Gold-Catalysed Oxidation of Lignin-Derived Building Blocks

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Abstract

Gold-Catalysed Oxidation of Lignin-Derived Building Blocks

PhD Dissertation of Amani Musharah submitted 23 April 2016 The University of Manchester, School of Chemistry

The use of heterogeneous catalysts containing Au nanoparticles supported on TiO₂ has been explored for oxidative aqueous phase transformations of sustainable phenolic and benzoic acid derivatives that can be obtained from lignin. Au/TiO₂ catalysts were chosen because of their high activity for ambient pressure oxidations of gas phase species, and because their synthesis is facile and reproducible through a modified depositionprecipitation method. The aerobic oxidation of syringic, vanillic, and ferulic acid as well as of guaiacol, eugenol and anisole was investigated at temperatures up to 70°C under (i) atmospheric air sparging in an open reactor and (ii) at 10 atm air pressure in a closed reactor system. The catalysts were characterised by Transmission Electron Microscopy (TEM), Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy and the reproducibility of their catalytic activity independently monitored by determining their activity for carbon monoxide oxidation in a gas flow reactor.

The oxidation of syringic acid, vanillic acid, ferulic acid over Au/TiO₂ resulted in the formation of 2,6-dimethoxy benzoquinone, guaiacol, and vanillin, respectively, indicating high selectivity for decarboxylation followed by selective oxidation at the position releasing the leaving group. Guaiacol was found to form tetraguaiacol, while eugenol produced quinone methide. Generally, higher air pressure strongly accelerated the transformations, indicating that availability of oxidants formed from O₂ is the rate limiting step in the observed transformations. No transformations took place when O₂ was excluded from the systems. Overall, guaiacol was found to be unreactive, even at elevated air pressure. The overall reaction pattern emerging from these studies is that the aerobic oxidation in the presence of Au/TiO₂ mimics known biotransformations, for example peroxidase-catalysed oxidations involving H_2O_2 .

To assess how the functional groups on the aromatic ring influence reactivity the oxidation of p-hydroxybenzoic acid and of 2,6-dimethoxybenzoic acid was also assessed. It was found that decarboxylation of p-hydroxybenzoic acid proceeds, albeit rather slowly, forming phenol, with no further oxidation to hydroquinone or benzoquinone. Taken together these results indicate that the methoxy moieties influence reactivity through both their inductive and resonance effects: leaving of the carboxylic acid group appears to be enhanced through the inductive effect, while further oxidation at the phenolic site seems to be activated through the resonance effect in ortho-position. In line with this hypothesis, it was recently found that dimethoxybenzoic acid converts fast.

Declaration

I declare that no potion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Amani H. Musharah

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List of Abbreviations

DMBA	2,6-Dimethoxybenzoic acid
DMBQ	2,6-Dimethoxybenzoquinone
ESEM	Environmental Scanning Electron Microscope
FA	Ferulic Acid
FT-ICR	Fourier Transform – Ion Cyclotron Resonance Mass Spectrometry
GC	Gas Chromatography
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectrometry
LC	Liquid Chromatography
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance Spectroscopy
PFR	Plug Flow Reactor
RGA	Residual Gas Analyser
SA	Syringic Acid
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TOF	Turnover Frequency
VA	Vanillic Acid

1. Introduction and background

1.1 Overview

The work presented in this thesis focuses on exploiting lignin, an underutilized natural resource, and studying the potential of upgrading lignin and lignin building blocks using a catalytic route. The objective is to produce higher value chemicals for use in pharmaceuticals, industry, and perhaps even in renewable fuels. In order to achieve this, a chemical method for the transformation of lignin building blocks into more useful chemicals in a relatively facile process must be found.

Energy use, the associated global warming and its environmental impact are among the top concerns in many societies, as the global climate system impacts the political climate. As the human population increases, natural resources become more limited; in addition, the activities of daily modern life and the human demand for food, water, timber and fuel are putting such a huge strain on natural resources that the earth's ability to sustain future regeneration can no longer be guaranteed. There is therefore a need to maximize the utilization of any natural resource and avoid wastage of any materials by using processes that can be improved.

Lignin is the second most abundant natural material after cellulose, and it represents about 30% of wood composition. Currently, lignin is produced mainly as a by-product of the paper industry. Almost 40-50 million tons of lignin are produced annually, and it is underutilized in its typical use as a low-grade fuel [1].

The catalytic upgrade of bio oils has been the subject of many studies. A lot of work has been done on upgrading cellulose- derived streams, while very limited attention has been paid to lignin-derived chemicals, although lignin could be an attractive precursor for some important aromatic chemicals, such as phenolics [2, 3].

Lignin is a low-cost material, and it has shown very promising potential for use as a source for renewable fuels and chemicals when it is decomposed into its smaller units. Lignin presents a very promising alternative for the production of petroleum fuels due to the possibility of using existing petroleum infrastructure for bio-fuel production [4, 5].

So far, the bio-fuels industry has relied on cellulose from starchy food crops such as corn and sugar cane as feedstock for fuel production. However, this has put the industry into direct competition with human food needs, and food prices have risen as a result. Cellulose represents only about a third of plant matter, however, and converting lignin, an essential component of wood, to fuels instead of converting cellulose could significantly increase fuel yields. [6-8]

The main aim of this study is to identify a process to upgrade lignin-derived building blocks into higher value specialty chemicals for use in industry or energy generation to maximize the value of a natural commodity rather than burning it for heat. One of the most likely routes to upgrading lignin would be depolymerization followed by catalytic transformation. Lignin degradation processes yield complex bio-oil mixtures of oxygen-containing chemicals, mainly syringols and guaiacols. Lignin pyrolysis products are considered to be corrosive, thermally and chemically unstable, and to have low heating value. They are also immiscible with other important chemicals such as petroleum fuels, which might limit their use. One of the most challenging issues concerning lignin-derived chemicals is their potential to be converted to fuels upon the removal of oxygen, which typically represents 35-40% of the molecular weight of lignocellulose. Removal of oxygen is essential as the presence of a high percentage of oxygen in fuels might lead to corrosion in refineries and engine parts [9]. Currently, the maximum allowed oxygen content in fuel should not exceed 10 wt.% [10].

The available literature on bio oil conversion is missing the fundamental chemistry governing the conversion steps. Knowledge about catalytic reaction networks is limited to primary products or to knowledge about a group of related compounds. Additionally, it is difficult to find sufficient data on reactions of individual lignin-derived chemicals. The complexity of the resulting streams of lignin pyrolysis limits the use of available data in predicting catalytic reaction performance. Understanding the conversion processes and reactions networks of bio-oils might be significant for development of the technologies of utilizing lignin and other biomass resources for the production of renewable fuels and higher value chemicals.

Hence, the aim of this study is to evaluate the catalytic transformation of lignin degradation products. This study aims to contribute to the overall knowledge about lignin

and lignin-derived chemicals by understanding the products of lignin pyrolysis, as well as their possible catalytic reactions, and understanding the products of those reactions.

Supported metal catalysts are among the most selective, highly active catalysts for various applications involving high-volume transformations. Pt, Pd, Au and Ag are among the most investigated catalysts, for wide range of applications [11, 12]. The properties of such catalysts can be influenced by the synthesis method, the type of support, and the pre-treatment conditions.

Gold had historically been considered to be inert to reactions. However, it was found in the late 1980s that gold supported on metal oxides could be an active catalyst for different reactions, including oxidation of CO. In 1985, Hutchings found that gold could be highly active in the hydrochlorination of acetylene in the production of vinyl chloride from hydrogen chloride [13]. In 1987, Haruta was able to define procedures to prepare gold catalysts using different supporting materials. Those catalysts were found to be catalytically active for the oxidation of CO at temperatures as low as -70°C [14]. These reports triggered a huge interest in gold catalysis globally. [15-17]

Gold-catalysed reactions fall into two main categories: heterogeneous and homogeneous catalysis. Heterogeneous catalysis includes catalysis by gold nanoparticles and thiolmonolayer gold surfaces. Homogeneous catalysis employs gold (I) or gold (III) compounds and is used mainly for organic synthesis. Catalysis by gold is considered appealing because both homogeneous and heterogeneous catalysts are found to be effective in oxidation reactions based on the use of air or oxygen, the most attractive oxidant, and that gold catalysed reactions can proceed selectively at room temperature with a satisfactory reaction rate and no significant decomposition of the catalyst [18]. Moreover, various studies have found that gold catalysts can be effective for organic synthesis and transformation with a reasonable conversion rate [19]. Gold has been found to be active as an oxidation catalyst by many research groups, including the host research group of the author.

