

Catalytic Wet Air Oxidation: Developing a Continuous Process



DAFYDD O. DAVIES

September 2016

Thesis submitted in accordance with the requirements of Cardiff
University for the degree of Doctor of Philosophy

Supervisor: Prof. Stanislaw Golunski

Acknowledgements

I would like to begin by thanking a number of people for their help and support throughout my PhD.

Firstly, I cannot thank my supervisor, Professor Stan Golunski, enough for giving me the opportunity to study at the Cardiff Catalysis Institute. He was very supportive in guiding me through my research and was always there, with his door open, if I needed his advice. I am also grateful of the time my post-doctoral supervisor, Dr David Selick spent supporting me during the initial stages of my PhD.

I would also like to extend my thanks to my industrial supervisors Dr. Peter Johnston, Dr. Andy York and Dr. Paul Collier from Johnson Matthey for their funding and guidance. Without their input, this project could not have gone ahead.

A special thanks also goes to: Dr. David Morgan for conducting the X-ray photo electron analyses; Dr. Georgi Lalev and the school of optometry, for letting me use their Tomographic electron microscopy; and to Chris Morgan, Steve Morris and Alun Davies for their technical assistance.

I must also express my gratitude to my friends and family for all the encouragement they have given me over the past couple of years.

And last but not least, for her patience, understanding and reassurance I'd like to thank my very supportive girlfriend, Kiera. We met just before I started my PhD so she's had to put up with the stress all the way through. Thank You.

Abstract

Past and present techniques to remove toxic organic pollutants from industrial wastewaters have involved biological, oxidative and thermal treatment, but long biological degradation lifetimes and harmful emissions released via incineration type processes poses an environmental problem. Much of the new and emerging technologies have steered away from chemical treatment and progressed towards more sustainable and environmentally friendly processes. Wet air oxidation (WAO), being one of them, uses air as the oxidant mixed with the wastewater solution to oxidise the pollutants. This technology has evolved over the years to include catalysis (CWAO) which offers a greener and more cost effective form of industrial wastewater treatment. The majority of CWAO studies involve batch treatment in autoclave reactors, but this project's aim was to make the treatment process continuous, using an active, stable heterogeneous catalyst in a trickle-flow reactor. Phenol was chosen as the model pollutant and the goal was to reduce its concentration from 1000 ppm to below the EPA limit under the least energy-intensive conditions possible.

The initial stages were made up of commissioning a reactor, followed by catalyst screening and optimisation, which included correlating activity with catalyst structure and composition. HPLC followed by UV detection was used to quantify phenol conversion, while a range of surface and bulk characterisation techniques were used to determine catalyst structure.

Of the catalysts screened platinum supported by silicon carbide provided the most successful results in terms of conversion. SiC's hydrophobic nature limits the wetting experienced during a CWAO reaction; a process that hinders oxygen activation. Doping with ceria improved the catalyst's performance, allowing the metal loading to be reduced while maintaining high conversion of phenol. However when ruthenium was the active component, the more hydrophilic alumina was the preferred support. The reaction with ruthenium relies more on catalyst wetting as it is already in the oxide form. When tests were subsequently carried out on Pt/alumina catalysts, they confirmed the need to increase the hydrophobicity in order to achieve high activity. It is proposed that when the active sites are metallic, the optimum support surface is highly hydrophobic; whereas when metal oxide provides the active sites, the optimum support surface is hydrophilic.

These findings explain how some of the catalytic components contribute towards CWAO's reaction mechanism, and activity controlled, in a way not yet shown by previous publications.

Contents

Declaration	i
Acknowledgements	iii
Abstract	iv
Contents	vi
Chapter 1 Introduction	1
1.1. Background and introduction to catalytic wet air oxidation.....	1
1.1.1. Environmental concerns	1
1.1.2. Pollution control	2
1.1.3. Pollution control for water courses	2
1.1.4. Legal limits for wastewater	4
1.1.5. Phenol as the model pollutant	7
1.1.6. Historic treatment of toxic wastewaters	12
1.1.7. Advanced water treatment of toxic waters	13
1.1.8. CWAO	22
1.2. Literature review – catalysts for CWAO	44
1.2.1. Introduction	44
1.2.2. Types of supports used in CWAO.....	44
1.2.3. Type of metals for CWAO	50
1.3. Conclusion	55

1.4.	References.....	56
Chapter 2 Developing a reactor for continuous flow operation.....		67
2.1.	Introduction.....	67
2.2.	Reactor design.....	68
2.3.	Reactor conditions	70
2.4.	Analysis method	72
2.5.	References.....	74
Chapter 3 Catalyst characterisation methods.....		75
3.1.	Introduction.....	75
3.2.	Temperature programmed reduction (TPR)	75
3.2.1.	Experimental procedure	76
3.3.	Brunauer-Emmett Teller (BET) and porosity.....	76
3.3.1.	Experimental procedure	77
3.4.	Powder X-ray diffraction (XRD).....	77
3.4.1.	Experimental procedure	78
3.5.	X-ray Photoelectron Spectroscopy (XPS)	79
3.5.1.	Experimental procedure	79
3.6.	Transmission Electron Microscopy, Scanning Transmission Electron Microscopy & Energy dispersive X-rays (TEM, STEM & EDX).....	80
3.6.1.	Experimental procedure	81
3.7.	Microwave Plasma – Atomic Emission Spectroscopy (MP-AES)....	82
3.7.1.	Experimental procedure	82

3.8.	Thermogravimetric analysis (TGA).....	82
3.8.1.	Experimental procedure	83
3.9.	References.....	83
Chapter 4 Catalyst screening for CWAO.....		85
4.1.	Preparation & Characterisation of platinum, ruthenium and ceria on alumina and silicon carbide supports	85
4.1.1.	Introduction	85
4.1.2.	Materials.....	85
4.1.3.	Catalyst Preparation	86
4.1.4.	Pre-reaction catalyst characterisation	87
4.1.5.	Conclusion.....	103
4.2.	Catalytic activity studies and correlation with structure.....	104
4.2.1.	Introduction	104
4.2.2.	Carbon based catalysts	104
4.2.3.	Active catalysts in the form of pellets	108
4.2.4.	Active catalysts in the form of granules	112
4.2.5.	Post-reaction catalyst characterisation	121
4.2.6.	Ruthenium catalysts	126
4.2.7.	Conclusion.....	128
4.3.	References.....	129
Chapter 5 The effect of catalyst hydrophobicity on CWAO.....		133

5.1. Preparation & Characterisation of hydrophobically modified platinum on an alumina support	133
5.1.1. Materials	133
5.1.2. Catalyst Preparation	134
5.1.3. Pre-reaction catalyst characterisation	135
5.1.4. Post reaction characterisation	153
5.1.5. Conclusion	154
5.2. Catalytic activity studies and correlation with structure.....	155
5.2.1. Conclusion	163
5.3. References.....	164
Chapter 6 The effect of ceria concentration on catalyst activity.....	166
6.1. Preparation & Characterisation of various loadings of ceria on Pt/SiC	166
6.1.1. Introduction	166
6.1.2. Materials	167
6.1.3. Catalyst Preparation	168
6.1.4. Pre-reaction catalyst characterisation	169
6.1.5. X-ray photoelectron spectroscopy (XPS).....	169
6.2. Catalytic activity studies and correlation with structure.....	174
6.2.1. Introduction	174
6.2.2. Ceria loading effect on activity	174
6.2.3. Conclusion.....	177

6.3. References.....	178
Chapter 7 Conclusions	180
Appendix	183

Chapter 1

Introduction

1.1. Background and introduction to catalytic wet air oxidation

1.1.1. Environmental concerns

Some of the biggest threats to humanity in recent times consist of: diminishing energy resources, climate change and population growth. These threats are the consequence of burning fossil fuels for energy and with an ever growing population, the pressure on countries to produce clean sources of energy has increased considerably^{1,2}. Clean sources of energy would not only decrease the need for the ever declining fossil fuel reserves but the earth's environment would also benefit from it. The risk of global warming from a rise in CO₂ would be reduced and the likelihood of a catastrophic natural disaster would also subside^{3,4}.

Another climate change issue, which is a risk to the earth's ecosystems, is water pollution. The majority of industrial and agricultural processes have some sort of waste management procedures in place, but in some cases rivers can be polluted by chemicals that have not been treated. This has some serious implications on aquatic life as the eutrophication process can occur when too many nutrients enter the river^{5,6}.

1.1.2. Pollution control

Renewable energy has been the way forward in recent years to tackle the increase in CO₂ emissions and a more stringent waste management philosophy has been adopted to address the issue of pollution. It is well known within modern society that recycling helps to decrease the amount of waste being sent to landfill and also lower the cost of production of materials. Recycling also reduces the need for the earth's ores to be mined which again lowers the impact on the planet's natural resources. Another method of waste management is the better designing of chemical processes; it helps minimise waste and optimise production in terms of cost and energy.

1.1.3. Pollution control for water courses

Pollution control for water courses already takes place in the form of wastewater treatment. Water not only gets treated so that it is safe to drink from the tap but it also gets treated after it has been used so that it is safe to be discharged back to the river.

1.1.3.1. Municipal wastewater treatment

There are many ways in which municipal wastewaters can be treated. These waters usually contain large quantities of chemical and biochemical materials as well as ammonia that are harmful to the river's aquatic wildlife.

Wastewater treatment techniques utilises bacterial growth to remove the chemical and biochemical particulates entering the treatment plant. This can be in the way of filter beds whereby bacteria attached to blast furnace slag media can feed off the wastewater's biochemical load as it trickles through. In turn the bacteria increases in mass and subsequently falls off the media and settles out as sludge in clarifying tanks further down the process⁷.

Other processes consist of process air being saturated into the wastewater which in turn activates the bacteria as part of an aerobic growth process. Once growth has occurred for a set number of days the sludge is again settled and taken for further treatment⁷.

Both processes would go on and produce a final effluent of a certain quality that complies with the river's discharge consent. This form of treatment therefore ensures that the river's ecosystem is not harmed by the chemicals present in the wastewater stream. The sludge that has been separated from the effluent would then be subjected to, thickening, dewatering and anaerobic digestion. Anaerobic digestion causes the destruction of volatile solids in the sludge and as a result produces methane. The methane can then be used as a source of energy to power the plant⁷.

1.1.3.2. Potable water treatment

The main reason for treating wastewater is to avoid watercourses getting polluted. If the pollution risk is minimised, not only will the threat to aquatic life be mitigated, the impact on potable water treatment plants will be alleviated.

This type of treatment uses clarifying and filtration techniques, along with disinfection, to reduce the water's colour, turbidity and microbial content. Chlorine and UV are predominantly used to disinfect the water and various acidic/alkaline solutions are used to adjust the pH to provide the optimum level of treatment^{8,9}.

In the event of the treatment works failing, the poor quality water will get diverted away from the point at which it failed and get discharged straight to the river. If chlorine dosing has already occurred then it would have to be de-chlorinated before reaching the river. Chlorine is very toxic to fish and therefore has to be avoided at all costs¹⁰. This

shows that though chlorine is beneficial for human consumption it is not for aquatic life and means that a large degree of precaution is required when discharging to watercourses.

1.1.3.3. Treatment of industrial wastewater

Industrial wastewater can contain a broad range of chemicals. They can also be very complicated in nature and very difficult to remove. The wastewater's biochemical content, for example, can vary depending on the industry it has come from. For a food processing manufacturer the biochemical concentration will be a lot higher compared to that of a petrochemical process. The petrochemical process, like other large chemical processes, will contain a plethora of more difficult to treat substances^{11,12}.

These compounds can be in the form of large, difficult to break down compounds, or even highly toxic ones that need to be removed before the wastewater can be discharged to rivers. Many industries will discharge their wastewater down sewers and get treated via conventional municipal wastewater treatment methods but due to the complicated nature of some of them they would have to be treated on site or be taken away for advanced specialised treatment^{11,13}. The wastewater would have to be biodegradable enough in order for it to be subjected to conventional treatment.

1.1.4. Legal limits for wastewater

Regulations provided by the European Union would determine how much and how concentrated UK's wastewaters can be¹⁴. For regular wastewater treatment, discharge consents are put in place to regulate these concentrations. The biochemical content would be measured in the form of biochemical oxygen demand (BOD) and the chemical content by chemical oxygen demand (COD). BOD and COD measures the amount of oxygen that it takes to fully oxidise the wastewater's biochemical or chemical

content to CO₂ and water^{15,16}. It is common for BOD and COD to be proportional to each other in wastewater solutions¹⁷.

Another parameter regulated is the concentration of ammonia or ammonium. These are measured in the form of ammoniacal nitrogen (AmN). Ammonia is associated with biological waste and therefore more commonly found in municipal wastewater streams, unless it is a process that produces products with considerable amounts of ammonia in it¹⁸. It is important to control ammonia as its presence in the river is toxic to aquatic organisms¹⁹.

Another threat to watercourses containing aquatic life is the discharge of phosphorus. Phosphorus promotes the growth of plantation in rivers through the eutrophication process²⁰. This results in the sunlight being blocked by overgrown algae on the water's surface which consequentially restricts photosynthesis of the plantation at lower depths. As a result, the river's oxygen concentration depletes and the fish suffocate.

Suspended solids are also monitored and regulated. They are measured in weight percentages, and depending on the nature of the wastewater solution, the mass would have some proportionality to BOD.

With regards to industrial wastewaters the discharge regulations are more rigorous. They can contain a range of chemicals and can be very toxic or harmful. With so many industrial processes operating in the world, each would have to have a waste management plan tailored for them. In order to mitigate any environmental pollution risk, almost every chemical is regulated before they can be discharged to watercourses.

Depending on the industrial process and how hazardous the wastewater is associated with it, the effluent will either be allowed to be discharged to the sewer, be treated at site, or be treated off site by a third party wastewater treatment facility. Once

treated to a specific standard, usually the residual chemical waste limit, they can be discharged for conventional treatment^{21,22}.

The table below is an example of some of the residual wastewater limits set as standard by the Singapore government²³. In the UK, the limits are set based on the type of industry and the nature of the watercourse the trader is discharging into.

Table 1.1 List of requirements for discharge of trade effluent into the public sewers (Singapore)

S/No	List of Substances	Limit in milligrams per litre of trade effluent (or otherwise stated)
1	5 Day Biochemical Oxygen Demand (BOD) at 20°C	400
2	Chemical Oxygen Demand	600
3	Total Suspended Solids	400
4	Total Dissolved Solids	3,000
5	Chloride (as chloride ion)	1,000
6	Sulphate (as SO ₄)	1,000
7	Sulphide (as sulphur)	1
8	Cyanide (as CN)	2
9	Detergents (linear alkylate sulphonate as methylene blue active substances)	30
10	Grease and Oil (Hydrocarbon)	60
11	Grease and Oil (Non-hydrocarbon)	100
12	Arsenic	5
13	Barium	10
14	Tin	10
15	Iron (as Fe)	50

16	Beryllium	5
17	Boron	5
18	Manganese	10
19	Phenolic Compounds (expressed as phenol)	0.5
20	Fluoride (expressed as fluoride ion)	15

1.1.5. Phenol as the model pollutant

The focus of this study was on the treatment and destruction of phenol. Phenol is commonly found in the wastewaters of the pharmaceutical and dyeing industries and it is regarded as toxic^{21,24,25}. Large quantities of phenol may be wasted over time and in 2005 alone, 45 metric tonnes was discharged from 677 reported facilities to surface waters in the USA²⁶. With it also being the chemical of choice for similar studies in the literature it is ideal as the model pollutant for this investigation²⁷⁻²⁹.

Phenol comes in the form of a hydroxyl group attached to an aromatic ring and was historically used to form bisphenol-A; a product used as a resin for coating applications³⁰.

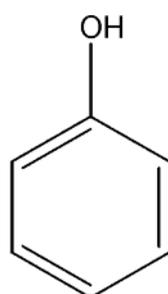


Figure 1.1 Phenol's molecular structure

Phenol can be absorbed into the blood via the skin, lungs and through ingestion and is regarded as toxic, corrosive and harmful³¹. According to this UK government's

document on the toxicological overview of phenol, the toxic compound can cause: “*cardiovascular and respiratory effects, respiratory failure and death*”. Phenol is considered a bactericide also and therefore would not be treated effectively by the biological processes of a sewage treatment plant³². It is important therefore that all, or almost all, of the phenol is removed before it can be discharged for conventional treatment.

The limit for residual phenol to be discharged into a conventional sewer depends on the governing body, the type of industry releasing the pollutant and the nature of the watercourse the pollutant is likely to end up in. Table 1.1 from the Singapore government indicates that no more than 0.5 mg/l should be discharged into the sewers; whereas in Suffolk county in the state of New York, USA, no more than an average of 1.5 mg/l should be discharged³³. The UK (via the Environment Agency) regulates industrial wastewaters on a case by case basis and concentrations of around 0.01 - 1 mg/l have been found in some sewers³⁴. Moreover, the admissible limit for it in drinking water is a stringent 0.5pg/l³⁵.

1.1.5.1. Phenol oxidation pathway and possible by-products

The aim of this study was to optimise the total mineralisation of phenol to CO₂ and water. During non-optimal conditions other intermediate products may be formed as part of the reaction.

Devlin and Harris proposed an oxidation pathway for aqueous phenol by molecular oxygen. The schematic is presented in the figure below.

The diagram shows, first of all, the phenol being oxidised to a group of quinone derivatives. The oxidation can proceed via two different pathways, one via hydroquinone and the other catechol. The hydroquinone pathway results in a *p*-benzoquinone being formed whereas *o*-benzoquinone is formed post catechol oxidation. Lastly, the oxidation pathway takes the reaction via a range of organic acid intermediates before mineralising to CO₂ and water. Here, a possible 15 organic acid compounds may be formed with the main pathway eventually reaching CO₂ and water. Alternatively, acetic or propanoic acid may be formed if there is not sufficient energy for total oxidation.

The two researchers came up with this schematic after isolating most the compounds in the post reaction solution. Some of the compounds are thought to be too short lived or not produced at all as they were not found in the solution and if CO₂ was produced early during the reaction. The acetic acid is thought to be a stable minor side product as only a trace of it was found compared to oxalic and formic acid. Propanoic acid is thought to be a side product also, but as it was not found in the post reaction solution, it is thought to be the product of an undesired pathway.

Below is a similar schematic, shown in a review by Kim *et al.*, that reinforces the route for the phenol oxidation pathway.

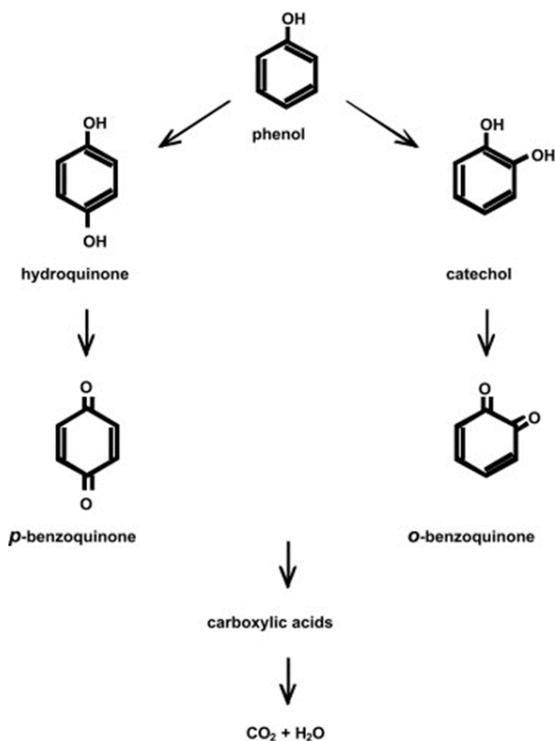


Figure 1.3 Another schematic of the phenol oxidation pathway²⁸

Phenol could polymerise during the process and then get oxidised to form other complex molecules. This was also reported by Alejandre *et al.*³⁷. It was proposed that phenol could react with the partial oxidation product glyoxal to form the polymer, or even via the polymerisation of glyoxal itself. This may also lead to molecules such as 4-hydroxybenzoic acid (4HBA) forming as part of a partial polymerisation/oxidation reaction.

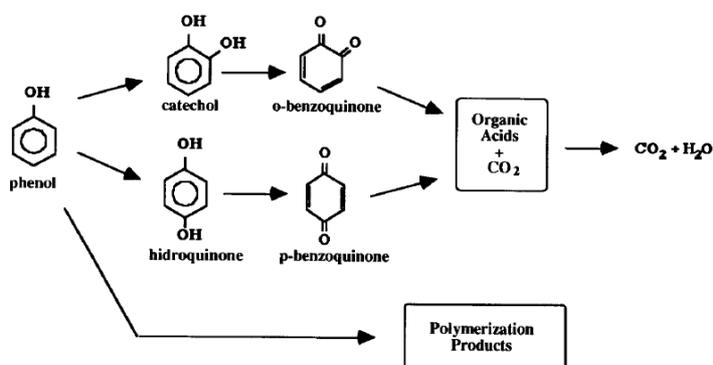


Figure 1.4 Possible polymerisation from phenol oxidation³⁷

1.1.6. Historic treatment of toxic wastewaters

Most organic compounds, as mentioned above, can be biologically treated via conventional sewage treatment-type techniques; but bactericides like phenol and difficult to break down inorganic salts require more advanced treatment methods.

Historically, these relatively untreatable compounds would have to be either, separated via adsorption, scrubbed, or even incinerated at very high temperatures and pressures³⁸. Incineration would require a substantial amount of energy not only to combust the pollutants but to vaporise the water they are in too. Not only is the process very energy intensive it also releases harmful, toxic gases like dioxins and furans as a consequence^{28,39}. The European Union (EU) set a target in 2005 to reduce dioxins being released to the atmosphere altogether⁴⁰.

Incineration does pose some advantages over its counterpart methods as it has fewer legal restrictions, as opposed to landfilling or using the chemical waste in agriculture, and manages to perform total destruction of the organic compounds. The heat produced as part of the process can also be recovered and used for power and there is less of an impact from odour in comparison to biodegradation⁴⁰.

On the other hand, temperatures of between 1000°C and 1700°C are used to combust these aqueous pollutants therefore, it is not surprising to see new advanced treatment techniques emerging to combat the carbon footprint associated with the process³⁹. Not only are the energy needs very high for incineration, the cost implications to industries are considerable also.

A study carried out by Wang *et al.* looked at the emission output implications of incineration⁴¹. The study set out to evaluate the amount of polycyclic aromatic hydrocarbons (PAHs) being emitted in the effluent of a liquid injection incinerator from

a petrochemical process. It was found that large amounts of high molecular weight PAHs of carcinogenic potency were released through the process and highlights how incineration has a major environmental impact. The operating temperature of this particular incinerator was 850-900°C.

As mentioned above, other ways of dealing with wastewaters is via landfilling or using its sludge for agricultural purposes. Sludge from more conventional domestic wastewaters can contain useful fertilizing properties for plant growth, but with industrial wastewaters the pulp is likely to contain more toxic substances such as the likes of phenolic compounds and heavy metals⁴⁰. Another limitation is that crop growth is seasonal and therefore fertilisers will not be required for prolonged periods of the year.

Although landfilling continues to be used as a waste disposal technique, the EU are proposing to reduce its use over time; the same as what happened to disposal of sewage sludge at sea. It is thought that stricter regulations are to be put on landfilling of more harmful wastes such as the toxic type discussed in this study. This therefore puts landfilling out of contention and indicates that incineration is the most feasible option out of the three.

1.1.7. Advanced water treatment of toxic waters

Historically, if the wastewater could not be treated biologically, incineration seemed the most favourable route, but over recent years, to minimise the impact on the environment and to optimise production, the need for a more cost effective, emission free technique was desired. To overcome the challenges presented by incineration, advanced oxidation technologies have been utilised as an alternative⁴².

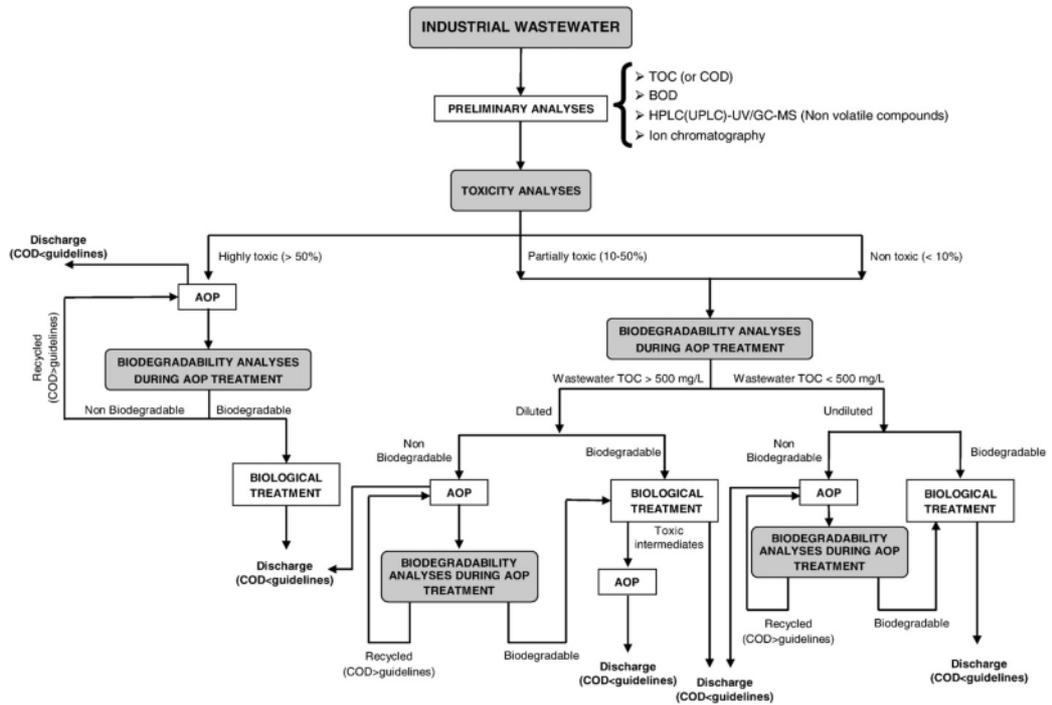


Figure 1.5 Treatment selection process of contaminated water⁴³

The schematic above shows the treatment selection process for dealing with polluted water. If the contaminants are not biodegradable then more advanced techniques are required.

Below are some advanced oxidation techniques that have been used to promote the destruction of organics in industrial wastewaters: -

1.1.7.1. Chlorine treatment

The use of chlorine is widely used in the water treatment industry. It is used as a disinfectant in the production of potable water whereby the microbial content get oxidised. The chlorine oxidant comes in the form of hypochlorite, and is dosed usually towards the end of the treatment process⁸.

Chlorine or hypochlorite is also used to treat industrial wastewaters. In the same way as it does for clean water disinfection, the chemical promotes the oxidation of

organics and inorganics⁴⁴. The limitation of this process is that chloride intermediates might be formed as part of the reaction and can be just as toxic as the chemicals in the water in the first place^{8,45,46}.

1.1.7.2. Hydrogen peroxide treatment

A large proportion of the advanced oxidation processes utilises hydrogen peroxide as an oxidant to oxidize harmful chemicals in industrial wastewaters. The oxidation process employs hydroxyl radicals from the peroxide to attack the organic content of the water⁴². The radicals are considered to be more effective oxidants than just the peroxide reagent itself but are a lot more unstable as they constantly get mopped up to form stable compounds. This means that the radicals need to be constantly generated, either chemically or via a photochemical reaction.

1.1.7.3. Ozone treatment

One of the ways in which these radicals can be formed is via the addition of ozone. Ozone by itself can generate radicals; but in combination with H_2O_2 it can artificially generate OH radicals to oxidise organic compounds more effectively⁴⁷. The down side of this application is that large quantities of ozone is required and therefore comes with significant cost implications.

1.1.7.4. Ultraviolet light (UV)

The radical can also be formed by the incorporation of ultraviolet light (UV). The UV wavelength has enough energy to excite the H_2O_2 to form the hydroxyl radicals; a process known as photolysis⁴⁸.

An advantage of this technique is that it can be used for disinfection as well as for advanced oxidation purposes. In conventional wastewater applications it is common to

find low pressure mercury UV lamps for these purposes. A low pressure UV setup would operate at two baseline wavelengths, 254 nm and 185 nm⁴⁹. The 254 nm radiation would provide the DNA destructing disinfection aspect of the operation and the 185 nm radiation would provide the energy required for advanced oxidation processes such as H₂O₂ activation.

Medium pressure lamps can also be used for this application. They provide a wider spectrum of UV radiation, have a small footprint and a higher UV flux compared to low pressure UV⁵⁰. The downside of medium pressure lamps, on the other hand, is that they have higher operating costs and the high levels of heat associated with them requires advanced thermal control. Low pressure systems are the most widely used systems in water treatment due to their lower running costs; but when the footprint capacity is small, the more compact medium pressure systems are preferred. A disadvantage of UV treatment in general is that H₂O₂ could create other toxic compounds in the wastewater stream^{48,51}.

1.1.7.5. Fenton's reagents

One of the most common ways of producing these hydroxyl species is via Fenton's reagents⁴³. The process uses the techniques mentioned above combined with an iron catalyst to promote the radical formation reaction even further. H₂O₂ decomposes over Fe²⁺ in acidic conditions to form the hydroxyl radical⁵².



It was shown that this process could be used to totally oxidise aqueous phenol. A study was carried out on various Fenton processes to see which was the most efficient at totally oxidising the pollutant⁵³. Fenton, solar-Fenton and UV-Fenton were all tested to determine the most efficient process. Of the three, the solar and UV type Fenton reactions

showed the highest degree of phenol conversion. They both managed to promote 96% conversion whilst the regular Fenton reaction could only promote 41% destruction. The UV-Fenton reaction managed to mineralise the phenol within 15 minutes, whereas the solar equivalent took 25 minutes. This aside, the latter would be preferred as it is significantly cheaper to run.

A review carried out by Esplugas *et al.* concluded that adding the Fenton (Fe^{2+}) reagent increased the phenol conversion rate 40 times that of using just UV and H_2O_2 alone⁵⁴. It was shown to be 5 times faster than ozonation also. However, the cost of ozonation is so low compared to that of the Fenton process, switching from the former to the latter would not be viable.

The advantages of using this technique are: the process is very active in terms of wastewater organics destruction, the chemicals used are widely available and any excess radicals formed decompose rapidly and safely⁵². The disadvantages on the other hand are: chemicals such as H_2O_2 are expensive in large industrial quantities and the use of UV increases the cost of running the reaction significantly.

1.1.7.6. Wet air oxidation

Dosing with chemicals are not considered to be the most sustainable method of treating industrial wastewaters. They can pose an environmental pollution risk if not controlled properly and can be very expensive when dealing with highly concentrated wastewaters^{55,56}.

In order to avoid these issues, techniques such as wet air oxidation (WAO) have been developed over the years. WAO provides a more environmentally friendly method of treating wastewater as it only uses air as the oxidant source. The process consists of atmospheric oxygen dissolving in the wastewater solution to promote the ideal

environment for oxidation to occur^{21,57}. The following reaction equation demonstrates the phenol oxidation reaction.

Equation 1.2

It uses the principles of oxygen interacting with water at high temperature to form hydroxide ions⁵⁸.

Equation 1.3

Oxygen is a relatively inert gas and would require significant amount of energy for it to be activated as an oxidant. It is common therefore to see WAO processes being operated at high temperature and high pressure to reach these activation levels^{57,59}.

WAO is often preferred over chemical treatment as it is a cheaper process to operate. Operating at high temperatures and pressures does come with significant cost implications, but nothing like what is incurred from constantly dosing with chemicals^{21,22}. Another advantage is that the process requires significantly less energy compared to traditional techniques such as incineration^{21,38}.

WAO does still require enough energy to achieve good reaction rates and with this comes the need to apply pressure to keep the solution as a liquid at temperatures above the boiling point of water. It is advantageous for the wastewater to be in the liquid phase because it increases the flux of pollutants through the process and no energy is wasted through vaporisation²¹. Increasing the pressure also increases the amount of oxygen that is able to dissolve in the water, which in turn increases the rate of oxidation²¹.

Below is a phase diagram that details the amount of pressure that is required to keep water as a liquid when the temperature increases.

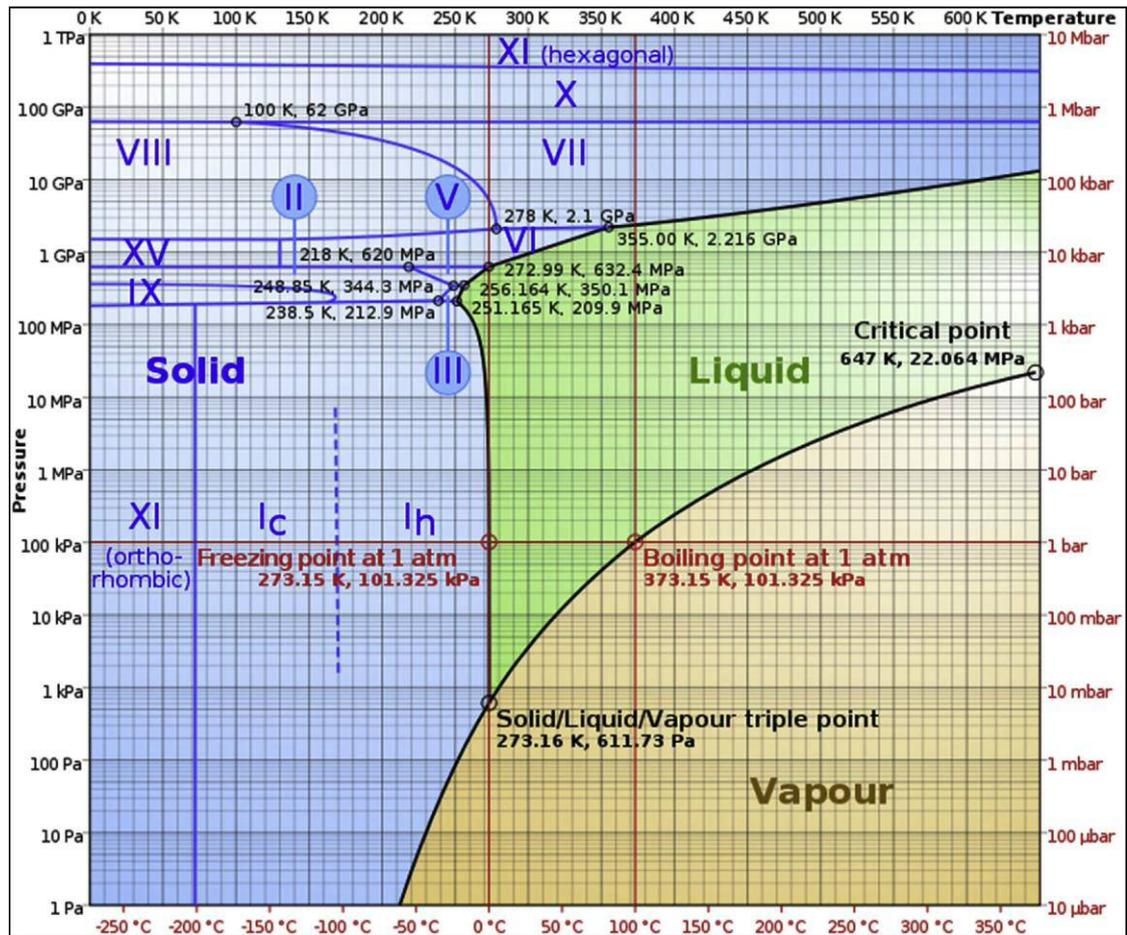


Figure 1.6 The water phase diagram⁶⁰

The rate of oxidation can be increased if the source of oxidant is changed from air to pure oxygen. Air only contains 21% oxygen, therefore increasing it to 100% would mean that more oxygen is able to dissolve in the water if the same volume is used.

The disadvantage of using pure oxygen is that it has to be synthesised to achieve 100% purity. Air on the other hand is readily available from the atmosphere and can be easily compressed to cylinders at a much lower cost. There is also a heightened fire risk associated with pure oxygen therefore the cost of the additional safety measures would have to be considered⁶¹.

WAO is often considered as an alternative process to chemical treatment but they can also be used in conjunction with one another; in other words take advantage of both

their capabilities. Chemicals such as H_2O_2 provides the very active radicals that are able to oxidise pollutants at ambient conditions therefore, if combined with WAO, less dependence is put on thermal oxygen activation. It is important that these chemicals are not over used as the cost of doing so would decrease the process' effectiveness. An efficient WAO process would require as little chemical as possible and rely on the oxygen from the atmosphere to carry out oxidation. A study carried out by Goi *et al.* confirms that adding H_2O_2 improves the WAO rate of landfill leachate removal⁶².

Below is a review of the research that has been conducted into WAO and shows how far the technology has come over time.

Mishra *et al.* reviewed the literature on WAO and stated clearly that the process had been tested for many industries. These included: distilleries, pulp and paper manufacturers and plants that dispose of cyanide and nitrile-type wastes²¹. They also concluded that the process comes with a significant capital cost due to the high pressure and temperatures involved; however, the operating costs were low. The review shows that not all COD waste can be mineralised using WAO. Some low molecular weight carboxylic acids for example were difficult to break down and the same went for large polymeric-type phenol compounds. Although there are some disadvantages, WAO is able to dramatically lower large concentrations of COD produced from industries. The review states that the process becomes self-sufficient at concentrations above 20,000 mg/l.

Gogate *et al.* agrees with the review in terms of WAO being self-sufficient at high concentrations, but reports that values of above 40,000 mg/l is required to make the process viable⁵⁶. Due to its high capital costs, Gogate *et al.* states that there are more efficient techniques being used to clean these types of wastewaters. Chlorine treatment for example has lower capital costs; but due to the risk of by-product formation, a small

scale WAO could be installed as a secondary treatment stage to ensure the wastewater was fit for disposal.

Glottvajn *et al.* showed that WAO could be used for sufficient removal of a drug used to control blood pressure⁶³. The study was carried out using an initial concentration of 800 mg/l, a temperature range of 240-280°C and an oxygen partial pressure (P_{O_2}) of 3.3-9.8 MPa. A first-order rate was observed whereby 80% DOC was removed after 120 mins. The biodegradability of the water had increased and the toxicity decreased in comparison to the initial feed. Although DOC reduction was successful, a significant amount of energy was required to provide the required oxidation. Also, some toxicity remained in the final water which would mean a secondary removal stage would be required to meet regulations and avoid polluting water courses.

Busca *et al.* on the other hand showed that the TOC of phenol could be reduced by 88% at 200°C and a P_{O_2} of 3 MPa⁵⁸. The review stated that a 100% TOC removal was impossible due to the restrictions of low molecular weight carboxylic acid removal using the technique. They also concluded that the solution's pH can highly influence the reaction and that the optimum pH for phenol destruction was between 2 and 7 and above 10. The reasons for this could be put down to O_2 solubility and the structure of phenol at different pH levels. The review also confirmed some of the most common partial oxidations products that are likely to be found during oxidation. These included the various quinone and organic and carboxylic acid formations shown in Figure 1.2 above. Again, the energy required to achieve significant removal of toxic waste species such as phenol using WAO is substantial and needs to be improved for it to be the most efficient and viable process.

The improvements can be found in the way of using catalysis. A catalyst is able to reduce the energy requirements associated with WAO and in turn, dramatically reduce the running costs. The process of combining WAO with catalysis is known as catalytic wet air oxidation (CWAO); the method used for phenol removal in this project.

1.1.8. CWAO

1.1.8.1. Background to catalysis

Catalysis has been used extensively over the last century to decrease the energy requirements of certain chemical reactions. Almost every industry that produces a product from chemical reactions, or tries to decrease the emissions of running a particular process, uses catalysis. As well as decreasing the operational costs, catalysis can be used to decrease pollution. It usually requires a lot of energy to oxidise or reduce certain harmful emissions but catalysis offers a ‘shortcut’ in terms of the energy profile required to reach the desired reaction.

Catalysis reduces the activation energy required to get over the hurdle of getting two molecules to react. When the activation energy is reduced, the energy input from temperature or UV to activate the reaction can be reduced; which results in lower operational costs and better emission control.

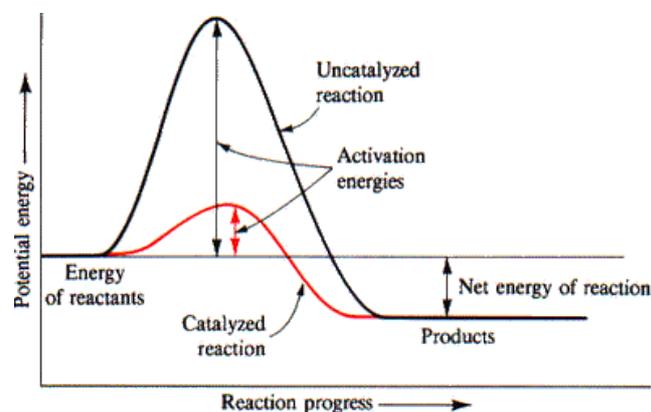


Figure 1.7 Catalyst effect on reaction activation energy⁶⁴

In physical terms the catalyst activates one or all the reagents as they come into contact and allows for them to react with each other with less difficulty. During the reaction phase, the catalyst's chemical structure is restored and is able to further activate the other reagents.

The reaction rate can be limited by the number of catalytic sites therefore, if the concentration of the substrate is high or the turn over frequency (TOF) is low (the number of substrate molecules a catalyst can react with in a given time) the rate cannot get any higher because all the sites are occupied⁶⁵. Increasing the substrate concentration further will have no effect on the rate as the adsorption and desorption of reactants and products have reached an equilibrium. It is therefore important to consider the number of active sites whilst designing a catalyst.

Catalysis may be operated homogeneously or heterogeneously. Homogeneous catalysis involves the reagents and the catalyst being in the same phase and therefore usually results in good activity as the contact between both would be optimised. Also if the reaction rate is limited by the number of active sites, it is easy enough to increase the catalyst's concentration in solution. The downfall of homogeneous catalysis is that much of the catalyst is lost after each batch of reaction as it is very difficult to separate compounds in the same phase once the reaction has finished²².

Heterogeneous catalysis, on the other hand, involves the reagents and the catalysts being in separate phases; usually the catalyst in the solid phase, and therefore allows it to be used repeatedly as the products can be separated at the end of the reaction. The disadvantage of heterogeneous catalysis is that the contact between the two phases is limited as the catalyst and reagents cannot be efficiently mixed in the way that it can be done in homogeneous reactions. Due to heterogeneous catalysis being a very attractive

process in terms of being able to reuse the catalyst after each process, much work has gone into optimising the catalyst-substrate contact time to make it the most efficient process. One way of achieving this is by selecting a catalytic support that is of a large surface area; this way the number of active sites can be controlled much better when designing the catalyst⁶⁶.

Most catalytic reactions, to do with emission control, is done via heterogeneous catalysis due to the practicality of having a fixed solid catalyst that can treat polluted gases at a fast rate and can regenerate without any product-catalyst separation issues⁶⁷.

In terms of emission control, this type of catalysis has played a major role in the management of global warming. A lot of industrial processes utilise a carbon source for energy such as, oil, gas or coal and produce environmentally harmful gasses as a result. One of these gases is CO₂ and much work has been carried out to create a system that minimises its release to the atmosphere. The process is known as carbon capture^{68,69}.

An example whereby emissions is a problem is in the automotive industry. Most vehicles use petroleum, diesel or some other type of hydrocarbon based fuel to power their engines and as a result, harmful gasses are emitted during the process. Carbon monoxide can be one of them and is highly toxic to living organisms if it enters the bloodstream^{70,71}. Although the gas is highly diluted once released to the atmosphere CO can be dangerous at very small doses⁷¹. This would be enhanced in a busy city where hundreds of vehicles may release the gas to the atmosphere every day. To limit vehicle CO emission, a catalyst is placed on the exhaust gas stream, ideally close to the engine, where the temperatures would be high enough to allow for an effective catalytic reaction to occur. Other gases present come in the way of nitrogen oxide species (NO_x). These gases would have to be reduced to form nitrogen and water so that no harmful species are

released to the general population^{67,72}. The catalyst used for this application is described as a three way catalyst and would provide the platform for hydrocarbon and CO oxidation as well as NO_x reduction. Below is an illustration of a similar catalyst system used for after-treatment; the NO_x trap system⁷³.

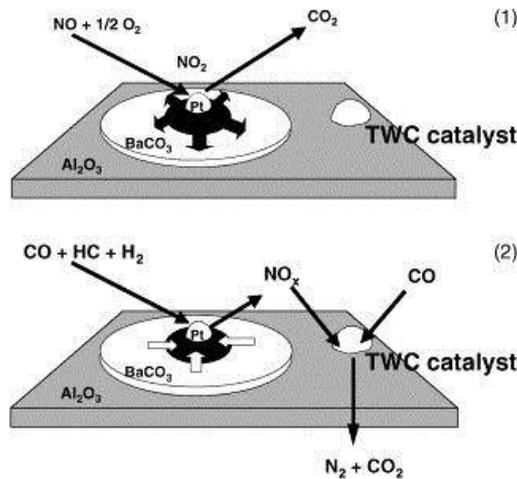


Figure 1.8 The NO_x trap catalyst mechanism

1.1.8.2. Catalysis in CWAO

The same concept has been developed for the catalytic oxidation of polluted water. The process uses air from the atmosphere as the oxidant source and a catalyst to lower the energy required for the oxidation reaction to take place. The equation below represents the total mineralisation of phenol when a catalyst is added to the wet air oxidation process.

