VANADIUM-BASED CATALYSTS FOR OXIDATION OF ORGANOSULFUR COMPOUNDS: SYNTHESIS, CATALYSIS AND MECHANISTIC STUDIES

By

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CO-SUPERVISOR             Dr. Adeniyi S. Ogunlaja
Declaration

I, Tendai Olsen Dembaremba, hereby declare that the dissertation for Master of Science is my own work and that it has not previously been submitted for assessment or completion of any postgraduate qualification to another University or for another qualification.

..................................................

Tendai Olsen Dembaremba
Foreword

The work herein contained was performed under the supervision of Professor Zenixole R. Tshentu and Doctor Adeniyi S. Ogunlaja as co-supervisor in the Nelson Mandela University Department of Chemistry as a Master of Science by research project.

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1. **T.O. Dembaremba, A.S. Ogunlaja, Z.R. Tshentu.** Investigating oxidovanadium(IV) complexes as potential catalysts for oxidative desulfurization. SACI Inorganic Chemistry Conference 2017, June 2017, Hermanus, South Africa. Oral (flash talk) and poster presentation. A silver award was received.

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I would be remiss not to recognize the undistinguished role played by my family, a family that believes in me, especially my wife Maria. Their generous support fortified my survival during this project.
Abstract

A series of oxidovanadium(IV) complexes based on the ligand, 2-(2’-hydroxyphenyl)imidazole, with substituent groups of different electronegativities on the phenolic para position, were successfully synthesized, characterized and investigated for their catalytic activities in the oxidation of dibenzothiophene (DBT), a typical refractory sulfur compound found in fuel. It was observed from catalytic oxidation studies that the presence of an electron withdrawing group on the phenolic para position of the ligand results in higher catalytic activity. SC-XRD data and DFT studies were used to explain the trends in activity observed. The highest activity was observed with 6.5 nmol of the nitro derivative catalyst [VO(PIMNO$_2$)$_2$] when 100% of 100 mg (0.543 mmol) of DBT was converted to its sulfone derivative dibenzothiophene sulfoxide (DBTO$_2$) using 2.0 mL (1.05 mmol) of $t$-BuOOH. Potential to immobilize the complex catalysts was demonstrated through the synthesis of oxidovanadium(IV) copolymer nanofibers. The oxidovanadium nanofibers were successfully employed in the oxidation of sulfur compounds in a real fuel sample (diesel 500) which were then removed through solvent extraction using acetonitrile to give clean fuel. SC-XRD, EPR and UV-Vis spectroscopy were instrumental in providing insight into the mechanism of the catalyzed reaction.

Vanadium oxides were also investigated as a cheaper alternative for the catalytic oxidation reaction. Phases of different vanadium oxides were synthesized by calcining NH$_4$VO$_3$ in air at different temperatures with an intention to investigate them for their catalytic activities. The catalyst obtained from calcination at 600$^\circ$C was predominantly the orthorhombic phase of V$_2$O$_5$. Potential to immobilize the vanadium oxides was demonstrated using a silica support where NH$_4$VO$_3$ was impregnated onto silica and calcined in air at 600$^\circ$C. The catalyst showed good potential in the oxidation of DBT to DBTO$_2$, with 10 mg (43.9 $\mu$mol) of catalyst successfully converting 100% of 100 mg (0.543 mmol) DBT to DBTO$_2$ using 2.0 mL (1.05 mmol) of $t$-BuOOH. The catalyst was also employed for a real fuel sample (diesel 500) with good results. The mechanistic aspects of vanadium oxides were also investigated in this study.

Keywords: Organosulfur, desulfurization, oxidation, oxidovanadium(IV), vanadium oxide.
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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BDS</td>
<td>Biodesulfurization</td>
</tr>
<tr>
<td>BT</td>
<td>Benzothiophene</td>
</tr>
<tr>
<td>DBT</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>DBTO</td>
<td>Dibenzothiophene sulfoxide</td>
</tr>
<tr>
<td>DBTO₂</td>
<td>Dibenzothiophene sulfone</td>
</tr>
<tr>
<td>DDS</td>
<td>Direct Desulfurization</td>
</tr>
<tr>
<td>DMDBT</td>
<td>Dimethyldibenzothiophene</td>
</tr>
<tr>
<td>DPBF</td>
<td>1,3-Diphenybisbenzofuran</td>
</tr>
<tr>
<td>EDG/EWG</td>
<td>Electron Donating Group/Electron Withdrawing Group</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GC-FID</td>
<td>Gas Chromatography equipped with a Flame Ionization Detector</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography equipped with a Mass Spectrometer</td>
</tr>
<tr>
<td>GC-SCD</td>
<td>Gas Chromatography equipped with a Sulfur Chemiluminescence Detector</td>
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<tr>
<td>HDS</td>
<td>Hydrodesulfurization</td>
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<tr>
<td>HYD</td>
<td>Hydrogenation</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductive Coupled Plasma-Optical Emission Spectroscopy</td>
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<tr>
<td>LC-TOF/MS</td>
<td>Liquid Chromatography coupled with a Time of Flight Mass Spectrometry</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>ODS</td>
<td>Oxidative Desulfurization (Oxydesulfurization)</td>
</tr>
<tr>
<td>P-XRD</td>
<td>Powder X-Ray Diffraction</td>
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<tr>
<td>SC-XRD</td>
<td>Single Crystal X-Ray Diffraction</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>t-BuOOH</td>
<td>tert-Butyl hydroperoxide</td>
</tr>
<tr>
<td>TOF</td>
<td>Turn Over Frequency</td>
</tr>
<tr>
<td>TOF-MS</td>
<td>Time of Flight Mass Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
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Outline

This Master’s thesis consists of five chapters. The first chapter is a general introduction which details the problem statement and presents the concept of oxidative desulfurization as a possible solution. A concise but extensive literature overview, around the oxidative desulfurization technique and how vanadium complexes and oxides can be applied to catalyze the oxidation step, is also covered in the chapter. The materials and methods used in the study are summarized in Chapter 2. Chapters 3 and 4 comprise the results from the research work illustrating the synthesis, characterization and use of vanadium complexes and oxides in the oxidation of dibenzothiophene. Finally, a general conclusion is given in Chapter 5.
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Chapter 1: Introduction

1.1 Crude oil
Crude oil is mainly sought due to its high hydrocarbon composition which generates large amounts of heat energy on combustion.\(^1\) Crude oil has become indispensable as a primary source of energy in modern civilizations and is a basis upon which the level of development of an economy is defined. Applications of crude oil range from domestic to industrial uses such as the generation of electricity.\(^2\) Crude oil is the backbone of the motorized industry of which over 95% of motorized transport relies on crude oil derived fuels which accounted for close to half of the crude oil consumed each year as of 2011.\(^1,2\)

Global demand for these fuel oils, particularly transportation fuel, has been escalating over the past few decades. Fuel oil consumption rose from around 70 million barrels per day in 1995 to over 80 in 2005 and is projected to grow to over 90 million barrels per day in 2020 (1 barrel = 159 L).\(^3\) **Figure 1.1** illustrates the increasing production levels of crude oils from which demand of the end-user oils from them can also be inferred.\(^4\)

![Figure 1.1 World conventional oil discoveries and production.\(^5\)](image)

1.2 Sources and availability
The use of fuel oils, especially in the motorized industry, is most likely to remain high for the unforeseeable future considering the various constraints research for alternative energy sources is facing.\(^1,4\) Only a fraction of these oil based fuels is derived from coal and natural gas through the Fischer-Tropsch process, most are derived from crude oil.\(^5\)

Crude oil is mainly recovered from tar sands and oil shale, usually after several studies; which include checking for the structural geology, sedimentary basin analysis and reservoir characterization, to confirm if the source is viable. These reserves require distillation and upgrading to produce synthetic
crude and petroleum.\textsuperscript{6} New wells are continuously being sought out, but it is increasingly becoming difficult to encounter new viable sources (\textbf{Figure 1.1}). Most discoveries are often in offshore hostile areas which cannot be exploited.\textsuperscript{2}

Production of synthetic oils (syncrudes) is an emerging field and may also become a viable source for oil. Syncrudes are produced from tar sands by a process of extraction and bitumen upgrading. Upgrading of the tar sands is difficult, with respect to hydrotreatment, since they contain two to four times as much sulfur and nitrogen compounds as standard crudes.\textsuperscript{2,7} These compounds need to be eliminated from fuel oils since they are a cause for environmental and human health concern.\textsuperscript{2}

It is also a growing concern to crude oil processing industries that quality of feedstock is depreciating.\textsuperscript{8} As crude oil sources get depleted, their feedstock progressively become heavier (density and viscosity) and sourer (high sulfur content) (\textbf{Figure 1.2}).\textsuperscript{9} Levels of sulfur compounds in fuels are also a direct product of crude diversity and source.\textsuperscript{2} Sulfur in crude oils is mainly present in the form of organosulfur compounds.\textsuperscript{1,2}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sulfur_content.png}
\caption{Increasing sulfur content as sources for crude oil get depleted over the years, from 1985 to 2010.\textsuperscript{9}}
\end{figure}

\subsection*{1.3 Organosulfur compounds in crude oil}

\subsubsection*{1.3.1 Classification of organosulfur compounds in fuel}

Organosulfur compounds may be classified as acidic, where they are mildly acidic when dissolved due to the presence of the dissociable proton or non-acidic in which case they do not influence the pH of water significantly. Acidic organosulfur compounds include thiols (mercaptans), while the thiophene, thioethers, and disulfides are examples of non-acidic organosulfur compounds (\textbf{Figure 1.3}).\textsuperscript{10}
1.3.2 Refractory sulfur compounds in fuel

Refractory organosulfur compounds (Figure 1.4) are a group of advanced polycyclic organosulfur compounds which poses challenges to the conventional methods of removing sulfur compounds from crude oil (e.g. hydrodesulfurization). Steric hindrance and electronic factors are claimed to be responsible for their low reactivities. They are classified into four groups according to their persistence:

(i) Sulfur compounds dominated by alkyl benzothiophenes (BTs).

(ii) Dibenzothiophenes (DBT) and alkyl benzothiophenes (DBTs) without alkyl substituents at the 4- and 6-positions.

(iii) Alkyl DBTs with only one alkyl substituent at either the 4- or 6-position.

(iv) Alkyl DBTs with substituents at the 4- and 6-positions.

Figure 1.3 Classification of organosulfur compounds.\textsuperscript{10}

1.3.3 Challenges associated with the presence of organosulfur compounds in fuel

The presence of sulfur compounds in end-user fuels will lead to release of sulfur oxides (SO\textsubscript{x}) which have several immediate and secondary deleterious effects on human health and on the environment. The following are some of the growing concerns surrounding these compounds:\textsuperscript{2,5,11}

(i) SO\textsubscript{3}, an oxidation product of SO\textsubscript{2} in the presence of a catalyst (e.g. NO\textsubscript{x}), reacts with atmospheric moisture to form H\textsubscript{2}SO\textsubscript{4}, hence acid rain.

(ii) Sulfur oxides may attach to dust and soot particles in the atmosphere to form particulates which increase severity of existing respiratory and pulmonary difficulties (e.g. asthma and heart disease).
(iii) Poisoning of catalysts used in emission control systems (catalytic converters) for cars which are crucial for reducing release of nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO) and unburnt hydrocarbons into the atmosphere which contribute to global warming.

(iv) Sulfur oxides are also known to have tendencies to incapacitate catalysts which are used in the fuel refining industries and acids formed from their reaction with moisture corrode engine parts.

(v) Flocculation of the sulfur compounds together with other compounds in the fuel can lead to a sediment (sludge) in the storage tanks.

Following growing environmental awareness and concerns for human health associated with the release of sulfur oxides (SO\textsubscript{x}) into the atmosphere, various countries around the globe passed mandatory legislations for end-user fuels, especially diesel, in a drive to minimize the release of sulfur oxides. Most countries, especially in the European Union and the United States of America, are looking forward to using fuels with ultra-low levels of sulfur, about 10 ppm.\textsuperscript{12-14} Figure 1.5 shows the trends of legislations being passed in different countries around the globe.\textsuperscript{2} Taking sulfur levels down to 10 ppm has been recommended in South Africa.\textsuperscript{12}

![Figure 1.5 Trends in diesel sulfur fuel specifications in the United States (US), United Kingdom (UK), European Union (EU) and South Africa (SA) over the years.\textsuperscript{17}](image)

Conventionally, hydrodesulfurization is used to remove the sulfur compounds from the fuel, albeit with some limitations.\textsuperscript{15,16} Other techniques such as bio-desulfurization, adsorption, solvent extraction and oxidative desulfurization coupled with adsorption or solvent extraction, are being explored as
alternative or complementary methods to remove the sulfur compounds from crude oil derived fuel. These techniques are discussed in greater detail in Section 1.4.

1.4 Desulfurization of crude oil
Desulfurization is a technique employed in processing crude oil to minimize the levels of sulfur in end-user fuels. Several methods have been proposed in that regard such as biodesulfurization, adsorption and extraction, but hydrodesulfurization has been the most prominent due to its efficiency on the wider spectrum of sulfur compounds in fuels. Other methods include biodesulfurization and desulfurization by adsorption or solvent extraction.

1.4.1 Hydrodesulfurization (HDS)
Hydro-desulfurization (HDS) involves the hydrogenation of organosulfur compounds in crude oil to produce hydrogen sulfide (H$_2$S) in the presence of a catalyst, usually CoMo/Al$_2$O$_3$ under high temperatures and pressure. Temperatures are normally between 300°C and 350°C and pressures range from 15 to 90 bars. The H$_2$S formed is then scrubbed off the fuels and further processed through the Claus process to give the elemental sulfur.$^{15,16}$

Hydrodesulfurization of polycyclic organosulfur compounds (dibenzothiophene and its analogues) proceeds via two routes; direct desulfurization (DDS) or hydrogenation (HYD).$^2$ DDS simply involves the hydrogenation of the sulfur group thereby removing it from the ring leaving a biphenyl in the case of DBT. HYD involves hydrogenation of one of the benzene rings of DBT to give tetrahydrodibenzothiophene and then further desulfurization to cyclohexylbenzene (Scheme 1.1).$^{18,19}$

![Scheme 1.1 Direct (DDS) and hydrogenation (HYD) pathways for hydrodesulfurization of dibenzothiophene.](image)
In polycyclic organosulfur compounds, HYD occurs preferentially over the DDS route especially if alkyl substituents are introduced in the 4- and/or 6-positions of DBT molecules.\textsuperscript{20} Introduction of the groups affects reactions by reducing the reaction rate of the two routes and changing the ratio between the two routes where HYD will become more dominant.\textsuperscript{21}

Obtaining ultra-low sulfur fuels through HDS is however limited by the presence of advanced polycyclic (refractory) organosulfur compounds as they pose steric hindrance to the hydrogenation catalysts. Figure 1.6 shows typical refractory organosulfur compounds which remain in high concentrations after HDS treatment.\textsuperscript{2,22} The majority of organosulfur compounds remaining in diesel fuels at a sulfur level below 500 ppm are DBTs with alkyl substituents at the 4-and/or 6-position because of lower HDS reactivity. Sulfur compounds remaining in hydrotreated oil at 30 ppm sulfur level will be DBTs with alkyl substituents at the 4-and 6-position because of lower HDS reactivity due to the increased steric hindrance.\textsuperscript{2}

\begin{center}
\textbf{Figure 1.6} Relative reactivity of advanced polycyclic organosulfur compounds towards hydrogenation.\textsuperscript{22}
\end{center}

In an effort to meet the mandatory sulfur levels specified by most legislations (below 10 ppm), intensification of the conditions (temperature and pressure) and improvement of the catalysts used for the conventional hydrodesulfurization process have been explored.\textsuperscript{2, 23, 24} This process is usually referred to as ultra-deep hydrodesulfurization. However, under extremely high temperatures and high pressures, it is difficult to selectively hydrogenate the sulfur compounds without saturating olefinic compounds.
in the oil. These compounds contribute to the other fuel specifications such as the octane rating. Hydrogenating the compounds will result in fuels which will fall out of these requirements. The high costs involved in such extreme conditions such as the use of excess hydrogen gas and energy also makes the method less viable as an alternative. Further development of the catalysts used for HDS in order to avoid the use of extreme conditions seems challenging, since only minor improvements were achieved over the past five decades. These need to be improved by a factor of about 3.2 to 7 to meet the prospective low sulfur fuel specifications, which is seemingly far-fetched. Conditions imposed for deep HDS also result in inhibiting effects by different poisons on the reactivity of the sterically hindered DBTs. These poisons include; nitrogen compounds, organic sulfur compounds, aromatics, oxygen compounds and \( \text{H}_2\text{S} \), and their inhibition order decreases respectively.

### 1.4.2 Biodesulfurization (BDS)

Biodesulfurization involves the use of microorganisms which consume organosulfur compounds in a bid to reduce the sulfur levels in fuel oils. Various microorganisms, of which bacteria make up the majority, require sulfur for their growth and biological functionality. These microorganisms can obtain the sulfur they need from various sources. Some of the bacteria can consume thiophenic compounds such as DBT. Examples are the *Brevibacterium sp.* and the *Pseudomonas sp.* which are reported to be good and degrading DBT. These bacteria can be exploited into consuming sulfur compounds in fuels thereby reducing the sulfur levels. Two major metabolic pathways for DBT utilization have been reported; (i) ring destructive and (ii) sulfur specific pathways (Scheme 1.2).

(i) Ring destructive pathway

The ring destructive pathway (Kodama pathway) involves the initial dioxygenation of the peripheral aromatic ring of dibenzothiophene, followed by cleavage of the ring. This leads to the accumulation of 3-hydroxybenzothiophene-2-carbaldehyde as a water-soluble end product with lower carbon content than dibenzothiophene. No desulfurization occurs, in this pathway but the mineralization of DBT can be exploited.

(ii) Sulfur-specific (desulfurization) pathway

Another ring-destructive pathway proposed by van Afferden *et al.* results in the mineralization of DBT with the release of the sulfur as sulfite stoichiometrically. The pathway is sulfur-specific and involves a series of oxidation steps where dibenzothiophene (DBT) is oxidized to DBT sulfoxide (DBTO), DBT sulfone (DBTO\(_2\)), hydroxy phenyl benzene sulfinate (HPBS) to yield hydroxybiphenyl (HBP) and sulfite in the presence of oxygen and water under ambient temperature and pressure conditions. The pathway relies on biocatalysts for specificity.
Scheme 1.2 Pathways of biodesulfurization of DBT, (a) ring destructive pathway and (b) the sulfur specific pathway.²

Although the technique is a green and very attractive approach, most bacteria reported so far can only take down the sulfur content to 50 - 200 ppm at best. This is due to the much lower activity of the bacteria witnessed at low sulfur concentrations.² There is a wider range of bacteria which can act on dibenzothiophene and alkyl sulfides but only a few are known for benzothiophene, and thiophene.²⁶ Biodesulfurization is also faced with several other limitations which include:¹⁷

(i) Production of active resting cells (biocatalysts) with a high specific activity;
(ii) Preparation of a biphasic system containing oil fraction, aqueous phase and biocatalyst;

(iii) Biodesulfurization of a wide range of organosulfur compounds at a suitable rate;

(iv) Separation of desulfurized oil fraction, and recovery of the biocatalyst and its return to the bioreactor; and


1.4.3 Desulfurization by adsorption or solvent extraction

1.4.3.1 Adsorption

Several sorbents have been reported, and some of the major groups of sorbents are summarized in Table 1.1. Metal-organic frameworks and Ni-ZnO have shown a lot of potential in each category.

Table 1.1 Sorbent materials used for desulfurization.

<table>
<thead>
<tr>
<th>Adsorptive desulfurization</th>
<th>Reactive desulfurization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolites(^{29,30})</td>
<td>Cu-ZnO</td>
</tr>
<tr>
<td>Mesoporous materials(^{31})</td>
<td>Ni-Al(_2)O(_3)</td>
</tr>
<tr>
<td>Activated carbons(^{32,33})</td>
<td>Ni-SiO(_2)</td>
</tr>
<tr>
<td>Metal-organic frameworks (MOFs)(^{34,35})</td>
<td>Ni-ZnO</td>
</tr>
</tbody>
</table>

Sulfone specific molecularly imprinted fibres are an avenue that is closely being followed in conjunction with the oxidative technique (Section 1.4.4), for example polybenzimidazole nanofibers have been developed for this purpose.\(^{36}\) Where the interaction of the S-compound with the surface of the sorbent is physical, it is usually referred to as adsorptive desulfurization and when the interaction is chemical it is called reactive adsorption desulfurization. The physical interactions in adsorptive desulfurization are weak forces (van der Waals) and the spent sorbent can be easily flushed by using an inert gas or solvent regenerating the sorbent. In chemical adsorption S-compounds are fixed in sorbent by chemical bonds usually as sulfide, with release of the S-free hydrocarbons. Oxidation of the sulfides to SO\(_x\) in the presence of air is then used to regenerate the spent sorbent. The success of desulfurization on these techniques is banked on the adsorption capacity, selectivity, durability and regenerability of these sorbents which are still a big challenge at the moment.\(^2\)

1.4.3.2 Solvent extraction

Solvent extraction is based on the increased solubility of the relatively more polar sulfur compounds in an appropriate solvent compared to the fuel matrix. Fuel oil is contacted with a non-miscible solvent that is selective for the relatively more polar, sulfur containing compounds. The solvent containing the extracted organosulfur compounds can then be separated from the oil by decantation. The solvent can be recovered from the mixture by distillation.\(^{37}\) A desirable solvent must have a number of properties, some of which are been listed on the next page.\(^{37}\)
(i) Organosulfur compounds must be highly soluble in the solvent compared to the rest of the fuel matrix.

(ii) The boiling point of the solvent must be quite different from that of the organosulfur compounds.

(iii) The solvent must be inexpensive for process viability.

Solvents such as methanol, furfural and ethylene glycol have been reported to reduce the sulfur content of hydrotreated middle distillate sevenfold (from 0.2% to 0.029%). Acetonitrile, lactones such as a γ-butyrolactone, DMF, nitrogen-containing solvents such as amines and pyrrolidines, and sulfur-containing solvents such as DMSO and solfolane are also reported to be potential solvents for extractive desulfurization. Ionic liquids (ILs) have also been explored over the years. ILs containing Cu(I) and Ag(I) ions showed good activity due to their tendency of forming π complexes with thiophene derivatives. ILs containing 1-butyl-3-methylimidazolium, tetrafluoroborate, hexafluorophosphate, octyl sulfate, ethyl sulfate and dimethyl phosphate have shown high efficiency for desulfurization of diesel fuel. Ionic liquids can be regenerated by treating the extract with an excess of low-boiling paraffins. The biggest challenge with the use of ILs is that they are costly. ILs are actually more expensive compared to most common organic solvents. More effort needs to be put in making them cheaper and improving their recycling strategies.

1.4.4 Oxidative desulfurization

It can be noted from the discussions around desulfurization by adsorption or solvent extraction, that it is crucial for the sulfur compounds to be relatively more polar than the rest of the compounds in the fuel matrix. The polarity of the organosulfur compounds can be easily increased by incorporating an extra step of oxidizing the sulfur in the organosulfur compounds to form sulfoxides and sulfones of the respective compounds. Oxidation of these compounds followed by adsorption or solvent extraction of the relatively more polar compounds can be used to complement the traditional hydrodesulfurization technique to obtain deep-desulfurized fuels. This technique is known as oxidative desulfurization (ODS).

1.4.4.1 Description of technique

The first ODS process was proposed in 1974 where NO₂ would be used as the oxidant followed by extraction using methanol to remove sulfur containing compounds from oil fractions. In 1988, a process for purifying hydrocarbon aqueous oils containing sulfur compounds, such as shale oils, by first reacting the oil with an oxidizing gas containing NO₂ and then extracting the oxidized oil with solvents in two stages (amines and formic acid) was described. ODS involves the oxidation of the sulfur containing compounds under ambient conditions using an appropriate oxidant to form compounds that can be easily removed from oil, through extraction or adsorption, due to their increased relative polarity. The method is particularly effective for the advanced polycyclic organosulfur compounds due to their high electron density on the sulfur group (Scheme 1.3).
Scheme 1.3 Oxidative desulfurization of typical refractory organosulfur compound in fuel (dibenzo thiophene).

The oxidation of dibenzothiophene, a typical refractory organosulfur compound, goes through steps where it is oxidized into dibenzothiophene sulfoxide (A), and the gets further oxidized into dibenzothiophene sulfone (B) which is relatively much more polar and can be easily removed from the fuel through adsorption or solvent extraction to give low sulfur fuel (C). The method is quite advantageous since it is carried out under ambient conditions; low temperature and pressure, and in the absence of pressurized hydrogen which is expensive. However, the amount of oxidant consumed in the process is too high compared to the sulfur removed. Very strong oxidants and catalysts which improve the rate of oxidation and yields of oxidized organosulfur compounds are therefore required.

Choice of oxidant is quite important considering the properties of the fuel matrix. It must be noted that NO₂, which was used when the technique was first proposed, is of environmental concern since it is greenhouse gases. Nitrous oxides, including NO₂, have a long average lifetime (~150 years) which result in a net greenhouse effect of about 300 times greater than that of CO₂. Strong oxidants, capable of oxidizing organosulfur compounds, are required to donate oxygen atoms to the sulfur containing molecules to form their respective sulfoxides and/or sulfones. There is a large pool of oxidants from which to pick from. Some of the potential oxidants are discussed in the next section.