The compounds studied were syringic acid, vanillic acid, ferulic acid, guaiacol, eugenol and anisole. These compounds were reacted in the liquid phase in the presence of gold on titania (Au/TiO₂) as a solid catalyst.

A recent study by the US department of energy suggested various areas of development in the field of lignin upgrading, listing a number of lignin-derived building blocks and potential routes of upgrade [20]. The oxidation reactions of some of the listed compounds over supported gold catalyst were selected for study.

There are several 'conventional' analytical techniques widely used to provide information on the chemical structure and content of chemical liquid and solid samples, such as UV-visible absorbance and electrospray mass spectrometry, chromatography and NMR. UV-visible absorbance spectroscopy is used to detect any change in light absorbance. This will be followed by liquid chromatography (LC) and gas chromatography (GC) [21]. Chromatography is used to determine the weight percentage of each component in a reaction mixture, and whether change has occurred in the concentration of each component before and after the reaction. NMR analyses provide further additional information about the structure of the compounds [22].

General materials and methods for the oxidation of lignin-derived chemicals will be presented in chapter 2. Catalyst characterisation techniques will be described, specifically the CO oxidation test as a basic test for catalyst activity. Analytical methods used for monitoring the progress of the catalytic reaction and analysing products will be presented in detail. These methods include NMR, UV-visible spectroscopy, and gas and liquid chromatography. The two reactors used to perform the catalytic reactions will be explained and illustrated, and reaction conditions will be discussed.

Chapter 3 will present the method for producing highly active supported catalysts for oxidative transformations. The morphology and oxidation performance of the produced catalyst will be described. Findings about the effects of different catalyst pre-treatment procedures will be presented as well.

Chapter 4 illustrates the experimental results of the catalytic oxidation of syringic acid. This includes the control experiments carried out to confirm the role of the gold catalyst in the reaction, as well as a number of experiments that contributed to understanding the reaction mechanism of syringic acid oxidation that led to the identified products.

Chapter 5 reports the experimental data for vanillic acid oxidation over a gold catalyst, and the control experiments carried out, followed by a discussion section. Ferulic acid oxidation reaction over the supported gold catalyst will be presented in Chapter 6.

Findings of guaiacol oxidation reaction and experimental data are discussed in Chapter 7. Different theories and conclusions on guaiacol transformation are presented.

Chapter 8 will discuss the catalytic transformation of eugenol, a lignin-derived compound, over the prepared gold catalyst. Experimental data will be presented and discussed, and a conclusion presented at the end of this section.

Chapter 9 reports the experimental data and findings of the oxidation of other chemicals, including one lignin-derived compound, anisole, and two non-lignocellulosic compounds (p-hydroxybenzoic and dimethoxybenzoic acids). The reactions of these compounds were studied in order to provide a better understanding of the relationship between chemical structure and reactivity towards gold as a catalyst.

A general discussion of the experimental data of lignin-derived chemicals subject to this study will be presented in detail in Chapter 10. Reaction mechanisms and proposed reaction networks will be illustrated. The relationship between the structure of these compounds and their conversion rates will be discussed. Challenges and recommendations will be highlighted at the end of this section. A conclusion on the findings of this work will end this report, followed by suggestions of future work and a listing of referenced work.

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1.2 Lignocellulosic resources

The word lignin is derived from the Latin word "lignum," which means wood. Lignin is found in the plant cells (Figure 1-1) and it is responsible for the rigidity and impermeability of the plant's structure, acting as a cementing material for cellulose wood fibres [23, 24].



Figure 1-1: Wood composition

Lignin is also the generic term for a large group of complex aromatic polymers resulting from the dehydrogenative polymerization of three different phenylpropane- or monolignols derived from wood: p-coumaryl, coniferyl and sinapyl alcohol (Figure 1-2). This polymerization process starts with the enzymatic oxidation of the phenolic hydroxyl groups in the monolignol when an electron is transferred from a lower to a higher energy level. This results in the production of free radicals and reactive monolignol species, which can couple with each other to produce lignin [25]. The degradation of each one of these monolignols produces different compounds, depending on the functional group on the main structure. Guaiacols, syringols, and phenols result from the thermal degradation of coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol respectively [26, 27].

Hemicellulose links lignin and cellulose [28]. Lignin can make up to 15–36% of the dry weight of the wood, depending on the type of plant and its need for structural support and water transport. Thus, lignin is considered the second most abundant natural polymer after cellulose [29-31].



Figure 1-2: Mono-lignols as the main units of lignin

1.2.1 Types of lignin

Lignin is called 'protolignin' in its natural form. Lignins can be grouped into different types based on their origin and structure. There are many variations in each type of lignin, as lignin characteristics differ based on the species, and even based on the different tissues and cells in the same plant [32]. For instance, softwood (gymnosperm) lignin contains guaiacyl units, while hardwood (dicotyledonous angiosperm) lignin contains both guaiacyl and syringyl units. Figure 1-3 is an illustration of the complex molecular structure of wood lignin.



Figure 1-3: Molecular structure of lignin [33]

Many techniques can be used to isolate lignin, but most of these techniques mainly involve dissolving lignin out of the cell wall, or dissolving the non-lignocellulosic wall that surrounds lignin. Each technique used to isolate lignin from other wall components produces a different type of material. Lignins are usually known by the name of the method used for the isolation, and can be also classified according to their origin and their chemical structure. However, the isolation process used to remove lignin from the plant may result in some changes to the chemical structure, which makes it hard to determine the exact structure of each type of isolated lignin precisely.

One of the most common processes for lignin isolation is kraft pulping. During this process, cellulosic fibres are separated from each other by removing lignin. This results in the production of the pulp used for paper manufacturing [34].

During conventional Kraft cooking to produce pulp, wood chips are reacted with a solution of sodium hydroxide and sodium sulphide, known as white liquor. The mixture is heated to about 170°C and allowed to cook for two hours in a pressure vessel known as a digester. This process results in lignin fragmentation into smaller, water-soluble units as a result of the reaction of lignin with hydroxide and hydrosulphide anions. Lignin fragmentation continues via the cleavage of the linkages between phenylpropane units, 'monolignols', which generate free phenolic hydroxyl groups. The resulting monolignols tend to survive the pulping process as their carbon–carbon linkages are considerably more stable.

During Kraft pulping, two main types of lignin reactions can occur: degradation and condensation. Degradation reactions release lignin fragments and enhance their dissolution, whereas condensation reactions lead to the formation of alkali-stable linkages, which makes these reactions less desirable [25].

Lignin contains carbon-oxygen-carbon (C-O-C) bonds that connect smaller hydrocarbon chains together. To release the smaller hydrocarbons and produce alkanes and alcohol from lignin, C-O-C bonds must be broken prior to any treatment. However, there are other C-O-C bonds within the small hydrocarbon units that must be kept un-broken, as they are essential for alcohol production. Breaking the C-O-C bonds between chains, while leaving those within chains undamaged, is a challenge [35].

Lignin is a large polymer with a very high molecular weight. It can give a wide range of products depending on the reaction it has gone through. For instance, lignin produces vanillic acid and syringic acid when it is oxidized. The complex structure of lignin and the presence of hydroxyl group substituents in its structure make it a good candidate for oxidation. Based on the reaction conditions, the oxidation products of lignin range from aromatic aldehydes to carboxylic acids. In some studies, wet oxidation of guaiacol, syringol, and phenol, used as model lignin compounds, resulted in the production of acetic acid. Nitrobenzene, metal oxides, and hydrogen peroxide are the most popular oxidants for lignin, while catalytic oxidation with gaseous oxygen is another alternative. [6, 36, 37]

Recently, the upgrading of lignocellulosic biomass has gained significantly more attention. Because of their low cost and abundance, lignocellulosic materials represent a promising source for the production of renewable fuels and high-value chemicals (Figure

1-4). Fuel production from lignocellulosic biomass may reduce the conflict between using cellulosic materials in food and fuel [2, 38].



