (Figure 5.3), a constant concentration of NO is not reached after 20 minutes and the NO concentration does not equal the inlet NO concentration. In the presence of oxygen, not only NO but also NO\textsubscript{2} adsorption occurs. During the first 10 minutes of the adsorption period, the detected outlet concentration of NO\textsubscript{2} is ca. 40 ppm lower than the inlet NO\textsubscript{2} concentration. After catalyst saturation, the NO\textsubscript{2} concentration increases until it exceeds the inlet value. After 30 minutes of adsorption, the outlet NO concentration (≈ 400 ppm) is lower than the inlet NO concentration (≈ 900 ppm) and the outlet concentration of NO\textsubscript{2} (≈ 600 ppm) is much higher than the inlet NO\textsubscript{2} concentration (≈ 50 ppm), the N\textsubscript{2}O concentration does not change (≈ 1.8 ppm) and the N\textsubscript{2} balance is 100 % ± 11 %. This indicates that NO is oxidised to NO\textsubscript{2} by the catalyst. Again, the presence of CO\textsubscript{2} confirms carbonate decomposition during the adsorption of NO and NO\textsubscript{2}.

After 30 minutes of adsorption, the NO and O\textsubscript{2} feeds are interrupted and the FTIR cell is flushed with He (100 %) until the NO\textsubscript{x} concentration reaches a stable 0 ppm. Following a purge with He (15 minutes, 30 °C) a TPD is carried out, from 30 °C to 500 °C. NO, NO\textsubscript{2}, H\textsubscript{2}O, CO\textsubscript{2} and a low concentration of CO are detected during the TPD. Desorption profiles for NO, H\textsubscript{2}O and CO\textsubscript{2} are similar to those obtained in the absence of oxygen (Figure 5.2).
NO desorption peaks at 30 °C and 100 °C correspond to physisorbed and weakly chemisorbed NO on the surface. Distinctively, NO\textsubscript{x} desorption occurs mainly in the form of NO\textsubscript{2}. Four NO\textsubscript{2} desorption peaks are observed, at 30 °C, 100 °C, 250 °C and 350 °C. The desorptions at 30 and 100 °C are attributed to desorption of NO\textsubscript{2} physisorbed over the catalyst surface. The desorption at 250 °C is due to moderately thermally stable species and the highest temperature desorption (350 °C) to nitrate species. This profile is comparable to that obtained in previous work\textsuperscript{8}.

Figure 5.4. Typical concentration profile over the zeolite-based catalysts during \(\text{NO}_x\) adsorption at 30 °C (\(\text{NO}:\text{O}_2 = 1:75\)) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He
Chapter 5 NO\textsubscript{x} storage on metal-exchanged zeolites

Figure 5.5 shows the same adsorption-desorption experiment, for Cu/ZSM-5 (30), including only the NO\textsubscript{x} profiles and the integrated areas for quantification. The evolution of NO and NO\textsubscript{2} during the TPD is a measure of the thermal stability of stored and adsorbed NO\textsubscript{x} species.

---

Temperature in °C (dashed line) (---) N\textsubscript{2}O ppm (---) NO ppm (---) NO\textsubscript{2} ppm

Figure 5.5. Typical NO\textsubscript{x} concentration profile over the zeolite-based catalysts during NO\textsubscript{x} adsorption at 30 °C (NO:O\textsubscript{2} = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He

In the presence of oxygen, desorption at high temperatures is ascribed to formation of more thermally stable nitrate species, promoted by the initial oxidation of NO to NO\textsubscript{2}.

This thesis chapter is dedicated to screening the NO\textsubscript{x} storage capacity of a variety of zeolite-based catalysts in the presence and absence of O\textsubscript{2}. This is quantified through performing
Chapter 5  

**NO\textsubscript{x} storage on metal-exchanged zeolites**

Isothermal NO\textsubscript{x} adsorption followed by TPD in He. While the total amount of NO\textsubscript{x} adsorbed/desorbed differs significantly between different catalysts, their adsorption/desorption profiles are similar to those explained in Figures 5.2 and 5.4. The NO\textsubscript{x} storage capacities of zeolite catalysts are summarised in separate figures which illustrate quantified values for the total amount of NO\textsubscript{x} (NO\textsubscript{2} and NO) adsorbed/desorbed and the % of NO converted to NO\textsubscript{2}.

Results are expressed as mg NO\textsubscript{x}/g catalyst. Total NO\textsubscript{x} desorption does not include the reversibly adsorbed NO\textsubscript{x}, meaning that the physisorbed NO\textsubscript{x} which desorbs at 30 °C (prior to the TPD) is excluded from calculations. As explained previously, the total amount of NO\textsubscript{x} adsorbed is under-quantified due to limitations of the experimental method. However, the total amount of NO\textsubscript{x} desorbed during the TPD is an accurate estimation of the storage capacity. Since oxidation of NO is an essential first step in the storage mechanism and the NO\textsubscript{x} adsorption capacities are under-quantified, only the % of NO converted to NO\textsubscript{2} is included in the results for experiments performed in the presence of O\textsubscript{2}.

When comparing the storage capacities of the different zeolite-based catalysts, non-exchanged H\textsuperscript{+}-ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 30) is used as a baseline and a commercial diesel NO\textsubscript{x} abatement autocatalyst prototype is used as the reference. Quantified NO\textsubscript{x} adsorption/desorption results obtained for these two systems are presented in Table 5.1. The storage capacity of the reference catalyst prototype in Table 5.1, is much higher than that of the baseline catalyst, H\textsuperscript{+}-ZSM-5 (30). The objective then, is to find a zeolite-based system with superior performance to the prototype. It should be mentioned that it is not only the absolute storage capacity but also the NO\textsubscript{x} desorption distribution at different temperatures which should be compared to determine the performance of a catalyst. An ideal storage system should possess both the ability to oxidise NO to NO\textsubscript{2} and to store the NO\textsubscript{2} formed up to high temperatures.
The chemical composition, structure and extra-framework cations of zeolites greatly influence molecular adsorption and interaction with the active sites, thus influencing catalytic and storage properties.

The nomenclature used for zeolite-based catalysts is defined as follows;

\[ \text{M}^X/\text{ZEO (Y)}_{\text{PREP}} \]

where;

- \( \text{M} \) = metal ion-exchanged/supported,
- \( X \) = oxidation state of the metal in the metal precursor,
- \( \text{ZEO} \) = zeolite name, associated with its structure,
- \( Y \) = zeolite SiO\(_2\)/Al\(_2\)O\(_3\) ratio, associated with its acidity,
- \( \text{PREP} \) = preparation method.
Whilst the zeolite-based catalysts used in this study are named as metal-exchanged zeolites, it should be noted that both ion-exchanged and supported metal species are present on the zeolite support. Hence, M/ZEO is used instead of M-ZEO.
5.3 Monometallic zeolitic systems

5.3.1 Wet ion exchange

There are several techniques to modify zeolites by ion exchange. Among them, wet ion exchange (WIE) is the most common as it is simple and feasible for industrial applications, involving few steps and with easily controlled experimental variables.

A detailed description of the WIE procedure is given in Chapter 3, Section 3.2.2.1. Extra-framework cations are introduced by ion-exchange of the H⁺ form zeolite with an aqueous solution of the metal precursor.

Because of the reversible nature of the exchange process, multiple exchanges are necessary to accomplish complete exchange. Thus, the metal exchange level should be determined by a bulk chemical analysis technique such as ICP-AES.

5.3.1.1 Exchanged metal

Cu/ZSM-5 catalysts have been reported to show good performance for NOx SCR with HC and NH₃, and NO decomposition. Fe/ZSM-5 catalysts are also very active for NOx SCR with HC and NH₃, as well as for N₂O decomposition. Pt/ZSM-5 catalysts have also been investigated for HC SCR. Deeba et al. reported that Pt/ZSM-5 enhances NOx conversion due to a cooperative effect between acid sites and Pt. The Pt sites enhance the formation of active intermediates such as NO₂. NO must be oxidised to NO₂ prior to reduction. Additionally, as NO is much more weakly adsorbed onto zeolites than NO₂, this oxidation also enhances total NOx storage. In fact, commercial NSR catalysts are composed of an adsorbent, such as BaO, combined with an oxidation component, such as Pt, that favours the oxidation of NO to NO₂.
Fe/ and Cu/ZSM-5 are promising catalysts, with durability at high temperatures and resistance to poisoning. Meanwhile supported Pt catalysts possess favourable oxidation properties. Hence, the storage capacities of a series of base (Fe and Cu), and precious (Pt), metal-exchanged zeolites were evaluated.

The physicochemical properties of the metal-exchanged zeolites prepared by wet ion exchange and calcined at (550 °C for 3 hours in static air) are summarised in Table 5.2.

### Table 5.2. Physicochemical properties of the metal-exchanged zeolites:

<table>
<thead>
<tr>
<th></th>
<th>Surface area BET [a]</th>
<th>Pore volume [a]</th>
<th>Acidity [b]</th>
<th>H₂ Consumption[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m²/g</td>
<td>mL/g</td>
<td>µmol NH₃/g</td>
<td>µmol H₂/g</td>
</tr>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>412</td>
<td>0.383</td>
<td>1299</td>
<td>260</td>
</tr>
<tr>
<td>Cu²⁺/ZSM-5 (30) <em>WIE</em></td>
<td>394</td>
<td>0.282</td>
<td>1439</td>
<td>707</td>
</tr>
<tr>
<td>Fe³⁺/ZSM-5 (30) <em>WIE</em></td>
<td>350</td>
<td>0.381</td>
<td>1064</td>
<td>207</td>
</tr>
<tr>
<td>Fe²⁺/ZSM-5 (30) <em>WIE</em></td>
<td>X</td>
<td>X</td>
<td>1128</td>
<td>233</td>
</tr>
<tr>
<td>Pt⁴⁺/ZSM-5 (30) <em>WIE</em></td>
<td>X</td>
<td>X</td>
<td>1477</td>
<td>263</td>
</tr>
</tbody>
</table>

[a] Surface area and pore volume measured by N₂ physisorption, [b] acidity measured by NH₃-TPD and [c] hydrogen consumption obtained from H₂-TPR profiles

All adsorption isotherms were characteristic of Type 1 according to the IUPAC classification. The surface area of the unmodified support, H⁺-ZSM-5 (30), is 412 ± 8 m²/g, in good agreement with the value provided by the supplier (400 m²/g). Incorporation of metal oxide particles diminishes the total surface area by 4.4 % for Cu and 15 % for Fe.

The pore volume distribution calculated from the nitrogen adsorption isotherms using the DFT & Monte-Carlo method is described in Table 5.3. It is known that incorporation of
metal oxide particles can lead to blockage of the zeolite channels and decrease the adsorption properties. Results show that the pore volume distribution does change after exchange, however the decrease in total pore volume is more significant for the Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE} catalyst. Reduction of the micro-, meso- and macro- porous volume indicates that CuO is distributed inside the pores, leading to the diminution in surface area and pore volume. In the case of the Fe\textsuperscript{III}/ZSM-5 (30)\textsubscript{WIE} catalyst, only the microporous volume is reduced (by 15%).

Table 5.3. Pore volume distribution of the metal-exchanged zeolites:

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Microporous (&lt; 2 nm)</th>
<th>Mesoporous (2 nm – 50 nm)</th>
<th>Macroporous (&gt; 50 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsuperscript{+}-ZSM-5 (30)</td>
<td>0.383</td>
<td>0.142</td>
<td>0.209</td>
<td>0.033</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE}</td>
<td>0.282</td>
<td>0.110</td>
<td>0.169</td>
<td>0.003</td>
</tr>
<tr>
<td>Fe\textsuperscript{III}/ZSM-5 (30)\textsubscript{WIE}</td>
<td>0.381</td>
<td>0.121</td>
<td>0.219</td>
<td>0.040</td>
</tr>
</tbody>
</table>

The acidity of the zeolite-based catalysts was probed using NH\textsubscript{3}-TPD, with NH\textsubscript{3} adsorbed at 30 °C. The NH\textsubscript{3}-TPD profiles are shown in Figure 5.6. In agreement with previous work\textsuperscript{51 71 72 73 74} the profile presents two main NH\textsubscript{3} desorptions, at 250 °C and 450 °C. These represent different acid sites strengths, with the peak at 250 °C attributed to desorption of NH\textsubscript{3} from weak Brønsted and Lewis acid sites and that at 450 °C assigned to desorption of NH\textsubscript{3} from strong Brønsted acid sites. Quantification of the concentration of acid sites was obtained by integration of the curves and correlation with the response factor. Results reported in Table 5.2 are given as total acid site density (μmol NH\textsubscript{3}/g support) and acid density at 250 °C and 450 °C. The total amount of acid sites is proportional to the Al content of the zeolite. The loading of different metals onto H\textsuperscript{+}-ZSM-5 (30) reduces the strong Brønsted acid- site density. The high temperature peak is shifted 50 °C higher and its
intensity decreases due to loss of Brønsted acid sites through metal ion exchange. In addition, the profile for Cu$^{II}$/ZSM-5 (30)\textsubscript{WIE}, Figure 5.6 b), shows that the peak at 250 °C is broader and more intense. The shoulder at 320 °C, suggests that Cu-exchange generates new medium strength acid sites, attributed to desorption of NH$_3$ from Cu(NH$_3$)$_2^{2+}$ complexes\textsuperscript{72}.

![Figure 5.6. NH$_3$-TPD profiles of the metal-exchanged zeolites:](image)

\begin{itemize}
\item a) H$^+$-ZSM-5 (30)
\item b) Cu$^{II}$/ZSM-5 (30)\textsubscript{WIE}
\item c) Fe$^{III}$/ZSM-5 (30)\textsubscript{WIE}
\item d) Fe$^{II}$/ZSM-5 (30)\textsubscript{WIE}
\item e) Pt$^{IV}$/ZSM-5 (30)\textsubscript{WIE}
\end{itemize}

For a complete characterisation of the acidity of zeolite-based catalysts it is necessary to determine the distribution of acid sites (Lewis and Brønsted) on the surface. Therefore, IR spectra of adsorbed pyridine should be collected.
In metal-exchanged zeolites, the redox properties of the metal species are an important factor in determining catalytic performance. Reducibility of the zeolite-based catalysts was investigated via H$_2$-TPR and H$_2$ uptake profiles are shown in Figure 5.7. Quantified hydrogen consumption (μmol H$_2$/g catalyst) determined from the TPR profiles is included in Table 5.2.

The small reduction peak that appears between 30 °C and 100 °C is an artefact and can be attributed to residual Ar. Cu$^{II}$/ZSM-5 (30)$_{WIE}$, Figure 5.7 b), exhibits two distinct reduction events. The first reduction peak, at 225 °C, is attributed to reduction of Cu$^{2+}$ cations located at exchanged sites and supported CuO species, to Cu$^{+}$. The second reduction event is broad and centred at 400 °C, corresponding to reduction of Cu$^{+}$ to Cu$^{0}$.$^{71,72,75}$ This could be
deconvoluted into two different peaks, at 375 °C and 450 °C. For Fe-exchanged ZSM-5 systems, the first TPR peak, at 375 °C, corresponds to the reduction of Fe₂O₃ to Fe₃O₄, and the second, at 500 °C, is assigned to the reduction of Fe₃O₄ to Fe⁰. Reduction of Fe₃O₄ to Fe⁰ proceeds via FeO, thus, the shoulder at 450 °C could be attributed to the reduction of FeO. Fe³⁺/ZSM-5 (30) WIE (Figure 5.7 d) exhibits the typical TPR profile, suggesting that Fe is present as a mixture of Fe³⁺ and Fe⁵⁺ species. Contrarily, as shown in Figure 5.7 c), the H₂-TPR for Fe³⁺/ZSM-5 (30) WIE, Fe-exchanged ZSM-5 obtained through WIE using FeCl₃ does not show the Fe₂O₃ and Fe₃O₄ reduction peaks but rather a negative peak centred around 300 °C. Reduction of PtOₓ species to Pt⁰ occurs at ≈ 80 °C. Due to the low temperature desorption of residual Ar it is not possible to distinguish those reduction peaks attributed to Pt in Figure 5.7 e), whilst the reduction events observed at higher temperatures are similar to those obtained for the unmodified H⁺-ZSM-5 (30) which correspond to reduction of the zeolite.

The nature and distribution of Cu and Fe species was investigated using diffuse-reflectance UV-Vis spectroscopy. The UV-Vis spectra are presented in Figure 5.8. It is known that for Fe-exchanged zeolites, Fe³⁺ ← O charge-transfer (CT) bands (200-350 nm) and weak Fe³⁺ (3d⁵) d-d transitions (350-550 nm) are expected. The first band (200-250 nm) is attributed to isolated Fe³⁺ species in the zeolite framework. The second band (250 nm - 350 nm) corresponds to isolated or small oligonuclear FeₓOᵧ extra-framework species. Larger FeₓOᵧ clusters appear between 350 and 450 nm and those bands at wavelengths over 450 nm correspond to surface FeₓOᵧ nanoparticles. In the case of Cu-exchanged zeolites, d-d transitions of Cu²⁺ (3d⁹) appear over 700 nm, hence electronic spectra analysis is only possible using UV-Vis-NIR spectroscopy.

Fe³⁺/ZSM-5 (30) WIE, Figure 5.8 c), presents a mixture of Fe species. The two bands at 225 and 250 nm are attributed to t₁ → t₂ and t₁ → e CT transitions, confirming the presence...
of tetrahedral and octahedral Fe$^{3+}$ species. Additionally, the spectrum suggests the presence of extra-framework Fe$_2$O$_3$ species in the micropores, which is in agreement with a decrease in micropore volume after Fe-exchange, as shown in Table 5.3. Fe is also distributed as larger clusters and iron crystallites on the external surface of the zeolite. Those UV bands observed for the unmodified H$^+$-ZSM-5 (30), Figure 5.8 a), are attributed to CT transitions of the contaminant iron, intrinsic within commercial zeolites. It has been reported that commercial zeolites contain trace levels of Fe and Ti within the MFI structure that are highly active for oxidation reactions $^{83}$. The spectrum of the Cu$^{II}$/ZSM-5 (30) WIE catalyst differs from that obtained for the non-exchanged H$^+$-ZSM-5 and exhibits one absorption band at 200-260 nm which could be assigned to charge-transfer from $\text{O}^{2-}$ to Cu$^+$ or Cu$^{2+}$ $^{29, 35, 91}$, and also to Fe$^{3+}$ ions in the framework.

![Figure 5.8. UV-Vis spectra of the metal-exchanged zeolites:](image)

- a) H$^+$-ZSM-5 (30)
- b) Cu$^{II}$/ZSM-5 (30)$_{WIE}$
- c) Fe$^{III}$/ZSM-5 (30)$_{WIE}$
Characteristic absorption bands of the parent zeolite \(^5\), H\(^+\)-ZSM-5 (30), are observed in the FTIR spectrum shown in Figure 5.9. The spectrum in the surface hydroxyl (OH) vibrational region (inset) contains three main bands at 3560, 3660 and 3750 cm\(^{-1}\). The band at 3560 cm\(^{-1}\) is associated with Brønsted acid groups; bridging hydroxyl groups with tetrahedrally coordinated framework aluminium (-Si-OH-Al-), the band at 3660 cm\(^{-1}\) is associated with hydroxyls of extra-framework aluminium (Al-OH), and the sharp peak at 3750 cm\(^{-1}\) with terminal silanol groups (Si-OH) inside the zeolite channels and on the surface \(^75\) \(^83\) \(^87\).

**Figure 5.9.** DRIFT spectra of the parent zeolite: H\(^+\)-ZSM-5 (30)

FTIR spectra in the OH vibrational region of the metal-exchanged zeolites are shown in Figure 5.10. As reported in the literature \(^76\) \(^92\), exchange of H\(^+\) with metal cations results in differences in the relative concentration of the different –OH groups. The relative intensity
of the band associated with bridging hydroxyl groups decreases after metal ion-exchange. Although the resolution of the spectra is not good enough, it seems that the relative intensity of the band at 3560 cm$^{-1}$ is lower for Cu$^{II}$ and Fe$^{III}$-exchanged ZSM-5, Figure 5.10 b) and c). This suggests that the level of exchange is much lower for these last two metal ion-exchanged ZSM-5 catalysts. Fe/ZSM-5 (30) catalysts present a new band at 3715 cm$^{-1}$ which is attributed to the stretching vibration of hydrolysed Fe species.

![Figure 5.10. DRIFT spectra in the OH vibrational region of the metal-exchanged zeolites:](image)

- a) H$^+$/ZSM-5 (30)
- b) Cu$^{II}$/ZSM-5 (30)$_{WIE}$
- c) Fe$^{III}$/ZSM-5 (30)$_{WIE}$
- d) Fe$^{II}$/ZSM-5 (30)$_{WIE}$
- e) Pt$^{IV}$/ZSM-5 (30)$_{WIE}$

The NO$_x$ storage capacities of the metal-exchanged ZSM-5 (30) catalysts were evaluated in the presence and absence of O$_2$. Figure 5.11 shows the NO$_x$ adsorption capacities in the absence of O$_2$ and quantification of the amount of NO$_x$ species desorbed during the TPD.
After adsorbing NO in the absence of O₂, desorption occurs mainly in the form of NO and at temperatures below 250 °C.