1.4.4.2 Oxidants
Peroxides have received a lot of attention because they are highly reactive. The O-O bond is weak (35-40 kcal/mol) whereas the O-H (>105 kcal/mol), C-O (80-85 kcal/mol), and C=O (160-165 kcal/mol) bonds are quite strong. Hydrogen peroxide is one of the best candidates as an oxidizing agent due to its high amount of active oxygen by mass unit (47%). The main challenge is that it can only be applied if two reaction phases are to be used – the fuel oil phase with the organosulfur compounds and a polar phase in which it can dissolve. Phase transfer catalysis, which involves the use of a transfer agent to facilitate the transfer of reagents and products at the polar-apolar phase, has been proposed to try and overcome this challenge. Mass transfer limitations make this reaction slow for industrial applications.

Organic hydroperoxides, such as tert-butyl hydroperoxide which tend to be more specific, can be used to overcome the challenge of mass transfer limitations due to their good solubility in the fuel oil. These also come with challenges of their own, such as; the high cost and low amount of active oxygen (17-10%). Hydrocarbon oxidation units can be set-up on-site to produce the hydroperoxides.
products after oxidation when using some of the organic hydroperoxides, such as tert-butyldihydroperoxide which produces tert-butyl alcohol, increase the cetane number of the fuel oil.\textsuperscript{9,49} Although organic peracids are another alternative and are even more powerful oxidants; they have to be produced \textit{in situ} by reacting hydrogen peroxide with a carboxylic acid and they tend to be highly reactive and corrosive.\textsuperscript{2,50} Some classes of peroxides which are commonly used in chemistry are presented in Table 1.2.\textsuperscript{47}

\textbf{Table 1.2} Some classes of peroxides.\textsuperscript{47}

<table>
<thead>
<tr>
<th>Class (Graphical)</th>
<th>Functional Group</th>
<th>Example</th>
<th>Functional Group</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>alkyl hydroperoxide</td>
<td>(t)-BuOOH</td>
<td>ozonide</td>
<td>1,2,4-trioxolane</td>
</tr>
<tr>
<td></td>
<td>dialkyl peroxide</td>
<td>(t)-BuOOt-Bu</td>
<td>1,2,4,5-tetraoxane</td>
<td>1,2,4,5-tetraoxane</td>
</tr>
<tr>
<td></td>
<td>peracid</td>
<td>peracetic acid</td>
<td>cyclic peroxide (endoperoxide)</td>
<td>1,2-dioxane</td>
</tr>
<tr>
<td></td>
<td>bisacyl peroxide</td>
<td>benzoyl peroxide</td>
<td>perester</td>
<td>(t)-butyl perbenzoate</td>
</tr>
</tbody>
</table>

Amount of oxidant, reaction conditions and timing are important. Contacting too much oxidant at extreme conditions with the oil for a long time may cause oxidant attacks on other less reactive oil components which may affect fuel quality.\textsuperscript{2} In some cases, washing, extraction and chemical post-treatment can be used to regenerate the oxidant for re-use.\textsuperscript{2,37,51} ODS requires large amounts of oxidants in order to get good yields. Catalysts are required to minimize the amounts of oxidants needed and to improve the rates of the oxidation process.\textsuperscript{52}

\textbf{1.5 Catalysis}

\textbf{1.5.1 Definition}

The term catalysis was coined by Berzelius in 1836 to identify a new entity capable of promoting the occurrence of a chemical reaction without necessarily getting consumed.\textsuperscript{53} It is a phenomenon by which chemical reactions are accelerated by small quantities of foreign substances, called catalysts.\textsuperscript{54} A catalyst is capable of accelerating the reaction rate or to change the selectivity of the reaction towards different products. During a reaction, an energy barrier must be overcome by the system so that products
are formed in the reaction. This barrier is usually expressed as $k_1$, and is quantified in terms of reaction rate dependency on temperature through the Arrhenius equation: $k_1 = A \times e^{\frac{-\Delta H_a}{RT}}$; where $A$ is the geometric factor, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the temperature of the reaction in (K) and $E_a$ is the activation energy (J mol$^{-1}$). A catalyst is intimately associated with the mechanism of the chemical reaction where it modifies the energy profiles of reactions so that alternative reaction pathways featuring lower activation energies are offered.$^{55}$

The oxidation of organosulfur compounds with hydroperoxides can only be efficiently carried out in the presence of catalysts.$^{52}$ Transition metals in their high oxidation states (strong Lewis acids) are required as active centres for such reactions. Mo(IV), Ti(IV), V(V) and W(IV) have been reported to show very good activity for catalysing the oxidation of the sulfur compounds into their respective sulfoxides and sulfones. Molybdenum has been the most prominent among these, although it tends to get leached into the reaction medium and the main part of its catalytic activity is due to solubilized molybdenum.$^{56-61}$ Ti-based systems, especially those supported on silica have shown the highest activity. Although Platinum Group Metals (PGMs) are very attractive due to their high catalytic activity, their high cost discourages their use.$^{62}$ As such, catalysts based on vanadium; a cheaper, abundant and readily available transition metal in South Africa which has also been reported to show good activity, have formed the basis of this study.$^{53,63}$

Catalysis can either be homogeneous where the catalyst is in the same phase as the reaction, or heterogeneous where the catalyst is in a different phase to the reaction.$^{64}$ Homogeneous and heterogeneous catalysts are compared in Table 1.3 below.$^{64}$

<table>
<thead>
<tr>
<th>Heterogeneous catalysts</th>
<th>Homogeneous catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple separation and recyclability</td>
<td>Often difficult to separate</td>
</tr>
<tr>
<td>Diverse process applicability</td>
<td>Limited process applicability (batch only)</td>
</tr>
<tr>
<td>Diffusion controlled</td>
<td>Diffusion limitations practically absent</td>
</tr>
<tr>
<td>Lower selectivity</td>
<td>Generally high selectivity</td>
</tr>
<tr>
<td>Thermally stable</td>
<td>Lower thermal stability</td>
</tr>
<tr>
<td>Well defined structure</td>
<td>Structure can be difficult to identify</td>
</tr>
</tbody>
</table>

1.5.2 Vanadium catalysed oxidation processes
Vanadium complexes and oxides are the basis for many commercial catalytic oxidation catalysts.$^{65}$ Some of the articles which cover areas where catalysts based on vanadium have been used are summarized in Table 1.4.
Table 1.4 Overview of the reactions catalysed by supported vanadium and its complexes as described in the open literature.  

<table>
<thead>
<tr>
<th>Catalytic Process</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective oxidation of alkanes and alkenes</td>
<td>67-68</td>
</tr>
<tr>
<td>Selective catalytic reduction of NO (_x) with NH(_3)</td>
<td>69-71</td>
</tr>
<tr>
<td>Oxidation of o-xylene to phthalic anhydride</td>
<td>72-73</td>
</tr>
<tr>
<td>Ammoxidation of aromatics and methylaromatics</td>
<td>74-75</td>
</tr>
<tr>
<td>Selective oxidation of methanol to formaldehyde</td>
<td>76</td>
</tr>
<tr>
<td>Oxidation of SO(_2)</td>
<td>77-79</td>
</tr>
<tr>
<td>Oxidation of aliphatic and aromatic hydrocarbons</td>
<td>80-81</td>
</tr>
<tr>
<td>Oxidation of H(_2)S</td>
<td>82-83</td>
</tr>
<tr>
<td>Oxidative dehydrogenation of alkanes</td>
<td>84-85</td>
</tr>
<tr>
<td>Decomposition of isopropylalcohol</td>
<td>86</td>
</tr>
<tr>
<td>Total oxidation of benzene</td>
<td>87</td>
</tr>
<tr>
<td>Selective oxidation of 4-methylanisole</td>
<td>88</td>
</tr>
<tr>
<td>Photo-oxidation of CO</td>
<td>89</td>
</tr>
<tr>
<td>Oxidative coupling of methane</td>
<td>90</td>
</tr>
<tr>
<td>Partial oxidation of methane to formaldehyde</td>
<td>91-93</td>
</tr>
<tr>
<td>Polymerization of olefins</td>
<td>94</td>
</tr>
<tr>
<td>Direct conversion of methane to aromatics</td>
<td>95-96</td>
</tr>
<tr>
<td>Oxidation of organosulfur compounds</td>
<td>97-103</td>
</tr>
</tbody>
</table>

The activity and selectivity of the vanadium oxide catalysts are mainly attributed to the changes in the oxidation state during the reaction hence the chemistry of vanadium is an important factor to be considered when designing catalysts based on vanadium.  

1.5.3 The chemistry and availability of vanadium  

Vanadium has an electron configuration of [Ar]4s\(^2\)3d\(^3\) and can be found in a variety of oxidation states which comprises +2 (lilac), +3 (green), +4 (blue) and +5 (yellow) as presented in Figure 1.7. V\(^{5+}\) (d\(^0\)) can be present in tetrahedral (VO\(_4\)), pentahedral (VO\(_5\)) and octahedral (VO\(_6\)) coordination environment and tends to form polyxoanions. V\(^{4+}\) (d\(^1\)) is also stable and mostly present in square pyramidal or pseudo-octahedral coordination geometry. Five-membered coordination is also observed with V\(^{3+}\) (d\(^2\)). Vanadium in the oxidation states of +3, +4 and +5 are relatively stable, while the +2 is less stable and only present under reducing conditions.  

![Image of vanadium ions](image_url)  

Figure 1.7 The colour of vanadium in some of the common oxidation states.
Dissolution of $V^{3+}$ and $V^{4+}$ species in water leads to rapid oxidation into the pentavalent state (vanadate). The pentavalent species may further polymerize mainly into the dimeric and trimeric forms, particularly at higher concentrations.\textsuperscript{105}

First discovered in 1801, vanadium is widely dispersed and relatively abundant in the earth’s crust at an average concentration of 150 mg/kg. South Africa is one of the largest producers and is estimated to be contributing 43% to the world’s vanadium production.\textsuperscript{63,105} Vanadium pentoxide ($V_2O_5$), in which vanadium is in the +5 oxidation state, is the most common commercial form. Other common commercial forms of vanadium(V) are usually obtained from the $VO_3^-$ ion, and these include ammonium metavanadate ($NH_4VO_3$), sodium metavanadate ($NaVO_3$), and sodium orthovanadate ($Na_3VO_4$). Vanadium(IV) compounds are usually derived from the vanadyl ion ($VO_2^+$) and these include vanadyl dichloride ($VOCl_2$) and vanadyl sulfate ($VOSO_4$).\textsuperscript{105}

**1.6 Catalysts based on oxidovanadium(IV) complexes**

**1.6.1 Coordination chemistry of vanadium(IV)**

Several advances have been made in understanding the catalytic properties of vanadium complexes. This is mainly inspired by understanding the biochemical aspects of the complexes since vanadium is found in haloperoxidases. This has further promoted understanding the coordination chemistry of vanadium. The coordination chemistry and stereochemical arrangements possible for vanadium are diverse (Figure 1.8). The complexes are mostly square pyramidal or distorted octahedral. Trigonal bipyramidal and pentagonal bipyramidal geometries are also possible.\textsuperscript{104,106}

![Figure 1.8](image)

**Figure 1.8** Typical stereochemical arrangements observed in vanadium species.

In order to elucidate the molecular orbital description of the vanadyl ion ($VO_2^+$), Ballhausen and Gray,\textsuperscript{107} considered $VO_2^+$ in an aqueous solution as its aquated form, the $VO(H_2O)_5^{2+}$ molecular ion. They proposed that bonding was between the vanadium 3d, 4s, and 4p orbitals, the 2s, 2p\(_x\) (2p\(_z\)) and 2p\(_z\) (2p\(_x\), 2p\(_y\)) oxide oxygen orbitals, and the sp\(_x\) hybrid oxygen orbitals (from water). The possibility of $\pi$-bonding of water oxygens was regarded as unlikely. The bonding strengths were arranged in the order ($V=O$) > (four square planar waters) > (axial water). Putting this into consideration, the following can be predicted:\textsuperscript{107}

1. A strong $\sigma$ bond between the sp\(_x\) oxygen hybrid orbital and the ($4s + 3d_z^2$) vanadium hybrid orbitals ($a_1$).
2. Two π-bonds between the oxygen $2p_x$ and $2p_y$ orbitals and the vanadium $3d_x^2$ and $3d_y^2$ (e).

3. Four σ-bonds between $sp_x$ orbitals of the water oxygens and the vanadium $(4s-3d_z^2)$ (a$_1$), $4p_x$ and $4p_y$ (e), and $3d_{x^2}$ and $3d_{y^2}$ (b$_1$) orbitals.

4. The axial water oxygen is bonded to the remaining $4p_z$ (a$_1$) orbital.

5. The vanadium $3d_{xy}$ (b$_2$) is non-bonding.

As such, energy levels can be predicted, and these are presented in Figures 1.9 and 1.10, making it possible to predict and interpret electromagnetic properties of vanadium species.$^{107}$

![Figure 1.9 Molecular orbital scheme for VO(H$_2$O)$_5^{2+}$](image)

Selbin et al.$^{108}$ also came up with an almost similar model to predict the electronic transitions that occur in vanadyl species. According to the authors, when using a ligand field approach the π-bonding of the equatorial ligands should not be neglected. Therefore, the order of the $b_1^*$ and $e_x^*$ energy levels is affected. However, depending on the nature of ligands in question, if these energy levels are so close together an inversion may occur. For example, in the case of a vanadyl complex of $C_{4v}$ symmetry, it can be predicted from the model that three electron transitions can occur as shown below.$^{108-110}$
Figure 1.10 Clustered energy level scheme for vanadyl(IV) complexes.

These three transitions typically appear in the UV-Vis range of 330 nm to 1000 nm. Spectra of complexes are also accompanied by bands at wavelengths lower than 200 nm which can be attributed to charge transfer. The lower transition band may overlap with or become occluded by the charge transfer bands.

Bonding in the vanadyl complexes can also be characterized through infrared spectroscopy since the energies of the vibrations of the bonds are in the infrared range. The vibrations are dependent primarily on \( \sigma \)-bonding although metal-ligand \( \pi \)-bonding also contributes significantly. These factors are discussed below:

1. **\( \sigma \)-Bonding**: The V-O bond involves donation of electrons from \( p_\pi \)(oxygen) orbitals to the \( d_\sigma \)(vanadium) orbitals. The stretching frequency of this bond, therefore, depends on the donating ability of the oxygen to the metal and the capacity of the metal to accept the electron density. The latter is mainly dependent on the nature of the coordinated ligands. Strong Lewis base ligands increase the electron density within the d-orbitals of the metal, thereby lowering the V-O stretching frequency and vice versa.

2. **\( \pi \)-Bonding**: Same as for \( \sigma \)-bonding, except that overlaps constitute a smaller factor.

3. **\( \pi_l \)-Bonding**: Contribution of charge from the ligand to the original \( b_2 \) atomic orbital.

### 1.6.2 Vanadium complex catalysts

**1.6.2.1 Naturally occurring catalytic vanadium complexes**

Several naturally occurring catalytic vanadium complexes have been noted to catalyze key reactions in nature, especially in biological systems. Of the enzymes found, two classes have been established: vanadate-dependent haloperoxidases and vanadium nitrogenases. Of interest to this study is the major class, vanadium-dependent haloperoxidases, which oxidize halides (iodide, bromide, chloride) in the presence of hydrogen peroxide to form halogenated organic compounds.

Vanadium atoms form part of their active sites, where they are five-coordinated in a trigonal-bipyramidal geometry. In the binding site of all these enzymes, one of the axial positions of vanadium, trans to the oxo group in the trigonal-
bipyramid, is coordinated to the azomethine nitrogen of the imidazole group from a histidine residue (Figure 1.11).\textsuperscript{111-113}

![Figure 1.11 Vanadate binding site structure of a typical vanadium-dependent haloperoxidase, Z. galactanivorans, showing the involvement of the imidazole azomethine nitrogen.\textsuperscript{113}]

These enzymes are quite robust, capable of withstanding temperatures of up to 70\textdegree C as well as surviving in organic solvents and excess H\textsubscript{2}O\textsubscript{2}.\textsuperscript{114} Their intricate designs, which afford their catalytic activity, have motivated the development of a vanadium(IV) complexes based on the imidazole group.\textsuperscript{115-117} Geometry and electronic properties play a huge role in the catalytic activity of the complex. These can be manipulated by altering some of the groups in the ligands.\textsuperscript{118}

1.6.2.2 \textit{Imidazole ligand based complex catalysts}

Imidazole refers to the parent compound of formula C\textsubscript{3}H\textsubscript{4}N\textsubscript{2}, a 5-membered aromatic heterocyclic classified as an alkaloid, while imidazoles are a class of heterocycles derived from a similar ring structure. The nitrogen double bonded to the carbon is described as the ‘azomethine’ nitrogen while the one single bonded both sides and bonds with hydrogen is described as the ‘pyrrole’ nitrogen. The boiling point is unusually high (256\textdegree C) compared other 5-membered heterocyclic compounds due to the strong hydrogen bonding in the ring.\textsuperscript{119} Several catalysts based on the imidazole and benzimidazole group have been reported over the years. Some of the ligands used to design the catalysts are shown in Table 1.5 on the next page.
Table 1.5 Structures of typical imidazole and benzimidazole ligands used to design vanadium based catalysts.104,120-125

<table>
<thead>
<tr>
<th>Imidazole</th>
<th>Benzimidazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>Name</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>1H-imidazole</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>1H-imidazole-4-carboxylic acid</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(2-pyridyl)-1H-imidazole</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(2-hydroxyphenyl)-1H-imidazole</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(2-pyridyl)-1H-benzimidazole</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(4-pyridyl)-1H-benzimidazole</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(2-benzimidazolyl) ethan-1-ol</td>
</tr>
<tr>
<td>![imidazole structure]</td>
<td>2-(hydroxyphenyl)-1H-benzimidazole</td>
</tr>
</tbody>
</table>

An attempt will be made to reproduce or improve the catalytic properties of vanadium complexes in the oxidation of sulfur compounds through a series of catalysts based on the ligand 2’-(2-hydroxyphenyl)imidazole coordinated to vanadyl. There is a large pool of techniques from which the synthesis of particular ‘imidazole’ of interest can be derived considering the plethora of imidazole synthesis techniques published over the years. Synthesis approaches include; the Debus synthesis126, Radiszewski synthesis127-129, dehydrogenation of imidazolines130, from alpha-halo ketones130, Wallach synthesis131-134, from aminonitrile and aldehyde135 and Markwald synthesis130.

1.6.2.3 Effects of electron withdrawing or donating groups on the properties of the complex catalysts
It is often observed that the introduction of electron donating and electron withdrawing substituents on complex catalysts changes the rate of organic reactions, even if the substituent is not directly involved in the reaction. This is attributed to the influence of the groups on the electronic systems of the reactants.136,137 There are two main electronic effects that substituents can exert, and these can be explained using aromatic hydrocarbon systems (arenes):138

(i) Resonance effects are those that occur through the π system and can be represented by resonance structures. These can be either electron donating where π electrons are pushed toward the arene or electron withdrawing where pi electrons are drawn away from the arene.

(ii) Inductive effects are those that occur through the σ system due to electronegativity effects. These too can be either electron donating electron donating where σ electrons are pushed toward the arene or electron withdrawing where σ electrons are drawn away from the arene.
The H atom is recognized as the standard and is regarded as having no effect in terms of the electron donating or withdrawing properties. Electron donating groups (EDG) are recognised by lone pairs on the atom adjacent to the π system, eg: -OCH$_3$ except -alkyl, -arene or -vinyl (hyperconjugation, π electrons). Electron withdrawing groups (EWG) are recognised either by the atom adjacent to the π system having several bonds to more electronegative atoms, or, having a formal +ve or δ +ve charge, eg: -CO$_2$R, -NO$_2$.$^{138,139}$ These groups are summarized in Table 1.6.$^{138}$

Table 1.6 Examples of electron donating and withdrawing groups.$^{138}$

<table>
<thead>
<tr>
<th>Electron donating groups (EDGs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-O$_2^-$</td>
</tr>
<tr>
<td>Electron withdrawing groups (EWGs)</td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>-X</td>
</tr>
</tbody>
</table>

R = alkyl groups and X = halides.

The effect of these groups on the electronic properties of the ligands, and the electronic properties and geometry of their complexes cannot be undermined as has been realized from the manifestation of the variations of these groups in various electronic spectra (e.g. EPR and UV-Vis) reported in various publications herein referenced.$^{136-140}$ Several researchers have also carried out Density Functional Theory (DFT) studies to understand the influence of having these groups in specific positions of the ligands.$^{141}$

1.6.3 Catalytic oxidation mechanism based on oxidovanadium(IV) complexes

The potential for vanadium complexes to enhance the reactivity of peroxides, particularly hydrogen peroxide and alkylhydroperoxides, is a well-known phenomenon. In most cases, the high activity is based on the interaction of the peroxides with the vanadium to form a high-valent peroxido catalytic vanadium species. The species is considered among the most active oxidants towards a variety of organic and inorganic substrates.$^{142}$ Understanding the mechanism of the reaction is of great importance in order to improve the catalysts and to extend the oxidation chemistry to other substrates and predict the nature of products. In cases where the vanadium precursors are in lower oxidation states, the first step involves oxidation of the metal centre with peroxide, to d$^0$ level, followed by the formation of the peroxido metal complex.$^{142-146}$ Although in most cases a peroxo complex is formed$^{142-144}$, some authors, usually working with Schiff base ligands have proposed the interaction of oxidovanadium(V) Schiff bases species with H$_2$O$_2$ to form an active species$^{145,146}$, VO(V)L−OOH$.^{*}$ In some cases, an equilibrium between the two is proposed.$^{142}$ However, of major discussion over the years has been the oxygen transfer step.
1.6.3.1 Mechanism of the oxygen transfer step
Several studies have been carried out over the years to try and clarify the mechanism of the oxygen transfer step. V. Conte et al.\textsuperscript{142} summarized three mechanistic pathways from literature data of the electrophilic epoxidation reaction.

1. The first pathway proposed involves a direct attack of the substrate by the electrophilic peroxido oxygen (Scheme 1.4). No intermediates are expected through this pathway but only a spirocyclic transition state (Sharpless-type mechanism).\textsuperscript{147-149}

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme_1.4.png}
\end{center}

**Scheme 1.4** Sharples-type polar mechanistic pathway for the electrophilic oxidation of double bonds with peroxo vanadium complexes.\textsuperscript{142}

2. The second pathway proposed is based on the double bond preliminarily coordinating to a vacant or labile site of the metal (Scheme 1.5), strongly reducing the nucleophilic character of the substrate resulting in the formation of a five membered peroxymetallacycle intermediate through an intramolecular 1,3-dipolar cycloaddition of the peroxido group to the coordinated alkene (Mimoun-type mechanism).\textsuperscript{150,151} Such a cyclic intermediate has been isolated, in some cases, with Pt and Pd peroxo complexes, while no direct evidence on it has been obtained with d\textsuperscript{0} peroxido species.