Figure 1-4: Illustration of different lignin decomposition processes and their corresponding products

1.2.2 Lignin degradation processes and products

As a macromolecule with a high molecular weight, lignin can be converted into smaller units with lower molecular weight by pyrolysis, gasification, liquefaction or combustion. These processes involve pyrolysis as either the sole cause or an important cause of fragmentation.

Pyrolysis is a relatively simple thermochemical route to breaking down lignin into low molecular weight compounds in the absence of oxygen (air). It is an irreversible process that results into numerous chemical species and different forms. Pyrolysis products of lignin are usually classified into three categories based on their physical state: char (solid), bio-oil (liquid) and non-condensable gases (gas). Char is the solid residue consists of the non-volatile fragments of hemicellulose, cellulose and lignin resulting from pyrolysis as a result of dehydration, condensation and re-polymerization. A bio-oil

is a dark-coloured liquid with a smoky odour that results from the condensation of the pyrolysis vapours and aerosols. The non-condensable fraction of pyrolysis vapours usually consists of gaseous species such as carbon monoxide, carbon dioxide, methane and hydrogen. The relative ratio between these three products varies depending on the conditions of the decomposition process employed.

Depending on the composition of the biomass feedstock, different types of biomass can yield bio oils of up to 60-95 wt.%. Wood can yield 72-80 wt.% bio oil based on the relative amount of cellulose and lignin in the wood material. Mixed paper streams typically yield more than 75 wt. % [39]. Figure 1-5 shows some examples of the compounds resulting from lignin degradation.



Figure 1-5: Lignin-derived compounds

1.2.3 Recent advances in lignin upgrading

The rapid depletion of fossil fuels means that finding a renewable, non-fossil based source of energy has become a necessity. Many forms of alternative energy have been investigated, including solar, wind, and bioenergy. Increasing attention is being paid to renewable energy generation from biomass, as it is a readily available renewable resource. Many technologies based on the use of biomass have been developed. Lignin represents a very attractive source of renewable fuels because of its complex structure and the low oxygen content compared to cellulose. The potential of producing fine and bulk compounds and the low oxygen content makes lignin more suitable for the production of streams in the range low oxygenates fuels [40].

The idea for better utilization of lignin started as early as 1975, when Gaetano proposed a method to polymerize lignin derivatives using different solvents in order to increase its economic value [41]. In 1988, Afifi proposed that lignin depolymerisation followed by selective upgrading would result in industrial grade chemicals such as phenol or BTX (benzene, toluene and xylene), or to deoxygenated fuel streams. They used anisole (methoxy benzene), a prototype of the aromatic methoxy linkage in lignin degradation products to study lignin pyrolytic pathways under high temperatures and pressures. The study was performed in the presence and absence of tetralin, a hydrogen donor solvent. The homogenous upgrading reaction of anisole produces various compounds including benzene and cresols, in addition to phenol and toluene. This group showed that a free radical initiates the reaction that breaks the methoxy linkage leading to methyl and phenoxy radicals [42].

In 1991, Bridgwater and Cottam used zeolite and hydrotreating catalysis to upgrade lignin bio oils. However, they found that the products of their process could not compete with conventional fuels, and that more advanced technologies would be necessary to produce high-quality products from bio oils [43].

The first breakthrough in upgrading biomass lignin was reported in the same year, when Sharma and Bakhshi studied the catalytic upgrading of biomass-derived oils to transportation fuels and chemicals. Their work showed that bio-oil resulting from fast pyrolysis of wood could be upgraded to transportation fuels and useful chemicals. They reported that the hydro-treatment catalysis of bio oils at 250- 450°C and 15-20 MPa H_2 pressures yielded up to 55 wt. % of liquid product containing 40-50 wt. % of gasolinequality hydrocarbons [44, 45].

The work by Sharma and Bakhshi sparked a huge interest in the field of lignin upgrading. Many studies were subsequently done using different methods to upgrade lignin bio-oil. In 1997, Wang and his group succeeded in producing hydrogen clean fuel using catalytic steam reforming of fast pyrolysis oils. Their strategy was to apply fast pyrolysis of biomass to produce bio oil, followed by catalytic steam reforming and shift conversion of specific fractions of the resulting oil. The conversion was done over a commercial nickelbased steam-reforming catalyst. Hydrogen yields as high as 85% of the stoichiometric value were obtained [46].

Later, in 2004, Czernik and Bridgwater reviewed the applications of bio oils produced from fast pyrolysis. The review showed that bio-oil represented a renewable source for liquid fuels and chemicals, and that the work done by Maggi and Elliott [47] in which bio oil was added to diesel in the presence of a surfactant suggested that using bio oil as a fuel component could be successful. However, this method has some drawbacks, such as a high cost of the surfactant required to overcome the issue of immiscibility between bio oils and hydrocarbon fuels. Additionally, the relatively high content of oxygen in bio oils compared to diesel fuel alone would lead to higher corrosion rates in engine parts. This means that deoxygenation would be required before bio-oils can be used as fuel components [48].

In 2007, Telysheva and her research group were able to obtain phenol, guaiacol (2methoxy phenol) and substituted guaiacols, in addition to eugenol and vanillin from the pyrolysis of kraft lignin [49]. These compounds can be catalytically converted into useful chemicals and fuel components, as found by several studies [30, 50-58].

In 2008, Yuan Kou showed that a reaction that breaks lignin down into the alkanes and alcohols required to synthesise bio-fuels. After experimenting with different catalysts and organic additives to optimize the reaction, they found that a high yield of monomers and dimers could be produced using a combination of organic additives and a platinum-carbon catalyst.

Kou reported that it is theoretically possible to produce monomers and dimers in yields of 44 to 56 wt.% and 28-29 wt.%, respectively, using ideal conditions. Impressively,

those theoretical ideals were nearly achieved, producing monomer yields of 45 wt.% and dimer yields of 12 wt.%. The hydrocarbons were then separated by simply cooling the solution, automatically separating the hydrocarbons as an oily layer of monomers and dimers that can be converted into useful products. This process yields three product types: alkanes with eight or nine carbon atoms suitable for gasoline, alkanes with 12 to 18 carbons for use in diesel, and methanol [59, 60].

In 2009, Zhao and co-workers reported successfully converting phenolic bio oil components including phenols, guaiacols and syringols into alkanes using a supported noble metal catalyst and mineral acid [57]. The reaction was performed in aqueous media, as water has been found to be a good medium for the selective hydrogenation or oxidation of some bio-derived compounds such alcohols under mild conditions [61]. Phenol was selected as a model compound to explore principal hydrogenation and deoxygenation routes. Full conversion of phenol over Pd/C catalyst was achieved with high selectivity towards cycloalkanes. Other supported noble metal catalysts have been tested where similar conversion rates were achieved. Guaiacol and eugenol were converted at high conversion rates and selectivity under the same conditions [57]. The down side of this conversion method over metal catalysts is the high pressure (50 bar) and high temperature (above 200°C) required to perform the reaction, which might make it costly to apply on an industrial scale.

Very recently, Gates's research group carried out extensive work on the catalytic upgrading of lignin-derived compounds, including the conversion of lignin-derived compounds such as guaiacol, anisole, 4-methylanisole as reaction feedstock over different catalysts [2, 3, 52, 53]. Pt supported on Al_2O_3 or SiO_2 - Al_2O_3 and zeolite were used in continuous flow reactors, with the lignin-derived compounds vaporised into a flowing gas stream, in the presence of N_2 for zeolite experiments and with H_2/N_2 for Pt/Al_2O_3 . These reactions were performed under a slightly elevated pressure (~1.4 bar) and a temperature of about 300°C. Product analysis showed that the transformation of lignin-derived compounds yields dozens of compounds, with some being more abundant than others [2, 53, 54].