Equation 1.4

The catalyst would be either homogeneous or heterogeneous, depending on the technique used, and would aid the total oxidation of toxic chemicals, such as phenol, at conditions that are less extreme compared to incineration for example. The process usually relies on an increase in temperature to activate the catalysts; but there have been examples of where UV has been used for the activation.

Duffy *et al.* showed that photocatalytic oxidation could be used as a secondary treatment method to remove difficult to break down acetic acid after WAO⁷⁴. Acetic acid is one of the partial oxidation products of phenol which can be difficult to break down compared to others. The reaction mechanism uses UV light with the aid of a semiconductor catalyst such as TiO₂ to form reactive hydroxyl radicals from water and O₂. These would then go on to oxidise organic compounds to CO₂ and H₂O. The study showed that photocatalysis can be used as an alternative to WAO and that the solution pH highly influences the promotion of acetic acid oxidation.

TiO₂ is among the most common catalyst for this type of oxidation reaction, along with CdS and ZnS⁷⁵. The review by Pera-Titus *et al.* showed that photocatalysis can be successfully utilised to mineralise chloro-phenols which can be further improved by the introduction of heavy metals such as platinum. The review also confirms that pH can have an effect on the reaction. TiO₂ for example carries a net positive charge after reducing the pH which means that the adsorption of the negatively charged chloro-phenol will be more favourable. It also reports that the temperature does not affect the oxidation rate at ambient conditions. One particular study showed that there was no improvement in activity ranging the temperature from 15 to 65°C⁷⁶.

Similarly, reactions involving the Fenton process uses UV to remove pollutants from wastewater. With the addition of H₂O₂ and activation from UV the iron component would act as a catalyst in their mineralisation. Esplugas *et al.* showed that introducing UV along with H₂O₂ promoted wet oxidation five times more than just UV alone⁵⁴.

The focus of this study was on a thermal catalytic reaction as oppose to a photocatalytic one. As explained previously, CWAO can be carried out homogeneously or heterogeneously and both are reviewed below.

1.1.8.2.1. CWAO using a homogeneous catalyst

A homogeneous catalyst would be an advantage to a particular catalytic reaction due to the increase in activity when the catalyst-reagent contact rate is increased. The reaction rate can therefore be improved with adequate mixing. Its limitation, on the other hand, is that the catalyst would be lost amongst the products as it would be difficult to separate compounds of the same phase. Saying this, there are examples of homogeneous catalysis being used for CWAO.

An example at a pilot scale is the LOPROX process²². This is a form of low pressure wet oxidation technology and occurs within a bubble column reactor with an iron ion catalyst. With a residence time of around 2 hours the process is able to oxidise 90% of COD with 65% selectivity towards CO₂.

Another homogeneous process used is the Ciba-Geigy process²². This is used commercially for pharmaceutical wastewaters. It uses air as the oxidant along with a copper ion catalyst and is able to achieve 99% conversion of organic carbon. It is a relatively energy intensive process as the temperature required to achieve this was above 300°C.

Below are some of the studies carried out on the research scale of homogeneous CWAO.

Arena *et al.* concluded, in their study, that a homogeneous CWAO reaction involving a copper, iron or manganese cation catalysts led to unselective single and double carbon partial oxidation products being formed from phenol⁷⁷. This was down to the free radical mechanism involved with a homogeneous catalytic reaction. Even the very active Cu⁺ catalyst had poor selectivity towards CO₂. The heterogeneous version of

the catalysts proved to be more active and was thought to be down to the kinetics of the adsorption-reaction, Langmuir-Hinshelwood mechanism.

The free radical mechanism of the homogeneous CWAO of phenol was explained by Wu *et al.*⁷⁸. It was explained that electron transfer from the copper cation catalyst to the phenol promoted radical formation. The reaction orders with regards to phenol, copper and oxidation concentrations were 1, 0.5 and 0.5 respectively. It was also shown that increasing the temperature increased the phenol conversion rate.

Pintar and Lavec proposed a mechanism for the homogeneous CWAO pathway of phenol⁷⁹.

The pathway highlights the formation of the activating free radicals ROH \cdot and ROOH \cdot from the reaction between phenol, catalyst and oxygen.

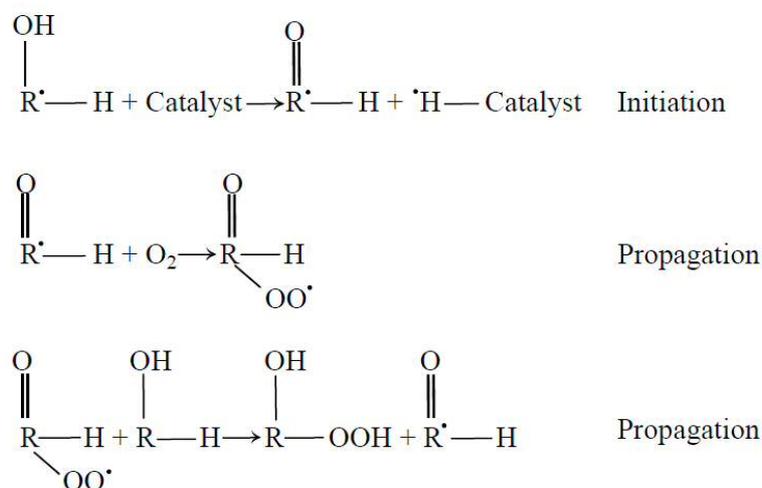


Figure 1.9 Homogeneous CWAO of phenol mechanism

Garg *et al.* compared two copper catalysts; one a homogeneous CuSO₄ and the other a heterogeneous CuO-ZnO/CeO₂⁸⁰. The homogeneous catalyst was tested at 90°C and atmospheric pressure and the heterogeneous was tested at above 160°C and 0.8MPa of pressure. Of the two, the homogeneous catalyst performed the best; converting 90% of

phenol and 83% COD. The heterogeneous catalyst managed to promote 82% phenol and 54% COD conversion.

Even though the homogeneous catalyst was the most active, the process can only be carried out in batch mode. This is down to difficulty separating the catalyst from the solution post reaction. A heterogeneous catalyst on the other hand can be separated and may be utilised continuously. Its activity can also be improved and lifetime enhanced with more research and, in turn, the process' whole life cost can outweigh the homogeneous operation.

1.1.8.2.2. CWAO using a heterogeneous catalyst

Heterogeneous catalysis offers a key advantage in that the catalyst is in a separate phase to the reactants and therefore can be recovered at the end of the reaction. In the case of CWAO, the catalyst is in the solid phase, the pollutant solution is in the liquid phase and the oxidant is in the gas phase. This therefore is considered a tri-phase heterogeneous catalytic system.

Heterogeneous CWAO has been proved to be a popular technique in the removal of phenol from wastewaters and below are examples of how it has been implemented.

A review carried out by Lavec *et al.* reported that the most successful catalysts for CWAO are of the heterogeneous types²⁷. The catalyst would require a stable support with an active component, such as a precious metal on its surface, to ensure the best chance of pollutant oxidation and preserving catalyst lifetime. They also stated that a single catalyst cannot accomplish total mineralisation of all pollutants alone; they would have to be specifically designed depending on the wastewater makeup. They also highlight the limitations of homogeneous catalysts; i.e. the difficulty involved with catalyst separation and the problems associated with metals carry-over to the final effluent after the reaction.

Kim *et al.* reiterates the problems associated with homogeneous catalysis in its review of CWAO processes²⁸. As well as the need to recover the ionic metal catalyst, a substantial amount of cost would come with ensuring they do not elute into the final effluent as they can be very toxic. This has steered developing the technology to more stable, easy to separate, heterogeneous catalysts.

Luck's review highlights the negative aspects of heterogeneous catalysis²². Not only will the process face difficulty treating a complex mixture of chemical waste, but also the catalyst faces the prospect of hydrothermal sintering. On the other hand, this review is slightly dated and the technology has progressed significantly since then.

Besson *et al.* reported that metal oxides containing copper, manganese or cobalt for example exhibit good activity for the removal of toxic pollutants; however they are prone to leaching⁸¹. This means that the active component of the catalyst may be lost during the reaction, causing it to deactivate over time. Also, if the leaching component is toxic and manages to reach a watercourse untreated, there could be a risk of environmental pollution. This has triggered the development of more stable precious metal catalysts to be produced, as they are less prone to leaching.

The research has shifted towards favouring heterogeneous CWAO over time because of the recovery issues presented by homogeneous reactions. Though the reaction rates tend to be higher in the latter, heterogeneous catalysts have been shown to successfully treat polluted wastewaters. There is also room for these catalysts to be optimised even further and therefore, for these reasons, only heterogeneous-type catalysts were developed for this project.

1.1.8.3. CWAO operations

There are many ways in which the CWAO reaction can operate; mainly via the batch or continuous flow setups. They both present advantages and disadvantages in terms of cost and practicality and it usually depends on the scale of the reaction to determine which method should be used.

1.1.8.3.1. Batch treatment

Batch CWAO reactions can be carried out using either a homogeneous or a heterogeneous catalyst. The former would be preferred if the reaction rate's efficiency outweighed the cost of losing the catalyst amongst the products, but the latter would be preferred if catalyst recovery was paramount.

A batch CWAO setup therefore requires the catalyst to be mixed in with the reagents in a fixed reactor volume. The diagram below illustrates its set-up.

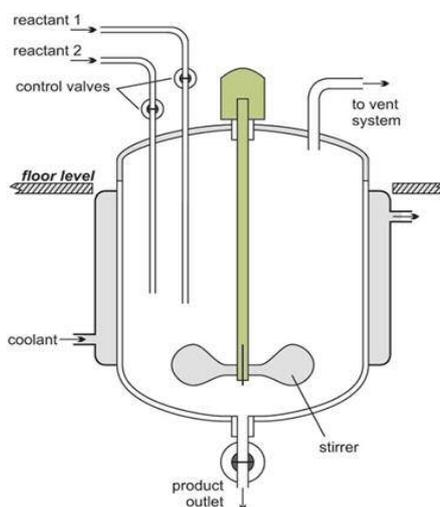


Figure 1.10 Diagram of a typical batch reactor⁸²

Lavec *et al.* reported that although pollutant conversion would be greater in batch reactors there is a chance that polymerisation may occur between the organic components and lead to catalyst fouling²⁷. This would be caused by the pollutants experiencing long

residence times within the reactor; which in turn would increase the probability of polymerisation. This review stated that only half of the converted phenol pollutant oxidised to CO₂ and the rest formed poly-aromatic species. In contrast to fixed bed continuous reactors, propagation reactions are more likely to occur due to the large liquid to solid volumetric ratios.

The study carried out by Stuber *et al.* agrees with what was found by Lavec *et al.* in that polymeric compounds are likely to be formed in batch reactors during CWAO⁸³. This has previously been observed during the CWAO of phenol using a copper oxide catalyst, but in this study it seems to be enhanced by using activated carbon. Activated carbon is able to strongly adsorb organics such as phenol therefore the pathway to oxidative coupling enhances. A batch reactor would further amplify this effect as the catalyst and reagents experience longer residence times.

Yang *et al.* investigated the performance of phenol CWAO over a CeO₂-TiO₂ catalyst in a batch reactor as well as a continuous flow packed bed reactor³⁵. The results showed that the catalyst promoted a 100% phenol conversion with 77% total organic carbon (TOC) removal in the batch reactor; whereas in the continuous flow reactor the results were 91% and 80% respectfully. This shows that the catalyst activity is superior in the batch set-up initially, but after a couple of cycles the activity dropped to 87% 65% respectfully. This indicates that the catalyst was deactivating in the batch reactor; whereas no signs of this was occurring in the continuous flow reactor. The paper suggests that it was the polymerisation of phenol causing the decrease in activity and hence the reason why the TOC conversion was always lower in the batch reactor.

All of these studies highlight the fact that phenol polymerisation is more likely to occur in a batch reactor. This was put down to the long residence time the pollutant

solution experiences within batch reactors and therefore allows time for propagation reactions to occur. Due to this reason, and the lengthy stepwise nature of the batch reaction process, the continuous flow method was selected as the basis for this CWAO project.

1.1.8.3.2. Continuous treatment

In view of an industrial sized wastewater treatment plant being able to process thousands of cubic meters per day, in most cases, a continuous flow setup would be preferred over the batch equivalent. This method allows for better catalyst sustainability; as deactivation through polymeric deposition is less likely to occur. For this particular scaled down investigation, a continuous flow setup was developed.

Below is an illustration of how the catalyst would be packed inside a continuous flow reactor. The wastewater solution would flow through the catalyst, along with air, to enable pollutant oxidation.



Figure 1.11 Continuous flow packed bed reactor

1.1.8.4. Continuous flow methods

The continuous flow process can be set up in two different ways: the wastewater and air flowing co-currently to one another, or with both flowing counter-currently. These processes are detailed below.

1.1.8.4.1. Co-current (concurrent) trickle bed reactor

This continuous setup consists of the air and wastewater solution flowing downwards alongside one another, through the fixed bed of catalyst. The way in which the liquid enters the reactor can be adapted so that it mixes efficiently with the air before it reaches the catalyst bed. This can be carried out with the aid of spray nozzles or baffles so that the solution does not enter as one big droplet⁸⁴. Varying the droplet size enables better control over catalyst wetting efficiency and in turn promotes better oxygen-to-pollutant contact time. It also enables the air and wastewater solution to mix efficiently before reaching the catalyst.

The following diagram demonstrates how the air and water would mix prior entering the catalyst bed: -

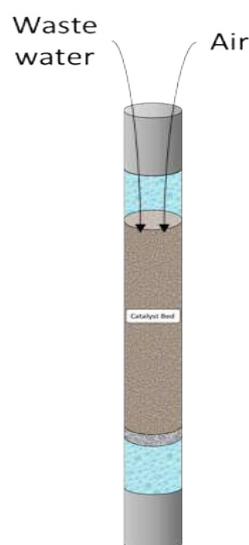


Figure 1.12 The co-current continuous flow CWAO reactor

Most of the research into continuous flow CWAO is carried out with a co-current flow operation. Examples of some of these studies are presented below.

Pintar's review into CWAO processes highlights a number of examples whereby this co-current setup was used to successfully remove organics from wastewater⁸⁵. The CALIPHOX process uses a bed of activated carbon to adsorb the organics from solution followed by a backwashing stage to send them on for CWAO treatment in a trickle bed reactor. Here, the wastewater solution and air flowed concurrently to one another. This phase also allows for the activated carbon to get regenerated - ready for the next cycle.

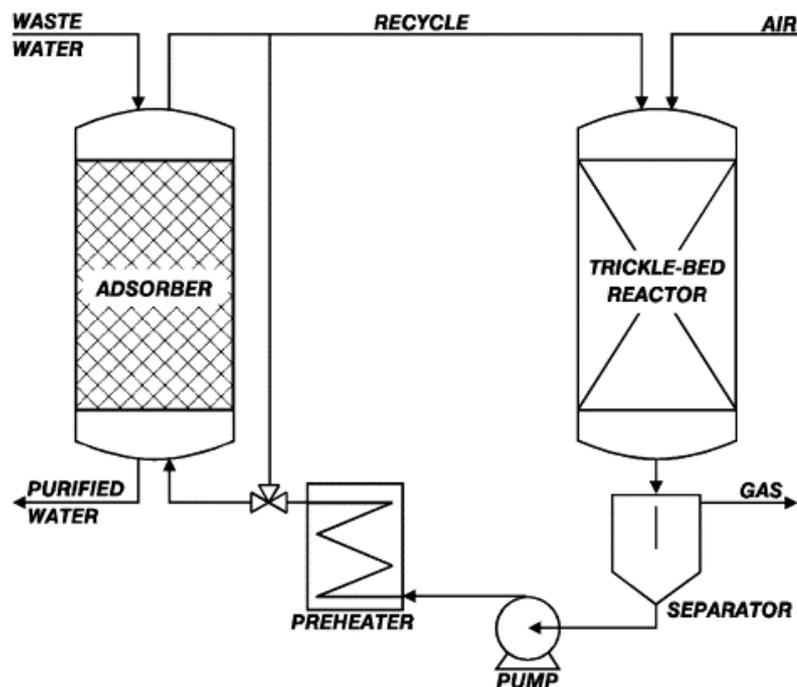


Figure 1.13 The CALIPHOX process

Another example of a study focussing on the co-current CWAO continuous process is the one conducted by Suarez-Ojeda *et al.*⁸⁶. This study looked at the CWAO of a number of phenol containing compounds using activated carbon as the catalyst. The wastewater would trickle through the catalyst bed under gravity and the air driven from a compressed air cylinder by pressure. The extent of oxidation could be controlled by the

wastewater feed rate as this highly influences catalyst-pollutant contact time. Faster flow rates compromise activity; whereas slower flow rates promote activity. This means that activity can be fine-tuned midway through a reaction and provides a great deal of flexibility in comparison to running in the batch mode.

Dudukovic *et al.* underlined the benefits of concurrent flow reactors by expressing the flexibility involved with throughput demands⁸⁷. A downward flow trickle bed reactor allows flows to be reduced much more than in a counter current up-flow reactor, for example, as the force of air aids its passage through the reactor. This therefore gives the operator the ability to decrease the flow as much as possible to achieve the desired activity. The counter current flow setup is discussed further below.

1.1.8.4.2. Counter current

The counter current continuous flow set up requires a flow of air and pollutant solution going against each other through a catalyst bed. In most cases the solution would gravitate and trickle through the catalyst and the air would flow against it. The advantage of this process is that the air going against gravity would have a scouring effect on the catalysts bed and therefore aid the de-lodging of unwanted fines that have built up in some of the crevasses over time. This means that the catalyst's active sites are constantly regenerated and preserved much better than if it were in a co-current flow reactor.

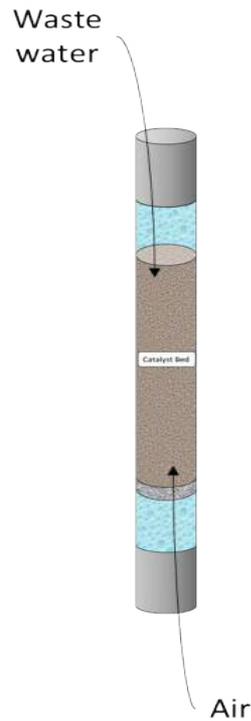


Figure 1.14 The counter-current continuous flow CWAO reactor

A catalyst in a co-current flow setup is likely to have more impurities on its surface and thus causes restrictions to the number of pathways the wastewater can take through its pores. As a result, ‘slugs’ of wastewater form and the contact efficiency between the pollutants and active sites diminish. This effect is less likely to occur when using a counter-current flow reactor as the air would continuously agitate the catalyst bed and decrease the deposition of impurities in the pores.

The paper by Dudukovic *et al.* also mentions the counter current flow packed bed reactor⁸⁷. The paper supports what was said above in that the up-flow rate of air promotes better wastewater distribution through the catalyst bed. It also states that pollutant residence time is likely to be longer in a counter current reactor as the air would be slowing down the wastewater’s flow rate. This promotes activity as longer residence times encourages more oxidation.

Though the counter-current setup offers its fair share of advantages in promoting CWAQ, it is impractical for small lab-scaled investigations such as this one. At low flow rates, the wastewater solution would not have enough static head to gravitate against the upward flow of air; whereas with the co-current method this would not be an issue. Due to this reason the reactor was set up in the co-current manner. If the process were to be scaled-up for a pilot plant study the counter current process would probably be more favourable.

1.1.8.5. Typical reaction conditions

Most heterogeneous catalytic reactions require an external source of energy for the active components to work efficiently. This can be in the form of an increase in temperature or by the application of UV light. Without a catalyst in place, the kinetics would call for a significantly higher activation energy level for the reaction to proceed. Some catalysts may reduce the activation energy enough so that no external source of energy is required and that the reaction can proceed at ambient conditions.

For this study, heat was applied to generate activity along with pressure to keep the solution in the liquid phase. The initial phenol concentration of the wastewater was kept consistent with what has been used in previous studies, and most importantly, what is typically found in industrial wastewaters. As well as the variables pointed out above, the phenol concentration can highly influence catalyst performance also^{86,88}. Phenol conversion diminishes at high concentrations as the catalyst's active sites are more likely to be filled quicker. It was important to keep the reaction conditions aligned with previous studies as they set a benchmark for further investigations.

The following tables show the typical reactor conditions used in CWAQ studies.

Table 1.2 Typical conditions for a phenol CWAO reaction³⁹

Oxide	Support	Substrate	T (°C)	P MPa
Cu/Cr oxides		phenol	>127	0.32
Cu/Cr/Ba/Al oxides		phenol	127	0.8
Co, Fe, Mn, Zn oxides with Cu oxides	$\gamma - Al_2O_3$	phenol	140	0.9
CuO	$\gamma - Al_2O_3$	phenol	>120	>0.6
CuO	$\gamma - Al_2O_3$	phenol	140	0.9
Cu/Ni/Al oxides		phenol	140	0.9
CuO/ZnO/CoO	cement	phenol	>130	7
CuO/ZnO/CoO	cement	phenol	>150	(*)
CuO/ZnO	$\gamma - Al_2O_3$	phenol	>105	>0.15
CuO	$\gamma - Al_2O_3$	phenol	>113	>0.44
CuO/CeO ₂		phenol	130	0.73
K - MnO ₂ /CeO ₂		phenol	110	0.5
MnO ₂ /CeO ₂		phenol	>80	>0.2
CuO	C	phenol	>160	>2.6
CuO	$\gamma - Al_2O_3$	phenol	>95	>0.1
MnO ₂ , Co ₂ O ₃		phenol	>170	>1.3
Ni - oxide		phenol	>15	-
Cu/Zn/Cr/Ba/Al oxides		phenol	>110	>0.1

Table 1.3 Typical conditions for a phenol CWAO reaction²⁹

Catalyst	Reactor type	C _{Ph} (g/L)	T (K)	P _{O₂} (MPa)	X _{Ph} (%)
Cu/Ni/Al	Batch slurry	5	423	0.9	>99
Hydrotalcite	Trickle bed				>75
Active Carbon	Trickle bed	5	433	0.2	>99
CeO ₂	Semibatch-slurry	5	453	1.5	~95
CuO/AC	Spinning basket	2.4	453	3.6	>99
Ru-CeO ₂ /AC	Batch slurry	2.2	433	2.0	>99
Cu/Zn/Co-oxides	Trickle bed	3.0	423	0.7	~50
K-Mn-Ce-O	Batch slurry	1.0	383	0.5	>99
Pt/TiO ₂	Batch Slurry	1.2	473	0.8	~99
	Trickle Bed				
CuO/MCM-41	Batch slurry	1.3	473	3.4	>99
CuO-CeO ₂	Semibatch-Slurry	1.0	432	0.73	>99
CuO-2(CuO)-Cr ₂ O ₃	Fixed bed	1.2	433	1.6	>99

Both tables give the typical reaction conditions required for a batch or continuous reaction and the second shows the conversion values expected (X_{Ph}) over certain catalysts.

The goal of this study therefore was to design an active and stable catalyst that exceeded the performance levels presented above.

1.1.8.6. Catalyst shape and size

Once a continuous process had been established, the focus turned to catalyst design. Before the composition could be developed it was important to identify what shape and size the catalyst particulates needed to be in to perform well in a continuous flow reactor. The particulate structure was therefore optimised in order to promote an effective CWAO reaction.

One of the factors effected by the size and shape of the particulates is the ease of flow through the fixed catalyst bed. Large particulates encourage large voids to form within the catalyst bed as a result of inefficient packing and as a consequence, makes it easier for the liquid to travel through unhindered. On the other hand, small particulates would pack more efficiently and the ease of flow will become more restricted³⁹.

Small particulates such as from a fine powdered catalyst would amplify this effect as the voids would become relatively non-existent. It is therefore important to consider a catalyst particulate that is big enough to create the required space for the appropriate flow rate to get through, otherwise it would get backed up and cause a pressure drop in the system⁸³.

The diagram below illustrates how catalyst packing efficiency within a reactor may highly influence the ease of flow.

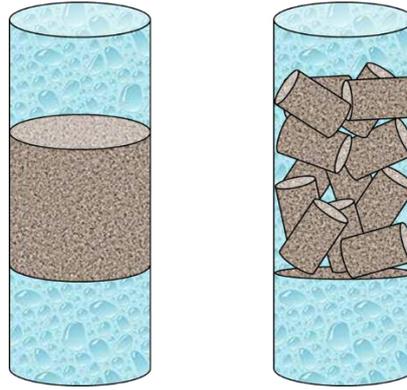


Figure 1.15 Catalyst particle packing efficiency within a continuous flow reactor (Left: small particulates, Right: large particulates)

Both examples would be of the same composition and weight, but due to different particulate structures their packing efficiencies become totally different.

Another factor affected by this is mass transfer. The particulates would have to be as small as possible to ensure the highest degree of pollutant-catalyst contact time is achieved. Having more efficient packing means that the probability of the pollutant coming into contact with the catalyst increases significantly. If this were to happen then the ease of flow through the bed would have to be sacrificed^{83,89}.

The graph below highlights how phenol conversion dramatically falls as the catalyst particulate size increases from 0.05 to 3 mm in diameter⁹⁰. It also shows the effect on pressure drop as the particulates get smaller.

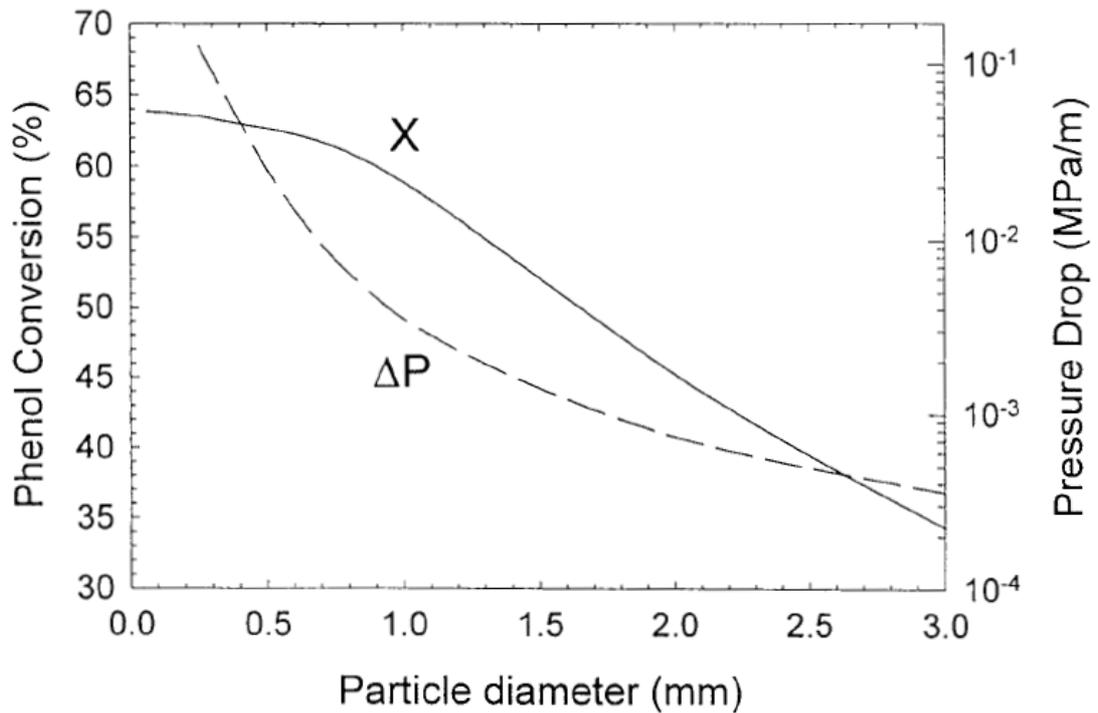


Figure 1.16 The effect of a catalyst's particle size on phenol conversion and pressure drop

It is therefore important to design a catalyst of optimum particulate size so that the ease of flow does not get compromised by mass transfer and *vice versa*.

Catalysts can also be fixed to continuous flow reactors as monoliths. Monoliths are structures that can be tailor-made to specific processes as their shape and size can be manipulated in a way that is best suited to that application. They are commonly found in continuous processes, especially ones dealing with gas streams. Honeycomb shaped monoliths, for example, are used as the catalytic supports in vehicle exhaust gas systems. There are no separate elements to the structure therefore it has to be developed via an extrusion process. A monolith of this kind would have hexagonal channels lined by the active components⁹¹.

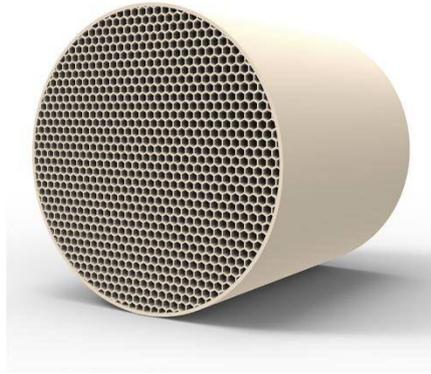


Figure 1.17 An example of a monolithic catalyst⁹²

These monolithic setups have been developed as they are a lot more practical than having a fixed bed of pellets in the exhaust gas stream. The flow pattern through a bed of pellets would differ from vehicle to vehicle; whereas through a monolith it would be consistent. A monolith would also be designed to optimise mass transfer productivity whilst allowing as much flow through as possible⁹¹.

With this being said, a structure of this kind could be suitable for CWAO. It would provide enough void volume to allow the wastewater to trickle through with ease and enough surface area to achieve optimum mass transfer conditions^{91,93,94}. On the other hand, developing monolithic structures for lab based studies would not be cost effective. Monoliths are more suited for up-scaled industrial size systems where the pollutant flux is more consistent and the catalyst composition optimised. For this reason only packed bed arrangements were investigated.

1.2. Literature review – catalysts for CWAO

1.2.1. Introduction

Once the optimum particulate size has been established the focus turns to catalyst composition. A heterogeneous catalyst requires an active component to promote the catalytic reaction and a support to keep it in place.

1.2.2. Types of supports used in CWAO

In order to prolong catalyst lifetime, the support has to be able to withstand the harsh conditions of a CWAO reaction. Not only will it be exposed to high temperatures and pressures but also face a constant flow of hot air and a stream of acidic wastewater. Below are examples of supports that have been used in previous CWAO investigations.

It is well established, in the water treatment industry, that carbon can be used to adsorb unwanted organic content from water. This is carried out using a process known as granular activated carbon treatment (GAC). Organic content, if not removed, can go on and react with chlorine during the disinfection stage to form toxic tri-halo methane compounds (THMs). These are regarded as a health risk to animals and signifies the need for an adsorption stage^{8,95}.

High surface area activated carbon removes organic material by adsorbing the unwanted molecules into its pores. As the carbon gets filled with impurities over time it gets less effective at removing organic matter. Once the carbon has aged, the GAC beds are removed so that they can be regenerated for future utilisation⁹⁶.

In a continuous flow CWAO reactor, the carbon would constantly be regenerated by oxidation at high temperature and there would not be a need for a separate regeneration stage, as is required in conventional GAC treatment. Having a catalyst in place also

lowers the activation energy required for regeneration as it promotes the oxidation of adsorbed organic matter.

In terms of this study, the phenol would get adsorbed by the carbon support and then get oxidised by air with promotion from an active catalyst. The use of carbon is well suited for this application as one of the key issues with continuous flow operation is contact time. If the carbon is able to delay phenol elution, the risk of it escaping without being oxidised is decreased. Its increase in retention time would allow for catalytic oxidation to take place.

Below are some examples whereby carbon has been used as a support for CWAO studies:-

Benhamed *et al.* studied the effect of transition metal impregnation on the oxidative regeneration of activated carbon by CWAO⁹⁷. They found that the inclusion of transition metals promoted phenol oxidation as well as oxidising the carbon support itself. This meant that further phenol adsorption was compromised by a deformation in the carbon's structure. Adding transition metals therefore has a positive effect on activity but a negative effect on regeneration.

Bingzheng *et al.*, on the hand, reported that doping with metals influenced phenol adsorption only if it was in high concentrations⁹⁸. There was no change in uptake at 100 mg/L of phenol but at 2500 mg/L, almost 20 mg/L less was adsorbed. Increasing the metal (iron) loading further exaggerated this effect. They showed that an increase in phenol concentration caused the carbon's pores to get filled quicker; meaning the adsorption-desorption equilibrium reaches its peak a lot sooner. With this being said, the mass transfer of phenol does increase when activated carbon is selected as the catalyst. This is beneficial as it allows more time for oxidation to occur.

Fortuny *et al.* concluded that activated carbon had catalytic properties without the need of an active metal present⁹⁹. However, similar to what was reported by Benhamed *et al.*, the carbon support was oxidised as well as the phenol; causing the catalyst to deactivate over time. This, in turn, caused phenol conversion to decrease from 100% initially to 48% once the reaction had finished. A non-carbon copper based catalyst was also tested in this study and although it had some leaching issues, it remained the better of the two in terms of phenol oxidation.

Another support that is widely used for CWAO is alumina. Alumina (Al_2O_3) has a proven track record and a strong reputation as a support in catalytic applications over time¹⁰⁰⁻¹⁰³. Alumina's inert features make it a suitable support as it usually can withstand the harsh conditions of a catalytic process.

Two types of alumina are usually used in catalytic systems, α and γ -Alumina^{104,105}. α -Alumina has a much lower surface area compared to γ -Alumina, therefore it is a lot less susceptible to thermal degradation^{106,107}. The advantages of having a high surface area alumina, on the other hand, is that it can be loaded with more of the active component and it will also have a higher degree of functionality¹⁰⁸. This would come in the way of Al-OH groups which are very beneficial in terms of controlling catalyst substrate interaction^{109,110}. On the other hand, this can make the material more vulnerable to thermal degradation over time and decrease the catalyst's lifetime^{111,112}. Saying this, CWAO reactions usually operate at relatively mild conditions and thermal deactivation, therefore, is less likely to occur.

Alumina has been used numerous times in CWAO studies, due to the reasons given above, and below are some examples of where it has been implemented.

Chang *et al.* studied the effect of introducing alumina as a support to ceria in a batch phenol CWAO reaction¹⁰³. Replacing some of the ceria with alumina meant that the catalyst's production cost come down significantly. However, its relative level of activity did not get affected. It was also reported that out of a number of supports tested (SiO₂, TiO₂ and AlPO₄₋₅) alumina came out on top as the best support to ceria in promoting phenol CWAO. The study found that 20 wt% Ceria, impregnated on alumina, promoted 100% phenol conversion and 80% TOC removal after 2 hours, at 180°C and with a catalyst loading of 3 g/L. With this being said, it took 2 hours to fully convert the phenol, which is relatively long for a batch reactor. The residence time of a continuous flow reactor would be a lot less, more like seconds, therefore there are limitations to this type of catalyst.

A similar study was also carried out with copper oxide impregnated on alumina. The report, carried out by Pires *et al.*, showed that out of a number of support, again, alumina was the most successful in supporting the active component¹¹³. The purpose of the study was to evaluate the cost of catalyst production in relevance to activity. Not only was the CuO/Alumina catalyst the most successful in terms of phenol and TOC removal, it was also the most cost effective overall. Be it not for its leaching problems, the pillared clay catalyst could have been the most cost effective. This meant that the alumina based catalyst was the most appropriate support overall. Again, 2 hours was taken to reach 100% phenol conversion; whereas in a continuous flow system this timeframe would have to come down significantly.

Fortuny *et al.*, on the other hand, evaluated the performance of the CuO/Alumina catalyst in a trickle flow reactor, as opposed to the previously presented batch methods^{114,115}. Although the study concentrated on comparing kinetic models, the catalyst managed to promote almost 100% phenol conversion with a reaction space time of 0.6 h

¹ (flow rate divided by catalyst volume). This was also achieved at 160°C, as opposed to the 180°C used in the previous study and a starting phenol concentration of 5 g/L. This shows that, at low flow rates, the continuous flow CWAO reaction can be very successful in oxidising phenol.

Below are examples of other supports used in CWAO: -

As mentioned previously, TiO₂ can be very useful as a catalyst in CWAO. Yang *et al.* reported on the activity of a ceria/TiO₂ catalyst in both batch and packed bed reactors³⁵. Interestingly, ceria with TiO₂ promoted better oxidation than pure ceria or TiO₂ alone. It promoted 100% COD conversion and 77% TOC removal at below 150°C in a batch reactor. The study also showed that its activity could be increased by increasing the reaction temperature and decreased by increasing the initial phenol concentration. In the continuous flow reactor, on the other hand, 91% COD conversion and 80% TOC removal could be achieved at 140°C and with a liquid flow rate of 0.5 ml/min. By calculation, the batch mode was able to convert all of the phenol within 2 hours; whereas the continuous flow mode was only able to convert it by 91% in just over 16 hours. The effectiveness of one technique over another would therefore come down to whole life cost analysis. TiO₂ promoted similar results to alumina, but due to it being the more expensive of the two, the latter is usually favoured (alumina: \$379-411/tonne¹¹⁶, TiO₂: \$900/tonne¹¹⁷).

It was shown earlier that ceria could be used as an active catalyst in CWAO. It can also be used as a dopant to improve the activity of other catalytic systems¹¹⁸. Ceria has the ability to promote oxygen to regenerate active metals quickly; which is beneficial for catalytic systems in situations of low atmospheric oxygen concentration^{119,120}. This is likely to occur in batch reactors where oxygen concentration can reach low levels.

There have been examples of where ceria is preferred to be doped into a catalyst system rather than using it in its pure form. Chen *et al.* showed that ceria alone was the poorest catalyst in terms of aiding phenol conversion in comparison to it being doped on SiO₂, TiO₂ and alumina¹¹⁹.

Silicon carbide (SiC) is also an inert material, but in comparison to γ -Alumina it is a much harder material and able to tolerate the harsh conditions of a reactor much better (SiC hardness: 2800 kg/mm², Alumina hardness: 1440 kg/mm²¹²¹). SiC, as a support, has not been studied for CWAO reactions before therefore it could be a promising alternative to the more common materials used.

SiC has a much smaller surface area compared to γ -Alumina, therefore its surface functionality is a lot different (e.g. β -SiC: 29 m²/g¹²², γ -alumina: 204 m²/g¹²³). SiC has fewer hydroxyl groups on its surface whereas alumina would have plenty. Hydroxyl functionality plays an important role in the hydrophobicity of a catalyst, which, in this study, was found to be highly influential. The SiC support would therefore be more hydrophobic than the alumina and influence how the oxygen gets activated during the catalytic process.

SiC has been used previously for other catalytic type applications therefore it would not pose any problems in terms of getting active metal components to impregnate onto its surface¹²⁴⁻¹²⁶.

Out of all the possible supports, carbon, alumina, ceria and SiC were chosen for this project. Carbon for its adsorption capabilities, alumina for its high surface area, inertness and good reputation for CWAO applications, ceria for its oxygen donation ability and SiC for its robustness and hydrophobic nature.

1.2.3. Type of metals for CWAO

Catalytic systems often contain metals as their active components. Metals are usually very active due to the free movement of electrons associated with their atomic structures. The metal would provide the electron transfer platform required for a catalytic reaction to occur¹²⁰.

It is common to find metallic active components in solid heterogeneous catalytic systems as the reaction deals with reagents in either the gas or liquid phases.

The active components used in this project focused mainly on platinum group metals (PGMs). Some of these metals are renowned for their ability to aid the total oxidation of pollutants¹²⁷⁻¹²⁹. They are often used for emission control in the automotive industry as they are able to promote total oxidation of toxic pollutants such as soot and carbon monoxide^{130,131}. Of these PGMs platinum has shown to be one of the most successful in promoting total oxidation.

Platinum can be in either the metallic or oxide form during the reaction process. It is usually prepared as a metal, but it can get further oxidised as it reacts with air at high temperature. Its oxide form can then act as a catalyst by oxidising the pollutant and go back to its metallic form once the cycle has finished¹²⁰. This is signified by the reaction equations below; whereby the target pollutant is represented by *A*: -

Equation 1.5

Equation 1.6

For the case of phenol oxidation, the platinum would provide the activated oxygen required for its mineralisation to CO₂ and water.

Below is a review of some of the studies that have used platinum in their CWAO reactions.

Cybulski and Trawczyński reported a shift in recent times from studies looking at copper oxide type catalyst to platinum group metal catalysts¹³². Copper oxide catalysts are very active in promoting phenol conversion, but they are also prone to leaching which causes deactivation. Platinum catalysts are less likely to leach and are more stable in the long term. Platinum catalysts also show good selectivity towards total oxidation; whereas the copper equivalent did not. Keav *et al.* highlights what is stated above in that a noble metal such as Pt demonstrates very good activity and stability in these types of catalytic applications¹³³.

Rocha *et al.* investigated the effect of various loadings of ceria on a Pt/TiO₂ catalyst¹²⁰. Leaving the ceria effect aside, the platinum was found to be in two oxidation states post calcination when measured by X-ray photoelectron spectroscopy: Pt²⁺ & Pt⁰. The catalyst that had the largest oxidising potential, i.e. the Pt²⁺, showed the best performance in terms of phenol conversion. The ceria being in the highest oxidation state (Ce⁴⁺) also promoted the best phenol conversion performance whilst also decreasing the chances of carbon build up on the surface. The findings and explanations of the mechanism are also in accordance with what was proposed by Monteros *et al.*¹³⁴. They proposed that the reaction followed the following mechanism: -

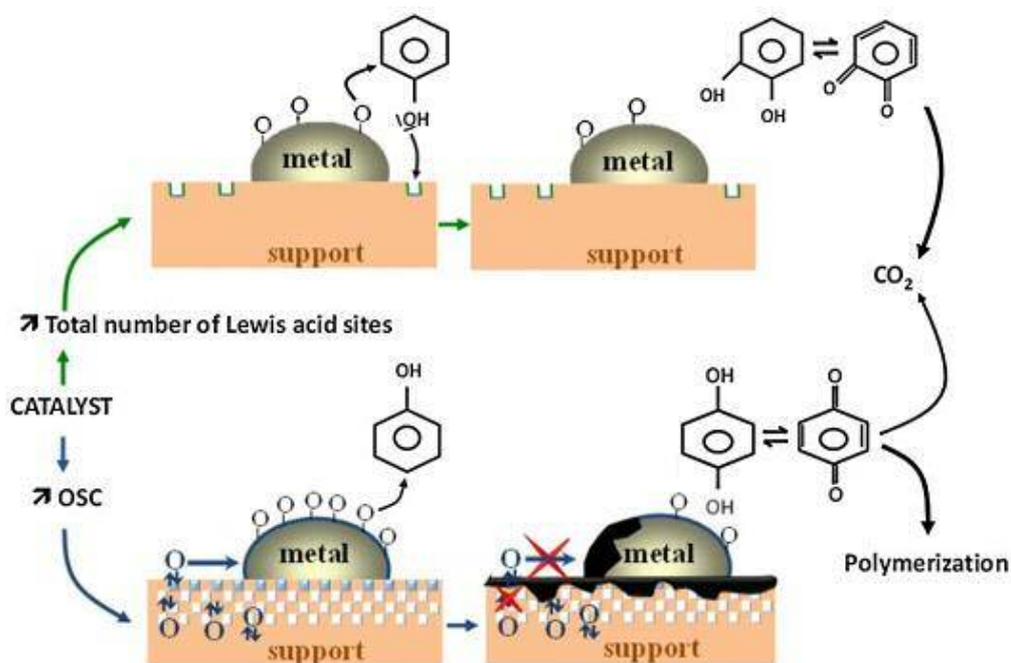


Figure 1.18 Mechanism of the phenol oxidation reaction over a Pt catalyst on a ceria/TiO₂ support¹³⁴

They reported that the phenol conversion increased with an increase in oxygen storage capacity (OSC), but not necessarily via total oxidation to CO₂. They proposed that the oxidation of phenol occurs via the *para* position as that would be the most sterically preferred orientation. This results in the *para*-benzoquinone formation, which can lead to polymerisation rather than total oxidation and consequentially result in coke formation on the surface. Increasing the number of Lewis acid sites on the surface, on the other hand, causes the phenol's hydroxyl group to interact head down and promote oxidation via the *ortho* position. Oxidising in this manner would decrease the chances of polymerisation occurring as the *ortho*-benzoquinone inhibits a chain-like reaction. This shows that though platinum in its highest oxidation state promotes the best phenol conversion performance, total oxidation will not necessarily be preferred if the support highly influences the way in which the phenol interacts with the surface.

Nousir *et al.* supports the papers discussed above by presenting an example of whereby zirconia was introduced into the ceria's lattice to increase the mobility potential of the oxygen atoms¹³⁵. The catalyst with the most zirconia present also decreased the chances of polymer formation. Zirconia increases the Lewis acidity of the surface and hence promotes the oxidation of phenol via the preferred orientation discussed above. It was also shown that polymer deposition was limited by low catalyst surface areas. This hints that the SiC based catalysts, for example, would serve longer in terms of catalyst lifetime.