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme_1.5.png}
\end{center}

**Scheme 1.5** Mimoun-type polar mechanistic pathway for the electrophilic oxidation of double bonds with peroxo vanadium complexes.\textsuperscript{142}

3. The third pathway is a free radical mechanism (Scheme 1.6), in which formation of a V(IV) superoxido species, invoked in a reaction catalyzed by a vanadium polyoxometalate.\textsuperscript{152} The free radical mechanism will be discussed in Section 1.6.3.2.
1.6.3.2 Free radical mechanism oxygen transfer step
Discussions by V. Conte et al.\textsuperscript{142} around the radical reactivity of a peroxide derived from monoperoxo vanadium picolinate complex, VO(O\textsubscript{2})pic give a lot of insight on the oxygen transfer step to the substrate. They noted the formation of a radical cation-anion pair within the solvent cage as the key step. The electrophilicity of the peroxo complex is then reduced by the ligand allowing the competitive radical process to take place (Scheme 1.7).

\begin{equation}
\text{R}_{\text{S}} \sim \text{R}' \rightarrow \text{R}_{\text{S}} \sim \text{R}' + \text{oxidized substrate}
\end{equation}

Scheme 1.7 Free radical mechanism involving formation of a radical cation-anion pair.\textsuperscript{153}

The homolytic rupture of one metal-peroxo bond to form the active free radical species has also been proposed (Scheme 1.8).

\begin{equation}
\text{substrate} \rightarrow \text{oxidized substrate}
\end{equation}

Scheme 1.8 Free radical mechanism involving the homolytic rupture of one metal-peroxo bond to form the active free radical species.\textsuperscript{154}

The reactivity of the peroxo-vanadium is characterized by the simultaneous vanadium catalyzed decomposition of H\textsubscript{2}O\textsubscript{2} to form dioxygen. The interaction of two molecules of the vanadium-peroxo complex can also form an active radical anion species (Scheme 1.9).
Scheme 1.9 Interaction of two vanadium-peroxo complex molecules to form an active radical anion species.\textsuperscript{155,156}

The kinetic behavior in several decomposition reactions and reactions with substrates is reported to be autocatalytic, which is typical of radical chain mechanisms.\textsuperscript{142} The generation of free radical species such as HO• and HOO• has also been proposed to be involved in the transfer of oxygen from the active oxygen species to the substrate to be the ones which directly oxidize the substrates to give their respective products.\textsuperscript{157,158}

1.6.4 Immobilization of vanadium complex catalysts onto polymers

Heterogeneous catalysts which can be easily handled in industrial applications can be obtained by adding groups added onto ligands of the complex catalysts which allow them to be incorporated into polymers (functionalization). Polymers are desirable since their properties (e.g. functionality and chemical stability) can be easily manipulated through chemical modifications to produce unique materials with desirable functionalities.\textsuperscript{159,160}

1.6.4.1 Synthesis of polymers

Polymers are mostly synthesized, either through condensation or addition polymerization. In condensation polymerization bifunctional monomers are reacted to form the polymer with the
elimination of small molecules, usually water. Polyesters, polyamides, proteins and polysaccharides are such polymers where \(-\text{COOH}\), \(-\text{OH}\), and \(-\text{NH}\) functionalities are used. Addition polymers usually involve reactions between unsaturated organic entities to form the polymers and no molecules are eliminated in the process. Below are some of the advantages and disadvantages of the two techniques (Table 1.7).\textsuperscript{161}

**Table 1.7** Comparison between condensation and addition polymerization.\textsuperscript{161}

<table>
<thead>
<tr>
<th>Condensation polymerization</th>
<th>Addition polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only monomers are added to an active end of the forming chain. Termination from the reaction of two active chains rarely occurs.</td>
<td>Any molecules present (monomer, oligomer, polymer) can react with each other.</td>
</tr>
<tr>
<td>Monomer exists throughout the reaction and its concentration decreases steadily with time as it gets added to polymer chains.</td>
<td>Monomer also exists throughout the reaction although large quantities are consumed early in the reaction (to form oligomers that can react with each other).</td>
</tr>
<tr>
<td>Polymer forms throughout the duration of the reaction.</td>
<td>Polymer forms at the very end of the reaction, by long oligomers reacting with each other.</td>
</tr>
<tr>
<td>Molecular weight of polymer does not depend on time. Long reaction times give high degrees of conversion but do not have a major influence on the molecular weight of the polymer.</td>
<td>Long reaction times, among several other factors (e.g. stoichiometry and contaminations), plays a huge role on the synthesis of high molecular weight polymers.</td>
</tr>
<tr>
<td>The reaction mixture contains primarily monomer and polymer, and very small amounts of growing chains. Monomer concentration decreases as the polymer chains grow as the reaction proceeds.</td>
<td>Intermediate molecular species (oligomers of any length) exist throughout the reaction, with the length distribution broadening and shifting to higher molecular weight as the reaction proceeds.</td>
</tr>
</tbody>
</table>

Polymers are mostly synthesized through radical initiated addition polymerization, where reagents are used to generate radicals which then react with vinylic monomers leading to continuous chain propagation reactions which continue until they are terminated by radical coupling, combination or disproportionation.\textsuperscript{161}

1.6.4.2 *Functionalization of polymer supports*

Methods which are commonly used to functionalize polymers with the desired ligands are discussed below.\textsuperscript{104,162}

1. **Ligand immobilization strategy:** A suitable functional group in the ligand of interest is reacted with one in the polymer onto which the ligand is to be functionalized.

2. **Graft polymerization:** Reactive radicals are introduced onto the polymer surface using chemicals or radiation followed by radical polymerization with a polymerizable ligand.

3. **Co-polymerization:** A polymerizable group is added to the ligand of interest (monomerization) followed by (co)polymerization.\textsuperscript{161}

The ligand immobilization strategy is the simplest and most commonly used method. The technique is limited in cases where other required functional groups may also end up reacting with the functionality in the polymer where the ligand is being introduced.\textsuperscript{104} An alternative would be to react the ligands with
the metal of interest before incorporation into the polymer. However, this may pose challenges if the final polymer is to be fabricated into nafibers as discussed in Section 1.6.4.5. This challenge may be overcome by adding suitable functionality for polymerization to the ligand followed by polymerization or co-polymerization with a passive monomer. Techniques for synthesizing monomerized ligands are discussed in Section 1.6.4.4.

1.6.4.3 Copolymerization
To (co)polymerize the ligands of interest, suitable functionality must be added to the ligands (monomerization). The groups which can be added will depend on whether condensation or addition polymerization is to be carried out. In light of the previous discussion comparing condensation and addition polymerization, it is clear that applying the condensation polymerization technique can be difficult in cases where functionality has to be reserved for the formation of complexes since the groups are related. In such cases, addition polymerization can be explored. A number of groups (e.g. allyl, acrylates and acrylamides) can be added to the ligands using various techniques.\textsuperscript{163} The introduction of the vinyl group which was used in this study is discussed below.

1.6.4.4 Introduction of vinyl group
Unlike most techniques for adding polymerizable groups which exploit nucleophilic substitution reactions, the vinyl group cannot be directly introduced. Coupling reactions are commonly used to introduce the vinyl group to produce the desired monomers. These include; Suzuki\textsuperscript{164}, Grignard\textsuperscript{165}, Wittig-type\textsuperscript{166}, elimination\textsuperscript{167}, decarboxylation\textsuperscript{168} and the Stille coupling\textsuperscript{169,170} reactions which are summarized in Table 1.8.

Protecting groups are required, since certain nucleophilic groups may hinder carbon coupling reactions by coordinating to the catalyst and to also make sure the group is added to the desired position. There is also a risk that monomers may undergo conjugate addition and premature polymerization, which may be either radical induced or ionic hence special storage conditions need to be followed, usually in the dark at low temperatures. Radical inhibitors may also be used.\textsuperscript{170}
### Table 1.8 Examples of reactions used to introduce the vinyl group.

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Suzuki coupling</strong></td>
<td><img src="image" alt="Suzuki coupling example" /></td>
</tr>
<tr>
<td><strong>Grignard</strong></td>
<td><img src="image" alt="Grignard example" /></td>
</tr>
<tr>
<td><strong>Wittig-type</strong></td>
<td><img src="image" alt="Wittig-type example" /></td>
</tr>
<tr>
<td><strong>Elimination</strong></td>
<td><img src="image" alt="Elimination example" /></td>
</tr>
<tr>
<td><strong>Decarboxylation</strong></td>
<td><img src="image" alt="Decarboxylation example" /></td>
</tr>
<tr>
<td><strong>Stille coupling</strong></td>
<td><img src="image" alt="Stille coupling example" /></td>
</tr>
</tbody>
</table>

1.6.4.5 Fabrication of polymer fibers

Having a high surface area is very important in catalysis and this can be achieved by the use of nanometric sized catalytic material. Polymer nanofibers can be fabricated using a variety of methods which include; drawing, template synthesis, thermally induced phase separation and spinning. These methods are discussed below, and their advantages and disadvantages are summarized in Table 1.9.

1. **Drawing:** Fibers are drawn from a microdroplet of polymer solution by dipping an object, for example a micropipette, into the droplet and then drawing at a certain speed. This discontinuous process requires viscoelastic materials and has a lower limit for fiber diameters of 100 nm.

2. **Template Synthesis:** This technique utilizes a nanoporous template through which the polymer solution is pushed to produce polymer fibers which are then solidified in a suitable solvent. The diameter of the fibers is directly related to the diameter of the pores of the template and as such, excellent reproducibility can be obtained.
3. **Phase Separation:** Several steps are used in this process to produce a porous nanofibrous structure. These include: polymer dissolution, gelation, solvent extraction, freezing and freeze drying. The formation of fibers occurs due to physical incompatibility.\(^\text{174}\)

4. **Self-Assembly:** This is a ‘bottom-up’ approach in which atoms and molecules arrange through weak non-covalent interactions into well-defined structures to yield ultrafine fibers with diameters typically less than 100 nm.\(^\text{175}\)

5. **Spinning:** Electrospinning is the most common technique employed among the spinning technique and this technique is discussed in greater detail in **Section 1.6.4.6.**\(^\text{104,176}\)

### Table 1.9 Comparison of different polymer fiber fabrication techniques.\(^\text{104}\)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drawing(^\text{171})</td>
<td>- Repeatable&lt;br&gt;- Convenient&lt;br&gt;- Minimum equipment required</td>
<td>- Poor control of fiber diameters&lt;br&gt;- Discontinuous process</td>
</tr>
<tr>
<td>Template Synthesis(^\text{172,173})</td>
<td>- Repeatable&lt;br&gt;- Convenient&lt;br&gt;- Good control of diameters – different diameters obtained using different templates</td>
<td>- Limited fiber length&lt;br&gt;- Difficult to upscale process</td>
</tr>
<tr>
<td>Phase Separation(^\text{174})</td>
<td>- Excellent control over pore shape and size&lt;br&gt;- Excellent control over 3D shape&lt;br&gt;- Good consistency</td>
<td>- Little control over fiber diameter and orientation&lt;br&gt;- Longer fabrication times (many steps involved)&lt;br&gt;- Limited to specific polymers</td>
</tr>
<tr>
<td>Self-Assembly(^\text{175})</td>
<td>- Simple fabrication&lt;br&gt;- Repeatable&lt;br&gt;- Excellent control of 3D shape&lt;br&gt;- Good for obtaining smaller nanofibers</td>
<td>- Inconvenient/complex process&lt;br&gt;- Poor control of fiber diameters&lt;br&gt;- Difficult to control pore size and shape</td>
</tr>
<tr>
<td>Spinning(^\text{176})</td>
<td>- Up-scalable&lt;br&gt;- Repeatable&lt;br&gt;- Conveniet (and cheap)&lt;br&gt;- Can control fiber size and orientation to an extent&lt;br&gt;- Well established technique&lt;br&gt;- Cost effective&lt;br&gt;- Long continuous fibers produced</td>
<td>- Difficult to control porosity and pore shape&lt;br&gt;- Has lower limit to fiber diameter&lt;br&gt;- Jet instability&lt;br&gt;- Difficult to fabricate 3D shapes&lt;br&gt;- Can be time consuming&lt;br&gt;- Harmful solvent vapors</td>
</tr>
</tbody>
</table>

### 1.6.4.6 Electrospinning

Records of the electrostatic attraction of liquids date back to the 1600s as observed by William Gilbert. In 1887 Charles Vernon Boys described the process in a paper on nanofiber manufacture and in 1900 John Francis Cooley filed the first electrospinning patent.\(^\text{177}\) Electrospinning is quite a convenient and economical means to produce nanoscale fibers, as conferred in **Table 1.9.**\(^\text{104,176}\) The setup consists of a hypodermic syringe with a tube which has a needle at the end (spinneret) and a ground collector which are both connected to an electrode of a high voltage direct current power supply (**Figure 1.12\(^\text{178}\).**
A polymer solution is pumped from the syringe and extruded through the needle tip at a constant rate where it experiences the high voltage being supplied. The high voltage charges the body of the extruded polymer solution on the tip of the needle and electrostatic repulsion counteracts the surface tension and the solution is stretched. At a critical point a stream of polymer solution erupts from the surface (Taylor cone). With high molecular cohesion of the polymer solution, a continuous stream (charged liquid jet) is obtained. The continuous stream of polymer solution generated dries in flight and the mode of current flow changes from ohmic to convective as the charge migrates to the surface of the fiber. The jet is then elongated by electrostatic repulsion initiated at small bends in the fiber, until it is finally deposited on the grounded collector. Uniform fibers with diameters in the nanoscale range are obtained as a result of the elongation and thinning of the fiber from the electrostatic repulsions experienced initiated in the bends. In cases where the cohesion is not sufficient, droplets of the polymer solution are released (electrospraying) which is not ideal. The polymer, polymer solution, and other properties influence the ability to electrospin a solution as well as the morphology of the fibers obtained. These parameters are summarized in Table 1.10 below.

Table 1.10 Parameters which affect the morphology of fibers obtained through electrospinning.

<table>
<thead>
<tr>
<th>Polymer properties</th>
<th>Solution properties</th>
<th>Other properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>Viscosity</td>
<td>Substrate properties</td>
</tr>
<tr>
<td>Molecular weight distribution</td>
<td>Viscoelasticity</td>
<td>Solution feed rate</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>Concentration</td>
<td>Field strength</td>
</tr>
<tr>
<td>Solubility</td>
<td>Surface tension</td>
<td>Geometry of electrodes</td>
</tr>
<tr>
<td></td>
<td>Electrical conductivity</td>
<td>Vapor pressure of the solvent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Relative humidity</td>
</tr>
</tbody>
</table>

It is desirable to have aligned nanofibers and varying degrees of fiber alignment have been achieved through the several advancements that have been made in the collection apparatus such as using patterned electrodes, conductive substrates separated by a nonconductive gap, disc collectors, etc.
Efforts have also been made to make it possible to up-scale and increase the production rate of the electrospinning process, through for example the use of multiple jet electrospinning.179,183

1.7 Catalysts based on vanadium oxides

1.7.1 Vanadium oxides

Vanadium oxides are receiving significant attention in various applications because of their structural versatility combined with chemical and physical properties. On that basis, they have also found applications in catalysis. Vanadium is analogous to phosphorous in its higher valence states and forms covalent linkages with oxygen.184 Vanadium oxides exist in a range of single and mixed valency states (V$^{5+}$, V$^{4+}$, V$^{3+}$ and V$^{2+}$) with a large variety of structures.185 A variety of chemical classifications are used to structurally categorize vanadium-oxygen compounds. The conditions of acidity during their formation are primarily used. Orthovanadates (XVO$_4$) are formed at relatively high pH, pyrovanadate salts (X$_4$V$_2$O$_7$) at intermediate alkalinity, metavanadates (XVO$_3$) at or near neutral pH values, while under acidic conditions complex polyvanadates (X$_2$V$_6$O$_{16}$, X$_6$V$_{10}$O$_{28}$) are obtained, where X represents the cation.184 Among the naturally occurring sources of vanadium, the minerals hummerite (K$_2$.Mg$_2$.V$_{10}$O$_{28}$.16H$_2$O), metahewettite (CaV$_6$O$_{17}$.3H$_2$O), and pascoite (Ca$_6$.V$_{10}$O$_{28}$.15H$_2$O) have been established to contain vanadium in the polyvanadate class.186 Vanadium(V) oxide (V$_2$O$_5$) is the most important vanadium oxide which has been employed in a wide range of industrial applications.105 The majority of vanadium compounds are obtained in their crystalline form.184

1.7.2 Characterization of vanadium oxides

Since most vanadium oxides exist in mixed valence states and a wide range of structures, they can only be successfully characterized through a multi-technique approach. Powder XRD, FT-IR and EPR are primarily used to characterize vanadium oxides.184-189 The energy level diagram of vanadium was presented in the form of VO(H$_2$O)$_5^{2+}$ in Section 1.6.1.107 It is important in this study to clarify discussions around characterization of vanadium oxides through EPR due to their unusual behavior.187

Different types of EPR signals are obtained from vanadium oxides.185,187,190,191 A high vanadium content leads to a broad resonance line (Zeeman’s effect) in which the $^{51}$V hyperfine lines cannot be resolved, and the g-factor is less than 2.187,191 The VO$^{2+}$ ion shows hyperfine splitting of 8 equidistant lines which result from the interaction of the electron of spin $s = 1/2$ and the vanadium nucleus of spin $I = 7/2$.187,191 Further splitting may be observed with change in symmetry.190 EPR parameters of typical VO$^{2+}$ minerals are summarized in Table 1.11, where g and A are the Hamiltonian parameters, the g-factor and hyperfine splitting factor [parallel ($\parallel$) and perpendicular ($\perp$)] corresponding to the Z-axis being parallel or perpendicular to the external magnetic field, respectively.187
### Table 1.11 Typical EPR parameters of VO$^{2+}$ minerals.$^{187}$

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>$g|$</th>
<th>$g\perp$</th>
<th>$A|$ mT</th>
<th>$A\perp$ mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kainite</td>
<td>1.932</td>
<td>1.983</td>
<td>17.70</td>
<td>6.90</td>
</tr>
<tr>
<td>Apopyllite</td>
<td>1.933</td>
<td>1.982</td>
<td>18.02</td>
<td>6.02</td>
</tr>
<tr>
<td>Pascoite site I</td>
<td>1.933</td>
<td>1.988</td>
<td>18.50</td>
<td>7.60</td>
</tr>
<tr>
<td>Pascoite site II</td>
<td>1.946</td>
<td>1.976</td>
<td>20.00</td>
<td>8.20</td>
</tr>
</tbody>
</table>

EPR spectra of high vanadium concentration samples of V$_2$O$_5$ supported on TiO$_2$, Al$_2$O$_3$, SiO$_2$ have been reported to show the symmetrical Zeeman’s effect line. The signals have also been reported to exhibit an underlying hyperfine structure of isolated V$^{4+}$. Similar lines have also been observed in some samples of V$_2$O$_5$ prepared by various methods. V$_2$O$_5$ is expected to be EPR silent since it does not have unpaired electrons. Occhiuzzi et al.$^{185}$ attributed the signal to partial reduction of V$_2$O$_5$ where the V$^{4+}$ species are located in the bulk. Gupta et al.$^{191}$ discussed the same observations in one of their papers as a manifestation of a super-exchange interaction of the form V$^{4+}$-O-V$^{5+}$. Concentration of V$^{4+}$ ions is much less than the concentration of V$^{5+}$ ions. As such, the amount of V$^{4+}$ ions is the one which determines the number of V$^{4+}$-O-V$^{5+}$ chains obtained. An increase in the amount of V$_2$O$_5$ results in increased V$^{4+}$ ions which yields more V$^{4+}$-O-V$^{5+}$ chains, resulting in increased super-exchange interactions. Concentrations of supported V$_2$O$_5$ beyond a certain critical concentration result in overlapping of hyperfine lines.$^{191}$

### 1.7.3 Preparation of vanadium oxides

NH$_4$VO$_3$ is a well appreciated precursor to several other oxides of vanadium where it can be modified through hydrothermal, electrochemical, thermal and other techniques to obtain the desired oxides.$^{192-194}$ The thermal decomposition of NH$_4$VO$_3$ in air is described by the equation below.$^{192}$

$$6\text{NH}_4\text{VO}_3 \xrightarrow[\Delta]{\text{air}} (\text{NH}_4)_3\text{V}_6\text{O}_{16} \xrightarrow[\Delta]{\text{air}} (\text{NH}_4)_2\text{V}_6\text{O}_{16} \xrightarrow[\Delta]{\text{air}} \text{V}_2\text{O}_5$$

From the studies carried out by Biedunkiewicz et al.$^{192}$, it was noted that the decomposition of NH$_4$VO$_3$ proceeds in three endothermic stages with elimination of NH$_3$ being observed in all three stages. Based on XRD investigations, the final product was concluded to be V$_2$O$_5$, and the intermediates being (NH$_4$)$_2$V$_6$O$_{16}$ and (NH$_4$)$_3$V$_6$O$_{16}$. However, the conclusion on (NH$_4$)$_3$V$_6$O$_{16}$ being the product of the first stage was made based on mass balance.$^{192}$

### 1.7.4 Immobilization of vanadium oxides

#### 1.7.4.1 Catalyst preparation

The heterogeneous form of the vanadium oxide catalysts is a preferred form and as such, vanadium oxides can be supported on inorganic oxides such as Al$_2$O$_3$, TiO$_2$ and ZrO$_2$. Other commonly used supports have also been exploited, such as silica, zeolites and carbon.$^{196-202}$ Choice of support material
is important depending on the reaction since it may influence the performance of the catalyst. Silica has become an extremely popular choice as support material due to the low cost, wide availability, mechanical stability and high porosity. The following are some of the most common techniques used to disperse the vanadium oxides onto support materials.

(i) Incipient wetness method

The incipient wetness method is one of the simplest procedures for dispersing a catalyst precursor onto a support. The method involves dissolving the catalyst precursor salt in a suitable volume (usually equal to the support pore volume) of a solvent. The solution is then added to the support which will draw the solution into the pores via capillary forces. Upon drying of solvent, the crystallites of the precursor are deposited onto the support. The rate of drying of the solvent is very crucial to control the distribution of crystallites uniformly in the pores.

(ii) Ion exchange method

The ion exchange method is suitable for support materials with surfaces which can have anionic or cationic sites with the oppositely charged catalyst precursor counter-ions. The ions can then be exchanged. Catalyst systems, which need charge compensation ions are ideal materials for ion exchange. Examples are zeolites, cationic clays or layered double hydroxides, since their crystalline lattice bears electric charges. It is important to control the isoelectric point of the solution to ensure that the ions exchange. The number of ions exchanged depends on the ion exchange sites. Although the method gives a uniform distribution of isolated metal centers, it is only suitable for low concentration metal loadings.

(iii) Deposition by precipitation

The precipitation method involves precipitation of the catalyst precursor in the pores of the support material as a hydroxide by adjusting the pH of the solution followed by drying. The method is usually more demanding due to the necessity of product separation after precipitation and large volumes of salt-containing solutions generated in precipitation processes. The method is still, however frequently applied to several catalytically relevant materials, especially for support materials. Supported metal catalysts are usually prepared by, either co-precipitation or deposition-precipitation methods.

1.7.4.2 Catalyst activation

Supporting of the precursor is usually followed by activation of the catalyst into the correct form required for catalysis. Calcination and reduction are normally employed to achieve the correct catalyst form. Calcination involves heating the catalyst precursor salt impregnated on the support at high temperatures in air in order to produce the metal oxide.
Calcination is also meant to decompose and volatilize undesirable species such as hydroxides, nitrates and carbonates. It is important to dry the mixture to avoid cracking of particles due to rapid evaporation of water trapped in the pores.\textsuperscript{203-205}

(ii) Reduction is used to convert the catalyst precursor salt or metal oxides using hydrogen, carbon monoxide or other gases. Temperature is an important factor to be considered as it has a lot of influence on the percentage dispersion, surface area and extent of reduction.\textsuperscript{203}

1.7.5 Vanadium oxides in catalytic oxidation reactions
Vanadium oxide based catalysts have been widely applied in the laboratory and industry for important reactions which include the oxidation of SO\textsubscript{2} to SO\textsubscript{3},\textsuperscript{77-79} conversion of H\textsubscript{2}S into elemental sulfur,\textsuperscript{82,83} and selective oxidation of several hydrocarbon molecules into value-added chemicals.\textsuperscript{67,80} The molecular structure and surface vanadia species, especially in supported catalysts, have been investigated for their role during hydrocarbon oxidation reactions. Below are some of the aspects which have been explored.\textsuperscript{208}

(i) The role of terminal vanadium oxide bonds.
(ii) The number of surface vanadia sites.
(iii) The influence of metal oxide additives.
(iv) The influence of surface acidic and basic sites.
(v) The influence of preparation methods.
(vi) The influence of the specific oxide support phase.

In studies of vanadium cluster species with hydrocarbon molecules carried out by Yuan \textit{et al.},\textsuperscript{209} it was reported that the anionic cluster series (V\textsubscript{2}O\textsubscript{3})\textsubscript{n}O\textsuperscript{n-} (V\textsubscript{2}O\textsubscript{6}\textsuperscript{n-}, V\textsubscript{4}O\textsubscript{11}\textsuperscript{n-}, V\textsubscript{6}O\textsubscript{16}\textsuperscript{n-}, etc.) is much less reactive than its cationic and neutral counterparts (V\textsubscript{2}O\textsubscript{3})\textsubscript{n+} and (V\textsubscript{2}O\textsubscript{3})\textsubscript{n}VO\textsubscript{3}. The aspects covered in their paper could also have an influence on the catalytic activities of the vanadium oxide clusters towards oxidation of sulfur compounds.\textsuperscript{209}

It is also becoming more apparent in catalysis that the activity of these oxides depends on the size and morphology of the particles. There is a drive towards the use of nanometric size catalysts.\textsuperscript{104}

1.7.6 Catalytic mechanism based on V\textsubscript{2}O\textsubscript{5}
The catalytic oxidation mechanism based on V\textsubscript{2}O\textsubscript{5} was described by Xu \textit{et al.}\textsuperscript{210} to involve the dissociation of V\textsubscript{2}O\textsubscript{5} to form V\textsubscript{3}O\textsuperscript{+} in solution, which gets oxidized into VO(O\textsubscript{2})\textsuperscript{+} on addition of H\textsubscript{2}O\textsubscript{2}. The peroxovanadium compound, VO(O\textsubscript{2})\textsubscript{2}\textsuperscript{-} with H\textsuperscript{+} as a counter-ion, is formed on further reaction of VO(O\textsubscript{2})\textsuperscript{+} with H\textsubscript{2}O\textsubscript{2}. VO(O\textsubscript{2})\textsubscript{2}\textsuperscript{-} is the active species in the reaction where the active oxygen is transferred to the S atom of dibenzothiophene and the sulfoxide to form the dibenzothiophene sulfone in the end.
(Scheme 1.10) \( \text{VO}(\text{O}_2)^2^- \) was noted to be very effective for the oxidation of sulfur compounds (DBT) to sulfoxides and the sulfoxide to sulfone.\(^{210,211}\)

**Scheme 1.10** Proposed mechanism of \( \text{V}_2\text{O}_5 \) catalysed oxidation of DBT to DBTO\(_2\).\(^{210}\)

### 1.8 Aims and objectives

The aim of this study was to develop catalysts based on; (i) vanadium-‘imidazole ligand’ complexes, and (ii) vanadium oxides, for the oxidation of refractory organosulfur compounds in fuel oil into organosulfone compounds which can be removed through adsorption or solvent extraction with a goal to obtain sulfur-free fuel.