Another paper presented the conversion reaction of lignin-derived representative compounds such as guaiacol, anisole and phenol. Hydrodeoxygenation reactions (HDO) were assessed over different noble metals and metal sulfide catalysts. Pt on different

supports, as well as Pd, Rh, Ni, Co, Mo catalysts was used to study the transformation reactions in different types of reactors. Data showed that transformation reaction of the lignin-derived compounds yielded numerous products in most reactions as a result of number of side reactions besides the HDO [11].

Gates's work on lignin-derived chemicals has contributed significantly to the understanding of the reaction mechanisms and networks of such chemicals, and the potential of using these reactions to produce high-value chemicals and fuel streams. However, although Gates has done a lot of work on different catalysts, including supported gold and tantalum catalysts [62-64], the studies of reactions of lignin-derived compounds has been limited to a few compounds using only two different catalysts. Moreover, reactions were carried out with the reactants in the gas phase, which require additional energy to vaporise the compounds in the liquid phase, in addition to the high temperature used to perform the reaction. The use of H_2 as a reactant involves a high cost, which may make this type of reaction unattractive for industrial scale applications.

According to the U.S. Department of Energy [65], lignin is considered to be one of the higher-value biomass products and presents economic opportunities and the potential to significantly increase the amount of liquid transportation fuels. The report published in 2007 listed various lignin-derived compounds that have a high potential for upgrade into higher-value chemicals. Chemical upgrading processes and likely reactions were proposed for each compound. The report shows that the gap in understanding the chemistry of lignin-derived chemicals is wide and needs lot of research in order to increase the knowledge in this important field that represents a very promising source for alternative energy. The areas of development include developing processes to upgrade lignin-derived chemicals. Among the proposed areas is studying the catalytic oxidation of syringols and guaiacols represented by vanillic acid, syringic acid and guaiacol. Other compounds that are thought to have high potential for chemical transformation include eugenol and vanillin, in addition to quinones [65].

1.3 Gold as an Oxidation Catalyst

1.3.1 History and early development

Comprehensive studies of colloidal gold were started in the early 1950s by Turkevich, who characterised various formulations of colloidal gold using electron microscopy. These studies highlighted the impact of contaminants on colloidal gold preparation [66].

In the 1970s and early 1980s, studies of the absorbance of O_2 and CO on the surfaces of gold particles and the preparation of gold nanoparticles supported on inactive ceramic oxides such as SiO₂, Al₂O₃ and TiO₂ were published [67-71]. Then, in 1985, it was found for the hydrochlorination of ethyne to vinyl chloride that gold can be effective in catalysing the reaction [13]. Shortly after, Haruta published preparation procedures of supported metal catalysts in 1987- 1989 [69, 72]. These catalysts, which included Au/ α -Fe₂O₃ and Au/NiO, were found to be active for CO oxidation at temperatures as low as -70° C.

In 1990, it was thought that an oxidation reaction using gaseous O_2 would be difficult to control, as radical reactions would reduce selectivity when oxygen is activated on metal sites [73, 74]. This belief changed in 1996, when propene was successfully oxidised to the industrially valuable propene oxide (used to produce polyurethane) with Au/TiO₂ as a catalyst [75]. This was a major breakthrough in gold catalysis studies, as it demonstrated that gold nanoparticles could achieve both high conversion and selectivity in catalytic oxidation.

Over the last two decades, attention has increased for metal oxide-supported gold catalysts for their wide range of reactions under ambient conditions and high selectivity towards certain chemicals. These features implied a potential significance of gold catalysis in industrial applications, and made them worth investigating. Gold catalysis has demonstrated activity in selective oxidation, hydrogenation, and reduction with the oxidation of different chemicals [13, 15, 16, 71].

In 2002, Biella reported new applications of gold catalysts investigated for selective oxidation of organic molecules. Those reactions were carried out under mild conditions using molecular oxygen in aqueous solution. It was proven that in the presence of alkali, polyhydroxylated aliphatic molecules could be oxidised to monocarboxylates with high selectivity towards the primary alcoholic group, whereas the phenyl group enhanced the

reactivity of a benzylic alcoholic group, as it limited selectivity toward mandelate, starting from phenyl-1, 2-ethanediol [76-81].

The mechanism of oxidation using gold catalysts is currently thought to begin by cleavage of the C-H bonds in the phenol molecule to form Au-H species. This hydrogen needs to be removed from the Au surface to restore catalytic activity, and the removal is thought to occur by O_2 reacting to form H_2O - or H_2O_2 , which decomposes to form H_2O ; the extra hydrogen comes from the –OH bond, which is broken to form a carboxyl group [82-85].

The oxidation reaction mechanism must include an oxygen activation step, as oxygen would not be active as an oxidant unless energy is provided to break the O-O double bond. For gold catalysts, it is thought that oxygen can be activated in two pathways: one directly on the gold surface and the other on the defects of the oxide support. For a reducible support such as TiO_2 , it has been suggested that the activation process proceeds on the support particles, which provides active oxygen to the gold cluster required for the oxidation reaction [86-89]. However, it is still not known precisely whether it is the supported gold or the gold nano-clusters that catalyses the reaction. Catalytic oxidation activity had been found to increase in the presence of gold cations, which act as active catalytic sites [90].

1.3.2 Effect of the support material on catalyst activity

Many studies have shown that the catalytic properties of gold depend on the supporting material, as well as the preparation method and the size of the Au clusters [65, 80, 91, 92]. In 1997, it was found that gold exhibits extraordinarily high activity when it is dispersed as ultrafine particles on a metal oxide support such as TiO₂. This type of catalyst was found to be highly active for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides [80].

Schüth and his group assessed the effect of the support material on the activity of gold as a catalyst. Catalysts prepared with TiO_2 and Al_2O_3 were found to be the most active, while ZnO and ZrO₂ gave substantially less active catalysts. Particularly, Au/TiO₂ showed high reproducibility and thermal stability compared to zirconia and zinc oxide, and exhibited a remarkably high reactivity, especially toward O₂ at 300 K. The catalyst also showed good stability upon long-term storage and stability under reaction conditions

[93, 94]. Another study compared TiO_2 and SiO_2 as supporting materials for gold as a catalyst for low- temperature CO oxidation. Au/TiO₂ was found to have a higher catalytic activity after high-temperature reduction [95].

Our research group has produced highly active gold catalysts using TiO_2 as a support, according to a specific preparation method developed by former group members [87, 88].

1.3.3 Low temperature Au catalysis for oxidations

Supported gold catalysts are becoming popular, as they can be active for selective oxidations under moderate conditions. With appropriately selected support and controlled gold particle size, high catalytic activity could be achieved using gold catalysts supported on metal oxides or activated carbon [96, 97]. Supported gold on TiO₂ was chosen as the catalyst for lignin-derived building block oxidation. Numerous studies with supported gold catalysts have found that gold supported on titania is a good catalyst for gas and liquid phase oxidations [1, 15, 16, 75, 90, 98]. Moreover, the catalyst preparation method was developed and tested within our research group and proved to be active for different oxidation reactions.

Previous work by Haruta showed that supported gold catalysts prepared from an aqueous solution of $HAuCI_4$ and the nitrates of various transition metals were highly active for H_2 and CO oxidation. These catalysts exhibited high catalytic activities, even at temperatures as low as -70°C [72].

Various studies have shown that oxidation using supported gold catalysts can use air instead of molecular oxygen as a source of O_2 . The identification of catalytic systems using oxygen from air is preferred for 'green' processing of a reaction intended to be operated on a large scale; this would be appealing to industry because of the low energy consumption and the utilisation of natural resources [72, 99-102].

1.3.4 Activation of O₂ by Au catalysts

The oxidation reaction mechanism must include an oxygen activation step, as oxygen would not be active as an oxidant unless energy is provided to break the O-O double bond. The path of oxygen activation in oxidation reactions using gold catalysts has been extensively studied, although no consistent conclusion has yet been reached. This could be due to the fact that it is hard to determine whether activated oxygen derives from the metal site or from the oxygen site. In 2010, Zhu carried out an experiment in which
catalysts with controllable oxygen content were tested for the oxidation of CO in the gas phase and of benzyl alcohol in the liquid phase. It was found that the metal site is not capable of activating molecular oxygen and that the activity of the catalyst depends on oxygen content [87, 89].