Two kinds of NOₓ adsorption sites are present on metal ion-exchanged zeolites: weak adsorption sites, attributed to the parent zeolite, and strong adsorption sites, attributed to the metal species exchanged and supported on the zeolite ¹⁵.

The NOₓ adsorption and desorption capacity of the parent zeolite (H⁺-ZSM-5) is lower than that of the metal-exchanged ZSM-5 (30) catalysts.

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**Figure 5.11.** NOₓ storage capacities of metal-exchanged / H⁺-ZSM-5 (30) catalysts

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h⁻¹, 0.1 % NO in He / He

Catalysts prepared by WIE at 25 °C for 24 h and calcined at 550 °C for 3 h in static air

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¹⁵
Among the different metal-exchanged zeolites, Cu\textsuperscript{II}/ZSM-5 \textsuperscript{(30) WIE} exhibits the highest NO adsorption capacity at three times that of unmodified H\textsuperscript{+}-ZSM-5 \textsuperscript{(30)}. While the NO\textsubscript{x} desorption capacity is also around three times greater than the parent zeolite, it is similar to that of the Fe-exchanged zeolites. This indicates that NO adsorption on the Cu\textsuperscript{II}/ZSM-5 \textsuperscript{(30) WIE} catalyst is mainly reversible, with most of the NO being desorbed at the adsorption temperature (30 °C). As discussed previously, the desorption capacity represented in the bar graphs does not include the amount of NO\textsubscript{x} desorbed at 30 °C. These results correlate with earlier studies in which Cu/ZSM-5 showed greater reversible NO adsorption compared to a series of metal-exchanged ZSM-5 zeolites\textsuperscript{24}.

The NO\textsubscript{x} adsorption and desorption behaviour of both Fe-exchanged zeolites, Fe\textsuperscript{II}/ZSM-5 \textsuperscript{(30) WIE} and Fe\textsuperscript{III}/ZSM-5 \textsuperscript{(30) WIE}, is similar. This is despite variations in the redox properties of the supported Fe species shown in Figure 5.7, and suggests that the storage capacity is not affected by the Fe precursor, Fe(SO\textsubscript{4}) or FeCl\textsubscript{3}, used for WIE.

Pt\textsuperscript{IV}/ZSM-5 \textsuperscript{(30) WIE} presents the lowest adsorption and desorption capacity, comparable with that of unmodified H\textsuperscript{+}-ZSM-5 \textsuperscript{(30)}. A potential explanation is low exchange of Pt achieved during WIE. Characterisation of Pt\textsuperscript{IV}/ZSM-5 \textsuperscript{(30) WIE} shows minor changes in the acid and redox properties when compared with the unmodified zeolite. In addition, the platinum solution used is much less concentrated (0.5 mM) than the copper and iron solutions (50 mM).

In the absence of O\textsubscript{2}, limited desorption is observed at temperatures above 150 °C. It is known that NO is more weakly adsorbed on zeolites than NO\textsubscript{2}. Therefore, to improve the storage capacity, NO should be converted to NO\textsubscript{2}. The NO\textsubscript{x} storage capacities of the metal-exchanged ZSM-5 \textsuperscript{(30)} catalysts were evaluated in the presence of O\textsubscript{2}. Figure 5.12 shows the amount of NO\textsubscript{x} desorbed after NO was adsorbed in the presence of O\textsubscript{2}.
Figure 5.12. NO$_x$ storage capacity of metal-exchanged / H$^+$-ZSM-5 (30) catalysts

NO$_x$ adsorption at 30 °C (NO:O$_2$ = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO + 7.5 % O$_2$ in He / He

Catalysts prepared by WIE at 25 °C for 24 h and calcined at 550 °C for 3 h in static air

NO$_x$ is mainly desorbed in the form of NO$_2$. Cu$^{II}$/ZSM-5 (30)$_{WIE}$ exhibits the highest NO$_x$ desorption, double of unmodified H$^+$-ZSM-5 (30). On the other hand, the storage capacity of the parent zeolite, H$^+$-ZSM-5 (30) is not changed after Pt ion-exchange in Pt$^{IV}$/ZSM-5 (30)$_{WIE}$. In contrast to the results obtained for adsorption in absence of O$_2$, Fe-exchanged zeolites present the lowest NO$_x$ desorption capacity at 33 % below the baseline value set by unmodified H$^+$-ZSM-5 (30).

In the absence of O$_2$, NO adsorbed over metal ion-exchanged zeolites is converted to N$_2$O and N$_2$O$_3$ via a disproportionation reaction. The N$_2$O is easily desorbed and the N$_2$O$_3$
species, appearing as a NO⁺-NO₂⁻ ion pair, are more strongly chemisorbed. In the presence of O₂, NO oxidises to NO₂, which forms N₂O₄. This then ionizes into NO⁺ and NO₃⁻.

Hadjiivanov et al.⁴ proposed that in the presence of O₂, NO adsorption on Cu/ZSM-5 at ambient temperature leads to the formation of nitrate and Cu²⁺-NO species. In the presence of O₂, the NO species are converted via the following reaction sequence⁴:

\[
\text{NO} \rightarrow \text{N}_2\text{O}_3 \rightarrow \text{N}_2\text{O}_4 \rightarrow \text{NO}_2 \rightarrow \text{NO}_3^-
\]

Equation 5.1

Hence, the presence of O₂ in the feed promotes the formation of nitrates⁴ ¹⁵ ¹⁰ ² ¹⁶ ²⁴. As nitrates are more thermally stable, desorption of these species occurs at higher temperatures.

It has been reported that although the main role of the O₂ is to oxidise NO to NO₂ and convert the NOₓ into highly reactive surface nitrates⁴, an excess of oxygen is also required to keep the catalyst surface clean from carbonaceous deposits and the metal ions in a high oxidation state⁹³.

A distribution of the NOₓ species desorbed at different temperatures is shown in Figure 5.13.

Reversible adsorption at 30 °C is predominant over unmodified H⁺-ZSM-5 (30). When compared with Cu and Fe ion-exchanged ZSM-5 catalysts, Pt⁴⁺/ZSM-5 (30) also exhibits considerable reversible adsorption, with a greater amount of NOₓ desorbed at 30 °C.

NOₓ desorption over the Fe ion-exchanged ZSM-5 catalysts occurs mainly at 250 °C, being non-significant at 100 °C and 350 °C.

Among the zeolite catalysts studied, only Cu²⁺/ZSM-5 (30) exhibits a high degree of NOₓ desorption at 350 °C. This is attributed to formation of surface Cu(NO₃)₂ species that are more thermally stable.
Based on these results, Cu$^{II}$/ZSM-5 (30) not only shows the highest activity for NO adsorption, but also a superior degree of NO$_x$ desorption at high temperatures than either Fe or Pt ion-exchanged ZSM-5 (30).

![Figure 5.13](image)

**Figure 5.13.** Total amount of NO$_x$ desorbed during the TPD carried out after NO$_x$ adsorption (0.1 % NO, 7.5 % O$_2$, He) on metal-exchanged / H$^+$-ZSM-5 (30) at each desorption temperature.
5.3.1.2 Zeolite structure and aluminium content

The role of the zeolite framework in the adsorption/desorption process and effect of varying the Si/Al ratio, which determines a zeolites hydrophilic/hydrophobic character, was investigated. Cu and Fe ions were exchanged into different medium and large pore zeolites including; Y, ZSM-5 and BETA, by WIE.

Zeolite Y has a Faujasite- type structure and possesses highly ordered cavities, denoted as supercages, with a diameter of 13 nm. It is also very hydrophilic.

Among the different zeolites available, ZSM-5 is widely used and studied. It has a MFI framework type and belongs to the pentasil family of zeolites. ZSM-5 is formed by 10 ring channels system with apertures of 0.51 nm x 0.55 nm and 0.53 nm x 0.56 nm. It ranges from moderately hydrophilic to hydrophobic, depending on the Si/Al ratio. Its acid resistance and thermal stability together with the special pore structure, possessing channel dimensions equal to the diameter of an aromatic ring, make ZSM-5 based catalysts suitable for multiple applications.

BETA is an attractive zeolite because of its widely open structure with a three dimensional channel system and narrow pore size distribution. With a disordered BEA framework type, it consists of 12 membered ring apertures with two perpendicular straight channels, each with a cross-section of 0.76 nm x 0.64 nm, and a sinusoidal channel of 0.56 nm x 0.56 nm. Within this type of open distorted framework, aluminium is present in a octahedral framework coordination site and as extra-framework species. The open structure provides greater accessibility to aluminium sites and compensating extra-framework cations, and makes it promising for shape-selective reactions. NH$_4^+$-exchanged BETA is known to contain a substantial concentration of defects, which gives it unique acid properties. BETA contains nine types of different T sites and seventeen environments of
Chapter 5

NO₃ storage on metal-exchanged zeolites

oxygen. In addition, compared to ZSM-5, zeolite BETA possesses high hydrothermal ability.

The channel dimensions of a zeolite not only affect its adsorption/desorption properties but also the effectiveness of metal ion-exchange. Larger channel dimensions could have a beneficial effect on WIE as it facilitates the diffusion of hydrated metal ions into the pores.

Figure 5.14. Powder X-Ray diffraction patterns of the parent zeolites:

a) H⁺-Y (5.1)  b) H⁺-Y (30)  c) H⁺-ZSM-5 (23)  d) H⁺-ZSM-5 (30)

e) H⁺-ZSM-5 (50)  f) H⁺-BETA (38)

XRD patterns in Figure 5.14 show the characteristic diffraction peaks of each framework type. Figure 5.14 a) and b) show distinctive diffraction peaks at 2θ of 6.3°, 10.3°, 12.1°, 15.9° and 24.1°, typical of FAU-type zeolites. XRD pattern of ZSM-5, Figure 5.14 c), d) and e), is consistent with an MFI-type zeolite, with typical diffraction peaks at 2θ of 7.9°,
8.8°, 23.1°, 23.9°, and 24.4°. Typical diffraction peaks of H⁺-BETA, Figure 5.14 f), appear at 2θ of 7.8°, 22.4°, 29.6° and 43.5°.

Figure 5.15 illustrates the effect of varying the zeolite framework and acidity on NOₓ storage in the absence of O₂, over Cu-exchanged zeolites.

![Figure 5.15. NOₓ storage capacity of Cu-exchanged zeolites](image)

**Figure 5.15.** NOₓ storage capacity of Cu-exchanged zeolites

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h⁻¹, 0.1 % NO in He / He

Catalysts prepared by WIE at 25 °C for 48 h and calcined at 550 °C for 3 h in static air

Both NO adsorption and desorption are dependent on the structure and aluminium content of the zeolites. As before, NOₓ desorption occurs mainly in the form of NO at low temperatures. Two different peaks are observed in the desorption profile, corresponding to reversible adsorption of NO at 30 °C and NO desorption at 100 °C.
Cu-exchanged Y catalysts, $\text{Cu}^{II}/Y$ (5.1) \text{WIE} and $\text{Cu}^{II}/Y$ (30) \text{WIE}, exhibit the lowest NO adsorption capacities. While NO adsorption over $\text{Cu}^{II}/Y$ (30) \text{WIE} is mainly reversible, NO desorption ($T > 30^\circ\text{C}$) is more significant for the $\text{Cu}^{II}/Y$ (5.1) \text{WIE} catalyst. Among the zeolite catalysts studied, $\text{Cu}^{II}/\text{BETA}$ (38) \text{WIE} presents the highest NO adsorption and desorption capacity. However, around 50\% of the NO adsorption is reversible and the amount of NO\_x desorbed at 100 °C is similar to that of the Cu-exchanged ZSM-5 catalysts.

The NO adsorption performance of Cu-exchanged ZSM-5 catalysts increases with the SiO\_2 content of the ZSM-5, though no clear trend is observed regarding their desorption capacity. Although the amount of NO desorbed at 100 °C is similar for both $\text{Cu}^{II}/\text{ZSM-5}$ (23) \text{WIE} and $\text{Cu}^{II}/\text{ZSM-5}$ (50) \text{WIE} catalysts ($\approx 1.6 \text{ mg NO}_x/\text{g}$), the desorption capacity of the $\text{Cu}^{II}/\text{ZSM-5}$ (30) \text{WIE} catalyst is lower. It should be noted that the catalysts denoted as ‘‘$\text{Cu}^{II}/\text{ZSM-5}$ (30) \text{WIE}’’ in Figures 5.11 and 5.15 were prepared by WIE over 24 and 48 h respectively. The desorption capacity is comparable but not the NO adsorption, hence, these differences are related to the amount of reversible NO adsorption. Mass transfer limitations could affect the NO\_x desorption at low temperatures \(^{98}\), slowing the desorption of physisorbed NO\_x at 30 °C.

Concordant with the results discussed here, Chang et al. \(^{15}\) found that H\(^{+}\)-BETA zeolites perform better for adsorbing NO\_x at 40 °C than Na\(^{+}\)-Y, H\(^{+}\)-ZSM-5, mordenite or activated carbon.

In order to study desorption at high temperatures, the NO\_x storage capacities of Cu-exchanged ZSM-5 (30) catalysts were evaluated in the presence of O\_2. Figure 5.16 shows the amount of NO\_x desorbed after adsorption in the presence of O\_2, as well as the NO oxidation activity.
Figure 5.16. \(\text{NO}_x\) storage capacity of Cu-exchanged zeolites

\(\text{NO}_x\) adsorption at 30 °C (\(\text{NO}:\text{O}_2 = 1:75\)) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\(^{-1}\), 0.1 % NO + 7.5 % O\(_2\) in He / He

Catalysts prepared by WIE at 25 °C for 48 h and calcined at 550 °C for 3 h in static air

Again, the main component of desorbed \(\text{NO}_x\) is \(\text{NO}_2\) and desorption at high temperatures becomes significant.

\(\text{Cu}^{II}/\text{ZSM-5 (23)}\) \(_{\text{WIE}}\) exhibits the highest \(\text{NO}_x\) desorption capacity. Among the Cu-exchanged ZSM-5 catalysts, desorption is clearly enhanced with the \(\text{Al}_2\text{O}_3\) content of the ZSM-5 support. The amount of \(\text{NO}_x\) desorbed from \(\text{Cu}^{II}/\text{ZSM-5 (23)}\) \(_{\text{WIE}}\) is more than 4 times that for \(\text{Cu}^{II}/\text{ZSM-5 (50)}\) \(_{\text{WIE}}\). Hence, decreasing the \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio increases the \(\text{NO}_x\) storage capacity. This is potentially due to the fact that hydrophilicity and cation exchange capacity increase with the \(\text{Al}_2\text{O}_3\) content of the zeolite. In order to correlate the
storage capacity with an improvement in the cation exchange properties, elemental analysis should be carried to determine the actual loadings of supported metals.

The total amount of NO$_x$ desorbed over Cu$^{II}$/Y (30)$_{WIE}$, Cu$^{II}$/ZSM-5 (30)$_{WIE}$ and Cu$^{II}$/BETA (38)$_{WIE}$ is approximately 6 mg NO$_x$/g. Accordingly, the storage capacity of Cu-exchanged zeolites with different structure but similar acidity is comparable.

Interestingly, the superior acidity of Zeolite Y, which has a SiO$_2$/Al$_2$O$_3$ ratio of 5.1, is not beneficial for the storage capacity of Cu ion-exchanged catalysts. This is because NO$_x$ adsorption over Cu$^{II}$/Y (5.1)$_{WIE}$ is exclusively reversible, with one peak observed at 30 °C attributed to desorption of physisorbed NO and NO$_2$.

As reported previously in the literature, the first reaction that takes place in the presence of NO and O$_2$ is the oxidation of NO to NO$_2$ 15:

\[
2 \text{NO} + \text{O}_2 \leftrightarrow 2 \text{NO}_2 \leftrightarrow \text{NO}^+ + \text{NO}_3^- \quad \text{Equation 5.1}
\]

In general, a high desorption capacity correlates with high oxidation activity. The amount of NO$_x$ desorbed is greater for those catalysts which oxidise NO to NO$_2$ during the 30 °C adsorption period. Cu$^{II}$/ZSM-5 (23)$_{WIE}$ not only presents the greatest desorption capacity but also the highest conversion of NO to NO$_2$. Surprisingly, despite negligible NO oxidation, considerable desorption is observed for Cu$^{II}$/Y (30)$_{WIE}$.

Desorption over the H$^+$ form of zeolites is attributed to decomposition of surface HNO$_3$ species. Nitric acid could be formed by interaction of adsorbed NO$_x$ with H$_2$O or via NO$_2$ disproportionation following:

\[
\text{ZEOb-OH}^+ + \text{NO}^+ + \text{NO}_3^- \leftrightarrow \text{ZEOb-O-NO}^+ + \text{H}^+ \text{NO}_3^- \quad \text{Equation 5.2}
\]
HNO$_3$ species formed through both reaction mechanisms have similar thermal stability. It has been reported that deposition of HNO$_3$ onto the surface of zeolites could induce contraction of the unit cell$^{98}$. 

Over Cu-exchanged zeolites, NO$_x$ is adsorbed in the form of nitrates. The following reaction sequence has been previously proposed$^{15}$:

\[
2 \text{ZEO-CuO} + 2 \text{NO}^+ + 2 \text{NO}_2^- \rightarrow \text{ZEO-Cu(NO}_2)_2 + \text{ZEO-Cu(NO}_3)_2
\]

\[
\rightarrow 2 \text{ZEO-Cu(NO}_2)_2 + 2 \text{NO}_g
\]

Equation 5.3

The distribution of NO$_x$ species desorbed at different temperatures is shown in Figure 5.17.

The purpose of this work is to enhance the high temperature desorption of NO$_x$. Accordingly, based on the amount of NO$_x$ desorbed at temperatures above 200 °C, the storage capacity of the Cu-exchanged zeolites decreases as follows:

Cu$^{II}$/ZSM-5 (23) WIE > Cu$^{II}$/BETA (38) WIE > Cu$^{II}$/ZSM-5 (30) WIE > Cu$^{II}$/Y (30) WIE > Cu$^{II}$/ZSM-5 (50) WIE > Cu$^{II}$/Y (5.1) WIE

Integration of desorption peaks at 250 °C and 350 °C allowed quantification of the amount on NO$_x$ desorbed from these catalysts. In this way, Cu$^{II}$/Y (30) WIE Cu$^{II}$/ZSM-5 (30) WIE and Cu$^{II}$/BETA (38) WIE show desorption of 4.7, 5.2 and 5.3 mg NO$_x$/g respectively. Thus, the storage capacity of Cu-exchanged zeolites with different frameworks but similar acidity is comparable, when comparing the total amount of NO$_x$ desorbed and the amount desorbed at high temperatures.

The amount of NO$_x$ desorbed at high temperature over Cu$^{II}$/ZSM-5 (23) WIE is 6 mg NO$_x$/g. This is 15 % higher than that of Cu$^{II}$/ZSM-5 (30) WIE. However, when considering total NO$_x$ desorption across the whole temperature range, Cu$^{II}$/ZSM-5 (23) WIE
shows double the amount of desorbed NO\textsubscript{x} compared to Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE}. This is attributed to the fact that Cu\textsuperscript{II}/ZSM-5 (23) \textsubscript{WIE} also presents a high concentration of weakly adsorbed NO\textsubscript{x} species, which desorb at 30 °C and 100 °C and account for up to 11.2 mg NO\textsubscript{x}/g of the total desorption.

Figure 5.17. Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on Cu-exchanged zeolites at each desorption temperature

The results in Figures 5.15 show that in the absence of O\textsubscript{2}, the NO adsorption capacity is influenced by both the zeolite structure and acidity. Meanwhile Figure 5.17 shows that in the presence of O\textsubscript{2}, while the oxidation activity is influenced by both the zeolite framework type and acidity, the NO\textsubscript{x} desorption capacity is found to be more dependent on the Brønsted acidity of the zeolite than on the framework structure.
The NO\textsubscript{x} storage capacity of Cu-exchanged zeolites depends on two factors: i) Selective adsorption sites attributed to ion-exchanged Cu\textsuperscript{2+}/Cu\textsuperscript{+} and supported oxides (CuO) and ii) physical and weak chemical adsorption on the zeolite support itself, which correlates with its physicochemical properties including structure, acidity, surface area and micropore volume.

The superior total NO\textsubscript{x} desorption at 30 °C and 100 °C over the Cu\textsuperscript{II}/ZSM-5 (23) \textit{WIE} catalyst could be attributed to intrinsic adsorption properties of the unmodified H\textsuperscript{+}-ZSM-5 (23). H\textsuperscript{+}-ZSM-5 (23) possesses relatively high Brønsted acidity due to the higher aluminium content. This promotes the formation of surface HNO\textsubscript{3} species through the reactions shown in Equation 5.2. Adsorption/desorption studies over the bare H-form zeolites are required to determine the extent to which the support contributes to the storage capacity of Cu-exchanged catalysts. This will also determine whether there is a synergistic effect between the zeolite support and CuO species.