In order to achieve the research aim, the following objectives were carried out:

1. Synthesizing and characterizing the vanadium-‘imidazole’ complexes and vanadium oxides to be used as catalysts;
2. Investigating the effect having electron withdrawing and donating groups on the ligands of the complex catalysts.
3. Investigating possibilities of hosting the catalysts on suitable supports, polymers and silica for the complexes and oxides, respectively;
4. Optimizing the catalytic conditions [temperature, and amounts of the catalysts, and oxidant (\(t\)-BuOOH)] in the oxidation of a model fuel sample (dibenzothiophene dissolved in acetonitrile);
5. Investigating the mechanisms of the catalyzed reactions.
6. Carrying out catalytic oxidation using a continuous flow system;
7. Applying the optimal flow system conditions in the oxidation of a real fuel sample.
Chapter 2: Experimental

2.1 Materials
The following chemicals were used in this study:
Ammonium metavanadate (99%, Sigma-Aldrich), fumed silica (powder, 0.2–0.3 µm avg., Sigma Aldrich), salicylaldehyde (99%, Sigma-Aldrich), 5-bromosalicyaldehyde (98%, Sigma-Aldrich), 5-methoxysalicyaldehyde (98%, Sigma-Aldrich), 5-nitrosalicyaldehyde (97%, Sigma-Aldrich), ammonia solution (25%, ACE), glyoxal solution (40 wt% in water, Sigma-Aldrich), benzoyl chloride, triethyl amine (99%, Merck), tributyl(vinyl)tin (97%, Sigma–Aldrich), 3,5-diterbutylcatechol (98%, Sigma–Aldrich), sodium (99%, Sigma–Aldrich), styrene (99% Sigma–Aldrich), azobisisobutyronitrile (98%, Sigma–Aldrich), vanadyl sulfate pentahydrate (98%, Sigma–Aldrich), ethanol (99.5%, Merck), sodium hydroxide (98.5%, ACE), diethyl ether (99%, Merck), dimethylformamide (99%, VWR Prolabo), glacial acetic acid (98%, Merck), tetrahydrofuran (99.5%, Merck), toluene (HPLC grade, Merck), acetonitrile (99.9% HPLC grade, Merck), hexane (HPLC grade, Merck), tert-butylhydroperoxide (t-BuOOH) (5.0-6.0M solution in decane, <4% water, Sigma-Aldrich), dibenzothiophene (99%, Merck) and 5,5-dimethyl-1-pyrroline N-oxide (97%, Sigma-Aldrich), 1.3 diphenylisobenzofuran (97%, Sigma Aldrich) and Sasol Diesel 500 (100%, Sasol).

2.2 Instrumentation

2.2.1 Nuclear Magnetic Resonance (NMR)
$^1$H NMR spectra of the ligands and oxidation products were determined using a Bruker Topspin 300 MHz spectrometer and reported relative to tetramethylsilane (δ 0.00 ppm).

2.2.2 Fourier Transform Infra-Red (FT-IR)
All infrared spectra were acquired using a Bruker Platinum ATR Tensor 27 FT-IR spectrophotometer in the mid-IR range (4000–380 cm$^{-1}$).

2.2.3 Melting point analysis
Melting points were determined using a Stuart Scientific SMP3 melting point apparatus equipped with a thermometer (0-400 °C).
2.2.4 Elemental Analysis (CHNS)

A Vario Elementary ELIII Microcube CHNS elemental analyzer was used for the CHNS elemental analysis. Calibration of the instrument was done with the use of the following standards in a linear curve adjustment within the total working range.

Standard 2: Acetanilide – C: 71.09, H: 0.67, N: 10.36%

2.2.5 X-Ray Fluorescence (XRF) analysis

Elemental composition of the \( V_xO_y \)-600°C catalyst was determined using a Bruker S1 Titan handheld XRF analyzer which was already calibrated and had its LOD determined. 0.2 g of the sample was prepared in a XRF sample cup with a 6 mm thick Mylar film window. The XRF testing was bracketed with NIST 2709 CRM standard.

2.2.6 Ultraviolet-Visible (UV-Vis) Spectroscopy

UV-Vis spectra of the complexes in acetonitrile were recorded from 200 nm to 800 nm on a Perkin Elmer Lambda 25 UV-Vis spectrophotometer using a slit width of 1 and 1 cm quartz cells.

2.2.7 Electron Paramagnetic Resonance (EPR)

EPR spectra were obtained using a Bruker ESP 300E X-band spectrometer. The parameters used during the analyses are presented in Table 2.1.

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>EPR analysis parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fields</strong></td>
<td><strong>Vanadium oxides</strong></td>
</tr>
<tr>
<td>Center Field</td>
<td>3500 G</td>
</tr>
<tr>
<td>Resolution in X</td>
<td>5000 G</td>
</tr>
<tr>
<td><strong>Microwave</strong></td>
<td></td>
</tr>
<tr>
<td>Frequency</td>
<td>9.790252 GHz</td>
</tr>
<tr>
<td>Power</td>
<td>200.00 mW</td>
</tr>
<tr>
<td><strong>Receiver</strong></td>
<td></td>
</tr>
<tr>
<td>Receiver Gain</td>
<td>(8.93\times10^3)</td>
</tr>
<tr>
<td>Mod. Phase</td>
<td>0.0 deg</td>
</tr>
<tr>
<td>Harmonic</td>
<td>1</td>
</tr>
<tr>
<td>Mod. Frequency</td>
<td>100 kHz</td>
</tr>
<tr>
<td>Mod. Amplitude</td>
<td>16.05 G</td>
</tr>
<tr>
<td><strong>Signal Channel</strong></td>
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<tr>
<td>Conversion</td>
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</tr>
<tr>
<td>Time Constant</td>
<td>1.25 msec</td>
</tr>
<tr>
<td>Sweep Time</td>
<td>100.00 sec</td>
</tr>
</tbody>
</table>
2.2.8 Powder and single crystal X-ray Diffraction (P-XRD and SC-XRD)

(i) P-XRD: P-XRD studies were performed on the vanadium(V) catalysts using a D2 Phase Bruker with Cu-Kα radiation in the range 10 < 2θdegrees < 70. Topas version 4.1 software was used to analyze the reflections.

(ii) SC-XRD: Intensity data for all the single crystals was collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo Kα radiation using APEX 2 data collection software.213 The structures were solved by direct methods applying SHELXS-2013 and refined by least-squares procedures using SHELXL-2013.214 The crystal structure diagrams were drawn with ORTEP-3 for windows.215

2.2.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Perkin-Elmer TGA 7 thermogravimetric analyser. The samples in platinum pans were heated at a rate of 10 °Cmin⁻¹ from 0ºC to 600ºC under a constant stream of nitrogen gas was used.

2.2.10 Energy Dispersive Spectroscopy (EDS) & Scanning Electron Microscopy (SEM)

Elemental analysis of samples using energy dispersive spectroscopy (EDS) was also carried out without any modifications of the samples. The samples were then gold coated for SEM analysis and viewed using a TESCAN Vega TS 5136LM Scanning Electron Microscope typically operated at 20 kV at a working distance of 20 mm.

2.2.11 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra X-ray Photoelectron Spectrometer equipped with a monochromatic Al Kα source (1486.6 eV). The base pressure of the system was below 3 x 10⁻⁷ Pa. A 75 W power source using a hybrid-slot spectral acquisition mode and an angular acceptance angle of ±20° was used to obtain the spectra. The analyzer axis made an angle of 90° with the specimen surface, with the specimen surface making an angle of 45° with the X-ray angle. A charge neutraliser was used due to the insulating surface used to prepare the sample. The elemental analysis and metal core level were recorded with a step of 1 eV and pass energy of 160 eV. The XPS data was processed using Kratos version 2 programs.216
2.2.12 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The amount of vanadium in the catalysts was determined using a Thermo Electron (iCAP 6000 Series) inductively coupled plasma (ICP) spectrometer equipped with an Optical Emission Spectrometer (OES) as a detector. The most sensitive wavelengths with minimum interferences were chosen for vanadium detection (290.88, 292.40, 309.31, and 311.07 nm). Additional instrument operating parameters are presented in Table 2.2 below.

Table 2.2 ICP-OES Operating parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Ar gas flow rate</td>
<td>5.0 Lmin⁻¹</td>
</tr>
<tr>
<td>Auxiliary Ar gas flow rate</td>
<td>1.00 Lmin⁻¹</td>
</tr>
<tr>
<td>Nebulizer Ar gas flow rate</td>
<td>0.90 Lmin⁻¹</td>
</tr>
<tr>
<td>Sampling depth</td>
<td>8.5 mm</td>
</tr>
<tr>
<td>Pump rate</td>
<td>100 rpm</td>
</tr>
<tr>
<td>N₂ addition flow rate</td>
<td>0.5 Lmin⁻¹</td>
</tr>
<tr>
<td>Cooled spraying chamber temperature</td>
<td>4°C</td>
</tr>
<tr>
<td>Selected wavelengths (Vanadium)</td>
<td>290.88 nm, 292.40 nm, 309.31 nm, 311.07 nm</td>
</tr>
<tr>
<td>Sample flush time</td>
<td>30 s</td>
</tr>
<tr>
<td>Points per peak</td>
<td>3</td>
</tr>
<tr>
<td>Time scan acquisition</td>
<td>50 ms/point</td>
</tr>
<tr>
<td>RF power</td>
<td>1150 Watts</td>
</tr>
</tbody>
</table>

2.2.13 Gas Chromatography (GC)

(i) GC-FID and GC-MS

Progress of the catalytic oxidation process was monitored using an Agilent 7890A Gas chromatograph (GC) equipped with a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column and a flame ionization detector (FID). The products for the catalytic oxidations were characterized using an Agilent 7890A GC equipped with a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column and an Agilent 5975C VL MSD mass spectrometer (MS). The conditions for the GC-FID are presented in Table 2.3 on the next page.
Table 2.3 GC-FID and MS conditions used for monitoring the progress of the oxidation.

<table>
<thead>
<tr>
<th></th>
<th>GC-FID</th>
<th>GC-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GC conditions</strong></td>
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(ii) GC-TOFMS

Analysis of fuel samples; in its original state, after oxidation of the sulfur compounds and after solvent extraction of the sulfur compounds with acetonitrile, was carried out using a LECO Pegasus GC × GC-HRT equipped with a LECO Pegasus 4D GC × GC-TOFMS detector. The conditions used for the analyses are presented in Table 2.4 on the next page.
Table 2.4 GC-HRT/TOFMS conditions used to analyse the fuel samples.

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<td>Acquisition Rate</td>
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2.3 General Methods

2.3.1 Determination of vanadium content in catalysts

The amount of vanadium in the catalysts was determined by weighing out 10 mg of each catalyst into a vial and leaching the vanadium into solution by adding 0.5 mL H₂SO₄, 0.3 mL H₂O₂ and 5 mL deionized distilled water. The solutions were filtered using 0.45 µM Millipore® filters to prevent nebulizer blockages, and diluted with deionized distilled water to 100 mL. All the solutions were analyzed by ICP-OES against six vanadium standards (1 ppm, 2 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm) standards prepared by appropriate dilutions of a 1000 ppm stock solution.

The vanadium oxide catalysts were also analyzed in solid form using X-ray fluorescence (XRF).

2.3.2 Determination of t-BuOOH concentration

To determine the concentration of the t-BuOOH sample, 5.0 mL of the t-BuOOH sample in 150 mL of water and 20 mL of 50% sulfuric acid was warmed up and then titrated using a freshly prepared 0.02 M KMnO₄ solution. The concentration of the t-BuOOH sample was the determined by relating the number of moles involved in the reaction using the equation below:

\[ 3H_2O_2 + 2KMnO_4 \rightarrow 3O_2 + 2H_2O \]
2.3.3 Catalytic oxidation studies

2.3.3.1 Oxidation of a model fuel sample under batch conditions

100 mg (0.543 mol) of dibenzothiophene dissolved in 10 mL of acetonitrile was used as a model fuel sample. Optimization studies for the catalytic oxidation reaction were carried out by varying the amount of catalyst, temperature and the amount of oxidant (t-BuOOH). For the vanadium oxide catalysts, V<sub>x</sub>O<sub>y</sub>/SiO<sub>2</sub>-600° C was used in the optimization studies and the oxidovanadium(IV)-2-(2’-hydroxyphenyl)imidazole complex, [VO(PIMH)<sub>2</sub>], was used for the complex catalyst series. The reactions were carried out at set temperatures with stirring. The required number of moles of the oxidant was added last and marked the beginning of the reaction. Progress of each oxidation reaction was monitored by drawing 100 μL aliquots after every 30 minutes and dissolving them in 0.5 mL acetonitrile before analysis using GC-FID.

Crystals of the product were obtained after filtering the reaction mixtures of any solids and allowing the acetonitrile to dry off slowly at room temperature. The oxidovanadium(IV) complex catalysts were compared for their efficiency in the catalytic oxidation of dibenzothiophene (DBT).

2.3.3.2 Oxidation of a model fuel sample under flow conditions

The optimal conditions (temperature and amount of oxidant) were adopted into a flow system where the supported catalysts (7.5 mg of V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and p(ST-co-VPIM)-VO fibers) were compared in the oxidation of 100 mg of dibenzothiophene dissolved in 10 mL acetonitrile. An improvised flow set-up (Figure 2.1) consisting of a pump driving a 20 mL syringe with an outlet leading to PTFE tubing which leads to a makeshift catalyst chamber loaded with the catalyst under investigation, where the reaction occurs before the mixture containing the oxidized sulfur compounds comes out into a collection vial. The catalyst chamber is encircled with a heating blanket maintained at 60° C during the reaction. The flow rate was varied from to 0.6 mL/hr down to 0.1 mL/hr. Three 100 μL aliquots were collected at each flow rate and dissolved in 0.5 mL acetonitrile before analysis using GC-FID.
2.3.3.3 Oxidation of a real fuel sample under flow conditions and solvent extraction of the oxidized sulfur compounds

Oxidation of a real fuel sample, Sasol Diesel 500, was carried out under the same conditions employed in the oxidation of the model fuel samples at flow rates of 0.01 mL/hr for the V₂O₅/SiO₂ catalyst and 0.02 mL/hr for p(ST-co-VPIM)-VO fibers. 100 µL of the samples were dissolved in 1500 µL of heptane and analysed using GC-SCD and TOF. The oxidized fuel samples were also washed three times using volumes of acetonitrile equivalent to the fuel, to extract the oxidized sulfur compounds. 100 µL of the desulfurized fuel samples were also dissolved in 1500 µL of heptane for GC-SCD and TOF analysis. The acetonitrile fraction was analysed without any further modifications.

2.3.4 Catalytic oxidation mechanistic studies

2.3.4.1 Electron Paramagnetic Resonance (EPR)
(i) Neat reactions

The catalytic reactions using the V₂O₅/SiO₂ catalyst and VO(PIMH)₂ were monitored using EPR spectroscopy where the signal typical for ⁵¹V (I = 7/2) was checked in the neat catalysts, after adding the oxidant and then after adding the substrate (dibenzothiophene) to the mixture. The solid V₂O₅/SiO₂ experiment was carried out in a normal EPR tube and the liquid reaction mixture of VO(PIMH)₂ was run in a flat cell.
(ii) Using a spin trap

Attempt were made to trap free radicals that may be produced during the catalytic reactions of the $V_2O_5/SiO_2$ catalyst and VO(PIMH)$_2$, using the spin trap, 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The addition of oxidant, $t$-BuOOH, to a solutions of VO(PIMH)$_2$ in DMSO which would also act as the substrate, was immediately followed by DMPO dissolved in DMSO. The solution was immediately run several times in a flat cell. An attempt was also performed using a similar strategy on the $V_2O_5/SiO_2$ catalyst albeit in a tube due to the solid nature of the catalyst.

2.3.4.2 Ultraviolet-Visible Spectroscopy (UV-Vis)

(i) VO(PIMH)$_2$ speciation upon addition of oxidant

UV-Vis spectra of a 2.9 mL solutions of 0.000104 M VO(PIMH)$_2$ in acetonitrile were recorded, upon addition of 100 µL of 0.00105 M oxidant in acetonitrile (0.100 nmol $t$-BuOOH into 0.0300 nmol catalyst), after every 20 minutes at different temperatures (30, 40, 50 and 60°C).

(iii) Singlet oxygen quenching studies

A singlet oxygen scavenger, 1,3-diphenylisobenzofuran (DPBF), was used to determine whether singlet oxygen is produced from the oxidant ($t$-BuOOH) in the presence of the catalyst [VO(PIMH)$_2$]. 1 mL volumes from each of 0.000100 M catalyst, 0.000100 M DPBF and 0.0100 M $t$-BuOOH in acetonitrile, were mixed and promptly added to a UV-Vis cuvette and spectra were then recorded every 20 minutes.
Chapter 3: Oxidovanadium(IV) complexes as catalysts

3.1 Introduction

Naturally occurring vanadium-dependent haloperoxidases, which oxidize halides (iodide, bromide, chloride) in the presence of hydrogen peroxide into halogenated organic compounds, have inspired the development of catalysts for the oxidation of sulfur compounds into their sulfoxides and sulfones.\(^{111-118}\) The oxidized products are more polar and can be easily removed from fuel using adsorbents or solvent extraction.\(^2\) The catalysts will be based on their 5-coordinated square pyramidal or trigonal bipyramidal vanadyl active sites.\(^{111-113}\) Oxidovanadium(IV)-2′-(2′hydroxyphenyl)imidazole will be used as a starting point. A series of catalysts will be prepared by substituting the phenolic para position of the catalyst with groups of different electronic properties (electron donating or withdrawing groups) to try and understand the influence of such groups in the catalytic activities of the catalysts. It will also be demonstrated through the synthesis of a copolymer between styrene and the monomerized version of the ligand that it is possible to immobilize the catalyst into polymeric materials. Due to better performances reported for nanometric sized catalysts, nanofibers will be targeted in these studies.\(^{104}\) The following studies are covered in this chapter.

1. Synthesis and characterization of a series of -H, -Br, -MeO and -NO\(_2\) substituted vanadium(IV) complexes; [VO(PIMH)\(_2\)], VO(PIMBr)\(_2\), VO(PIMMeO)\(_2\) and VO(PIMNO\(_2\))\(_2\)].
2. Synthesis and characterization of a polymer supported VO(PIMH)\(_2\) catalyst, p(VPIM-co-ST)-VO nanofibers.
3. Optimizing the catalytic oxidation conditions [temperature, amounts of the VO(PIMH)\(_2\) catalyst and amount of oxidant (t-BuOOH)] in the oxidation of a model fuel sample (dibenzothiophene dissolved in acetonitrile).
4. Comparing the vanadium complex catalysts for their catalytic activities and investigating the effect thereof, of having groups of different electronegativities in the ligands of the catalysts.
5. Catalytic oxidation of model and real fuel samples using the p(VPIM-co-ST)-VO nanofibers in a continuous flow system.
6. Investigating the mechanism of VO(PIMH)\(_2\) catalyzed oxidation reactions.
3.2 Preparatory work
3.2.1 Preparation of ligands
The ligands were prepared by following a procedure reported in literature by Gerber et al.\textsuperscript{217} for related substituted imidazoles (Scheme 3.1). 0.02 mol. of starting material [3.7 g salicyaldehyde for 2'- (2-hydroxyphenyl)imidazole (PIMH), 4.0 g 5-bromosalicyaldehyde for 2'- (2-hydroxy-5-bromophenyl)imidazole (PIMBr), 3.0 g 2-hydroxy-5-methoxybenzaldehyde for 2'- (2-hydroxy-5-methoxyphenyl)imidazole (PIMMeO) and 3.3 g 2-hydroxy-5-nitrobenzaldehyde for 2'- (2-hydroxy-5-nitrophenyl)imidazole (PIMNO\textsubscript{2})] in 25 mL ethanol (except in the case of PIMNO\textsubscript{2} where dimethyl sulfoxide was used) was mixed with 5.0 mL of a 40 % aqueous glyoxal solution at 0\textdegree C. 10.0 mL of an ice-cold 25 % aqueous ammonia solution was added and stirred for 30 minutes at 0\textdegree C. The yellow-brown mixture was then stirred overnight at room temperature. The ethanol was then removed using a rotary evaporator and the residue was extracted several times using 20 mL aliquots of diethyl ether. The diethyl ether was then removed using a rotary evaporator and the oil obtained was recrystallized from ethyl acetate to afford pure crystals of the ligands.

![Scheme 3.1 Synthesis of substituted imidazole ligands.\textsuperscript{217}](image)

3.2.1.1 Synthesis of the ligand 2'- (2-hydroxyphenyl)imidazole (PIMH)
Yield: 72%. FT-IR: 1554 cm\textsuperscript{-1}, ν (C=\textit{N}) and 1264 cm\textsuperscript{-1}, phenolic ν (C-O). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.75 (s, 1H), 7.63 (d, 1H), 7.24 (t, 1H), 7.12 (s, 2H), 7.07 (d, 1H), 6.86 (t, 1H), 5.73 (s, 1H).

3.2.1.2 Synthesis of the ligand 2'- (2-hydroxy-5-bromophenyl)imidazole (PIMBr)
Yield: 83%. FT-IR: 1528 cm\textsuperscript{-1}, ν (C=\textit{N}) and 1248 cm\textsuperscript{-1}, phenolic ν (C-O). \textsuperscript{1}H NMR (300 MHz, DMSO) δ 12.44 (s, 1H), 8.09 (s, 1H), 7.37 (dd, 1H), 7.28 (s, 2H), 7.07 (s, 1H), 6.91 (d, 1H).

3.2.1.3 Synthesis of the ligand 2'- (2-hydroxy-5-methoxyphenyl)imidazole (PIMMeO)
Yield: 63%. FT-IR: 1532 cm\textsuperscript{-1}, ν (C=\textit{N}) and 1219 cm\textsuperscript{-1}, phenolic ν (C-O). \textsuperscript{1}H NMR (300 MHz, CDCI\textsubscript{3}) δ 7.19 (s, 1H), 7.08 (s, 1H), 7.05 (s, 1H), 7.02 (s, 2H), 6.91 (s, 1H), 6.89 (s, 1H), 6.75 (d, 2H), 3.63 (s, 3H).
3.2.1.4 Synthesis of the ligand 2’-(2-hydroxy-5-nitrophenyl)imidazole (PIMNO₂)
Yield: 88%. FT-IR: 1560 cm⁻¹, ν (C=⁻N) and 1300 cm⁻¹, phenolic ν (C-O). ¹H NMR (300 MHz, DMSO) δ 13.88 (s, 1H), 8.93 (s, 1H), 8.11 (d, 1H), 7.35 (s, 2H), 7.07 (d, 1H).

3.2.2 Preparation of complexes
Complexes were prepared from the ligands using literature techniques used for similar bis-coordinated complexes (Scheme 3.2). To a solution of each ligand in methanol (except in the case of PIMNO₂ where dimethyl sulfoxide was used) was added a solution of two-fold molar quantity of vanadyl sulfate in water. Precipitates were formed immediately. These were filtered off and washed with a methanolic solution and allowed to dry in the open to yield the complexes from the different ligands.

![Scheme 3.2 Preparation of oxidovanadium complexes.](image)

3.2.2.1 Complex formation oxovanadium(IV)-2’-(2-hydroxyphenyl)imidazole [VO(PIMH)₂]
Yield: 62%. FT-IR (v, cm⁻¹): 1563, ν(C=⁻N); 1148, ν(C-O); 964, ν(V=O); 446, ν(V-N) and 409, ν(V-O). CHNS Analysis, expected (found) for C₁₈H₁₃N₄O₃V (%): C, 56.26 (56.11); H, 3.41 (3.66); N, 14.58 (14.52).

3.2.2.2 Complex formation oxovanadium(IV)-2’-(2-hydroxyphenyl)imidazole [VO(PIMMeO)₂]
Yield: 56%. FT-IR (v, cm⁻¹): 1570, ν(C=⁻N); 1099, ν(C-O); 920, ν(V=O); 466, ν(V-N) and 430, ν(V-O). CHNS Analysis, expected (found) for C₂₀H₁₇N₄O₅V (%): C, 54.06 (53.94); H, 3.86 (4.07); N, 12.61 (12.58).

3.2.2.3 Complex formation oxovanadium(IV)-2’-(2-hydroxyphenyl)imidazole [VO(PIMBr)₂]
Yield: 69%. FT-IR (v, cm⁻¹): 1563, ν(C=⁻N); 1107, ν(C-O); 920, ν(V=O); 464, ν(V-N) and 421, ν(V-O). CHNS Analysis, expected (found) for C₁₈H₁₃N₄O₃V (%): C, 39.88 (39.81); H, 2.05 (2.33); N, 10.34 (10.32).