One of the most difficult to oxidise intermediates post phenol oxidation is acetic acid. Mikulová *et al.* reported on the effect of platinum crystallite size on acetic acid oxidation¹³⁶. Its crystallite size and dispersion is highly influenced by the pre-treatment reduction temperature. Whilst increasing the temperature promotes larger crystallite sizes its dispersion decreases. The results show that an optimum dispersion percentage and crystallite size resulted in the best acetic acid conversion. This meant that a large enough crystallite size is required whilst maintaining a relatively good dispersion.

Another of the PGMs considered was ruthenium. Ruthenium has also been studied in the literature as an active component for CWAQ, but it is not as established as platinum in terms of its total oxidation capabilities.

Lafaye *et al.* reported that oxygen storage capacity (OSC) does not affect ruthenium catalytic performances in the way that it does for platinum catalysts¹³⁷. It was shown previously that increasing the OSC after introducing ceria promoted phenol polymerisation, but this does not seem to occur for ruthenium as the performance remains the same regardless of ceria concentration. Lewis acid sites are key in preventing polymerisation as they promote phenol oxidation via the total oxidation pathway instead.

These Lewis acid sites diminish when ceria is added to platinum but remain for the ruthenium equivalent. This therefore explains why ceria did not cause ruthenium catalysts to degrade over time.

Cybulski *et al.* compared ruthenium to platinum in their performance to oxidise phenol on silica-titania supports¹³². They concluded that the platinum active sites would promote total oxidation; whilst ruthenium would promote a route via intermediates that are difficult to oxidise. This better performance of platinum was also reported by Keav *et al.*¹³³. They showed that the platinum catalyst outperformed the ruthenium equivalent even when both metals were of similar dispersion levels.

Espinosa *et al.* also showed this but, most importantly, built on what was shown by Lafaye *et al.* in that OSC does not affect the ruthenium's performance, only the lifetime of the platinum catalysts¹³⁴. This was put down to the number of Lewis acid sites not being affected by the addition of ceria in the case of the ruthenium catalyst.

Yang *et al.* reported that ruthenium is predominantly in the oxide form following calcination; whereas platinum is likely to be both metallic as well as oxide^{138,139}. This is likely to influence their relative activities, especially when comparing different supports that may influence phenol-catalyst interaction.

As well as acting as a support, ceria can be considered as the active component also. Oxygen atoms are able to migrate freely across its surface and create holes whereby atmospheric oxygen can be activated. This means that expensive precious metals can be thrifted if ceria is introduced in small concentrations. Yu *et al.* reported that adding ceria to a ruthenium/alumina catalyst improved activity towards a number of pollutants¹⁴⁰. The ceria would not only improve the ruthenium's dispersion on the surface but it would also add more active sites for the pollutant and oxygen to react. Yang *et al.* also showed that

increasing the ceria concentration had a positive effect on catalyst activity¹⁴¹. The diagram below illustrates how adding ceria increases performance in the CWAO of succinic acid.

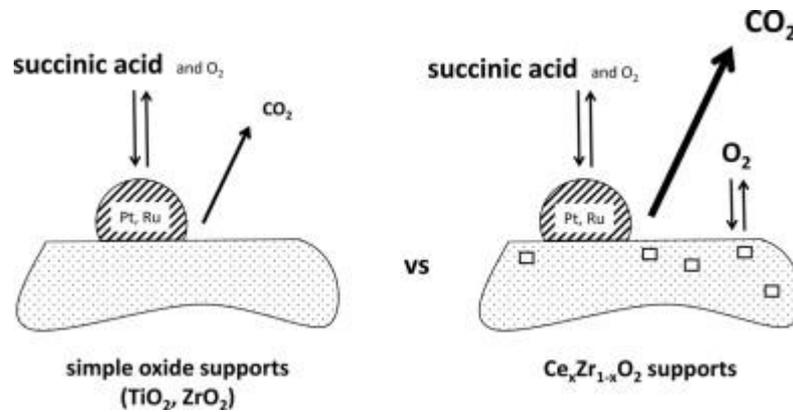


Figure 1.19 The effect of ceria on the CWAO of succinic acid¹⁴¹

The effect ceria had on carbon deposition during oxidation was also reviewed by Keav *et al.*¹³³. The general consensus was that with an increase in OSC comes an increase in the amount of substances that is able to adsorb on the surface. Although this is good for oxidation mass transfer, the amount of difficult to oxidise intermediates, such as polymers and carbonaceous material, increases as a consequence.

1.3. Conclusion

Platinum, ruthenium and ceria have shown to be very effective in promoting oxidation of unwanted pollutants in wastewater, which is why they have also been chosen for this investigation.

One of the goals of this study was to develop an innovative and successful catalyst for CWAO. Therefore, as well as the more conventional catalytic supports, SiC was also investigated. It is thought that its hydrophobic nature plays an important role in controlling the interaction the wastewater has with the catalyst, especially in a trickle bed reactor.

The catalyst granule's shape and size also influences the process' performance. It is imperative that an optimum particle size is designed so that activity does not get compromised by the ease of flow through the reactor.

It was found that the most appropriate model pollutant to investigate was phenol. Phenol is considered a toxic pollutant that is largely wasted from industrial processes and is the most researched compound for this particular application.

In terms of whole life cost, there has been a shift away from batch type processes towards more continuous flow CWAQ systems. For this reason, as well as producing an active and stable catalyst, a well-engineered reactor was developed in order to achieve a successful continuous flow CWAQ process.

1.4. References

- 1 G.-R. Walther, E. Post, P. Convey, A. Menzel, C. Parmesan, T. J. C. Beebee, J.-M. Fromentin, O. Hoegh-Guldberg and F. Bairlein, *Nature*, 2002, **416**, 389–95.
- 2 C. Parmesan and G. Yohe, *Nature*, 2003, **421**, 37–42.
- 3 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci.*, 2006, **103**, 15729–15735.
- 4 C. Song, *Catal. Today*, 2006, **115**, 2–32.
- 5 D. W. Kolpin, E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton, *Environ. Sci. Technol.*, 2002, **36**, 1202–1211.
- 6 Livingstone, *Mar. Pollut. Bull.*, 2001, **42**, 656–666.
- 7 E. Metcalf and H. Eddy, *Wastewater engineering: treatment and reuse*, 2003.
- 8 S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny and D. M. DeMarini, *Mutat. Res. - Rev. Mutat. Res.*, 2007, 636, 178–242.

- 9 W. A. M. Hijnen, E. F. Beerendonk and G. J. Medema, *Water Res.*, 2006, 40, 3–22.
- 10 M. Ferraris, E. Chiesara, S. Radice, A. Giovana, S. Frigerio, R. Fumagalli and L. Marabini, *Chemosphere*, 2005, **60**, 65–73.
- 11 M. Takht Ravanchi, T. Kaghazchi and A. Kargari, *Desalination*, 2009, **235**, 199–244.
- 12 R. Crisafully, M. A. L. Milhome, R. M. Cavalcante, E. R. Silveira, D. De Keukeleire and R. F. Nascimento, *Bioresour. Technol.*, 2008, **99**, 4515–4519.
- 13 D. G. J. Larsson, C. de Pedro and N. Paxeus, *J. Hazard. Mater.*, 2007, **148**, 751–755.
- 14 European Union law - http://eur-lex.europa.eu/legal-content/EN/LKD/?uri=celex:31991L0271_04/06/2016, .
- 15 American Public Health Association, American Water Works Association and Water Environment Federation, *Stand. Methods*, 1999, 541.
- 16 G. C. Gil, I. S. Chang, B. H. Kim, M. Kim, J. K. Jang, H. S. Park and H. J. Kim, *Biosens. Bioelectron.*, 2003, **18**, 327–334.
- 17 A. . Vlyssides, M. Loizidou, P. . Karlis, A. . Zorpas and D. Papaioannou, *J. Hazard. Mater.*, 1999, **70**, 41–52.
- 18 M. Shrimali and K. . Singh, *Environ. Pollut.*, 2001, **112**, 351–359.
- 19 R. V. Thurston, R. C. Russo and G. A. Vinogradov, *Environ. Sci. Technol.*, 1981, 15, 837–840.
- 20 S. Carpenter, N. Caraco, D. . Correll, R. W. Howarth, A. N. Sharpley and V. H.

- Smith, *Ecol. Appl.*, 1998, **8**, 559–568.
- 21 V. S. Mishra, V. V. Mahajani and J. B. Joshi, *Ind. Eng. Chem. Res.*, 1995, **34**, 2–48.
- 22 F. Luck, *Catal. Today*, 1999, **53**, 81–91.
- 23 National Environment Agency Singapore - <http://www.nea.gov.sg/anti-pollution-radiation-protection/water-pollution-control/allowable-limits>, .
- 24 L. Keith and W. Telliard, *Environ. Sci. Technol.*, 1979, **13**, 416–423.
- 25 L. Martinkova, M. Kotik, E. Markova and L. Homolka, *Chemosphere*, 2016, 149, 373–382.
- 26 ATSDR - <http://www.atsdr.cdc.gov/> 04/06/2016, .
- 27 J. Levec and A. Pintar, *Catal. Today*, 2007, **124**, 172–184.
- 28 K. H. Kim and S. K. Ihm, *J. Hazard. Mater.*, 2011, 186, 16–34.
- 29 F. Stuber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias and A. Fabregat, *Top. Catal.*, 2005, **33**, 3–50.
- 30 M. Weber and M. Weber, in *Phenolic Resins: A Century of Progress*, 2010, pp. 9–23.
- 31 <https://www.gov.uk/government/publications/phenol-properties-incident-management-and-toxicology> 05/06/2016, .
- 32 A. Fortuny, *J. Hazard. Mater.*, 1999, **64**, 181–193.
- 33 S. C. N. York, 2015.
- 34 <https://www.gov.uk/government/publications/m18-monitoring-of-discharges-to>

water-and-sewer 05/06/2016, .

- 35 S. Yang, W. Zhu, J. Wang and Z. Chen, *J. Hazard. Mater.*, 2008, **153**, 1248–1253.
- 36 H. R. Devlin and I. J. Harris, *Ind. Eng. Chem. Fundam.*, 1984, **23**, 387–392.
- 37 A. Alejandre, F. Medina, A. Fortuny, P. Salagre and J. E. Sueiras, *Appl. Catal. B Environ.*, 1998, **16**, 53–67.
- 38 S. . Kolaczowski, P. Plucinski, F. . Beltran, F. . Rivas and D. . McLurgh, *Chem. Eng. J.*, 1999, **73**, 143–160.
- 39 A. Eftaxias, Rovira i Virgili University, 2002.
- 40 D. Fytili and A. Zabaniotou, *Renew. Sustain. Energy Rev.*, 2008, **12**, 116–140.
- 41 L. C. Wang, I. C. Wang, J. E. Chang, S. O. Lai and G. P. Chang-Chien, *J. Hazard. Mater.*, 2007, **148**, 296–302.
- 42 E. Kattel, N. Dulova, M. Viisimaa, T. Tenno and M. Trapido, *Environ. Technol.*, 2016, **37**, 352–359.
- 43 I. Oller, S. Malato and J. A. Sanchez-Perez, *Sci. Total Environ.*, 2011, **409**, 4141–4166.
- 44 G. Chen, *Sep. Purif. Technol.*, 2004, **38**, 11–41.
- 45 S. W. Krasner, H. S. Weinberg, S. D. Richardson, S. J. Pastor, R. Chinn, M. J. Scilimenti, G. D. Onstad and A. D. Thruston, *Environ. Sci. Technol.*, 2006, **40**, 7175–7185.
- 46 W. A. Mitch and D. L. Sedlak, *Environ. Sci. Technol.*, 2002, **36**, 588–595.
- 47 Y. Yoon, Y. Hwang, M. Kwon, Y. Jung, T. M. Hwang and J. W. Kang, *J. Ind. Eng. Chem.*, 2014, **20**, 2801–2805.

- 48 J. J. Rueda-Marquez, M. G. Pintado-Herrera, M. L. Martin-Diaz, A. Acevedo-Merino and M. A. Manzano, *Chem. Eng. J.*, 2015, **270**, 80–90.
- 49 S. Sven, A. Volker, A. Erich, B. Karl, V. Alex and W. Hans-Dieter, *IUVA News*, 2005, **8**, 32–37.
- 50 <http://www.xylem.com/treatment/us/categories/disinfection-and-oxidation/uv-disinfection-systems> 05/06/2016, .
- 51 M. B. Heringa, D. J. H. Harmsen, E. F. Beerendonk, A. A. Reus, C. A. M. Krul, D. H. Metz and G. F. Ijpelaar, *Water Res.*, 2011, **45**, 366–374.
- 52 J. A. Zazo, J. A. Casas, A. F. Mohedano, M. A. Gilarranz and J. J. Rodriguez, *Environ. Sci. Technol.*, 2005, **39**, 9295–9302.
- 53 V. Kavitha and K. Palanivelu, *Chemosphere*, 2004, **55**, 1235–1243.
- 54 S. Esplugas, J. Gimenez, S. Contreras, E. Pascual and M. Rodriguez, *Water Res.*, 2002, **36**, 1034–1042.
- 55 <http://www.lenntech.com/library/oxidation/cwao/cwao.htm> 05/06/2016, .
- 56 P. R. Gogate and A. B. Pandit, *Adv. Environ. Res.*, 2004, **8**, 501–551.
- 57 H. S. Joglekar, S. D. Samant and J. B. Joshi, *Water Res.*, 1991, **25**, 135–145.
- 58 G. Busca, S. Berardinelli, C. Resini and L. Arrighi, *J. Hazard. Mater.*, 2008, **160**, 265–288.
- 59 F. Luck, *Catal. Today*, 1996, **27**, 195–202.
- 60 X. Zhang, P. Sun, T. Yan, Y. Huang, Z. Ma, B. Zou, W. Zheng, J. Zhou, Y. Gong and C. Q. Sun, *Prog. Solid State Chem.*, 2015, **43**, 71–81.
- 61 H.-J. Reinhardt, H.-D. Obermeyer, B. Schreiner and S. Wolf, *Lindle Gr.*, 2015.

- 62 D. Goi, G. Di Giorgio, I. Cimarosti, B. Lesa, G. Rossi and G. Dolcetti, *Chem. Biochem. Eng. Q.*, 2009, **23**, 343–349 ST – Treatment of Landfill Leachate by H₂.
- 63 A. Ž. Gotvajn, J. Zagorc-Končan and T. Tišler, *J. Environ. Eng.*, 2007, 133, 89–94.
- 64 <http://www.chem.uiuc.edu/rogers/text13/tx133/tx133fr.html> 11/06/2016, .
- 65 L. J. Burcham and I. E. Wachs, *Catal. Today*, 1999, **49**, 467–484.
- 66 H. J. Fecht and M. Werner, *The Nano-Micro Interface: Bridging the Micro and Nano Worlds*, 2005.
- 67 A. Fritz and V. Pitchon, *Appl. Catal. B Environ.*, 1997, **13**, 1–25.
- 68 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939–943.
- 69 D. M. D’Alessandro, B. Smit and J. R. Long, *Angew. Chemie - Int. Ed.*, 2010, 49, 6058–6082.
- 70 C. McAtee, G. McCullough and R. Douglas, *Jpurnal Automob. Eng.*, 2012, **226**, 1536–1546.
- 71 A. P. Jones, *Atmos. Environ.*, 1999, **33**, 4535–4564.
- 72 R. Gläser, J. A. Lercher, K. Vorlop, J. Weitkamp and M. V. Twigg, *Appl. Catal. B Environ.*, 2007, **70**, 2–15.
- 73 J. Kašpar, P. Fornasiero and N. Hickey, in *Catalysis Today*, 2003, vol. 77, pp. 419–449.
- 74 J. E. Duffy, M. A. Anderson, C. G. Hill and W. A. Zeltner, *Ind. Eng. Chem. Res.*, 2000, **39**, 3698–3706.

- 75 M. Pera-Titus, V. Garcia-Molina, M. A. Banos, J. Gimenez and S. Esplugas, *Appl. Catal. B Environ.*, 2004, **47**, 219–256.
- 76 L. Rideh, a Wehrer, D. Ronze and a Zoulalian, *Ind. Eng. Chem. Res.*, 1997, **36**, 4712–4718.
- 77 F. Arena, C. Italiano, A. Raneri and C. Saja, *Appl. Catal. B Environ.*, 2010, **99**, 321–328.
- 78 Q. Wu, X. Hu and P. Yue, *Chem. Eng. Sci.*, 2003, **58**, 923–928.
- 79 A. Pintar and J. Levec, *J. Catal.*, 1992, **135**, 345–357.
- 80 A. Garg, I. M. Mishra and S. Chand, *CLEAN - Soil, Air, Water*, 2010, **38**, 27–34.
- 81 M. Besson, C. Descorme, M. Bernardi, P. Gallezot, F. di Gregorio, N. Grosjean, D. P. Minh and a Pintar, *Environ. Technol.*, 2010, **31**, 1441–1447.
- 82 <http://www.essentialchemicalindustry.org/processes/chemical-reactors.html>
11/06/2016, .
- 83 F. Stuber, I. Polaert, H. Delmas, J. Font, A. Fortuny and A. Fabregat, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 743–751.
- 84 D. I. Enache, P. Landon, C. M. Lok, S. D. Pollington and E. H. Stitt, in *Industrial and Engineering Chemistry Research*, 2005, vol. 44, pp. 9431–9439.
- 85 A. Pintar, in *Catalysis Today*, 2003, vol. 77, pp. 451–465.
- 86 M. E. Suarez-Ojeda, F. Stuber, A. Fortuny, A. Fabregat, J. Carrera and J. Font, *Appl. Catal. B Environ.*, 2005, **58**, 105–114.
- 87 M. P. Duduković, F. Larachi and P. L. Mills, *Catal. Rev.*, 2002, **44**, 123–246.
- 88 F. Stuber, K. M. Smith, M. B. Mendoza, R. R. N. Marques, A. Fabregat, C. Bengoa,

- J. Font, A. Fortuny, S. Pullket, G. D. Fowler and N. J. D. Graham, *Appl. Catal. B Environ.*, 2011, **110**, 81–89.
- 89 F. Arena, G. Trunfio, J. Negro and L. Spadaro, *Appl. Catal. B Environ.*, 2008, **85**, 40–47.
- 90 A. Eftaxias, F. Larachi and F. Stüber, *Can. J. Chem. Eng.*, 2008, **81**, 784–794.
- 91 J. Zhao and X. Yang, *Build. Environ.*, 2003, **38**, 645–654.
- 92 <http://www.techinstroautomation.com/page/ceramic-honeycomb/> 11/06/2016, .
- 93 P. Forzatti, *Appl. Catal. A Gen.*, 2001, 222, 221–236.
- 94 A. A Klinghoffer, R. L. Cerro and M. A Abraham, *Catal. Today*, 1998, **40**, 59–71.
- 95 T. H. Boyer and P. C. Singer, *Water Res.*, 2005, **39**, 1265–1276.
- 96 S. Babel and T. A. Kurniawan, *J. Hazard. Mater.*, 2003, **97**, 219–243.
- 97 I. Benhamed, L. Barthe, R. Kessas, C. Julcour and H. Delmas, *Appl. Catal. B Environ.*, 2016, **187**, 228–237.
- 98 B. Li, K. Sun, Y. Guo, J. Tian, Y. Xue and D. Sun, *Fuel*, 2013, **110**, 99–106.
- 99 A. Fortuny, J. Font and A. Fabregat, *Appl. Catal. B Environ.*, 1998, **19**, 165–173.
- 100 A. M. Cassell, J. a. Raymakers, J. Kong and H. Dai, *J. Phys. Chem. B*, 1999, **103**, 6484–6492.
- 101 D. M. Ciuparu, M. R. Lyubovsky, E. Altman, L. D. Pfefferle and A. K. Datye, *Catal. Rev. Sci. Eng.*, 2002, **44**, 593–649.
- 102 A. Corma, A. Martinez, V. Martinezsoria and J. B. Monton, *J. Catal.*, 1995, 153, 25–31.

- 103 L. Chang, I.-P. Chen and S.-S. Lin, *Chemosphere*, 2005, **58**, 485–492.
- 104 J.-C. Liu, Y. Tang, C.-R. Chang, Y.-G. Wang and J. Li, *ACS Catal.*, 2016, **6**, 2525–2535.
- 105 A. R. Keshavarz, M. Rezaei and F. Yaripour, *J. Nat. Gas Chem.*, 2011, **20**, 334–338.
- 106 S. Imamura, H. Sasaki, M. Shono and H. Kanai, *J. Catal.*, 1998, **177**, 72–81.
- 107 C. Morterra and G. Magnacca, *Catal. Today*, 1996, **27**, 497–532.
- 108 D. Chan, S. Tischer, J. Heck, C. Diehm and O. Deutschmann, *Appl. Catal. B Environ.*, 2014, **156-157**, 153–165.
- 109 E. Heracleous and A. A. Lemonidou, in *Catalysis Today*, 2006, vol. 112, pp. 23–27.
- 110 J. G. Weissman, *Catal. Today*, 1996, **28**, 159–166.
- 111 C. H. Bartholomew, *Appl. Catal. A Gen.*, 2001, **212**, 17–60.
- 112 Q. Xu, K. C. Kharas, B. J. Croley and A. K. Datye, *Top. Catal.*, 2012, **55**, 78–83.
- 113 C. A. Pires, A. C. C. dos Santos and E. Jordao, *Brazilian J. Chem. Eng.*, 2015, **32**, 937–848.
- 114 A. Fortuny, C. Bengoa, J. Font, F. Castells and A. Fabregat, *Catal. Today*, 1999, **53**, 107–114.
- 115 A. Eftaxias, J. Font, A. Fortuny, J. Giralt, A. Fabregat and F. Stuber, *Appl. Catal. B Environ.*, 2001, **33**, 175–190.
- 116 <http://www.reuters.com/article/china-aluminium-alumina-idUSL3N0YX1XD20150611> 16/06/16, .

- 117 http://www.sheffieldresources.com.au/market_hm/ 16/06/16, .
- 118 I. P. Chen, S. S. Lin, C. H. Wang and S. H. Chang, *Chemosphere*, 2007, **66**, 172–178.
- 119 I. P. Chen, S. S. Lin, C. H. Wang, L. Chang and J. S. Chang, *Appl. Catal. B Environ.*, 2004, **50**, 49–58.
- 120 M. A. L. Rocha, G. Del Ángel, G. Torres-Torres, A. Cervantes, A. Vázquez, A. Arrieta and J. N. Beltramini, *Catal. Today*, 2015, **250**, 145–154.
- 121 <http://accuratus.com/silicar.html> 16/06/16, .
- 122 N. Keller, C. Pham-Huu, C. Estournes and M. J. Ledoux, *Appl. Catal. A Gen.*, 2002, **234**, 191–205.
- 123 D. S. Maciver, H. H. Tobin and R. T. Barth, *J. Catal.*, 1963, **2**, 485–497.
- 124 F. E. Tuler, R. Portela, P. Avila, J. P. Bortolozzi, E. E. Miro and V. G. Milt, *Microporous Mesoporous Mater.*, 2016, **230**, 11–19.
- 125 Q. Wei, G. Yang, Y. Yoneyama, T. Vitidsant and N. Tsubaki, *Catal. Today*, 2016, **265**, 36–44.
- 126 H. Yang, Y. Zhang, J. Zhou, Z. Wang, J. Liu and K. Cen, *Int. J. Hydrogen Energy*, 2016, **41**, 3339–3348.
- 127 M. Koek, O. P. Kreuzer, W. D. Maier, A. K. Porwal, M. Thompson and P. Guj, *Resour. Policy*, 2010, **35**, 20–35.
- 128 D. Fino, S. Bensaid, M. Piumetti and N. Russo, *Appl. Catal. A Gen.*, 2016, 509, 75–96.
- 129 Y. Sato, S. Y. Takizawa and S. Murata, *J. Photochem. Photobiol. A Chem.*, 2016,

- 321**, 151–160.
- 130 J. Giménez-Mañogil and A. García-García, *Fuel Process. Technol.*, 2015, **129**, 227–235.
- 131 P. V. Gosavi and R. B. Biniwale, *J. Power Sources*, 2013, **222**, 1–9.
- 132 A. Cybulski and J. Trawczynski, *Appl. Catal. B Environ.*, 2004, **47**, 1–13.
- 133 S. Keav, A. E. de los Monteros, J. Barbier and D. Duprez, *Appl. Catal. B Environ.*, 2014, **150-151**, 402–410.
- 134 A. E. D. L. Monteros, G. Lafaye, A. Cervantes, G. Del Angel, J. Barbier and G. Torres, *Catal. Today*, 2015, **258**, 564–569.
- 135 S. Nousir, S. Keav, J. Barbier, M. Bensitel, R. Brahmi and D. Duprez, *Appl. Catal. B Environ.*, 2008, **84**, 723–731.
- 136 J. Mikulova, J. Barbierjr, S. Rossignol, D. Mesnard, D. Duprez and C. Kappenstein, *J. Catal.*, 2007, **251**, 172–181.
- 137 G. Lafaye, J. Barbier and D. Duprez, *Catal. Today*, 2015, **253**, 89–98.
- 138 S. Yang, Y. Feng, J. Wan, W. Zhu and Z. Jiang, *Appl. Surf. Sci.*, 2005, **246**, 222–228.
- 139 M. Y. Smirnova, O. V. Kikhtyanin, M. Y. Smirnov, A. V. Kalinkin, A. I. Titkov, A. B. Ayupov and D. Y. Ermakov, *Appl. Catal. A Gen.*, 2015, **505**, 524–531.
- 140 C. Yu, P. Zhao, G. Chen and B. Hu, *Appl. Surf. Sci.*, 2011, **257**, 7727–7731.
- 141 S. Yang, M. Besson and C. Descorme, *Appl. Catal. B Environ.*, 2015, **165**, 1–9.

Chapter 2

Developing a reactor for continuous flow operation

2.1. Introduction

The aim of this study was to develop a continuous flow process for CWAO. An extensive amount of time was allocated to re-commissioning a reactor that was stagnant for many years. This reactor served a batch recycle process originally, but was then adapted for this project's requirements. To remove the risk of contamination, all the stainless steel lines were fully replaced and adapted to suit the setup required for a continuous flow process. This also involved installing several pumps and incorporating a high performance liquid chromatography (HPLC) instrument to analyse the products. With this came the lengthy period of building a method for product separation and detection. Phenol can oxidise to form many oxidation products therefore specific mobile and stationary phase compositions were required for their analysis. To ensure CWAO could take place, various catalysts had to be developed. Catalysts were methodically prepared, characterised and tested for their activity in aiding the total oxidation of phenol.

2.2. Reactor design

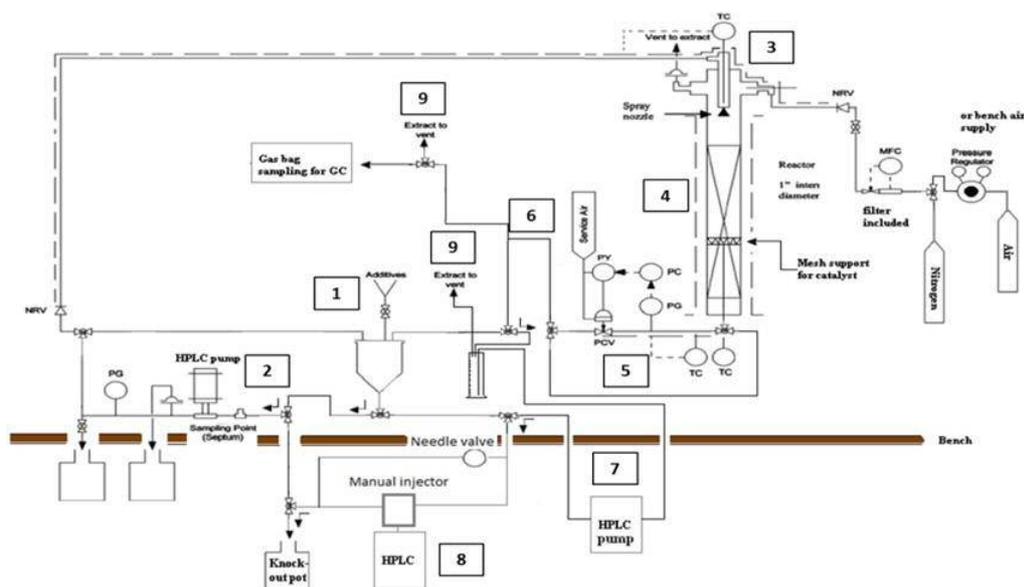


Figure 2.1 Reactor Schematic

- | | |
|-------------------------------|-----------------------------|
| 1. Phenol/water additives pot | 6. Gas-liquid separation |
| 2. Inlet HPLC pump | 7. Outlet HPLC pump |
| 3. Air from cylinder | 8. Shimadzu HPLC instrument |
| 4. Catalyst bed | 9. Venting of gases |
| 5. Pneumatic actuator | |

The diagram above illustrates the rig design as a schematic whereby each component required for the CWAO operation is labelled numerically.

The phenol/water solution inlet stage consisted of an additives pot (1) and a HPLC pump (2). The required weight of phenol was dissolved in a Winchester bottle of HPLC water which connected to the pot (1) via nylon tubing. The Winchester bottle was positioned above the additives pot, so when the valve positioned between both was opened, the solution could flow down until it was full. This allowed for periodic filling

of the pot and ensured that there was enough phenol solution in place for the reaction. The pump (2) enabled the delivery of the liquid from the additives pot to the top of the catalyst bed at the desired flow rate. It was important to make sure that there were no air-locks in the inlet system as this would have hindered the pumping efficiency. To overcome this issue, the pump was configured in a way so that it could be purged for a while before starting up.

The air required for oxidation was delivered from a pressurised cylinder and was controlled by a mass flow controller (MFC) linked to a control box. The air joined the phenol solution at the top of the reactor where they could subsequently flow co-currently through the catalyst bed (3). The catalyst bed sat inside a reactor tube (1.27cm diameter) in a furnace linked to the same control box (4). Here, the liquid solution could trickle through the bed along with air at the desired operating temperature. Glass wool and insulating tapes were placed around the tubing where heat loss was most likely to occur.

Situated on the outlet side of the reactor was a pneumatic actuator to control the reaction pressure whilst keeping the process continuous (5). A supply of air from the lab's compressed air system was required to open the actuator's spring loaded valve. With the relevant pressure selected on the control box, the actuated valve would shut enough to keep the system pressurised whilst still maintaining a continuous flow at the same time.

Once past the pneumatic actuator, the effluent flowed into a liquid/gas separator made up of a sealed measuring cylinder (6). This allowed for the liquid to collect at the bottom and the gas to be vented off to the fume cupboard (9). A third line ran to the bottom of the cylinder whereby the liquid was sucked via a secondary HPLC pump (7) to the Shimadzu[®] HPLC instrument where separation and detection took place (8).

2.3. Reactor conditions

The conditions set for the reactor were kept as consistent as possible in order to compare catalyst activity. Only one variable at a time was changed during each experiment. This enabled kinetic studies to be carried out without confusing what effect was responsible for activity.

In order to compare results to what has been found in the literature, each reactor variable was kept consistent with what was used by Fortuny *et al.*¹. Their studies have shown the most successful results in terms of phenol CWAO using a continuous flow reactor. The table below represents the typical conditions that were selected for this CWAO study.

Table 2.1 Set conditions used for each CWAO reaction

Reactor variable	Value
Temperature (°C)	120-160
Pressure (bar(g))	13.1
Air flow rate (ml/min)	144
Liquid hourly space velocity (h ⁻¹)	26.6
Phenol concentration (mg/L)	1000

The temperature value selection depended highly on the catalysts activity. At temperatures above 160°C, catalysts were able to promote 100% phenol conversion and therefore required it to be reduced in order to measure true activity. Tests were also conducted over a range of temperatures in order to gain an insight into activation energies.

Most of the tests carried out were kept at a constant pressure of 13.1 bar (gauge). Bar (gauge) is what is measured by the pressure gauges and is always 1 bar below the absolute pressure. At atmospheric pressure, the absolute value would be 1 bar, but on the gauge it would be 0. Therefore, if the gauge pressure read 13.1 bar, like what was used in this study, the absolute pressure would be 14.1 bar. Bar gauge is represented by bar(g), and bar absolute is represented by bar(a). In this thesis, bar(g) was used. For most reactions, 13.1 bar(g) was selected as this equated to 2 bar(g) of oxygen partial pressure. This meant that the oxygen was always in excess and poor activity could not be put down to oxidant concentration deficiency.

For the same reason as mentioned above, 144 ml/min of air was selected to exceed the stoichiometric requirements of oxygen. The air required to deliver the oxygen came from a compressed air cylinder (BOC); whereas air for the pneumatic actuator came from the laboratory supplied system.

In addition to temperature, the liquid hourly space velocity (LHSV) had an effect on catalyst activity too. LHSV equates to the amount of liquid flowed per unit time through a specific volume of space; in this case, the volume of catalyst. Decreasing the catalyst volume enhances LHSV; whereas increasing the volume lowers it. The equation below shows how it is calculated²: -

Equation 2.1

The phenolic solution was made up by dissolving 2.5 g of phenol (Sigma-Aldrich®) in 2.5 L of HPLC grade water (Fisher Scientific) to reach a concentration of 1000mg/L. This value was representative of what was used in previous phenol CWAO studies and was also realistic of what is usually found in phenolic wastewaters.

All the stainless steel tubing and fittings were supplied by Swagelok® and the mass flow controller (MFC) was a Brooks 5850 TR.

2.4. Analysis method

The analysis technique consisted of high performance liquid chromatography (HPLC) separation followed by ultraviolet (UV) detection. HPLC separates the products so that they can be individually analysed by the UV detector. The reactor effluent was continuously linked to a sample loop inside the HPLC where periodic analysis injections could take place.

Similar to gas chromatography, a mobile liquid phase was required to carry the eluents through a separating column and on to the detector. Depending on the nature of the products and the degree of separation required, the mobile phase composition could be tailored in a way that was best suited. In this case, the polarity of the stationary phase and the organic nature of the mobile phase highly influenced product retention time. When both the stationary phase and the products were of a polar nature, their affinity towards each other increased significantly. This in turn increased their retention time within the column. An organic mobile phase, on the other hand, allowed the more organic products to elute faster. The organic mobile phase would attract the organic eluents through van der Waal forces and reduce their retention on the stationary phase³.

A reverse phase (*C18-Shim-pack XR-ODS*: 3mm diameter and 50 mm in length) packed bed column was used to separate the eluted products along with a mobile phase consisting of water and methanol. Being hydrophobic, the reverse phase column had the better affinity for the hydrophobic eluents. The mobile phase, on the other hand, was hydrophilic and therefore allowed the more hydrophilic products to elute faster. The mobile phase mix was applied using a gradient flow method; starting off nearly totally

hydrophilic (4.7% MeOH in H₂O (*Fisher Scientific*®)), then ramping linearly up to a less hydrophilic mix of 60% MeOH in water. Manipulating the mobile phase in this way not only provides great flexibility in terms of compound separation, but also allows for the analysis run time to be optimised.

To minimise peak tailing and maximise retention consistency, phosphoric acid was added to the mobile phase. This ensured the stationary phase stayed protonated when the organic acids eluted through. This can highly influence the organic acids' retention times over the column therefore an optimum balance of mobile phase acidity was required. For this C-18 column, a pH of around 3 (0.22vol%H₃PO₄ in water (*Sigma Aldrich*®)) was sufficient⁴. The temperature in the HPLC instrument was kept at a constant 30°C to allow for the best possible separation and to stay within the column's optimum working conditions.

Once the products were separated, a dual wavelength UV detector quantified them in order of elution. This allowed for compounds with large differences in UV-visible adsorption energies to be detected. Along with phenol, the quinone-type products strongly absorbed at 254 nm; whereas the organic acids absorbed at a higher energy of 210 nm.

Each of the products were calibrated from standards (obtained from *Sigma Aldrich*®) by calculating their peak areas at different known concentrations. Along with knowledge of their retention times, all the possible products were identified and quantified from their calibration curves (The calibration curves are presented in the Appendix). Below is a typical chromatogram of the products that were formed during the CWAO reaction.

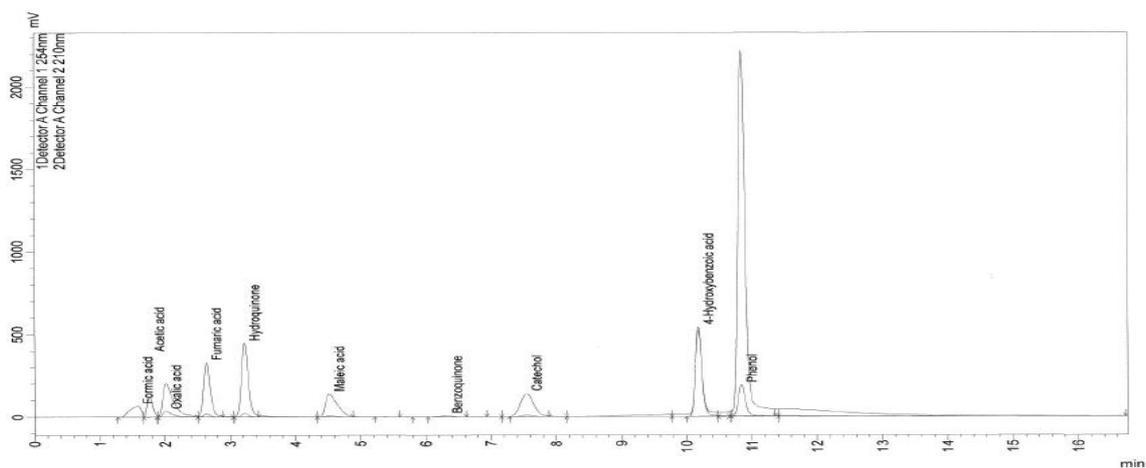


Figure 2.2 Chromatogram of phenol and its partial oxidation product

2.5. References

- 1 M. E. Suarez-Ojeda, F. Stuber, A. Fortuny, A. Fabregat, J. Carrera and J. Font, *Appl. Catal. B Environ.*, 2005, **58**, 105–114.
- 2 A. Eftaxias, Rovira i Virgili University, 2002.
- 3 https://www.shimadzu.eu/sites/default/files/Tips_for_practical_HPLC_analysis-Separation_Know-how.pdf 16/06/16, .
- 4 P. Ergunul and C. Nergiz, *Czech J. Food Sci.*, 2010, **28**, 202–205.

Chapter 3

Catalyst characterisation methods

3.1. Introduction

In order to understand and correlate structure with activity each catalyst was characterised using the various techniques available. A mix of batch and surface sensitive techniques were used to build a full picture of how the catalysts might behave in terms of promoting catalytic wet air oxidation. Techniques such as X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett Teller (BET) and transmission electron microscopy (TEM) were used to analyse the surface; whereas techniques such as X-ray diffraction (XRD) and temperature programmed reduction (TPR) were used to analyse the bulk.

3.2. Temperature programmed reduction (TPR)

The temperature programmed reduction (TPR) technique consisted of determining the reduction potential of the catalysts as a function of temperatures¹. A thermal conductivity detector (TCD) was used to quantify how much H₂ was consumed as a result of catalyst reduction². From this, oxidation states could be established as each compound usually has characteristic reduction profiles. Compound interaction within the catalyst itself can also influence reduction potentials. Another phenomenon that can occur is that compounds can reduce at different temperatures depending on which part of the

catalyst they reside on. For example, the compounds sitting on the surface can reduce at different temperatures to the ones embedded in the bulk.

The catalysts in this study were pre-treated under various oxidising/reducing atmospheres and consequentially resulted in very different activity behaviours. Knowing which oxidation state the successful catalysts were in allows for future CWAO systems to be optimised.

3.2.1. Experimental procedure

0.050-0.100g of catalyst was weighed out on an analytical balance and placed within the sample tube sandwiched between two layers of quartz wool to prevent contamination. A Thermo TPDRO1100 instrument was used to obtain the temperature programmed reduction profiles. Samples were first pre-treated in flowing argon (20mL/min) at 110°C for 45 minutes at a rate of 20°C/min. For the analysis, a flow of 10% H₂/Ar was passed over the catalyst at a rate of 10°C/min from ambient temperature to 800°C. At the end of the programme the catalyst was cooled at a rate of 50°C/min.

3.3. Brunauer-Emmett Teller (BET) and porosity

BET (Brunauer-Emmett Teller) is a surface area analysis technique that measures the ability of a solid to adsorb gas at different pressures³. There is a positive, linear relationship seen between the pressure at which the gas is adsorbed and the surface area of the catalyst. The gas used in this study was nitrogen.

BET analysis can provide pore size information. To gain an insight into the pore size distribution, density functional theory (DFT) was used to analyse the adsorption isotherms. This gives a volume profile over a range of pore widths and helps determine what type of pore structure the catalyst has⁴.

The CWAO reaction relies heavily on mass transfer to promote a successful oxidation reaction therefore, it was important to establish how much surface area and porosity contributed to this effect.

3.3.1. Experimental procedure

A Quantachrome Quadrasorb was used to gather surface area and pore volume profiles. Initially, the catalyst had to be pre-treated under a vacuum at 120°C for 2 hours to remove any moisture or impurities. Once treated, the catalysts were placed in a suitable analysis tube and weighed using an analytical balance. The optimum weight required should have equated to ca. 15-20 m² of catalyst surface area. The catalyst weight was used to calculate the total pore volume. Once the tubes were fitted the analysis could start (4 samples could be analysed per run on this particular instrument). The sample tubes were kept in liquid nitrogen during the analysis period so that heat could not affect the adsorption process. A flow of N₂ gas was passed over the catalysts at various pressures to obtain the data required to determine surface area and pore volumes.

3.4. Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) is used to characterise the crystallinity of materials⁵. It involves radiating a beam of X-rays onto a crystallite powdered sample. Crystalline compounds consist of layered lattices that can diffract X-ray beams in specific directions and can be quantified by the angle they are diffracted by. Diffraction only occurs if the angle between the radiated beam and the diffracted beam is 2θ ⁶. Lattice spacing can be calculated from diffraction angles using Bragg's law below:-

Equation 3.1

λ	wavelength	d	lattice spacing
θ	diffraction angle	n	integer

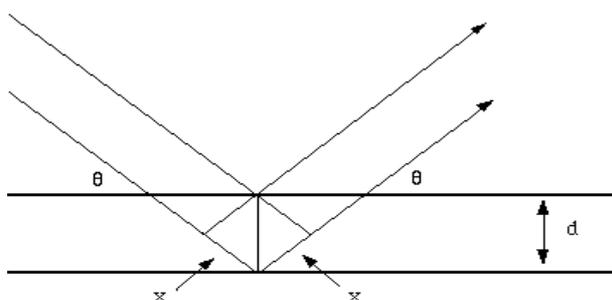


Figure 3.1 X-ray diffraction

Crystalline components have unique diffraction patterns. This means that they can be used to confirm whether the catalysts were synthesised successfully during preparation. Moreover, the technique is able to identify the different phases of the same compound. This was significant in identifying the components that were responsible for promoting activity.

3.4.1. Experimental procedure

The analysis was carried out using a diffractometer with a Cu K α X-ray source. To load the sample, the pellets were crushed to a powder and placed in a sample holder. Once in the instrument, an automated robotic arm would take the sample and place it in line with the X-ray beam ready to be analysed. The analysis was carried out using a tension of 40KV and a current of 40mA between 2 θ angles of 10 $^{\circ}$ and 80 $^{\circ}$. The crystallite size and lattice strains were also computed using the Debye-Scherrer equation and a

highly crystalline reference (FWHM = $0.0925^\circ 2\theta$) silicon sample was used to quantify peak broadening.

3.5. X-ray Photoelectron Spectroscopy (XPS)

XPS (Photo-electron spectroscopy) is a surface sensitive technique that uses X-ray radiation to ionise a compound to determine its elemental composition⁷. The ejected electrons are detected by an electrostatic detector whereby kinetic energies are measured. As the incident X-ray beam wavelength is known, electron binding energies can be calculated using the formula below³.

$$- \quad \text{Equation 3.2}$$

Where:-

h Plank's constant

ν Frequency of radiation

m_e Mass of an electron

I_i Ionisation energy of an electron from an orbital i

Binding energies were plotted against the emitted electron intensities and were compared to plots from a reference database. These allowed for the surface elements to be identified and also provide information regarding their electronic states. The software was also able to quantify them as a percentage of the surface measured.

3.5.1. Experimental procedure

A Kratos Axis Ultra DLD system was used to collect XPS spectra using monochromatic Al Ka X-ray source operating at 144 W (12mA x 12 kV). Powdered

samples were prepared in a similar fashion to SEM, specifically the catalysts powder was pressed on to double sided scotch tape attached to 6mm diameter stubs and any excess material tapped off.

Data was collected with pass energies of 160 eV for survey spectra, and 40 eV for the high resolution scans. The system was operated in the Hybrid mode, which utilises a combination of magnetic immersion and electrostatic lenses to improve sensitivity and acquisition occurred over an area approximately $300 \times 700 \mu\text{m}^2$.

A magnetically confined charge compensation system was used to minimize charging of the sample surface, and all spectra were taken with a 90° take off angle. A base pressure of $\sim 1 \times 10^{-9}$ Torr was maintained during collection of the spectra.

Spectra were analysed using CasaXPS (V2.3.17) and calibrated to the C(1s) line for adventitious carbon taken to be 284.8 eV. Elemental molar ratios (at%) calculated after subtraction of a Shirley background and using sensitivity factors supplied by the manufacturer.