The impact of the oxidation state and redox properties of Cu\textsuperscript{n+} ions upon NO\textsubscript{x} storage capacity has been studied in previous work \textsuperscript{24 37 75 99}. In general, catalysts where Cu\textsuperscript{2+} is more readily reduced to Cu\textsuperscript{+} are more active in generating intermediates for deNO\textsubscript{x} reactions, such as the oxidation of NO to NO\textsubscript{2}, which favours the formation of more thermally stable adsorbed nitrate species. Additionally, higher activity is observed for catalysts with more stable Cu\textsuperscript{+} species, which show a higher Cu\textsuperscript{+} to Cu\textsuperscript{0} reduction temperature.

The H\textsubscript{2}-TPR profiles of the Cu-exchanged zeolites are shown in Figure 5.18.

As discussed previously, Cu-exchanged zeolites generally exhibit two reduction peaks, at 225 °C and 400 °C. The first reduction peak is attributed to reduction of Cu\textsuperscript{2+} to Cu\textsuperscript{+} located at cation-exchange sites and supported CuO species.
Cu^{2+} + H_2 \rightarrow Cu^{0} + H_2O \quad \text{Equation 5.4}

The second peak corresponds to reduction of Cu^+ to Cu^0.

Cu^+ + \frac{1}{2} H_2 \rightarrow Cu^{0} + \frac{1}{2} H_2O \quad \text{Equation 5.5}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.18.png}
\caption{H_2-TPR profiles of Cu-exchanged zeolites:}
\begin{itemize}
  \item a) Cu^{II}/Y (5.1)_{\text{WIE}}
  \item b) Cu^{II}/Y (30)_{\text{WIE}}
  \item c) Cu^{II}/ZSM-5 (23)_{\text{WIE}}
  \item d) Cu^{II}/ZSM-5 (30)_{\text{WIE}}
  \item e) Cu^{II}/ZSM-5 (50)_{\text{WIE}}
  \item f) Cu^{II}/BETA (38)_{\text{WIE}}
\end{itemize}
\end{figure}

The reduction profile is highly dependent on the support as the reduction temperature is affected by the interaction of the Cu ions with the zeolite. The temperature at which Cu^{2+} is reduced to Cu^+ depends on the presence of Cu^{2+} located at exchange sites and as supported CuO species. In addition, the reduction temperature is known to be affected by the acidity of the support. Cu ions exchanged on a low SiO_2/Al_2O_3 ratio zeolite are likely
to be reduced at a higher temperature, as the high negative framework charge means that Cu cations are more strongly bonded to the framework oxygen.

Total hydrogen consumption, determined from the TPR profiles, is shown in Table 5.4. Despite variations in the total amount of H₂ consumed, reduction profiles are comparable for all catalysts, except Cu²⁺/BETA (38) WIE.

<table>
<thead>
<tr>
<th></th>
<th>High/Low temperature area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺/Y (5.1) WIE</td>
<td>0.0</td>
</tr>
<tr>
<td>Cu²⁺/Y (30) WIE</td>
<td>1.4</td>
</tr>
<tr>
<td>Cu²⁺/ZSM-5 (23) WIE</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu²⁺/ZSM-5 (30) WIE</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu²⁺/ZSM-5 (50) WIE</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu²⁺/BETA (38) WIE</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Cu supported on H⁺-BETA (38) presents a distinctive reduction profile with a small peak appearing at 235 °C and a sharp intense peak at 255 °C. It should be noted that the high/low temperature area ratio of this catalyst is 4, much higher than that of Cu supported on H⁺-Y and H⁺-ZSM-5. The TPR profile for Cu²⁺/BETA (38) WIE is similar to that observed for over-exchanged zeolites in previous work, where the reduction peak at 250 °C is assigned to cationic oligomers located at exchanged sites. Although compositional analysis is required to determine the Cu loadings, TPR results suggest that the level of exchange is superior in the case of Cu supported on H⁺-BETA (38). The superior NO adsorption capacity, Figure 5.15, and NOₓ desorption at high temperature, Figure 5.17, could be attributed to a high level of metal ion-exchange.
The NO\textsubscript{x} storage capacity of Fe-exchanged zeolites prepared by WIE using FeCl\textsubscript{3}, was also investigated.

Figure 5.19 illustrates the effect of the zeolite structure and acidity on NO\textsubscript{x} storage, in the absence of O\textsubscript{2}, over Fe-exchanged zeolites.

![Figure 5.19. NO\textsubscript{x} storage capacity of Fe-exchanged zeolites](image)

**Figure 5.19.** NO\textsubscript{x} storage capacity of Fe-exchanged zeolites

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO in He / He

Catalysts prepared by WIE at 25 °C for 48 h and calcined at 550 °C for 3 h in static air

Fe\textsuperscript{III}/BETA (38)\textsubscript{WIE} exhibits the highest NO adsorption and desorption capacity, 6.3 and 3.6 mg NO\textsubscript{x}/g. This is superior to its Cu analogue catalyst Cu\textsuperscript{II}/BETA (38)\textsubscript{WIE}, and nearly 8 times that of Fe exchanged onto H\textsuperscript{+}/ZSM-5 (30). Unlike the results obtained for
Cu-exchanged zeolites, in the absence of O$_2$ Fe/ZSM-5 catalysts present poor NO storage activity, with performance comparable with that of the unmodified zeolites. Additionally, an increase in the amount of NO adsorbed at 30 °C is observed for Fe/Y catalysts when compared with Cu analogues in Figure 5.15.

Figure 5.20 shows the degree of NO conversion and amount of NO$_x$ desorbed following adsorption in the presence of NO and O$_2$.

In agreement with the trend found for Cu-exchanged ZSM-5 catalysts, NO$_x$ desorption is clearly enhanced with the Al$_2$O$_3$ content of the ZSM-5 support. The amount of NO$_x$ desorbed for the Fe$^{III}$/ZSM-5 (23)$_{WIE}$ catalyst is more than 7 that of the Fe$^{III}$/ZSM-5 (50)$_{WIE}$ catalyst. The total NO$_x$ desorption capacity of the two more active catalysts; Fe$^{III}$/ZSM-5 (23)$_{WIE}$ and Fe$^{III}$/BETA (38)$_{WIE}$, is comparable with that of their Cu analogues, Cu$^{II}$/ZSM-5 (23)$_{WIE}$ and Cu$^{II}$/BETA (38)$_{WIE}$.

For Fe-exchanged zeolites, the NO$_x$ storage capacity is also influenced by the zeolite structure. Both the amount of NO adsorbed on the catalyst in the absence of O$_2$ and the amount of NO$_x$ desorbed following adsorption in the presence of O$_2$ are affected by the zeolite structure. Figure 5.20 shows that there is a significant change in the NO$_x$ desorption capacity of catalysts with comparable SiO$_2$/Al$_2$O$_3$ ratio but different zeolite frameworks, being Fe$^{III}$/BETA (38)$_{WIE}$ > Fe$^{III}$/ZSM-5 (30)$_{WIE}$ > Fe$^{III}$/Y (30)$_{WIE}$. However, Fe supported on BETA zeolite does not always present superior NO$_x$ storage performance compared to Fe supported on ZSM-5. Pan et al. $^{14}$ reported that Fe/ZSM-5 (30) presents higher NO$_x$ adsorption capacity than Fe/BETA (25), under 470 ppm of NO and 5 % of O$_2$ at 300 °C.
The distribution of NO\textsubscript{x} species desorbed from Fe-exchanged zeolites at different temperatures is shown in Figure 5.21.

It is important to highlight the decrease in the amount of total NO\textsubscript{x} desorbed at high temperature, especially at 350 °C, when comparing Fe-exchanged zeolites with analogous Cu catalysts (Figure 5.17). While, the amount of NO\textsubscript{x} desorbed at 350 °C is 4.3 mg NO\textsubscript{x}/g over Cu\textsuperscript{II}/BETA (38) \textit{WIE}, this value decreases to 1.3 mg NO\textsubscript{x}/g for Fe\textsuperscript{III}/BETA (38) \textit{WIE}. However the difference in the total amount of NO\textsubscript{x} desorbed at high...
temperatures (T > 200 °C) over metal-exchanged BETA (38) is not as significant: 5.3 mg NO\textsubscript{x}/g for Cu\textsuperscript{II}/BETA (38)\textsubscript{wie} and 4.9 mg NO\textsubscript{x}/g for Fe\textsuperscript{III}/BETA (38)\textsubscript{wie}.

Based on the amount of NO\textsubscript{x} desorbed at temperatures above 200 °C, the storage capacity of the Fe-exchanged zeolites decreases as follows:

Fe\textsuperscript{III}/BETA (38)\textsubscript{wie} > Fe\textsuperscript{III}/Y (5.1)\textsubscript{wie} > Fe\textsuperscript{III}/ZSM-5 (23)\textsubscript{wie} \approx Fe\textsuperscript{III}/ZSM-5 (30)\textsubscript{wie} > Fe\textsuperscript{III}/ZSM-5 (50)\textsubscript{wie} > Fe\textsuperscript{III}/Y (30)\textsubscript{wie}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 \% NO, 7.5 \% O\textsubscript{2}, He) on Fe-exchanged zeolites at each desorption temperature}
\end{figure}

Despite the superior desorption capacity of the Fe\textsuperscript{III}/ZSM-5 (23)\textsubscript{wie} catalyst (12.1 mg NO\textsubscript{x}/g), most NO\textsubscript{x} is desorbed at 30 °C and 100 °C. As found for its Cu analogue, the large amount of NO\textsubscript{x} desorbed at low temperature is attributed to intrinsic adsorption properties of the zeolite support (H\textsuperscript{+}-ZSM-5 (23)) and formation of surface HNO\textsubscript{3} species.
The nature of metal-exchanged ions and their redox properties greatly affect the NO\textsubscript{x} storage capacity of zeolite catalysts. H\textsubscript{2}-TPR profiles of the Fe-exchanged zeolites are shown in Figure 5.22.

![Figure 5.22. H\textsubscript{2}-TPR profiles of Fe-exchanged zeolites:](image)

- a) Fe\textsuperscript{III}/Y (5.1)\textsubscript{WIE}
- b) Fe\textsuperscript{III}/Y (30)\textsubscript{WIE}
- c) Fe\textsuperscript{III}/ZSM-5 (23)\textsubscript{WIE}
- d) Fe\textsuperscript{III}/ZSM-5 (30)\textsubscript{WIE}
- e) Fe\textsuperscript{III}/ZSM-5 (50)\textsubscript{WIE}
- f) Fe\textsuperscript{III}/BETA (38)\textsubscript{WIE}

As discussed previously, a typical reduction profile for Fe ion-exchanged zeolites presents two peaks. The first peak at 375 °C corresponds to the reduction of Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}. The second peak, at 500 °C, is assigned to the reduction of Fe\textsubscript{3}O\textsubscript{4} to Fe\textsuperscript{0} via FeO. In addition to these characteristic Fe reduction peaks, a distinctive negative event centred around 250 °C is observed for Fe\textsuperscript{III}/Y (5.1)\textsubscript{WIE} and Fe\textsuperscript{III}/BETA (38)\textsubscript{WIE}.

Total hydrogen consumption determined through integration of the H\textsubscript{2}-TPR curves is included in Table 5.5. In concordance with the absence of intense reduction peaks in...
Figure 5.22, H₂ consumption is much lower for Fe exchanged onto ZSM-5 zeolites. Elemental analysis of Fe loadings should be performed to determine if variations in H₂ consumption are due to the metal exchange level achieved, influenced by the zeolite structure, or to a change in the reducibility of the Fe species induced by the support.

**Table 5.5.** Hydrogen consumption obtained from the H₂-TPR profiles of the Fe-exchanged zeolites:

<table>
<thead>
<tr>
<th></th>
<th>H₂ consumption (µmol H₂/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺/Y (5.1)</td>
<td>281</td>
</tr>
<tr>
<td>Fe³⁺/Y (30)</td>
<td>119</td>
</tr>
<tr>
<td>Fe³⁺/ZSM-5 (23)</td>
<td>49</td>
</tr>
<tr>
<td>Fe³⁺/ZSM-5 (30)</td>
<td>23</td>
</tr>
<tr>
<td>Fe³⁺/ZSM-5 (50)</td>
<td>44</td>
</tr>
<tr>
<td>Fe³⁺/BETA (38)</td>
<td>93</td>
</tr>
</tbody>
</table>

Iron possesses high oxygen storage capacity and oxygen mobility because of its equilibrium:

\[
\text{Fe}^{3+} \leftrightarrow \text{Fe}_2\text{O}_3 \leftrightarrow \text{Fe}^{2+}
\]

Equation 5.6

Low storage capacity is related with a low content of Fe³⁺ as both the oxygen storage capacity and oxygen mobility are lower. It has been reported previously that the presence of Fe₂O₃ species plays a crucial role in the oxidation of NO to NO₂. Hence, the larger amount of H₂ consumed could explain the superior NOₓ storage capacity of the Fe³⁺/BETA (38) WIE catalyst, potentially due to a higher Fe³⁺ content.
5.3.2 Chemical vapour impregnation

The method by which metal ion-exchanged zeolites are prepared is crucial in optimising NO\textsubscript{x} storage capacity, through control of metal loadings, nature and distribution of active species and crystallite size.

Sublimation of FeCl\textsubscript{3} vapour onto the H\textsuperscript{+} form of a zeolite is an effective method to introduce Fe into exchange sites\textsuperscript{43 49 101 102 47}. Over-exchanged Fe-MFI prepared by sublimation shows high activity for deNO\textsubscript{x} technologies. Several authors have reported a method by which anhydrous FeCl\textsubscript{3} is sublimed onto H\textsuperscript{+}-ZSM-5, with Brønsted protons replaced by [FeCl\textsubscript{2}]\textsuperscript{+} according to the following reaction\textsuperscript{43}:

\[
\text{H}^+ + \text{FeCl}_3 \rightarrow [\text{FeCl}_2]^+ + \text{HCl}
\]

Equation 5.7

As introduced in Chapter 4, chemical vapour impregnation (CVI) is a simple, facile, reproducible and easily controlled metal vapour deposition technique developed by Forde \textit{et al.}\textsuperscript{103} It has been demonstrated that CVI is an effective technique to achieve highly dispersed metal oxide nanoparticles on H+-ZSM-5\textsuperscript{84 104 105}. A detailed description of the experimental procedure is found in Chapter 3, Section 3.2.2.2.

5.3.2.1 Exchanged metal

1 wt. % Cu-, Fe- and Pt-exchanged ZSM-5 (30) were prepared by CVI using copper (II) acetylacetonate, iron (III) acetylacetonate and platinum (II) acetylacetonate as metal precursors.

The physicochemical properties of the metal-exchanged zeolites, prepared by chemical vapour impregnation and calcined at 550 °C for 3 hours in static air are summarised in Table 5.6.
Table 5.6. Physicochemical properties of metal-exchanged zeolites prepared by CVI:

<table>
<thead>
<tr>
<th></th>
<th>Surface area BET [a]</th>
<th>Pore volume [a]</th>
<th>Acidity [b]</th>
<th>H2 Consumption[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m²/g</td>
<td>mL/g</td>
<td>µmol NH₃/g</td>
<td>µmol H₂/g</td>
</tr>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>412</td>
<td>0.383</td>
<td>1299</td>
<td>260</td>
</tr>
<tr>
<td>CuII/ZSM-5 (30) CVI</td>
<td>337</td>
<td>0.319</td>
<td>1290</td>
<td>512</td>
</tr>
<tr>
<td>FeIII/ZSM-5 (30) CVI</td>
<td>375</td>
<td>0.357</td>
<td>1077</td>
<td>82</td>
</tr>
<tr>
<td>PtII/ZSM-5 (30) CVI</td>
<td>307</td>
<td>0.208</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

[a] Surface area and pore volume measured by N₂ physisorption, [b] acidity measured by NH₃-TPD, and [c] hydrogen consumption obtained from the H₂-TPR profiles.

Impregnation of H⁺-ZSM-5 (30) via CVI diminishes the total surface area by 18 % for Cu, 9 % for Fe and 25 % for Pt. The total pore volume also decreases after metal exchange. This pore blockage is extensive for the PtII/ZSM-5 (30) CVI catalyst, with a 46 % decrease in pore volume.

Table 5.7. Pore volume distribution of metal-exchanged zeolites prepared by CVI:

<table>
<thead>
<tr>
<th></th>
<th>Pore volume/mL·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>0.383</td>
</tr>
<tr>
<td>CuII/ZSM-5 (30) CVI</td>
<td>0.319</td>
</tr>
<tr>
<td>FeIII/ZSM-5 (30) CVI</td>
<td>0.357</td>
</tr>
<tr>
<td>PtII/ZSM-5 (30) CVI</td>
<td>0.208</td>
</tr>
</tbody>
</table>
Chapter 5

The pore volume distributions of the metal-exchanged ZSM-5 (30) catalysts prepared by CVI are presented in Table 5.7. A decrease in the micro- and meso-porous volume is common for Cu, Fe and Pt/ZSM-5 (30) catalysts.

Representative transmission electron microscopy images and particle size distribution for the Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} catalyst are shown in Figure 5.23. Highly dispersed Pt particles with a mean particle size of 6.2 ± 3.3 nm are observed. The majority of the distribution falls into the 2 - 10 nm size range, with a low population in the 0 -2 nm and 10 -18 nm ranges. The morphology of the nanoparticles should be considered, as not all particles present the same shape, spherical and larger cubic crystallites are observed. The homogeneously distributed Pt nanoparticles are likely the cause of the macro- porous volume reduction of the Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} catalyst in Table 5.7.

Quantitative analysis obtained from TEM coupled with EDX, presented in Table 5.8, confirms the presence of approximately 1 wt. % of Pt in Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI}. Thus, the actual metal loading achieved is equal to the theoretical total loading expected based on the amount of Pt precursor used during CVI. In addition, the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio correlates with that of the commercial zeolite (30).

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>O</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt. %</td>
<td>σ</td>
<td>wt. %</td>
<td>σ</td>
</tr>
<tr>
<td>Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI}</td>
<td>40.49</td>
<td>0.61</td>
<td>2.54</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Figure 5.23. Selected HRTEM and STEM images and platinum particle size distribution for Pt/ZSM-5 (30) CVI
NH$_3$-TPD profiles for these catalysts are shown in Figure 5.24. The intensity of the peak at 450 °C, attributed to NH$_3$ chemisorbed at Brønsted acid sites, decreases considerably after Cu exchange. This is due to exchange of Brønsted acid protons. Fe$^{III}$/ZSM-5 (30)$_{CVI}$ presents a different profile with a characteristic event at low temperature and a peak centred at 350 °C suggesting that Fe exchange generates new medium-strength acid sites.

![NH$_3$-TPD profiles of metal-exchanged zeolites prepared by CVI](image)

**Figure 5.24.** NH$_3$-TPD profiles of metal-exchanged zeolites prepared by CVI:

a) H$^+$/ZSM-5 (30)  b) Cu$^{II}$/ZSM-5 (30)$_{CVI}$  c) Fe$^{III}$/ZSM-5 (30)$_{CVI}$

H$_2$-TPR profiles of the metal-exchanged ZSM-5 (30) catalysts prepared by CVI are presented in Figure 5.25. Cu$^{II}$/ZSM-5 (30)$_{CVI}$ exhibits the typical reduction profile discussed previously for Figure 5.7, with two peaks at 225 °C and 400 °C attributed to the reduction of Cu$^{2+}$ to Cu$^0$ at exchanged sites and supported CuO species to Cu$^0$. On the other hand, the TPR profile of Fe$^{III}$/ZSM-5 (30)$_{CVI}$ is formed by a broad peak centred at 300 °C with shoulders at 220 °C and 375 °C. No peak at 500 °C, assigned early in this chapter to reduction of Fe$_3$O$_4$ to Fe$^0$, is observed. This indicates that those Fe$_3$O$_y$ species formed by
CVI are more easily reduced as the reduction temperature is shifted towards lower values. Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} presents a sharp negative peak at 375 °C followed by a positive peak of similar intensity, these events represent H\textsubscript{2} uptake via a spillover mechanism which is characteristic of supported Pt species\textsuperscript{106}. The low temperature reduction of PtO species at 80 °C is accompanied by H\textsubscript{2} uptake in Figure 5.25 d)\textsuperscript{107}.