3.2.2.4 Complex formation oxovanadium(IV)-2’-(2-hydroxyphenyl)imidazole [VO(PIMNO₂)₂]
Yield: 76%. FT-IR (v, cm⁻¹): 1560, ν(C=⁻N); 1148, ν(C-O); 992, ν(V=O); 482, ν(V-N) and 421, ν(V-O). CHNS Analysis, expected (found) for C₁₈H₁₃N₄O₃V (%): C, 45.59 (45.49); H, 2.34 (2.54); N, 17.72 (17.68).
3.2.3 Preparation of the monomerized ligand, 2’-(2-benzoxy-5’-ethenylphenyl)imidazole (PIMEthenyl)

A monomerized version of the ligand 2-(2’-hydroxyphenyl)imidazole was synthesized through a series of steps, starting off with the 5-bromo-substituted ligand (PIMBr), protection of the -NH and -OH functionalities with benzoyl groups, followed by substitution of the -Br on the phenolic para position with a vinyl group and finally removing the benzoyl protecting groups to yield the monomerized ligand with a goal to copolymerize it together with styrene to make the immobilized version of the complex [VO(PIMH)₂] (Scheme 3). Literature procedures were used for all the steps.²¹⁹,²²⁰

![Scheme 3.3 Synthesis of the monomerized ligand 2’-(2-benzoxy-5’-ethenylphenyl)imidazole, (PIMEthenyl).²¹⁹,²²⁰](image)

3.2.3.1 Synthesis of N-benzyol-2-(2’-benzoxy-5’-bromophenyl)imidazole (dibenzoyl-PIMBr)

2-(2’-Hydroxy-5’-bromophenyl)imidazole (PIMBr) 1, synthesized previously, was used as the precursor where the -OH and -NH groups were protected with benzoyl groups to give product 2 using procedures from literature.²¹⁹,²²⁰ Yield: 78%. FT-IR: 1705 and 1747 cm⁻¹, ν(C=O) from the benzoyl groups. ¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, 1H), 7.76 (d, 2H), 7.70 (d, 2H), 7.64 – 7.42 (m, 6H), 7.42 – 7.31 (m, 1H), 7.26 – 7.15 (m, 1H), 7.07 (d, 1H), 7.02 (d, 1H). CHNS Analysis, expected (found) for C₂₃H₁₅BrN₂O₃ (%): C, 61.76 (61.91); H, 3.38 (3.83); N, 6.26 (6.17).

3.2.3.2 Synthesis of N-benzyol-2-(2’-benzoxy-5’-ethenylphenyl)imidazole (dibenzoyl-PIMEthenyl)

The bromide group was substituted by the vinyl group to give product 3 using procedures from literature.²¹⁹,²²⁰ Yield: 73%. FT-IR: 1706 and 1744 cm⁻¹, ν(C=O) from the benzoyl groups. ¹H NMR
(300 MHz, CDCl₃) δ 8.18 – 8.11 (m, 2H), 7.88 – 7.77 (m, 1H), 7.64 (dd, 1H), 7.59 – 7.35 (m, 6H), 7.28 (dd, 2H), 7.18 – 7.12 (m, 1H), 7.08 (d, 1H), 7.02 (d, 1H), 6.75 – 6.59 (m, 1H, vinyl-H), 5.70 (t, 1H, vinyl-H), 5.25 (dd, 1H, vinyl-H). CHNS Analysis, expected (found) for C₂₅H₁₈N₂O₃ (%): C, 76.13 (76.23); H, 4.60 (4.66); N, 7.10 (7.25).

3.2.3.3 Synthesis of 2-(2'-hydroxy-5'-ethenylphenyl)imidazole (PIMEthenyl)
The vinyl substituted precursor was deprotected to obtain the product 4 using procedures from literature.²¹⁹,²²⁰ Yield: 53%. FT-IR: 1490 cm⁻¹, ν(C=N) and 1247 cm⁻¹, phenolic ν(C-O). ¹H NMR (300 MHz, DMSO) δ 14.28 (s, 1H), 8.29 (d, 1H), 8.02 – 7.85 (m, 1H), 7.85 – 7.43 (m, 3H), 7.35 – 7.14 (m, 1H), 6.66 (dd, 1H, vinyl-H), 5.88 (d, 1H, vinyl-H), 5.21 (d, 1H, vinyl-H). CHNS Analysis, expected (found) for C₁₁H₁₀N₂O (%): C, 70.95 (71.01); H, 5.41 (5.43); N, 15.04 (14.99).

3.2.3 Preparation of a 2-(2'-hydroxy-5'-ethenylphenyl)imidazole-styrene copolymer p(VPIM-co-ST)
The literature procedure by Walmsley et al.²¹⁹ was followed to produce the 2-(2'-hydroxy-5'-ethenylphenyl)imidazole-styrene copolymer (Scheme 3.4). FT-IR: ν(C=N) = 1494 cm⁻¹ and phenolic ν(C-O) = 1263 cm⁻¹. CHNS analysis found for the copolymer (%): C, 84.81; H, 7.38; N, 2.19.

![Scheme 3.4 Preparation of the monomerized ligand-styrene copolymer.](image)

3.2.4 Fabrication of p(VPIM-co-ST) nanofibers
Nanofibers were obtained from electrospinning a 20% solution of p(VPIM-co-ST) in DMF/THF (4:1) as reported in literature.²¹⁹ FT-IR: ν(C=N) = 1493 cm⁻¹ and 1263 cm⁻¹, phenolic ν(C-O). CHNS analysis, found for the nanofibers (%): C, 84.81; H, 7.38; N, 2.19.

3.2.5 Preparation of p(VPIM-co-ST)-VO nanofibers
Oxidovanadium(IV) was hosted onto the nanofibers as reported in literature (Scheme 3.5).²¹⁹ FT-IR (ν, cm⁻¹): 1530, (C=N); 1273, (C-O); 964, (V=O); 447, (V-N) and 415, (V-O). CHNS analysis, expected (found) for the VO-nanofibers (%): C, 77.83; H, 7.245; N, 4.55.
Scheme 3.5 Preparation of p(VPIM-co-ST)-VO fibers.\textsuperscript{219}

3.3 Results and discussion

3.3.1 Proton Nuclear Magnetic Resonance Spectroscopy (\textsuperscript{1}H NMR)

3.3.1.1 Characterization of ligands

The \textsuperscript{1}H NMR for the synthesized ligands; 2'- (2-hydroxyphenyl) imidazole (PIMH), 2'-(2-hydroxy-5- bromophenyl)imidazole (PIMBr), 2'-(2-hydroxy-5-nitrophenyl)imidazole (PIMNO\textsubscript{2}) and 2'-(2-hydroxy-5-methoxyphenyl)imidazole are presented in Figures 3.1-3.4. The splitting patterns and integrals of the proton peaks observed were as expected.\textsuperscript{104} The general chemical shifts in the aromatic regions are downfield-shifted as the substituent groups become more electronegative can be easily noted. The aromatic peaks were found between; (6.74-7.19 ppm for PIMMeO), (6.85-7.75 ppm for PIMH), (6.90-8.09 ppm for PIMBr) and (7.06-8.93 ppm for PIMNO\textsubscript{2}). These groups are clearly expected to have an influence on the donicity of the ligands \textit{via} their azomethine nitrogen and phenolic oxygen groups which are directly attached to the aromatic groups.

Figure 3.1 \textsuperscript{1}H NMR of 2'-(2-hydroxyphenyl)imidazole (PIMH).
Figure 3.2 $^1$H NMR of 2'-{(2-hydroxy-5-bromophenyl)imidazole (PIMBr).

Figure 3.3 $^1$H NMR of 2'-{(2-hydroxy-5-methoxyphenyl)imidazole (PIMMeO).

Figure 3.4 $^1$H NMR of 2'-{(2-hydroxy-5-nitrophenyl)imidazole (PIMNO$_2$).
3.3.1.2 Synthesis of the monomerized ligand (PIMEthenyl)

In the synthesis steps of the monomerized ligand (PIMEthenyl), successful protection of the pyrrolic nitrogen and phenolic oxygen by a benzoyl group can be noted from the disappearance of the protons are ascribed to the -NH and -OH groups (2). Upon substitution of -Br with the vinyl group, the vinyl peaks appear in the region 5.25-6.73 ppm (3). The protons ascribed to -NH and -OH reappear upon deprotection (4) (Figure 3.5).²¹⁹,²²⁰

Figure 3.5 ¹H NMR of the intermediate steps in the synthesis of the monomerized ligand (PIMEthenyl).

3.3.2 Fourier Transform Infra-Red (FT-IR) spectroscopy

3.3.2.1 Characterization of the complexes [oxidovanadium(IV)-2-(2'-hydroxyphenyl)imidazole and its -MeO, -Br and -NO₂ derivatives].

In the FT-IR spectra of the ligands (PIMH, PIMMeO, PIMBr and PIMNO₂), the azomethine stretch [ν(C=N)] peaks were observed at 1554, 1532, 1528 and 1560 cm⁻¹ respectively.²²¹ Coordination to oxidovanadium(IV) resulted in a shift of the azomethine peaks to lower frequencies; 1563, 1570 and 1563 for VO(PIMH)₂, VO(PIMMeO)₂ and VO(PIMBr)₂, respectively. In the case of VO(PIMNO₂)₂, the azomethine peak remained at 1560 cm⁻¹. The shift in frequencies could be a manifestation of bond lengths being influenced by the geometries assumed upon coordination as will be discussed later in
Section 3.3.3. The peaks at 1264, 1219, 1248 and 1300 cm\(^{-1}\) were tentatively assigned to the phenolic \(\nu(C-O)\) stretches of the ligands, PIMH, PIMMeO, PIMBr and PIMNO\(_2\), respectively. These peaks shifted to higher wavenumbers, 1297, 1226, 1262 and 1303 cm\(^{-1}\), for VO(PIMH)\(_2\), VO(PIMMeO)\(_2\), VO(PIMBr)\(_2\) and VO(PIMNO\(_2\))\(_2\), respectively. It can therefore be resolved from the FT-IR data that there was less influence of the geometry assumed by VO(PIMNO\(_2\))\(_2\) on the azomethine and phenolic bond lengths, whereas VO(PIMMeO)\(_2\) was extremely affected, while VO(PIMH)\(_2\) and VO(PIMBr)\(_2\) were moderately affected and to roughly the same extent.\(^{222,223}\)

In addition, the appearance of new peaks in the regions 920-992, 446-482 and 409-430 cm\(^{-1}\) which are positions typical for \(\nu(V=O)\), \(\nu(V-N)\) and \(\nu(V-O)\) stretches, respectively, also confirmed the formation of the complexes.\(^{224,225}\) Stacked spectra for the ligands against the complexes are presented in Figures 3.6-3.9, and Table 3.1 summarizes major peaks of interest.

![Figure 3.6 FT-IR spectra of PIMH and its complex VO(PIMH)\(_2\).](image-url)
Figure 3.7 FT-IR spectra of PIMMeO and its complex VO(PIMMeO)$_2$.

Figure 3.8 FT-IR spectra of PIMBr and its complex VO(PIMBr)$_2$. 
Figure 3.9 FT-IR spectra of PIMNO$_2$ and its complex VO(PIMNO$_2$)$_2$.

Table 3.1. FT-IR spectral data for VO(PIMH)$_2$ and its; -MeO, -Br and -NO$_2$ derivatives (PIMMeO, PIMBr and PIMNO$_2$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(C=N) (cm$^{-1}$)</th>
<th>ν(C-O) (cm$^{-1}$)</th>
<th>ν(V=O) (cm$^{-1}$)</th>
<th>ν(V-N) (cm$^{-1}$)</th>
<th>ν(V-O) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(PIMH)$_2$</td>
<td>1563</td>
<td>1148</td>
<td>964</td>
<td>446</td>
<td>409</td>
</tr>
<tr>
<td>VO(PIMMeO)$_2$</td>
<td>1570</td>
<td>1099</td>
<td>920</td>
<td>466</td>
<td>430</td>
</tr>
<tr>
<td>VO(PIMBr)$_2$</td>
<td>1563</td>
<td>1107</td>
<td>920</td>
<td>464</td>
<td>421</td>
</tr>
<tr>
<td>VO(PIMNO$_2$)$_2$</td>
<td>1560</td>
<td>1148</td>
<td>992</td>
<td>482</td>
<td>421</td>
</tr>
</tbody>
</table>

3.3.2.2 Synthesis of copolymer and characterization of copolymer, poly(styrene-co-5'-ethenyl-2-hydroxyphenylimidazole) copolymer, [p(ST-co-VPIM)]

FT-IR was used to follow each step in the synthesis of the polymerizable ligand (VPIMEthenyl) (Figure 3.10). Stretching vibrations, ν(N-H) and ν(O-H), observed in region 3400–3120 cm$^{-1}$ for PIMBr disappear after protection with benzoyl groups. Peaks at 1706 and 1747 cm$^{-1}$ which can be attributed to the O- and N-substituted benzoyl groups in dibenzoyl-PIMBr further confirm successful protection of the functional groups. Deprotection to obtain PIMEthenyl was noted by the disappearance of the benzoyl protecting group peaks and the re-emergence of the O-H and N-H functional group peaks.$^{219,220}$
Figure 3.10 FT-IR spectra showing changes at each stage in the synthesis leading to 2-(2’-hydroxy-5-ethenylphenyl)imidazole. 1: 2-(2’-hydroxy-5-bromophenyl)imidazole; 2: N-benzoyl-2-(2’-benzoxy-5-bromophenylimidazole; 3: N-benzoyl-2-(2’-benzoxy-5-ethenylphenyl)imidazole and 4: 2-(2’-hydroxy-5-ethenylphenyl)imidazole.

3.3.2.3 Characterization of the oxidovanadium(IV)-containing poly(styrene-co-5’-ethenyl-2-hydroxyphenylimidazole) nanofibers [VO-p(ST-co-VPIM)].

In the FT-IR spectrum of the copolymer (Figure 3.11), the band at 1494 cm\(^{-1}\) can be attributed to the azomethine stretch \([\nu(C=\text{N})]\).\(^{221}\) Coordination to the metal centre oxidovanadium(IV) results in a shift of the azomethine band to 1530 cm\(^{-1}\).\(^{222}\) The peak at 1263 cm\(^{-1}\) was tentatively assigned to the phenolic \(\nu(\text{C-O})\) stretches in the copolymer, and the peak shifted to 1273 cm\(^{-1}\) upon coordination.\(^{223}\) Bands which emerged at 964, 447 and 415 cm\(^{-1}\) which are positions typical for \(\nu(\text{V=O}), \nu(\text{V-N})\) and \(\nu(\text{V-O})\) stretches, respectively, also confirmed successful hosting of oxidovanadium(IV) on the copolymer.\(^{224,225}\)
3.3.3 X-ray crystallography

Recrystallization of the complex catalyst VO(PIMH)$_2$ and its -Br and NO$_2$ derivatives in a mixture of DMSO and ethyl acetate produced dark blue-green single crystals suitable for single crystal X-ray diffraction analysis. The molecular structures of the complexes are presented in Figures 3.12-3.14. Crystal data and details for the determination of the molecular structures are presented in Table 3.2, and selected bond lengths and angles are presented in Table 3.3.

3.3.3.1 Oxovanadium(IV)-2’-(2-hydroxyphenyl)imidazole complex catalyst, [VO(PIMH)$_2$]

The bidentate ligand, 2-(2’-hydroxyphenyl)imidazole, coordinates to the vanadyl ion through the neutral azomethine nitrogen and phenolate oxygen to produce a neutral bis[(imidazole)phenolato]oxidovanadium(IV) complex. The average bite angle of the ligands is 84.88(6)$^\circ$. The average lengths for the V–phenolate O and V–imidazole N bonds were 1.908 and 2.062(15) Å, respectively. The length of the V=O bond is 1.6101 Å, slightly above those reported in literature which fall in the range 1.591-1.605 Å. With a $\tau_5$ value of 0.26, the geometry of the complex [VO(PIMH)$_2$] can be described as a highly distorted square pyramidal with the vertical plane defined by the V(1)-O(1) bond and the equatorial plane by the O(2), O(3), N(21) and N(31) donor

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Figure 3.11 FT-IR spectra of the copolymer [p(ST-co-VPIM)] and the oxidovanadium(IV)-containing copolymer nanofibers [VO-p(ST-co-VPIM)].
ligands.\textsuperscript{218} The angles O(2)-V(1)-O(3) and N(21)-V(1)-N(31) are 136.92(6)° and 152.35(6)°, respectively and are far from the ideal 180°.

\textbf{Figure 3.12} An ORTEP view of VO(PIMH)\textsubscript{2} with ellipsoids drawn at 50% probability level.

3.3.3.2 Oxidovanadium(IV)-2′-(2-hydroxy-5-bromophenyl)imidazole complex catalyst, [VO(PIMBr)\textsubscript{2}]

The bromine derivative, 2-(2’-hydroxy-5-bromophenyl)imidazole, also coordinates in a similar fashion as observed for the oxidovanadium(IV)-2′-(2-hydroxyphenyl)imidazole complex [VO(PIMH)\textsubscript{2}] to produce the neutral bis[(imidazole)-5-bromophenolato]oxovanadium(IV) complex. The length of the V=O bond is, 1.6143 Å, higher than that of VO(PIMH)\textsubscript{2} and those reported in literature.\textsuperscript{226,227} The average bite angle of the ligands is 85.68(19)°. The average length for the V–phenolate O bonds is than that of VO(PIMH)\textsubscript{2}, the complex is more square pyramidal compared to VO(PIMH)\textsubscript{2}. A higher $\tau_5$ value\textsuperscript{228} of signifies a shift from square planarity towards the trigonal bipyramidal geometry, and clearly the phenolic para position substitution effected the change in geometry.\textsuperscript{218} The angles O(11)-V(1)-O(21) and N(11)-V(1)-N(21) are 144.5(2)° and 152.08(19)°, respectively are also far from the ideal 180°.
Figure 3.13 An ORTEP view of VO(PIMBr)$_2$ with ellipsoids drawn at 50% probability level.

3.3.3.3 Oxidovanadium(IV)-2'- (2-hydroxy-5-nitrophenyl)imidazole complex catalyst, [VO(PIMNO)$_2$]$_2$

The nitro group derivative, 2-(2'-hydroxy-5-nitrophenyl)imidazole, also coordinates in a similar fashion as observed for the other complexes to produce the neutral bis[(imidazole)-5-nitrophenolato]oxovanadium(IV) complex. The length of the V=O bond is, 1.604 Å, lower than that of VO(PIMH)$_2$ and VO(PIMBr)$_2$, and falls within the literature range; 1.591-1.605 Å.$^{226,227}$ The average bite angle of the ligands is 85.42(8)$^\circ$. The average lengths for the V–phenolate O and V–imidazole N bonds were 1.910 and 2.0615(19) Å, respectively. With a lower $\tau_5$ value$^{228}$ of 0.15, VO(PIMNO)$_2$ is more square pyramidal than VO(PIMH)$_2$. The angles O(11)-V(1)-O(21) and N(11)-V(1)-N(21) are 142.42(8)$^\circ$ and 151.30(8)$^\circ$, respectively are also far from the ideal 180$^\circ$. 
**Figure 3.14** An ORTEP view of VO(PIMNO$_2$)$_2$ with ellipsoids drawn at 50% probability level.

**Table 3.2** Selected crystal data for VO(PIMH)$_2$, VO(PIMNO$_2$)$_2$, and VO(PIMBr)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>VO(PIMH)$_2$</th>
<th>VO(PIMBr)$_2$</th>
<th>VO(PIMNO$_2$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{18}$H$</em>{14}$N$_4$O$_3$V 2(C$_2$H$_6$OS)</td>
<td>C$<em>{16}$H$</em>{12}$Br$_2$N$_4$O$_3$V 2(C$_2$H$_6$OS)</td>
<td>C$<em>{18}$H$</em>{12}$N$_6$O$_7$V (C$_2$H$_6$OS)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>541.53</td>
<td>699.31</td>
<td>553.40</td>
</tr>
<tr>
<td>Crystal colour</td>
<td>dark blue-green</td>
<td>dark blue-green</td>
<td>dark blue-green</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$ (No. 14)</td>
<td>$P2_12_12_1$ (No. 19)</td>
<td>$P2_1/c$ (No. 14)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>$a$, $b$, $c$ (Å)</td>
<td>15.8192(9)                      10.5686(6)                      14.8615(8)</td>
<td>15.3157(7)                      15.8806(8)                      22.1939(13)</td>
<td>13.8817(5)                      13.0525(5)                      13.1235(5)</td>
</tr>
<tr>
<td>$\alpha$, $\beta$, $\gamma$ (°)</td>
<td>90, 94.964(2), 90</td>
<td>90, 90, 90</td>
<td>90, 108.646(2), 90</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>2475.3(2)</td>
<td>5398.1(5)</td>
<td>2253.05(15)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{calc}$ (g/cm$^3$)</td>
<td>1.453</td>
<td>1.721</td>
<td>1.632</td>
</tr>
<tr>
<td>Radiation (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Total reflections</td>
<td>43888</td>
<td>56689</td>
<td>26442</td>
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<tr>
<td>Unique reflections</td>
<td>6170</td>
<td>13338</td>
<td>5606</td>
</tr>
<tr>
<td>R, wR2, S</td>
<td>0.0370, 0.1025, 1.07</td>
<td>0.0453, 0.1210, 1.04</td>
<td>0.0443, 0.1264, 1.06</td>
</tr>
</tbody>
</table>
Table 3.3 Selected bond lengths (Å) and angles (°) for VO(PIMH)\(_2\), VO(PIMBr)\(_2\) and VO(PIMNO\(_2\))\(_2\).

<table>
<thead>
<tr>
<th></th>
<th>VO(PIMH)(_2)</th>
<th>VO(PIMBr)(_2)</th>
<th>VO(PIMNO(_2))(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)-O(1)</td>
<td>1.6101(13)</td>
<td>1.6143(18)</td>
<td>1.604(5)</td>
</tr>
<tr>
<td>V(1)-O(2)</td>
<td>1.9141(13)</td>
<td>1.908(2)</td>
<td>1.919(5)</td>
</tr>
<tr>
<td>V(1)-O(3)</td>
<td>1.9023(12)</td>
<td>1.9125(18)</td>
<td>1.916(4)</td>
</tr>
<tr>
<td>V(1)-N(21)</td>
<td>2.0620(15)</td>
<td>2.0588(19)</td>
<td>2.060(5)</td>
</tr>
<tr>
<td>V(1)-N(31)</td>
<td>2.0617(15)</td>
<td>2.0642(19)</td>
<td>2.072(5)</td>
</tr>
<tr>
<td>O(1)-V(1)-O(2)</td>
<td>109.90(6)</td>
<td>108.61(10)</td>
<td>108.3(2)</td>
</tr>
<tr>
<td>O(1)-V(1)-O(3)</td>
<td>113.16(6)</td>
<td>108.96(9)</td>
<td>107.2(2)</td>
</tr>
<tr>
<td>O(1)-V(1)-N(21)</td>
<td>103.26(6)</td>
<td>105.63(8)</td>
<td>104.2(2)</td>
</tr>
<tr>
<td>O(1)-V(1)-N(31)</td>
<td>104.39(6)</td>
<td>103.07(8)</td>
<td>103.7(2)</td>
</tr>
<tr>
<td>O(2)-V(1)-O(3)</td>
<td>136.92(6)</td>
<td>142.42(8)</td>
<td>144.5(2)</td>
</tr>
<tr>
<td>N(21)-V(1)-N(31)</td>
<td>152.35(6)</td>
<td>151.30(8)</td>
<td>152.08(19)</td>
</tr>
<tr>
<td>Ligand average bite angle</td>
<td>84.88(6)(^\circ)</td>
<td>Ligand average bite angle</td>
<td>85.68(19)(^\circ)</td>
</tr>
</tbody>
</table>

3.3.4 Ultraviolet-Visible Spectroscopy (UV-Vis)

Three low intensity \(d-d\) transitions, in the range of 330–1000 nm, are expected for oxidovanadium(IV) complexes.\(^{110,140}\) These bands, as demonstrated by VO(PIMH)\(_2\), were observed in the ranges 500-560 nm and 580-650 nm, for the \(b_2 \rightarrow b_1\) and \(b_2 \rightarrow e\) transitions, respectively, and the high energy transition \(b_2 \rightarrow a_1\) was observed in the range 410-440 nm as a shoulder to a charge transfer band high energy transition, hence the higher intensity. (Figure 3.15). Intraligand transitions associated with the aromatic rings, \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\), and are normally expected to occur in the ranges 242-267 nm and 317-384 nm, were observed for VO(PIMH)\(_2\) at maxima of 245 and 316 nm, respectively.\(^{140}\) Major changes were realized in these transitions for the other complexes inferring a huge influence of the different electronic properties of the substituent groups on the electronic properties of the complexes (Figure 3.16). However, the overwhelming absorptions of the nitro group in the same region occlude appearance of the two transitions.\(^{104}\)
3.3.5 Electron Paramagnetic Resonance (EPR)

The EPR spectra of the solid and solution forms of the complex catalyst [VO(PIMH)₂] and that of the polymer supported catalyst [VO-p(ST-co-VPIM)] are presented in Figure 3.17. The origin of the paramagnetic peaks in the solution spectrum of the complex and the polymer spectra can be attributed to the oxidovanadium(IV) ion (⁵¹V, I = 7/2), g-factor = 2.0087. While the solution spectrum of VO(PIMH)₂ exhibited the almost isotropic 8-line hyperfine splitting, the signal observed for the powder...
form of the complex was not well resolved with humps on the larger peak ascribed to the Zeeman’s effect. Loss of resolution in powder spectra can be attributed to line broadening due to dipolar interactions between neighboring molecules. The dipolar interactions in solution and in solid polymer are weak since there is more separation between molecules. An anisotropic signal was observed for the polymer catalysts which could be due to restrictions on isotropic tumbling.