3.6. Transmission Electron Microscopy, Scanning Transmission Electron Microscopy & Energy dispersive X-rays (TEM, STEM & EDX)

Transmission electron microscopy was used to determine the physical shape and structure of the catalysts as well as determining the size distribution of the active particle components. The technique produces an image from electrons that interact with a thin layer of catalyst sample after transmission⁸. For the difficult to resolve small crystalline particles, scanning transmission electron microscopy (STEM) was used to analyse incoherently scattered electrons at high angles^{9,10}. EDX on the other hand analyses the X-

rays that are emitted. These X-rays are characteristic of each element and therefore can be identified as a fraction of the sample at the site of emission. This technique therefore provides bulk elemental characterisation.

The above techniques were also used to determine catalyst active component particle size distribution. This helped to understand if varying size distributions affected activity.

Tomographical images were also taken to see how water behaved on hydrophobic catalysts. This had to be carried out under CRYO conditions so that the water droplet froze as soon as it hit the catalyst. This information was important as hydrophobicity played a major role in the CWAO mechanism.

3.6.1. Experimental procedure

A high-resolution transmission electron microscope (HR-TEM) JEOL 2100 (LaB6) system was employed. The state-of-the-art instrument was equipped with a high-resolution Gatan digital camera (2k x 2k). For HRTEM analysis, after preparing a water suspension from the samples, a drop of about 2 mL was put on the TEM grid and dried. For the CRYO TEM images, once the sample was affixed to the sample holder, HPLC water was sprayed from a bottle fitted with an atomiser onto the catalyst. The samples were pre-frozen in liquid nitrogen by plunge freezing the water sprayed catalyst samples which were then transferred on to a high-tilt Gatan CRYO transfer tomography holder (Model 914) using a Gatan CRYO station. The holder is specifically designed for prolong analysis of frozen samples. To maintain the temperature of -175 °C, the holder is equipped with a CRYO Dewar for liquid nitrogen with a zeolite CRYO pump inside. During the experiments, the sample temperature was constantly monitored by a Gatan SmartSet cold

stage controller (Model 900). Once ready, the sample could be imaged using the correctly set software settings.

3.7. Microwave Plasma – Atomic Emission Spectroscopy (MP-AES)

MP-AES was used to quantify the amount of active components that were leached during the CWAO reaction^{11,12}. The technique uses nitrogen plasma to atomise or ionise the metal leachate followed by detection of the electromagnetic radiation emitted through relaxation. The emitted spectra goes through a monochromator and a detector which allows the leachate to be quantified. The element in question must be calibrated from known concentrations beforehand to allow for quantification to be made. The leachate analysed was platinum.

3.7.1. Experimental procedure

The MP-AES was an *Agilent 4100* with nitrogen plasma of 5000K. Three standard solutions of platinum were prepared (4, 8 and 12ppm in water) for calibration. The stabilisation and uptake time for each measurement was 15 seconds. Once calibrated, an effluent sample was taken from the continuous flow CWAO reactor and pumped into the MP-AES analyser. If any leaching occurred, the instrument would detect the platinum and quantify it in terms of its concentration.

3.8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique that measures the weight of a sample as a function of temperature¹³. It can also be carried out under various atmospheres. The sample is likely to chemically react with the atmosphere at elevated temperatures and cause its mass to change. The outcome can then be correlated to the experimental conditions during testing.

TGA is useful for CWAO studies because it shows whether catalysts deactivated as a result of fouling or not. If it was down to fouling, polymeric carbon impurities would get oxidised to CO₂ and cause the catalyst to decrease in mass. Below is an example of carbon being oxidised over various catalysts under TGA conditions¹⁴: -

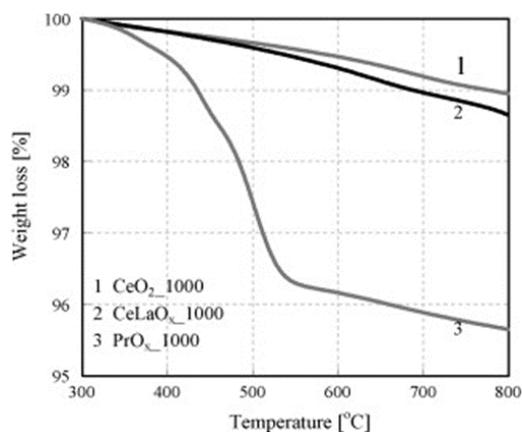


Figure 3.2 TGA example

For this project, some catalysts also underwent surface modifications to improve catalytic activity. They were modified with an organic silane to increase hydrophobicity. TGA was therefore used to evaluate their stability in an oxidative environment and to see whether they would survive the elevated temperatures of a CWAO reactor.

3.8.1. Experimental procedure

The instrument used was a *Perkin Elmer TGA 4000*. Catalyst samples (ca.50mg) were added to ceramic crucibles before their initial weights were recorded. The temperature programme ran from 30°C to 995°C at a rate of 20°C/min in an atmosphere of air. The *Pyris* software, linked to the instrument, recorded the thermogravimetric data and produced a table showing sample mass as a function of temperature.

3.9. References

- 1 F. Arena, G. Trunfio, J. Negro and L. Spadaro, *Appl. Catal. B Environ.*, 2008, **85**,

40–47.

- 2 C. Costello, J. Guzman, J. Yang, Y. Wang, M. Kung, B. Gates and H. Kung, *J. Phys. Chem. B*, 2004, **108**, 12529–12536.
- 3 E. P. H. & T. E. Brunauer S, *J. Am. Chem. Soc.*, 1938, **60**, 1938.
- 4 G. Leofanti, M. Padovan, G. Tozzola and B. Venturelli, *Catal. Today*, 1998, **41**, 207–219.
- 5 I. E. Wachs, in *Catalysis Today*, 2005, vol. 100, pp. 79–94.
- 6 B. Warren, *X-ray diffraction*, Reading, Mass., Addison-Wesley Pub. Co., 1969.
- 7 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- 8 G. Spoto, E. N. Gribov, G. Ricchiardi, A. Damin, D. Scarano, S. Bordiga, C. Lamberti and A. Zecchina, *Prog. Surf. Sci.*, 2004, **76**, 71–146.
- 9 <http://www.imaging-git.com/16/06/16>, .
- 10 E. D. Boyes and P. L. Gai, *Ultramicroscopy*, 1997, **67**, 219–232.
- 11 I. Gandarias, E. Nowicka, B. May, S. Alghareed, R. Armstrong, P. Miedziak and S. Taylor, *Catal. Sci. Technol.*, 2016, **6**, 4201–4209.
- 12 Y. Huang, Z. Lin and R. Cao, *Chem. - A Eur. J.*, 2011, **17**, 12706–12712.
- 13 H. L. Fang and H. F. M. DaCosta, *Appl. Catal. B Environ.*, 2003, **46**, 17–34.
- 14 K. Krishna, A. Bueno-López, M. Makkee and J. A. Moulijn, *Appl. Catal. B Environ.*, 2007, **75**, 189–200.

Chapter 4

Catalyst screening for CWAO

4.1. Preparation & Characterisation of platinum, ruthenium and ceria on alumina and silicon carbide supports

4.1.1. Introduction

CWAO is a relatively novel area of research in comparison with other catalytic studies. Not only is there a lack of knowledge in explaining the mechanistic nature of a CWAO reaction, but also there has not been a specific catalyst system that clearly outperforms other systems in terms of activity. Also, due to the complexity involved with treating wastewater made up of many possible pollutants, there have only been a few catalyst systems studied for phenol CWAO; even fewer for continuous flow operation. With this in mind, the initial area of work was focused on screening catalysts to get an idea of what type of system performs best for this type of reaction.

In this section, an overview is given on how the catalysts were prepared, characterised and eventually tested to see which type of system was the most active for phenol CWAO.

4.1.2. Materials

All the catalyst supports (alumina and silicon carbide 3 mm pellets) were supplied by Johnson Matthey[®]. The metal precursor platinum(II) 2,4-pentandionate (minimum of

48% Pt) was supplied by Alfa Aesar, and the ruthenium(III) 2,4-pentandionate (97% assay) and cerium(III) nitrate hexahydrate (99.99%) were supplied by Sigma Aldrich. The solvents used for impregnation, depending on the type of metal precursor used, consisted of HPLC grades of toluene and water supplied by Sigma-Aldrich and Fischer Scientific respectfully.

4.1.3. Catalyst Preparation

There are many ways to prepare a catalyst for heterogeneous catalytic applications. In this study an incipient wetness method was used, followed by drying and calcination. Due to the novelty of CWAO, in terms of the literature published, most of the work carried out is based on discovering the best type of catalyst and not so much on catalyst development. For this reason, more focus was put on catalyst screening and keeping the preparation technique consistent. However, some investigations involved varying calcination conditions.

As mentioned above, an incipient wetness technique was used to initially prepare the catalyst. A metal precursor was dissolved in a minimum amount of solvent followed by the catalyst support to initiate impregnation. For the impregnation of platinum and ruthenium, toluene was used to dissolve the precursors; whereas for ceria, HPLC water was used. The precursor and support were weighed separately on an analytical balance (4.d.p) to ensure the correct weight percentage of active metal component was achieved. The solution was left in a 250 ml round bottomed flask for 24 hours to allow for sufficient impregnation.

A large proportion of the catalysts required the supports to be in the granular form. This was achieved by crushing and sieving the provided pellets to the desirable grade (0.425-0.6mm).

After an impregnation period of 24 hours, the solution was evaporated using a rotary evaporator. The temperature of the water bath was set to 80-90°C and the pressure set to below 400 mbar. This allowed the solvent to be evaporated without the need of excessive heat. The instrument was fitted with a condenser with a flow of water to allow the evaporated solvent to condense in a separate collection vessel. The flask's rotation speed could also be controlled to further aid evaporation. Once all the solvent was gone, the sample was left to dry overnight at 120°C to ensure all residual solvent was evaporated.

The next stage of the catalyst preparation process consisted of a calcination step. Calcination not only removes impurities from the catalyst, but also treats the active components until preferred oxidation state is reached. In this study, the catalysts were placed in a furnace at 500°C in static air for 2 hours with an initial ramp rate of 10°C/min. Once cooled, the catalysts were fully prepared for testing.

If a bimetallic catalytic system was being prepared, the first metal would be impregnated, rotary evaporated, dried and calcined before repeating the process for the second active metal component.

It was important to keep the preparation steps as consistent as possible in order to compare catalyst performance during the screening process. Keeping preparation and reaction conditions consistent means that only changes in catalyst composition can have an effect on phenol oxidation.

4.1.4. Pre-reaction catalyst characterisation

Various characterisation techniques were used to identify and confirm catalytic composition and explain activity.

4.1.4.1. X-ray diffraction (XRD)

This bulk technique gave an insight into catalyst structure. Below are a series of diffractograms that show their XRD profiles. Each diffraction angle is characteristic to the type of crystal structure present. The components can therefore be identified and confirmed from the reference database or the literature.

The figure below shows the diffraction profile of various platinum-type catalysts on an alumina and silicon carbide support.

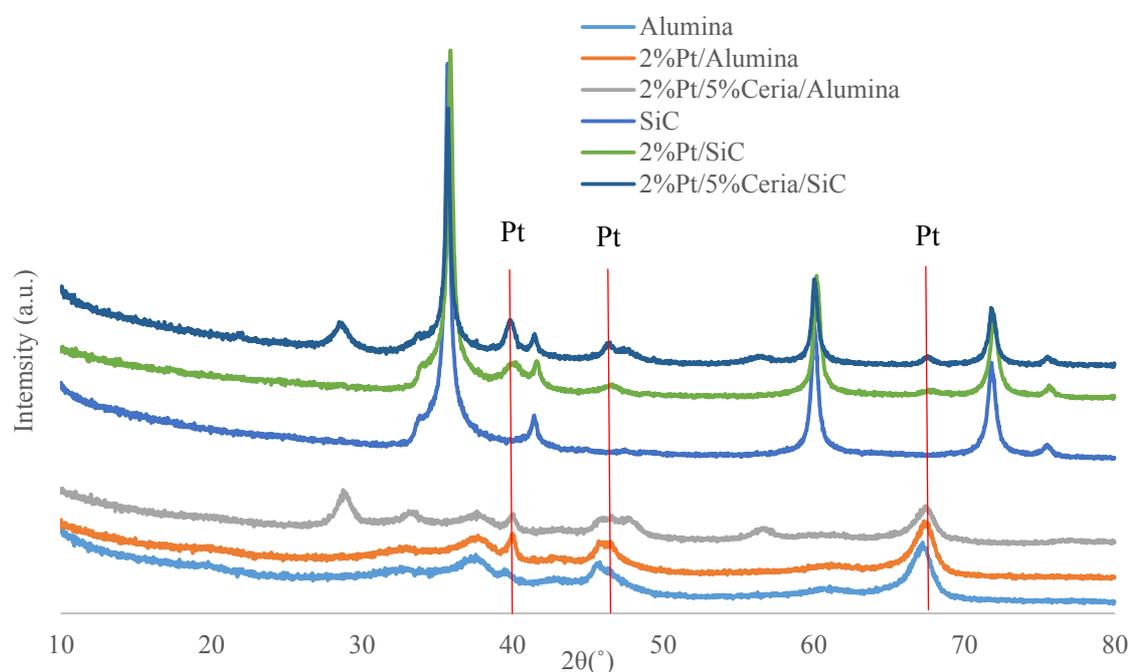


Figure 4.1 Diffractogram illustrating the diffraction angles of various platinum-type catalyst

The diffractogram shows the platinum diffracting the X-rays at the three positions highlighted. The peaks appear small as the percentage loading of the platinum was relatively low. For the SiC supported catalysts, the peaks appeared at 40°, 47° and 68°. These were not present when pure SiC was analysed. These peaks were further confirmed by a study which investigated the XRD pattern of supported platinum catalysts¹. The XRD profile suggests that the platinum was mainly metallic. Platinum oxide (α -PtO₂)

diffracts X-rays at different angles to the metal. But as it is only a bulk technique, there could have been small concentrations of amorphous oxide species not being detected². For the alumina catalysts, it was more difficult to identify the Pt peaks amongst the support's peaks. Nevertheless, the peak positions appear stronger with the Pt present and are consistent with what was found for the SiC catalysts.

By comparing the different type of supports, it is clear which peaks relate to the ceria components and which relate to the platinum. The ceria diffracted the X-rays at 29°, 33°, 48° & 57° and were consistent with what was found in a study investigating ceria nanospheres³.

The diffraction angles of both supports (γ -alumina and β -SiC) also agreed with what has been shown in the literature^{4,5}. Each of the components prepared during impregnation were therefore identified by this bulk characterisation technique.

The figure below shows the same type of diffractogram as above but with ruthenium as the active metal component.

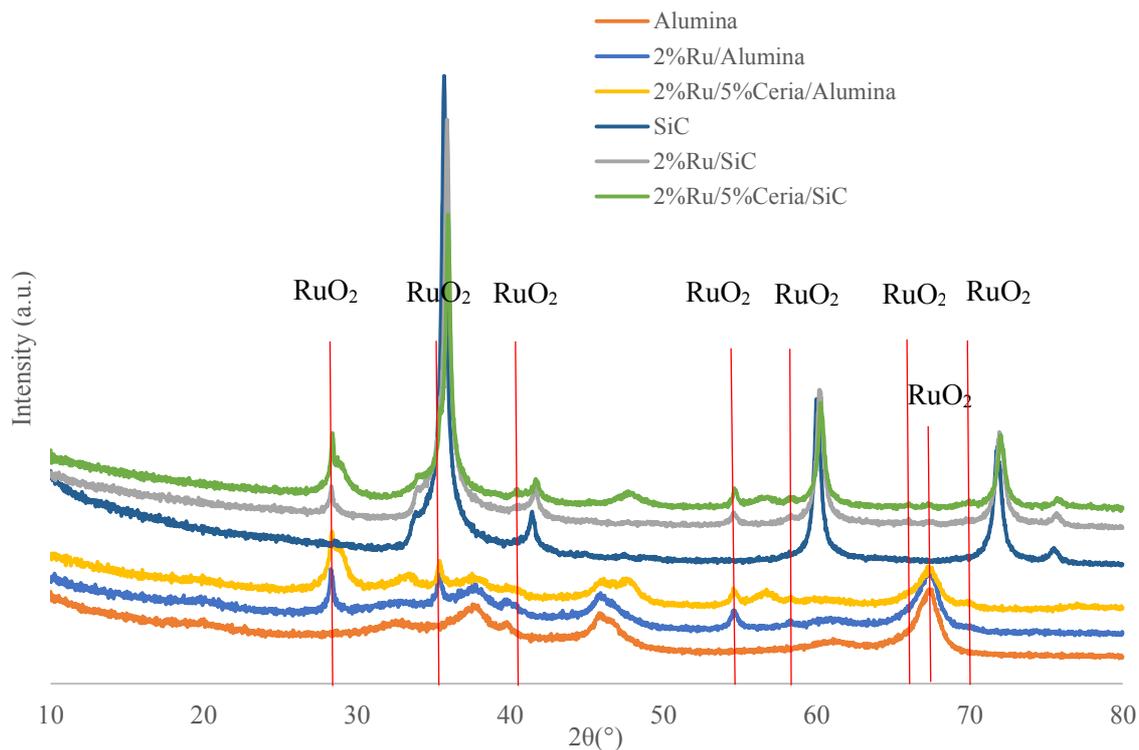


Figure 4.2 Diffractogram illustrating the diffraction angles of various platinum-type catalysts

In contrast to the platinum, the ruthenium's diffraction angles suggested it was in its oxide form rather than the metal. Literature studies show that metallic ruthenium diffracts X-rays at angles of: 45° , 48° , 50° , 51° , 55° & 69° ⁶. The diffractogram above, on the other hand, show traces for ruthenium at 29° , 35° , 40° , 55° , 58° , 66° , 67° & 70° , which is characteristic of the oxide form. Literature studies also supports this observation^{7,8}. Similar to the platinum catalyst diffractogram, the ceria peaks showed up at the same diffraction angles. This indicates that the active component, be it platinum or ruthenium oxide, did not affect the ceria's phase behaviour.

Even though the platinum and ruthenium catalysts were pre-treated in the same manner, XRD showed that they were in different oxidation states. Regardless of support type, the platinum was predominantly in its metallic form, and the ruthenium was predominantly in its oxide form.

4.1.4.2. Temperature programmed reduction (TPR)

TPR plays an important role in identifying which oxidation state the catalytic system is in. The following TPR profiles represent hydrogen consumption as a function of temperature. The first set of the graphs represent the reduction profiles of the platinum-type catalysts; with alumina as the support on the left and SiC as the support on the right.

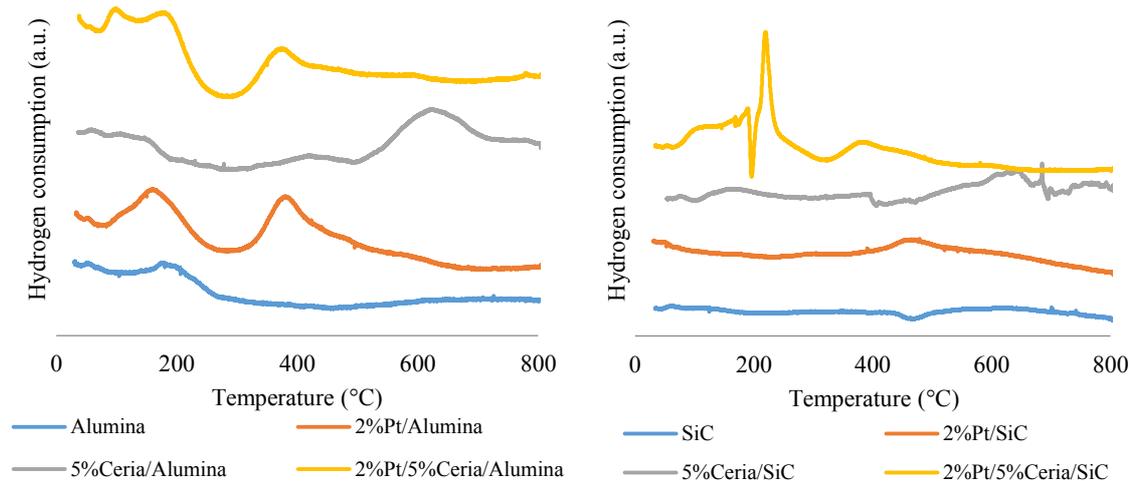


Figure 4.3 TPR profiles of platinum catalysts on alumina and SiC supports

By comparing alumina with 2%Pt/Alumina, it is clear which peaks are responsible for the platinum components. One shows up at just below 400°C and another as a shoulder to the alumina peak seen above 100°C. XRD showed that the bulk of the platinum was metallic, however the peaks in the profiles above suggests that there are oxide species present. Ciambelli *et al.* and Contreras-Andrade *et al.* highlighted that the first peak at 100°C relates to the reduction of the bulk PtO_x species, weakly bound to the alumina and that the peak below 400°C relates the more strongly interacting PtO_x being reduced^{9,10}. These peaks were not present for the 2%Pt/SiC catalyst, on the other hand, only a small broad peak showing up at above 400°C. This indicates that the SiC catalyst has more platinum bound as a metal and that any PtO_x species present are only strongly interacting. It can be said, therefore, that the alumina support promotes better PtO_x formation in

comparison to SiC as the calcination conditions were exactly the same. Also, as it was believed earlier that the majority of the platinum was metallic, but TPR has shown that there are oxide species present.

With the incorporation of ceria into the catalytic system, reduction peaks appeared at the same temperatures for both alumina and SiC supports; be it more pronounced for the alumina series. The dip and a spike seen around 200°C for the 2%Pt/5%Ceia/SiC catalyst was down to an error on the instrument; the profile settled after this. For the 5%Ceia/support profiles, the main hydrogen consumption activity occurs upwards of 600°C. This agreed with the study carried out by Yao *et al.*, where it was proposed that the peaks at high temperatures (600°C) increased and got more complex with an increased concentration of ceria on the alumina support¹¹. It was also shown that when adding a precious metal to the catalyst, the familiar peaks associated with platinum appeared and the high temperature peak associated with ceria was not affected much. In this case, that high temperature peak has almost totally disappeared. This could have been down to the second calcination step having an effect, or that the interacting platinum has changed the reducibility of the ceria in some way. A study carried out by Triki *et al.* explained how adding a precious metal enhances the reducibility of ceria due to the hydrogen spill over effect¹². This would explain again why the ceria peak was affected when adding the platinum. There is another peak at 400°C, though small, it is thought that it relates to the surface reducing before the bulk at higher temperatures¹².

The next pair of TPR profiles represent the ruthenium equivalent of the catalysts: the alumina type on the left and the SiC type on the right.

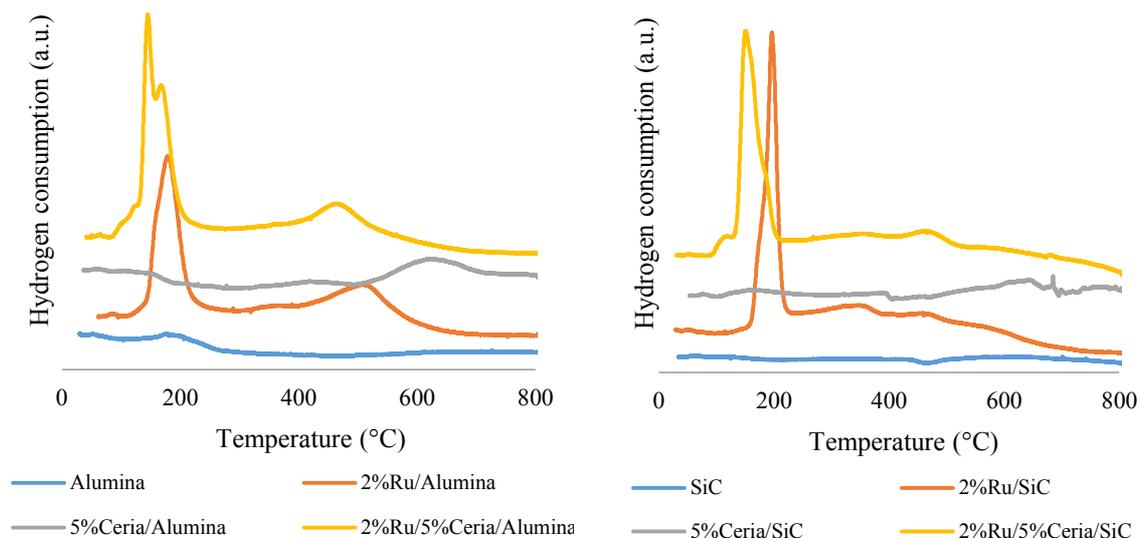


Figure 4.4 TPR profiles of ruthenium catalysts on alumina and SiC supports

The ruthenium peaks are a lot more pronounced in comparison to the platinum; indicating a higher concentration of oxide species. This confirms what was shown by the XRD diffractograms. The double peak just below 200°C relates to the reduction of RuO₂ phases^{13,14}. Wang *et al.* showed that a ruthenium/alumina catalyst, calcined in air at 400°C for 2 hours after an incipient wetness impregnation, reduced at the same temperatures as in the graphs above¹⁴. The study explained that the peaks related to the reduction of RuO₂ phases.

Similar to the platinum TPR profiles, the ceria peak at just above 600°C disappeared when Ru was introduced to 5%Ceia/Alumina. This suggests that the hydrogen spill over effect comes into force when ruthenium is incorporated. Interestingly, the ruthenium oxide peaks become more reducible when ceria is included. Also, the first ruthenium peak becomes more prominent. This indicates that a large proportion of the RuO₂ species bind weaker to a support already containing ceria.

Changing the type of support does not affect the reduction profiles significantly. However, the peak at 500°C is a lot more pronounced for the ruthenium-alumina

catalysts. This suggests that the alumina promoted more difficult to reduce ruthenium species compared to SiC. Wang *et al.* also established that the peak at 500°C was down to a strongly interacting ruthenium oxide-alumina complex¹⁵.

4.1.4.3. Surface area Brunauer Emmett Teller (BET)

BET was used to determine catalyst surface areas. The surface area can differ greatly between supports, especially if they are doped with active components.

The following table contains surface area measurements for the alumina and SiC supported catalysts.

Table 4.1 Surface area of alumina and SiC type catalysts

Catalyst	Surface area (m²/g)	Catalyst	Surface area (m²/g)
<i>Alumina</i>	<i>107</i>	<i>SiC</i>	<i>24</i>
<i>2%Pt/Alumina</i>	<i>97</i>	<i>2%Pt/SiC</i>	<i>23</i>
<i>5%Ceia/Alumina</i>	<i>96</i>	<i>5%Ceia/SiC</i>	<i>25</i>
<i>2%Ru/Alumina</i>	<i>103</i>	<i>2%Ru/SiC</i>	<i>24</i>
<i>2%Ru/5%Ceia/Alumina</i>	<i>95</i>	<i>2%Ru/5%Ceia/SiC</i>	<i>24</i>

The main difference between the two types of supports is that the alumina catalyst, be it with an active component present or not, has a larger surface area compared to SiC. The type of alumina used for this study consisted of the high surface area γ -alumina which in general has a higher surface area compared to SiC¹⁶. The SiC used was β -SiC and is notorious for having low surface area properties¹⁷.

The surface area of alumina is usually higher than SiC due to there being more hydroxyl functionality on the surface. They are more commonly found on alumina as there are more oxygen containing species, protruding from the surface, that are exposed to air¹⁸. This type of alumina is also very porous because its structure has a very disordered cubic close packed lattice¹⁹. SiC, on the other hand, has a more ordered lattice

(Si-C tetrahedral bonding) which can result in it having a relatively low surface area²⁰. Its ordered crystallinity was seen in the XRD diffractograms as large sharp peaks, much larger than what was seen for the less crystalline γ -alumina phases.

The effect of introducing active components to the support however is discussed below. This also includes explanations from a pore size distribution perspective.

4.1.4.4. Pore size distribution (Using a DFT method)

Alumina's surface area was measured at 107 m²/g. When an impregnation step was added, such as incorporating active components in the form of platinum, ruthenium or ceria, the overall surface area dropped. This suggests that some of the alumina's pores get filled during the process.

The figure below shows the pore size distribution of the alumina supported catalysts. It shows the majority of the volume being between pore widths of 1 and 5 nm. The pore volumes reduced in size when the active components were added and suggests that the impregnating particles were of a similar size to the voids. This consequentially reduces alumina's surface area which can be seen in the table above.

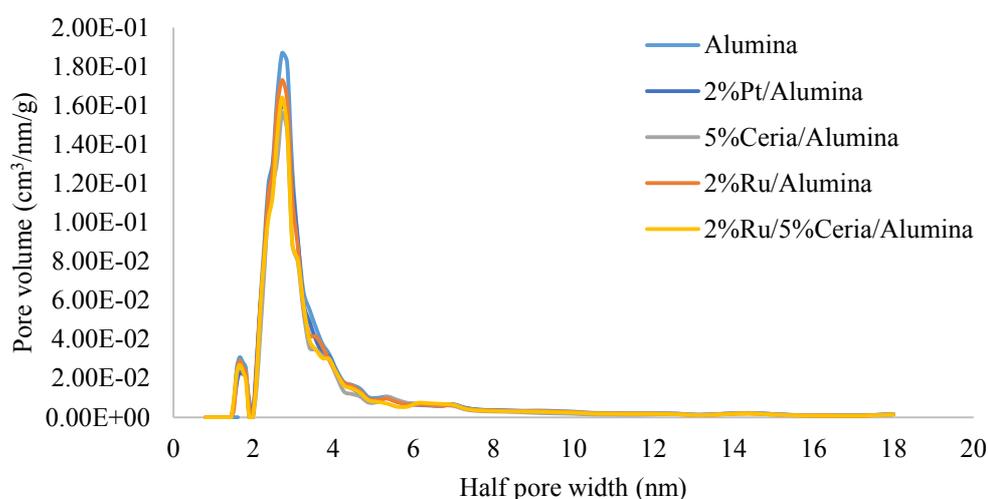


Figure 4.5 The pore size distribution of alumina catalysts

In comparison, the SiC's surface areas have not changed significantly after incorporating the active components. Compared to alumina, SiC is not as porous at the lower pore width end. This is evident from the figure below as the pore size distributions show volumes much lower than that of the alumina catalysts. The alumina's pore volume gets as high as $0.18 \text{ cm}^3/\text{nm/g}$, whereas the SiC's only gets as high as $0.02 \text{ cm}^3/\text{nm/g}$. SiC shows a lack of porosity compared to alumina therefore the impregnated particles are less likely to have an effect on surface area. This effect is also seen in the table above. Interestingly, introducing ceria to the SiC support increased the surface area. However, this could be down to experimental error or ceria itself increasing the overall value.

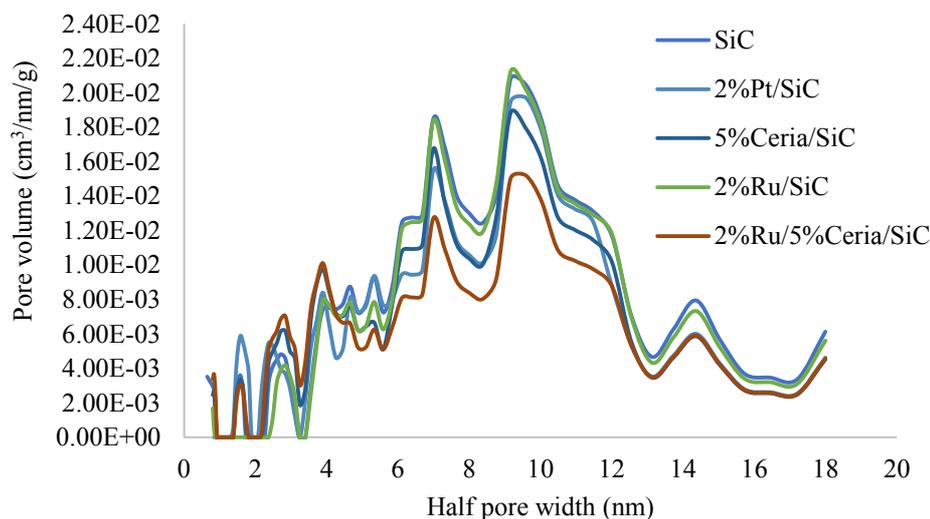


Figure 4.6 The pore size distribution of SiC catalysts

The effect of adding an active component on alumina was obvious due to the significant change in pore volume between 1 and 5 nm. However, it is difficult to highlight which active component had the biggest effect on porosity as the differences are very small. This is also the case for the SiC catalysts.

4.1.4.5. Transmission electron microscopy (TEM)

TEM was used to visually analyse the catalyst surfaces. Information such as the particle shape, size and distribution could be obtained from the images produced by the instrument.

Below are images of the platinum catalysts.

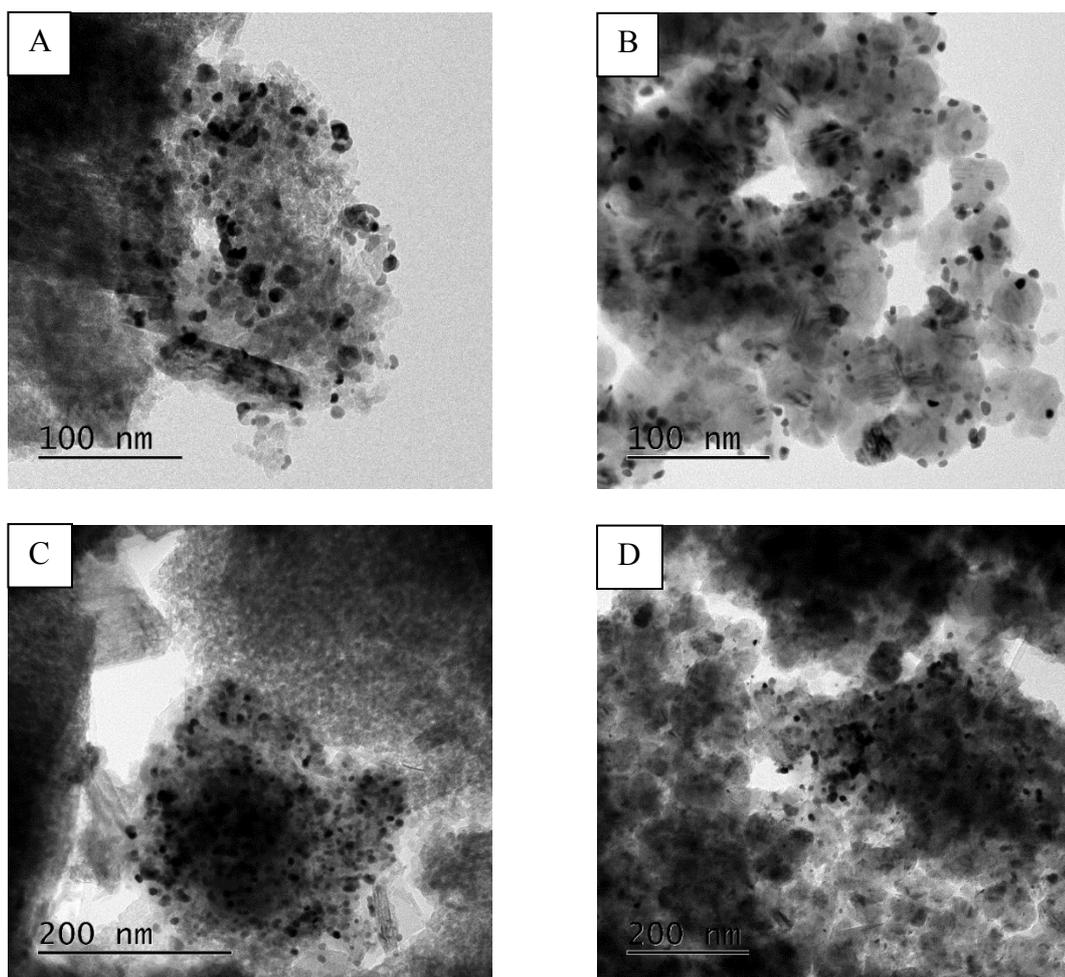


Figure 4.7 TEM images of the various platinum catalysts. A) 2%Pt/Alumina, B) 2%Pt/SiC, C) 2%Pt/5%Cerium/Alumina, D) 2%Pt/5%Cerium/SiC

The dark patches on the images relate to the active components sitting on the support. Without the recognisable features of each type of support, it would be difficult to distinguish between the catalysts. The active components also appear to be very similar

in terms of particle size. This means that they will not be responsible for any differences seen in catalyst activity.

Although the active components appear to be similar in terms of shape, size and distribution, there are differences between the supports. The SiC is made up of relatively large, inconsistently shaped particles; whereas the alumina seems to have smaller and more closely packed particles. This observation can be explained by the porosity data. The alumina's pores were more consistent compared to SiC as the majority of the volume resided between 1 and 5 nm pore width. The SiC on the other hand had significantly less pore volume distributed over a wider range of pore widths.

In support of these findings, *ImageJ*[®] software was used to measure the average diameter of the particles in the images. The table below shows the mean particle size along with the standard deviation for each catalyst.

Table 4.2 Particle size information about the platinum-type catalysts

Catalyst	Active component's particle size (nm)	
	Mean	Standard deviation
2%Pt/Alumina	8.115	4.563
2%Pt/SiC	7.729	4.098
2%Pt/5%Ceia/Alumina	7.910	2.869
2%Pt/5%Ceia/SiC	8.055	3.969

The table shows that the active component particle size was very similar for each catalyst, confirming previous observations. The average diameters ranged from 7.7 nm for 2%Pt/SiC to 8.1 nm for 2%Pt/Alumina which means that support did not have a

significant effect on particle size. This suggests that the impregnation method was adequate enough for producing a catalyst with consistently sized particles.

These particle sizes could explain why the pore blocking effect was seen during the pore size distribution study of alumina. A large proportion of the pores resided between 1 and 5 nm pore widths which is almost the same as the average particle size. This means that any particles between 1 and 5 nm were likely to affect the pore volume.

The standard deviations were also calculated for each sample. They ranged between 3 and 5 nm, indicating that there were some variations in sizes. In some cases, particles could be as small as 1 nm or as large as 20 nm in diameter. These results, however, showed that the incipient wetness technique produced catalysts with quite consistent active component particle sizes.

4.1.4.6. Energy dispersive X-ray spectroscopy (EDX)

It was very difficult to distinguish between platinum and ceria from the electron images above because they both show up as dark spots on the supports. EDX was therefore used to determine the elemental makeup of the catalysts and highlight where they were positioned on the surface. The software translated this information by highlighting the elements in different colour. The first EDX images were of the 2%Pt/Alumina catalyst.

4.1.4.6.1 2%Pt/Alumina

The elements in this catalyst consisted of platinum, aluminium and oxygen. The majority of the oxygen was bonded to aluminium whereas the minority was bound to platinum. The alumina's elements are very evenly distributed but the platinum, on the other hand, showed areas of uneven distribution. This is evident in the image below as

there appears to be a couple of clusters of platinum in places. Apart from these clusters, however, the platinum does appear to be evenly distributed.

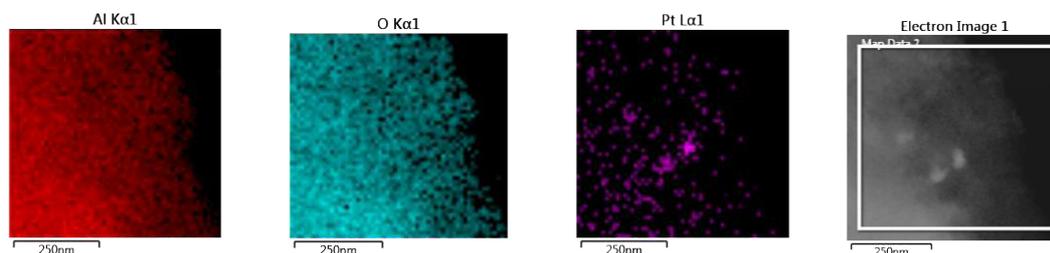


Figure 4.8 EDX images of 2%Pt/Alumina

4.1.4.6.2 2%Pt/SiC

The next catalyst analysed was the 2%Pt/SiC system. Here, Si and C were observed as well as the Pt and O elements. These images showed good distribution of all the elements. It is worth noting that some of the carbon and oxygen elements were detected from the background sample holder also. It can be seen from both the oxygen and platinum images that not all the O atoms are associated with platinum. This could be down to oxygen being accounted as SiO₂ amongst the SiC support²¹.

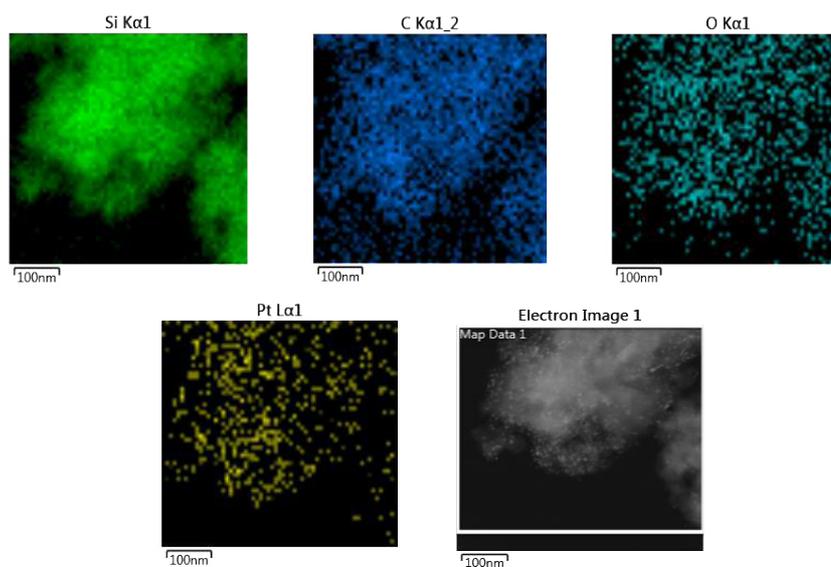


Figure 4.9 EDX images of 2%Pt/SiC

4.1.4.6.3 2%Pt/5%Cerium/Alumina

2%Pt/5%Cerium/Alumina also showed good elemental distribution. However, there were some clusters of Pt and ceria in places. The oxygen atoms are distributed all over the catalyst and can be attributed to alumina, platinum and ceria.

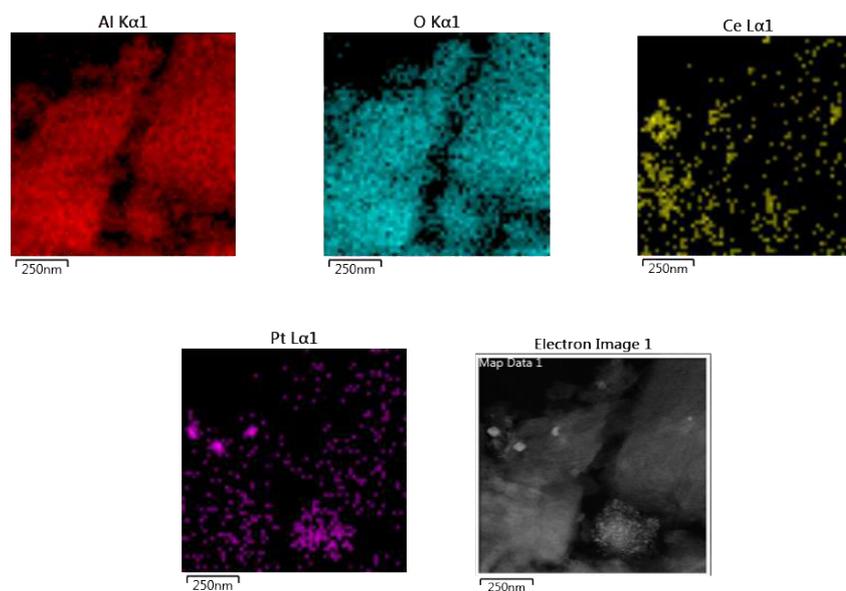


Figure 4.10 EDX images of 2%Pt/5%Cerium/Alumina

4.1.4.6.4 2%Pt/5%Cerium/SiC

The 2%Pt/5%Cerium/SiC was the final catalyst to be analysed. Along with the observation that the elements are evenly distributed, oxygen atoms show up again in places where platinum and ceria were not. This shows that SiC can contain oxygenated species.