Adsorption and dissociation of molecular O_2 on different gold surfaces have been extensively investigated in order to investigate the mechanism of O_2 activation. In 2010, Boronat identified three modes of O_2 adsorption (Figure 1-6), two of which are important from the catalytic point of view: (a), a weak interaction end-on mode that occurs only on small gold particles with low coordinated atoms, (b), a top-bridge-top mode stable on all gold surfaces and particles; and (c), a bridge-bridge mode that requires the presence of four gold atoms arranged in a specific way, and usually gives the highest molecular activation. The two latter modes are more important from a catalytic point of view.



Figure 1-6: Illustration of different adsorption and dissociation modes of oxygen on gold [86]

It was also suggested that the gold particle size and morphology as well as the electron density from the catalyst to O_2 are key factors that can heavily influence the adsorption and dissociation characteristics of the catalyst. Most importantly, the study suggested that when gold nanoparticles are supported on TiO₂, the most stable positions for O_2 adsorption and the most active sites for O_2 dissociation are found at the metal-support interface, not on the gold particle [86, 103].

1.3.5 Au catalysts for H₂O₂ generation

Hydrogen peroxide is an important oxidant that can be used in selective oxidation reactions over support metal catalysts. It has been suggested that the surface of gold is capable of generating H_2O_2 in situ, when gold supported on titanosilicate is used as a catalyst [104]. It has been found that over an Au/TiO₂ catalytic system, it is possible to reach an equilibrium state between Ti⁴⁺-O-Au, Ti³⁺-O-Au⁺ at the interface of Au and TiO₂ [82]. A study by Haruta involving the epoxidation of propylene over Au/TiO₂ suggests that oxygen is activated over a Ti³⁺ cation site to a negatively charged oxygen species, which forms hydroperoxo- or peroxide-like species through the direct reaction with hydrogen. Subsequently, oxygen species adsorbed on the Ti site react with propylene adsorbed on the surface of Au particles. The role of gold is probably to provide binding sites for propylene and to aid electron transfer from H₂ to O₂ [96, 105, 106]. Hutchings suggested that gold catalysts are active for the direct synthesis of peroxide through the selective redox process [99, 102].

On the other hand, it was found that when titania is used as support, H_2O_2 can decompose easily to 2 -OH[•] on metal nanoparticles, while interaction with surface hydroxyls on TiO₂ promotes the formation of OOH species on the surface [107].

1.3.6 Proposal of gold catalysis for the selective oxidation of lignin-derived compounds

Previous work, summarised in section 1.3.3, has shown that gold is an active catalyst for oxidations at low temperatures. The aim of this work is to identify a catalytic route to the upgrade of lignin-derived compounds. Although some work has been carried out with different catalysts, including Pt, Pd, Ni and other metals, no reference was found that reports the effect gold has on the transformation reaction of lignin-derived compounds. Thus, it was decided to study the catalytic reaction over a supported gold catalyst of a number of lignin-derived building blocks that are representative of lignin decomposition products. The outcome of this work might contribute to the overall understanding of transformation and reaction networks of lignin and its degradation products.

1.3.7 Common preparation methods

Various methods can be used to prepare highly active gold catalysts. The most common methods include co-precipitation, sol-immobilisation, wet impregnation and deposition-precipitation. A brief overview of these methods is presented in this section.

i. Co-precipitation

Co-precipitation was one of the first methods developed for the preparation of catalysts and is still in use currently. In this method, gold catalysts are prepared by adding an aqueous solution of gold – typically chloroauric acid – and a transition metal nitrate into an aqueous solution of sodium carbonate. After continuous stirring, the precipitate is collected and washed, vacuum dried, and calcined in air at temperatures as high as 400°C. This method produced ultrafine gold particles uniformly dispersed on the transition metal oxides. These catalysts were found to be highly active for H₂ and CO oxidation even at temperature as low as -70°C. Haruta concluded that the significantly enhanced catalytic activities were caused by combined effect of gold and the transition metal oxides [72, 108]. The calcination step is intended to convert hydroxides of the support metal into metallic oxides, where Auⁿ⁺ forms Au(OH)₃, which is turned into metallic gold [92, 109].

ii. Sol-immobilisation

One of the widely used methods to prepare gold catalysts is sol-immobilisation. This method is based on the preparation of Au nanoparticles in the presence of a stabilising agent (polymer, surfactant, polar molecule, etc.). Then, the support is added to the solution to form slurry in which gold adsorbs onto the support. The catalyst is then washed and calcined to remove any residual protecting agent on the surface of gold. The catalyst properties can be significantly influenced by the presence of the protective layer that acts a mediator between metal-support and reactant-metal interactions. Polyvinyl alcohol (PVA) is the most common used protecting agent. The activity and selectivity of gold catalysts can be associated with a number of parameters: morphology, dispersion and interactions between gold particles and the support. This method allows sufficient control of metal particle size in order to reduce the influence of the support on metal dispersion.

The surface properties and morphology of the support are critical determinants of metal dispersion during the immobilisation step. Prati demonstrated that one of the important advantages of the sol-immobilisation method is the possibility of achieving better metal dispersion over the support compared to conventional preparation methods such as wet impregnation. This is due to the low melting point of gold, which depending of the type of support, can lead to poor dispersion of gold particles [110-114].

iii. Wet impregnation

Also called "incipient wetness impregnation," this is a straightforward and simple method for preparing active catalysts. To prepare gold catalyst using this method, an aqueous solution of HAuCl₄ is added to the support (such as TiO₂) to form a paste of viscous slurry, which is thoroughly mixed and dried. This would be typically followed by a calcination step [110-113, 115]. However, HAuCl₄ may not be the ideal source for gold in wet impregnation, as the method does not involve a washing step to remove Cl⁻ ions that can poison the catalyst [109]. Schuth demonstrated that impregnation could be a good method to synthesise active gold catalysts, finding that wet impregnation followed by ammonia gas-phase treatment prior to finally washing with water resulted in the formation of gold catalysts containing 2 nm-diameter gold particles [116]. These findings contradicted the belief that it is difficult to produce active catalysts containing individual Au particles smaller than 10 nm using this method.

iv. Deposition-precipitation

Deposition-precipitation is the most commonly used method to prepare gold catalysts, and is the easiest method to handle, which makes it the preferred method to produce catalysts on a commercial scale [14]. Typically, an HAuCl₄ solution is used as the source for Au, to which the support material is added to form slurry. The pH of the mixture is adjusted to the desired value by adding a base material, usually to pH values between 6-10, at which gold would exist in the form of Au(OH)₃, which is adsorbed on the surface of the support material [117, 118]. The resulted slurry is then filtered, washed and dried to produce the final supported gold catalyst. The washing step removes any Cl⁻ ions that might exist in the catalyst and lead to catalyst poisoning, and is thus an important advantage of the deposition-precipitation method over wet-impregnation.

1.4 Summary

Bio-fuels are a significant renewable energy source, considering the future outlook of the fossil fuels. Lignin, a complex polymer derived from wood, is a promising source of bio-fuels. Lignin consists of many carbon chains with different functional groups that could possibly be oxidised to various compounds. Development of selective and robust catalytic processes to selectively break and make bonds will be an important area of technology development in the area of lignin upgrading studies that aim for better utilization of this material in the production of valuable chemicals and fuels [36].

If lignin and/or lignin-derived chemicals could be upgraded into value-added products, specifically to be used in the bio-fuels industry, many benefits could be achieved. Finding an alternative to petroleum fuels would provide energy security for future generations in an environmentally friendly way, without the need for a major investment in refining facilities due to the possibility of using existing petroleum infrastructure. Moreover, the overall economics of the bio-fuels industry will be improved [119].