![EPR spectra](Figure 3.17) EPR spectra of; VO(PIMH)\(_2\) powder and solution (DMF), and VO-[p(ST-co-VPIM)] powder.

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

XPS analysis of the nanofibers confirmed the presence of all the expected elements; carbon, nitrogen, vanadium, and oxygen. These appeared at 279.8, 597.6, (514.6/521.5) and 527.3 keV, respectively (Figure 3.18). The position of the V 2p\(_{3/2}\) signal confirms that vanadium is in its +4 oxidation state and the additional V 2p\(_{1/2}\) signal shows the effect of spin orbit coupling.
3.3.7 Energy Dispersive Spectroscopy
Analysis of the oxidovanadium(IV)-containing poly(styrene-co-5’-ethenyl-2-hydroxyphenyl) imidazole nanofibers VO-[p(ST-co-VPIM)] fibers with EDS showed that vanadium was successfully hosted on the fibers from the peaks at ~0.5 and ~5 keV, which can be attributed to O from V-O and V, respectively. However, a second smaller peak for vanadium, of different energy, ~5.5 keV and a sulfur peak at ~2.4 keV can be attributed to unreacted VOSO₄ which remained even after washing the fibers (Figure 3.19).

Figure 3.18 Wide scan XPS spectrum of VO-[p(ST-co-VPIM)]. Inserts show the high resolution XPS scans for N 1s and V 2p.

Figure 3.19 EDS of VO-[p(ST-co-VPIM)] nanofibers.
3.3.8 Scanning Electron Microscopy (SEM)

Successful fabrication of p(ST-co-VPIM) nanofibers through electrospinning can be noted from the almost uniform fibers with diameters in the range 2-5 µm (Figure 3.20). Upon coordination of vanadyl to form the polymer catalyst, VO-p(ST-co-VPIM), the integrity of the fibers is maintained with diameters in the range 2-10 µm.

Figure 3.20 SEM micrographs of (a) p(ST-co-VPIM), (b) VO-p(ST-co-VPIM).

3.3.9 Thermogravimetric Analysis and Differential Scanning Calorimetry (TG/DSC)

The TG curves of p(ST-co-VPIM) (Figure 3.21) and VO-p(ST-co-VPIM) (Figure 3.22) start off with gradual losses in weight in the region below 350°C which can be attributed to loss of solvents. Although the loss is less apparent for p(ST-co-VPIM), in the case of VO-p(ST-co-VPIM) it amounts to about 10%, in the range 25°C to 350°C. Major weight losses of about 95% and 80%, which can be attributed to the collapse of the polymer backbone were observed in the ranges 350-475°C and 350-450°C, for p(ST-co-VPIM) and VO-p(ST-co-VPIM), respectively.
Figure 3.21 TGA and DSC curves of the copolymer, p(ST-co-VPIM).

Figure 3.22 TGA and DSC curves of the copolymer catalyst, VO-[p(ST-co-VPIM)].
The stability of the p(ST-co-VPIM) and VO-p(ST-co-VPIM) can also be easily concluded from the TG-DSC curves. $T_{\text{max}}$ for p(ST-co-VPIM) was $\sim 410 \, ^\circ\text{C}$, slightly higher than that of polystyrene, $T_{\text{max}} = 401 \, ^\circ\text{C}$. However, the $T_{\text{max}}$ for VO-p(ST-co-VPIM) is even lower than that of polystyrene, at $\sim 385 \, ^\circ\text{C}$. The $T_{\text{max}}$ for VO-p(ST-co-VPIM) is still rational considering that the fibers are going to be applied in reactions which will be carried out under ambient conditions. After the decomposition of p(ST-co-VPIM) fibers, 0% weight remained, whereas VO-p(ST-co-VPIM) fibers left behind ~5% weight after decomposition. The 5% weight can be attributed to mainly vanadium oxides and possibly small amounts of residual carbon, if any.

More details for the thermal events can be noted from the DSC curves and the one for VO-p(ST-co-VPIM) was accompanied by many artifacts compared to the one for p(ST-co-VPIM). Of major significance was the exothermic event noted after complete decomposition of VO-[p(ST-co-VPIM)] which can be attributed to the oxidation of the vanadium into its oxides.

### 3.3.10 Catalytic oxidation studies

#### 3.3.10.1 Characterization of products of oxidation

From GC-FID and GC-MS analyses, dibenzothiophene sulfone (DBTO$_2$) was the only product for all reactions after 270 minutes of oxidation under optimal conditions. Formation of DBTO$_2$ as the only product after 270 mins of reaction qualifies the catalysts as a specific catalyst in the oxidation of DBT to DBTO$_2$. Relatively small amounts of dibenzothiophene sulfoxide (DBTO) were noted during the reaction. DBTO is an intermediate in the oxidation of DBT to DBTO$_2$. GC-MS studies on an aliquot sampled during the reaction showed the presence of the sulfone and sulfoxide at 20.690 min ($m/z = 200$) and 20.605 min ($m/z = 216$) respectively. The FT-IR spectrum of the final oxidation product shows intense peaks at 1161 cm$^{-1}$ and 1286 cm$^{-1}$ which are typical for S=O bonds. A shift in the peak characteristic for the C-S bond from 733 cm$^{-1}$ in DBT to 750 cm$^{-1}$ in the product also indicates the introduction of an electronegative oxygen group onto sulfur (Figure 3.23). DBT and product $^1$H NMR spectra in Figure 3.24, also showed different spitting patterns due to the introduction of the electronegative oxygen to DBT. DBT: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 – 8.02 (m, 2H), 7.82 – 7.72 (m, 2H), 7.41 – 7.31 (m, 4H) and DBTO$_2$: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (dd, 4H), 7.65 (t, 2H),
7.54 (t, 2H). The single crystal for the oxidation product was also isolated and its ORTEP representation is presented in Figure 3.25, and the information pertaining it is presented in Tables 3.4 and 3.5.

Figure 3.23 FT-IR spectra comparing DBT and the product of oxidation, DBTO₂.

Figure 3.24 ¹H NMR spectra comparing DBT and the product of oxidation, DBTO₂.
**Figure 3.25** ORTEP representation of DBTO$_2$ showing 50% thermal probability ellipsoids.

**Table 3.4** Selected crystal data for dibenzothiophene sulfone (DBTO$_2$).

<table>
<thead>
<tr>
<th><strong>Compound</strong></th>
<th>Dibenzothiophene sulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$_{12}$H$_8$O$_2$S</td>
</tr>
<tr>
<td>Formula weight</td>
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<tr>
<td>Crystal colour</td>
<td>colourless</td>
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<tr>
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<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
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</tr>
<tr>
<td>a (Å)</td>
<td>10.0514(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.8184(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.0487(4)</td>
</tr>
<tr>
<td>$\alpha, \gamma, \beta$ ($^\circ$)</td>
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<tr>
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<td>$\rho_{calc}$ (g/cm$^3$)</td>
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</tr>
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<td>Unique reflections</td>
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</tr>
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</tr>
<tr>
<td>wR2</td>
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</tr>
<tr>
<td>S</td>
<td>1.08</td>
</tr>
</tbody>
</table>
Table 3.5 Bond distances (Å) and angles (°) of dibenzothiophene.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-O(1)</td>
<td>1.4390(13)</td>
<td>O(1)-S(1)-C(1)</td>
<td>110.28(7)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.7562(14)</td>
<td>O(1)-S(1)-O(1a)</td>
<td>117.36(8)</td>
</tr>
<tr>
<td>S(1)-O(1a)</td>
<td>1.4390(13)</td>
<td>O(1)-S(1)-C(1a)</td>
<td>111.48(7)</td>
</tr>
<tr>
<td>S(1)-C(1a)</td>
<td>1.7562(14)</td>
<td>O(1a)-S(1)-C(1)</td>
<td>111.48(7)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.3942</td>
<td>C(1)-S(1)-C(1a)</td>
<td>93.45(7)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.3822</td>
<td>O(1a)-S(1)-C(1a)</td>
<td>110.28(7)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.3892</td>
<td>S(1)-C(1)-C(2)</td>
<td>110.42(10)</td>
</tr>
<tr>
<td>C(2)-C(2a)</td>
<td>1.4752</td>
<td>S(1)-C(1)-C(6)</td>
<td>126.08(12)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.3873</td>
<td>C(2)-C(1)-C(6)</td>
<td>123.49(14)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.3783</td>
<td>C(1)-C(2)-C(3)</td>
<td>118.12(14)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.3863</td>
<td>C(1)-C(2)-C(2a)</td>
<td>112.84(12)</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.9500</td>
<td>C(2a)-C(2)-C(3)</td>
<td>129.03(13)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.9500</td>
<td>C(2)-C(3)-C(4)</td>
<td>119.01(15)</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.9500</td>
<td>C(3)-C(4)-C(5)</td>
<td>121.63(17)</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.9500</td>
<td>C(4)-C(5)-C(6)</td>
<td>120.64(16)</td>
</tr>
</tbody>
</table>

3.3.10.2 Optimization of oxidation conditions using $\text{VO(PIMH)}_2$

(a) Optimizing amount of oxidant

In the presence of 100 mg (0.543 mol) of dibenzothiophene and 7.5 mg (19.5 nmol) of catalyst [VO(PIMH)$_2$] dissolved in 10 mL of acetonitrile and a temperature of 60°C, the amount of oxidant ($t$-BuOOH) was increased from 0.5 mL to 2.0 mL (from 0.263 to 1.05 mmol) resulting in an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 63.3% to 100%. The turn over frequency (TOF) at 1 hour increased from 932.9 h$^{-1}$ to 2291.4 h$^{-1}$ (Figure 3.26 and Table 3.6).
Figure 3.26 Percentage conversion of DBT with time using various amounts of oxidant (t-BuOOH). Amount of catalyst [VO(PIMH)$_2$] = 7.5 mg (19.5 nmol); DBT = 100 mg (0.543 mol); t-BuOOH = 0.5, 1.0, 1.5 and 2.0 mL (0.263, 0.526, 0.789 and 1.05 mmol respectively); acetonitrile solvent = 10 mL; Temperature = 60°C.

The effect of adding excessive oxidant on the complex catalysts was investigated by adding 5 mL t-BuOOH (2.63 mmol) to a solution of 7.5 mg (19.5 nmol) VO(PIMH)$_2$ catalyst in acetonitrile. The solution turned red and red crystals formed upon slow recrystallization. SC-XRD analysis revealed the crystals to be a cluster of V$_{10}$O$_{28}$ with the ligands (Figure 3.27). Rapid oxidation of vanadium(IV) into pentavalent species which may further polymerize into other forms, has been reported. Amounts of oxidant must therefore be kept to a minimum to avoid disintegration of the catalyst.
The isolated cluster of $\text{V}_{10}\text{O}_{28}^{6-}$ and the ligands which is possibly a sign of disintegration of $\text{VO(PIMH)}_{2}$ in the presence of excessive amounts of oxidant.

(b) Optimizing temperature

Optimization of temperature was carried out using 100 mg (0.543 mol) of dibenzothiophene, 7.5 mg (19.5 nmol) of catalyst [VO(PIMH)$_2$] and 2.0 mL (1.05 mmol) of $t$-BuOOH dissolved in 10 mL of acetonitrile. Increasing temperature from 30$^\circ$C to 60$^\circ$C resulted in an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 75% to 100%. The turn over frequency (TOF) at 1 hour increased from 830.9 h$^{-1}$ to 2291.4 h$^{-1}$. Increasing temperature results in a larger number of molecules with enough energy to overcome the activation energy barrier (Figure 3.28 and Table 3.6).
Figure 3.28 Percentage conversion of DBT with time at different temperatures. Amount of catalyst [VO(PIMH)$_2$] = 7.5 mg (19.5 nmol); DBT = 100 mg (0.543 mol); $t$-BuOOH = 2.0 mL (1.05 mmol); acetonitrile solvent = 10 mL. Temperatures used = 30°C, 40°C, 50°C and 60°C.

c) Optimizing amount of catalyst
Optimization to find the best amount of catalyst [VO(PIMH)$_2$] was carried out using 100 mg (0.543 mol) of dibenzothiophene and 2.0 mL (1.05 mmol) of $t$-BuOOH dissolved in 10 mL of acetonitrile at 60°C. As the amount of catalyst was increased from 1 mg to 7.5 mg (2.6 - 19.5 nmol) an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 93.6% to 100% was noted. In the absence of the catalyst, the overall percentage conversion of DBT to DBTO$_2$ was only 31.2%. Increase in activity can be explained in terms of the kinetics of the reaction, where an increase in amount of catalyst increases the number of active sites which participate in the catalytic oxidation process.$^{64}$ The turn over frequency (TOF) at 1 hour decreased from 10408.7 h$^{-1}$ to 2291.4 h$^{-1}$ since the number of moles of catalysts was increasing (Figure 3.29 and Table 3.6).
Figure 3.29 Percentage conversion of DBT using different amounts of catalyst [VO(PIMH)$_2$]. Amount of DBT = 100 mg (0.543 mol); t-BuOOH = 2.0 mL (1.05 mmol); Acetonitrile solvent = 10 mL; Temperature = 60°C.

3.3.10.3 Comparing vanadium complexes for catalytic activity
The effect of substituting the hydrogen in position 5' of the ligand used to make the vanadium complex [VO(PIMH)$_2$] with an electron withdrawing group (-NO$_2$), an electron donating group (-MeO) and bromine (-Br); on the catalytic activity of the complex was investigated. The comparative catalytic oxidation studies were carried out using the optimal conditions obtained [100 mg (0.543 moles) of DBT, 2.0 mL (1.05 mmol) of t-BuOOH and 6.5 nmol of catalyst in 10 mL of acetonitrile at 60°C].

After 210 minutes; 100, 94.9, 90.5 and 82.3% conversions were realized for the -NO$_2$, -H, -Br and -MeO derivatives respectively (Figure 3.30 and Table 3.6). The turnover frequencies after 1 h also decreased from VO(PIMNO$_2$)$_2$ = 5725.4 h$^{-1}$, VO(PIMH)$_2$ = 5144.3 h$^{-1}$, VO(PIMBr)$_2$ = 4121.1 h$^{-1}$ and VO(PIMMeO)$_2$ = 3592.6 h$^{-1}$. The decrease in activity can be attributed to the different electronegativities of the substituent groups which has an influence on the electron density on the
catalytic metal centre and the geometries of the complexes.\textsuperscript{136-141} The nitro group is very electronegative and the methoxy group is electron donating. Bromine is quite electronegative but has a lone pair of electrons which can form part of the resonance in the phenyl ring.\textsuperscript{138}

Analysis of SC-XRD data coupled with Density Functional Theory (DFT) studies were used to provide a more detailed explanation of how these different substituent groups influence the properties of the complexes and their catalytic activities. The discussions are covered in Sections 3.3.10.4 and 3.3.10.5.

![Graph comparing catalytic activities](figure30.png)

**Figure 3.30** Comparing the catalytic activities of the complex catalysts; VO(PIMH)\(_2\), VO(PIMBr)\(_2\), VO(PIMMeO)\(_2\) and VO(PIMNO\(_2\))\(_2\).
Table 3.6 Summary of results from the catalytic oxidation studies.

<table>
<thead>
<tr>
<th>VO(PIMH)₂ catalyst</th>
<th>Dibenzothiophene</th>
<th>t-BuOOH</th>
<th>Temp. °C</th>
<th>% Conversion after 210 mins</th>
<th>TOF (h⁻¹) after 1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg</td>
<td>nmol</td>
<td>mg</td>
<td>mmol</td>
<td>mL</td>
<td>mmol</td>
</tr>
<tr>
<td>Varying amount of oxidant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>1.5</td>
<td>0.789</td>
<td>0.688</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>1.0</td>
<td>0.526</td>
<td>1.03</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>0.5</td>
<td>0.263</td>
<td>2.06</td>
</tr>
<tr>
<td>Varying temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>Varying amount of catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 mg 0 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>1.0 mg 2.6 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>2.5 mg 6.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>5.0 mg 13.0 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>7.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
<td>0.517</td>
</tr>
<tr>
<td>Comparing catalysts (6.5 nmol. of each catalyst was used)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VO(PIMH)₂</td>
<td>6.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>VO(PIMBr)₂</td>
<td>6.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>VO(PIMMeO)₂</td>
<td>6.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>VO(PIMNO₂)₂</td>
<td>6.5 mg 19.5 mmol</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
</tbody>
</table>

*TOF(h⁻¹): (turnover frequency), moles of substrate (DBT) converted per mole of metal ion per hour; t-BuOOH mol eq., moles of t-BuOOH:moles of substrate (DBT).

3.3.10.4 Trends in catalyst activity based on analysis of SC-XRD data

Analysis of the crystal data of the complex catalysts shows that substituting the phenolic para position of the ligand with groups of different electronegativities has an influence on the geometry of the complex. The geometry index/structural parameter (r), which indicates the geometry of the metal center, varied with substitution of the phenolic para position with groups of different electronegativities. In the case of these 5-coordinate complexes r distinguishes whether the complex is square pyramidal or trigonal bipyramidal as the parameter increases from 0 to 1, respectively.²²⁸ The r-value was noted to be 0.33, 0.26 and 0.15 for VO(PIMBr)₂, VO(PIMH)₂ and VO(PIMNO₂)₂ respectively, implying a shift towards the square pyramidal geometry on addition of an electron withdrawing group.

The distance between vanadium and the plane, defined by the azomethine nitrogens and oxygens of the ligand (N₂O₂ plane), was also expected to follow a similar trend but no definite trend was realized. This
distance was noted to be 0.541, 0.597 and 0.563 Å for VO(PIMBr)$_2$, VO(PIMH)$_2$ and VO(PIMNO$_2$)$_2$ respectively. Lack of trend can be attributed to the different degrees of twisting of the N$_2$O$_2$ planes in the structures mainly due to changes around the coordination of vanadium to the phenolic oxygen and azomethine nitrogen, which is a direct influence of the different electron withdrawing properties of the groups on the phenolic para position. It can be noted from the crystal data presented in Table 3.3 that there is no clear trend in the V-O and V-N bond lengths, and angles which result from them, as the groups on the phenolic para position are changed. Since the plane is defined by the phenolic oxygens and azomethine nitrogens, no clear trend in the distance between the N$_2$O$_2$ plane and vanadium will be realized with change from H, to -Br and -NO$_2$.

It is proposed that a shift from the trigonal bipyramidal geometry to square planarity makes the vanadium centre more labile to attack by the oxidant which is the first step in the catalytic oxidation mechanism. The relevant crystal data of the complexes has been summarized in Figure 3.31, against the catalytic activities of the complexes observed in the oxidation of dibenzothiophene (expressed as % conversion).

**Figure 3.31** Plot relating the geometry index ($\tau$) to the catalytic activities of the complexes.

3.3.10.5 Trends in activity based on Density Functional Theory (DFT) studies
Natural Bonding Order (NBO) analysis was performed on all complexes at the DFT level with 6-311G++ (d, p) in order to elucidate the intramolecular re-hybridization and delocalization of electron
density within the complexes. The differences in activity noted for the catalysts are explained in terms variations in the bonding situations, natural bond charges, perturbation energies and the HOMO-LUMO energy gaps of the complexes due to the differences in the electronegativities of the substituent groups. There was no clear trend in the changes in these parameters with changes in the electronegativities of the groups. However, there was a clear disparity between VO(PIMNO$_2$)$_2$ and the other complexes. The discussion will be limited to comparing the complex with the highly electron withdrawing group VO(PIMNO$_2$)$_2$ to the other complexes. Figure 3.32 is used as a reference.

Figure 3.32 Schematic for referencing DFT atoms in the complexes.

(a) Bond lengths and angles
The SC-XRD and DFT bond lengths and angles of the complexes [VO(PIMH)$_2$, VO(PIMBr)$_2$, VO(PIMNO$_2$)$_2$ and VO(PIMMeO)$_2$] are compared in Tables 3.7 and 3.8. The data for the DFT modelled structures of the complexes tallies with the SC-XRD data qualifying the DFT level for analysis of the complexes. The different electronegativities of the substituent groups are expected to effect changes in the bond lengths and angles of the complexes.

Table 3.7 DFT and SC-XRD bond lengths of the complexes.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>VO(PIMH)$_2$</th>
<th>VO(PIMBr)$_2$</th>
<th>VO(PIMNO$_2$)$_2$</th>
<th>VO(PIMMeO)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>XRD</td>
<td>DFT</td>
<td>XRD</td>
</tr>
<tr>
<td>C2-O2</td>
<td>1.3325</td>
<td>1.333</td>
<td>1.3315</td>
<td>1.322</td>
</tr>
<tr>
<td>C11-O3</td>
<td>1.3241</td>
<td>1.324</td>
<td>1.3387</td>
<td>1.329</td>
</tr>
<tr>
<td>O2-V</td>
<td>1.9137</td>
<td>1.9141</td>
<td>1.9191</td>
<td>1.924</td>
</tr>
<tr>
<td>O3-V</td>
<td>1.9029</td>
<td>1.9023</td>
<td>1.9160</td>
<td>1.915</td>
</tr>
<tr>
<td>N1-V</td>
<td>2.0610</td>
<td>2.0620</td>
<td>2.0695</td>
<td>2.066</td>
</tr>
<tr>
<td>N3-V</td>
<td>2.0619</td>
<td>2.0617</td>
<td>2.0723</td>
<td>2.078</td>
</tr>
<tr>
<td>V-O1</td>
<td>1.6111</td>
<td>1.6101</td>
<td>1.6043</td>
<td>1.597</td>
</tr>
</tbody>
</table>
Table 3.8 DFT and SC-XRD bond angles of the complexes.

<table>
<thead>
<tr>
<th>Bond angle (°)</th>
<th>VO(PIMH)₂</th>
<th>VO(PIMBr)₂</th>
<th>VO(PIMNO)₂</th>
<th>VO(PIMMeO)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>XRD</td>
<td>DFT</td>
<td>XRD</td>
</tr>
<tr>
<td>O1-V-O3</td>
<td>113.14</td>
<td>113.16</td>
<td>107.21</td>
<td>109.2</td>
</tr>
<tr>
<td>O1-V-O2</td>
<td>109.90</td>
<td>109.90</td>
<td>108.27</td>
<td>112.1</td>
</tr>
<tr>
<td>O1-V-N1</td>
<td>103.25</td>
<td>103.26</td>
<td>104.14</td>
<td>100.6</td>
</tr>
<tr>
<td>O1-V-N3</td>
<td>104.39</td>
<td>104.39</td>
<td>103.76</td>
<td>101.6</td>
</tr>
</tbody>
</table>

The Electron Withdrawing Group (EWG), -NO₂, decreases the electron density of the aromatic rings attached to the groups. As a result, carbon atoms, C2 and C11, attached to oxygen atoms O2 and O3 respectively become more electronegative. Therefore, decreasing the p-character of the atoms, thus leading to a decrease in the C-O bond length. A similar effect was also experienced between the bonding presented by N3 and N1 with vanadium atom. The opposite is true for the other complexes containing the Electron Donating Groups (EDGs).

(b) Bonding situation

To assess the bonding situation of [VO(PIMH)₂, VO(PIMBr)₂, VO(PIMNO)₂ and VO(PIMMeO)₂], especially the V=O bond, NBO analyses were conducted for all the complexes (Table 3.9). In all complexes, the d-orbital contribution to the bonds established between the vanadium atom and the atoms it is bonded to, respectively, is low. The hybridization of the vanadium atom in all complexes are mostly found to be predominantly at the d orbital for the V=O bond (V3d-O2p coupling). The V=O bond for VO(PIMH)₂, VO(PIMBr)₂, VO(PIMNO)₂ and VO(PIMMeO)₂, show vanadium character of around 28.31%, 28.56%, 30.27% and 28.79% respectively and with a hybridization of \( sp^{3.39}d^{0.09}, \)
\( sp^{3.28}d^{0.09}, \)
\( sp^{3.47}d^{0.09}\) and \( sp^{3.48}d^{0.08}\) on the oxygen atom respectively. VO(PIMNO)₂ contributed the highest degree of V3d-O2p coupling as well as a higher contribution of d-electron energies, thus leading to a higher electrophilicity and a higher affinity for oxidation reactions. The molecular hybridization of VO(PIMNO)₂ makes it more energetically favoured. The rest of the complexes contributed varying degrees of V3d-O2p coupling and d electron energies, much lower than those observed for VO(PIMNO)₂, thus leading to slightly lower electrophilicity and affinity for oxidation reactions as compared to VO(PIMNO)₂. The order of activity is VO(PIMNO)₂> VO(PIMBr)₂ > VO(PIMMeO)₂> VO(PIMH)₂.
Table 3.9 Selected hybridization of the complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bond</th>
<th>Atom</th>
<th>%</th>
<th>%s</th>
<th>%p</th>
<th>%d</th>
<th>H.O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(PIMH)$_2$</td>
<td>V1-O2</td>
<td>Vanadium</td>
<td>28.31</td>
<td>1.73</td>
<td>3.12</td>
<td>95.01</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen</td>
<td>71.69</td>
<td>22.76</td>
<td>77.15</td>
<td>0.09</td>
<td>sp$^{3.59}$</td>
</tr>
<tr>
<td>VO(PIMBr)$_2$</td>
<td>V3-O4</td>
<td>Vanadium</td>
<td>28.56</td>
<td>1.75</td>
<td>2.77</td>
<td>95.33</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen</td>
<td>71.44</td>
<td>23.37</td>
<td>76.55</td>
<td>0.09</td>
<td>sp$^{3.28}$</td>
</tr>
<tr>
<td>VO(PIMNO$_2$)$_2$</td>
<td>V1-O2</td>
<td>Vanadium</td>
<td>30.27</td>
<td>1.51</td>
<td>1.72</td>
<td>96.63</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen</td>
<td>69.73</td>
<td>22.36</td>
<td>77.55</td>
<td>0.09</td>
<td>sp$^{3.47}$</td>
</tr>
<tr>
<td>VO(PIMMeO)$_2$</td>
<td>V1-O2</td>
<td>Vanadium</td>
<td>28.79</td>
<td>1.39</td>
<td>2.88</td>
<td>95.57</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen</td>
<td>71.21</td>
<td>22.31</td>
<td>77.60</td>
<td>0.08</td>
<td>sp$^{3.48}$</td>
</tr>
</tbody>
</table>

(c) Natural bond charges (NBO)

The natural charge for the vanadium atom is positive for all complexes, and all other atoms bonded to the vanadium atom bear a negative natural charge (Table 3.10). Observed positive charges on these atoms are due to the electron-withdrawing nature of the complexes, while negative charges are due to their electron-donating nature of complexes. NBO atomic charges show that the vanadium atoms in complexes [VO(PIMBr)$_2$ and VO(PIMMeO)$_2$] have smaller positive atomic charges compared to the vanadium in VO(PIMNO$_2$)$_2$. An EWG results in a higher positive vanadium atom which will be more susceptible to nucleophilic attack.