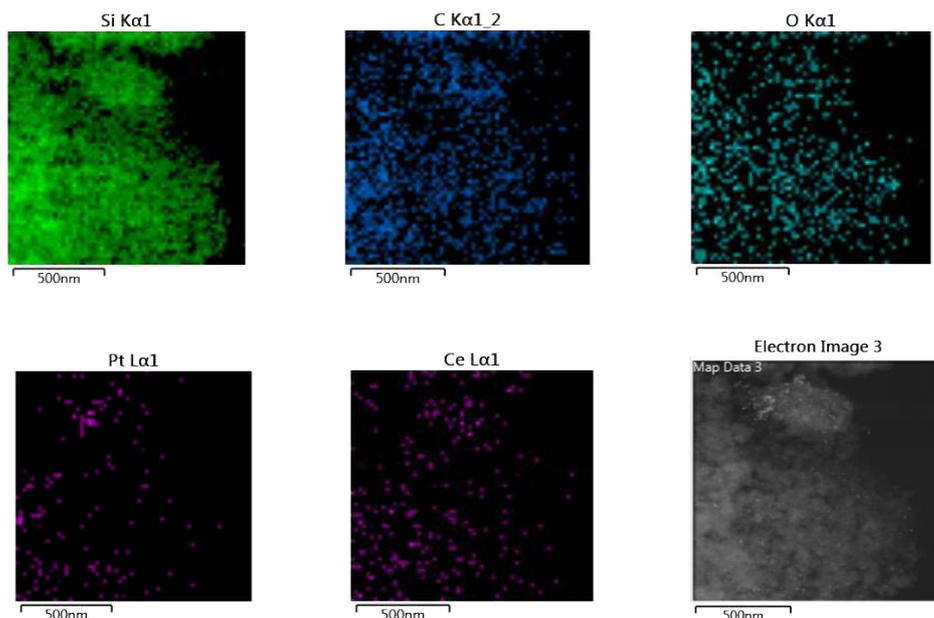


Figure 4.11 EDX images of 2%Pt/5%Ceia/SiC

Apart from the odd cluster, all the images showed good element distribution. However, these are only snapshots of one area of the surface and may not be a true representation of the elemental map. With this being said, the active component particle size, shape and distribution have been fairly even for each catalyst and it can be said that keeping the impregnation and preparation consistent could have contributed to this.

Presented in the table below are the elemental weight percentages for all the components. They were quantified using the same EDX elemental mapping technique. It needs to be taken into consideration that the values represent the percentage composition of one specific area and not the whole catalyst. These are therefore an estimation of what the catalyst may contain overall.

Table 4.3 EDX element weight percentages

Catalyst	weight% Active component					
	Pt	Ce	O	Al	Si	C
2%Pt/Alumina	2.20	0.00	49.78	48.02	0.00	0.00
2%Pt/SiC*	2.67	0.00	0.00	0.00	58.18	39.16
2%Pt/5%Cerium/Alumina	2.76	3.03	43.48	50.73	0.00	0.00
2%Pt/5%Cerium/SiC	1.68	3.1	8.78	0.00	51.11	35.34

*oxygen has not been taken into account

The platinum content varied from 1.68% to 2.76%. This could have been down to differences between the types of areas selected for the EDX analysis. The same could be said for the ceria as the value should be closer to 5% not 3%. This can be rectified by analysing multiple areas of the catalyst, not just one.

Most of the oxygen came from alumina as 2%Pt/5%Cerium/Alumina contributed 43.84% compared to only 8.78% from 2%Pt/5%Cerium/SiC. Theoretically, the Pt/Ce system would be 7% of the total weight which would mean that their associated oxygen components (PtO_2 or Ce_2O_3) would be less than 1%. For the Pt/Ce/SiC catalyst, the oxygen content was 8.78% which meant that the majority of it was associated with the SiC support.

4.1.5. Conclusion

This section showed how the catalysts were prepared and characterised for the CWAO of phenol. The preparation method consisted of an incipient wetness impregnation followed by drying and calcination. Characterisation, on the other hand, consisted of a number of bulk and surface sensitive techniques to chemically and physically interoperate structure and composition. This information was then used to explain the catalytic behaviours seen in the next section.

4.2. Catalytic activity studies and correlation with structure

4.2.1. Introduction

In this section the process of screening was used to identify the most appropriate catalysts for the low temperature, continuous flow, CWAO of phenol. Many catalysts were tested, including ones of various support types and active metals. The conditions were kept as consistent as possible and were based on the ones listed in chapter 2, unless stated otherwise.

4.2.2. Carbon based catalysts

The first set of catalysts tested were of the carbon type. Carbon was used due to it being a cheap material to manufacture and therefore lowers the cost of running the CWAO system²². The different carbon catalysts used were in the form of an extrudate pellet; one being an activated carbon and the other, 2%Ru/Carbon. Below is a graph representing the phenol conversion percentage as a function of time for both catalysts: -

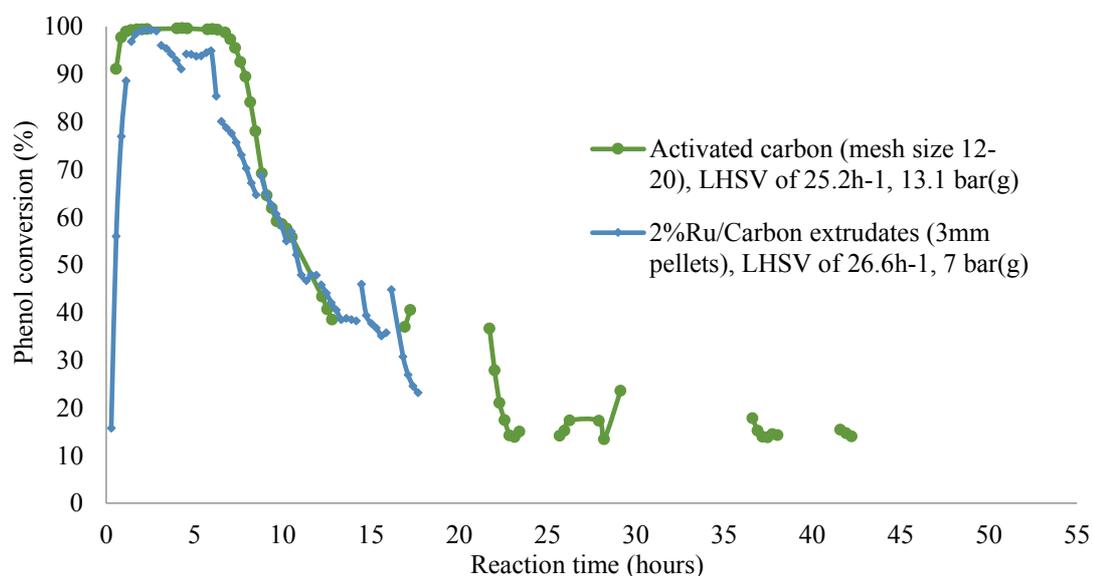


Figure 4.12 Phenol conversion profiles of carbon catalysts at 160°C

For the initial hour, the phenol conversion increased sharply until the maximum 100% was met. The next few hours remain unchanged for the activated carbon, indicating that all the phenol has been removed. This observation was short-lived as both showed a relatively fast drop in conversion later on. The 2%Ru/Carbon was the one to act first. The gaps in the profiles represent the shutdown period at the end of the day before restarting the reactor the next morning. Although the 2%Ru/Carbon was not tested past 18 hours, it followed the same trend as the activated carbon catalyst. This catalyst finally stabilises just before 25 hours and remains relatively stable for the rest of the test. It can be said that these catalysts have very similar profiles and therefore could have similar reaction mechanisms due to both having a type of carbon as its base support.

It could be said that the catalysts went through a phase of high activity towards phenol oxidation before deactivating sharply over the next few hours. If this was the case, catalyst deactivation should have continued until zero conversion. The true catalytic activity was at 15% as this is where conversion stabilised for the activated carbon. The 2%Ru/Carbon catalyst may have stabilised around this value too if it was tested for long enough. It is thought therefore, that these carbon catalysts adsorb the phenol strongly during the initial few hours until it has all been removed from the water. Once adsorption reaches an equilibrium with desorption, catalyst saturation causes the excess phenol to appear in the effluent again. This meant that a large proportion of the phenol was only adsorbed and not oxidised. The true activation is only observed when the profile reaches that stable 15%.

To see if this adsorption effect was the case, pure HPLC water was fed through a 1%Pt/Carbon catalyst after it had been tested for phenol conversion at various temperatures below 100°C. The water, in theory, would wash out any phenol residing

within the pores of the 1%Pt/Carbon catalyst after the regular test had taken place. This is shown in the two graphs below: -

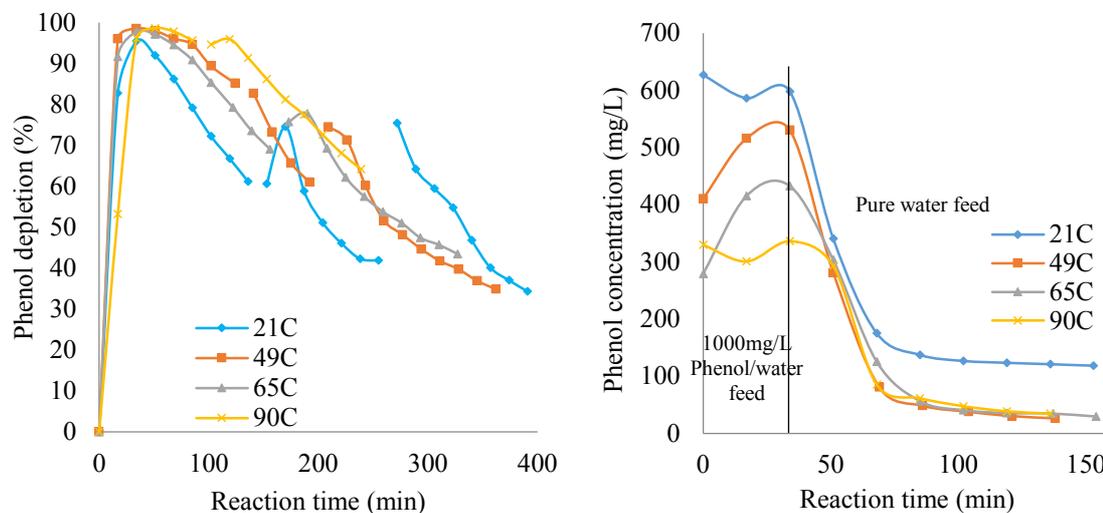


Figure 4.13 The adsorption and desorption of phenol in a 1%Pt/Carbon catalyst system ($C=^{\circ}C$)

A similar effect was seen on the graph on the left to what was seen for the activated carbon and 2%Ru/Carbon catalysts; a sharp increase in conversion before a gradual decrease over time. It is highly unlikely that any oxidation occurred because 100% conversion was reached at room temperature even. To see if any unreacted phenol resided within the pores of the carbon, pure water was fed through and the effluent analysed by the HPLC instrument. This is represented by the graph on the right. If there were no phenol molecules adsorbed on the catalyst surface the water would elute with no trace of it being present. As expected, there was a sharp drop in phenol concentration as it was diluted by the water. However, once stabilised, traces of phenol could be seen for a further hour after the water was fed through. It seems also that the cooler temperature of 21°C makes it more difficult for the water to remove the phenol from the catalysts pores. Once the temperature reaches 49°C or above the rate of phenol removal seems to be almost identical for each one. This therefore confirms that phenol can get adsorbed

rather than oxidised. Only after the adsorption-desorption equilibrium has been reached does the true activity show for these carbon supported catalysts.

There are many publications in the literature that support this notion of phenol adsorption by a carbon catalyst. Bingzheng *et al.* reported that the uptake of phenol could be separated into three stages: rapid adsorption, slow adsorption and equilibrium²³. These three stages can be seen for the carbon catalysts tested for this project. Rapid adsorption was observed initially, followed quickly by a long period of slow adsorption and finally an equilibrium phase of adsorption-desorption where the maximum uptake capacity of the catalyst was reached. From this, any excess phenol in the system eluted out of the reactor due to catalyst saturation. The same publication also reported that incorporating an active metal (iron) reduced the adsorption effect slightly. This was put down to the reason that incorporating a dopant lowered the number of adsorption sites on the surface. This effect was also seen when ruthenium was impregnated onto activated carbon in this study. The 2%Ru/Carbon catalyst, in comparison to the non-doped equivalent, reached the saturation point much sooner. This indicates that ruthenium decreased the number of adsorption sites like what iron did in the study carried out by Bingzheng *et al.* above.

Depending on how active the type of carbon catalyst is, in almost every case, there will be an adsorption phase followed by an oxidation phase. This effect has been reported many times in the literature^{24–26}.

Using a carbon based catalyst would be very useful if phenol adsorption was the aim. As the priority was phenol oxidation, the catalyst screening process was steered away from carbon type catalysts. The non-carbon catalysts performed much better in terms of oxidation and did not show any strong adsorption effects that complicated results

interpretation. However, carbon does have potential in the application of CWAO if adsorption is the rate limiting step.

4.2.3. Active catalysts in the form of pellets

Pellets were chosen for a couple of reasons: they limit pressure drop in the reactor, they reflect the type of catalyst that might be used on a larger scale and they are commonly produced as pellets by manufacturers. The pellets were supplied by Johnson Matthey® and were further manipulated to incorporate the active components.

The graph below shows the phenol conversion profiles of various pellet type catalysts. They consist of 2%Pt/Alumina, 2%Pt/5%Cerium/Alumina and 2%Pt/5%Cerium/SiC. The reactor was operated at similar conditions to what was used for the carbon type catalysts.

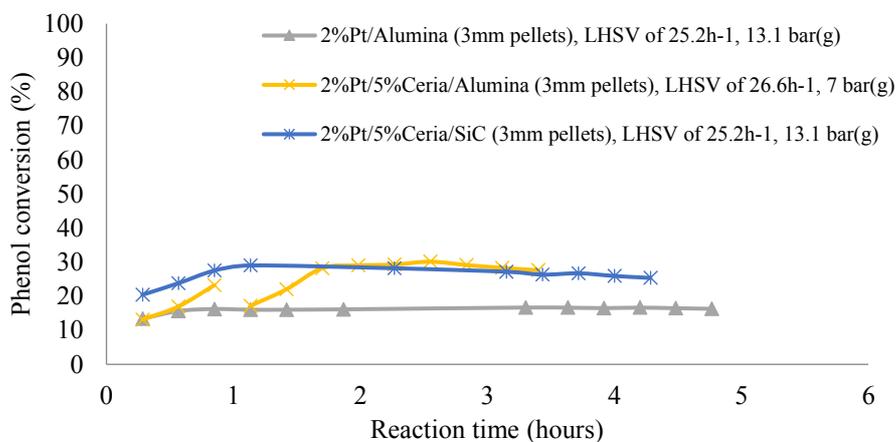


Figure 4.14 Phenol conversion profiles of various pellet-type catalysts at 160°C

The main difference between the profiles is that there is no strong adsorption observed like what there was for the carbon type catalysts. Carbon adsorbed phenol strongly in the initial stages of the reaction before stabilising after saturation. The pellet catalysts above show no adsorption phase and the conversion profiles are stable from almost the beginning. This suggests that carbon is either a lot more porous than the pellets

or has a much stronger physical affinity towards the phenol. The activities, on the other hand, are relatively at the same level. This is why non-adsorbent supports were investigated further.

The best performers were the catalysts with ceria incorporated alongside platinum on alumina and SiC, which achieved conversion percentages of 25-30%. In order to compare these two supports further, various compositions of platinum and ceria on alumina and SiC were investigated. The ruthenium catalysts were investigated in more detail later in the study.

Figure 4.15 below compares the various platinum and ceria incorporated alumina and SiC catalysts in terms of their average phenol conversion levels after stabilisation.

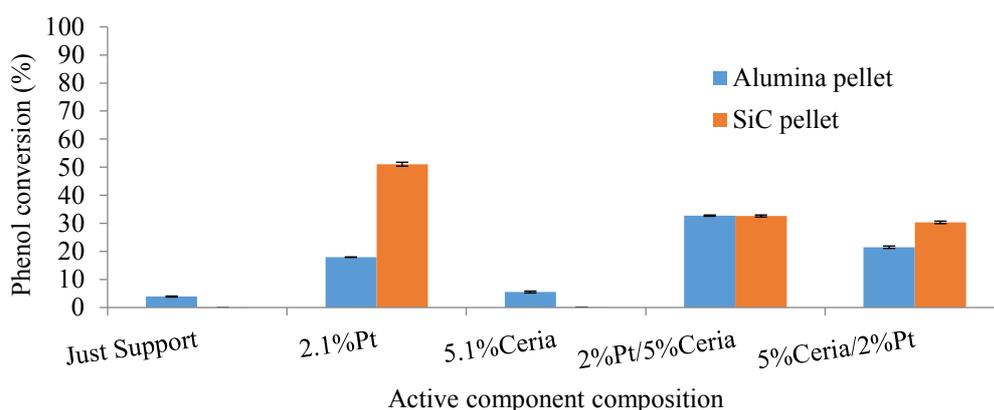


Figure 4.15 Average phenol conversions over various platinum incorporated catalyst pellets at 140°C

Operating with just the support provides little or no aid for the oxidation of phenol. Whilst SiC on its own shows no activity at all, alumina does promote some conversion. This could be down to alumina having more readily available oxygen atoms on its surface compared to SiC to promote oxidation. Another reason could be down to the acidic/basic nature of the alumina's surface influencing the affinity towards phenol, which in turn would influence the contact time to allow for oxidation. Figoli *et al.* showed that the

acidic-basic regions of the alumina get covered by phenol when it was flowed through the material²⁷. Phenol is acidic and therefore would attack the basic bridged oxygen sites of alumina. As a consequence, phenol's oxygen atom would be in close enough proximity to associate with the acidic aluminium centres and promote further affinity. SiC on the other hand is known not to being susceptible to any acid or alkali attacks²⁸.

Incorporating platinum to the catalyst increases its activity significantly, especially for the SiC supported type. In most cases, adding a precious metal such as platinum to a catalytic system will boost activity, especially with regards to catalytic oxidation²⁹. The platinum metal is able to activate adsorbed oxygen from the atmosphere which would then be available to oxidise the target phenol molecule³⁰. Characterisation studies suggested that the platinum was mostly metallic and therefore explains why there was such an increase in activity shown in the figure above.

Incorporating the platinum on the SiC support increased the activity a lot more than what it did when impregnated on alumina. This was believed to be down to the more hydrophobic nature of SiC compared to alumina. Its hydrophobicity decreases the phenol solution's wetting ability which, in turn, allows the metallic platinum to activate atmospheric oxygen more efficiently. Hydrophilic catalysts, on the other hand, get wetted more easily and therefore hinder the oxygen-metal transfer process. This effect was investigated in more detail in the next chapter.

Having ceria as the only active component, on the other hand, only produced better activity when it was incorporated onto alumina. However, the conversion values were a lot lower in comparison to using 2%Pt/Alumina. This shows that ceria is only active when the support is more hydrophilic and suggests that the catalyst needs to be wetted in order to promote oxidation. Ceria is well known for its oxygen storage capacity

and therefore is able to promote oxidation without relying too much on atmospheric oxygen activation³¹. SiC, on the other hand, does not allow for sufficient wetting and as a consequence inhibits ceria's ability to promote oxidation. This explains its inactivity in the graph above.

Impregnating Pt and ceria, in whichever order, on SiC did not promote phenol oxidation as much as it did when just Pt was present. This could have been down to ceria impeding the Pt active sites to promote oxygen activation under hydrophobic conditions. With regards to alumina on the other hand, the activities have increased. This can be explained by the reason that incorporating ceria enhances oxygen availability for oxidation under hydrophilic conditions.

The figure below shows their conversion profiles as a function of temperature. The SiC catalyst was a lot more active compared to alumina at lower temperatures, but eventually become nearly equal at higher temperatures. This suggested that the alumina catalyst was affected a lot more by temperature increases.

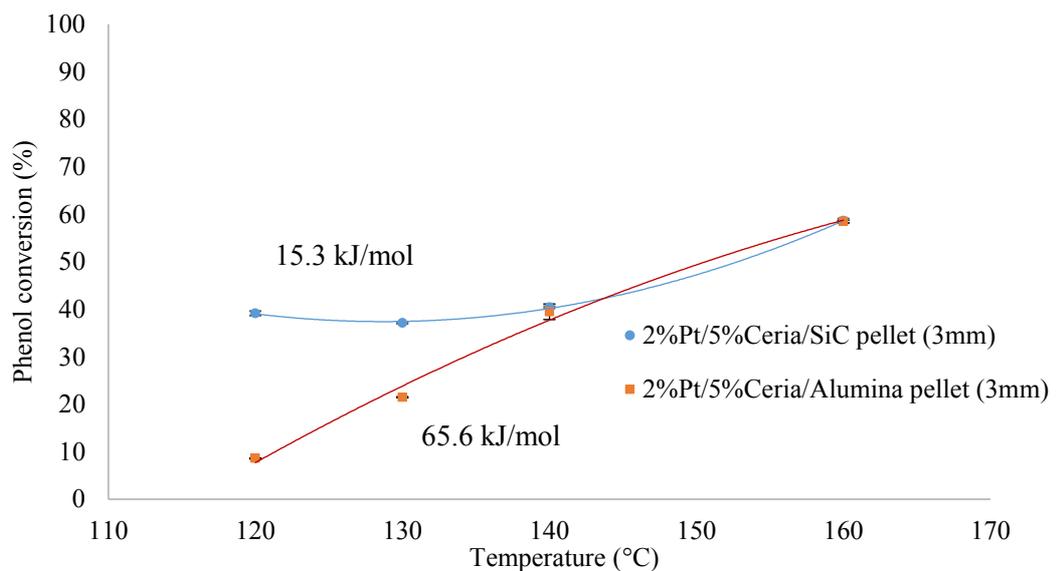


Figure 4.16 Phenol conversion profiles of Pt and Ceria on Alumina and SiC with a function of temperature

It was shown previously that alumina hindered metallic Pt from activating atmospheric oxygen due to catalyst wetting issues. It is believed therefore, that this effect becomes less significant as the temperature increases.

The SiC catalyst was affected less by the temperature increase. The Pt has already better access to the atmospheric oxygen at lower temperatures compared to when it was on alumina. As oxygen is in excess, increasing the temperature further did not affect conversion significantly.

The results so far have been based on pellet catalysts. It was important therefore to investigate how different pellet sizes affected phenol-catalyst mass transfer. It was discussed in the introduction that an optimum pellet size would maximise contact efficiency whilst minimising pressure drop effects. The direction of the study went towards lowering the pellet size enough so that mass transfer was at its optimum.

4.2.4. Active catalysts in the form of granules

To achieve the optimum pellet size, the supports were first crushed, sieved (to 0.425mm – 0.6mm) and later impregnated with the same active components used previously³².

4.2.4.1. Platinum catalysts

The following catalysts were based on platinum and ceria incorporated onto alumina and SiC supports. The graph shows their phenol conversion profiles as a function of time.

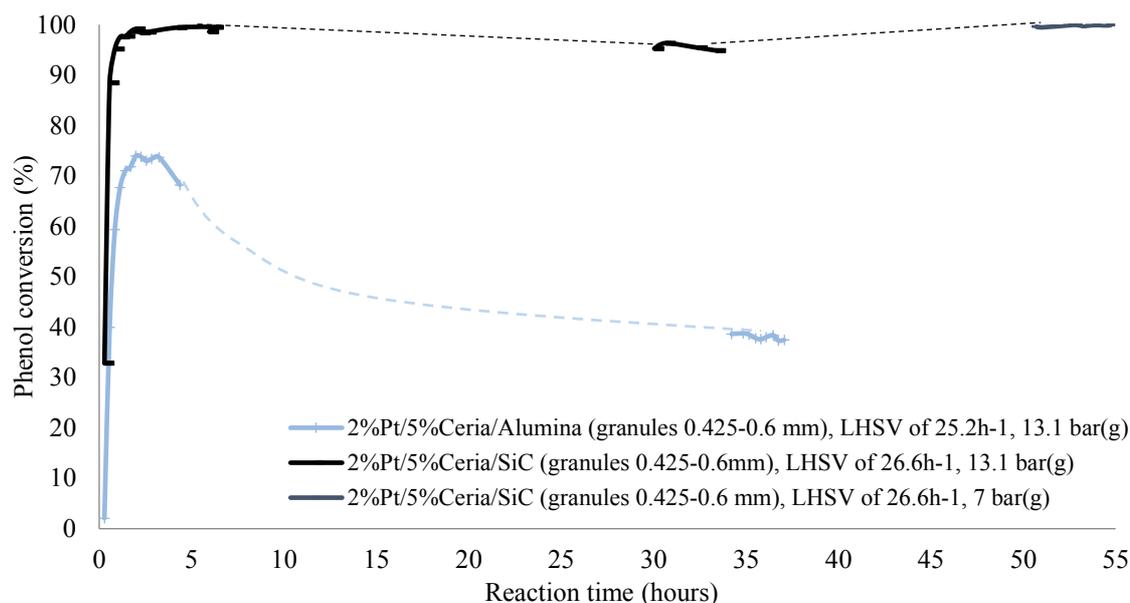


Figure 4.17 Phenol conversion profiles of granule catalysts at 160°C

It is clear that these granules out-performed the pellets greatly. With regards to the alumina catalyst, the activity has increased from 25% for the pellet to just above 70% as a granule. After 35 hours of testing this particular catalyst, phenol conversion dropped by 30%, indicating that there is some form of deactivation occurring. Deactivation could not be down to leaching as atomic emission spectroscopy confirmed otherwise. Roy *et al.* reported that deactivation could occur as a result of platinum metal over-oxidation or by coke deposition over time³³. TGA analysis showed the 2%Pt/5%Cerium/Alumina catalyst reducing in mass as a function of temperature. This led to the belief that there were carbon impurities deposited on the surface causing deactivation.

The SiC equivalent's activity, on the other hand, increased from 25% conversion for the pellet to 100% for the granule. Even after 55 hours' worth of testing the level of activity remained high and the catalyst was able to oxidise almost all of the phenol. Both of these catalysts had selectivity of above 95% towards total oxidation with the remaining 5% being selective towards partial oxidation products. These were the quinones and

organic acids highlighted previously. The catalyst also showed little or no signs of deactivation, but this cannot be confirmed as a conversion of 100% can give a false representation of true activity. The TGA analysis, on the other hand, did show some weight loss and indicated that some coke formation had occurred. However, it seems that the scale of deactivation was a lot less for the SiC catalyst in comparison to its alumina equivalent.

Of what has been shown thus far, it is clear that SiC has been the best support for the various catalysts tested. It manages to promote phenol conversion at double the amount the alumina catalysts could achieve, even after nearly 40 hours of testing. Decreasing the pellet size therefore has amplified the hydrophobicity effect.

Decreasing the pellet size also optimises mass transfer. It allows for better packing within the reactor and as a consequence, increases the phenol-catalyst contact time. A larger pellet causes inefficient packing and may result in some of the phenol escaping without sufficient contact time. Stüber *et al.* measured phenol conversion as a function of catalyst pellet size³². It showed that the pellets needed to be small enough to provide the best phenol-catalyst contact efficiency but large enough to avoid pressure drop issues.

The figure below compares the two types of pellets used for all the platinum and ceria incorporated alumina and SiC catalysts.

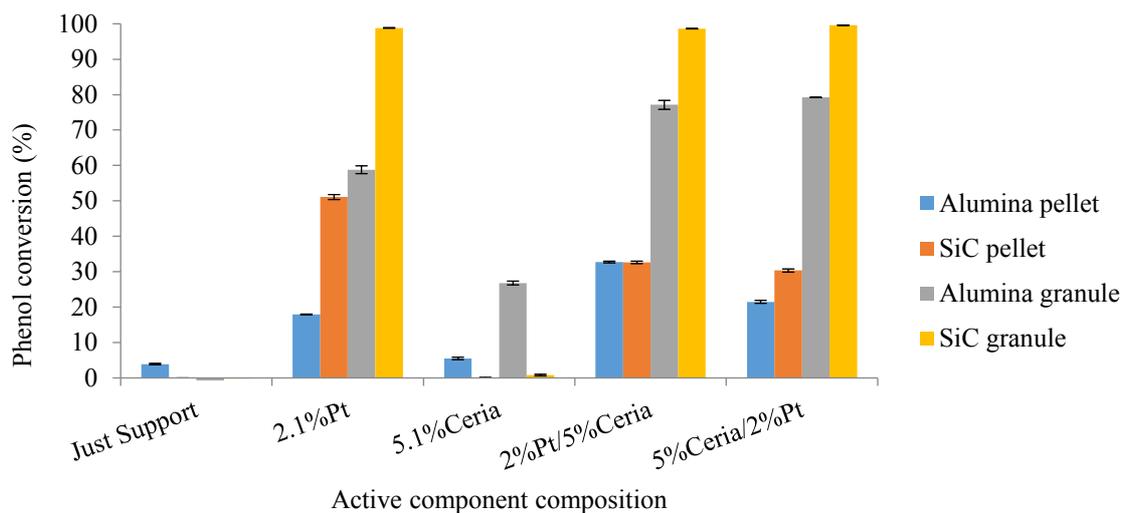


Figure 4.18 Average phenol conversions over various platinum and ceria incorporated catalyst at 140°C

As expected, the granule catalysts perform much better than the larger pellets. The graph also shows how active the SiC catalysts are compared to the alumina. The 2%Pt/SiC granule alone has managed to aid nearly 100% phenol conversion. The same effect was seen for both pellet and granule when just ceria was incorporated on the support. The best result came from alumina being the support, as ceria prefers the catalyst to be wetted in order to promote oxidation. SiC does not offer sufficient wetting for phenol to come into contact with the ceria to allow for oxidation to occur. Pt on SiC, on the other hand, allows for atmospheric oxygen to be activated as the more hydrophobic conditions are favoured.

It was explained previously that a catalyst's true maximum activity cannot be measured if conversion reaches 100%. The catalyst may have extra capacity which cannot be expressed. This was seen for three of the Pt-SiC catalysts: 2%Pt/SiC, 2%Pt/5%Cerria/SiC and 5%Cerria/2%Pt/SiC. In order to identify which catalyst promoted the best conversion, the temperature was reduced to 120°C: -

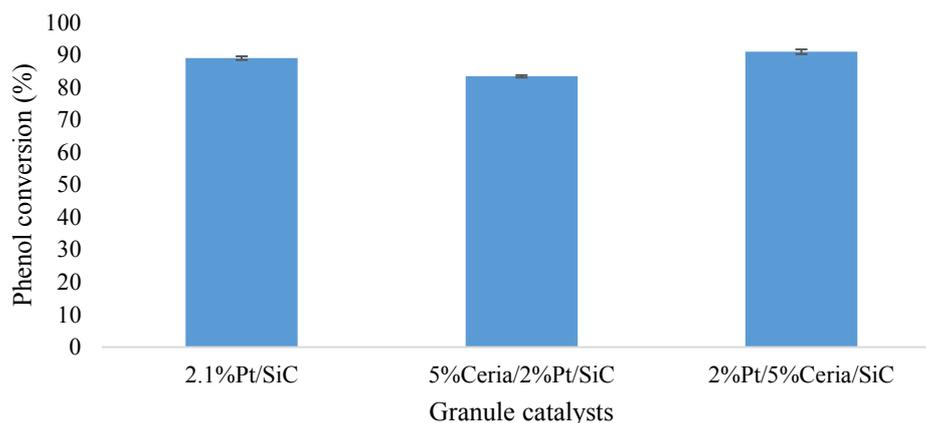


Figure 4.19 Average phenol conversions over various platinum and ceria incorporated catalyst at 120°C

Even at 120°C the activities remained relatively high with all three managing to promote over 80% phenol conversion. It is now appropriate to compare the catalysts as their true potentials have been shown. The 2%Pt/SiC promoted an average phenol conversion of 89%, whilst the ceria incorporated version (2%Pt/5%Cerium/SiC) promoted 91%. With only a difference of 2%, incorporating ceria did not increase the activity significantly. This shows that ceria does not provide much benefit when incorporated onto SiC catalysts. The ceria needs to be wetted in order to activate phenol, whereas the Pt does not. The oxidation pathway using platinum as the active component relied on a two stage process: the activation of atmospheric oxygen followed by oxidation of phenol.

These granule catalysts were further tested to see what effect temperature, space velocity, pressure and initial phenol concentration had on the reaction. These studies were able to show what conditions were required in order to promote the best phenol conversion.

4.2.4.2. Temperature

The first variable investigated was the operating temperature: -

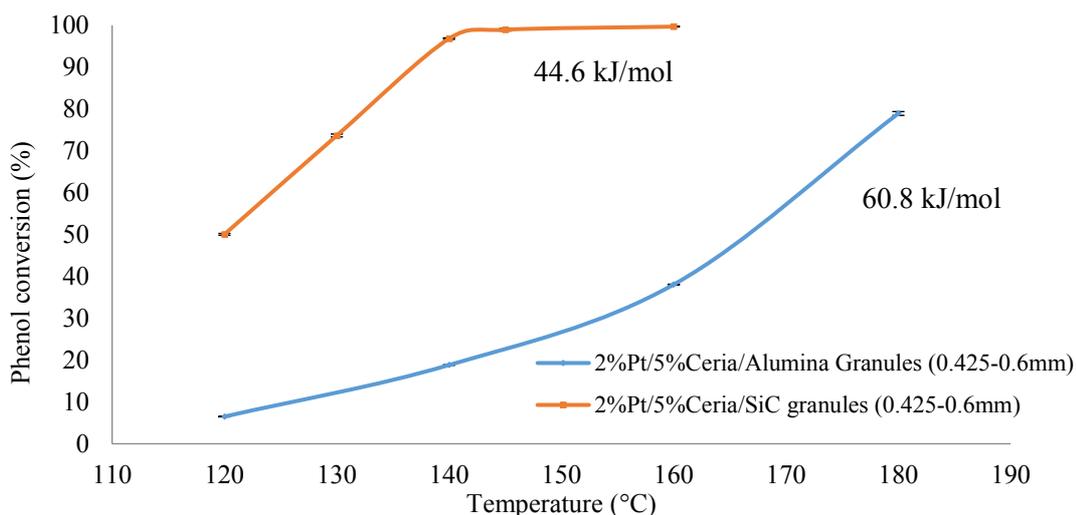


Figure 4.20 Phenol conversion profiles of Pt and ceria on alumina and SiC catalysts as a function of temperature

Both profiles show an increase in conversion as a function of temperature. Increasing the temperature increases the reaction kinetic energy which, in turn, increases the rate at which phenol is oxidised. Unlike the pellet profiles, the granules show a much bigger difference in conversion. It follows the same trend though, in the sense that the SiC catalyst has a lower activation barrier compared to alumina.

The activation energies for the alumina catalysts did not change significantly going from pellet to granule. Although it has come down marginally due to better mass transfer effects. The SiC catalyst, on the other hand, had a lower activation energy of 44.6 kJ/mol. The platinum required the support to be hydrophobic in order to promote the best possible oxidation; whereas the hydrophilic alumina slows this activation process down.

4.2.4.3. Liquid Hourly Space velocity (LHSV)

The next parameter investigated was the liquid hourly space velocity (LHSV). This investigates how changing the flow rates and catalyst volumes can affect phenol conversion. Below is a graph representing the results:-

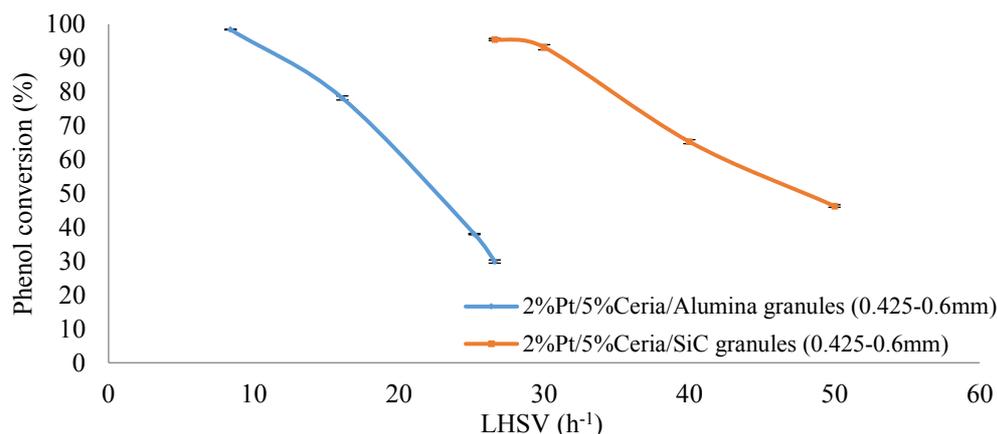


Figure 4.21 Phenol conversion as a function of LHSV over Pt and Ceria supported by alumina and SiC granules (160°C)

The figure above clearly indicates that the SiC is, again, the outperformer. At a space velocity of 25-30 h⁻¹ the alumina catalyst only promoted 30% conversion whilst the SiC catalyst promoted nearly 100% removal. At flow rates that represented 50 h⁻¹, the SiC catalyst could still achieve activity of over 45% conversion.

At high flow rates, or low catalyst volumes (to give a low LHSV), the alumina seems to cope less with the increased load. At higher loadings, the catalyst saturates quicker, meaning phenol oxidation turn-over becomes more difficult. This effect was amplified for the alumina catalyst, as faster wetting inhibits oxygen activation even further. This did not affect the hydrophobic SiC catalyst as much.

4.2.4.4. Pressure

As well as the temperature and space velocity, the effect of pressure was also investigated. On the left, below, is the profile for the 2%Pt/5%Cerium/Alumina catalyst and on the right the 2%Pt/5%Cerium/SiC catalyst.

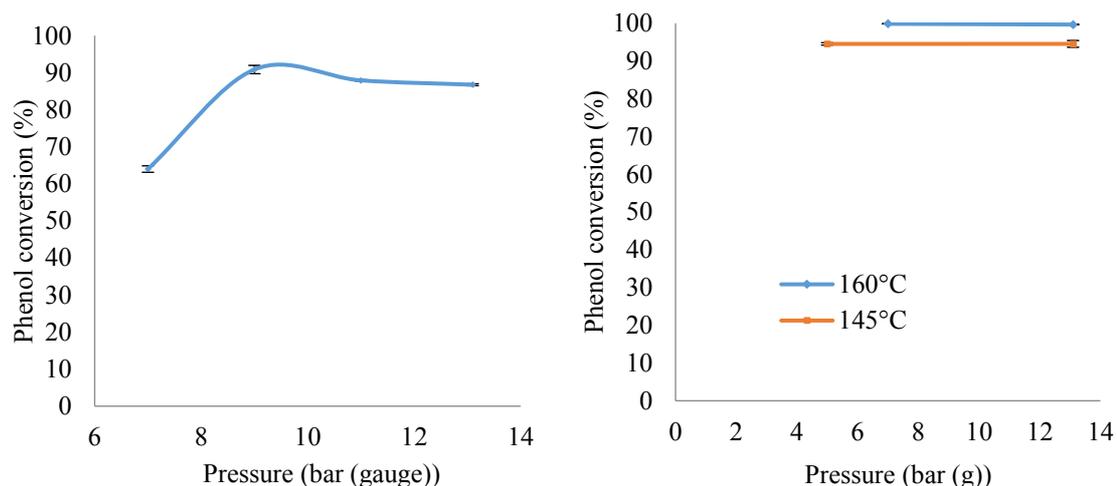


Figure 4.22 The pressure effect on phenol conversion (2%Pt/5%Cerium/Alumina (160°C, 8.4h-1) – left, 2%Pt/5%Cerium/SiC – right)

The alumina catalyst managed to promote conversion from 65% to 90% when the pressure was increased from 7 to 9 bar(g). Increasing the pressure increases the oxygen concentration within the reactor which is essential for an oxidation reaction to occur. Increasing the pressure further did not have an effect on conversion as the oxygen was likely to have passed its saturation point.

With the SiC catalyst, on the other hand, even at pressures as low as 5 Bar(g), the activity remained as consistent as it did at 13 Bar(g). The same was true at 145°C. This shows that oxygen already had good access to the active sites due to the hydrophobic nature of the support. This meant that the catalyst was already saturated and did not require more pressure. The alumina catalyst was subjected to more wetting therefore required an increase in pressure to deliver the oxygen to the active sites.

4.2.4.5. Concentration

Similar to the LHSV the initial concentration of the phenol feed also affects contact time. For this particular investigation, only the alumina supported catalysts were

tested. The graphs below depict the effect concentration had on both conversion and reaction rate.

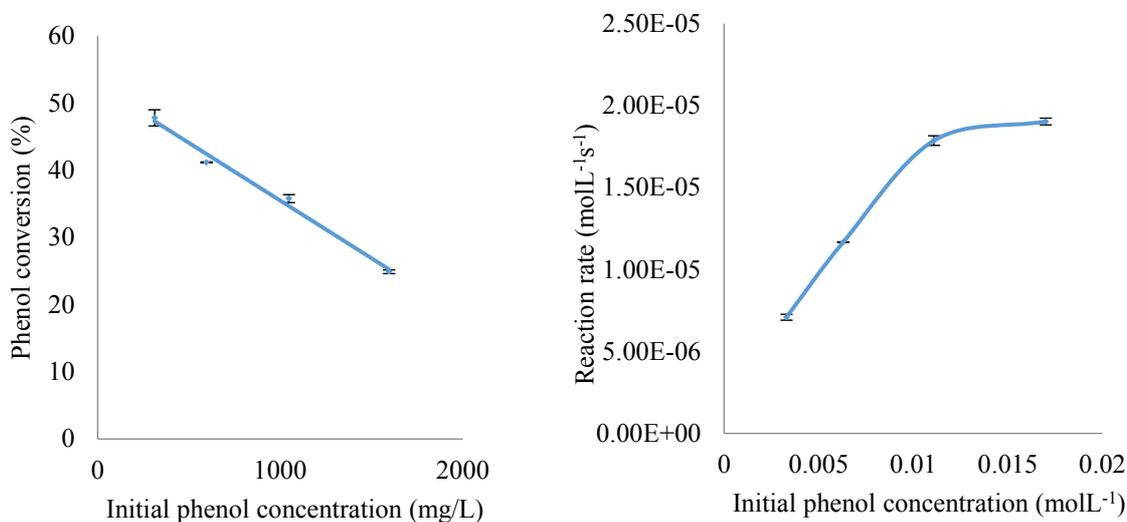


Figure 4.23 The effect of initial phenol feed concentration on conversion and reaction rate (160°C, 16.1 h-1)

Increasing the initial phenol concentration increases the ratio of phenol molecules to the available active sites on the catalyst. This therefore causes the molecules to compete for the remaining active sites. When the concentration gets too high, the number of free active sites diminish rapidly and causes the catalyst to reach its saturation point. This means that some phenol molecules would pass through without being oxidised because the active sites are all taken up. This effect was seen in the graph above when the phenol conversion decreased linearly with an increase in initial phenol concentration.

In terms of rate, the reaction seemed to be pseudo first order initially as the rate increased linearly as a function of concentration. It was pseudo first order because the second reactant, oxygen, was in excess. The reaction rate increased linearly initially as the catalyst had the capacity to take the increase in concentration. However, this increase slowed down past the saturation point and the rate turned into more of a zero order

reaction. This was reflected in the graph above as the curve reached a plateau past the saturation point.

4.2.5. Post-reaction catalyst characterisation

4.2.5.1. Catalyst deactivation

One of the main reasons for carrying out characterisation post-reaction was to determine whether the catalysts changed chemically or physically during testing. Any changes can affect the catalyst activity and durability within the reactor. The two catalysts tested were the 2%Pt/5%Cerium/Alumina and 2%Pt/5%Cerium/SiC. The alumina catalyst showed a significant amount of deactivation during the reaction; whereas the SiC did not. Adsorption effects were ruled out as the deactivation was gradual. The alumina catalyst showed a steady conversion profile for the first few hours but gradually decreased over the remaining 35 hours. The graph below shows the degradation profile of 2%Pt/5%Cerium/Alumina at two different LHSVs.

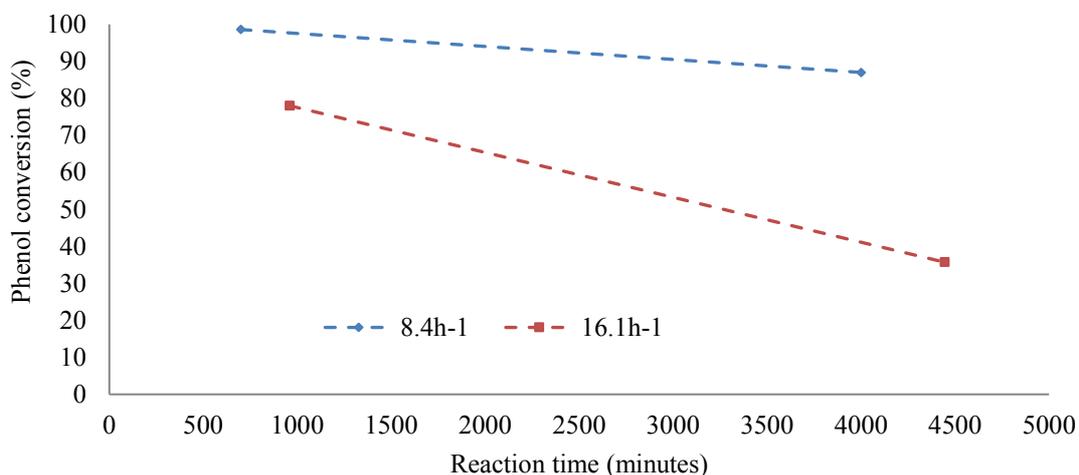


Figure 4.24 2%Pt/5%Cerium/Alumina degradation represented as phenol conversion profiles at two different space velocities

The graph shows a difference between the initial and the ending phenol conversion percentages for both space velocities. The tests were carried out for over 4000 minutes. For the 8.4 h^{-1} space velocity the catalyst degraded by 10% and for 16.1 h^{-1} it degraded by over 40%. There was such a big difference because the flow rate can amplify deactivation. Increasing the flow rate increases the probability of deactivation as the active sites are more likely to be saturated. This means that polymeric carbon formation is more likely to occur on the surface rather than phenol oxidation. At lower flow rates, carbon polymer formation is less likely to occur as the active sites are more accessible for oxidation to occur. Deactivation can also occur from structural changes in the catalysts. It was shown previously that alumina is susceptible to acid attacks. This would also get affected by increases in flow rate. .