1.5 Aims and Objectives

This work aims to examine the selective oxidation of lignin building blocks using supported gold on TiO_2 as a catalyst. The objective is to determine the effectiveness of the reaction in producing high-value chemicals for use as speciality chemicals, liquid transportation fuels, fuel streams or fuel additives [6, 37, 65]. Understanding the possible reactions and reaction mechanisms of lignin-derived compounds and their reaction networks might contribute to the overall knowledge in this fast-developing field.

Specifically, the project objectives include:

- Defining a clear procedure to prepare a highly active titania-supported gold catalyst as an oxidation facilitator.
- Characterising catalysts with conventional analytical techniques, and using catalytic CO oxidation activity as an indicator of catalyst quality.
- Evaluate the effect of different pre-treatment methods on the stability and performance of the prepared catalyst.
- Oxidising lignin-derived chemicals in aqueous phase, and optimising the reaction conditions to obtain the best results; ideally, the oxidation should be performed using air at ambient pressure as the oxidant, at a moderate to low reaction temperature.
- Characterising resultant chemicals to determine their potential use as specialty chemicals or as fuel streams or additives.

2. Fundamental Principles and General Methods and Materials

This chapter will describe the general experimental procedure used to characterise and test the supported gold catalyst and to study the oxidation reaction and products of the catalytic oxidation of lignin-derived compounds over the prepared catalyst. Fundamentals of analytical techniques and the sample preparation procedures used are presented. The Au/TiO₂ catalysts were prepared according to the preparation procedure described chapter 3.

2.1 Catalyst Testing

2.1.1 CO oxidation test

As indicated earlier, there is currently no clear or standardised method for testing the activity of gold catalysts, although considerable work has been done on this. The comparison of the efficiency of catalysts among different research groups is thus complicated by the fact that each group had to develop its own testing method. In this work, the CO oxidation reaction will be used as a standard test for the initial determination regarding whether a catalyst is active. It is a simple heterogeneously catalysed reaction of CO using O_2 as an oxidant represented by equation 2-1 for which a sufficient amount of data is available for comparison. Accordingly, the CO oxidation reaction was used to compare the activity of the prepared gold catalysts with that of other Au catalysts mentioned in the extant literature.

$$CO + \frac{1}{2}O_2 \xrightarrow{1\% \text{Au/TiO}_2} CO_2$$
(2-1)

The reactor used to test catalytic activity is a tubular plug-flow reactor (PFR), whereby CO is oxidised using O_2 as an oxidant and He as a carrier gas. The reaction chamber consists of a glass tube into which a thermocouple is inserted to monitor the reaction temperature. This setup is placed into a heating jacket that is used to increase the reaction temperature when needed. The catalyst being tested is usually packed in the glass tube (this type of reactor is also called a packed-bed reactor), in which the gaseous oxidant comes into contact with the catalyst. As the oxidant comes into contact with the catalyst,

the reaction starts to change temperature, which is monitored through the thermocouple (Figure 2-1).

The gas outlet is connected to an SRS RGA 100 mass spectrometer, allowing the distributions of products to be observed in real time. The mass spectrometer has a typical operating pressure of 5×10^{-7} bar, and the output readings are recorded every 25 seconds and tabulated as partial pressures. Figure 2-1 is a schematic illustration of the plug flow reactor used to perform the CO oxidation reaction over Au/TiO₂.



Figure 2-1: Illustration of the plug flow reactor for CO oxidation

It should be noted that this type of reactor usually uses N_2 as a carrier gas. However, He was used instead to avoid any possible overlap between N_2 and CO, which has the same molecular weight.

The rate of a catalytic reaction is proportional to the amount of catalyst in contact with the reagents. In the case of solid phase catalyst and gas phase reagents, the rate of reaction is proportional to the exposed area, efficiency of diffusion of reagents in and products out, and turbulent mixing or lack thereof. The rate of CO conversion was monitored as function of temperature.

Quadrupole Mass Spectrometry Analysis

A mass spectrometer measures the mass/charge ratio of ionised atoms of any other charged particles. Quadrupole mass spectrometry uses an analyser that consists of four cylindrical rods, set parallel to each other, with each opposite rod pair connected electrically. Ions are filtered based on their mass-to-charge ratio (m/z) as a result of the radio frequency voltage applied between each pair of rods [120].

Residual Gas Analyser (RGA) is a class of quadrupole mass spectrometers that typically covers masses ranging from 1 to 100 or 200 amu (atomic mass units). RGA provides online real-time analyses, and are usually used for the process control and contamination monitoring of the gasses present in high vacuum systems. The primary application of the RGA is to analyse the composition of a vacuum system. The composition can be used to detect impurities, monitor gas fills, or analyse chemistry that is occurring [121, 122]

The RGA analysis depends on the conversion of gas molecules into charged particles, typically positive ions. An MS signal is then produced depending on the species involved in the reaction. RGAs are used in most cases to monitor the quality of the vacuum and easily detect minute traces of impurities in the low-pressure gas environment. Utilising RGA in the standard glass reaction set up would help identify potential gaseous products of the oxidation reaction.

2.1.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is one of the most powerful tools used for imaging of microstructure in scientific and industrial applications. By tracing the scan pattern of a sample with a focused beam of electrons, SEM delivers high-resolution three-dimensional images that provide information about the morphology and composition of the analysed sample.

The technique utilises a beam of energetic electrons focused through a series of electromagnetic lenses. The electrons move down a column to a solid sample placed in a vacuum chamber (Figure 2-2). Most samples require some preparation prior to placement in the vacuum chamber, and the samples must be conductive or coated with a conducting material such as gold. When high-energy electrons come in contact with the sample, the sample surface releases electrons in the form of X-ray fluorescence. The scatter pattern of these electrons determines the shape, size, and composition of the sample. Different

detectors can be used to attract different types of scattered electrons, such as secondary and backscattered electrons as well as X-rays.



Figure 2-2: Illustration of Scanning Electron Microscope

SEM provides sample magnification down to 10 nanometres, with a great range of view and detailed surface information. In comparison, TEM can provide magnification down to nanometres, which makes it a more valuable tool for the analysis of the catalysts subject to this study, which are expected to have Au particles as small as 1 nanometre in diameter, although images obtained by TEM usually have a smaller field of view compared to SEM images.

The environmental scanning electron microscope (ESEM) is a type of SEM that permits wet and insulating samples to be imaged under vacuum or water vapour without prior specimen preparation, overcoming the disadvantage of SEM restriction to solid samples. However, the main disadvantage of ESEM is that the electron beam spreads and excites the entire specimen, not just the sample under the electron beam. This reduces the image contrast because of the detection of X-rays from outside the area of interest [123-125]. ESEM imaging was performed using a Quanta 400 FEI instrument. The catalyst sample was simply placed on a grid using carbon tape prior to ESEM imaging.

2.1.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a very powerful tool used for material science. TEM utilises the same principle as the light microscope, but it uses electrons instead of light. Electrons have much shorter wavelengths compared to light, which means that the resolution of TEM can be much higher than that of a light microscope. Hence, TEM can reveal details of the sample structure down to one atom.

In TEM, a high-energy beam of electrons is focused through condensing lenses and transmitted through a thin layer of a sample. The technique requires air to be pumped out of the vacuum chamber in order to create a space for the electrons to move. The specimen must be thin enough to allow a sufficient transmission of electrons in order to form an image with minimum energy loss.



Figure 2-3: Illustration of Transmission Electron Microscope

Figure 2-3 shows an illustration of the transmission electron microscope components. The interaction between atoms and electrons is focused through objective lenses, and generates an image that can reveal information about the structure of the sample with atomic resolution. This image can be captured with a phosphor screen or a camera, and is used to observe material features such as crystal structure and layer composition. The image produced is a high-resolution black and white image, where darker areas represent components of the sample where fewer electrons were transmitted through, while lighter areas represent those where more electrons were transmitted through [126-128].

Although manual determination of size distribution is time consuming and inefficient when several samples are being compared, it was used to determine the distribution using an inbuilt TEM tool that allows direct visualisation down to one atom [129]. The images obtained were separated into a 5×5 grid pattern, and particles were counted and divided into categories based on size. An FEI Technai microscope operating at 300 kV with a bright field was used for the imaging. The catalyst samples were placed on a carbon-coated grid forming a thin layer in preparation for the microscope imaging.