Table 3.10 NBO charges of select atoms of the complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>V</th>
<th>O1</th>
<th>O2</th>
<th>C2</th>
<th>N1</th>
<th>N3</th>
<th>O3</th>
<th>C11</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(PIMH)$_2$</td>
<td>1.021</td>
<td>-0.303</td>
<td>-0.564</td>
<td>0.358</td>
<td>-0.484</td>
<td>-0.482</td>
<td>-0.558</td>
<td>0.351</td>
</tr>
<tr>
<td>VO(PIMBr)$_2$</td>
<td>1.001</td>
<td>-0.301</td>
<td>-0.561</td>
<td>0.351</td>
<td>-0.519</td>
<td>-0.517</td>
<td>-0.566</td>
<td>0.361</td>
</tr>
<tr>
<td>VO(PIMNO$_2$)$_2$</td>
<td>1.121</td>
<td>-0.247</td>
<td>-0.528</td>
<td>0.383</td>
<td>-0.504</td>
<td>-0.449</td>
<td>-0.537</td>
<td>0.389</td>
</tr>
<tr>
<td>VO(PIMMeO)$_2$</td>
<td>1.003</td>
<td>-0.299</td>
<td>-0.557</td>
<td>0.316</td>
<td>-0.508</td>
<td>-0.504</td>
<td>-0.526</td>
<td>0.318</td>
</tr>
</tbody>
</table>

(d) Highest Occupied Molecular Orbitals and Lowest Unoccupied Orbitals (HOMOs and LUMOs)

It can be clearly realized from the computationally optimized structures of the complexes that the HOMOs are mainly located on the ligands and the oxido group while LUMOs are mainly located on vanadium centre (Table 3.11). HOMOs of higher energy tend to give electrons better (good Lewis bases) while LUMOs of lower energy have a tendency of attracting electrons (good Lewis acids).\textsuperscript{232} It is therefore clear that the vanadium centre is the one which is labile to attack by the oxidant.
Table 3.11 Computationally optimized structures of the complexes showing the HOMO and LUMO distributions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(PIMH)$_2$</td>
<td><img src="image1" alt="HOMO" /></td>
<td><img src="image2" alt="LUMO" /></td>
</tr>
<tr>
<td>VO(PIMBr)$_2$</td>
<td><img src="image3" alt="HOMO" /></td>
<td><img src="image4" alt="LUMO" /></td>
</tr>
<tr>
<td>VO(PIMNO$_2$)$_2$</td>
<td><img src="image5" alt="HOMO" /></td>
<td><img src="image6" alt="LUMO" /></td>
</tr>
<tr>
<td>VO(PIMMeO)$_2$</td>
<td><img src="image7" alt="HOMO" /></td>
<td><img src="image8" alt="LUMO" /></td>
</tr>
</tbody>
</table>

3.3.10.7 Catalytic oxidation using VO-[p(ST-co-VPIM)] nanofibers

The use of nanofibers is more applicable in flow-setups rather than batch process since mechanical actions makes them lose their integrity. Recyclability of the catalysts is a crucial factor to consider for industrial applications of these catalysts. When used in a flow set-up, only minor breakages of the fibers are encountered compared with use in a batch reaction (Figure 3.33). Although slight twisting of the fibers was observed after use in a flow set-up, their average diameters and texture was maintained attesting to their stability in an acetonitrile (or fuel), DBT and t-BuOOH system. The results for the application of VO-[p(ST-co-VPIM)] nanofibers on model and real fuel samples are discussed in this section.
Figure 3.33 SEM images of (a) fibers in their original state, (b) after use in a batch reaction and (c) after use in a flow set-up.

(a) Catalytic oxidation studies of model fuel sample under flow conditions
Using 1.05 mmol t-BuOOH and 100 mg VO-[p(ST-co-VPIM)] nanofibers at 60°C in the flow set-up, varying the flow rate from 0.6 mL/h down to 0.2 mL/h resulted in percentage conversion of DBT to DBTO₂ in the model fuel sample (100 mg of DBT in 10 mL of acetonitrile) increasing from 49.2% to 100% due to increased contact time of the feed with the catalyst (Figure 3.34).

Figure 3.34 Change in % conversion of DBT to DBTO₂ with change in flow rate.

(b) Catalytic oxidation studies of real fuel sample under flow conditions
A flow rate of 0.2 mL/h was then adopted in the oxidation of a real fuel sample. Due to the complex nature of the fuel matrix, analysis for the real fuel sample; in its original state, after oxidation and after solvent extraction of the oxidized sulfur compounds with acetonitrile; was carried out using GC coupled
to a Sulfur Chemiluminescence Detector (SCD) as well as a Time of Flight-Mass spectrometer (TOF-MS), and the results are presented below (Figures 3.35 to 3.37). The peaks for sulfur can be noted in the original fuel sample in the region, 3600 to 4000 s (Figure 3.35 A and B). No significant shifts or changes in the intensity were noticed in the GC-SCD sulfur peaks of original fuel compared to oxidized fuel (Figures 3.35 A and B, and 3.36 A and B). However, a significant shift of the TOF-MS peak from ~3400 s to ~3700 s for the peak of highest intensity, assumed to be a peak for the dibenzothiophenes since they are the major compounds in hydrotreated fuel, indicates that ‘dibenzothiophenes’ were successfully oxidized together with the other sulfur compounds (Figures 3.35 C and 3.36 C). GC-SCD sulfur compound peaks disappeared in the fuel sample upon solvent extraction of the oxidized sulfur compounds using acetonitrile demonstrating the success of the oxidation technique coupled with solvent extraction as a complementary method to obtain ultra-low sulfur fuels (Figures 3.37 A, B and C).

The GC-SCD and TOF-MS data will be analysed further to determine the quantities of sulfur compounds before and after solvent extraction.
Figure 3.35 GC-SCD plots from the analysis of the original fuel sample (A) grid image, (B) XIC image and (C) the TOF-MS plot.
Figure 3.36 GC-SCD plots from the analysis of the oxidized fuel sample (A) grid image, (B) XIC image and (C) the TOF-MS plot.
Figure 3.37 GC-SCD plots from the analysis of the oxidized fuel sample after solvent extraction of the sulfur compounds with acetonitrile (A) grid image, (B) XIC image and (C) the TOF-MS plot.
3.3.11 Mechanistic studies
Several studies were carried out to try and understand the mechanism of the oxidation reaction catalysed by the oxidovanadium(IV) complex, VO(PIMH)$_2$. These studies and the proposed reaction mechanism are discussed in this section.

3.3.11.1 Colorimetry
The catalyst in acetonitrile goes through colour changes during the catalytic oxidation reaction where the solution quickly goes from its blue-green colour through a yellow colour to become red-brown (Figure 3.38). The blue-green colour is recovered upon completion of the reaction although the tone of the colour is different, which could be a result of a different coordination environment. The recovery of the green colour from the red-brown colour is the slower step and it depends upon the temperature of the reaction, and the amount of substrate and oxidant present. The complex is proposed to go from V$^{4+}$ to V$^{5+}$ upon addition of oxidant, where V$^{5+}$ is the active species that oxidizes the substrate to recover its original V$^{4+}$ state. The catalyst goes through this cycle until the oxidant has been spent allowing it to display its green colour in the mixture.

![Figure 3.38 Colour changes of VO(PIMH)$_2$ (A) upon addition of the oxidant, (B) during the reaction with dibenzothiophene and (C) upon consumption of the oxidant.](image)

3.3.11.2 EPR studies on the complex
The complex VO(PIMH)$_2$, was used to investigate the catalytic oxidation reaction mechanism of the oxidovanadium(IV) complexes. Oxidation of the V$^{4+}$ catalyst to the diamagnetic V$^{5+}$ was recognized from the gradual disappearance of the 8-line hyperfine signal, where the $^{51}$V ($I = 7/2$), upon addition of oxidant to the solution of the catalyst in DMF. The signal was recovered after addition of dibenzothiophene to the mixture and standing it for about 24 h (Figure 3.39).
Figure 3.39 Changes in the EPR spectrum of the complex catalyst [VO(PIMH)₂] upon addition of oxidant (t-BuOOH) and substrate (dibenzothiophene). (a) Spectrum of neat VO(PIMH)₂, (b and c) disappearance of 8 hyperfine lines upon addition of oxidant, and (d) signal after 24 h recovery. Concentrations; 0.300 M catalyst in DMF and neat (0.526 M) t-BuOOH.

3.3.11.3 EPR studies using the spin trap
Four distinct lines were obtained in the EPR spectrum when the spin trap, 5,5-dimethyl-1-pyrroline N-oxide, was used to trap free radicals produced during the catalytic oxidation reaction (Figure 3.40). There is an ambiguity in the signal on whether HO• or HOO• free radicals were trapped or oxygen-centred radicals (e.g. singlet oxygen and superoxide, O₂•⁻). HO• radicals typically give four lines whose intensity are in the ratio, 1:2:2:1. HOO• radicals give four lines of equal intensity with the lines showing further splitting especially the middle ones. The presence of both species may result in a convolution of the peaks unless there is an improved resolution. Trapped oxygen radicals decay to form DMPO/•OOH which further decays to form DMPO/•OH. Interpretation for oxygen radicals and DMPO/•OOH are made difficult by the short life time (t₁/₂ ≈ 45 seconds) of the species which decay into DMPO/•OOH. The use of the free radical trap, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) would be ideal due to the longer lifetime of the species generated, or even an analog of DMPO called 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) which gives a species of
Further investigations for the possibility of singlet oxygen being produced were carried out through quenching studies.

**Figure 3.40** EPR spectrum of the DMPO/• free radical species.

### 3.3.11.4 Singlet oxygen quenching studies

An attempt was made to determine if singlet oxygen is generated by the highly reactive dioxidoperoxidovanadium(V) species. A singlet oxygen (\(^1\)O\(_2\)) quencher; 1,3-diphenylisobenzofuran (DPBF), with maximum absorption peak at 415 nm, is normally employed for the quantification of singlet oxygen by monitoring its decay into o-dibenzoylbenzene and comparing the rate of decay to a standard, usually methylene blue, and then determining the quantum yield. Preliminary studies were promising, where a higher decay rate in the lambda max of DPBF was noticed in the presence of catalyst and oxidant compared to when there was no catalyst (Figure 3.41). However, in this particular vanadyl complex catalyzed reaction, the generation of HO• or HOO• free radicals was also proposed to be a possibility, and these can have the same effect as singlet oxygen on DPBF and the study can therefore be dismissed as inconclusive for determining the presence of singlet oxygen, among other challenges. Furfuryl alcohol has been reported in other publications to be more specific to singlet oxygen and could be used to overcome this challenge and other challenges around the use of DPBF.
3.3.11.5 UV-Vis studies on the complex

Since the catalyst goes through colour changes upon addition of the oxidant, the changes were monitored spectrophotometrically. As expected, the d-d transitions disappeared gradually upon addition of the oxidant confirming the oxidation of the catalyst from $V^{4+}$ to $V^{5+}$. From the apparent changes in the charge transfer bands (Figure 3.42), it is also proposed that the complex changes to other species as a result, as can be noted in the proposed mechanism. The reaction was also monitored at different temperatures and the results are presented in Figure 3.43. It can be clearly noted that the rate at which the intensities of the charge transfer bands decrease or increase, changes with temperature. More work is being carried out to deconvolute the superimposed spectra for the supposed species. After that the kinetic studies of the speciation (based on the rate of change of the intensities of the charge transfer bands) will then be carried out in order to understand the reaction mechanism.
Figure 3.42 Changes in the UV-Vis spectrum of the complex upon addition of oxidant (t-BuOOH). Concentrations: 0.1 mL (0.100 nmol) t-BuOOH to 2.9 mL (0.0300 nmol) catalyst solution at 30°C.

Figure 3.43 UV-Vis spectra for the oxidation of the complex upon addition of oxidant (t-BuOOH) at different temperatures. Concentrations: 0.100 mL (0.1 nmol) t-BuOOH to 2.9 mL (0.0300 nmol) catalyst solution at (A) 20°C, (B) 40°C, (C) 50°C and (D) 60°C.
3.3.11.6 SC-XRD
A single crystal of one of the intermediates in the oxidation of the catalyst was isolated, the
dioxidovanadium complex, VO$_2$(PIMH)$_2$ (Figure 3.44). It is proposed that it is formed in a reaction
where one of the bidentate 2-(2’-hydroxyphenyl)imidazole ligands releases its azomethine N to
vanadium bonds, to pave way for oxygen to react with vanadium to form the dioxidovanadium(V)
centre as shown in Scheme 3.6 (Section 3.3.11.8). The azomethine N of the mono-coordinated ligand
is protonated to give a positive charge which neutralizes the negative charge in the complex.
VO$_2$(PIMH)$_2$, with $\tau = 0.22$, can also be best described as having highly distorted square pyramidal
geometry with the vertical plane defined by V(1)-O(1) and the equatorial plane by the O(2), O(11),
O(21) and N(22) donor ligands. The angles O(2)-V(1)-O(21) and O(11)-V(1)-N(22) are 141.61(10) and
155.01(8) respectively and are quite far from the expected 180°.

Figure 3.44 ORTEP diagram of VO$_2$(PIMH)$_2$ showing 50% thermal probability ellipsoids.
Table 3.12 Selected crystal data for VO$_2$(PIMH)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>VO$_2$(PIMH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical</td>
<td>C$<em>{18}$H$</em>{15}$N$_4$O$_4$V</td>
</tr>
<tr>
<td>Formula weight</td>
<td>402.28</td>
</tr>
<tr>
<td>Crystal colour</td>
<td>yellow</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P212121 (No. 19)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>200</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>7.2579(3) 13.8117(5) 16.2980(6)</td>
</tr>
<tr>
<td>α, γ, β (°)</td>
<td>90, 90, 90</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>1633.78(11)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g/cm$^3$)</td>
<td>1.635</td>
</tr>
<tr>
<td>Radiation (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Total reflections</td>
<td>15488</td>
</tr>
<tr>
<td>Unique</td>
<td>4064</td>
</tr>
<tr>
<td>R, wR2, S</td>
<td>0.0284, 0.0757, 1.06</td>
</tr>
</tbody>
</table>

Table 3.13 Selected bond lengths (Å) and angles (°) of VO$_2$(PIMH)$_2$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)-O(1)</td>
<td>1.636(2)</td>
<td>O(1)-V(1)-O(2)</td>
<td>106.68(11)</td>
</tr>
<tr>
<td>V(1)-O(2)</td>
<td>1.635(2)</td>
<td>O(1)-V(1)-O(11)</td>
<td>102.48(9)</td>
</tr>
<tr>
<td>V(1)-O(11)</td>
<td>1.948(2)</td>
<td>O(1)-V(1)-O(21)</td>
<td>111.35(9)</td>
</tr>
<tr>
<td>V(1)-O(21)</td>
<td>1.9610(17)</td>
<td>O(1)-V(1)-N(22)</td>
<td>97.92(9)</td>
</tr>
<tr>
<td>V(1)-N(22)</td>
<td>2.084(2)</td>
<td>O(2)-V(1)-O(21)</td>
<td>141.61(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(11)-V(1)-N(22)</td>
<td>155.01(8)</td>
</tr>
</tbody>
</table>

3.3.$\text{H}_1.7$ LC-MS
Analysis of a solution of VO(PIMH)$_2$ with t-BuOOH in acetonitrile using Liquid Chromatography coupled to a Time of Flight Mass Spectrometer (LC-TOF/MS) revealed masses very close to some of the expected intermediates. Most of the masses were slightly higher than the expected masses and possible protonation of the vanadium species. A slightly higher mass was also observed even in the case of a pure VO(PIMH)$_2$ sample in acetonitrile. The starting material and the major intermediates expected are presented in Table 3.14. The MS spectrum obtained from the analysis is also presented (Figure
3.45). Of major interest are the high masses observed which confirm possible dimerization of the vanadyl oxidoperoxido species as proposed by Conte et al.\textsuperscript{142}

**Table 3.14** Vanadium species in the mixture of VO(PIMH)\textsubscript{2} with t-BuOOH in acetonitrile.

<table>
<thead>
<tr>
<th>Species</th>
<th>MW-molecular weight</th>
<th>Predicted masses (m/z)</th>
<th>Observed masses (m/z)</th>
<th>Comments</th>
</tr>
</thead>
</table>
| 1       | \[\text{MW}=385.27\] | 385.05  
386.05  
387.06 | 385.16 | VO(PIMH)\textsubscript{2}, the initial complex. [M\textsuperscript{+}] |
| 2       | \[\text{MW}=402.28\] | 402.05  
403.06  
404.06 | 403.25 | VO\textsubscript{2}(PIMH)\textsubscript{2}, the dioxido species possibly accompanied by an extra proton. [MO\textsuperscript{+} + H\textsuperscript{+}] |
| 3       | \[\text{MW}=418.28\] | 418.05  
419.05  
420.05 | 417.22  
476.28  
434.25 | VO\textsubscript{2}(PIMH)\textsubscript{2}, the dioxidoperoxido species possibly deprotonated or accompanied by tert-butyl to give 476.28 MW. The 434.25 observed in the spectrum is proposed to be due to the addition of dioxygen to the species although it’s not yet fully understood. [MO\textsubscript{2}\textsuperscript{+} - H\textsuperscript{+}]; [MO\textsubscript{2}\textsuperscript{+} + C\textsubscript{4}H\textsubscript{9}\textsuperscript{+}] and [MO\textsubscript{2}\textsuperscript{+} + O\textsubscript{2}] |
| 4       | \[\text{MW}=484.21\] | 484.98  
484.98  
485.99 | 487.37  
467.32 | The dimeric species possibly protonated on the peroxide oxygens. Loss of an oxygen from the dimeric species is believed to yield 467.32 MW. [M\textsubscript{2}\textsuperscript{+} + 2H\textsuperscript{+}] |
Proposed catalytic oxidation mechanism

From all the studies carried out in a bid to try and understand the mechanism of the catalytic oxidation reaction when using the oxidovanadium catalyst, the following mechanism is proposed (Scheme 3.6). In this mechanism, the oxidovanadium(IV) catalyst [VO(PIMH)₂] (a) is first oxidized into the dioxidovanadium(V) species (b), which is then further oxidized into the dioxidoperoxido species (c), a metal-activated highly reactive oxygen species which can oxidize the substrate, possibly with the involvement of free radicals. Dimerization of the dioxidoperoxido species (d) with liberation of oxygen species is possible, and in that case the liberated oxygen could be the active oxidant. The dimeric vanadyl species also has the potential to oxidize substrates. In each case the original vanadyl species (a) is recovered.

Figure 3.45 LC-TOF/MS spectrum showing various species present in solution.
Scheme 3.6 Proposed catalytic oxidation reaction mechanism when using oxidovanadium(IV) complex catalysts.

3.4 Conclusions

The oxidovanadium(IV)-2-(2'-hydroxyphenyl)imidazole catalyst [VO(PIMH)₂] and its derivatives, where the phenolic para position of the ligand was substituted by groups of different electron withdrawing/donating properties (-Br, -MeO and -NO₂), were successfully synthesized and characterized. An interesting trend in geometry was noted from the SC-XRD data of the crystals isolated for the VO(PIMH)₂ catalyst and its -Br and -NO₂ derivatives. From the geometry indices determined from the crystal data, it was concluded that having an electron withdrawing group (-NO₂) on the phenolic para position of the ligand results in a shift in geometry from the trigonal bipyramidal towards the square pyramidal geometry. The trend in shift towards the more square pyramidal geometry was as follows; VO(PIMNO₂)₂ > VO(PIMH)₂ > VO(PIMBr)₂ > VO(PIMMeO)₂. The observations made were synonymous with DFT predictions, although the trend was not clear in most cases.
The changes in geometry in the series of catalysts also manifested in catalytic activities of the catalysts where the catalyst with the most electronegative -NO₂ groups showed the highest activity and the rest followed the same trend observed for the geometries; VO(PIMNO₂)₂ > VO(PIMH)₂ > VO(PIMBr)₂ > VO(PIMMeO)₂. It can therefore be concluded that having an electronic group on the phenolic para position of the catalyst results in a geometry which is more square planar which allows the catalyst to have much higher catalytic activity. The catalyst with the electron withdrawing -NO₂ group [oxidovanadium(IV)-2-(2’-hydroxy-5-nitrophenyl)imidazole], therefore, has a lot of potential in oxidative desulfurization applications.

Potential to host the complex catalysts in a polymeric material was demonstrated through the synthesis of oxidovanadium(IV) copolymer nanofibers, VO-[p(ST-co-VPIM)]. Although their use under mechanical action was futile due to fracturing of the fibers, their application in a flow system was very successful and 100% conversion of DBT to DBTO₂ was achieved at a flow rate of 0.2 mL/h using the same conditions as optimized for VO(PIMH)₂ in the batch reaction.

Application on a real fuel system was also very successful as observed from preliminary analysis of GC-SCD and TOF-MS data. Although the use of such complexes enables tailoring of the catalysts to improve catalytic activity, one huge challenge is the intricate synthesis approaches, especially monomerizing the ligands.
Chapter 4: Vanadium oxides as catalysts

4.1 Introduction

Vanadium oxides are the basis for several industrial catalytic oxidation catalysts and have been applied in areas such as, the oxidation of SO$_2$ to SO$_3$ as in the Contact process$^{77,79}$ and selective oxidation of several hydrocarbon molecules into value-added chemicals.$^{67,80}$ Biedunkiewicz et al.$^{192}$ demonstrated that various vanadium oxides are produced during the thermal decomposition of NH$_4$VO$_3$, with (NH$_4$)$_3$V$_6$O$_{16}$, (NH$_4$)$_2$V$_6$O$_{16}$ and V$_2$O$_5$ being the predominant oxides. Yuan et al.$^{209}$ also indicated variations in the reactivities of vanadium cluster species with hydrocarbon molecules depending on their charges. This study set out to investigate the vanadium oxide phases that can be yielded through the calcination of NH$_4$VO$_3$ at different temperatures. These were to be investigated for their catalytic activities in the oxidation of dibenzothiophene (DBT), using $t$-BuOOH before hosting the most active oxide on a silica support to obtain a heterogeneous catalyst which can be applied in the oxidative desulfurization of fuel. Due to instrument constraints, an ICP to be particular – for determining the metal content of these oxides, the oxides were not compared for their catalytic activities but this will be done in the future. Only the V$_x$O$_y$/SiO$_2$-600$^\circ$C catalyst in which the vanadium oxide crystallites are uniformly dispersed over a fumed silica support to increase the exposed active sites for catalysis was applied. This chapter reports the following work that was covered:

1. Synthesis and characterization of the vanadium oxides through the calcination of NH$_4$VO$_3$ at different temperatures, i.e. 250, 300, 350, 400 and 600$^\circ$C, for 20 hr.
2. Synthesis and characterization of a silica supported catalyst, V$_x$O$_y$/SiO$_2$-600$^\circ$C.
3. Optimizing the catalytic conditions [temperature, amounts of the V$_x$O$_y$/SiO$_2$-600$^\circ$C catalyst and amount of oxidant ($t$-BuOOH)] in the oxidation of a model fuel sample (DBT dissolved in acetonitrile).
4. Carrying out catalytic oxidation of the model fuel sample using the V$_x$O$_y$/SiO$_2$-600$^\circ$C catalyst in continuous flow system.
5. Applying the optimal flow system conditions in the oxidation of a real fuel sample using the V$_x$O$_y$/SiO$_2$-600$^\circ$C catalyst.
6. Investigating the mechanisms of the V$_x$O$_y$/SiO$_2$-600$^\circ$C catalyzed oxidation reaction.
4.2 Preparatory work
The effect of calcination temperature on the distribution of vanadium oxide phases in the catalysts was studied by calcining 10 g samples of NH₄VO₃ samples in air at 250°C, 300°C, 350°C, 400°C and 600°C for 20 h (Scheme 4.1).