The 2%Pt/5%Ceia/SiC catalyst's deactivation, on the other hand, was presented as a function of temperature:-

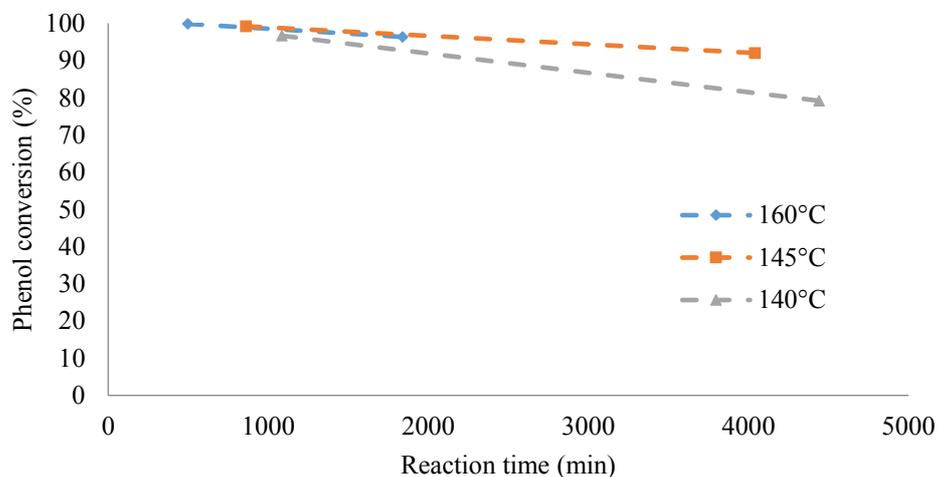


Figure 4.25 2%Pt/5%Ceia/SiC degradation represented as phenol conversion profiles at three different temperatures

It is worth noting that the three tests were carried out using a space velocity of 26.6 h^{-1} . It was clear from this graph that the deactivation was not as severe as it was for

the alumina catalysts and shows how well suited SiC is for the reaction. Even at this high a space velocity and a much lower temperature of 145°C, the SiC catalyst was able to perform just as well as the alumina (the alumina catalyst was tested at 160°C). In this instance the lowest temperature test related to the highest degree of degradation. At lower temperatures, the catalyst is less able to fully regenerate. This allows for carbon to build-up on the surface.

Even though deactivation was observed for the SiC catalyst, it is negligible in comparison to alumina. Deactivation over the alumina catalyst occurred using a space velocity of 16.1 h⁻¹; whereas 26.6 h⁻¹ was required to show the same over the SiC equivalent.

The main cause for deactivation therefore, is thought to be down to carbon build up on the catalyst surface. It could also be down to active components leaching from the catalyst as the phenol solution passes through. This might have occurred as the phenol solution was slightly acidic.

In order to get an idea of what might be causing deactivation, the following two characterisation techniques were used:-

4.2.5.2. Thermo-gravimetric analysis (TGA)

The first technique used to determine why deactivation occurred was thermo-gravimetric analysis. This technique was able to detect whether the catalyst experienced any weight loss as a function of temperature in an oxidative atmosphere. Any carbon impurities present would be oxidised and identified in terms of mass loss.

This technique was only carried out for the 2%Pt/5%Ceia/Alumina catalyst as it showed the highest degree of deactivation. The graph below depicts its mass loss as a function of temperature and also the rate at which the mass was lost (%/minute).

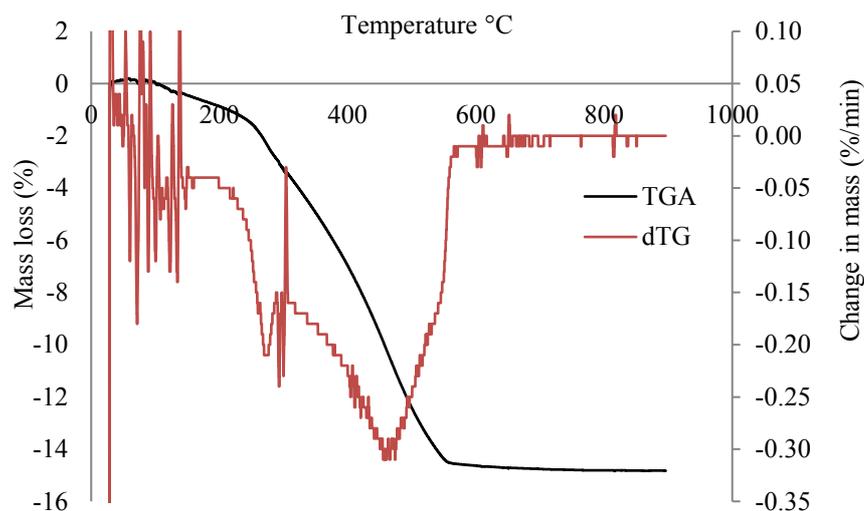


Figure 4.26 TGA profile of the used 2%Pt/5%Cerium/Alumina catalyst

The first bit of weight lost was seen at just above 100°C which was likely to be down to water boiling from the surface. This occurred gradually up until just above 200°C and then rapidly up until just above 500°C. Such a profile was characteristic of carbon groups in the form of carboxylic acids and phenolic compounds oxidising to form CO₂ and CO respectfully³⁴. These substances therefore may have caused deactivation through active site fouling.

Catalyst regeneration may have been possible if carbon deposition was solely responsible for deactivation. This could have been done by running the reactor at high temperature with only flow of air present. To ensure this was the case the catalysts were also tested for leaching using the following technique.

4.2.5.3. Atomic emission spectroscopy (AES)

AES was able to detect whether any leaching had occurred during testing. This may have led to the deactivation profile shown previously.

For this investigation, both 2%Pt/5%Ce/Alumina and 2%Pt/5%Ce/SiC were tested to see if any Pt leaching had occurred. They were also the ones represented in the

deactivation profiles above. In most cases, the biggest contribution to activity came from platinum.

After nearly 60 hours in the reactor, a sample of effluent was gathered in a vial and measured in the AES instrument for platinum. This was carried out after calibrating the platinum at different concentrations.

The table below represents the concentration of platinum in both effluents. The concentration was measured in parts per million (ppm).

Table 4.4 Concentration of platinum leached from the catalysts listed measured by AES

Catalyst	Pt concentration (ppm)
2%Pt/5%Ce/Alumina	0
2%Pt/5%Ce/SiC	0.14

No platinum was found in the solution from the 2%Pt/5%Ce/Alumina reaction, indicating that deactivation occurred as a result of carbon build-up. There was hardly any platinum found in the other catalyst's reaction effluent also, only 0.14 ppm. This indicates that leaching was not a problem and that carbon build-up was the cause for deactivation.

Nousir *et al.* confirms that polymeric carbon species can cause deactivation³⁵. They also stated that adsorption of these polymeric species are more likely to occur on high surface area catalysts. This may explain why the alumina catalyst suffered from deactivation more as it has a much higher surface area compared to SiC. This therefore inhibits phenol oxidation increasingly over time. Having ceria present might slow down the rate of deactivation as it improves oxygen mobility on the catalyst surface.

As carbon formation was the likely cause for deactivation, a regeneration step would have been useful to restore performance. This would have allowed for the impurities to get oxidised from the surface so that the active sites were free again to promote oxidation.

4.2.6. Ruthenium catalysts

A range of ruthenium catalysts were also investigated as part of the catalyst screening process. The figure below contains the average steady-state phenol conversion percentages over 2%Ru/SiC, 2%Ru/Alumina, 2%Ru/5%Cerium/SiC and 2%Ru/5%Cerium/Alumina (all in granule forms).

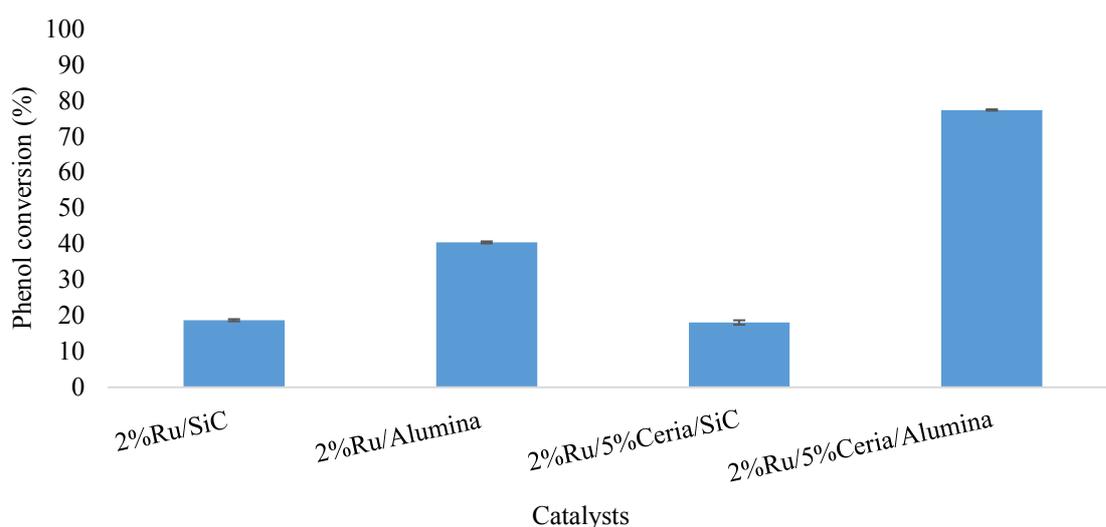


Figure 4.27 Phenol conversion of ruthenium catalysts (140°C)

The initial observation is that the highest phenol conversion value is not as high as some of the values seen for the platinum catalysts. It can be said therefore that the platinum catalysts, depending on the support used, are still the most active for this application.

The interesting outcome from this study, on the other hand, is that the reverse effect was seen in terms of hydrophobicity. In both cases, the alumina catalysts

outperformed the SiC equivalents, going against the effect observed for the platinum catalysts. This reverse effect, though, was seen for the ceria in figure 4.18 and was put down to the active component being a metal oxide and not metallic. The metal oxide does not rely on activating atmospheric oxygen and relies more on direct contact with phenol. This effect was enhanced during wetted conditions which explains why the more hydrophilic catalyst was the most active in this case. The same can be explained therefore for the ruthenium catalysts as the active component is more of an oxide rather than a metal, which means the more hydrophilic alumina catalyst performs better than the SiC equivalent.

From the XRD diffractograms, ruthenium oxide structures were detected and from TPR profiles, strong peaks appeared to indicate that a large bulk of the material was in the oxide form too. There is therefore, strong evidence that a large proportion of the ruthenium is in the oxide form which has been shown in the literature also³⁶.

Incorporating ceria into the catalyst enhances this effect if the support is hydrophilic. This can be seen when comparing the performances of both 2%Ru/Alumina and 2%Ru/5%Cerium/Alumina catalysts. Applying another metal oxide enhances the performance of RuO₂ on the hydrophilic support. There is not much change in activity when comparing the two SiC catalysts as they are more hydrophobic. Adding a metal oxide therefore would not improve performance. The catalyst would perform better if the active component was metallic.

4.2.6.1. Temperature study

A temperature study was also carried out on the ruthenium catalysts. This is shown in the graph below.

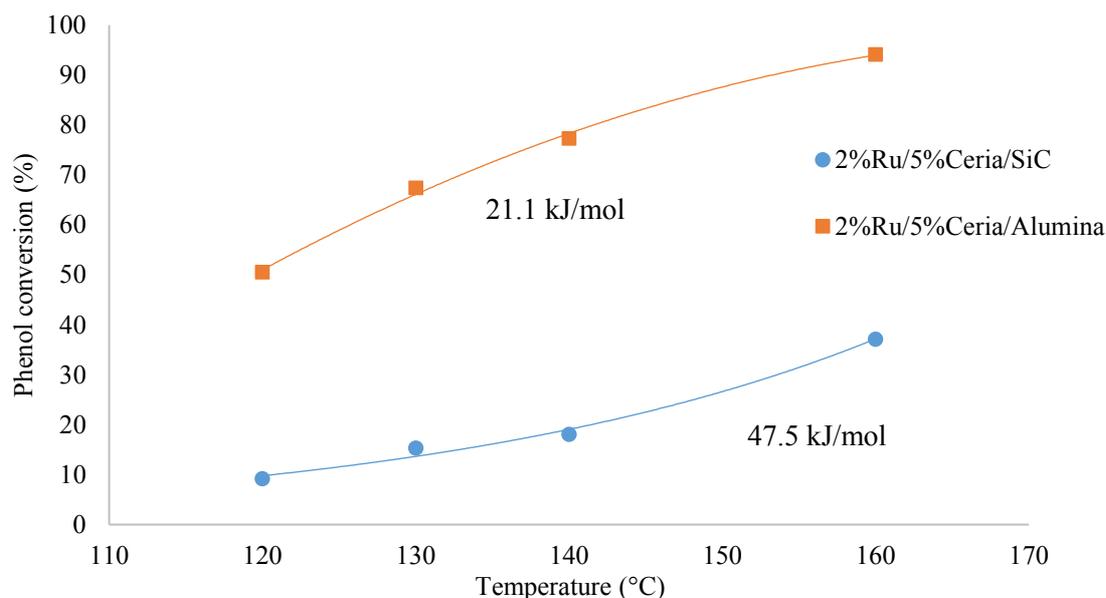


Figure 4.28 The effect of temperature on phenol conversion over ruthenium catalysts

The ruthenium catalysts composed of ruthenium and ceria incorporated on SiC and alumina. As discussed above, the alumina catalysts were more active than the SiC equivalents and the same was reflected in *Figure 4.28* above. As the temperature increased, the phenol conversion increased for both catalysts; more so for the alumina type.

In contrast to what was observed for the platinum catalysts, the activation energy was lower this time for the alumina catalyst. This was the case as the Ru-Alumina system prefers hydrophilic conditions. The metal oxide needs to be wetted in order to promote oxidation. Increasing the contact efficiency therefore, decreases the oxidation activation barrier.

4.2.7. Conclusion

To conclude, the SiC type catalysts, with Pt as the active metal, proved to be more active in terms of phenol conversion compared to the alumina catalyst. It was thought that the platinum needed to be in its metallic form to promote atmospheric oxygen activation.

This effect was enhanced by the hydrophobic nature of the catalyst as the platinum sites become more accessible for oxygen in less wetted conditions.

When the active metal was an oxide (ceria for example), the reverse effect was seen. This reaction depended on the phenol coming in contact with the metal oxide and preferred hydrophilic conditions. The best result was therefore seen when the ceria was impregnated on the more hydrophilic alumina support.

The next catalytic system to be investigated was ruthenium impregnated on both alumina and SiC supports. The best performance came from ruthenium impregnated on alumina. Here, the ruthenium was in its oxide configuration therefore preferred hydrophilic conditions to promote direct oxidation.

To summarise, if the active component was a metal oxide, the more hydrophilic support was preferred; whereas if it was a metal, the more hydrophobic support was preferred. Doping with ceria aided only the catalysts with metal oxides incorporated on a hydrophilic support. However, metallic platinum incorporated on SiC promoted the best activity overall, regardless of the type of catalyst it came up against.

4.3. References

- 1 T. Hyde, *Platin. Met. Rev.*, 2008, **52**, 129–130.
- 2 J. R. McBride, G. W. Graham, C. R. Peters and W. H. Weber, *J. Appl. Phys.*, 1991, **69**, 1596–1604.
- 3 M. L. Dos Santos, R. C. Lima, C. S. Riccardi, R. L. Tranquilin, P. R. Bueno, J. A. Varela and E. Longo, *Mater. Lett.*, 2008, **62**, 4509–4511.
- 4 S. A. Hosseini, *Open J. Phys. Chem.*, 2011, **01**, 23–27.
- 5 F. L. Wang, L. Y. Zhang and Y. F. Zhang, *Nanoscale Res. Lett.*, 2009, **4**, 153–156.

- 6 S. H. Joo, J. Y. Park, J. R. Renzas, D. R. Butcher, W. Huang and G. A. Somorjai, *Nano Lett.*, 2010, **10**, 2709–2713.
- 7 G. Borah and P. Sharma, *Indian J. Chem.*, 2011, **50**, 41–45.
- 8 M. Ramani, B. S. Haran, R. E. White and B. N. Popov, *J. Electrochem. Soc.*, 2001, **148**, A374.
- 9 P. Ciambelli, V. Palma, A. Ruggiero and G. Iaquaniello, in *9th International Conference on Chemical and Process Engineering*, 2009, pp. 19–24.
- 10 I. Contreras-Andrade, A. Vazquez-Zavala and T. Viveros, *Energy and Fuels*, 2009, **23**, 3835–3841.
- 11 H. C. Yao and Y. F. Y. Yao, *J. Catal.*, 1984, **86**, 254–265.
- 12 M. Triki, Z. Ksibi, A. Ghorbel and F. Medina, *J. Sol-Gel Sci. Technol.*, 2011, **59**, 1–6.
- 13 N. Abudukelimu, H. Xi, Z. Gao, Y. Zhang, Y. Ma, X. Mamat and W. Eli, *Adv. Mater. Sci. Eng.*, 2015, **1**, 31–37.
- 14 L. Wang, N. Abudukelimu, Y. Ma, S. Qing, Z. Gao and W. Eli, *React. Kinet. Catal. Lett.*, 2014, **112**, 117–129.
- 15 W. Wang, R. Ran and Z. Shao, *Int. J. Hydrogen Energy*, 2011, **36**, 755–764.
- 16 D. S. Maciver, H. H. Tobin and R. T. Barth, *J. Catal.*, 1963, **2**, 485–497.
- 17 P. Krawiec and S. Kaskel, *J. Solid State Chem.*, 2006, **179**, 2281–2289.
- 18 N. J. Schoenfeldt, 2008.
- 19 E. Yalamaç, A. Trapani and S. Akkurt, *Eng. Sci. Technol. an Int. J.*, 2014, **17**, 2–7.

- 20 A. H. Rashed, *Properties and characteristics of silicon carbide*, 2002.
- 21 J. Roy, S. Chandra, S. Das and S. Maitra, *Rev. Adv. Mater. Sci.*, 2014, **38**, 29–39.
- 22 F. Stuber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias and A. Fabregat, *Top. Catal.*, 2005, **33**, 3–50.
- 23 B. Li, K. Sun, Y. Guo, J. Tian, Y. Xue and D. Sun, *Fuel*, 2013, **110**, 99–106.
- 24 F. Stuber, K. M. Smith, M. B. Mendoza, R. R. N. Marques, A. Fabregat, C. Bengoa, J. Font, A. Fortuny, S. Pullket, G. D. Fowler and N. J. D. Graham, *Appl. Catal. B Environ.*, 2011, **110**, 81–89.
- 25 N. G. Habtu, 2011.
- 26 A. Eftaxias, Rovira i Virgili University, 2002.
- 27 N. S. Figoli and J. M. Parera, *J. Res. Inst. Catal. Hokkaido Univ.*, 1970, **18**, 142–149.
- 28 <http://accuratus.com/silicar.html> 16/06/16, .
- 29 A. K. Santra and D. W. Goodman, *Electrochim. Acta*, 2002, **47**, 3595–3609.
- 30 A. B. Anderson, J. Roques, S. Mukerjee, V. S. Murthi, N. M. Markovic and V. Stamenkovic, *J. Phys. Chem. B*, 2005, **109**, 1198–1203.
- 31 H. J. Freund, *Catal. Today*, 2014, **238**, 2–9.
- 32 F. Stuber, I. Polaert, H. Delmas, J. Font, A. Fortuny and A. Fabregat, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 743–751.
- 33 S. Roy and A. K. Saroha, *RSC Adv.*, 2014, **4**, 56838–56847.
- 34 M. Santiago, F. Stüber, A. Fortuny, A. Fabregat and J. Font, *Carbon N. Y.*, 2005,

- 43**, 2134–2145.
- 35 S. Nousir, S. Keav, J. Barbier, M. Bensitel, R. Brahmi and D. Duprez, *Appl. Catal. B Environ.*, 2008, **84**, 723–731.
- 36 S. Yang, Y. Feng, J. Wan, W. Zhu and Z. Jiang, *Appl. Surf. Sci.*, 2005, **246**, 222–228.

Chapter 5

The effect of catalyst hydrophobicity on CWAO

5.1. Preparation & Characterisation of hydrophobically modified platinum on an alumina support

It was evident from the previous chapter that the catalyst support had a big influence on CWAO activity. With regards to platinum, the difference came down to whether the support was in the form of alumina or SiC.

Catalyst characterisation studies helped determine that there was no significant difference between the active platinum components and that the only difference came from the type of support used. The SiC based catalyst was the clear outperformer with nearly 100% of the phenol being oxidised under the set conditions. The alumina type did not perform as well and the main difference was believed to be down to support hydrophobicity.

In this part of the study the alumina catalysts were modified in order to increase hydrophobicity and subsequently improve catalytic performance. They were modified by impregnating an organic silane on their surface.

5.1.1. Materials

The materials used to develop the platinum on alumina catalyst were mentioned in the previous chapter. The catalyst was in its granular form. The silane solution,

dichlorodiphenylsilane (99.5%), was purchased from *Sigma Aldrich*. The same toluene solution was used as the solvent for the impregnation process.

5.1.2. Catalyst Preparation

The silane catalysts were prepared via two routes. The first consisted of impregnating the silane onto the alumina support followed by the impregnation of the active platinum component; whereas the second consisted of impregnating the platinum before incorporating the silane component. The impregnation and pre-treatment stage of the platinum component followed the same procedure used in the previous chapter. Incorporating the silane, be it on alumina or Pt on alumina, was carried out slightly differently due to the nature of the chemical. The method was similar to what was found in the literature¹.

The dichlorodiphenylsilane was a solution made up of 99.5% purity therefore, the mass had to be calculated from its density in order to verify the weight percentage required. Various weight percentages of the silane catalyst were made for this study. Whether it was being impregnated on alumina alone or on the already prepared 2%Pt/Alumina, the method was the same for each. The required mass of the silane solution was dissolved in a minimum amount of toluene, along with the known mass of alumina or 2%Pt/alumina, in a round bottomed flask, in order for the impregnation to take place. Impregnation varied between 10 minutes and a number of hours to determine the optimum impregnation time. After the silane was impregnated, the catalyst was filtered using a Buchner flask/funnel setup, under a slight vacuum. The filtered catalyst was left to dry overnight, in a desiccator, before being treated under a flow of nitrogen at 200°C. This took place for 1 hour where the temperature was increased at a ramp rate of 1°C/min.

Two types of catalysts were therefore prepared: silane/2%Pt/Alumina and 2%Pt/silane/Alumina.

Some of the 2%Pt/Alumina catalysts were also prepared under various atmospheres. One method consisted a flow of air at 500°C for 2 hours; whereas the other consisted a flow of 5%H₂/Argon at 300°C for 1 hour. Both methods used a ramp rate of 10°C/min¹.

5.1.3. Pre-reaction catalyst characterisation

Catalyst characterisation was key in determining if the silane had been incorporated onto the catalyst successfully. Alumina and 2%Pt/Alumina were characterised in the previous chapter.

5.1.3.1. X-ray diffraction (XRD)

X-ray diffraction was used to see if incorporating the silane component had any effect on catalyst crystallinity. It was discovered previously that it was difficult to distinguish between the platinum and alumina diffraction peaks^{2,3}. It was expected that this would occur here as well.

Various loadings of silane on 2%Pt/Alumina were prepared, ranging from 1% to 4% and compared using XRD. These catalysts were subsequently tested in order to confirm whether hydrophobicity affects catalyst activity.

The figure below shows the diffractograms of all the catalysts mentioned above:-

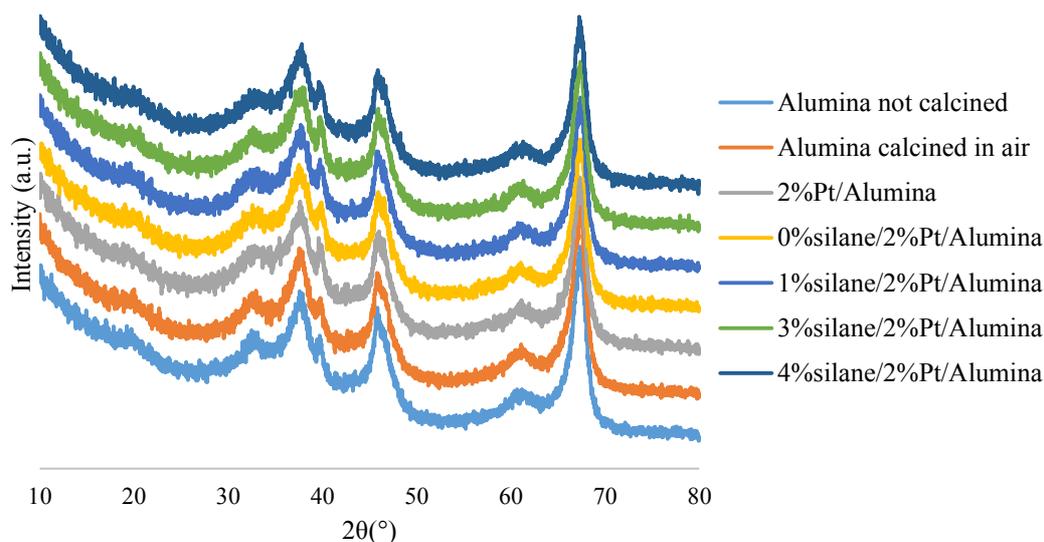


Figure 5.1 XRD diffractograms of various alumina catalysts with platinum and silane incorporated

It is very difficult to distinguish between all the profiles above, even between the 2%Pt/Alumina and just the support. There was no difference between the calcined and the non-calcined alumina supports which suggests that calcination did not affect its crystallinity. This was also shown in the literature⁴. Due to similarities in diffraction angles, it was thought beforehand that the platinum peaks would be undistinguishable amongst the alumina peaks. Only when the Pt-SiC catalysts were characterised could the peaks be found².

It was evident from the diffractograms that the incorporated silane, be it 1% or 4%, did not have an effect on alumina's crystallinity. However, as this was a bulk characterisation technique, it would have been difficult to recognise any changes in surface crystallinity. It makes it even more difficult by alumina masking what might have occurred with Pt crystallinity. Paul *et al.* also showed that alumina's overall crystallinity did not change after being grafted by three different organosilane components⁵.

5.1.3.2. Temperature programmed reduction (TPR)

TPR provided information with regards to the type of oxidation state the active components were in^{6,7}. Active component reducibility was different this time as the preparation of silane involved calcinations in different atmospheres. The silane catalysts had to be heat-treated in N₂ in order for them to be stable. The catalysts therefore had to be calcined in air in order to fix the Pt followed by N₂ post silane impregnation. This was done the other way round if the silane was impregnated first.

As making the silane catalysts involved both types of calcinations 2%Pt/Alumina, with and without N₂ pre-treatment, was analysed in order to compare the results. These showed that the pre-treatment atmosphere can have an effect on platinum oxidation state. These profiles were then compared to the silane incorporated catalysts to determine if they had any added effect.

Below are the profiles of the non-silanated catalysts, but pre-treated in various atmospheres.

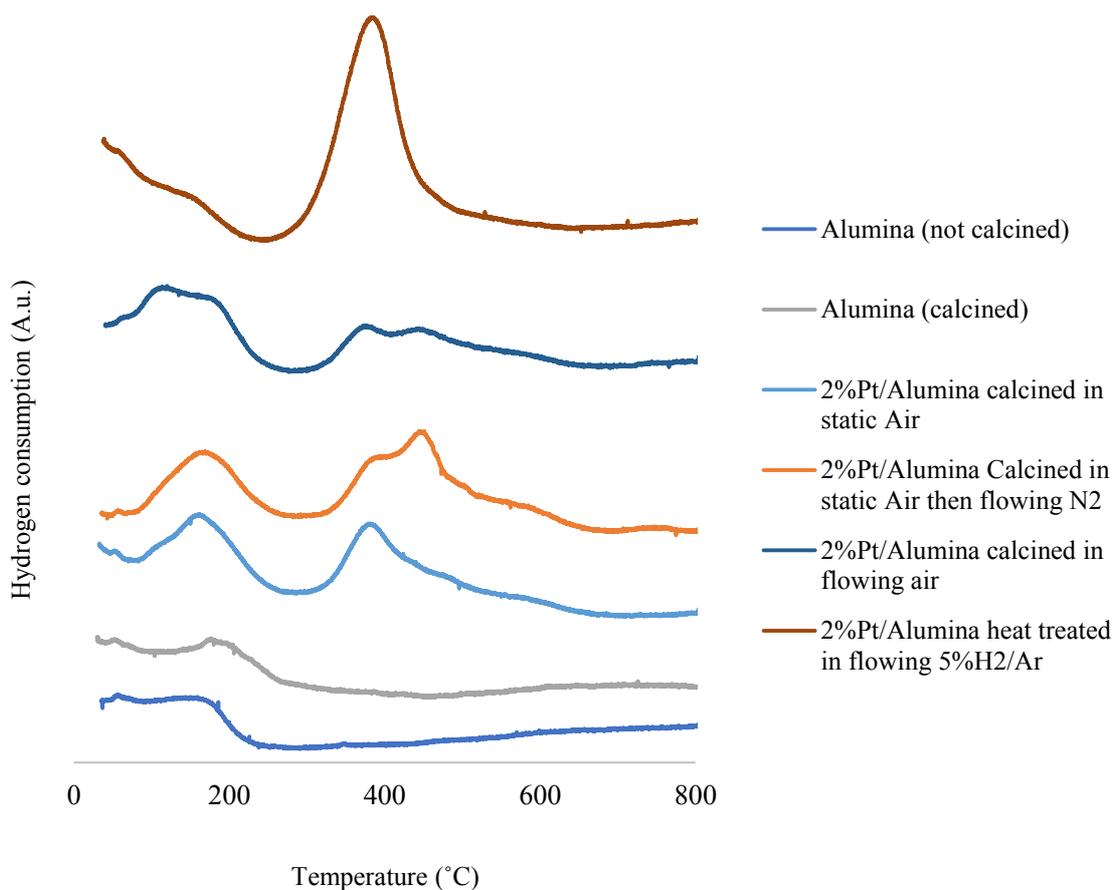


Figure 5.2 TPR profiles of the alumina catalysts pre-treated under various atmospheres

It was important to set a baseline for the TPR profiles by means of analysing just the alumina support. Calcining the alumina in static air did not change the hydrogen consumption profile in comparison to the non-calcined support. Introducing platinum, on the other hand, causes two peaks to appear between 100°C and 200°C and one near 400°C. The 2%Pt/Alumina was calcined in static air at 500°C therefore it would have formed some reducible PtO_x species. This was in accordance with what was found in the literature^{8,9}.

If silane were to be incorporated on 2%Pt/Alumina it would have had to incur a final N₂ treatment step at 200°C. To observe how this affected the catalyst alone, TPR analysis was conducted on 2%Pt/Alumina that had been treated by N₂ at 200°C for 1 hour.

This profile was represented as ‘2%Pt/Alumina calcined in static air then flowing N₂’. A new peak has appeared above 400°C and indicates that this extra treatment has introduced a more strongly bound oxide species. N₂ is considered to be inert therefore oxidation was not expected. However, flowing the gas over the catalyst rather than having it static may have had something to do with it.

Due to a flow of N₂ changing the oxidation state of the catalyst in this way, the same 2%Pt/Alumina precursor was pre-treated with a flow of air instead to see what affect this had on its reducibility. This catalyst’s TPR profile was very similar to that of the one treated with the flow of N₂ apart for the additional peak appearing at 100°C. This indicates that treating the catalyst in this way produces a catalyst with more strongly bound PtO_x species. Calcining in static air may not allow for effective platinum oxidation, whereas introducing a flow of air enables enough oxygen to oxidise the metal more effectively. This information may be able to explain why a flow of N₂ managed to produce new oxide species. The flow of N₂ may have had small concentrations of oxygen present that allowed the catalyst to oxidise further and therefore explain why a peak appeared above 400°C.

Heat-treating the catalyst under various atmospheres changes its characteristics significantly. The next step was to intentionally reduce the catalyst by introducing a flow of hydrogen during the heat treatment phase. The TPR trace showed one large broad peak just below 400°C and the peak at 150°C reduced dramatically. As referenced previously, the first peak at 150°C represented the reduction of the weakly bound oxide species, whereas the peaks up towards 400°C represented the more strongly bound oxide species^{8,9}. The large peak below 400°C, in this case, indicated that the oxide species were strongly bounded. The peak at 150°C reduced in size probably because the hydrogen pre-treatment step reduced the weakly bound oxide species. This was shown to be the case in a study reported by Barias *et al.*¹⁰.

The above characterised catalysts did not include silane, but showed how pre-treating in different atmospheres changed the nature of the active metals. The next set of catalysts characterised were the silane incorporated catalysts therefore, the above profiles needed to be taken into consideration to aid the analysis.

The figure below represents the various silane incorporated catalysts:-

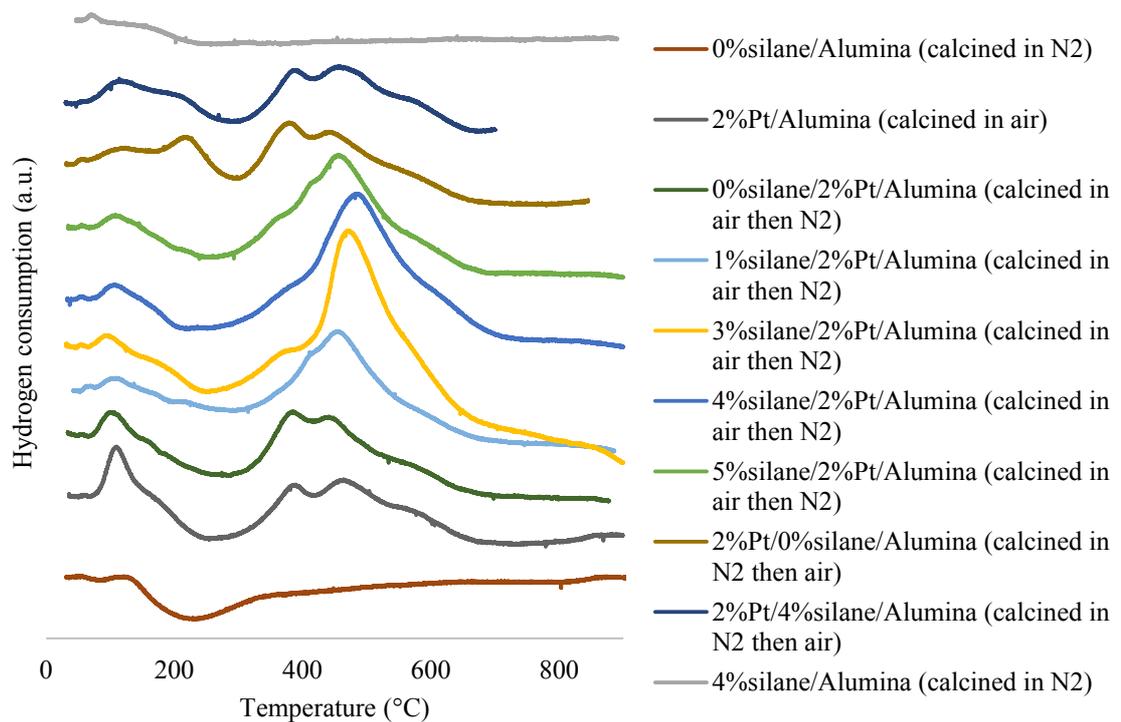


Figure 5.3 TPR profiles of silane on 2%Pt/alumina catalysts (catalysts calcined in air after Pt impregnation and treated in N₂ after silane treatment)

The alumina profile from the previous figure was very similar to that of the 0%silane/alumina profile in this figure. The 0%silane/alumina was calcined in N₂ and has not affected the TPR profile; the alumina in the previous figure was calcined in air. This suggested that only the active components were affected by changes in pre-treatment atmospheres.

A 2%Pt/alumina catalyst, calcined in static air, was also characterised as a baseline to show how incorporating silane affected the profiles. A peak appeared between 100°C and 150°C to represent the weakly bound oxide species; whereas a few peaks at 400°C appeared for the more strongly bound ones. The previous figure showed that the 2%Pt/Alumina calcined in static air did not produce a peak above 400°C therefore suggests there is a fine balance between producing strongly bound PtO_x species and not.

The next catalyst characterised was the 0%silane/2%Pt/Alumina calcined in N₂ which produced a profile almost identical to that of the 2%Pt/Alumina catalyst. It was also very similar to that of the 2%Pt/alumina catalyst calcined in N₂ which further confirms that pre-treating with flowing N₂ produces strongly bound PtO_x species.

A number of 2%Pt/Alumina catalysts were then produced with various loadings of the silane component; these varied from 1% to 5% weight %. They all showed peaks characteristic of that of the platinum on alumina catalyst but showed more complexity, broadness and intensity. This can be put down to either the silane itself being reduced or that PtO_x reducibility has been affected. This could be down to silane affecting how the platinum component is oxidised/reduced during the heat treatment phase of the preparation process.

Increasing the silane loading did not affect peak intensity that much, only complexity. This technique therefore could not be used to quantify the silane loadings, only to show that catalyst reducibility became more complex when the load was increased.

Other catalysts characterised consisted of platinum incorporated on an already silane impregnated alumina, which consisted of a N₂ calcination followed by static air. These catalysts were represented as 2%Pt/0%silane/Alumina and

2%Pt/4%silane/Alumina. These produced TPR profiles similar to that of the 2%Pt/Alumina catalyst but with an extra peak appearing at just above 200°C. Therefore, changing the order of preparation produced an oxide species with another level of binding strength. When silane was present, the complexity of the peaks increased again.

The last catalyst to be characterised was 4%silane/Alumina. There were no stand-out peaks present on this profile but there was some activity around 200°C. Alumina alone showed negative hydrogen consumption around this temperature; whereas the profile was neutral when silane was present. This indicated that silane was being reduced at this temperature.

To conclude, it can be confirmed that changing the heat treatment atmospheres during catalyst preparation highly influences the type of platinum oxide species produced. It was also confirmed that the silane can influence active component reducibility and also get reduced themselves. TPR therefore, confirmed that silane was present in some way on the catalyst; although it could not be quantified.

5.1.3.3. Surface area Brunauer Emmett Teller (BET)

When manipulating the catalysts with silane, it is possible that the surface gets affected in some way. It was important therefore to carry out surface area characterisation to determine if this was the case.

The table below shows the surface areas of all the catalysts measured using the Brunauer Emmett Teller (BET) technique.

Table 5.1 Surface areas of various silane incorporated catalysts

Catalyst	Surface area (m ² /g)
<i>Alumina calcined in air</i>	<i>107</i>
<i>Aumina not calcined</i>	<i>103</i>
<i>2%Pt/Alumina</i>	<i>97</i>

<i>4%silane/Alumina</i>	<i>104</i>
<i>0%silane/2%Pt/Alumina</i>	<i>105</i>
<i>1%silane/2%Pt/Alumina</i>	<i>104</i>
<i>3%silane/2%Pt/Alumina</i>	<i>104</i>
<i>4%silane/2%Pt/Alumina</i>	<i>102</i>
<i>5%silane/2%Pt/Alumina</i>	<i>108</i>
<i>2%Pt/0%silane/Alumina</i>	<i>108</i>
<i>2%Pt/4%silane/Alumina</i>	<i>98</i>

Calcining the alumina increased its surface area from 103m²/g to 107m²/g which perhaps occurs due to any impurities present on the non-calcined material being burned off. Incorporating platinum on the catalyst decreases the surface area significantly and can be put down to the metal filling the pores of the alumina after impregnation.

When silane was introduced and incorporated onto the alumina alone, the surface area did not change that much. This suggested that the silane either had no effect on surface area at all, or that its functionality increased the overall value. The net effect therefore is that the surface area did not change significantly. This can be said for all the silane catalysts as the surface area only fluctuated between 98m²/g and 108m²/g. This was only a difference of 10m²/g and indicated that surface manipulation is very minimal. This technique therefore was not that useful for quantifying the amount of silane present but did show that the surface area was not affected significantly.

5.1.3.4. Pore size distribution (using a DFT method)

Catalyst porosity, on the other hand, may have been affected by silane. The figure below shows the pore size distribution profiles of all the catalysts mentioned above.

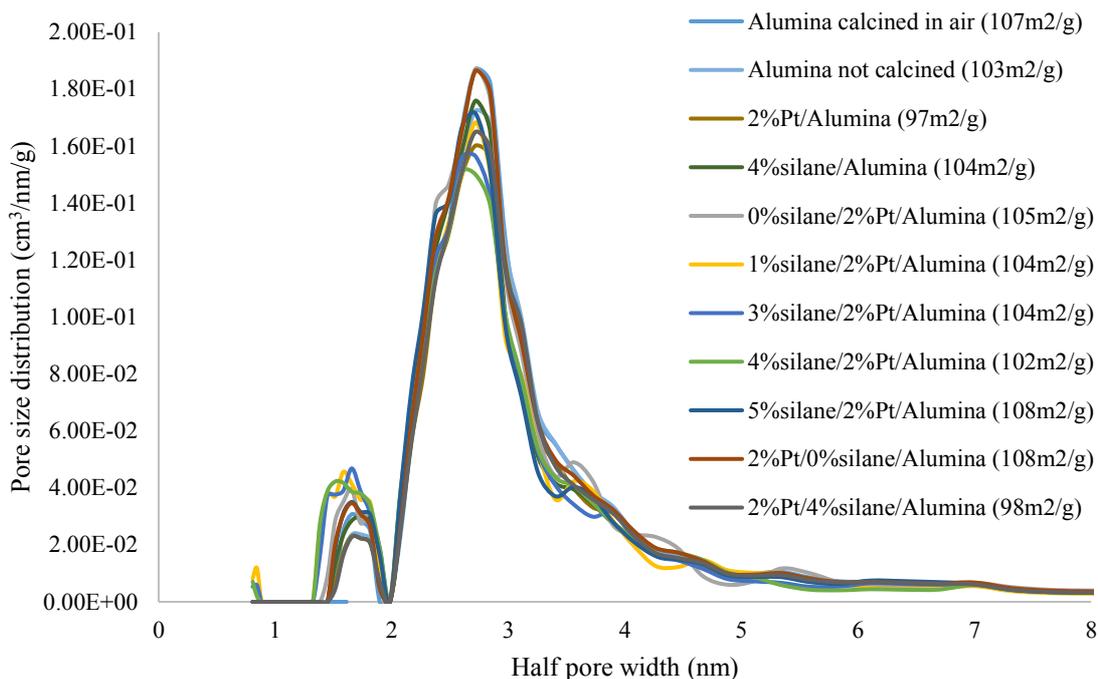


Figure 5.4 Pore size distribution of silane treated catalysts

There were two main peaks that appeared for all profiles, one at 1.75 nm half pore width and a main one at 3.75 nm half pore width. This indicated that the porosity profiles did not differ from the original alumina profile and no significant new areas of porosity were created post catalyst preparation.

Similar to the surface area measurements, the profiles were very close to each other and were difficult to tell apart. A lot of the measurements could be down to experimental error and therefore very difficult to interoperate. Incorporating the silane does show, to a certain extent, the biggest decrease in the main porosity peak (4%silane/2%Pt/Alumina), however the catalyst with no silane present (2%Pt/Alumina) showed a similar trend.

From this, it was very difficult to deduce any conclusions from the data other than the fact that the alumina's pore size distribution was not affected significantly. This

suggested that the alumina's pores were very large and that any impregnation of low silane concentrations did not affect the profile significantly.

It was mentioned in the previous chapter that the alumina has most of its pores between 1.5 nm and 6 nm half pore width and that the main bulk of distribution was around 2.75 nm. If there were a greater distribution of pores then the effect of incorporating platinum and silane might have been more noticeable.

Although it was difficult to quantify and identify silane in the techniques above it was shown to be present from TPR analysis. The main objective of adding the silane was to significantly increase the 2%Pt/Alumina's hydrophobicity. The next characterisation technique was able to show if this had occurred.

5.1.3.5. Transmission electron microscopy (TEM)

Previously, TEM was used to identify how the active components were distributed throughout the catalyst. For this part of the study, the instrument was used to qualitatively analyse catalyst hydrophobicity. This was carried out by analysing water droplet interactions with the catalyst surface. The process involved spraying the catalysts with a fine mist of water, before quickly being dunked in liquid nitrogen, so that they could be viewed cryogenically under the electron microscope. The water vitrified under rapid cooling which meant that no ice crystals were formed during the process. This also allowed for the droplets to remain in the same shape as they were when they initially came into contact with the catalyst. Catalyst hydrophobicity therefore governs the contact angles the droplets have with the surface. Hydrophobic catalysts would result in the droplets forming with large contact angles; whereas hydrophilic catalysts would result in the droplets forming with small contact angles.