2.1.4 ICP-OES

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is one of the most common techniques for elemental analysis of dissolved samples. It has high specificity and multi-element detection capability, as it utilises a plasma source to dissociate the sample into its component atoms. The principle of ICP-OES is that when excited electrons return to their ground state, they emit photons at a specific wavelength, depending on the chemical character of each element. The intensity of characteristic photon emission is proportional to the amount of the element that exists in the sample. Therefore, ICP allows the qualitative and quantitative analysis of elemental composition of the analysed sample relative to a reference standard. An illustration of the ICP-OES is presented in Figure 2-4.

ICP-OES analysis requires the sample to be in solution. Solid samples must be dissolved, typically by combined acid attack employing HF, HNO₃, and HCl acids [130-132].



Figure 2-4: Illustration of ICP with UV and OES detectors

While ICP requires samples to be in solution, the catalyst samples were in the solid phase. Due to the difficulty of dissolving TiO₂, samples were prepared for ICP analysis as follows [133, 134]:

200 mg of catalyst was placed in a microwave sample vessel, to which 1 ml of water, 3 ml of concentrated nitric acid, 6 ml of hydrofluoric acid (40%) were added, samples left to dissolve overnight. Mixtures were then digested in a microwave oven for 3.5 hours. After that, samples were heated to evaporate all solvents, and then dissolved in 10 ml of aqua regia (a 1:3 mixture of conc. aqueous HNO₃ and HCl), and the total volume was increased to 20 ml using deionised water. Samples were then analysed using ICP-OES for their Au and Ti content.

2.2 Liquid-phase catalytic reaction

2.2.1 Reaction apparatus setup

The main aim of this work is to identify the optimal reaction condition to transform lignin-derived compounds into useful chemicals over supported gold catalyst. Ideally, these conditions should be attractive for industrial applications. This means that the cost of the reaction should be kept at a minimum or that it must be cost effective for largescale applications. Thus, the transformation reaction of subject compounds will be assessed under ambient conditions, i.e. using air as an oxidant under ambient pressure and relatively low temperature.

Two reaction systems were designed. An open reaction system was designed using simple lab equipment to carry the reaction at atmospheric pressure.

a. Open system

This system was used for the reactions under ambient pressure, while varying other parameters such as temperature, catalyst ratio, gas saturation, gold loading and catalyst pre-treatment procedures. The system comprised a 500 ml 3-neck boiling flask placed in a heating mantle. A water-cooled condenser was attached to the central neck, and one of the side necks had a glass tube with an inner diameter of 2 mm connected to an air pump that delivered air to the solution to maintain continuous stirring while aerating the sample. The other neck serves as a measuring point, where a thermometer is attached, and can be removed for drawing samples. An illustration of the open reaction system is shown in Figure 2-5.



Figure 2-5: Illustration of the open system for liquid phase reactions

b. Closed high pressure system

A second reaction system utilising high pressure was used in order to capture potential gaseous products and to study the effect of high pressure on the reaction rate.

Figure 2-6 shows the closed reaction system comprising a stainless steel cylinder reactor coated internally with Teflon and heated using a heating jacket. The reactor was connected to a pressure gauge and a thermocouple to monitor pressure and temperature, with a gas inlet and a sampling point. The whole set-up was placed on a mechanical shaker in order to maintain homogeneity of the reaction mixture.



Figure 2-6: Illustration of the stainless steel closed reaction system



Figure 2-7: image of the pressurized reaction system

2.2.2 Reaction Parameters

Previous studies on the oxidation of lignin-derived chemicals suggest using relatively severe reaction conditions of 500°C and 900 psi pressure in order to achieve satisfactory conversion rates. Using these kinds of conditions would make the industrial application of this reaction economically unfavourable. It was decided that for this study to be of high value for the industrial sector, products should be obtained via the catalytic oxidation of subject chemicals under ambient conditions and in aqueous phase. Other studies on supported metal catalysts suggested the oxidation of similar compounds under ambient conditions [68, 82, 135-142]. The reaction temperature is a key parameter to optimize for the reaction. High temperatures would increase operational costs, and low temperatures might not be sufficient to attain satisfactory reaction rates. Therefore, reaction temperatures of 70-100°C will be investigated under atmospheric pressure.

The optimal compound: catalyst ratio required for oxidation with gold catalysts could not be precisely determined. Although the literature has a lot of information on the oxidation of lignin building blocks, those studies were performed under high pressure and high temperature with compound: catalyst ratios of, for example, 20:1 (mol:mol) using different catalysts including zeolite and supported metals, and no information about oxidation using gold catalysts was found [143-145]. Hence, we decided to utilise reaction parameters similar to those used in glycerol oxidation reaction as an initial testing ratio, as there are a lot of studies outlining different parameters of this reaction with gold catalysts. Typically, researchers in the field of glycerol oxidation employ a 500-3000:1 (mol: mol) ratio of glycerol:Au [98, 146-148]. However, since the aim of this project was to perform the oxidation on aromatic molecules that may require stronger reaction conditions, a low reactant: gold ratio was selected, meaning that less reactant molecules would be available to react against each gold atom. A ratio of 300:1 reactant:Au was chosen, in addition to the above mentioned 20:1 ratio suggested for lignin-derived compounds.

The oxidation reaction in the liquid phase of all compounds subject to this study was assessed according to the following procedure, except where it was explicitly stated:

Control experiments

A set of control experiments was designed and performed in order to have a better understanding of the compounds subject to study and the effect of each parameter on the reaction progression. These control experiments would help eliminating any uncertainties about the potential of any of the reaction parameters to contribute to the progression of the reaction in the absence of the catalyst.

Temperature effect

To find the effect of temperature on the reacting compounds, a 3 mM solution of the subject lignin-derived compound is heated at 70°C with no added catalyst under continuous air flow at atmospheric pressure using the open reaction system. Samples of the solution were analysed regularly via UV-visible spectrometer.

Effect of TiO₂

This experiment is carried out to exclude any potential for TiO_2 itself to catalyse the reaction of lignin-derived compounds oxidation. An equivalent weight of TiO_2 to the catalyst weight employing a 20:1 reactant to gold ratio (40 mg) was added to the solution. The mixture is then heated at 70°C and atmospheric pressure for 24 hours in the open reaction system, and monitored using a UV-visible spectrometer.

Effect of Dissolved Au Ions

This control experiment is probably the most important one, as it would help determine the actual form of Au that catalyses the reaction. Ideally, the reaction should be catalysed by the supported gold particles in the form of catalyst rather than by Au ions leached into the solution. HAuCl₄ solution was added to the reactant solution at a reactant:Au ratio of 20:1. The solution is heated to 70°C for 24 hours under continuous air flow.

Lignin-derived compounds transformation using 1% Au/TiO₂

The oxidation reactions are performed at 70°C with a continuous air flow of 1 ml min⁻¹ in an open glass reaction system where 44 mg of the catalyst (1% Au/TiO₂) is added to 150 ml of the reactant solution (3 mM). The reactions are monitored through regular sampling and prompt analyses at least at 1, 2, 4, 8, 24 hours. Reactions progression was monitored using UV-Visible spectroscopy and HPLC, whereas several analytical techniques were employed to identify and confirm the structure of the resulting oxidation products. Proton NMR, GC-MS and FT-ICR-MS were used for the products analysis as described in section 2.2.3.

2.2.3 Analytical techniques

This section outlines the analytical techniques used to monitor reaction progression and analyse reaction products. Samples were taken and analysed regularly using conventional analytical techniques. Syringe filters were used to remove residual catalyst to eliminate any interference with the reactant/product signals.

UV-visible spectroscopy was used as a basic test to monitor any changes in absorbency in the reaction mixture with time, while product analyses were performed using HPLC, GC-MS, LC-MS and NMR. FT-ICR MS was used only for the analysis of the syringic acid oxidation reaction using facilities in Research and Development Centre, Saudi Aramco.