![Figure 5.25. H\textsubscript{2}-TPR profiles of metal-exchanged zeolites prepared by CVI:](image)

**Figure 5.25.** H\textsubscript{2}-TPR profiles of metal-exchanged zeolites prepared by CVI:

a) H\textsuperscript{+}-ZSM-5 (30)  
 b) Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI}  
 c) Fe\textsuperscript{III}/ZSM-5 (30)\textsubscript{CVI}  
 d) Pt\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI}

FTIR spectra in the OH vibrational region are shown in Figure 5.26. Based on relative intensities of the bands, it is difficult to determine differences in the concentration of the different –OH groups. However, exchange of H\textsuperscript{+} by metal ions is known to decrease the intensity of the band at 3560 cm\textsuperscript{-1}, associated with Brønsted acid groups.
Figure 5.26. DRIFT spectra in the OH vibrational region of metal-exchanged zeolites prepared by CVI:

a) H⁺-ZSM-5 (30)  b) CuII/ZSM-5 (30)CVI  c) FeIII/ZSM-5 (30)CVI

d) PtII/ZSM-5 (30)CVI

The storage capacities of the Fe-, Cu- and Pt-exchanged ZSM-5 (30) catalysts prepared by CVI were evaluated in the presence and absence of O₂.

Figure 5.27 compares the adsorption/desorption capacity in the absence of O₂.

Desorption of NO adsorbed at 30 °C in the absence of O₂ occurs in the form of NO at 30 °C and 100 °C. The two desorption peaks correspond to reversible adsorption of NO and weak physical adsorption of NO on the surface of the catalyst.
Whereas an equal NO adsorption capacity is observed for Cu\textsuperscript{II}/ZSM-5 (30) \texttext{CVI} and Fe\textsuperscript{III}/ZSM-5 (30) \texttext{CVI}, Fe-exchanged ZSM-5 shows double the total NO\textsubscript{x} desorption. This indicates that NO adsorption over Cu\textsuperscript{II}/ZSM-5 (30) \texttext{CVI} is mainly reversible, as the amount of NO desorbed at 100 °C is similar to that of the parent zeolite H\textsuperscript{+}/ZSM-5 (30). Pt\textsuperscript{II}/ZSM-5 (30) \texttext{CVI} exhibits very low storage capacity, not much larger than that of the unmodified ZSM-5 (30).

NO\textsubscript{x} desorption at high temperatures is related to formation of more thermally stable nitrates on the catalyst surface. Oxidation of NO to NO\textsubscript{2} is known to be the first and limiting
step in this storage mechanism. Hence, the storage capacity in the presence of O₂ was assessed. Figure 5.28 represents the NOₓ desorption capacity following adsorption of NO in the presence of O₂.

Figure 5.28. NOₓ storage capacity of metal-exchanged/H⁺-ZSM-5 (30) catalysts

NOₓ adsorption at 30 °C (NO:O₂ = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h⁻¹, 0.1 % NO + 7.5 % O₂ in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air

NOₓ is desorbed mainly in the form of NO₂, at 30 °C, 100 °C 250 °C and 350 °C. The four desorption events represent adsorbed species of differing nature, reversible and weak physical adsorption of NO and adsorption of nitrates with different thermal stabilities.

Total NOₓ desorption is greater for Cu^{II}/ZSM-5 (30) CVI (5.8 mg NOₓ/g), which is comparable with that of the analogous catalyst prepared by WIE shown in Figure 5.12
(5.6 mg NO\textsubscript{x}/g). Desorption is not improved by exchanging Fe or Pt ions onto H\textsuperscript{+}-ZSM-5 (30). Thus, results are similar to those obtained for metal-exchanged ZSM-5 (30) prepared by WIE.

The total distribution of NO\textsubscript{x} species desorbed at different temperatures is shown in Figure 5.29.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_29}
\caption{Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on metal-exchanged/H\textsuperscript{+}-ZSM-5 (30) at each desorption temperature.}
\end{figure}

Total NO\textsubscript{x} desorption at temperatures above 200 °C is similar for both Cu- and Fe-exchanged ZSM-5 (30), 3.3 and 2.8 mg NO\textsubscript{x}/g respectively. Even so, the formation of thermally stable surface nitrates, which desorb at 350 °C, is only significant in the case of Cu\textsuperscript{II}/ZSM-5 (30) CVI.
5.3.2.2 Zeolite structure and aluminium content

The role of the zeolite framework and acidity in NO\textsubscript{x} storage over metal-exchanged zeolites prepared by CVI was investigated. The study comprises of evaluating the NO\textsubscript{x} adsorption/desorption capacities of Cu, Fe and Pt ions exchanged onto six different zeolites in the absence and presence of O\textsubscript{2}. Assessed zeolite supports include Y, ZSM-5 and BETA. Nevertheless, for simplification, only the most relevant results will be discussed.

Cu-exchanged zeolites were the first set of catalysts assessed. Figure 5.30 includes their NO\textsubscript{x} adsorption and desorption capacities in the absence of O\textsubscript{2}.

![Figure 5.30. NO\textsubscript{x} storage capacity of Cu-exchanged zeolites](image)

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air
The zeolite framework and SiO$_2$/Al$_2$O$_3$ ratio affect not only the total NO adsorption capacity but also the amount of reversibly adsorbed NO. As for Cu-exchanged zeolites prepared by WIE, a clear absolute trend is not found. However, some similarities are apparent. Cu$^{II}$/BETA (38) CVI exhibits the greatest NO adsorption but not desorption capacity due to the large amount of reversibly adsorbed NO. Among the ZSM-5 based catalysts Cu$^{II}$/ZSM-5 (50) CVI, that with the highest SiO$_2$ content, shows superior storage performance. Meanwhile larger pore size zeolite Y has a detrimental effect on the NO storage capacity.

![Figure 5.31. NO$_x$ storage capacity of Cu-exchanged zeolites](image)

**Figure 5.31.** NO$_x$ storage capacity of Cu-exchanged zeolites

NO$_x$ adsorption at 30 °C (NO:O$_2$ = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO + 7.5 % O$_2$ in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air
Results obtained for NO\textsubscript{x} storage in the presence of O\textsubscript{2} are shown in Figure 5.31. The total amount of NO\textsubscript{x} desorbed is similar for all the catalysts but two. As for those Cu-exchanged zeolites prepared by WIE in Figure 5.16, superior NO\textsubscript{x} desorption is observed for Cu\textsuperscript{II}/ZSM-5 (23)\textsubscript{CVI}. In addition, despite the lower NO oxidation activity of Cu\textsuperscript{II}/Y (5.1)\textsubscript{CVI}, the amount of NO\textsubscript{x} desorbed is 5.5 mg NO\textsubscript{x}/g, which is comparable with that of Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} (5.8 mg NO\textsubscript{x}/g).

Based on the distribution of NO\textsubscript{x} species at different temperatures, shown in Figure 5.32, it can be concluded that the amount of NO\textsubscript{x} desorbed at temperatures above 200 °C is much higher for Cu\textsuperscript{II}/ZSM-5 (23)\textsubscript{CVI}.

**Figure 5.32.** Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on Cu-exchanged CVI zeolites at each desorption temperature.
It should be noted that the distribution of adsorbed NO₂ species and their thermal stability differs between Cu²⁺/ZSM-5 (23) prepared by WIE (Figure 5.17) and CVI (Figure 5.32). Both catalysts present high NOₓ desorption capacity, with a large amount of NOₓ desorbed at high temperatures. Cu²⁺/ZSM-5 (23) prepared by WIE shows desorption of a similar amount of NOₓ at each temperature. Thus, not only reversibly adsorbed and physisorbed NO (desorbed at 30 °C) is detected, but also highly thermally stable nitrates - which are desorbed at 350 °C. On the other hand, when Cu²⁺/ZSM-5 (23) is prepared by CVI most of the NOₓ desorption occurs at 100 °C and 250 °C. This indicates that CVI favours the formation of active sites which form weakly adsorbed NOₓ species and nitrates of moderate thermal stability.

![H₂-TPR profiles of Cu-exchanged zeolites](image)

**Figure 5.33.** H₂-TPR profiles of Cu-exchanged zeolites:

a) Cu²⁺/Y (30) CVI  

b) Cu²⁺/ZSM-5 (30) CVI  

C) Cu²⁺/BETA (38) CVI

H₂-TPR profiles of Cu-exchanged zeolites with different frameworks but similar acidity are shown in Figure 5.33. The zeolite framework is found to have a greater effect on the
redox properties of Cu sites in -exchanged zeolite catalysts prepared by CVI than those prepared by WIE (Figure 5.18). Similar reduction profiles are shown in Figure 5.33. The absence of a high temperature reduction peak in Cu^{II}/Y (30) CVI (Figure 5.33 a) suggests that Cu is mainly in the form of CuO and as less stable exchanged Cu ions, which are reduced at lower temperatures. The broad high temperature reduction peak observed at ca. 360 °C for Cu^{II}/BETA (38) CVI is also less intense than that of Cu^{II}/ZSM-5 (30) CVI.

![Graph showing NOx storage capacity of Fe-exchanged zeolites](image)

**Figure 5.34.** NOx storage capacity of Fe-exchanged zeolites

NO adsorption at 30 °C and TPD with He up to 500 °C.

Reaction conditions: Flow reactor, GHSV = 35,000 h⁻¹, 0.1 % NO in He/He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air
NO$_x$ storage was also evaluated over Fe-exchanged zeolites prepared by CVI. Figure 5.34 illustrates the effect of the zeolite framework and acidity on NO$_x$ adsorption/desorption capacity in the absence of O$_2$.

Contrary to the results obtained for metal-exchanged zeolites prepared by WIE, Fe exchanged on BETA (Fe$^{III}$/BETA (38) CVI), does not show superior storage performance. In fact, the amount of NO adsorbed over this catalyst (1.6 mg NO$_x$/g) is 4 times lower than that of the WIE analogue (6.3 mg NO$_x$/g, Figure 5.19).

![Figure 5.35. NO$_x$ storage capacity of Fe-exchanged zeolites](image)

**Figure 5.35.** NO$_x$ storage capacity of Fe-exchanged zeolites

NO$_x$ adsorption at 30 $^\circ$C (NO:O$_2$ = 1:75) and TPD with He up to 500 $^\circ$C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO + 7.5 % O$_2$ in He / He

Catalysts prepared by CVI at 150 $^\circ$C for 2 h and calcined at 550 $^\circ$C for 3 h in static air

- 252 -
Based on results obtained during NO\textsubscript{x} adsorption/desorption experiments in the presence of O\textsubscript{2}, it can be concluded that the trends observed for Fe-exchanged zeolites prepared by CVI are similar to those observed in Figure 5.20 for their WIE analogues.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.36.png}
\caption{Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 \% NO, 7.5 \% O\textsubscript{2}, He) on Fe-exchanged zeolites at each desorption temperature}
\end{figure}

High storage capacity is noted for Fe\textsuperscript{III}/ZSM-5 (23) \textsubscript{CVI}, with 9.2 mg of NO\textsubscript{x} desorbed per g of catalyst. As shown in Figure 5.32, the majority of NO\textsubscript{x} desorption occurs at low temperature, indicating formation of weakly adsorbed surface species. In fact, NO\textsubscript{x} desorption at temperatures above 200 °C only accounts for 3 mg NO\textsubscript{x}/g (33 \% of total desorbed NO\textsubscript{x}). Interestingly, Fe\textsuperscript{III}/Y (5.1) shows almost double the total NO\textsubscript{x} desorption when prepared by CVI (7.2 mg NO\textsubscript{x}/g) compared with WIE (4 mg NO\textsubscript{x}/g). Fe\textsuperscript{III}/Y (5.1) \textsubscript{CVI} shows a large amount of NO\textsubscript{x} desorption above 200 °C (3.5 mg NO\textsubscript{x}/g), which exceeds the
amount desorbed by Fe$^{III}$/ZSM-5 (23) CVI (3.0 mg NO$_x$/g) or Fe$^{III}$/BETA (38) CVI (2.7 mg NO$_x$/g). The distributions of NO$_x$ species desorbed at different temperatures from Fe CVI catalysts are shown in Figure 5.36.

![Figure 5.36. Distributions of NO$_x$ species desorbed at different temperatures from Fe CVI catalysts.]

As shown in Figure 5.37, H$_2$-TPR profiles of the Fe-exchanged zeolites prepared by CVI exhibit a broad reduction peak centred at 300 °C. This can be deconvoluted into a series of peaks corresponding to reduction of Fe following the sequence: Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe$^0$. The structure of the zeolite induces changes in the reducibility of the Fe species. The reduction event is shifted towards higher temperature for Fe$^{III}$/Y (30) CVI, Figure 5.37 a). Reduction temperature shifts suggest variation in the relative Fe$^{3+}$/Fe$^{2+}$ concentration and the stability of Fe ions. Hence, reduction occurring at higher temperatures could imply
Chapter 5

NO\textsubscript{x} storage on metal-exchanged zeolites

A larger population of Fe species in a lower oxidation state and more strongly bonded Fe ions. Further characterisation is needed to confirm these suggestions.

NO\textsubscript{x} adsorption/desorption experiments in the absence and presence of O\textsubscript{2}, were also performed over Pt-exchanged zeolites prepared by CVI.

As presented in Figure 5.38, results for NO\textsubscript{x} adsorption and desorption in the absence of O\textsubscript{2} are comparable with those of the unmodified zeolites (Figure 5.27), indicating that the storage capacity is not enhanced with exchange of H\textsuperscript{+} by Pt ions on the parent zeolite.

![Figure 5.38. NO\textsubscript{x} storage capacity of Pt-exchanged zeolites](image)

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air
Chapter 5

NO\textsubscript{x} storage on metal-exchanged zeolites

Although in absolute numbers, the NO\textsubscript{x} storage capacity in the presence of O\textsubscript{2} over Pt-exchanged zeolites is lower than that of the Cu and Fe catalysts, the same trends are observed. As presented in Figure 5.39, Pt\textsuperscript{II}/Y (5.1) CVI and Pt\textsuperscript{II}/ZSM-5 (23) CVI present the highest degree of NO\textsubscript{x} desorption. In the case of the Fe\textsuperscript{III}/ZSM-5 (23) CVI catalyst, most desorption occurs at low temperatures, associated with the intrinsic adsorption capacity of unmodified H\textsuperscript{+}-ZSM-5 (23). The distributions of NO\textsubscript{x} species desorbed at different temperatures are shown in Figure 5.40. The largest amount of NO\textsubscript{x} desorption at 250 °C is observed for Pt\textsuperscript{II}/Y (5.1) CVI (1.8 mg NO\textsubscript{x}/g).

![Figure 5.39. NO\textsubscript{x} storage capacity of Pt-exchanged zeolites](image)

**Figure 5.39.** NO\textsubscript{x} storage capacity of Pt-exchanged zeolites

NO\textsubscript{x} adsorption at 30 °C (NO:O\textsubscript{2} = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air
The absence of NO₃ desorption at 350 °C for Pt ion-exchanged zeolites in Figure 5.40 should be noted. This indicates that no highly thermally stable nitrates are formed.

*Figure 5.40.* Total amount of NO₃ desorbed during the TPD carried out after NO₃ adsorption (0.1 % NO, 7.5 % O₂, He) on Pt-exchanged zeolites at each desorption temperature.
5.4 Bimetallic and trimetallic zeolitic systems

The effect of the exchanged metal, zeolite framework, acidity and preparation method on the NO\textsubscript{x} storage capacity of monometallic ion-exchanged zeolites has already been assessed. Bimetallic zeolitic systems prepared by introducing a second metal cation using ion exchange have been reported to show superior performance in deNO\textsubscript{x} reactions.\textsuperscript{38, 108} Sultana et al.\textsuperscript{110} reported that Cu-Fe/ZSM-5, prepared by consecutive wet ion exchanges, exhibits higher NO\textsubscript{x} conversion for NH\textsubscript{3} SCR compared with the monometallic analogues. This performance improvement was correlated to a change in redox properties of the constituent metals; that the presence of Cu increases the reducibility of Fe resulting in an increase in low temperature NO\textsubscript{x} conversion.

In order to study complementary and synergistic effects between Cu, Fe and Pt, a series of bimetallic and trimetallic zeolitic catalysts was prepared by CVI. Cu-Fe/ZSM-5 (30)\textsuperscript{CVI}, Cu-Pt/ZSM-5 (30)\textsuperscript{CVI}, Fe-Pt/ZSM-5 (30)\textsuperscript{CVI} and Cu-Fe-Pt/ZSM-5 (30)\textsuperscript{CVI} catalysts were prepared by simultaneous sublimation of the corresponding metal acetylacetonates precursors at 150 °C for 2 hours. These were then calcined in static air at 550 °C for 3 hours. NO\textsubscript{x} adsorption/desorption experiments, in the presence and absence of O\textsubscript{2}, were carried out using these bimetallic and trimetallic zeolitic catalysts.

While the theoretical metal loading of monometallic zeolitic systems prepared by CVI is 1 wt. %, that of bimetallic and trimetallic zeolitic systems is up to 3 wt. %. The theoretical metal loading is calculated based on the amount of metal precursor used during CVI. Hence, in order to compare the storage capacity, results are expressed as mg of NO\textsubscript{x} adsorbed/desorbed per gram of metal loaded.

Results presented in Figure 5.41 show that NO\textsubscript{x} storage capacity is not significantly improved by impregnation of a second metal onto the ZSM-5 (30) support.
Figure 5.41. NO$_x$ storage capacity of mono-, bi- and tri-metallic zeolites

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air

On the contrary, the addition of Pt to either Cu/ZSM-5 (30) CVI or Fe/ZSM-5 (30) CVI, results in a decrease in the amount of NO$_x$ adsorbed and desorbed. As presented in Figure 5.41, the amount of NO adsorbed in the absence of O$_2$ and subsequently desorbed decreases over the Cu-Pt/ZSM-5 (30) CVI, Fe-Pt/ZSM-5 (30) CVI and Cu-Fe-Pt/ZSM-5 (30) CVI catalysts when compared with their monometallic analogues. A similarly detrimental effect is found in Figure 5.42 for NO$_x$ adsorption and desorption in the presence of O$_2$. Cu-Pt/ZSM-5 (30) CVI, Fe-Pt/ZSM-5 (30) CVI and Cu-Fe-Pt/ZSM-5 (30) CVI present comparable NO$_x$ storage capacities to that of monometallic Pt/ZSM-5 (30) CVI. It should be noted that the NO...
oxidation activity is similar for all ZSM-5-based catalysts studied; mono-, bi- and trimetallic.

**Figure 5.42.** NO\textsubscript{x} storage capacity of mono-, bi- and tri-metallic zeolites

NO\textsubscript{x} adsorption at 30 °C (NO:O\textsubscript{2} = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He / He

Catalysts prepared by CVI at 150 °C for 2 h and calcined at 550 °C for 3 h in static air

A positive synergistic effect is only found for Cu-Fe/ZSM-5 (30)\textsuperscript{CVI}, for which the amount of NO\textsubscript{x} desorbed is increased by 10 % following adsorption in the absence of O\textsubscript{2}, and by 20 % following adsorption in the presence of O\textsubscript{2}, when compared with monometallic Cu/ZSM-5 (30)\textsuperscript{CVI} or Fe/ZSM-5 (30)\textsuperscript{CVI}. However, as shown in Figure 5.43 the addition of Fe to Cu/ZSM-5 (30)\textsuperscript{CVI} does not result in an improvement in the desirable high
temperature NO\textsubscript{x} desorption at 350 °C, which is associated with highly thermally stable adsorbed species.

**Figure 5.43.** Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on mono-, bi- and tri-metallic zeolites at each desorption temperature

As discussed previously, the reducibility of supported metals plays an important role in the NO\textsubscript{x} storage capacity. The incorporation of a second metal cation affects the structure, redox properties, stability and nature of the active sites on the zeolite. Hence, characterisation studies of these bi- and trimetallic zeolitic systems are required.
5.5 High temperature NO\textsubscript{x} desorption from zeolite catalysts

As introduced previously in this chapter and in the thesis objectives in Chapter 1, the main goal of this study is to find an adsorption catalyst which stores NO\textsubscript{x} below 250 °C and releases it at high temperature (T > 250 °C). It has been shown that the oxidation of NO to NO\textsubscript{2} is crucial to form those highly thermally stable species which are desorbed at higher temperature. Hence, only adsorption/desorption experiments in the presence of O\textsubscript{2} are considered.

Figures 5.44 and 5.45 summarise the high temperature NO\textsubscript{x} desorption capacities of metal-exchanged zeolites prepared by WIE and CVI respectively. Results include the amount of NO\textsubscript{x} calculated from the integrated area of desorption peaks appearing at 250 °C and 350 °C.

**Figure 5.44.** The total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on metal-exchanged zeolites prepared by WIE at temperatures of above 100 °C.
The high temperature NO\textsubscript{x} desorption capacity of the baseline catalyst, unmodified H\textsuperscript{+}-ZSM-5 (30), is, in most cases, clearly enhanced following metal exchange by both methods, WIE and CVI. In fact, the amount of NO\textsubscript{x} desorbed at high temperatures over a number of the catalysts studied even exceeds the 3.5 mg NO\textsubscript{x}/g desorbed from the commercial catalyst prototype, defined as reference catalyst in Table 5.1. Whilst the zeolite framework and acidity plays a crucial role in the NO\textsubscript{x} storage capacity and desorption at high temperatures, the effect is more significant for those zeolite-based catalysts prepared by WIE. In general, metal-exchanged zeolites prepared by WIE exhibit higher NO\textsubscript{x} desorption at high temperatures than analogous catalysts prepared by CVI. Among the catalysts studied, several present high NO\textsubscript{x} storage performance, though Cu\textsuperscript{II}/ZSM-5 (23) is of particular interest because of its intrinsic adsorption properties.