The TEM instrument was set up in a way so that the catalyst could be imaged from different angles. This meant that the droplets could be viewed with more confidence as a 2-D image raised concerns in terms of position and depth.

The first catalyst to be cryogenically viewed using TEM was the 2%Pt/Alumina catalyst. This catalyst was chosen as it was believed to be the least hydrophobic in nature compared to the others analysed. This also meant that the more hydrophobic samples had a catalyst that they could be compared with.

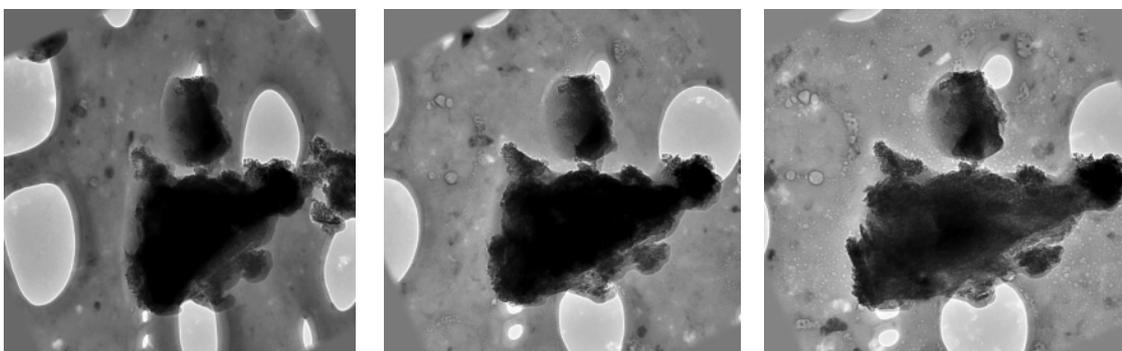


Figure 5.5 TEM images of 2%Pt/Alumina catalyst

The figure above shows the three different angles the images were taken from. The arc began with a side-on view before panning through to more of a front-on view as the scans progressed. In this instance, the sprayed water was seen as a thin layer around the edges of the catalyst. This was more pronounced around the south side of the catalyst and could be seen from every angle. This profile was indicative of a more hydrophilic material as there was no droplet formation on the catalyst. The water, instead, formed a frozen layer of vitrified water around the surface. Alumina is regarded as hydrophilic as it contains a large degree of hydroxyl functionality¹¹. The droplets therefore would rather spread out on the catalyst surface and come into contact with the hydroxyl groups through dipole interactions.

The next catalyst analysed was believed to be more hydrophobic due to its lack of hydroxide surface functionality. It consisted of platinum on a silicon carbide support. The images below show how this more hydrophobic catalyst interacted with the droplets: -

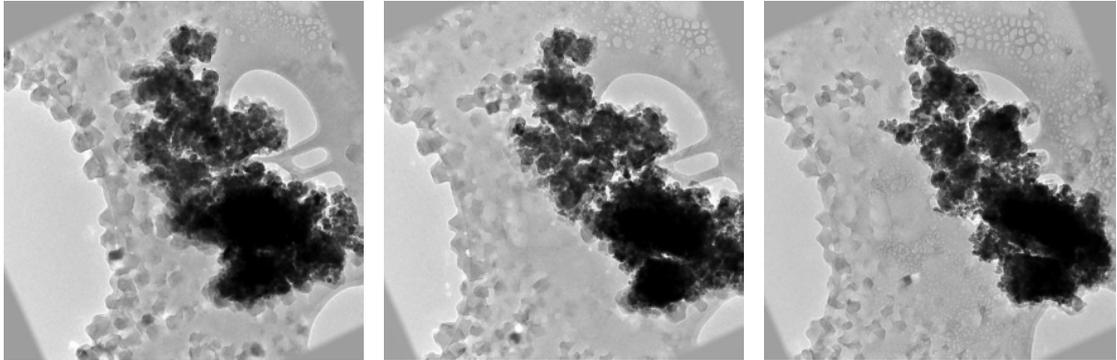


Figure 5.6 TEM images of 2%Pt/SiC

The droplets interacted differently with the SiC. At various points around the surface, the droplets appeared more like domes and less like an equally distributed layer. This was characteristic of water interacting with a more hydrophobic material^{12,13}. The larger the contact angle is between the droplet and the surface, the more hydrophobic the material is. Literature adsorption data have showed that a quarter of a passively oxidised SiC surface appears negatively charged and therefore hydrophilic, whereas the remainder was not charged and therefore hydrophobic¹⁴. As the 2%Pt/SiC catalyst underwent oxidation during the calcination phase a fraction of it must be hydrophilic as well as hydrophobic. But from the TEM images, there must have been some degree of hydrophobicity, due to the nature of the dispersed water droplets.

In order to truly identify whether hydrophobicity played a major role in the CWAO of phenol, the alumina was modified with a diphenyl silane in order to make it more hydrophobic. This allowed alumina's hydroxide components to be replaced with diphenyl silane which, in turn, increased its hydrophobicity. The catalyst imaged below consisted of 5%silane/2%Pt/Alumina.

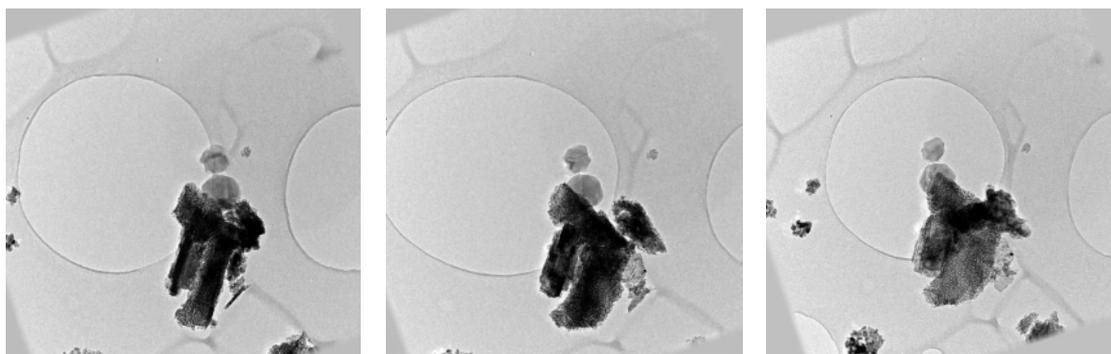


Figure 5.7 TEM images of 5%silane/2%Pt/Alumina

These three images showed a completely different water droplet profile to the other two. Here, there seemed to be no water present apart from a couple of large droplets in some areas. One of the droplets seemed to be loosely attached and in the shape of a sphere. The other droplet was not attached to the catalyst but loosely attached to the other droplet. This indicated that the catalyst much more hydrophobic than the others as there was a lack of water associated with it. Also, the shape of the droplet was characteristic of that of a very hydrophobic material as the contact angle was so large. This catalyst was exactly the same as 2%Pt/Alumina except for the silane component therefore, the modification certainly affected its hydrophobic nature. Introducing silane at 5% weight has altered the surface to be hydrophobic and therefore could have similar properties to that of the SiC support. It seemed that this modified alumina was more hydrophobic than the SiC even, as the spherical nature of the droplet formed on the surface was more pronounced.

From this study it was confirmed that having SiC instead of an alumina support made the catalyst more hydrophobic; even more so when silane was incorporated.

5.1.3.6. Thermogravimetric analysis (TGA)

As well as making successful hydrophobic catalysts, their stability in the reactor were also key. The catalysts had to be durable enough to withstand the harsh conditions

that occur during a CWAO reaction. One technique that sets out to test this is TGA. TGA allows for mass loss to be measured as a function of temperature in oxidative atmospheres. It was important therefore to analyse the modified catalyst as the stability of the silane was unknown. TGA was able to detect, through sample weight loss, at what temperature the silane oxidise at. In this case, compressed air was used as the oxidant and the temperature ranged from ambient to 800°C to ensure oxidation and mass loss was observed.

The graph below represented the TGA profiles of a range of silane modified catalysts. As the weight percentages of the silane were relatively low, it was difficult do analyse the differences between the TGA profiles. Comparing the silane and non-silane modified catalysts, on the other hand, did show that the profiles were different.

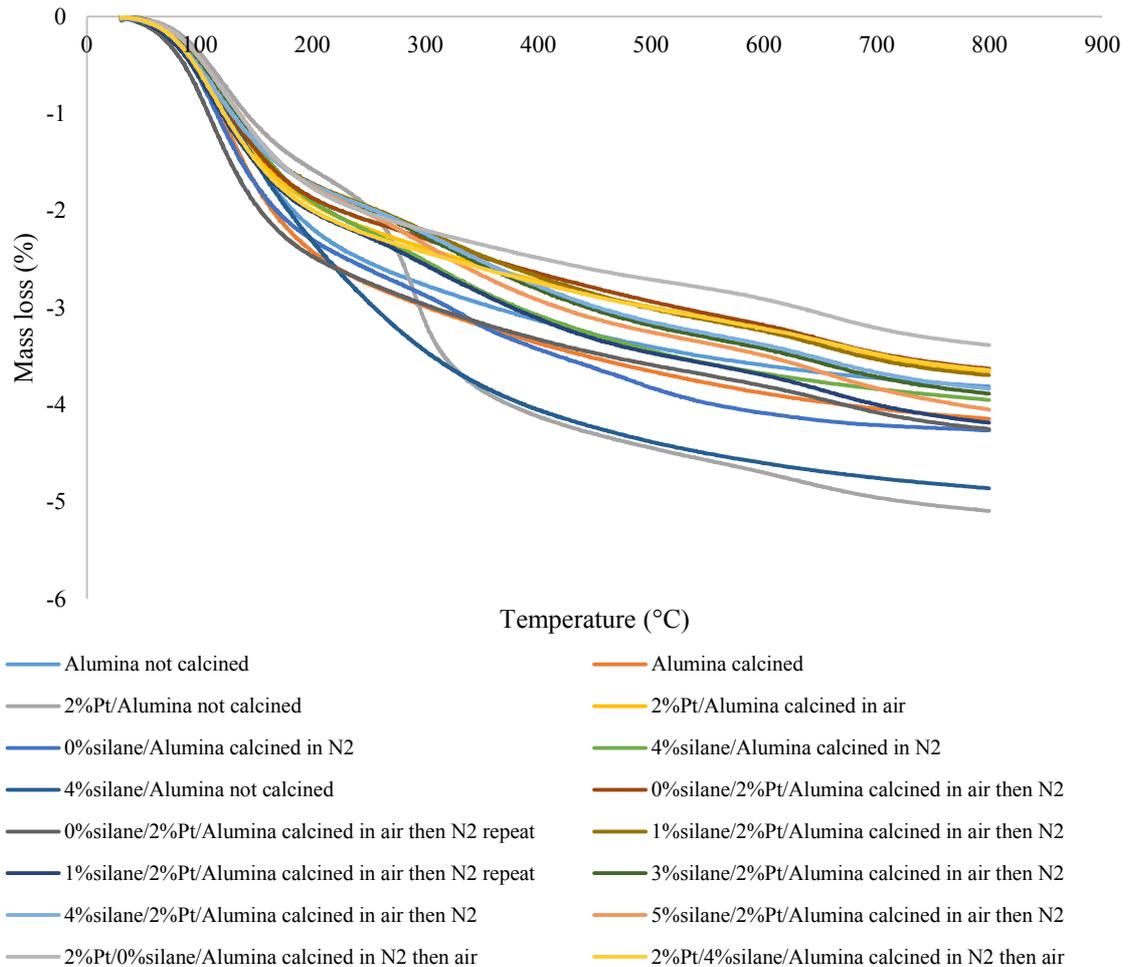


Figure 5.8 TGA profiles of the silane modified catalysts (catalysts were calcined in air after Pt impregnation and treated in N₂ after silane treatment)

All of the catalysts tested shared a common feature in their profiles which was a decrease in mass from ambient temperature to 200°C. This usually represents any moisture and low boiling point impurities that have accumulated on the surface since their pre-treatment. As the boiling point of water is 100°C it was not a surprise to observe a mass loss here.

All of the non-modified catalysts also shared similar TGA profiles. Although they did not follow the exact line in mass loss as a function of temperature, their profile shapes

were similar. Both the alumina catalysts (without any components added) shared similar mass loss rates after 200°C.

The platinum incorporated catalysts all showed another drop in mass loss just above 600°C. This could have been down to some strongly bounded material being oxidised from the surface. The non-calcined equivalent showed a decrease in mass at 270°C as there were likely to be more weakly bounded, oxidisable material on the surface.

When silane was incorporated without the platinum present, the decrease in mass at 600°C was not observed. It did however decrease in mass at just above 300°C. When platinum was also incorporated the mass loss at 600°C was seen in addition to the one at 300°C. It can be confirmed therefore, that silane was present after it was impregnated because the catalysts containing it had characteristic decreases in mass as a function of temperature. They also remained relatively stable as they showed the same trend in mass loss as the non-silanated catalysts around the reactor operating temperature.

This technique can also be used to compare catalysts of different silane loadings using relative mass loss. Due to the sensitivity of the profiles, it was important to compare silane catalysts prepared from the same batch of Pt/Alumina. The catalysts analysed below were the ones containing 0-5% silane incorporated on 2%Pt/Alumina. The graph below shows only the profiles of these catalysts.

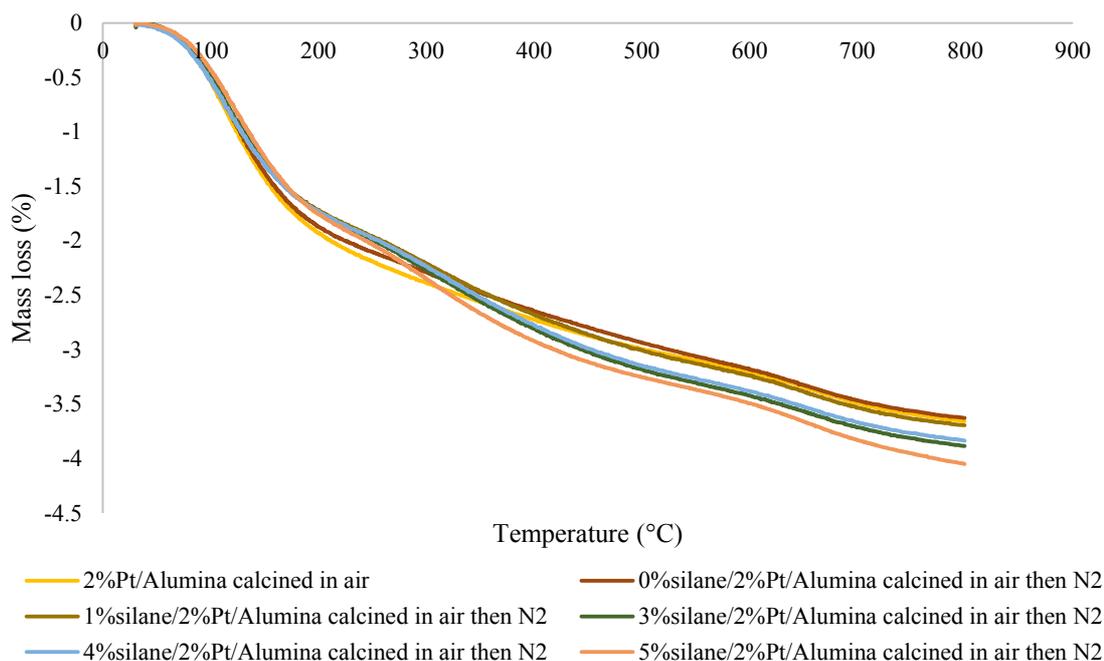


Figure 5.9 TGA profiles the catalysts with various silane loadings

When no silane was present the initial mass loss seems to be larger. This could be down to the lack of hydrophobicity with a non silanated catalyst allowing more moisture on the surface and therefore show a larger decrease in mass at above 100°C. Mass loss with regards to silane occurred at 300°C because no change was observed for the non-silane catalysts at this temperature. Also, the boiling point for dichlorodiphenyl silane is 305°C¹⁵. The mass lost at 600°C was attributed to the presence of platinum. It is possible that platinum was able to promote oxidation of very strongly bounded material.

Increasing the theoretical loadings of the silanes from 0% to 5% does show a significantly greater mass loss overall. Mass loss increased as the percentage of silane increased, except for the 3% and 4% loaded catalysts. The silane loading seemed to be very similar in both of these catalysts. Apart from these two, the theoretical values match up with the measured. It was predicted that the catalyst with the most silane present would result in the highest degree of hydrophobicity and thus, activity.

5.1.4. Post reaction characterisation

TGA was also used to characterise the catalysts that had been subjected to CWAO testing. The figure below compares the TGA profiles of both ‘fresh’ and ‘used’ catalysts; some containing silane and others without.

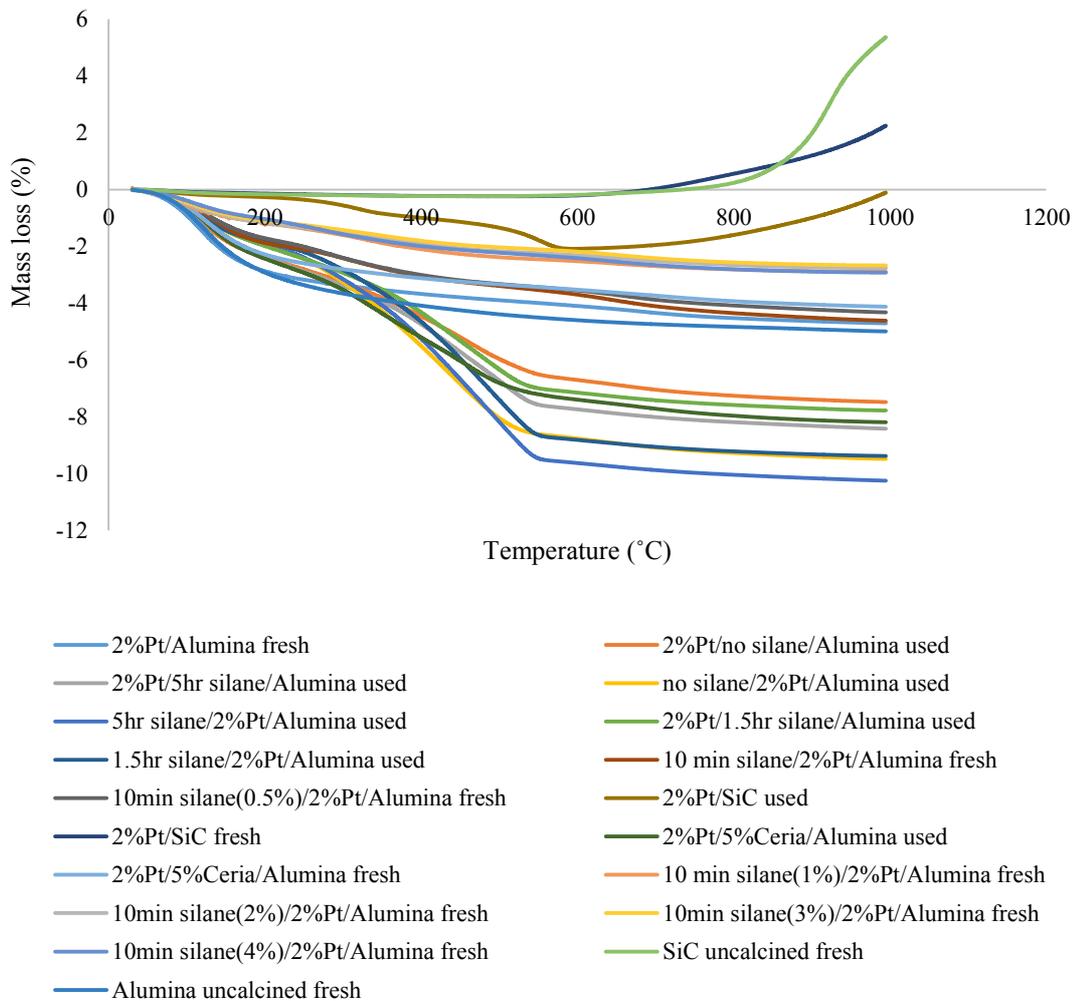


Figure 5.10 TGA profiles of used silane and non-silane modified catalysts

The profiles were grouped into three sets: used catalyst, fresh catalysts and SiC catalysts. The used set of catalysts experienced, as expected, a larger degree of mass loss compared to the catalysts that had not been tested. This was likely to be down to surface carbon formation during the CWAO reaction¹⁶. Any carbon formed would have been

oxidised at high temperature during TGA and result in more mass loss compared to the fresher catalysts. Carbon formation was the likely cause for catalyst deactivation.

The third set of catalysts had SiC as their support. These catalysts, be them used or not, showed an increase in mass. This effect was put down to SiC itself oxidising¹⁷. The used catalysts therefore, showed no net change as both mass loss and gain were occurring simultaneously.

5.1.5. Conclusion

In this section the silane modified alumina catalysts were characterised and analysed to see whether they had been impregnated successfully and whether or not they were hydrophobic. Although it was difficult to quantify and even identify silane from techniques such as XRD and porosity studies, they were detected using TPR and TGA. They could almost be quantified by TGA. TEM was also used to confirm the hydrophobic effect of the silane modification. The images showed the vitrified droplet of water as a sphere on the catalyst surface meaning that the contact angle was very large and therefore hydrophobic. The alumina catalyst alone showed no hydrophobicity therefore, it can be confirmed that a hydrophobic modification could be achieved through incorporating a silane. The SiC catalysts also possessed hydrophobic properties.

5.2. Catalytic activity studies and correlation with structure

In this section the catalysts were tested to see how surface modifications affected catalytic activity. The reason for manipulating the surface was to try and increase hydrophobicity. This highly influences how water physically interacts with the catalyst and therefore affect reaction rates¹⁸. It was highlighted in the previous chapter that the SiC type catalysts promoted better CWAO of phenol when Pt was the active metal. As the reaction depended on oxygen getting activated by Pt, it was thought that the active metal needed to have as little contact as possible with the water so that it could be more accessible. In order for this to happen, the surface needed to be of a hydrophobic nature so that water did not hinder oxygen activation. Alumina resulted in the catalyst not performing as well as the SiC because it was believed to be more hydrophilic.

In order to manipulate the surface properties of the catalyst in this way the alumina support was subjected to silanation. This process was carried out by impregnating the support with a silane-type compound so that the hydrophilic hydroxyl functionality could be replaced by a silicon-hydrocarbon species to make it more hydrophobic. It has previously been reported that incorporating hydrophobicity onto a catalyst can benefit activity. Massa *et al.* showed that incorporating PTFE onto a CuO/Alumina catalyst improved durability and decreased the chances of carbon fouling¹⁸. However, this did not improve initial activity.

The silane used in this study was in the form of dichlorodiphenyl silane. The chlorine components would have been substituted for the aluminium atoms on the catalyst support and produce an aluminium-silicon-diphenyl species. This in turned increased its hydrophobicity.

As this procedure was fairly unknown for the application of CWAO, a paper on alumina manipulation with organosilanes was used to help develop these catalysts¹. Although it had no reference to CWAO it contained the methodology required to manipulate the alumina surface to achieve a silinated surface

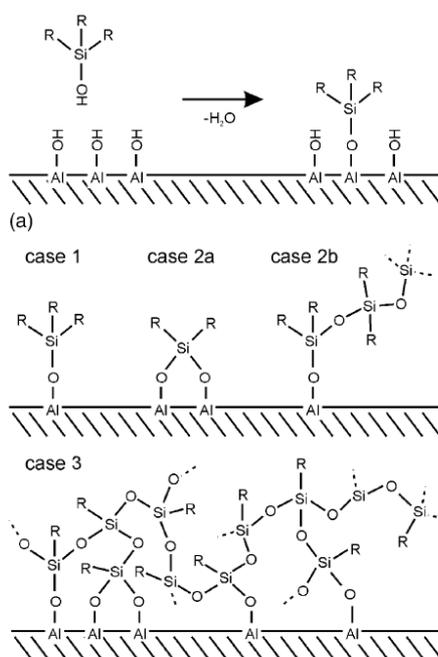


Figure 5.11 Hydrophobic modification with organosilanes¹

The paper also explained how the silane loadings were varied by changing impregnation immersion times. This was therefore used to produce the first set of hydrophobic catalysts. For the 2%Pt/silane/Alumina catalyst, the silane was impregnated on alumina and then calcined in N₂ before the impregnation of Pt could take place.

The following graph represents the phenol conversion profiles for the catalyst mentioned above. Three types of this particular catalyst were tested: one after 1.5 hours of silane immersion time, another after 5 hours of silane immersion time and another with no silane present. The loading of the silane was 5 wt.%. The reactions were carried out

using the same standard conditions as previously used throughout this project. The temperature was set at 140°C.

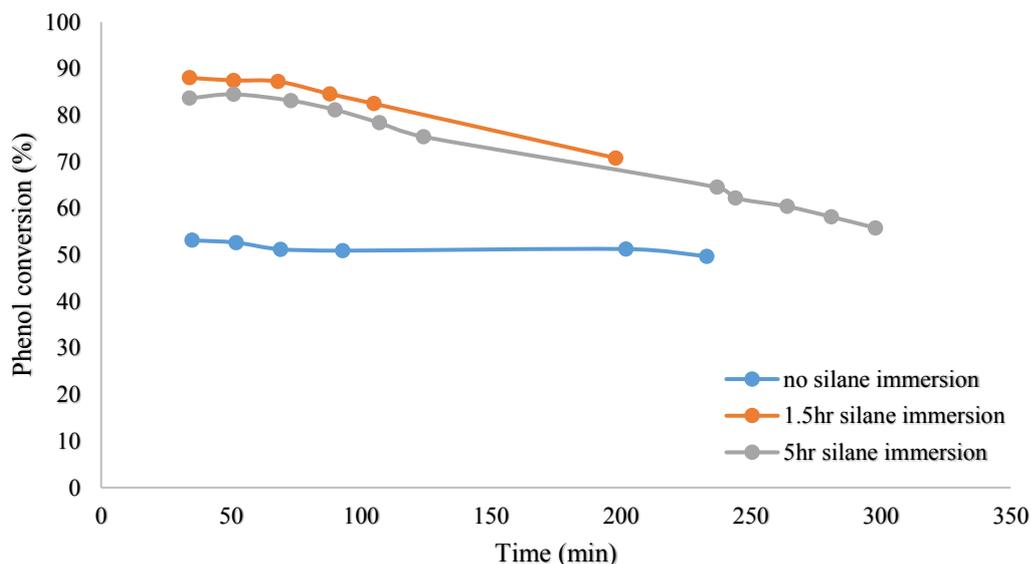


Figure 5.12 Alumina calcined in N₂ after silane immersion, then in air after 2%Pt impregnation (silane: dichlorodiphenylsilane) (140°C)

The graph compared the three catalysts mentioned above. The ‘blank’ catalyst (2%Pt/Alumina – no silane) behaved as it should have, delivering stable phenol conversion of just above 50%. This was comparable to previous tests done on Pt-Alumina. Even though the alumina had been immersed in toluene to mimic the silane preparation conditions it did not affect the activity. It is believed that the hydrophilic nature of the alumina allowed water to block oxygen activation at the active sites thus, delivering half the activity of what the more hydrophobic SiC catalyst could achieve.

The purpose of this study was to modify alumina by silane surface modification so that similar activities to that of the SiC catalysts could be achieved. The silane was shown to be very hydrophobic from TEM water droplet analysis, even more so than the SiC catalysts.

The next profiles in the graph were that of the modified alumina catalyst. One of them consisted of a 1.5 hour silane immersion impregnation period. For the entire length of the continuous flow reaction, this catalyst's activity remained higher than that of the 'blank' catalyst indicating that silane incorporation had improved catalyst performance. However, the deactivation it experienced was drastic compared to other lifetime profiles seen throughout this study. In this reaction, phenol conversion dropped from 90% to 70% in the space of around 3 hours. The blank catalyst did not show any significant deactivation which means that the increase in activity promoted by silane was short lived. It was thought therefore that the silane was becoming ineffective as time passed by. This was not down to adsorption effects, as was seen for the carbon type catalysts, because the porosity and surface area characterisation analysis showed no significant change when the silane was added. This could have been down to silane being impregnated before platinum. This may have resulted in the following:-

The final platinum pre-treatment calcination step may have stripped some of the silane off via high temperature oxidation. TGA analysis showed that a significant amount of mass was lost at just above 300°C and was put down to dichlorodiphenyl silane's boiling point being 305°C. This means that a calcination temperature of 500°C would have deactivated the silane somewhat. It may not have totally stripped the silane off but manipulated it in a way so that the hydrophobicity was not as effective.

Also, a lot of the platinum may have been sitting on top of the silane and if any deactivation occurred, then some of it may have got stripped off too.

The other catalyst in the graph consisted of silane incorporated in the same manner, but via a 5 hour immersion impregnation time. The same deactivation trend was seen but with it having a slightly lower activity compared to the 1.5 hour immersed

catalyst. This meant that the immersion time did not have any effect on improving hydrophobicity. The difference could have been down to slightly different concentrations of silane being loaded on to the catalyst after impregnation.

The next set of catalysts tested consisted of the same composition but with the impregnation carried out in reverse. The platinum was impregnated first this time followed by the silane. This was carried out to ensure that the silane was not affected by the second calcination stage and also to ensure that the platinum did not get affected by silane deactivation in the reactor.

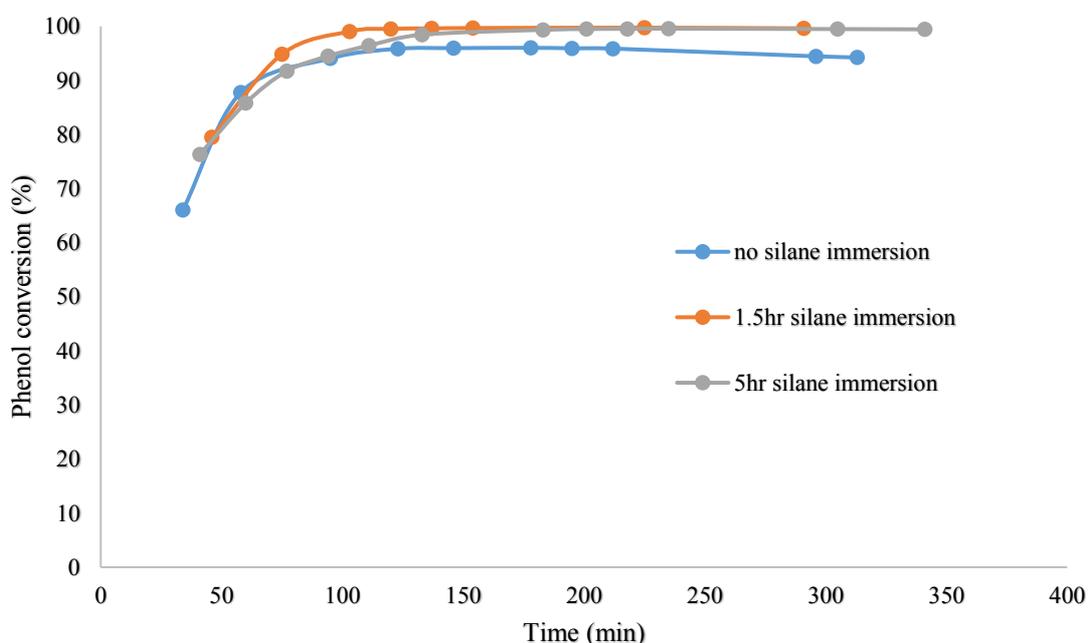


Figure 5.13 2%Pt/Alumina calcined in air after impregnation of Pt, then in N₂ after 5% silane immersion (140°C)

Instantaneously there was a large jump in activity, even for the blank 2%Pt/Alumina catalyst. This could be explained by the fact that the catalysts were calcined under N₂ after the silane impregnation instead of air. The nature of the N₂ calcination, shown by TPR analysis, caused a newly bonded PtO_x species to be formed

on the alumina surface. The jump in activity for the blank catalyst therefore could have been down to alumina's hydrophilicity allowing the phenol to come into contact with these newly formed PtO_x species. Calcining 2%Pt/Alumina in N_2 therefore increases its activity.

It is worth noting, however, that oxidation via activated atmospheric oxygen was more efficient than direct oxidation by PtO_x . However, as the blank catalyst was hydrophilic, the only way to increase its activity was by increasing the oxide concentration on the surface.

It seems from the graph that the blank catalyst managed to perform almost as well as the modified catalysts did. This, however, was not a fair comparison as the silane catalysts managed to promote total phenol conversion. In order to see their true potential, the reactions were repeated at a lower temperature. The following conversions were obtained from a reaction running at 120°C instead of 140°C .

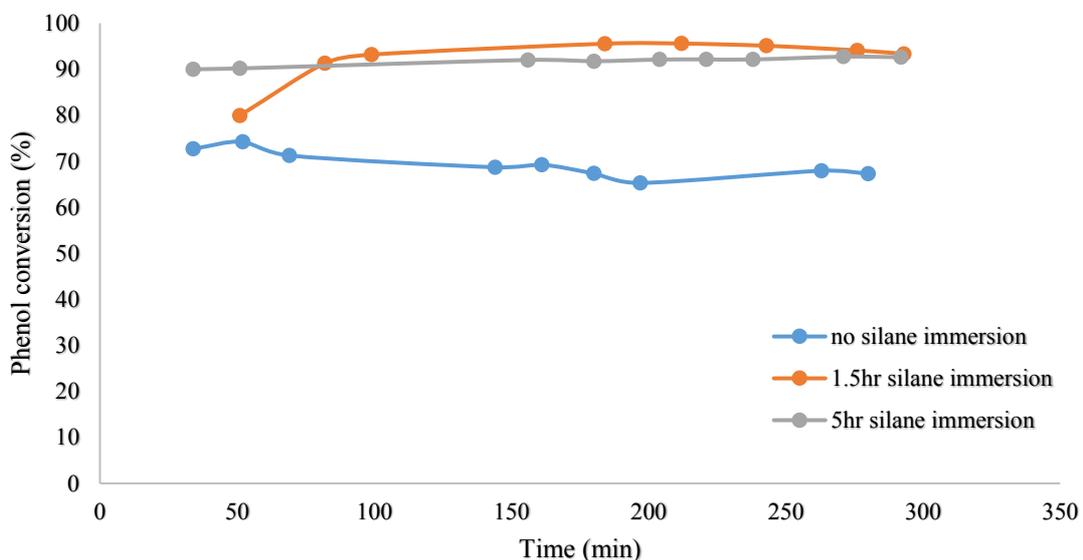


Figure 5.14 2%Pt/Alumina calcined in air after impregnation of Pt, then in N_2 after silane immersion (120°C)

By decreasing the temperature, the catalysts became less active and showed their true performance potentials in relation to each other. Phenol conversion decreased by only 10% for the silane catalysts; whereas almost 30% reduction was seen for the blank catalyst. This reinforced the evidence that having a hydrophobic silane present on a hydrophilic catalyst improved phenol conversion.

In contrast to the previous experiment, the catalysts in this case showed no signs of deactivation. This was put down to the change in preparation impregnation order. The silane was believed to be more stable after being impregnated last and that the platinum was less likely to leach during the reaction.

Once it was discovered that modifying the support had a major effect on catalyst activity, tests were carried out using different loadings of silane to see whether hydrophobicity and activity could be controlled. Previously, this was attempted by immersing the catalysts for different periods of time, however this did not affect overall activity. For this part of the study, different concentrations of silane were prepared and impregnated onto the 2%Pt/Alumina catalyst. The catalysts were submerged for only 10 minutes for this particular impregnation. Silane concentrations ranging between 0% and 5% were prepared, with the hope that different degrees of activity could be achieved.

In addition to the changes made above, a lower surface area alumina was tested as well as the usual high surface area equivalent. The thought behind using a lower surface area alumina was that its hydrophilic functionality would be lower and therefore, promote catalytic activity even further.

The following graph represents 3 types of catalysts with various degrees of silane loading. The first consisted of the, previously used, high surface alumina catalyst and the second, the lower surface area equivalent. The third catalyst tested was of the high surface

area alumina catalyst, but did not receive a N₂ treatment step once the silane was impregnated.

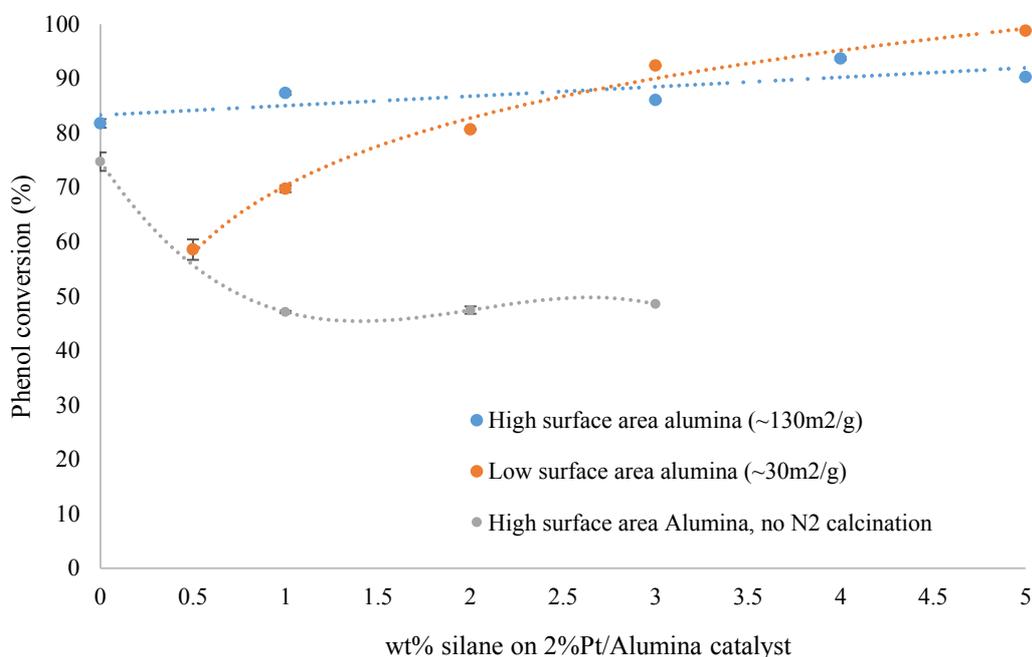


Figure 5.15 The effect of alumina surface area on the conversion of phenol over silane modified catalysts

The first two catalysts showed an increase in phenol conversion as a function of silane concentration. This was expected as it has been shown previously that hydrophobicity promotes activity.

This was not the case for the third catalyst tested as phenol conversion decreased suddenly once silane was introduced to the catalyst. This catalyst did not receive any N₂ treatment after impregnation therefore, shows that it was a key step in its preparation. As a result of not treating the impregnated silane, it was believed that unwanted precursor residuals, such as chlorates, interfered with the oxygen activation mechanism. The N₂ pre-treatment step at 200°C ensured that only pure silane species were left on the surface¹.

As well as investigating the effect of silane concentration on activity, alumina surface area was also investigated. As mentioned previously, the lower surface area alumina should have less hydrophilic functionality and therefore, improve activity; however, less surface area does have a negative impact on catalyst-substrate contact time.

Looking at the graph, both of these effects can be used to explain the profiles seen. The higher surface area catalyst showed the best activity initially, however it was overtaken by the low surface area catalyst as the silane concentration got higher.

When there was a lack of silane on the surface, hydrophobicity was less effective in improving catalyst activity therefore, the reaction depended more on surface area. When silane loading increased to more significant levels, above 2.5 weight %, the hydrophobicity effect took over and the surface area became less significant.

For the higher surface area catalyst, increasing the silane concentration had less of an effect on phenol conversion compared to its lower surface area equivalent. The phenol conversion only increased by up to 10% for the former but up to 40% for the latter. This effect was enhanced for the lower surface area catalyst as it was able to achieve better silane coverage. The above therefore explains why incorporating silane on a high surface area alumina did not change the activity as significant as it did for the lower surface area catalyst.

5.2.1. Conclusion

The results presented above showed that both the surface area and silane concentration could be optimised in order to control catalytic activity. It was shown that increasing the hydrophobicity through silane incorporation had a positive effect on activity. These results therefore explained why the more hydrophobic SiC was better in promoting phenol oxidation compared to the alumina. This investigation has shown that

the support can highly influence phenol CWAO and that activity does not just depend on the type of active metal present.

The next chapter looked at how ceria as an oxygen storage component affected catalyst activity.

5.3. References

- 1 A. Sah, H. L. Castricum, A. Blik, D. H. A. Blank and J. E. Ten Elshof, *J. Memb. Sci.*, 2004, **243**, 125–132.
- 2 T. Hyde, *Platin. Met. Rev.*, 2008, **52**, 129–130.
- 3 S. A. Hosseini, *Open J. Phys. Chem.*, 2011, **01**, 23–27.
- 4 J. Xu, A. Ibrahim and X. Hu, *Microporous Mesoporous Mater.*, 2016, **231**, 1–8.
- 5 B. Paul, W. N. Martens and R. L. Frost, *J. Colloid Interface Sci.*, 2011, **360**, 132–138.
- 6 F. Arena, G. Trunfio, J. Negro and L. Spadaro, *Appl. Catal. B Environ.*, 2008, **85**, 40–47.
- 7 C. Costello, J. Guzman, J. Yang, Y. Wang, M. Kung, B. Gates and H. Kung, *J. Phys. Chem. B*, 2004, **108**, 12529–12536.
- 8 P. Ciambelli, V. Palma, A. Ruggiero and G. Iaquaniello, in *9th International Conference on Chemical and Process Engineering*, 2009, pp. 19–24.
- 9 I. Contreras-Andrade, A. Vazquez-Zavala and T. Viveros, *Energy and Fuels*, 2009, **23**, 3835–3841.
- 10 O. A. Bariãs, A. Holmen and E. A. Blekkan, *J. Catal.*, 1996, **158**, 1–12.

- 11 M. Digne, P. Sautet, P. Raybaud, P. Euzen and H. Toulhoat, *J. Catal.*, 2002, **211**, 1–5.
- 12 D. Yang, Y. Xu and D. Wu, *J. Phys. Chem. C*, 2007, **111**, 999–1004.
- 13 Z. Yoshimitsu, a Nakajima, T. Watanabe and K. Hashimoto, *Langmuir*, 2002, **18**, 5818–5822.
- 14 V. Medout-Marere, A. El Ghzaoui, C. Charnay, J. M. Douillard, G. Chauveteau and S. Partyka, *J. Colloid Interface Sci.*, 2000, **223**, 205–214.
- 15 *Sigma Aldrich 03/09/16*.
- 16 M. Santiago, F. Stüber, A. Fortuny, A. Fabregat and J. Font, *Carbon N. Y.*, 2005, **43**, 2134–2145.
- 17 O. Ebrahimpour, J. Chaouki and C. Dubois, *J. Mater. Sci.*, 2013, **48**, 4396–4407.
- 18 P. Massa, F. Ivorra, P. Haure and R. Fenoglio, *Catal. Commun.*, 2009, **10**, 1706–1710.

Chapter 6

The effect of ceria concentration on catalyst activity

6.1. Preparation & Characterisation of various loadings of ceria on Pt/SiC

6.1.1. Introduction

It was shown previously that incorporating ceria affected the activity of the catalysts in different ways. It was also shown that a metal component supported by a hydrophobic support performed much better than a metal on a hydrophilic support and that a metal oxide on a hydrophilic support performed better than the oxide on a hydrophobic support.

This was believed to be down to wetting efficiency. A hydrophilic surface allows for sufficient wetting therefore, any catalytic component in the oxide form will be able to supply enough oxygen for oxidation¹⁻³. In this instance, a metallic component will be submerged and therefore unable to activate oxygen. When the support is hydrophobic, the wetting efficiency is reduced and the metallic components are able to activate oxygen for CWAO. Metallic catalytic components are usually preferred to promote oxidation⁴⁻⁸.

The results showed that a metal on a hydrophobic support was the more suited catalyst for this application due to atmospheric oxygen mass transfer effects. The transfer of phenol to the metal oxide was more difficult than that of the transfer of oxygen to the metal as the latter was in excess; whereas the former was not.

Incorporating ceria (5% weight loading) improved the activity in all cases. In the case of the metal oxide, the activity was enhanced due to the addition of another oxygen donating metal oxide⁹⁻¹². In the case of a metal, adding a metal oxide increased the activity as it not only aided oxygen mobility but also was able to oxidise the phenol through direct contact^{10,11}.

This chapter looked at the ‘ceria-effect’ in more detail and investigated how varying the concentration of ceria on a metallic-hydrophobic support system affected phenol oxidation activity. This catalytic system consisted of platinum supported by a ceria on a SiC support whereby only the ceria loading was changed. This therefore, was a subsidiary chapter to the previous work and further helped to gain an understanding of the CWAO mechanism.

This chapter gives an overview of catalyst preparation, characterisation and eventually catalyst testing to see how the various ceria loadings affected activity.

6.1.2. Materials

The same materials were used as for the previous catalyst preparation methods. The catalyst support (SiC 3mm pellets) was supplied by Johnson Matthey®; whereas the metal precursor platinum(II) 2,4-pentandionate (Pt 48% min) was supplied by Alfa Aesar and the cerium(III) nitrate hexahydrate (99.99%) supplied by Sigma Aldrich. The solvents used for the impregnations, depending on the type of active component precursor, were HPLC grade toluene and water supplied by Sigma-Aldrich and Fischer Scientific respectfully.