Scheme 4.1 Calcination of NH₄VO₃ at different temperatures to obtain vanadium oxides.

For the supported catalyst (VₓOᵧ/SiO₂-600°C), fumed silica was acidified by stirring in 0.2 M phosphoric acid for 24 h at room temperature. 10 g of ammonium metavanadate was then impregnated onto the acidified fumed silica by adding it to the mixture and stirring for 48 h. The mixture was then filtered, and the precipitate was dried in the open. The precipitate was further dried at 70°C for 72 h. The precipitate was then calcined in air at 600°C for 20 h to produce the supported catalyst (Scheme 4.2).

Scheme 4.2 Synthesis of the silica supported catalyst VₓOᵧ/SiO₂-600°C.
4.3 Results and discussion

4.3.1 Fourier Transform Infra-Red (FT-IR) spectroscopy

4.3.1.1 Optimization of calcination temperature

FT-IR spectra of the samples are compared in Figure 4.1. Absorptions in the 250°C sample which can be attributed to V=O stretching motion of distorted octahedral and square pyramids, respectively were observed at 1004 cm\(^{-1}\) and 968 cm\(^{-1}\), respectively.\(^{194,245}\) These merged into a single band typical of the square pyramidal geometry V=O stretching motion in samples prepared above 350°C.\(^{245}\) A band was observed around 850 cm\(^{-1}\) in the spectra for the 350°C–600°C samples and around 740 cm\(^{-1}\) for the 250°C and 300°C samples. These bands, together with those found in the region; 440–530 cm\(^{-1}\) in all the samples, can be ascribed to V-O-V symmetric and asymmetric stretching vibrations.\(^{194}\) Splitting of the V-O stretching band in the 440–530 cm\(^{-1}\) was also observed in the 250°C and 300°C samples. This can be attributed to the differences in the strengths of the V-O bonds.\(^{188,189,246}\) A shift of the V-O-V band from lower wavenumbers (738 cm\(^{-1}\) in the 250°C sample), to higher wavenumbers (856 cm\(^{-1}\) in the 600°C sample) with increase in calcination temperature can be explained as a manifest of changes in symmetry.\(^{188}\) The bands at 3587 cm\(^{-1}\) and 1624 cm\(^{-1}\) can be assigned to O–H stretching and H–O–H bending vibrations of water molecules, respectively. The bands at 3256 cm\(^{-1}\) and 1413 cm\(^{-1}\) are due to asymmetric stretching and the symmetric bending vibrations of NH\(_3\)\(^{+}\).\(^{194}\)

![Figure 4.1](image-url) 

**Figure 4.1** Changes in FT-IR spectra of calcined NH\(_4\)VO\(_3\) with calcination temperature.
4.3.1.2 Characterization of the (VₓOᵧ/SiO₂-600°C) catalyst

Very intense unsymmetrical peaks were observed at 1096 cm⁻¹ and 474 cm⁻¹ in the FT-IR spectrum for fumed silica (Figure 4.2). These, respectively, are characteristic of the anti-symmetric motion of silicon atoms in siloxane bonds (Si-O-Si) and the rocking motion of oxygen atoms bridging silicon atoms in the siloxane bonds. A much weaker peak was observed at 840 cm⁻¹ and is due to silanol (Si-OH) stretch vibrations.⁴⁴⁷ Corresponding peaks were observed in the spectrum for the silica-supported catalyst at 1095 cm⁻¹, 463 cm⁻¹ and 831 cm⁻¹. In addition to those peaks, peaks were observed at 952 cm⁻¹ and 576 cm⁻¹, and can be attributed to the formation Si-O-V linkages and V-O stretching, respectively, confirming that vanadium oxide was successfully supported on silica.⁴⁴⁸

![Figure 4.2 FT-IR spectra of fumed silica and the VₓOᵧ/SiO₂-600°C catalyst.](image)

4.3.2 Powder X-Ray diffraction (P-XRD)

4.3.2.1 Optimization of calcination temperature

The XRD for the 250°C sample showed the presence of significant amounts of a (NH₄)₂V₆O₁₆ monoclinic phase in the sample, 97.06% (Table 4.1 and Figure 4.3). The (NH₄)₂V₆O₁₆ phase decreased with increase in calcination temperature; from 97.06 %, 37.61 % and 1.98 %, down to 0 %, for the 250, 300, 350 and 400°C respectively. The 600°C sample was 100% V₂O₅ orthorhombic phase. A percentage of the VO₂ phase was also noted in the 350°C and 400°C samples. Biedunkiewicz et al.¹⁹² demonstrated that NH₄VO₃ decomposes through a series of steps which include the formation of (NH₄)₂V₆O₁₆. The distribution of phases formed is related to temperature and time, among other factors.⁶⁸ 600°C was
selected as the temperature for the synthesis of the vanadium(V) catalyst and 400°C as well to investigate if the presence of VO₃ had a significance of the catalytic reaction.

**Table 4.1** Distribution of phases in the NH₄VO₃ samples calcined at different temperatures.

<table>
<thead>
<tr>
<th>Calcination temperature</th>
<th>Phase composition (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V₂O₅</td>
<td>VO₂</td>
</tr>
<tr>
<td>600°C</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>400°C</td>
<td>99.98</td>
<td>0.02</td>
</tr>
<tr>
<td>350°C</td>
<td>97.97</td>
<td>0.05</td>
</tr>
<tr>
<td>300°C</td>
<td>62.39</td>
<td>-</td>
</tr>
<tr>
<td>250°C</td>
<td>2.94</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 4.3** Changes in XRD spectra of calcined NH₄VO₃ with calcination temperature and upon supporting on silica.

4.3.2.2 Characterization of the VₓOᵧ/SiO₂-600°C catalyst
The supported catalyst (VₓOᵧ/SiO₂-600°C) had 96.13 % of the V₂O₅ phase and 3.87 % of the VO₂ phase. (Figure 4.3). An amorphous halo characteristic of adding an amorphous silica support was observed between 2θ = 15 and 35 in the diffractogram for the supported catalyst. Significant broadening in reflections after 2θ = 40 and merging of several reflections which were close to each other (e.g. at 2θ = 41 and between 2θ = 46 and 60) was observed in the VₓOᵧ/SiO₂-600°C catalyst. The same broadening
and merging of reflections was also observed in the spectrum for the catalyst synthesized at 400°C (e.g. between 2θ = 47 and 48).

On adding an amorphous material to a crystalline material, the final pattern is expected to be a convolution of the amorphous and crystalline phase. The amorphous phase is detected as a broad reflection due to scattering from a wide range of directions compared to lattice scattering in crystals. Crystalline phase reflections are intense and narrow; hence the reflections for V2O5 appeared to be sitting on top of the amorphous silica phase. Peaks of a crystalline phase can also shift or broaden if the amount of amorphous phase added is enough to influence the lattice distance, the micro-strain or the "crystal size" itself. Broadening of reflections can also be attributed to the wider variety of sizes of the crystallites due to immobilization on silica. A wider range of crystallite sizes in the 400°C unsupported sample might have led to the broadening in some of the peaks.

4.3.3 Electron Paramagnetic Resonance (EPR)

The EPR spectra for the unsupported catalysts VₓOᵧ-400°C and VₓOᵧ-600°C, and the supported catalyst VₓOᵧ/SiO₂-600°C are presented in Figure 4.4. An anisotropic EPR spectrum was obtained for the supported catalyst. The spectrum showed hyperfine interaction lines typical for vanadium, derived from the interaction of unpaired electrons with the nuclear magnetic moment (⁵¹V, I = 7/2) with a g-factor = 1.9661. According to studies of supported V₂O₅ samples by Gupta et al., the response to EPR of the samples can be attributed to electron super-exchanges in the V⁴⁺-O-V⁵⁺ chains and these can manifest as a Zeeman’s effect signal with an underlying hyperfine structure of isolated V⁴⁺. Only the Zeeman’s effect signals, which originate from the interaction on the unpaired electrons in the samples with the external magnet, were observed in the spectra of the unsupported catalysts around g-factor = 1.9661. In the case of VₓOᵧ-600°C which was reported to be 100% V₂O₅, the signal could be as a result of partial reduction of the V₂O₅, by NH₃ produced from NH₄⁺, which could not be picked up by the XRD.
4.3.4 X-Ray Photoelectron Spectroscopy (XPS)
In the XPD spectrum of V$_2$O$_5$/SiO$_2$-600$^\circ$C, the presence of peaks at 103.0, (516.8/523.3/975.4) and 532.08 keV, confirms the presence of silica, vanadium, and oxygen, respectively, in the V$_2$O$_5$/SiO$_2$ catalyst, as expected (Figure 4.5). The effect of spin orbit coupling is noticed by the V2p$_{3/2}$ and V2p$_{1/2}$ peaks at 516.8 and 523.3 eV, respectively. A vanadium Auger electron peak is also observed at 925.4 eV.$^{229}$

Figure 4.4 EPR spectra for the supported and unsupported V$_2$O$_5$ catalysts.
Figure 4.5 Wide scan XPS spectrum of the $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ catalyst. The insert shows the high resolution XPS scan for V 2p.

4.3.5 Energy Dispersive Spectroscopy

Successful hosting of vanadium onto silica in the synthesis of the $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ catalyst can be noted from the shift in energy of the vanadium peak from ~5.5 keV down to ~5.0 keV. The presence of vanadium at ~5.0 keV is also noted in the EDS of the $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ catalyst after use (Figure 4.6).

Figure 4.6 EDS of (a) $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ and (b) $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ after use.

4.3.6 Scanning Electron Microscopy (SEM)

No definite shape or size range could be established for the fumed silica particles before or after hosting vanadium (Figure 4.7). No significant changes in the morphology of the $\text{V}_x\text{O}_y/\text{SiO}_2-600^\circ\text{C}$ particles could be established after use.
4.3.7 Catalytic oxidation studies VₓOᵧ/SiO₂-600°C

The goal to compare the catalytic activities of the vanadium oxide catalysts synthesized at different temperatures (VₓOᵧ-250°C; VₓOᵧ-300°C; VₓOᵧ-350°C; VₓOᵧ-400°C and VₓOᵧ-600°C) was not achieved since their exact vanadium contents were not determined. It is proposed that differences in activity must be realized due to the variations in phase compositions of the catalysts. Yuan et al.²⁰⁹ realized variations in the reactivities of vanadium cluster species in the oxidation of hydrocarbon molecules depending on their charges (cationic, neutral or anionic). Focus was therefore put on the VₓOᵧ/SiO₂-600°C catalyst. Optimization studies for amount of oxidant, temperature and amount of catalyst were carried out using the VₓOᵧ/SiO₂-600°C catalyst.

4.3.7.1 Optimizing amount of catalyst (VₓOᵧ/SiO₂-600°C)

Starting off with the optimal amount of oxidant (t-BuOOH), amount of dibenzothiophene (DBT) and temperature used for the complex catalyst [VO(PIMH)₂], i.e. 2 mL t-BuOOH (1.05 mol), 100 mg (0.543 mmol) of dibenzothiophene and 60°C, optimization to find the best amount of catalyst (VₓOᵧ/SiO₂-600°C) was carried out. As the amount of catalyst was increased from 2.5 mg to 10 mg (11-43.9 µmol), an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 80.7% to 100% was noted (Figure 4.8 and Table 4.2). In the absence of the catalyst, the overall percentage conversion of DBT to DBTO₂ was only 31.2%. Increase in activity can be explained in terms of the kinetics of the reaction, where an increase in amount of catalyst increases the number of active sites which participate in the catalytic oxidation.
The turnover frequency (TOF) decreased from 1958.0 h\(^{-1}\) to 773.9 h\(^{-1}\) since the number of moles of catalyst was increased. 10 mg of catalyst was used for subsequent studies.

**Figure 4.8** Percentage conversion of DBT using different amounts of catalyst (V\(_x\)O\(_y\)/SiO\(_2\)-600\(^\circ\)C) Amount of DBT = 100 mg (0.543 mmol); \(t\)-BuOOH = 2.0 mL (1.05 mmol); acetonitrile solvent = 10 mL; temperature = 60\(^\circ\)C.

4.3.7.2 **Optimizing amount of oxidant**
In the presence of 100 mg of dibenzothiophene and 7.5 mg (43.9 \(\mu\)mol) of catalyst (V\(_x\)O\(_y\)/SiO\(_2\)-600\(^\circ\)C) in 10 mL of acetonitrile and a temperature of 60\(^\circ\)C, the amount of oxidant (\(t\)-BuOOH) was increased from 0.5 mL to 2.0 mL (0.263 - 1.05 mmol) resulting in an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 46.7% to 100% (**Figure 4.9** and **Table 4.2**). The turnover frequency (TOF) increased from 367.1 h\(^{-1}\) to 773.9 h\(^{-1}\).
4.3.7.3 Optimizing temperature

Optimization of temperature was carried out using 100 mg of dibenzothiophene, 10 mg (43.9 µmol) of catalyst (VₓOᵧ/SiO₂-60°C) and 2.0 mL (1.05 mmol) of t-BuOOH dissolved in 10 mL of acetonitrile. Increasing temperature from 30°C to 60°C resulted in an increase in the rate of oxidation and the overall percentage conversion of dibenzothiophene to dibenzothiophene sulfone (after 210 minutes) from 55% to 100% (Figure 4.10 and Table 4.2). Increasing temperature results in a larger number of particles with enough energy to overcome the activation energy barrier. The turn over frequency (TOF) increased from 329.1 h⁻¹ to 773.9 h⁻¹.
Figure 4.10 Percentage conversion of DBT with time at different temperatures. Amount of V$_2$O$_5$/SiO$_2$-600°C catalyst = 10 mg (43.9 µmol); DBT = 100 mg (0.543 mmol); t-BuOOH = 2.0 mL (1.05 mmol); acetonitrile solvent = 10 mL. Temperatures used = 30°C, 40°C, 50°C and 60°C.

4.3.7.4 Comparing solvents
Changing the solvent from acetonitrile to cyclohexane under the same reaction conditions [10 mg (43.9 µmol catalyst; 100 mg (0.543 mmol) DBT; 2.0 mL (1.05 mmol) t-BuOOH and 60°C] resulted in a decrease in the rate of oxidation of DBT to DBTO$_2$ and the overall percentage yield from 100% in acetonitrile to 93.8% in cyclohexane (Figure 4.11 and Table 4.2). The TOFs at 1 h. were 773.9 h$^{-1}$ and 550.7 h$^{-1}$, respectively. This can be an indication that polar solvents may enhance the activity of the catalyst considering that the mechanism is redox in nature as discussed in Section 4.3.8.
Figure 4.11 Comparing catalytic activity between acetonitrile and cyclohexane. Amount of solvent = 10 mL; amount of $V_2O_5/SiO_2$-600°C catalyst = 10 mg (43.9 µmol); DBT = 100 mg (mol); t-BuOOH = 2.0 mL (1.05 mmol); temperature = 60°C.

### 4.3.7.5 Summary of optimization studies

#### Table 4.2 Summary of results from the catalytic oxidation studies.

<table>
<thead>
<tr>
<th>$V_2O_5/SiO_2$ catalyst</th>
<th>Dibenzothiophene</th>
<th>[t-BuOOH]</th>
<th>Temp. °C</th>
<th>% Conversion after 210 mins</th>
<th>TOF (h⁻¹) After 1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg</td>
<td>µmol</td>
<td>mg</td>
<td>mmol</td>
<td>mL</td>
<td>mmol</td>
</tr>
<tr>
<td>Varying amount of catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>2.5</td>
<td>11.0</td>
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<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>5.0</td>
<td>22.0</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>7.5</td>
<td>32.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>Varying amount of oxidant</td>
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<td></td>
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<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>1.5</td>
<td>0.789</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>0.5</td>
<td>0.263</td>
</tr>
<tr>
<td>Varying temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>10.0</td>
<td>43.9</td>
<td>100</td>
<td>0.543</td>
<td>2.0</td>
<td>1.05</td>
</tr>
</tbody>
</table>

*TOF(h⁻¹): (turnover frequency), moles of substrate (DBT) converted per mole of metal ion per hour; t-BuOOH mol eq., moles of t-BuOOH:moles of substrate (DBT).
4.3.7.6 Catalytic oxidation studies of model fuel sample under flow conditions
Oxidation of the model fuel sample was carried out using 1.05 mmol \( t \)-BuOOH and 10 mg (43.9 µmol) of the \( \text{V}_2\text{O}_5/\text{SiO}_2 \)-600° C catalyst at 60°C in a flow set-up, where the flow rate was varied from 0.6 mL/h down to 0.1 mL/h resulting in % conversion of DBT to DBTO \(_2\) in the model fuel sample [100 mg (0.543 mmol) of DBT in 10 mL of acetonitrile] increasing from 35.1 % to 100% (Figure 4.12).

![Figure 4.12](image)

**Figure 4.12** Change in % conversion of DBT to DBTO \(_2\) with change in flow rate.

4.3.7.7 Catalytic oxidation studies of real fuel sample under flow conditions
A flow rate of 0.1 ml/h was adopted in the oxidation of a real fuel sample. Analysis of the fuel sample in its original state, after oxidation and after solvent extraction of the oxidized sulfur compounds with acetonitrile; was carried out using GC coupled to a Sulfur Chemiluminescence Detector (SCD) as well as a Time of Flight-Mass spectrometer (TOF-MS), and the results are presented in Figures 4.13 to 4.15. The peaks for sulfur in the original fuel sample appear in the region, 3600 to 4000 s (Figures 4.13 A and B). No significant shifts or changes in the intensity were noticed in the GC-SCD sulfur peaks between the original fuel and oxidized fuel (Figures 4.13 A and B, and 4.14 A and B). Successful oxidation of the sulfur compounds is highlighted by a significant shift noted for the TOF-MS peak of highest intensity from ~3400 s to ~3700 s (Figures 4.13 C and 4.14 C). GC-SCD sulfur compound peaks disappeared in the fuel sample upon solvent extraction of the oxidized sulfur compounds using
acetonitrile confirming the success removal of the sulfur compounds from fuel (Figures 4.15 A, B and C).

Further analysis of the GC-SCD and TOF-MS data will be carried out to quantify the exact concentrations of sulfur compounds involved in each case.
Figure 4.13 GC-SCD plots from the analysis of the original fuel sample (A) grid image, (B) XIC image and (C) the TOF-MS plot.
**Figure 4.14** GC-SCD plots from the analysis of the oxidized fuel sample (A) grid image, (B) XIC image and (C) the TOF-MS plot.
Figure 4.15 GC-SCD plots from the analysis of the oxidized fuel sample after solvent extraction of the sulfur compounds with acetonitrile (A) grid image and (B) XIC image and (C) the TOF-MS plot.
4.3.8 Catalytic oxidation mechanistic studies

V$_x$O$_y$/SiO$_2$-600°C was used to investigate the catalytic oxidation reaction mechanism of vanadium oxide based catalysts. Disappearance of the EPR signal typical for vanadium ($^{51}$V, $I = 7/2$) on addition of oxidant ($t$-BuOOH) to the catalyst suggests the oxidation of the V$^{4+}$ to the diamagnetic EPR silent V$^{5+}$ in the catalyst (Figure 4.16). The signal is recovered, a long while after introduction of the substrate into the mixture indicating reduction of the V$^{5+}$ back to V$^{4+}$. However, there was a slight variation in the EPR signal. This may be due to slight changes in the coordination geometry of the V$^{4+}$-O-V$^{5+}$ system.

![Figure 4.16 First derivative EPR signals of (a) the neat catalyst; (b, c and d) on addition of the oxidant (t-BuOOH); (e and f) on addition of the substrate; and (g) the recycled catalyst. Neat (0.526M) t-BuOOH was used.](image)

The possible mechanism for the oxidation reaction using the supported catalyst is presented in Scheme 4.3. The reaction is proposed to involve the oxidation of V$^{4+}$ in the neat V$_x$O$_y$/SiO$_2$-600°C catalyst (a) into V$^{5+}$ (b) by the oxidant (t-BuOOH) and a possible formation of a highly reactive peroxo by another t-BuOOH molecule (c) which then oxidizes the substrate (d) to regenerate the V$^{4+}$ in the catalyst.
Scheme 4.3 Proposed catalytic oxidation reaction mechanism when using the V₄O₉/SiO₂-600°C catalyst.

4.4 Conclusions
Varying the calcination temperature of NH₄VO₃ in air from 250°C to 600°C yielded different compositions of vanadium oxides; from predominantly (NH₄)₂V₆O₁₆ with a slight VO₂ phase at 250°C, a mixture of (NH₄)₂V₆O₁₆ and V₂O₅ at 300°C, to predominantly V₂O₅ above 350°C. Successful hosting of vanadium oxides onto a silica support was also demonstrated with FT-IR and P-XRD. EPR confirmed the possibility of having V⁴⁺-O-V⁵⁺ sites in the system of the supported silica catalyst.

The silica supported catalyst proved to have good activity in the oxidation of DBT to DBTO₂ with 10 mg successfully converting 100% of 100 mg (0.543 mol) DBT to DBTO₂ using 2.0 mL (1.05 mol) t-BuOOH at 60°C. The catalyst also proved to be effective for the oxidation of the sulfur compounds in a real fuel sample when it was tested in an improvised flow set-up.

The reaction mechanism of the silica supported catalyst is proposed to be redox in nature where V⁴⁺ sites within the catalyst are the ones which are directly involved in the catalysis. Studying the mechanistic aspects of the reaction provided insight to aspects that can be considered in the development of the catalyst. It is essential to vary the synthesis approaches to obtain different quantities of the V⁴⁺-O-V⁵⁺ sites by having different vanadium oxide phase percentages, and also investigate the role of each oxide in the catalytic reaction to fully understand ways of improving the activity of the catalyst.
Chapter 5: Conclusions and Future work

5.1 Conclusions
Catalysts based on vanadium complexes and vanadium oxides were successfully synthesized and characterized. From the study conducted, they have shown good potential in the oxidation of dibenzothiophene, the major sulfur compound which remains in hydrotreated fuel. From the EPR studies carried out, it can be concluded that the reaction mechanisms for both the complex catalysts and vanadium oxide catalysts are redox in nature and could be somewhat related. A more detailed reaction mechanism was proposed for the complex catalysts due to the nature of the catalysts which allowed further tests, such as UV-Vis, to be conducted.

Choosing between the use of complexes or vanadium oxides is a matter of weighing between efficiency and cost, where the complexes can be easily engineered to achieve very high turn-over frequencies and vanadium oxides on the other hand are much cheaper to synthesize. The development of such viable catalysts for the oxidation of refractory sulfur compounds in fuel make oxidative desulfurization a worthwhile consideration for application as a complimentary technique to hydrodesulfurization to obtain low sulfur level fuels. However, more work needs to be carried out to understand how these catalysts work and to improve them further.

5.2 Future work
Although much ground has been covered in testing the catalysts and understanding how they work, several other studies still need to be conducted to improve the catalysts and fully understand their mechanistic aspects. The polymer catalyst and the silica supported vanadium oxide catalysts need to be examined for the surface area using the Brunauer-Emmett-Teller (BET) method. The active sites of the silica supported catalyst also need to be examined further.

Obtaining the single crystals of the methoxy derivative complex catalyst [VO(PIMMeO)₂] has been difficult due to the high solubility of the complex in most common laboratory solvents. Several recrystallization techniques will be attempted to obtain single crystals of the complex catalyst to complete the trends observed so far with the other catalysts. Attempts will be made to monomerize the -NO₂ ligand and incorporate it into a polymer as demonstrated using the neat complex [VO(PIMH)₂].
Determination of the exact vanadium content of the vanadium oxide catalysts is very crucial in order to compare the catalytic activities of the different phase compositions and resolve which mixture (or calcination temperature) gives the highest catalytic activity.

Further analysis of the GC-SCD and TOF-MS data will be required to quantify the amounts of sulfur compounds remaining after desulfurization of the real fuel samples (i.e. after oxidation using the nanofibers and silica supported vanadium oxides, and solvent extraction).

It will also be crucial to carry out other tests to critically evaluate the quality of the fuel after oxidative desulfurization considering the negative impacts the oxidation step may have on other compounds in the fuel matrix. Recyclability and leaching studies of the catalysts are just as important since contamination of fuel with vanadium metal is also detrimental to the environment.

Further tests for singlet oxygen will have to be conducted to understand the oxygen transfer step fully in the mechanism of VO(PIMH)\(_2\). The use of furfuryl alcohol which is more specific for singlet oxygen in singlet oxygen quenching studies\(^{239-243}\), and the free radical traps; 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) or 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) which generate species with longer lifetimes\(^{233-235}\), is also an avenue that will be followed to further understand the oxygen transfer step. Free radical traps will also have to be employed for the V\(_x\)O\(_y\)/SiO\(_2\)-600\(^\circ\)C catalyst. Ce\(^{4+}\) studies could also be used to confirm the generation of dioxygen.\(^{250}\)
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