**Figure 5.45.** The total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on metal-exchanged zeolites prepared by CVI at temperatures of above 100 °C
5.6 Conclusions

This chapter is dedicated to initial screening of metal-exchanged zeolites for NO\textsubscript{x} storage under different conditions and to study the effect of the silicon/aluminium ratio, internal channels and inclusion of base and precious metals. Of particular interest is desorption that occurs at high temperature, above 200 °C, essential to use a NO\textsubscript{x} adsorption catalyst in real applications. A series of metal-exchanged zeolites have been prepared by two post synthesis exchange methods; wet ion exchange and chemical vapour impregnation, and evaluated for NO\textsubscript{x} storage under different model conditions. Cu, Fe and Pt was exchanged into different medium and large pore zeolites, including Y, ZSM-5 and BETA. Although several promising candidates, with great storage performance and large amount of NO\textsubscript{x} desorbed at high temperature, have been found, reproducibility and durability studies are needed to reach robust conclusions.

All zeolite-based catalysts exhibit a high adsorption capacity for NO at 30 °C in the presence and absence of O\textsubscript{2}. He-TPD was conducted to investigate the desorption of NO\textsubscript{x} from these catalysts. During the desorption of NO\textsubscript{x}, other than NO and NO\textsubscript{2} no other N-containing products such as N\textsubscript{2} or N\textsubscript{2}O were observed. While in the absence of O\textsubscript{2}, desorption occurs as NO at 30 °C and 100 °C; in the presence of O\textsubscript{2}, desorption occurs mainly as NO\textsubscript{2} at four different desorption temperatures: 30 °C, 100 °C, 250 °C and 350 °C. Desorption at 30 °C is denoted as being reversible adsorption, associated with weakly physisorbed species on the catalyst surface. Variable temperature desorption studies suggest that NO\textsubscript{x} is adsorbed on different sites. High temperature desorption is attributed to formation of more thermally stable nitrates; NO is converted to nitrate species following the reaction sequence: NO $\rightarrow$ N\textsubscript{2}O\textsubscript{3} $\rightarrow$ N\textsubscript{2}O\textsubscript{4} $\rightarrow$ NO\textsubscript{2} $\rightarrow$ NO\textsubscript{3}. Hence the concentration of O\textsubscript{2} in the gas feed has an important role, as the first reaction step involved in forming more strongly adsorbed, thermally stable species is the oxidation of NO to NO\textsubscript{2}.
Two kinds of NO\textsubscript{x} adsorption sites are present on metal-exchanged zeolites: weak adsorption sites, attributed to the parent zeolite, and adsorption sites, attributed to the metal species exchanged and supported onto the zeolite.

When comparing the nature of the exchanged metal, in general, Cu- and Fe-exchanged zeolites present higher NO\textsubscript{x} storage capacity than Pt analogues, for which the storage capacity is comparable to that of the baseline catalyst H\textsuperscript{+}-ZSM-5 (30).

In agreement with previous work \cite{14, 24, 47, 82}, the zeolite framework and Si/Al ratio is found to play a crucial role in the NO\textsubscript{x} storage capacity of metal-exchanged zeolites. The framework and acidity of the zeolite have an influence not only on the total NO\textsubscript{x} adsorption/desorption capacity; but also on the amount of reversible and irreversible adsorption, on the degree of NO oxidation and on the distribution of NO\textsubscript{x} species desorbed at different temperatures. In addition, these behaviours are also dependent on the gas feed composition. Thus, relationships between the properties and storage capacities of zeolites are different for experiments carried out in the absence and presence of O\textsubscript{2}.

The zeolite framework determines the NO\textsubscript{x} storage activity and thermal stability of the catalysts. The widely open structure and three directional channel system of BETA zeolite is advantageous for NO adsorption in the absence of O\textsubscript{2}, as the superior storage performance of Cu\textsuperscript{II}/BETA (38) and Fe\textsuperscript{III}/BETA (38) suggests. Whereas, the medium and small average pore diameters of the ZSM-5 and BEA framework provide, in general, the most active catalysts; the larger pore sizes of Y zeolites have a detrimental effect on the NO storage capacity. This lower activity has been reported before for Cu/Y \cite{111} and Fe/Y \cite{47, 112}, where only a fraction of cations are active due to species located in inaccessible sites, sodalite cages and hexagonal prisms. The pore geometry of the parent zeolites also influences NO\textsubscript{x} storage capacities when NO is adsorbed in the presence of O\textsubscript{2}- narrow pore
zeolites are more active for the oxidation of NO to NO\textsubscript{2} and, therefore favour formation of more stable adsorbed species.

The Brønsted acidity of the zeolite support is also found to affect the NO\textsubscript{x} storage capacity. However, conflicting trends are found depending on the nature of the exchanged metal and the storage conditions. It has been found in previous work that whereas stability can be improved by using high SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios, a low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio results in highly active systems\textsuperscript{113,114}. The amount of NO adsorbed/desorbed in the absence of O\textsubscript{2}, over Cu-exchanged zeolites increases with a decreasing aluminium content of zeolites with the same framework topology. Contrarily, the storage capacity obtained in the absence of O\textsubscript{2} for Fe-exchanged zeolites increases with increasing aluminium content of ZSM-5 zeolites. When comparing zeolites with the same framework, a decrease in the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio (increase in Brønsted acidity) is also beneficial for NO\textsubscript{x} desorption and NO oxidation during NO adsorption in the presence of O\textsubscript{2}. Metal-exchanged ZSM-5 (23) catalysts exhibit high NO\textsubscript{x} storage capacity. Although desorption occurs mainly at low temperatures, due to the intrinsic adsorption capacity of the parent zeolite H\textsuperscript{+}-ZSM-5 (23), desorption at high temperatures is also significant. In addition, the high aluminium content zeolite Y studied, shows promising results for NO\textsubscript{x} storage in the presence of O\textsubscript{2}, Cu\textsuperscript{II}/Y (5.1) and Fe\textsuperscript{III}/Y (5.1) prepared by CVI present a greater NO\textsubscript{x} desorption, even at high temperatures.

Consistent with previous reports, the preparation method and degree of exchange are also believed to influence the stability and activity of metal-exchanged zeolites for deNO\textsubscript{x} reactions\textsuperscript{115}. Previous studies have reported the importance of achieving an optimum balance between the zeolite’s Brønsted acidity and degree of metal exchange, in order to improve catalyst activity\textsuperscript{114}. Whilst results presented in this chapter disagree as to which method produces the most active zeolites, the wet ion exchange preparation method is slightly favoured over CVI. Activity of metal, particularly Cu, -exchanged zeolites
prepared by WIE combine high NO adsorption capacity with high temperature NO\textsubscript{x} desorption.

The important role of the redox behaviour of metal sites on a zeolite’s storage performance is widely recognized\textsuperscript{2}. NO\textsubscript{x} adsorption and formation of stable surface nitrates is influenced by the initial catalyst redox state. The Cu\textsuperscript{2+}/Cu\textsuperscript{+} \textsuperscript{37} and Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio \textsuperscript{14} and bonding strength of the metal ions to the framework affect the reducibility of metal species and consequently the storage capacity.

Whilst initial reducibility studies have been performed; in order to identify the active sites, understand the storage capacity and propose a possible mechanism further characterisation is required. Complete characterisation of the zeolite catalysts should include an analysis of the structure, morphology, porosity, acidity, composition, degree of metal exchange, redox properties and distribution of metal species as well as identification of the adsorbed N-complexes.
5.7 References


67. Leistner, K.; Nicolle, A.; Da Costa, P., Modelling the kinetics of NO oxidation and NOx storage over platinum, ceria and ceria zirconia. *Applied Catalysis B-Environmental* 2012, 111, 415-423.


73. Inaba, M.; Murata, K.; Takahara, I.; Inoue, K.-i., Production of olefins from ethanol by Fe and/or P-modified H-ZSM-5 zeolite catalysts. *Journal of Chemical Technology and Biotechnology* 2011, 86 (1), 95-104.


Chapter 5

NOx storage on metal-exchanged zeolites


6

6.1 Introduction

Chapter 5 covers the initial screening of metal-exchanged zeolites for NO\textsubscript{x} storage and a study of the effect of the zeolite framework and Brønsted acidity, as well as the nature of the exchanged metal. Among the zeolite-based catalysts studied, several present high NO\textsubscript{x} storage performances. Those of particular interest are metal exchanged zeolites that exhibit greater NO\textsubscript{x} desorption at high temperatures above 200 °C.

A common approach for enhancing catalyst properties is to optimise a single variable while the other variables remain fixed. The experimental results obtained thus, do not reveal the interaction between the variables involved. The optimal values of the variable are difficult to determine from these experiments simply because of the large number of experiments required. Accordingly, use of the statistical design of experiments (DOE) is effective to speed up catalysts optimisation.

There are many factors affecting NO\textsubscript{x} storage capacity for metal exchanged zeolites. Focussing on the ion exchange preparation method, this study adopts the DOE method to enhance the adsorption/desorption properties of the Cu\textsuperscript{II}/ZSM-5 (30) catalyst system. In this chapter, experimental design is used to generate a set of data to evaluate the influence of ion exchange experimental variables on NO\textsubscript{x} storage. As described in section 6.3, completion of the study requires an associated statistical analysis, using the response values obtained to find interactions among different experimental variables. The optimum variable values are then determined statistically, in order to maximise the catalyst’s NO\textsubscript{x} storage performance.
6.2 Application of statistical design of experiments (DOE) to optimise NO\textsubscript{x} storage on Cu\textsuperscript{II}/ZSM-5 (30)

As introduced previously, the statistical design of experiments (DOE) provides the data to quantify the influence of experimental variables and associated interactions, with a relative small number of experiments. If there are many experimental variables, it is important to separate the important from the negligible ones. Only after identifying the main contributors and their interactions, can a detailed optimisation be performed.

Hence, Cu\textsuperscript{II}/ZSM-5 (30) catalysts were prepared by wet ion exchange (WIE) and chemical vapour impregnation (CVI) as part of a two level design, constructed using the Design-Expert® 9 statistical design and analysis software. These zeolite catalysts were evaluated for NO\textsubscript{x} storage under different reaction conditions and characterised by different techniques to correlate physicochemical properties with adsorption/desorption properties.

The storage capacity, in the absence of O\textsubscript{2}, was evaluated as explained in Chapter 5, Section 5.2, through performing isothermal NO\textsubscript{x} adsorption with 0.1 % NO balance in He, followed by a TPD with He. The adsorption-desorption profiles obtained are comparable with those shown in Figure 5.2 and 5.3. Those catalysts that exhibit high performance where also tested for NO\textsubscript{x} storage in the presence of O\textsubscript{2}. The adsorption-desorption profiles obtained, in this case, are comparable with those shown in Figures 5.4 and 5.5. The NO\textsubscript{x} storage capacities are summarised in bar plot figures which illustrate quantified values for the total amount of NO\textsubscript{x} (NO and NO\textsubscript{2}) adsorbed and desorbed.
6.2.1 Wet ion exchange

When using WIE, the experimental method and degree of exchange are known to influence the stability and activity of metal exchanged zeolites for deNO\textsubscript{x} reactions.

Over-exchanged Cu/ZSM-5 catalysts, where the amount of Cu\textsuperscript{II} ion exceeds the 1:2 ratio assumed by the ion exchange reaction shown in equation 6.1, are highly active for deNO\textsubscript{x}.

\[
\text{Cu}^{2+} + 2 \text{[H}^+\cdot\text{AlO}^2-\text{]} \leftrightarrow 2 \text{H}^+ + \text{Cu}^{2+}\cdot2\text{AlO}^2- \tag{Equation 6.1}
\]

High metal loading is achieved by repeated ion exchange- up to three to four cycles\textsuperscript{1,2}. However, it has been reported that the degree of metal exchange via WIE is also controlled by the solution contact time, temperature and pH\textsuperscript{3,4,5,6}. In addition, the washing procedure used, after contact between the zeolite support and the metal precursor solution, also affects the degree of metal exchange. Iwamoto et al.\textsuperscript{1,7} prepared active catalysts by a single ion exchange of Cu\textsuperscript{II} in basic ammonia hydroxide (NH\textsubscript{4}OH). By raising the pH of the copper precursor solution, [CuOH]\textsuperscript{+}, [Cu\textsubscript{2}OH]\textsuperscript{3+}, [Cu\textsubscript{2}(OH)\textsubscript{3}]\textsuperscript{2+} and [Cu\textsubscript{3}(OH)\textsubscript{2}]\textsuperscript{4+} exchangeable species are formed, allowing high exchange with aluminium sites\textsuperscript{8,9}. Hence, the pH of the suspension of the copper salt and the zeolite during WIE is a key factor in achieving highly active catalysts.

**Table 6.1.** Experimental variables and level assignments in a two level factorial design to optimise the Cu\textsuperscript{II}/ZSM-5 (30) catalytic system prepared by WIE

<table>
<thead>
<tr>
<th>Variable</th>
<th>Low level (-)</th>
<th>High level (+)</th>
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</thead>
<tbody>
<tr>
<td>Copper precursor concentration</td>
<td>0.025 M</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Solution temperature</td>
<td>25 °C</td>
<td>90 °C</td>
</tr>
<tr>
<td>Solution contact time</td>
<td>6 h</td>
<td>24 h</td>
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<tr>
<td>Solution pH</td>
<td>5.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Washing volume</td>
<td>50 mL</td>
<td>100 mL</td>
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</table>
The experimental parameters of the WIE preparation procedure that affect NO\textsubscript{x} storage on Cu\textsuperscript{II}/ZSM-5 (30) most significantly, were screened based on a fractional two-level factorial design \(2^{5-1}\). Copper (II) acetate was used as the metal precursor. Five variables (copper precursor concentration, solution temperature, solution contact time, solution pH and washing volume) were studied in 16 experiments. Calcination conditions were held constant, at 550 °C for 3 h in static air. As shown in Table 6.1, the concentration of each variable was set at two levels, high and low, denoted by (+) and (-) signs respectively.

Cu\textsuperscript{II}/ZSM-5 (30) catalysts were prepared by WIE based on the DOE matrix presented in Table 6.2.

Table 6.2. Mix proportions of the experimental design for studied variables to optimise the Cu\textsuperscript{II}/ZSM-5 (30) catalytic system prepared by WIE

<table>
<thead>
<tr>
<th>No.</th>
<th>Cu\textsuperscript{II} precursor concentration</th>
<th>Solution temperature</th>
<th>Solution contact time</th>
<th>Solution pH</th>
<th>Washing volume</th>
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Figure 6.1 shows the NO storage capacity obtained for Cu\textsuperscript{II}/ZSM-5 (30) \text{WIE.DOE} catalysts. Bar graphs include the total amount of NO adsorbed at 30 °C and NO desorbed during the TPD up to 300 °C. The amount of NO reversibly adsorbed and hence desorbed at 30 °C is excluded from calculations.

**Figure 6.1.** NO\textsubscript{x} storage capacities of Cu\textsuperscript{II}/ZSM-5 (30) \text{WIE.DOE[No.]} catalysts

NO adsorption at 30 °C and TPD with He up to 300 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO in He / He

Catalysts prepared by WIE DOE and calcined at 550 °C for 3 h in static air

The results reveal that variation of the different experimental variables affects the NO storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) \text{WIE.DOE} catalysts extensively. Not only the total amount of NO adsorbed and desorbed but also the extent of reversible NO adsorption is affected by WIE experimental conditions. Additionally, the resulting colour of the Cu\textsuperscript{II}/ZSM-5 (30) \text{WIE} catalyst is also dependant on the experimental parameters. As
presented in the x-axis of Figure 6.1, wet ion exchange of Cu$^{ll}$ onto the white support, H$^+$-ZSM-5 (30), results in a gradient of colours including light blue, light grey, grey and dark grey. The reason for colour variation is the chemical environment, as these colours are associated with different speciation of copper. While Cu(OH)$_2$ is light blue, CuO is black and Cu$_2$O is red.

Cu$^{Il}$/ZSM-5 (30) WIE DOE 4 and Cu$^{Il}$/ZSM-5 (30) WIE DOE 8 catalysts exhibit the greatest NO adsorption at 2.7 mg NO/g, 4.5 times higher than that of the unmodified ZSM-5 (30). A significant amount of the total NO adsorbed corresponds to reversible adsorption, 48 and 61\% for Cu$^{Il}$/ZSM-5 (30) WIE DOE 4 and Cu$^{Il}$/ZSM-5 (30) WIE DOE 8 respectively. Based on the results it can be concluded that Cu$^{Il}$/ZSM-5 (30) WIE DOE 4 presents the highest storage capacity, with 2.7 and 1.4 mg NO/g adsorbed and desorbed. On the other hand, Cu$^{Il}$/ZSM-5 (30) WIE DOE 16 presents the lowest storage capacity, with only 0.9 and 0.1 mg NO/g adsorbed and desorbed. While the highest amount of NO adsorbed (Cu$^{Il}$/ZSM-5 (30) WIE DOE 4, 2.7 mg NO/g) is 3 times greater than the lowest amount of NO adsorbed (Cu$^{Il}$/ZSM-5 (30) WIE DOE 16, 0.9 mg NO/g) the highest amount of NO desorbed is 14 times greater than the lowest amount of NO desorbed.

It should be noted that Cu$^{Il}$/ZSM-5 (30) WIE DOE 5 represents the catalyst prepared using experimental conditions defined as “standard,” used to prepare those WIE catalysts presented in Chapter 5 Figure 5.11 before the statistical approach was applied. Concordantly, based on NO adsorption, NO storage is enhanced by 35\% for the most active WIE catalyst Cu$^{Il}$/ZSM-5 (30) WIE DOE 4 when compared with the standard catalyst, Cu$^{Il}$/ZSM-5 (30) WIE DOE 5.

Results indicate that there is not a direct relationship between the Cu$^{ll}$ precursor concentration and NO$_x$ storage performance. Hence, using a 0.05 M aqueous solution of
copper (II) acetate is not preferable to a 0.025 M solution. While, the copper precursor solution temperature is found to have the greatest effect on the NO\textsubscript{x} storage capacity, its beneficial effect is also related with the Cu\textsuperscript{II} precursor concentration and solution contact time. At a pH of 5.5, an increase in the solution temperature up to 90 °C is clearly advantageous when using a 0.025 M solution of copper (II) acetate, independent of the solution contact time. Moreover, when using a more concentrated copper (II) acetate aqueous solution (0.05 M), a high temperature (90 °C) is only favourable at short solution contact times (6 hours). No significant differences are observed for Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie} catalysts prepared using different washing volumes. Contrarily to expectation, raising the pH of the Cu\textsuperscript{II} precursor solution by adding NH\textsubscript{4}OH does not give rise to more active catalysts for NO\textsubscript{x} storage. In fact, using a more basic solution generally has a detrimental effect on the NO adsorption/desorption properties of the Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie} catalysts. In addition, as the solution temperature increases, the negative effect of increasing the solution pH is more significant and the amount of NO adsorbed and desorbed drops considerably (Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie,doe 9} and Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie,doe 16}).

To obtain the results presented in Figure 6.1, only NO was quantified and the TPD was performed up to 300 °C rather than 500 °C. This should not affect the results because when NO is adsorbed in the absence of O\textsubscript{2}, desorption occurs mainly as NO at 30 °C and 100 °C. However, as shown in Figure 6.2, the NO\textsubscript{x} storage capacities of selected Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie,doe} catalysts were also obtained, quantifying the amount of NO and NO\textsubscript{2} adsorbed at 30 °C and desorbed during He TPD up to 500 °C. Although the amount of NO adsorbed/desorbed in Figure 6.3 and 6.4 is similar for the most active WIE catalyst (Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie,doe 4}) and standard catalysts (Cu\textsuperscript{II}/ZSM-5 (30)\textsc{wie,doe 5}), major differences (up to 1 mg NO/g) are found for reversible NO adsorption over the other catalysts. Besides, an important amount of the total NO\textsubscript{x} is desorbed as NO\textsubscript{2}, 42 % and 28 %
for Cu$^{II}$/ZSM-5 (30) WIE.DOE.4 and Cu$^{II}$/ZSM-5 (30) WIE.DOE.8 respectively. Despite variations, Cu$^{II}$/ZSM-5 (30) WIE.DOE.4 desorbs more than double the amount of NO$\_x$ when compared with the standard catalyst presented in Chapter 5 (Cu$^{II}$/ZSM-5 (30) WIE.DOE.5).