6.1.3. Catalyst Preparation

Catalyst preparation was carried out using the same method as shown previously. This involved the crushing and sieving of the SiC pellet support to obtain the desired 0.425-0.6 mm granular grade followed by incipient wetness of the chosen ceria loading.

The solvent for the solution was water as it was required to dissolve the cerium(III) nitrate hexahydrate salt. After being left to immerse overnight, the solution was evaporated using a rotary evaporator followed by a period of time in a 120°C oven to dry. The catalyst was then calcined at 500°C for 2 hours after a temperature ramp increase of 10°C/min.

The next step involved incorporating the platinum. The same steps as above were repeated but this time using the platinum(II) 2,4-pentandionate salt and toluene as the solution. These steps resulted in a platinum/ceria/SiC catalyst being made.

In this study four types of catalysts were prepared: 0%Pt/x%Cerium/SiC, 0.5%Pt/x%Cerium, 1%Pt/x%Cerium/SiC and 2%Pt/x%Cerium/SiC, whereby each type consisted of 0%, 1%, 2.5% and 5% as x% of ceria. This resulted in 16 different catalysts in total: -

Table 6.1 Catalysts prepared for the investigation

		Ceria wt. %			
		0	1	2.5	5
Pt wt%	2	2%Pt/SiC	2%Pt/1%Cerium/SiC	2%Pt/2.5%Cerium/SiC	2%Pt/5%Cerium/SiC
	1	1%Pt/SiC	1%Pt/1%Cerium/SiC	1%Pt/2.5%Cerium/SiC	1%Pt/5%Cerium/SiC
	0.5	0.5%Pt/SiC	0.5%Pt/1%Cerium/SiC	0.5%Pt/2.5%Cerium/SiC	0.5%Pt/5%Cerium/SiC
	0	SiC	1%Cerium/SiC	2.5%Cerium/SiC	5%Cerium/SiC

6.1.4. Pre-reaction catalyst characterisation

A 2%Pt/5%Ceia/SiC catalyst was prepared previously therefore, referral back to section 4.1.4 would provide characterisation information regarding the physical and chemical properties of the catalyst. These include X-ray diffraction, temperature programmed reduction, surface area and pore size distribution, transmission electron microscopy and energy dispersive X-ray spectroscopy.

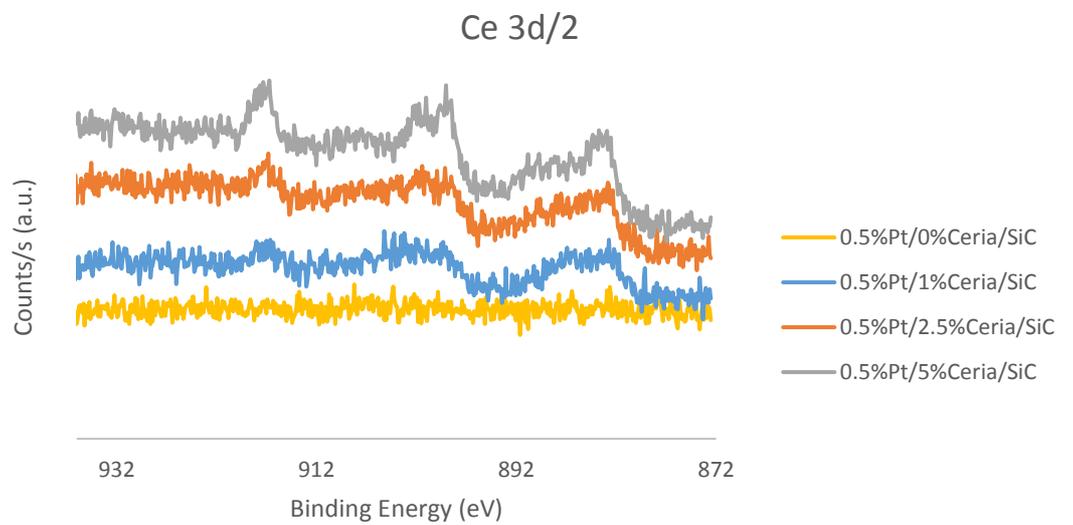
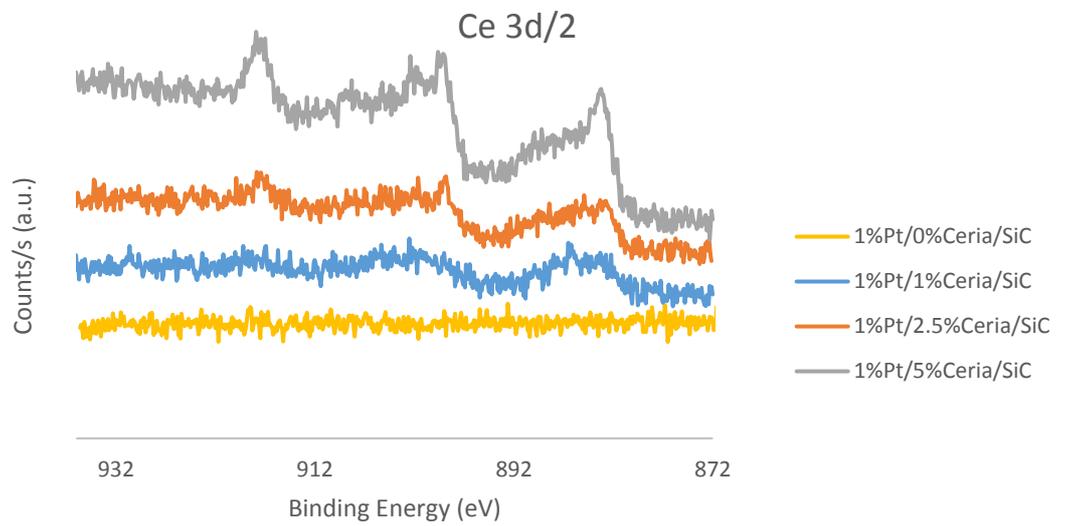
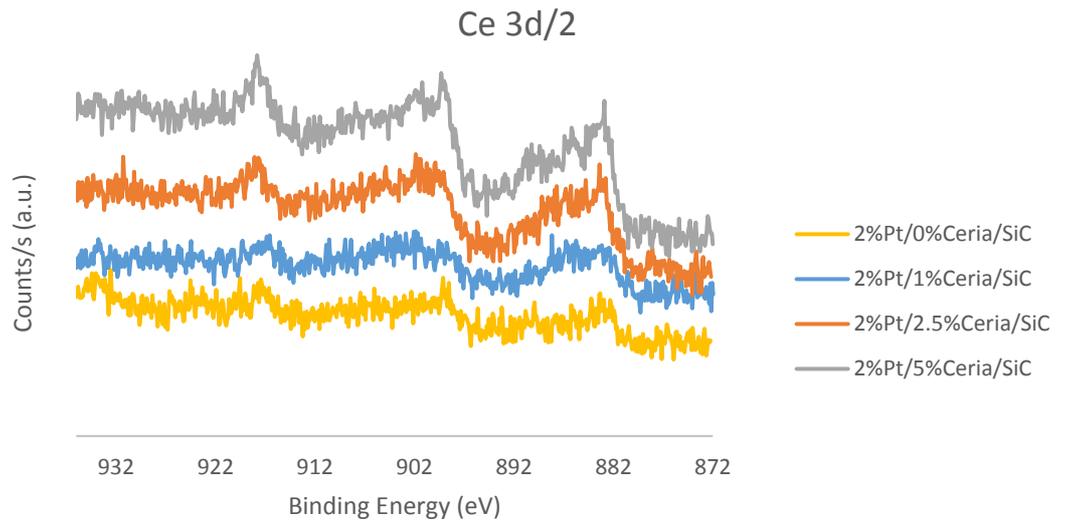
Post reaction characterisation can be found in section 4.2.5 where thermogravimetric analysis and atomic emission spectroscopy were carried out.

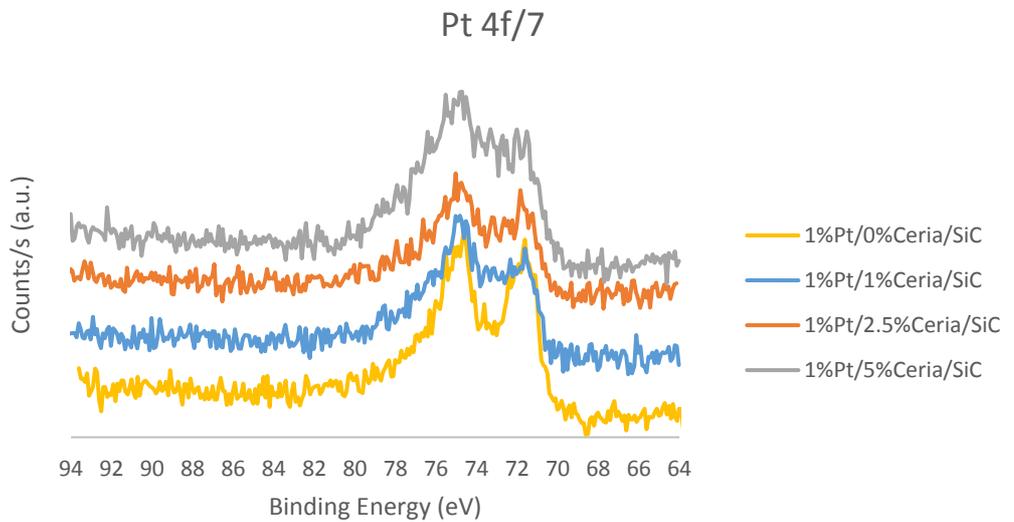
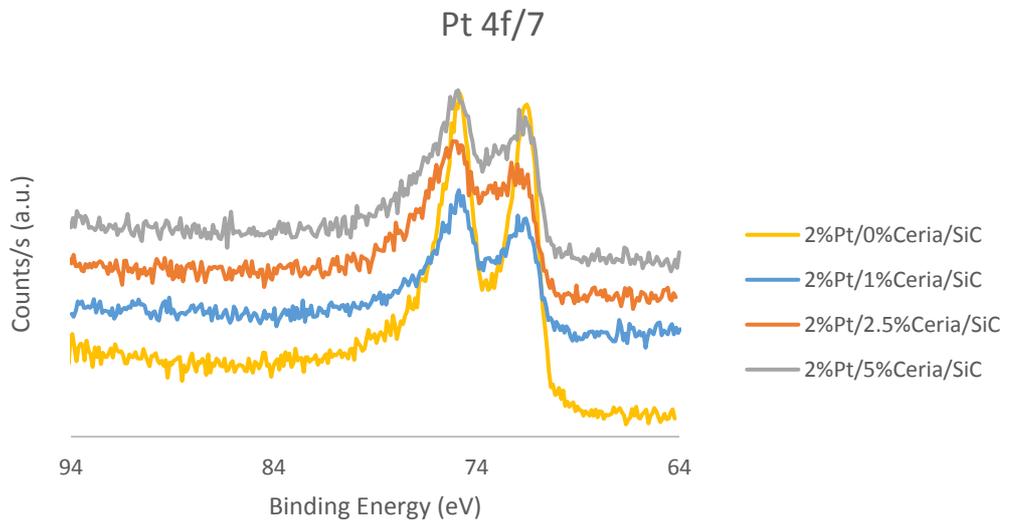
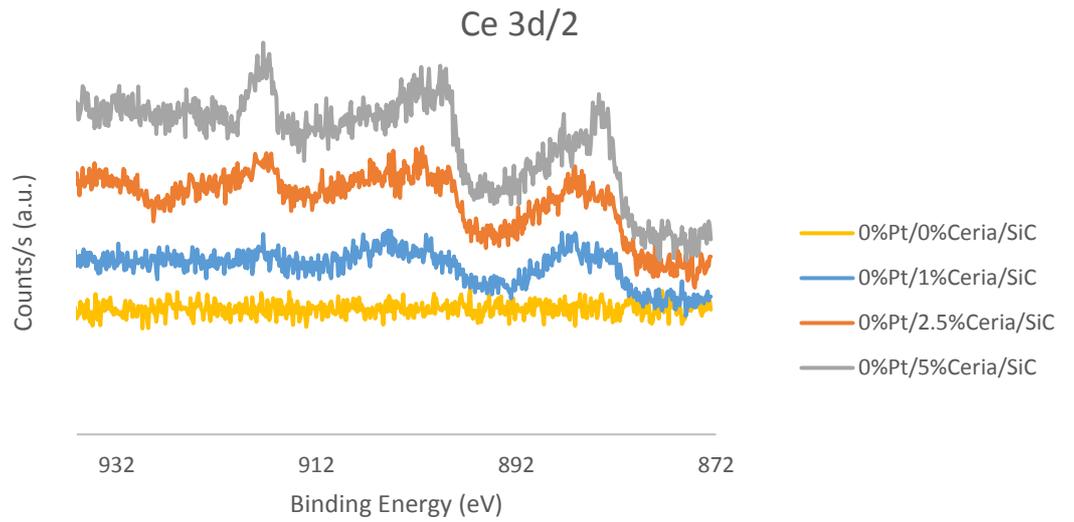
The characterisation shown here consisted of X-ray photoelectron spectroscopy (XPS) and provided information regarding the actual loading of the platinum and ceria on the SiC support

6.1.5. X-ray photoelectron spectroscopy (XPS)

XPS is a qualitative analysis technique and can give information with regards to the oxidation state of species at the surface of the catalyst¹³. Even though the technique can quantify surface elemental compositions, it is not able to quantify the bulk.

Below are XPS spectra of all the catalysts that were shown in the table above. The spectra focused on the ceria and platinum elements of the catalysts.





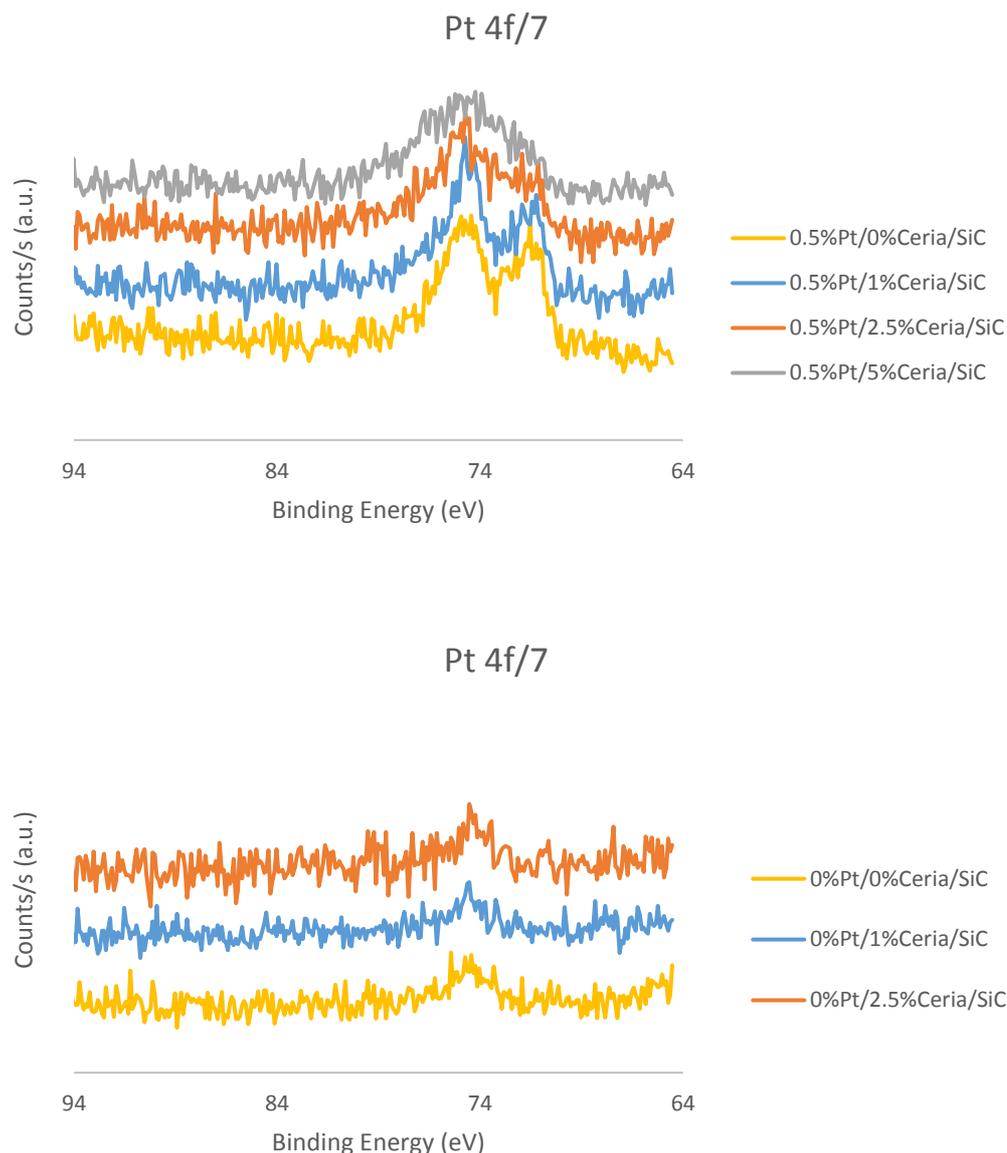


Figure 6.1 XPS binding energy profiles of ceria and platinum for all the catalysts tested

For the platinum spectra, the peak shown on the right is related to Pt^0 and the peak that shows up in between the two main peaks (73 eV) is related to Pt^{2+} ^{13–15}. The ceria, peaks on the other hand represent Ce^{4+} (900 eV) and Ce^{3+} (884 eV) ¹¹. It can be seen that when the ceria concentration is increased, so does the Pt^{2+} peak in relation to the Pt^0 peak. This can be put down to the ability of ceria being able to donate oxygen atoms to the Pt metal much better when it is in high concentrations ¹¹.

Once characterised, the focus turned to catalyst testing. The next section shows the impact ceria had on catalytic activity. The results from the XPS analysis above was therefore used to help explain some of the activities observed.

6.2. Catalytic activity studies and correlation with structure

6.2.1. Introduction

The following study focused on the effect the active metal loadings had on activity. It involved optimising the platinum and ceria loadings on SiC to deliver the best CWAO performance.

6.2.2. Ceria loading effect on activity

The following graph represents the phenol conversion achieved by the various platinum and ceria loaded catalyst. Due to the high level of activity achieved by the Pt/SiC system previously, the temperature was reduced to 120°C to ensure total phenol conversion was not achieved. This ensured that 100% conversion was not reached and that a better comparison between each of the catalyst could be made.

The following graph represents the phenol conversion as a function of increasing ceria concentration on four catalysts with different platinum loadings. The loadings were based on theoretical concentrations of platinum and ceria.

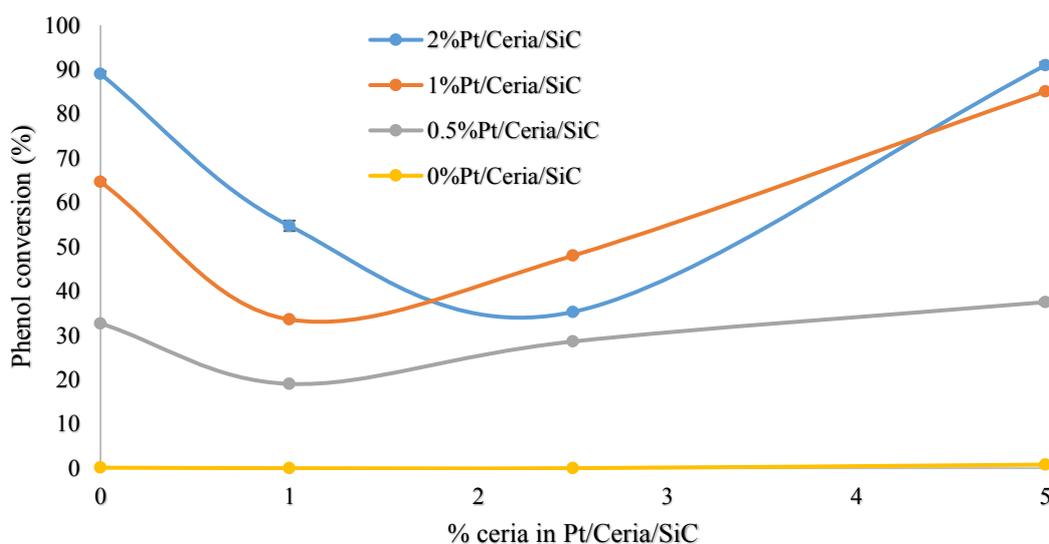


Figure 6.2 The effect of varying platinum and ceria loadings on SiC at 120°C

In general, the phenol conversion increased with increasing platinum concentration. This was true for every case apart from the anomaly seen for 2%Pt/2.5%Ce/SiC. Here the phenol conversion was less than what it was when only 1wt. % of platinum was present. It was established that increasing the platinum concentration increased the catalytic activity in every case apart from this one, therefore some other factor must have been responsible for the anomaly.

Increasing the ceria loading, on the other hand, decreased phenol conversion at low concentrations but increased as the loadings reached higher values. This formed a ‘U’ shaped conversion-ceria concentration profile. This phenomena was seen for each catalyst type apart from when there was no platinum present. It was expected that ceria would have had a positive effect on activity regardless of its concentration.

As platinum was the main contributor towards activity, it was not surprising to see a correlation between its loading and phenol conversion, regardless of the amount of ceria present. This effect was seen also when there was no platinum present; even at high concentration levels of ceria the conversion remained close to 0%.

The trend can be seen for each ceria loaded type apart from the anomaly at 2.5% ceria loading. This was the only occurrence where an increase in platinum had a negative effect on conversion. The reason for this was unknown. The graph also showed how adding some ceria had a negative impact on activity. This could be seen when comparing the catalyst where no ceria was present with the catalyst with a theoretical loading of 1%. This indicated that a small amount of ceria works against the promotion of phenol oxidation.

A similar result was seen by Rocha *et al.* where the activity dropped after introducing a low % loading of ceria in Pt-TiO₂-Ce and increased as the concentrations

got higher¹¹. The reasoning was put down to a number of factors. It was suggested that the particle sizes of the platinum were smaller for the most successful catalysts and that they were of the highest acidity compared to the ones that gave the lowest activity. It was stated also that the most active catalysts contained platinum and cerium with optimal oxidation state ratios. As the concentration of ceria increased so did the % ratio of $\text{Pt}^{2+}/\text{Pt}^0$. This occurs as the ceria allows oxygen transfer to occur in the form of oxygen to oxidise the platinum. The catalyst that predominantly consisted of Pt^{2+} (10% ceria) performed a lot worse than the catalyst that had Pt^0 in more equal proportions (3 & 5 % Ceria) and the same was true when Pt^{2+} was in low concentration compared to Pt^0 (1% Ceria). The concentration of Ce^{4+} was lower for the 3% and 5% Ce catalysts which meant that they converted less of the Pt^0 to Pt^{2+} .

When looking at the XPS spectra of the platinum for the catalysts in this project the Pt^{2+} peak increased as a function of ceria loading. It also showed the Pt^0 peak decreasing as ceria was added initially. Previous results showed that metallic Pt promoted the best phenol conversion therefore any small increases in Pt^{2+} disrupts the successful, hydrophobically driven, oxidation mechanism. Using the added information from Rocha *et al.* it would require enough additional ceria, with good oxygen storage capacity (low Ce^{4+} %) to reach an optimum $\text{Pt}^{2+}/\text{Pt}^0$ ratio and rectify the activity lost. It was predicted that increasing the ceria concentration further would have reduced activity again.

The anomaly, mentioned previously, could have been explained by the oxygen storage capacity aspect of this reasoning too. The XPS spectra for the 1%Pt/2.5%Cerium/SiC showed a relatively smaller peak for the Ce^{4+} than for the 2%Pt/2.5%Cerium/SiC which meant that there were less Pt^0 to Pt^{2+} reactions occurring in the former. Good phenol oxidation was observed for the catalysts with more Pt^0 present.

There was a fine balance as too much ceria can diminish activity, therefore the most successful catalysts with regards to Pt/Ce systems are the ones with a relatively equal Pt^{2+}/Pt^0 ratio. This ratio allows for good oxygen storage capacity to be provided by ceria without totally oxidising the platinum. The platinum is required to be in its metallic state for a hydrophobically driven CWAO mechanism.

It seemed like in this case that the theoretical 5% Ceria catalysts was the optimum loading concentration for this Pt/Ce system. Even though the activity decreased after introducing small amounts of ceria, increasing the load to 5% not only restored the original activity but has also improved it. The ceria may be able to use its transfer capabilities to deliver oxygen to the platinum to be activated but it can also directly oxidise phenol in locations where sufficient wetting might occur. Although SiC is predominantly hydrophobic, it is likely that there are some hydrophilic locations on the surface. This was true for RuO_2 on alumina as the wetting was significantly higher than that of the SiC support and the reaction relied more on direct oxidation.

It can be seen from the graph above that the platinum in Pt/5%Cerium/SiC could be thrifted from 2% to 1% wt. loading and not affect phenol conversion significantly.

6.2.3. Conclusion

To conclude, phenol CWAO was highly affected by the introduction of ceria. The results showed the relatively high activity achieved by the hydrophobic Pt/SiC system when no ceria was present and decreased when ceria was introduced in small concentrations. The activities did not get restored until higher amounts of ceria was added. This was thought to be down to the oxidation states of Pt reaching an optimum ratio to allow for the oxidation of phenol to occur more efficiently. Ceria, in its optimum concentration, ensured that not all the metallic platinum was oxidised whilst maintaining

good oxygen storage capacity. It therefore allowed platinum to be thrifted to lower concentrations whilst achieving the same level of phenol conversion.

It is worth noting though, with reference to previous research, that too much oxygen storage capacity, as with ceria, can have a detrimental effect on catalyst lifetime^{16,17}. It is thought that the ceria diminishes the amount of Lewis acid sites on the surface and therefore promotes phenol oxidation in the para position. This leads to polymer formation and, eventually, deposition of carbon on the surface.

6.3. References

- 1 F. Arena, G. Trunfio, J. Negro and L. Spadaro, *Appl. Catal. B Environ.*, 2008, **85**, 40–47.
- 2 F. Stuber, I. Polaert, H. Delmas, J. Font, A. Fortuny and A. Fabregat, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 743–751.
- 3 A. Eftaxias, F. Larachi and F. Stüber, *Can. J. Chem. Eng.*, 2008, **81**, 784–794.
- 4 M. Koek, O. P. Kreuzer, W. D. Maier, A. K. Porwal, M. Thompson and P. Guj, *Resour. Policy*, 2010, **35**, 20–35.
- 5 D. Fino, S. Bensaid, M. Piumetti and N. Russo, *Appl. Catal. A Gen.*, 2016, 509, 75–96.
- 6 Y. Sato, S. Y. Takizawa and S. Murata, *J. Photochem. Photobiol. A Chem.*, 2016, **321**, 151–160.
- 7 J. Giménez-Mañogil and A. García-García, *Fuel Process. Technol.*, 2015, **129**, 227–235.
- 8 P. V. Gosavi and R. B. Biniwale, *J. Power Sources*, 2013, **222**, 1–9.

- 9 I. P. Chen, S. S. Lin, C. H. Wang and S. H. Chang, *Chemosphere*, 2007, **66**, 172–178.
- 10 I. P. Chen, S. S. Lin, C. H. Wang, L. Chang and J. S. Chang, *Appl. Catal. B Environ.*, 2004, **50**, 49–58.
- 11 M. A. L. Rocha, G. Del Ángel, G. Torres-Torres, A. Cervantes, A. Vázquez, A. Arrieta and J. N. Beltramini, *Catal. Today*, 2015, **250**, 145–154.
- 12 A. E. D. L. Monteros, G. Lafaye, A. Cervantes, G. Del Angel, J. Barbier and G. Torres, *Catal. Today*, 2015, **258**, 564–569.
- 13 E. P. H. & T. E. Brunauer S, *J. Am. Chem. Soc.*, 1938, **60**, 1938.
- 14 A. S. Arico, A. K. Shukla, H. Kim, S. Park, M. Min and V. Antonucci, *Appl. Surf. Sci.*, 2001, **172**, 33–40.
- 15 S. Guo, S. Dong and E. Wang, *ACS Nano*, 2010, **4**, 547–555.
- 16 J. Mikulova, S. Rossignol, J. Barbier, D. Mesnard, C. Kappenstein and D. Duprez, *Appl. Catal. B Environ.*, 2007, **72**, 1–10.
- 17 G. Lafaye, J. Barbier and D. Duprez, *Catal. Today*, 2015, **253**, 89–98.

Chapter 7

Conclusions

In this study several catalysts were tested and screened for their performance in promoting CWAO of phenol in a trickle flow reactor. It was discovered from an intensive literature review of the relevant catalysts that there was room for improvement in terms of performance. The aim, therefore, was to develop a resilient and stable catalyst that was able to promote total oxidation of phenol without being affected by the harsh conditions of the reactor.

Not only was the focus on developing a successful catalyst, much work was carried out on commissioning a reactor and optimising the process. Moreover, an analysis method was developed in the way of a HPLC with a UV detector to quantify the catalytic performance.

Each of the catalysts tested were characterised to determine their structure. These characterisation methods consisted both of surface and bulk techniques to give the information required to correlate activity to structure.

The initial screening process intended to attain the best metal and support combination for this CWAO reaction. It was discovered that the carbon based catalysts strongly adsorbed phenol and did not provide much activity in terms of oxidation. Platinum, on the other hand, promoted phenol oxidation to a much higher level, regardless of the type of support. Of the two supports tested, the more hydrophobic SiC promoted

the best phenol conversion result; alumina's more hydrophilic nature hindered the oxygen activation process through wetting.

The reaction with ruthenium, on the other hand, preferred alumina as the support. In this case, due to the metal being in the oxide form, catalyst wetting was favoured as this provided optimal mass transfer conditions. It was therefore proposed that when the active sites are metallic, the optimum support surface is highly hydrophobic but when they consisted of metal oxides, the optimum support surface is hydrophilic. Of the two successful catalysts (Pt/SiC and Ru/Alumina), the former promoted the greatest phenol conversion and oxidation. 2%Pt/SiC managed to promote >99% conversion and >95% selectivity towards total oxidation at 160°C and 13.1 bar(g), even after 55 hours of testing. Its performance remained at a high level (98%) even after lowering the temperature to 140°C.

This led to a more in-depth study being carried out on the effect of hydrophobicity on activity. The study consisted of Pt/Alumina catalysts being hydrophobically modified in order to confirm the effect seen during the catalyst screening phase. Pt/Alumina were hydrophobically modified through their immersion in various concentrations of silane solutions. Increasing the catalyst silane loadings improved phenol oxidation during CWAO tests and confirmed the need to increase the hydrophobicity in order to achieve high activity. It was also shown that surface area plays a significant role in the reaction. Increasing the silane concentration on a low surface area alumina increased the activity more than it did for a high surface area alumina. However the high surface alumina showed better activity at low silane loadings due to surface functionality becoming more significant. In each case though, increasing the silane concentration did improve activity. Another factor to consider was whether the silane incorporated catalyst was heat-treated with N₂ or not. A catalyst that had not been pre-treated in this way caused a decrease in

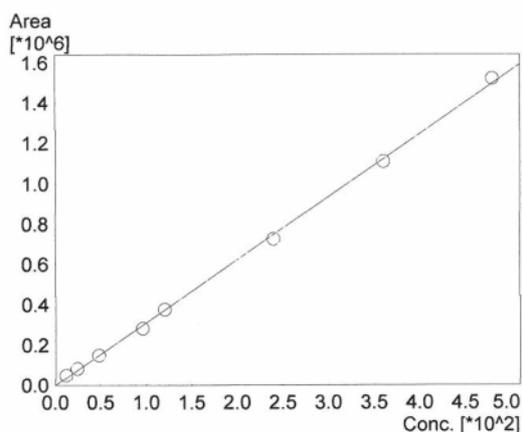
activity with the addition of silane and it was put down to precursor impurities (such as chlorine species) interfering with the oxygen activation mechanism.

A third study was carried out on the effect of doping with ceria. It was discovered during the screening phase that doping with ceria promoted oxidation over Pt/SiC and allowed the belief that the active metal could be thrifted in order to maintain performance. The study showed that although this was the case, the effect of increasing ceria concentration was not linear. Dosing with a small amount of ceria decreased activity but as the concentrations got higher the activity was restored and even improved. This was put down to ceria needing to be in an optimum ratio to the active metal in order to achieve the best activity.

To conclude, a continuous process was successfully developed for the catalytic wet air oxidation of phenol. Novel catalysts with unique characteristics were developed and could promote total phenol oxidation in a low energy intensive atmosphere. Further research is recommended to be carried out into CWAO as it has been shown to be an effective and environmentally friendly technology for treating and removing toxic compounds in advanced wastewaters.

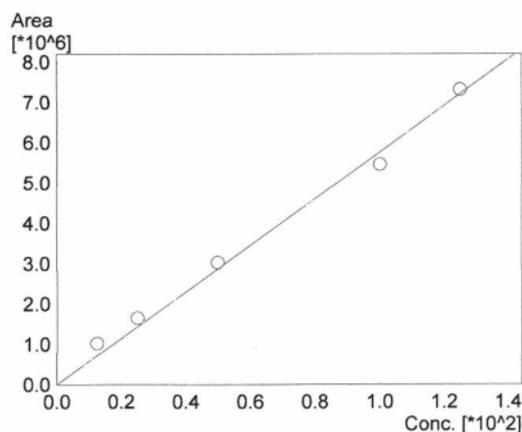
==== Shimadzu LabSolutions Calibration Curve ====

ID# : 1
 Name : Formic acid
 Quantitative Method : External Standard
 Function : $f(x)=3118.74*x+0$
 Rr1=0.9995512 Rr2=0.9991026 RSS=1.824325e+009
 MeanRF: 3.263407e+003 RFSD: 4.031657e+002 RFRSD: 12.354136
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



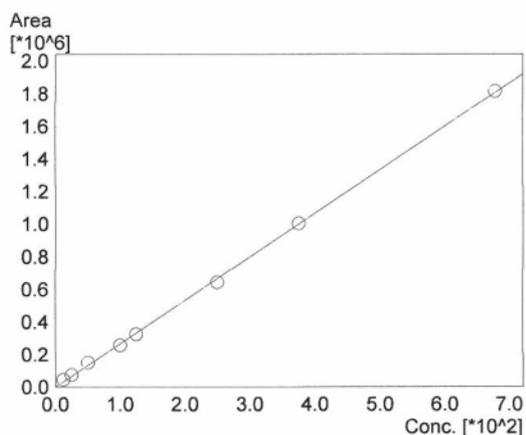
#	Conc.(Ratio)	MeanArea	Area
1	12	50163	50163
2	24	83569	83569
3	48	149007	149007
4	96	281895	281895
5	120	375665	375665
6	240	725716	725716
7	360	1109228	1109228
8	480	1520983	1520983

ID# : 2
 Name : Oxalic acid
 Quantitative Method : External Standard
 Function : $f(x)=57687.2*x+0$
 Rr1=0.9977464 Rr2=0.9954978 RSS=2.633398e+011
 MeanRF: 6.437887e+004 RFSD: 1.055446e+004 RFRSD: 16.394292
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



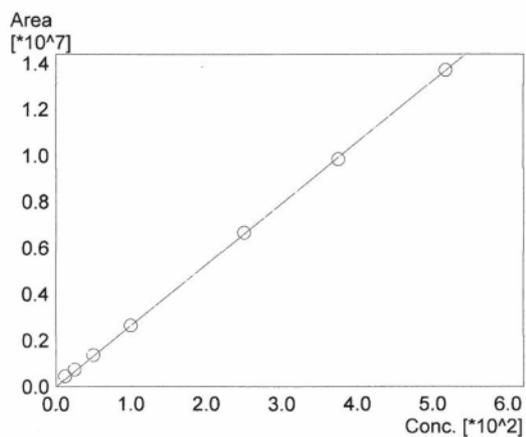
#	Conc.(Ratio)	MeanArea	Area
1	12.5	1021256	1021256
2	25	1656826	1656826
3	50	3035355	3035355
4	100	5464866	5464866
5	125	7320628	7320628

ID# : 3
 Name : Acetic acid
 Quantitative Method : External Standard
 Function : $f(x)=2665.00 \cdot x+0$
 Rr1=0.9997575 Rr2=0.9995151 RSS=1.265501e+009
 MeanRF: 2.846904e+003 RFSD: 3.881949e+002 RFRSD: 13.635685
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



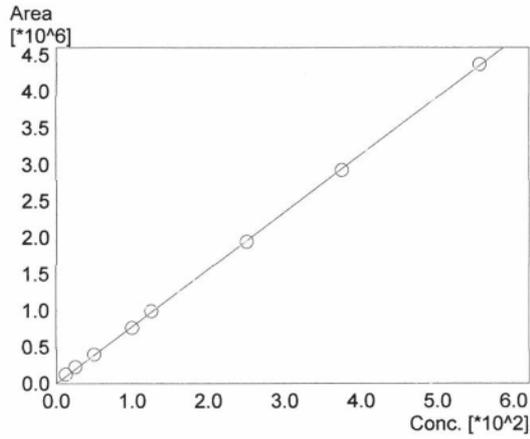
#	Conc.(Ratio)	MeanArea	Area
1	12.5	46381	46381
2	25	74414	74414
3	50	149698	149698
4	100	257416	257416
5	125	324939	324939
6	250	643061	643061
7	375	1001577	1001577
8	677	1812655	1812655

ID# : 4
 Name : Fumaric acid
 Quantitative Method : External Standard
 Function : $f(x)=26483.7 \cdot x+0$
 Rr1=0.9999415 Rr2=0.9998829 RSS=3.642154e+010
 MeanRF: 2.857017e+004 RFSD: 3.930235e+003 RFRSD: 13.756430
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



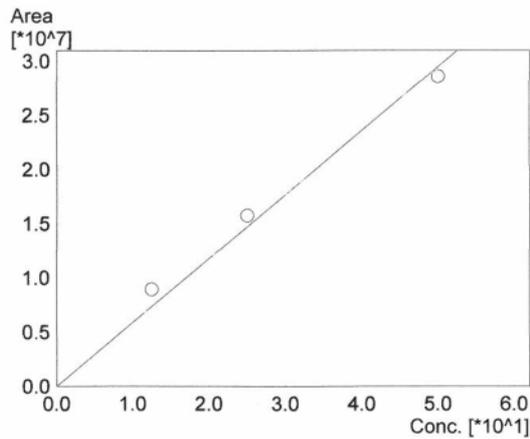
#	Conc.(Ratio)	MeanArea	Area
1	12.5	463156	463156
2	25	743978	743978
3	50	1363402	1363402
4	100	2640222	2640222
6	250	6679682	6679682
7	375	9849325	9849325
8	517	13713807	13713807

ID# : 5
 Name : Hydroquinone
 Quantitative Method : External Standard
 Function : $f(x)=7843.99*x+0$
 Rr1=0.9999156 Rr2=0.9998312 RSS=3.181576e+009
 MeanRF: 8.264010e+003 RFSD: 8.183704e+002 RFRSD: 9.902824
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



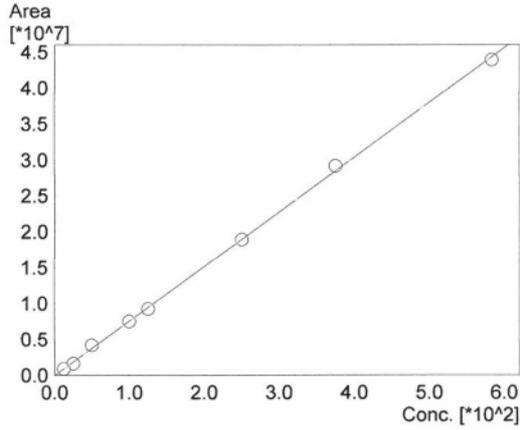
#	Conc.(Ratio)	MeanArea	Area
1	12.5	124820	124820
2	25	225956	225956
3	50	401268	401268
4	100	766084	766084
5	125	994321	994321
6	250	1944838	1944838
7	375	2921935	2921935
8	555	4371331	4371331

ID# : 6
 Name : Maleic acid
 Quantitative Method : External Standard
 Function : $f(x)=590426*x+0$
 Rr1=0.9998767 Rr2=0.9997534 RSS=4.340235e+012
 MeanRF: 6.399821e+005 RFSD: 7.234945e+004 RFRSD: 11.304917
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



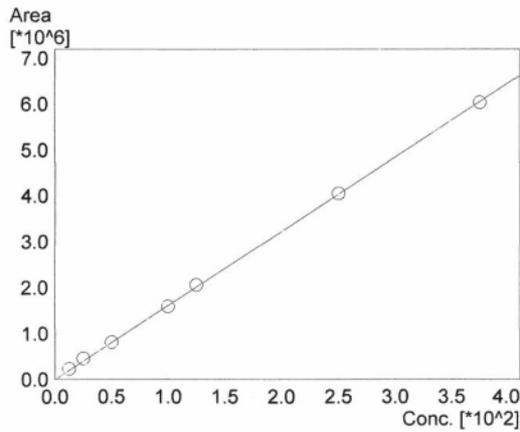
#	Conc.(Ratio)	MeanArea	Area
1	12.5	8953181	8953181
2	25	15784110	15784110
3	50	28616375	28616375

ID# : 7
 Name : Benzoquinone
 Quantitative Method : External Standard
 Function : $f(x)=75958.9 \cdot x+0$
 Rr1=0.9997185 Rr2=0.9994371 RSS=9.208797e+011
 MeanRF: 7.524121e+004 RFSD: 5.057569e+003 RFRSD: 6.721807
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



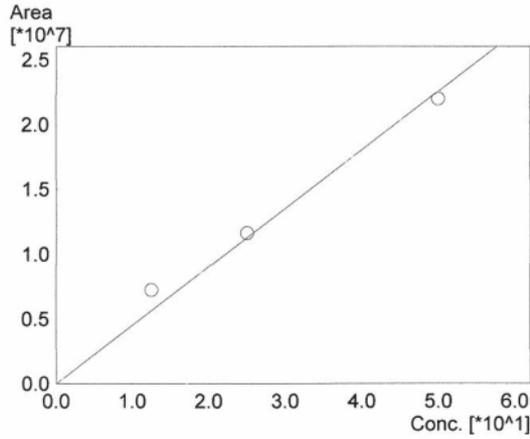
#	Conc.(Ratio)	MeanArea	Area
1	12.5	918330	918330
2	25	1643499	1643499
3	50	4203471	4203471
4	100	7546161	7546161
5	125	9296626	9296626
6	250	18929153	18929153
7	375	29183352	29183352
8	583	43888464	43888464

ID# : 8
 Name : Catechol
 Quantitative Method : External Standard
 Function : $f(x)=16163.2 \cdot x+0$
 Rr1=0.9999289 Rr2=0.9998578 RSS=7.623881e+009
 MeanRF: 1.690684e+004 RFSD: 1.208394e+003 RFRSD: 7.147365
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



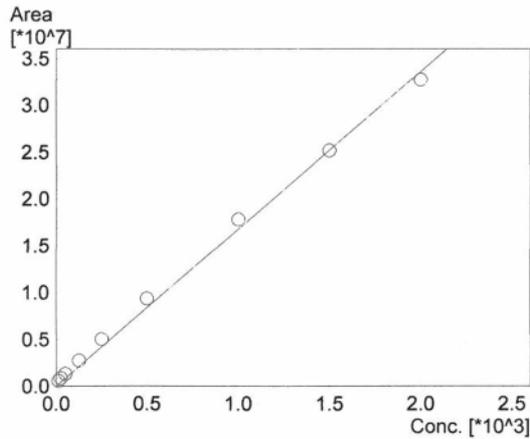
#	Conc.(Ratio)	MeanArea	Area
1	12.5	234469	234469
2	25	463912	463912
3	50	811598	811598
4	100	1597216	1597216
5	125	2065013	2065013
6	250	4051645	4051645
7	375	6038668	6038668

ID# : 9
 Name : 4-Hydroxybenzoic acid
 Quantitative Method : External Standard
 Function : $f(x)=451198*x+0$
 Rr1=0.9992775 Rr2=0.9985556 RSS=2.975215e+012
 MeanRF: 4.944308e+005 RFSD: 7.359527e+004 RFRSD: 14.884849
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



#	Conc.(Ratio)	MeanArea	Area
1	12.5	7226166	7226166
2	25	11637766	11637766
3	50	21984417	21984417

ID# : 10
 Name : Phenol
 Quantitative Method : External Standard
 Function : $f(x)=16805.1*x+0$
 Rr1=0.9993146 Rr2=0.9986297 RSS=4.415468e+012
 MeanRF: 2.440159e+004 RFSD: 1.026598e+004 RFRSD: 42.070943
 FitType : Linear
 ZeroThrough : Through
 Weighted Regression : None
 Detector Name : Detector A



#	Conc.(Ratio)	MeanArea	Area
1	12.5	587171	587171
2	25	867984	867984
3	50	1315858	1315858
4	125	2732784	2732784
5	250	5006029	5006029
6	500	9369208	9369208
7	1000	17837024	17837024
8	1500	25176197	25176197
9	2000	32716353	32716353