Reusability of the most active WIE catalyst, Cu$^{II}$/ZSM-5 (30) WIE.DOE.4, was investigated by performing three consecutive NO adsorption-desorption experiments over the same catalyst bed. Results in Figure 6.3 show no catalyst deactivation upon reuse and variations in the amount of NO adsorbed and desorbed are within the experimental error (0.3 mg NO$\_x/g$ catalyst).

**Figure 6.2.** NO$\_x$ storage capacities of Cu$^{II}$/ZSM-5 (30) WIE.DOE.[No.] catalysts

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO in He / He

Catalysts prepared by WIE DOE and calcined at 550 °C for 3 h in static air
As explained in Chapter 5, O\textsubscript{2} is necessary to obtain high temperature desorption because NO\textsubscript{2} is more strongly adsorbed than NO. Thus, the storage capacity of selected Cu\textsuperscript{II}/ZSM-5 (30) WIE DOE catalysts was also evaluated in the presence of O\textsubscript{2}.

Figure 6.3. Reusability of Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE} for NO\textsubscript{x} storage

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO in He / He

Catalysts prepared by WIE DOE and calcined at 550 °C for 3 h in static air

Figure 6.4 shows the amount of NO\textsubscript{x} desorbed after NO adsorption in the presence of O\textsubscript{2} over; unmodified H\textsuperscript{+}-ZSM-5 (30), the most active WIE catalyst, Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE} 4, the catalyst prepared using standard experimental conditions, Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE} 5 and the Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE} 1 catalyst.
Cu\textsuperscript{II}/ZSM-5 (30) \textit{WIE DOE} 4, also exhibits the highest NO\textsubscript{x} desorption, 8.5 mg NO\textsubscript{x}/g. This is almost double that of the standard catalyst and is 2.5 times that of unmodified H\textsuperscript{+}-ZSM-5 (30).

**Figure 6.4.** NO\textsubscript{x} storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) \textit{WIE DOE} catalysts

NO\textsubscript{x} adsorption at 30 °C (NO:O\textsubscript{2} = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He / He

Catalysts prepared by \textit{WIE DOE} and calcined at 550 °C for 3 h in static air

The distribution of NO\textsubscript{x} species desorbed at different temperatures is shown in Figure 6.5. The amount of NO\textsubscript{x} desorbed at high temperature (T > 200 °C) for Cu\textsuperscript{II}/ZSM-5 (30) \textit{WIE DOE} 4 is double that of the Cu\textsuperscript{II}/ZSM-5 (30) \textit{WIE catalyst} prepared using standard experimental conditions, DOE [5]. Thus, Cu\textsuperscript{II}/ZSM-5 (30) \textit{WIE DOE} 4 shows not only the highest activity for NO adsorption in the absence of O\textsubscript{2}, but also a superior degree of NO\textsubscript{x} desorption above 200 °C after NO\textsubscript{x} adsorption in the presence of O\textsubscript{2}. High concentration of physisorbed NO\textsubscript{2},
desorbed at 30 °C, and thermally stable nitrate species, desorbed at high temperature, are formed on Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE.DOE.4}.

![Figure 6.5. Total amount of NO\textsubscript{x} desorbed during the TPD carried out after NO\textsubscript{x} adsorption (0.1 % NO, 7.5 % O\textsubscript{2}, He) on Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE.DOE} catalysts at each desorption temperature](image)

In order to correlate the physicochemical properties of the Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE} catalysts with their NO\textsubscript{x} storage performance, characterisation of the most active WIE catalyst, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE.DOE.4}, was performed and results were compared with that of unmodified H\textsuperscript{+}ZSM-5 (30) and the standard catalyst, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE.DOE.5}.

As shown in Table 6.3, incorporation of Cu\textsubscript{2}O\textsubscript{y} species on H\textsuperscript{+}ZSM-5 (30) decreases the total BET surface area. The decrease in surface area is greater in the case of Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE.DOE.4}, 25 % vs. the 4 % decrease obtained for the standard Cu\textsuperscript{II}/ZSM-5(30)\textsubscript{WIE.DOE.5} catalyst prepared before the statistical approach was applied. The total pore volume of
H⁺-ZSM-5 (30) also decreases after Cu exchange. In this case, the decrease in total pore volume is more significant for the standard catalyst.

Table 6.3. Physicochemical properties of Cu⁺/ZSM-5 (30) WIE catalysts

<table>
<thead>
<tr>
<th></th>
<th>Surface area BET [a]</th>
<th>Pore volume [a]</th>
<th>Acidity [b]</th>
<th>H₂ Consumption [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m²/g</td>
<td>mL/g</td>
<td>µmol NH₃/g</td>
<td>µmol H₂/g</td>
</tr>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>412</td>
<td>0.383</td>
<td>1299</td>
<td>260</td>
</tr>
<tr>
<td>Cu⁺/ZSM-5 (30)</td>
<td>394</td>
<td>0.282</td>
<td>1439</td>
<td>707</td>
</tr>
<tr>
<td>Cu⁺/ZSM-5 (30) WIE DOE 4</td>
<td>311</td>
<td>0.331</td>
<td>1993</td>
<td>784</td>
</tr>
</tbody>
</table>

[a] Surface area and pore volume measured by N₂ physisorption, [b] acidity measured by NH₃-TPD and [c] hydrogen consumption obtained from the H₂-TPR profiles

The pore volume distribution is described in Table 6.4. Loss of micro-, meso- and macroporous volume indicates that incorporation of copper oxide particles leads to blockage of the zeolite channels and pores. The microporous and mesoporous volumes are reduced by 23 % and 19 % for the Cu⁺/ZSM-5 (30) WIE catalyst prepared using standard conditions (Cu⁺/ZSM-5 (30) WIE DOE 5); and by 24 % and 11 % for the most active WIE catalyst (Cu⁺/ZSM-5 (30) WIE DOE 4).

Table 6.4. Pore volume distribution of Cu⁺/ZSM-5 (30) WIE catalysts

<table>
<thead>
<tr>
<th></th>
<th>Pore volume/mL·g⁻¹</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Microporous</td>
<td>Mesoporous</td>
<td>Macroporous</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt; 2 nm)</td>
<td>(2 nm – 50 nm)</td>
<td>(&gt; 50 nm)</td>
<td></td>
</tr>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>0.383</td>
<td>0.142</td>
<td>0.209</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>Cu⁺/ZSM-5 (30) WIE</td>
<td>0.282</td>
<td>0.110</td>
<td>0.169</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Cu⁺/ZSM-5 (30) WIE DOE 4</td>
<td>0.331</td>
<td>0.108</td>
<td>0.186</td>
<td>0.037</td>
<td></td>
</tr>
</tbody>
</table>
Changes in the acidity of the zeolite catalysts were probed by NH$_3$-TPD and profiles are shown in Figure 6.6. As explained in Chapter 5, the NH$_3$ desorption peak at 250 °C is attributed to weak Brønsted and Lewis sites and that at 450 °C is assigned to strong Brønsted acid sites. Results obtained from quantification of the concentration of acid sites are listed in Table 6.3. The loading of Cu onto H$^+$-ZSM-5 (30) reduces the strong Brønsted acid site density. In addition, the peak appearing at 325 °C suggests that Cu exchange generates new, medium strength acid sites. As reported before, this is attributed to desorption of NH$_3$ from Cu(NH$_3$)$_2^{2+}$ complexes and is more pronounced for the most active WIE catalyst, Cu$^{II}$/ZSM-5 (30)$_{\text{WIE DOE 4}}$. It should be noted that the optimised catalyst presents a characteristic sharp desorption peak at 425 °C, indicating the presence of a high population of strong acid sites.

![NH$_3$-TPD profiles of Cu$^{II}$/ZSM-5 (30)$_{\text{WIE}}$ catalysts:](image)

**Figure 6.6.** NH$_3$-TPD profiles of Cu$^{II}$/ZSM-5 (30)$_{\text{WIE}}$ catalysts:

a) H$^+$-ZSM-5 (30)  

b) Cu$^{II}$/ZSM-5 (30)$_{\text{WIE}}$  

c) Cu$^{II}$/ZSM-5 (30)$_{\text{WIE DOE 4}}$
These results are in agreement with those presented in previous publications\textsuperscript{11}. Zeolites exchanged with divalent cations show a clear decrease in Brønsted acidity and an increase in Lewis acidity.

Due to the influence of the metal species’ redox properties on storage performance, reducibility was investigated via H\textsubscript{2}-TPR. H\textsubscript{2} uptake profiles of selected Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE} catalysts are presented in Figure 6.7.

As previously shown in Figure 5.7, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE} presents two reduction events. The first reduction peak at 225 °C is attributed to reduction of Cu\textsuperscript{2+} to Cu\textsuperscript{+} located at cation...
exchange sites and reduction of supported CuO species. The second reduction broad peak centred at 400 °C corresponds to reduction of Cu$^+$ to Cu$^0$. Although the TPR profile of the same Cu$^{II}$/ZSM-5 (30) WIE catalyst, presented in Figure 6.9 a), shows the same reduction events, it appears as almost a flat line. This is due to relatively low H$_2$ uptake when compared with the other catalysts in the same figure. As presented in Table 6.3, while Cu$^{II}$/ZSM-5 (30) WIE consumes 192 µmol of H$_2$ per g catalyst, Cu$^{II}$/ZSM-5 (30) WIE DOE 4 consumes 898 µmol of H$_2$ per g catalyst. The superior H$_2$ uptake exhibited for those Cu$^{II}$/ZSM-5 (30) WIE catalysts prepared following the statistical approach, indicate higher concentrations of reducible Cu$_x$O$_y$ species and hence, higher Cu loadings. However, elemental analysis is required to determine the actual metal loading and degree of exchange. The H$_2$-TPR profiles of those catalysts with superior storage performance are shown in Figure 6.7 c), Cu$^{II}$/ZSM-5 (30) WIE DOE 4 and Figure 6.9 d), Cu$^{II}$/ZSM-5 (30) WIE DOE 8. They present a similar reduction profile comprising of a first reduction peak at 240 °C with a shoulder at 220 °C and a second reduction peak at 300 °C with a shoulder at 350 °C. The small peak at 220 °C is assigned to CuO species, the peak at 240 °C corresponds to cationic oligomers such as [Cu-O-Cu]$^{2+}$ and [Cu$^+$-Cu$^+$] at cation exchange sites$^{12}$ and the reduction at 350 °C is consistent with reduction of bulk CuO. Reducibility of Cu$^{II}$/ZSM-5 (30) WIE catalysts prepared at higher pH is illustrated in Figure 6.7 e), f) and g), these H$_2$-TPR profiles are characteristic of over-exchanged Cu/ZSM-5 catalysts with two types of zeolite – Cu interactions. Schreier and co-workers$^9$ suggested that metal cations interact with zeolites by two mechanisms: i) ion exchange at the Al exchange sites and ii) electrostatic adsorption at silanol groups. Whilst the first is the dominant mechanism at low to mid pH, the second dominates at high pH. The latter is more clearly manifested in zeolites with low aluminium content such as ZSM-5, where electrostatic adsorption at high pH gives rise to over-exchanged of metal cations.
Based on these results, it can be concluded that the distribution and speciation of Cu sites on ZSM-5 (30) is affected by the experimental conditions used during WIE. Hence, the Cu$^{2+}$/Cu$^{+}$ ratio and bonding strength of the metal ions to the framework affect the reducibility of Cu$_x$O$_y$ species and consequently the NO$_x$ storage capacity. Hadjiivanov et al. 13 showed that NO is selectively adsorbed at Cu$^{2+}$ cations because, whereas NO forms a strong bond with Cu$^{2+}$, the bond with Cu$^{+}$ is weak.

To study the oxidation state of the surface Cu species, XPS was performed. The XPS spectra of the Cu$^{II}$/ZSM-5 (30) WIE catalysts prepared using standard conditions, Cu$^{II}$/ZSM-5 (30) WIE DOE 5, and optimised the most active WIE catalyst, Cu$^{II}$/ZSM-5 (30) WIE DOE 4, are presented in Figure 6.8.

![Figure 6.8. XPS spectra in the Cu 2p binding energy region of a) Cu$^{II}$/ZSM-5 (30) WIE b) Cu$^{II}$/ZSM-5 (30) WIE DOE 4](image)
The spectra show two prominent peaks at 933.5 and 953.5 eV which are assigned to Cu 2p₃/₂ and Cu 2p₁/₂ respectively. These peaks are attributed to reduced Cu species (Cu⁺/Cu⁰). A minor Cu²⁺ contribution is also observed as a weak shoulder at 934.5 eV and 954.5 eV, comparable with the values of bulk CuO (934 and 954 eV). As proposed in previous publications, the presence of shake-up features at ca. 10 eV above the Cu 2p₃/₂ and Cu 2p₁/₂ signals is evidence of an open 3d⁹ shell corresponding to Cu³⁺. Hence, those peaks shown in Figure 6.8 b) at ca. 943 and 953 eV confirm the presence of surface CuO species on Cu⁰/ZSM-5 (30).

Surface compositions calculated by quantitative analysis of the XPS spectra are shown in Table 6.5. An increase in the surface concentration of aluminium following incorporation of copper, suggests migration of framework Al³⁺ to extra framework sites. The Cu/Al ratio is equal to 0.07 for Cu⁰/ZSM-5 (30) WIE and 0.12 for Cu⁰/ZSM-5 (30) WIE DOE 4. Thus, although a less concentrated copper salt solution was used during WIE, a higher concentration of surface copper species, 2.76 wt.%, is achieved under the conditions used to prepare the most active WIE catalyst, Cu⁰/ZSM-5 (30) WIE DOE 4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si At %</th>
<th>Si Wt. %</th>
<th>Al At %</th>
<th>Al Wt. %</th>
<th>O At %</th>
<th>O Wt. %</th>
<th>Cu At %</th>
<th>Cu Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺-ZSM-5 (30)</td>
<td>27.7</td>
<td>39.8</td>
<td>1.4</td>
<td>1.9</td>
<td>71.1</td>
<td>58.2</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Cu⁰/ZSM-5 (30) WIE</td>
<td>29.4</td>
<td>40.7</td>
<td>5.0</td>
<td>6.7</td>
<td>65.3</td>
<td>51.5</td>
<td>0.36</td>
<td>1.11</td>
</tr>
<tr>
<td>Cu⁰/ZSM-5 (30) DOE 4</td>
<td>28.5</td>
<td>38.9</td>
<td>7.3</td>
<td>9.5</td>
<td>63.5</td>
<td>49.3</td>
<td>0.89</td>
<td>2.76</td>
</tr>
</tbody>
</table>

Representative TEM images for the Cu⁰/ZSM-5 (30) WIE DOE 4 catalyst are shown in Figure 6.9. Not only small nanoparticles (1.5 – 3 nm) but also large CuO clusters (20-500 nm) are found. Quantitative analysis obtained from TEM, coupled with EDX,
confirms the presence of heterogeneously distributed copper. This accounts for between 4 and 10 wt. % of the total composition, depending on the region analysed.

**Figure 6.9.** Selected HRTEM and STEM images for Cu\(^{II}\)/ZSM-5 (30)
6.2.1 Chemical vapour impregnation

Selecting the correct temperature is crucial when preparing metal exchanged zeolites by CVI. Thus, the temperature should be enough to allow sublimation but not decomposition of the acetylacetonate precursor. Thermogravimetric analysis of the copper (II) acetylacetonate precursor, presented in Figure 6.10, shows that decomposition starts at ca. 200 °C.

![Figure 6.10. TG curve of the copper (II) acetylacetonate precursor in air](image)

The key experimental variables for the CVI preparation technique and their effect on NO\textsubscript{x} storage over Cu\textsuperscript{II}/ZSM-5 (30) were screened based on a fractional two-level factorial design $2^3$. Copper (II) acetylacetonate was used as the metal precursor. Three variables (copper precursor concentration, impregnation temperature and time) were studied in 8 experiments. Calcination conditions were held constant (550 °C for 3 h in static air). As shown in Table
6.6, each variable was set at two levels, high and low, denoted by (+) and (-) signs respectively.

**Table 6.6.** Experimental ranges of all five variables in a two-level factorial design to optimise the 
Cu\(^{II}/ZSM-5\) (30) catalytic system prepared by CVI

<table>
<thead>
<tr>
<th>Variable</th>
<th>Low level (-)</th>
<th>High level (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical copper loading</td>
<td>1 wt. %</td>
<td>2.5 wt. %</td>
</tr>
<tr>
<td>Impregnation temperature</td>
<td>140 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>Impregnation time</td>
<td>1 h</td>
<td>2 h</td>
</tr>
</tbody>
</table>

Cu\(^{II}/ZSM-5\) (30) catalysts were prepared by CVI based on the DOE matrix presented in Table 6.7.

**Table 6.7.** Mix proportions of the experimental design for studied variables to optimise the 
Cu\(^{II}/ZSM-5\) (30) catalytic system prepared by CVI

<table>
<thead>
<tr>
<th>No.</th>
<th>Theoretical Cu loading</th>
<th>Impregnation temperature</th>
<th>Impregnation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>[2]</td>
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<tr>
<td>[3]</td>
<td>+</td>
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</tr>
<tr>
<td>[4]</td>
<td>-</td>
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<tr>
<td>[5]</td>
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<td>[6]</td>
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<td>+</td>
</tr>
<tr>
<td>[7]</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>[8]</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

The NO\(_x\) storage capacities of the Cu\(^{II}/ZSM-5\) (30) \(CVI_{DOE}\) catalysts were evaluated in the absence of O\(_2\). Figure 6.11 shows the amount of NO adsorbed at 30 °C and the amount of NO desorbed during the TPD up to 500 °C. The amount of NO desorbed at 30 °C, corresponding to reversible adsorption, is excluded from calculations.
Figure 6.11. NO$_x$ storage capacities of Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE \{No.\}}}$ catalysts

NO adsorption at 30 °C and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h$^{-1}$, 0.1 % NO in He / He

Catalysts prepared by CVI DOE and calcined at 550 °C for 3 h in static air

Concordant with results obtained for catalysts prepared by WIE, variation of the different experimental variables affects NO storage capacity when Cu$^{II}$/ZSM-5 (30) catalysts are prepared by CVI. Not only the total amount of NO adsorbed and desorbed but also the extent of the reversible NO adsorption is affected by CVI experimental conditions. Both, Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 6}}$ and Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 7}}$, present the greatest storage performance, with 3.3 and 2.3 mg NO/g adsorbed and desorbed respectively. 30 % of the total amount of NO adsorbed corresponds to reversible adsorption. In this case, Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 8}}$ represents the catalyst prepared under experimental conditions defined as “standard,” used to prepare those catalysts presented in Chapter 5 Figure 5.27,
before the statistical approach was applied. The most active CVI catalyst, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE 6}, shows double the NO adsorption capacity when compared with the standard catalyst, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE 8}.

Results show that for Cu\textsuperscript{II}/ZSM-5 (30) systems prepared by CVI, the 2.5 wt.% catalysts exhibit higher NO adsorption and desorption capacities than 1 wt. % catalysts. Figure 6.12 shows the NO\textsubscript{x} storage capacity of the same catalysts expressed as mg of NO\textsubscript{x} adsorbed/desorbed per gram of metal loaded. The theoretical metal loading is calculated based on the amount of metal precursor used. When considering the theoretical metal loading, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE 5} exhibits a higher storage capacity, with NO desorption 2.5 times higher than that obtained for the standard catalyst.

**Figure 6.12.** NO\textsubscript{x} storage capacities of Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE [No.]} catalysts expressed as mg NO\textsubscript{x}/g metal loaded

- 297 -
The impregnation temperature is found to have the greatest effect on the NO\textsubscript{x} storage capacity. In addition, the optimum temperature is found to be dependent on the Cu\textsuperscript{II} precursor concentration. Hence, while 150 °C is the optimum sublimation temperature to enhance NO\textsubscript{x} storage over 2.5 wt.% Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} catalysts, 1 wt.% Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI} catalysts perform better when prepared at 140 °C. Impregnation time is not significant, with equivalent NO\textsubscript{x} storage for catalysts where copperCu is sublimed at the same temperature for 1 or 2 hours.

**Figure 6.13.** NO\textsubscript{x} storage capacity of Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE} catalysts

NO\textsubscript{x} adsorption at 30 °C (NO:O\textsubscript{2} = 1:75) and TPD with He up to 500 °C

Reaction conditions: Flow reactor, GHSV = 35,000 h\textsuperscript{-1}, 0.1 % NO + 7.5 % O\textsubscript{2} in He / He

Catalysts prepared by CVI DOE and calcined at 550 °C for 3 h in static air

The NO\textsubscript{x} storage capacity of selected Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE} catalysts was also evaluated in the presence of O\textsubscript{2}. Figure 6.13 displays the amount of NO\textsubscript{x} desorbed after NO adsorption.
in the presence of O$_2$ over unmodified H$^+$-ZSM-5 (30), the catalyst prepared using standard experimental conditions, Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 8}}$, the most active 1 wt. % Cu catalyst, Cu$^{II}$/ZSM-5 (30)$_{\text{WIE DOE 5}}$ and the most active 2.5 wt. % Cu catalyst, Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 6}}$.

Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE 6}}$ exhibits the highest NO$_x$ desorption, 10.2 mg NO$_x$/g, almost double that of the standard catalyst and 3 times la that of unmodified H$^+$-ZSM-5 (30). Optimisation of the CVI sublimation temperature for 1 wt. % Cu catalysts results in a 22 % increase of the amount of NO$_x$ desorbed.

**Figure 6.14.** Total amount of NO$_x$ desorbed during the TPD carried out after NO$_x$ adsorption (0.1 % NO, 7.5 % O$_2$, He) on Cu$^{II}$/ZSM-5 (30)$_{\text{CVI DOE}}$ catalysts at each desorption temperature

The distribution of NO$_x$ species desorbed at different temperatures is shown in Figure 6.14. The amount of NO$_x$ desorbed at high temperature (T > 200 °C) is 7.7 mg NO$_x$/g for
Chapter 6

Optimising Cu\textsuperscript{II}/ZSM-5 (30) for NO\textsubscript{x} storage

Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 6, double than that of the most active 1 wt. % Cu catalyst, Cu\textsuperscript{II}/ZSM-5 (30) CV1 DOE 5. While Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 5 presents a high concentration of physisorbed and weakly chemisorbed NO\textsubscript{2}, a large amount of thermally stable nitrate species are formed on Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 6.

**Table 6.8.** Physicochemical properties of Cu\textsuperscript{II}/ZSM-5 (30) CVI catalysts

<table>
<thead>
<tr>
<th></th>
<th>Surface area BET [^{a}]</th>
<th>Pore volume [^{a}]</th>
<th>Acidity [^{b}]</th>
<th>H\textsubscript{2} Consumption [^{c}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m\textsuperscript{2}/g</td>
<td>mL/g</td>
<td>µmol NH\textsubscript{3}/g</td>
<td>µmol H\textsubscript{2}/g</td>
</tr>
<tr>
<td>H\textsuperscript{+}-ZSM-5 (30)</td>
<td>412</td>
<td>0.383</td>
<td>1299</td>
<td>260</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}/ZSM-5 (30) CVI</td>
<td>337</td>
<td>0.319</td>
<td>1290</td>
<td>512</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 6</td>
<td>353</td>
<td>0.281</td>
<td>1081</td>
<td>674</td>
</tr>
</tbody>
</table>

\[^{a}\] Surface area and pore volume measured by N\textsubscript{2} physisorption, \(^{b}\) acidity measured by NH\textsubscript{3}-TPD and \(^{c}\) hydrogen consumption obtained from the \textsubscript{H2}-TPR profiles

Characterisation of Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 6, the catalyst which exhibits the greatest NO\textsubscript{x} storage capacity in the absence and presence of O\textsubscript{2}, was performed. In order to determine the cause of its superior performance, results were compared with that of the unmodified zeolite support and the standard catalyst, Cu\textsuperscript{II}/ZSM-5 (30) CVI.

**Table 6.9.** Pore volume distribution of Cu\textsuperscript{II}/ZSM-5 (30) CVI catalysts

<table>
<thead>
<tr>
<th></th>
<th>Pore volume/mL·g\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>H\textsuperscript{+}-ZSM-5 (30)</td>
<td>0.383</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}/ZSM-5 (30) CVI</td>
<td>0.319</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}/ZSM-5 (30) CVI DOE 6</td>
<td>0.281</td>
</tr>
</tbody>
</table>
As shown in Table 6.3, incorporation of Cu$_2$O species onto H$^+$/ZSM-5 (30) diminishes the total surface area by 18 % for Cu$^{ll}$/ZSM-5 (30) CVI and 14 % for Cu$^{ll}$/ZSM-5 (30) CVI DOE 6. The total pore volume of H$^+$/ZSM-5 (30) is also reduced after Cu exchange, decreasing by 26 % for the most active CVI catalyst Cu$^{ll}$/ZSM-5 (30) CVI DOE 6.

The pore volume distribution is quantified in Table 6.9. Loss of micro-, meso- and macro-porous volume indicates that incorporation of copper oxide particles leads to blockage of the zeolite channels and pores. Cu$^{ll}$/ZSM-5 (30) CVI DOE 6 shows a large decrease in micropore volume (64 %).

![Figure 6.15. NH$_3$-TPD profiles of Cu$^{ll}$/ZSM-5 (30) CVI catalysts:](image)

a) H$^+$/ZSM-5 (30)  b) Cu$^{ll}$/ZSM-5 (30) CVI  c) Cu$^{ll}$/ZSM-5 (30) CVI DOE 6
NH$_3$-TPD results shown in Figure 6.15 present the characteristic profile of metal exchanged zeolites, with a low temperature desorption peak attributed to weak Brønsted and Lewis sites and a high temperature desorption peak assigned to strong Brønsted acid sites. Results obtained from quantification of the concentration of acid sites are listed in Table 6.8. Loading of Cu onto H$^+$-ZSM-5 (30) lowers the strong Brønsted acid site density. In addition, new strong acid sites are generated on Cu$^{II}$/ZSM-5 (30) CVI DOE 6, as indicated by the small amount of NH$_3$ desorbed at ca. 650 °C.

![H$_2$-TPR profiles of Cu$^{II}$/ZSM-5 (30) CVI catalysts](image)

**Figure 6.16.** H$_2$-TPR profiles of Cu$^{II}$/ZSM-5 (30) CVI catalysts:

a) Cu$^{II}$/ZSM-5 (30)$_{CVI}$  b) Cu$^{II}$/ZSM-5 (30)$_{CVI, DOE 1}$  c) Cu$^{II}$/ZSM-5 (30)$_{CVI, DOE 5}$

d) Cu$^{II}$/ZSM-5 (30)$_{CVI, DOE 6}$

H$_2$-TPR profiles shown in Figure 6.16 confirm that the reducibility of Cu species is not affected by the experimental conditions used during CVI. Cu$^{II}$/ZSM-5 (30)$_{CVI}$ catalysts show similar Cu$^{2+}$/Cu$^+$ ratios and comparable reduction temperatures. As presented in Table 6.8, while Cu$^{II}$/ZSM-5 (30)$_{CVI}$ consumes 152 µmol of H$_2$ per g of catalyst,
Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI DOE 6} consumes 316 µmol of H\textsubscript{2} per g of catalyst. Hence, catalysts with higher theoretical Cu loading (2.5 wt. %), exhibit a larger uptake of H\textsubscript{2}, attributed to an increase in the concentration of reducible Cu\textsubscript{x}O\textsubscript{y} species.

XPS spectra of the Cu\textsuperscript{II}/ZSM-5 (30) catalysts prepared by CVI are shown in Figure 6.17. As for the spectra of catalysts prepared by WIE, presented in Figure 6.10, the Cu 2p\textsubscript{3/2} peak appearing at 933.5 eV is attributed to reduced Cu\textsuperscript{+}/Cu\textsuperscript{0} species with a minor contribution of Cu\textsuperscript{2+} species. In this case, no shake-up features associated with surface CuO species were observed.

![Figure 6.17. XPS spectra in the Cu 2p binding energy region of a) Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI} b) Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI DOE 6}](image)

Quantitative analysis obtained from XPS spectra is presented in Table 6.10. Despite different theoretical metal loadings, 1 wt. % Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI} and 2.5 wt. % Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI DOE 6} show a similar concentration of surface Cu species.
Table 6.10. Quantitative analysis of the Cu$^{II}$/ZSM-5 (30) CVI catalysts obtained from XPS spectra

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si At %</th>
<th>Si Wt %</th>
<th>Al At %</th>
<th>Al Wt %</th>
<th>O At %</th>
<th>O Wt %</th>
<th>Cu At %</th>
<th>Cu Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$-ZSM-5 (30)</td>
<td>27.7</td>
<td>39.8</td>
<td>1.4</td>
<td>1.9</td>
<td>71.1</td>
<td>58.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu$^{II}$/ZSM-5 (30) CVI</td>
<td>30.2</td>
<td>41.8</td>
<td>3.8</td>
<td>5.1</td>
<td>65.6</td>
<td>51.7</td>
<td>0.47</td>
<td>1.49</td>
</tr>
<tr>
<td>Cu$^{II}$/ZSM-5 (30) CVI DOE 6</td>
<td>30.1</td>
<td>41.6</td>
<td>4.7</td>
<td>6.2</td>
<td>64.8</td>
<td>51.0</td>
<td>0.39</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Representative TEM images and the particle size distribution for Cu$^{II}$/ZSM-5 (30) CVI DOE 6 are shown in Figure 6.18. Highly dispersed spherical copper particles with a mean particle size of $2.3 \pm 0.7 \text{ nm}$ are observed.

Figure 6.18. Selected HRTEM and STEM images and platinum particle size distribution for Cu$^{II}$/ZSM-5 (30) CVI DOE 6.
6.3 Statistical analysis of NO\textsubscript{x} storage on Cu\textsuperscript{II}/ZSM-5 (30)

Results presented in this chapter show the application of the DOE method in order to investigate the effect of catalyst preparation variables on the NO\textsubscript{x} storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) catalysts. As mentioned previously, completion of the study requires an associated statistical analysis.

Statistical analysis will be performed using the same Design-Expert\textsuperscript{®} 9 software. The set of data discussed in this chapter generates response values that should be added to the DOE matrix in the software. For NO\textsubscript{x} storage experiments in the absence of O\textsubscript{2}, two different response factors should be considered: the amount of NO adsorbed and amount of NO desorbed. After completion of NO\textsubscript{x} storage experiments in the presence of O\textsubscript{2}, the same statistical analysis could be applied using the total amount of NO\textsubscript{x} desorbed as the response factor. In this case, using the amount of NO\textsubscript{x} desorbed at high temperature (T > 200 °C) as the response factor will provide information which is more relevant for application of the storage catalysts under real conditions. For each response, the minimum change the design should assign as being statistically significant and the estimated standard deviation must be entered as Delta ("Signal") and Sigma ("Noise") respectively. The ratio will be calculated as Delta/Sigma. Power should exceed 80 % to ensure seeing the desired difference. Standard deviation has been estimated to be 0.1 mg NO\textsubscript{x}/g catalyst by repeating the same storage experiment up to 3 times over selected catalysts.

After the response data has been entered, the software will apply statistical analysis to establish:

- Quantification of the influence of each experimental variable on the response.
- Identification of important individual factors dominating the NO\textsubscript{x} storage capacity.
- Interaction between the different experimental variables studied. Determination of dependent and independent variables and of linear or nonlinear relationships between variables.

- Determination of the regression equation that calculates NO\textsubscript{x} storage capacity as a function of the experimental variables studied.

- Representation of a three-dimensional response surface, where the highest point reveals the optimal experimental variable values to maximise the NO\textsubscript{x} storage capacity.

- Experimental validation of the statistical model.

An optimum Cu\textsuperscript{II}/ZSM-5 (30) catalyst for NO\textsubscript{x} storage will then be prepared using the optimal predicted values for the WIE and CVI experimental variables studied. In order to confirm the effectiveness of the statistical model developed, the NO\textsubscript{x} storage capacity obtained experimentally should be comparable within the predicted optimum response value.
6.4 NO\textsubscript{x} storage under real working conditions

After application of the statistical approach to optimise Cu\textsuperscript{II}/ZSM-5 (30) prepared by WIE and CVI, several catalysts demonstrate promising performance for NO\textsubscript{x} storage. Among them, Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE 4} and Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI DOE 6} exhibit the highest NO\textsubscript{x} storage capacity, with a large amount of NO\textsubscript{x} desorbed at high temperature. Hence, they have been selected as potential candidates for application under real working conditions.

The performance of selected Cu\textsuperscript{II}/ZSM-5 (30) catalysts under conditions similar to the composition of diesel exhaust effluent was evaluated. A detailed description of the experimental procedure is given in Chapter 3.3.2.1. In summary, quantitative analysis was carried out by continuously monitoring the effluent gas composition using a FTIR.

![Figure 6.25. Typical temperature profile for reaction under real conditions](image)

Pretreatment up to 500 °C with 10 v. % O\textsubscript{2} + 5 v. % H\textsubscript{2}O + 5 v. % CO\textsubscript{2} balanced in N\textsubscript{2}

Storage at 80 °C and TPD up to 500 °C with 10 v. % O\textsubscript{2} + 5 v. % H\textsubscript{2}O + 5 v. % CO\textsubscript{2} + 200 ppm NO + 200 ppm CO + 500 ppm C\textsubscript{3}H\textsubscript{8} balanced in N\textsubscript{2}
Figure 6.25 shows the temperature profile and reaction conditions for evaluation of the catalytic activity under realistic conditions.

---

Temperature in °C (dashed line)  
(---) H₂O v. %  
(---) CO₂ v. %  
(---) CO ppm

(---) N₂O ppm  
(---) NO ppm  
(---) NO₂ ppm  
(---) C₃H₈ ppm

**Figure 6.26.** Effluent concentration profile over the Cu²⁺/ZSM-5 (30) catalyst

Reaction conditions: Flow reactor, GHSV = 30,000 h⁻¹

Pretreatment up to 500 °C with 10 v. % O₂ + 5 v. % H₂O + 5 v. % CO₂ balanced in N₂

Storage at 80 °C and TPD up to 500 °C with 10 v. % O₂ + 5 v. % H₂O + 5 v. % CO₂ + 200 ppm NO + 200 ppm CO + 500 ppm C₃H₈ balanced in N₂

Figures 6.26 and 6.27 show the evolution of the different compounds over Cu²⁺/ZSM-5 (30) catalysts during on-line testing under real conditions. Similar profiles are obtained for the two catalysts evaluated. The H₂O concentration profile shows several adsorption and
Chapter 6

Optimising CuII/ZSM-5 (30) for NOx storage

desorption peaks. H2O is firstly adsorbed at room temperature and is rapidly desorbed as the temperature starts to increase during the pretreatment. A second H2O adsorption event is observed during cool down at ca. 50 min. and is desorbed again as the temperature increases during the TPD. The CO2 concentration remains constant during the experiment. During the storage period at 80 °C (60 – 62 min.), the amount of NO and NO2 adsorbed is negligible and only adsorption of C3H8 occurs. C3H8 is then desorbed during the TPD at 200 °C, at which temperature H2O also desorbs. The CO concentration drops considerably (from 150 ppm to 50 ppm) as the temperature increases, reaching a minimum concentration of 50 ppm at 450 °C. The concentration of C3H8 and NO starts to decrease when the temperature reaches 350 °C. At 500 °C, the concentration of C3H8 is 58 % lower than the feed concentration (from 600 to 250 ppm) and that of NO decreases by 33 % (from 300 to 200 ppm).

Consumption of C3H8 via oxidation reactions is not considered because the concentration of H2O and CO2 is not increased and other partial oxidation products, such as C3H6, are not detected. This results suggests that under these conditions, NO is reduced to N2 by C3H8 at temperatures above 350 °C. Thus, NO reduction is favoured over hydrocarbon combustion. Although NO reduction by propane over Cu/ZSM-5 has been reported in previous publications21 22 23, in order to confirm C3H8-SCR, NOx conversion should be determined from N2 formation. Hence, the effluent gas concentration must be monitored using a different technique, such as GC-TCD.

Evolution of NO2 over both catalysts is shown in Figure 6.28. A small desorption peak at 325 °C and 350 °C is observed for CuII/ZSM-5 (30) WIE DOE 4 and CuII/ZSM-5 (30) CVI DOE 6 respectively. The contribution of NOx storage is minimal as only 0.1 mg NOx/g catalyst is
desorbed.

--- Temperature in °C (dashed line)  
(---) H$_2$O v. %  
(---) CO$_2$ v. %  
(---) CO ppm  
(---) N$_2$O ppm  
(---) NO ppm  
(---) NO$_2$ ppm  
(---) C$_3$H$_8$ ppm

**Figure 6.27.** Effluent concentration profile over the Cu$^{II}$/ZSM-5 (30) CV1DOE catalyst

Reaction conditions: Flow reactor, GHSV = 30,000 h$^{-1}$

Pretreatment up to 500 °C with 10 v. % O$_2$ + 5 v. % H$_2$O + 5 v. % CO$_2$ balanced in N$_2$

Storage at 80 °C and TPD up to 500 °C with 10 v. % O$_2$ + 5 v. % H$_2$O + 5 v. % CO$_2$ + 200 ppm NO + 200 ppm CO + 500 ppm C$_3$H$_8$ balanced in N$_2$

It is widely known that the presence of H$_2$O decreases the NO$_x$ adsorption capacity and causes deactivation of the catalysts because H$_2$O competes for the selective adsorption sites and can even blocks the pores$^{24}$. When water vapour is added, surface reactions convert
the Cu adsorption sites into Cu(OH)$_2$, resulting in a decrease in the storage capacity Cu/ZSM-5 (30) catalysts. The presence of NO in the feed gas can also have a negative effect on the NO$_x$ storage capacity. The interaction of NO with the stored nitrates shifts the equilibrium back to NO$_2$ and desorption of nitrates occurs at lower temperatures (150 °C instead of 300-400 °C).

In this study, the main storage contribution over the Cu/ZSM-5 (30) catalysts is the adsorption of C$_3$H$_8$ at 80 °C. High hydrocarbon adsorption capacity over metal exchanged zeolites has been reported before, where a large desorption of C$_3$H$_6$ during TPD experiments was attributed to intrinsic adsorption on the zeolite support. It is believed that the HC molecules stored in the zeolite support are unlikely to be involved in the NO reduction mechanism.$^{25}$

![Figure 6.28. Evolution of NO$_2$ during storage and TPD under real conditions](image)

- 311 -
6.5 Conclusions

This study adopts the statistical design of experiments (DOE) method to investigate the experimental variables which affect the NO\textsubscript{x} storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) prepared by WIE and CVI.

Temperature is found to have the greatest effect on the NO\textsubscript{x} storage capacity. In addition, its influence is dependent on the copper precursor concentration. Increasing the solution temperature for WIE correlates with an increase in NO\textsubscript{x} storage where a low copper precursor concentration is used. An increase in the CVI impregnation temperature also correlates with an increase in NO\textsubscript{x} storage, however only at a high loading of Cu.

The data set generated and the relative influence of the experimental variables studied is required for subsequent optimisation via statistical analysis.

The optimal values of the studied experimental variables that maximise NO\textsubscript{x} storage over Cu\textsuperscript{II}/ZSM-5 (30) prepared by WIE are: 0.025 M (Cu precursor concentration), 90 °C (solution temperature) and 5.5 (solution pH). The solution contact time is not significant.

The most active WIE catalyst, Cu\textsuperscript{II}/ZSM-5 (30) \text{WIE DOE 4}, exhibits a NO\textsubscript{x} storage capacity which is higher than that of the catalyst prepared using standard conditions. The amount of NO\textsubscript{x} desorbed is 1.4 and 8.5 mg NO\textsubscript{x}/g after NO adsorption in the absence and presence of O\textsubscript{2} respectively. Additionally, reusability studies show no deactivation of the catalyst over consecutive adsorption-desorption experiments.

The values of the experimental variables studied which affect optimal NO\textsubscript{x} storage over Cu\textsuperscript{II}/ZSM-5 (30) prepared by CVI are: 2.5 wt. % (theoretical Cu loading) and 150 °C (impregnation temperature). The impregnation time is not significant. The most active CVI
catalyst, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE 6}, exhibits a superior NO\textsubscript{x} storage capacity to that of the catalyst prepared using standard conditions. The amount of NO\textsubscript{x} desorbed is 2.3 and 10.2 mg NO\textsubscript{x}/g after NO adsorption in the absence and presence of O\textsubscript{2} respectively.

While the total amount of NO\textsubscript{x} desorbed is greater for the most active catalyst prepared by CVI than that prepared by WIE, the amount of NO\textsubscript{x} desorbed at high temperature (T > 200 °C) is comparable for both catalysts, approximately 7.5 mg NO\textsubscript{x}/g.

In order to find correlations between the physicochemical properties and the NO\textsubscript{x} storage capacity of the most active catalysts, Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{WIE DOE 4} and Cu\textsuperscript{II}/ZSM-5 (30)\textsubscript{CVI DOE 6}, characterisation using different analytical techniques was performed.

Experimental conditions used during WIE affect the distribution and speciation of the Cu sites on the ZSM-5 (30) support as shown by H\textsubscript{2}-TPR, NH\textsubscript{3}-TPD and XPS. On the other hand, characterisation of the standard and most active CVI catalysts show no apparent difference in Cu speciation, despite the difference in theoretical Cu loading.

Whilst initial characterisation studies have been performed, further investigation is required for better understanding of the nature of these catalysts.

Catalytic activity of the most active Cu\textsuperscript{II}/ZSM-5 (30) catalysts under conditions similar to the effluent in a real working diesel exhaust was evaluated. Evolution of the different compounds suggests that the contribution of NO\textsubscript{x} storage is minimal and that C\textsubscript{3}H\textsubscript{8}-SCR could be taken place, reducing the amount of NO considerably.
6.6 References


Conclusions & Future Work

7.1 Conclusions

The title and objective of this thesis arises from a novel approach, the diesel oxidation NO\textsubscript{x} adsorption catalyst (DONAC), where NO\textsubscript{x} is to be stored by a diesel oxidation catalyst (DOC).

Diesel oxidation catalysts are the most used technology for abatement of carbon monoxide, gas phase hydrocarbons and the soluble organic fraction (SOF) of diesel particulate matter. Much of the DOC’s development has focussed on decreasing the light-off temperature in order to improve oxidation activity, principally during cold starts. On the other hand, NO\textsubscript{x} storage-reduction (NSR) catalysts (Pt/BaO/Al\textsubscript{2}O\textsubscript{3}) are one of the most practical technologies for NO\textsubscript{x} emission control technologies applied in lean-burn gasoline and diesel vehicles\textsuperscript{1}. Despite very interesting results being obtained with each class of catalyst, further studies are needed to find a catalytic system sufficiently active, selective and stable.

Among DOCs, the most efficient catalysts belong to two categories: supported noble metal (Pt and Pd) catalysts\textsuperscript{2,3,4,5,6,7,8,9} and transition metal oxide catalysts, such as Cr, Fe, Co and Mn oxides\textsuperscript{10,11,12,13}. The noble metal-based catalysts are more active but rather unstable and expensive. Platinum-based diesel oxidation catalysts are still the most used technology. Although Al\textsubscript{2}O\textsubscript{3} has been extensively used as a support, the use of other metal oxide supports has yielded more active HC oxidation catalysts\textsuperscript{8,14,15,16,17,18}. It is then interesting to investigate the effect of the support, to obtain more economically viable supported platinum catalysts with a high sulphur tolerance.
Yazawa, Kobayashi and co-workers have published several studies which investigate the support effect in the low temperature catalytic combustion of propane over palladium and platinum catalysts by using a series of metal oxide and mixed metal oxide supports. However, a degree of uncertainty persists in determining whether the reaction is structure sensitive and in the true nature of the active site. One of the aims of this thesis is to rationalise the effect of a series of mixed TiO$_2$ and Al$_2$O$_3$ based supports on propane combustion in an oxidising atmosphere over platinum catalysts. The novelty of this work is that it uses a systematic study to explore the effect of multiple variables. This work addresses not only the effect of the support, platinum loading, preparation method, calcination conditions and platinum precursor, but also the effect of the titania phase composition (anatase or anatase-rutile) and an investigation of the oxidation of NO to NO$_2$. The latter have not previously been reported to the same level.

The most active supported platinum catalyst was found to be 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 % mol Si, A-R). This catalyst exhibits a T$_{50}$ of 270 °C for propane oxidation and T$_{50}$ of 350 °C for NO oxidation. Because different metal loadings and experimental conditions were used, it is difficult to compare results in absolute numbers with previous publications. However, the same trends were found. Hence, in general, increasing the SiO$_2$ content of the TiO$_2$ and Al$_2$O$_3$ mixed supports gives rise to Pt catalysts which are more active for propane and NO oxidation. Variations in the oxidation properties of the supported platinum catalysts studied are mainly related to the nature of the support material rather than other variables such as preparation method, metal precursor or calcination conditions.

In order to determine the effect of the support on the structural and electronic properties of the Pt catalysts and correlate these with oxidation performance, full characterisation was performed. The oxidation state of platinum varies with the support material. In general, the presence of metallic platinum becomes more favourable with increasing SiO$_2$ content of
the support. There is a linear relationship between the oxidation state of platinum and catalytic activity for NO oxidation, with conversion clearly higher with an increasing presence of Pt\(^0\). However, for the total oxidation of propane this relationship is not as unequivocal. For the anatase-rutile TiO\(_2\) based supports, propane oxidation activity is enhanced by increasing the concentration of metallic platinum. On the other hand, anatase TiO\(_2\) based catalysts present superior activity for propane oxidation despite platinum being present predominantly as PtO.

An interesting finding is that platinum catalysts prepared using anatase-based supports, TiO\(_2\)-(SiO\(_2\)) (A), present high performance for the total oxidation of propane but not for the oxidation of NO. These supports not only possess a high surface area but a “cloud shape” morphology with highly dispersed small TiO\(_2\) crystallites. Morphology and phase composition play an active role in the redox properties of the support and its interaction with supported metal particles. Thus, metal-support interactions are of great importance to understand the observed differences in catalytic activity. Results suggest that the extraordinary activity of 1 wt.% Pt/TiO\(_2\) (A) is due to highly reactive oxygen species within the titania support, which promote the total oxidation of propane but not the oxidation of NO to NO\(_2\).

The activity of the supported platinum catalysts was found to depend strongly on oxidation state, with platinum in metallic state being most active. However, it is not only the platinum oxidation state, but the combination of several factors including metal dispersion, BET surface area, morphology and phase composition of the support that explains the variations in catalytic activity.

NSR catalysts are usually formed of precious metals, NO\(_x\) storage components and support metal oxides. NSR catalysts work in a periodic mode, switching between lean and rich
conditions. DONAC provides an alternative for NO\textsubscript{x} abatement and requires an adsorption catalyst that stores NO\textsubscript{x} at low temperature (T < 250 °C) and releases it at high temperatures. While BaO is the most commonly studied NO\textsubscript{x} trapping component, metal exchanged zeolites have been widely used not only for NH\textsubscript{3}- and HC-SCR but also as NO\textsubscript{x} storage components. A study of the NO\textsubscript{x} storage capacity of metal (Cu, Fe and Pt) -exchanged zeolites with different compositions (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 5.1 – 50) and structures (Y, ZSM-5 and BETA) prepared by two different exchange methods (WIE and CVI) has been addressed in this thesis.

While investigations of NO\textsubscript{x} adsorption-desorption on metal exchanged zeolites have been reported in a number of publications, the effect of the silicon/aluminium ratio, internal channels and inclusion of base and precious metals has not previously been investigated in the level of detail presented here. In addition, the NO\textsubscript{x} storage capacity of catalysts prepared by the CVI method, developed by Forde et al.\textsuperscript{19}, has not been reported before. This study also adopts the DOE method to enhance the adsorption/desorption properties of a Cu\textsuperscript{II}/ZSM-5 (30) catalytic system prepared by WIE and CVI. Application of statistical design of experiments is a novel approach that allows the identification of important individual variables and interactions among them in order to optimise catalytic activity with a relatively low number of experiments.

NO\textsubscript{x} storage capacities were investigated in the absence and presence of O\textsubscript{2}. However, NO is more weakly adsorbed on zeolites than NO\textsubscript{2} and thus, oxidation of NO to NO\textsubscript{2} is necessary to improve NO\textsubscript{x} desorption at high temperature (T > 200 °C). Desorption at high temperatures is attributed to formation of more thermally stable nitrates. For application under real conditions, results for NO\textsubscript{x} storage in the presence of O\textsubscript{2} are more telling.
When comparing different metal exchanged zeolites, it is important to consider not only the total amount of NO\textsubscript{x} adsorbed and desorbed but also the degree of NO oxidation and distribution of NO\textsubscript{x} species desorbed at different temperatures. The zeolite framework and acidity are found to play a crucial role in the NO\textsubscript{x} storage capacity of metal exchanged zeolites. The DOE method was applied to investigate the way in which experimental variables affect the NO\textsubscript{x} storage capacity of Cu\textsuperscript{II}/ZSM-5 (30). Whilst the data set generated provided information about the relative influence of the experimental variables studied, statistical analysis is required for subsequent optimisation. Temperature is found to have the greatest effect on the NO\textsubscript{x} storage capacity. In addition, its influence is dependent on the copper precursor concentration.

Among the zeolite based catalysts studied, potential candidates for application under real working conditions are those that exhibit greater NO\textsubscript{x} desorption at high temperatures above 200 °C. Due to the intrinsic adsorption capacity of the parent zeolite, H\textsuperscript{+}-ZSM-5 (23), Cu\textsuperscript{II}/ZSM-5 (23) catalysts prepared by WIE and CVI exhibit high NO\textsubscript{x} storage capacities with a large amount of NO\textsubscript{x} being desorbed at high temperatures, 6 mg NO\textsubscript{x}/g catalyst (200 μmol NO\textsubscript{x}/g catalyst) for Cu\textsuperscript{II}/ZSM-5 (23) \textsubscript{WIE} and 10.9 mg NO\textsubscript{x}/g catalyst (363 μmol NO\textsubscript{x}/g catalyst) for Cu\textsuperscript{II}/ZSM-5 (23) \textsubscript{CVI}. The statistical approach allowed for a significant enhancement in the storage capacity of Cu\textsuperscript{II}/ZSM-5 (30) and, in particular, the amount of NO\textsubscript{x} desorbed at high temperature. NO\textsubscript{x} desorption at temperature above 200 °C is found to be 8.5 mg NO\textsubscript{x}/g catalyst (283 μmol NO\textsubscript{x}/g catalyst) for Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{WIE DOE 4} and 10.2 mg NO\textsubscript{x}/g catalyst (340 μmol NO\textsubscript{x}/g catalyst) for Cu\textsuperscript{II}/ZSM-5 (30) \textsubscript{CVI DOE 6}.

Once again, due to differences in the experimental reaction conditions used, it is difficult to compare the NO\textsubscript{x} storage capacity obtained for the catalysts presented in this thesis with
those of similar catalysts presented in previous publications. However, the most active catalysts seem to exhibit higher performance than previously studied analogues $^{20,21}$.

The catalytic activity of the most active Cu$^{II}$/ZSM-5 (30) catalysts under conditions similar to the effluent of a real working diesel engine was evaluated. Results suggest that the contribution of NO$_x$ storage is minimal and that C$_3$H$_8$-SCR takes place, decreasing the amount of NO$_x$ storage considerably.

In order to correlate the physicochemical properties of the metal exchanged zeolites with their NO$_x$ storage performance, characterisation studies were performed. Results confirmed differences in the distribution and speciation of the metal sites on the zeolite support. H$_2$-TPR was found to provide key information in understanding the NO$_x$ storage capacity. The initial redox state, Cu$^{2+}$/Cu$^+$ and Fe$^{3+}$/Fe$^{2+}$ ratio, and bonding strength of the metal ions to the framework affect the reducibility of metal species and consequently the storage capacity.

In summary, studies carried out during the course of this thesis have led to a significant enhancement in the performance of supported platinum catalysts, for the catalytic oxidation of propane and NO, and of metal exchanged zeolites for NO$_x$ storage. Whilst future work is required to fully understand these catalytic systems, the detailed investigations presented here provide key information to address actual needs in diesel exhaust emissions abatement.
7.2 Recommended Future Work

7.2.1 Oxidation properties of supported platinum catalysts

Completion of this work will require further characterisation studies to fully understand the catalytic systems studied. Stability tests under realistic conditions should then be carried out for those promising catalysts found.

Among the further characterisation needed, the following analytical techniques have been suggested:

ICP-MS

Quantification of the total metal loading and composition of the catalyst is crucial for determination of the active phase nature and to more accurately compare the activity of different catalysts.

CO$_2$-TPD and IR spectra of adsorbed pyridine.

Acidity trends obtained in this thesis for the TiO$_2$ (A-R) supports are inconsistent with those obtained in previous studies$^{22-25}$, which showed that the Brønsted acidity of TiO$_2$ based supports increases with an increasing SiO$_2$ content. In addition, the NH$_3$-TPD experiments performed do not provide information about the nature of Lewis and Brønsted acid sites. Hence, further studies would be beneficial in understanding the surface acidity and basicity of the supports and catalysts in greater detail.

Propane, NO and O$_2$ uptake studies.

As reported previously$^{26-28}$, measuring the density of adsorbed molecules, including propane, NO and O$_2$, over the supported platinum catalysts will provide useful information
in understanding the effect of the support on the oxidation properties and deactivation of catalysts.

**In situ** Raman and IR spectroscopy

Shifts in the XPS binding energy of supported platinum catalysts exposed to different conditions have been associated with SMSI. It is widely recognised that metal-support interactions are of great importance in understanding differences in catalytic activity. Thus, probing metal-support interactions under oxidising and reducing conditions by **in situ** techniques would be of great interest.

**TPR-TPO redox cycles, oxygen storage and oxygen mobility studies**

Initial H$_2$-TPR experiments suggest that the oxidation properties of supported platinum catalysts depend extensively upon the inherent reducibility of the support. The extraordinary activity of 1 wt. % Pt/TiO$_2$ (A) is attributed to highly reactive oxygen species within the titania support, which promote the total oxidation of propane. In order to confirm this theory and understand the redox properties of the supports, repeated TPR/O cycles, oxygen storage and oxygen mobility experiments are required.

**HRTEM-TEAM**

Analysis of TEM images is a powerful tool for determination of the structural properties of catalysts and the structure sensitive nature of a reaction. To assess the real effect of dispersion on catalytic activity, the oxidation activities of platinum catalysts which differ in metal dispersion and particle size, but are supported on the same metal oxide, should be evaluated.

In addition, SMSI is, in many cases, related to structural modification via encapsulation. A limitation of this technique is the resolution of the instrument used. Metal particles are
sometimes overlooked as their size is below the detection limit of the instrument. Hence, use of a transmission electron microscope with higher resolution or other instrument such as an electron aberration-corrected electron microscope, will allow for more complete analysis of these catalysts.

With the development of the catalysts, understanding the reaction mechanism involved in the different oxidation reaction studies is a key issue.

**Determination of kinetics for propane and NO oxidation reactions**

Changing the reaction mixture composition, this is the C$_3$H$_8$:O$_2$ or NO:O$_2$ ratio, is known to affect catalyst performance. Determination of the reaction orders with respect to the reactants and products, the activation energy and Arrhenius plots allows elucidation of the rate determining step and might suggest possible mechanisms.

**Assessment of the supports’ oxidation activity**

Although many studies have confirmed that metal oxide supports present negligible intrinsic oxidation activity, with the noble metal known to be the active phase, propane and NO oxidation should be performed over the bare supports to determine the inherent oxidation properties of the support.

Whilst more active supported platinum catalysts have been developed through this study, for application in real DOCs further extensive studies under conditions similar to the composition of diesel exhaust effluent are required.

**Calculation of turnover frequencies**

ICP-MS analysis and completion of stability tests over all catalysts is needed to calculate their TOFs at steady state.
Transient temperature cycles

Transient temperature cycles simulate changes in engine load. It has been demonstrated that when tested for propane oxidation under a transient temperature cycles Pt catalysts exhibit hysteresis behaviour. Similar tests for NO oxidation should be performed to determine variations in catalytic activity at constant exhaust composition and confirm the inverse hysteresis which was previously reported \(^{31}\).

Reaction mixture composition

It is known that the oxidation reaction is hindered when using a more complex reaction mixture \(^{32}\) \(^{33}\) \(^{34}\) \(^{35}\). Studying the inhibitory effect of CO\(_2\), H\(_2\)O and SO\(_2\) would allow for estimation of how the catalysts would perform under real working conditions.

Based on the results presented in this thesis, further work should be addressed to optimise and design supported metal catalysts for DOC technologies.

Other supports

Further investigations to assess the effect of other metal oxide and mixed metal oxide supports on the oxidation activity of supported platinum catalysts are needed in order to identify catalysts with high oxidation activity. Previous studies have shown that CeO\(_2\), ZrO\(_2\) and CeO\(_2\)-ZrO\(_2\) supports present potential for application in hydrocarbon oxidation \(^{36}\).

Different noble metals

Investigation of potential support effects on the oxidation properties of other noble metals, such as Pd, Ru or Rh, will allow identification of candidate DOCs. A study of synergism in bimetallic catalyst systems is also of interest when designing catalysts.
Additives

The low temperature propane oxidation activity, thermal stability and poisoning resistance of supported noble metal catalysts under an oxidising atmosphere has been reported to be enhanced with the electronegativity of additives. Hence, the effect of addition of elements including Nb, V and W, on the oxidation activity of the catalysts studied should be investigated.

7.2.2 Optimising NO\textsubscript{x} storage in metal exchanged zeolites

Although several candidates which show promising NO\textsubscript{x} storage performance and a large amount of high temperature NO\textsubscript{x} desorption have been found, reproducibility and durability studies are needed to reach robust conclusions.

Whilst initial characterisation studies have been performed, these should be extended, with full analysis of the structure, morphology, porosity, acidity, composition, degree of metal exchange, redox properties and distribution of metal species as well as identification of the adsorbed N-complexes. The following analytical techniques have been suggested:

**ICP-MS**

Quantification of the total metal loading and composition of the catalyst is crucial in determining the degree of metal exchange and speciation.

**CO\textsubscript{2}-TPD and IR spectra of adsorbed pyridine**

Further studies would be beneficial in understanding in more detail the nature of acid and base sites, both Lewis and Brønsted. While pyridine is adsorbed as pyridinium ion on a Brønsted site, it is coordinatively bonded to Lewis sites. These adsorption species present
different vibrational frequencies. Lewis acid sites are associated with the bands appearing at 1450 and 1600 cm\(^{-1}\) and Brønsted acid sites with those at 1520 and 1620 cm\(^{-1}\). \(^{37}\)

**XRD**

Although unlikely because only extra framework exchange is expected, XRD investigations should be performed to determine possible changes in the crystallinity and unit cell dimensions of the zeolites after metal exchange.

As described in Chapter 6, completion of the optimisation by DOE requires statistical analysis of the data generated. Statistical analysis provides quantification of the influence of each experimental variable and of the interactions between different variables. Experimental validation should address the effectiveness of DOE in maximising the NO\(_x\) storage performance by preparing and assessing a catalyst under the optimal experimental conditions predicted by the statistical model.

With the development of the catalysts, understanding the mechanism involved in the formation of nitrates is a key issue. *In situ* DRIFTS studies should be used to determine the NO\(_x\) storage mechanism, identify reaction intermediates and assess the thermal stability of adsorbed surface species. Often, multiple M\(_x\)O\(_y\) species are formed on the surface of zeolites and determining the contribution of each type of site is difficult. Transient analysis techniques would help to elucidate the nature of the active phase and identify spectators.

Results presented in this thesis have already demonstrated changes in performance when a catalyst that shows a high NO\(_x\) storage capacity under model conditions, is tested under conditions similar to those in the diesel engine. Insufficient activity, narrow operating windows and sensitivity to H\(_2\)O and sulphur poisoning hinder their practical application for
NO\textsubscript{x} storage. Hence, further investigations are required to determine how a catalyst will perform under real working conditions.

**Adsorption temperature**

Investigation of the effect of varying the adsorption temperature on NO\textsubscript{x} storage would be interesting, as it affects the degree of NO oxidation and, consequently, the thermal stability of the adsorbed species formed.

**Reaction mixture composition**

It is known that the presence of other molecules decreases the NO\textsubscript{x} adsorption capacity and causes deactivation of catalysts through competition for the selective adsorption sites and pore blockage\textsuperscript{21, 38, 39, 40}. Studying the inhibitory effect of CO\textsubscript{2}, CO, H\textsubscript{2}O and SO\textsubscript{2} allows for estimation of how the catalysts would perform under real working conditions.

In order to continue with optimisation of the NO\textsubscript{x} storage capacity, different zeolite frameworks and exchanged metals should be studied to design novel metal exchanged catalysts. Due to their abundance, low cost and high NO\textsubscript{x} storage capacity, natural zeolites are of interest\textsuperscript{38}.

A conclusion to the study will consist of applying findings to the design of a selective hybrid catalyst with high poisoning resistance. The combination of a catalyst with high oxidation activity and an adsorbent with the capacity to store NO\textsubscript{x} at high temperatures would be of great interest.
7.3 References


32. Catalytic control of diesel engine particulate emission: Studies on model reactions over a EuroPt-1 (Pt/SiO$_2$) catalyst


APPENDIX A

Analysis by XPS and TEM-EDX confirms the presence of tungsten, W, on the TiO$_2$-SiO$_2$ (10 % mol Si, A) support.

XPS wide spectrum of the TiO$_2$-SiO$_2$ (10 % mol Si, A) support

EDX spectrum of the TiO$_2$-SiO$_2$ (10 % mol Si, A) support
APPENDIX B

Representation of the typical linear and “u-shaped” CO uptake of the supported platinum catalysts.

CO Chemisorption pulses obtained for 1 wt. % platinum supported catalysts

Pretreatment: 300 °C, 2 h, H₂. CO chemisorption performed at room temperature using 77 µL pulses of CO. Sample mass used ca. 500 mg
APPENDIX C

Absence of diffraction lines corresponding to platinum – 2θ of 39° (111), 46° (200) and 67° (220) - on the XRDs of the supported platinum catalysts.

Powder X-Ray diffraction patterns of the supports and supported platinum catalysts:

a) TiO$_2$ (A-R)  

b) 1 wt. % Pt/TiO$_2$ (A-R)  

c) TiO$_2$-SiO$_2$ (16 mol % Si, A-R)  

d) 1 wt. % Pt/TiO$_2$-SiO$_2$ (16 mol % Si, A-R)