UV-visible spectroscopy

Many molecules absorb ultraviolet or visible light. In organic compounds, absorption of ultraviolet and visible radiation is restricted to those compounds that contain functional groups with electrons of low excitation energy. An absorption spectrum may show a number of absorption bands corresponding to the functional groups with electrons of low excitation energy within the molecule.

According to Beer's Law, the absorbance of a molecule is directly proportional to the path length, and the concentration of that molecule. An absorption spectrum may show a number of absorption bands corresponding to the functional groups within the molecule. Figure 2-8 is an illustration of the UV-visible spectrometer.



Figure 2-8: Illustration of the UV-Visible spectrometer

UV-Visible spectroscopy was performed using a Bechman DU 520 Spectrometer, with 10 mm standard path length quartz cuvettes (Sigma). The wavelength range of the spectrometer was 190-1000 nm. Sample solutions were diluted 100 fold with deionised water to ensure spectra within the absorbance rage of the spectrometer.

Disposable plastic cuvettes (Sigma) were initially used, but at wavelengths close to 200 nm, the spectra become noisy, and obtaining reliable results in this region was somewhat difficult. This is because the disposable cuvettes have a minimum absorption range of 230 nm; using quartz cuvettes instead of the plastic ones solved this problem.

Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy was used for determining the content and the molecular structure of the sample. In NMR, a molecule is placed within a magnet, which generates a magnetic field around the analysed molecule, since the nuclei of that molecule have a charge and are in motion. NMR typically uses magnetic fields ranging from 200 to 900 MHz, requiring superconductor magnets that must be cooled using liquid helium (-269°C).

When an external magnetic field is applied to nuclei, energy transfer between the ground and higher energy levels available to the nuclear spin becomes possible. This transfer takes place at specific wavelengths in the radio frequency range, which are the same frequencies at which energy is emitted when the spin returns to the ground state. These transfers of energy are measured and processed into signals to produce the NMR spectrum. The precise resonant frequency of the energy transition is based on the magnetic field of the nucleus. This means that when the nucleus is more electronegative, its nuclear spin transition occurs at a higher frequency.

One of the most important factors in acquiring good NMR spectra is the stability and homogeneity of the magnetic field. Fluctuations in the magnetic field strength during data acquisition might result in broad spectrum with poor resolution. The 'lock system' is a mechanism used by the spectrometer to correct drifts in the magnetic field as they occur and keep the magnetic field stable. The resonance frequency of the deuterium atom in the used solvent is measured (the lock signal) and used to determine the drift. The spectrometer uses a dedicated detector to monitor the deuterium signal and apply an electric current through coils to correct the strength of the magnetic field and keep the signal in the same position.

Another factor that could contribute to improving the quality of the NMR spectrum is shimming. In order to get a high-resolution spectrum of a sample, the magnetic field over the whole volume of the sample has to be homogeneous to avoid getting distorted line shapes. Therefore, the homogeneity of the magnetic field needs to be optimised or "shimmed" to every analysed sample. Shimming is the process in which the field homogeneity is adjusted by applying different electrical currents through coils placed around the sample tube inside the magnet. Figure 2-9 is a schematic illustration of the NMR instrument.



Figure 2-9: Illustration of Nuclear Magnetic Resonance instrument

Proton NMR analyses were performed using a B400 Bruker Avance III 400 MHz using deuterated methanol (MeOD) as the lock agent. Proton NMR analysis results in a spectrum that corresponds to the ¹H environments of the analysed molecule. This spectrum can be interpreted directly or compared to spectral libraries. Tetramethylsilane (TMS) is used as internal reference for proton resonance frequency. Samples were prepared by adding 0.5 ml of MeOD (d, 99.8% from CIL) to 1 ml of the analysed sampled in the aqueous solution using 5 mm thin-walled glass tubes, 203 mm in length suited for 400 MHz frequency supplied by Sigma-Aldrich.

Fourier Transform – Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is an ultrahigh resolution and mass accuracy MS technique based on the detection of ion cyclotron motion within a magnetic field [149]. FT-ICR MS coupled to ionisation sources has been widely used to study molecular complexes [150].

In a typical closed, cylindrically shaped ICR cell, the ions are injected into the cell along the axial direction. The cyclic motions of confined ions are typically detected by measuring the image current induced by ions in the detection plates of the ICR trap.

Use of this high-resolution analyser enables the determination of the mass-to-charge ratio (m/z) of an ion by measuring the frequency at which the ion proceeds in a magnetic field. Ranging from 100 KHz to MHz, these frequencies can be very accurately measured, enabling the precise determination of ion mass to within ±0.000005 amu. FTICR-MS is significantly different from other mass spectrometry techniques in that ions are detected as they pass near detection plates rather than as they hit a detector. In this work, spectra were acquired in positive mode electrospray ionisation (ESI) on an Apex Qe 9.4 Tesla fourier transform – ion cyclotron resonance mass spectrometer (FT-ICR MS), manufactured by Bruker Daltonics, Bremen, Germany, equipped with an Apollo II atmospheric pressure ion source. Samples were diluted 100 fold in methanol (Sigma-Aldrich, p.a. grade). Data were acquired using ApexControl software (v3.0, Bruker Daltonics, Bremen, Germany). Elemental formula assignments were achieved using Data Analysis (v3.4, Bruker Daltonics, Bremen, Germany) with a tolerance of 1 ppm and unlimited number of C and H, and N₀₋₁₅, O₀₋₁₅, Na₀₋₁. An illustration of the FT-ICR MS is presented in Figure 2-10.



Figure 2-10: Illustration of FT-ICR-MS

The implementation of ionisation techniques enables the extension of mass spectrometric methods to large molecules and molecular complexes. Methods such as electrospray and laser desorption can be used for the ionisation of complex compounds, which remarkably expands the applications of mass spectrometry.

There is no specific ionisation process that can ionise all compounds in a mixture simultaneously. Different ionisation techniques can be used for different chemical structures. Each technique has its advantages, such as selectivity towards different groups of compounds or heterogeneous mixtures [151]. Ionisation techniques include the following:

i. Electrospray Ionisation

Electrospray (ESI) is a low-fragmentation ionisation technique that is used to ionise polar functional groups using high electric field to assist the transfer of ions from solution into the gaseous phase prior to mass spectrometric analysis. Using ESI prior to chromatography allows characterisation of macromolecules. In ESI, a continuous stream of analysed solution is passed through a high-voltage capillary tube, typically made of stainless steel or quartz, producing a mist of highly charged droplets that have the same polarity as the capillary tube. The charged droplets exit the electrospray tip, passing down a pressure gradient toward the analyser region of the mass spectrometer [152]. ESI is best suited for polar and ionic compounds, which are already charged, resulting in better ionisation.

ii. Atmospheric Pressure Chemical Ionisation

In this technique, the ionisation takes place in the gas phase, where the solution is evaporated, then used to form charged plasma by a corona discharge electrode under atmospheric pressure. Atmospheric pressure chemical ionisation can be used for less polar solutions, but not for non-polar solutions.

iii. Atmospheric Pressure Photoionisation

Atmospheric pressure photoionisation (APPI) is an ionisation method developed for less polar compounds. This method utilises photons from a discharge lamp, where low energy compounds can be ionised by the emitted photons. Analytes including large molecules can be ionised selectively with minimum background interference, as most of the used solvents and gases are unaffected by the ionisation method.

iv. Laser-Induced Acoustic Desorption Ionisation

This ionisation method utilises laser to generate acoustic waves in a thin metal foil. When generated waves travel through the foil, deposited molecules on the opposite side are desorbed. This allows ionisation of large, low-energy molecules that are not responsive to other ionisation methods [153].

High Performance Liquid Chromatography (HPLC)

HPLC is a separation technique that involves the injection of a small volume of liquid sample into a column packed with a stationary phase; using a pump, individual components of the sample are forced at high pressure into the column with a mobile phase. The components of the sample are then separated by the interaction between those components and the column packing. A detector measures the amount of each component at the exit. The type of detector depends on the sample type (Figure 2-11).



Figure 2-11: Illustration of HPLC

Reverse phase liquid chromatography separates molecules based on their interaction with the column component according to polarity. Analysed molecules are bound to the mobile phase (polar) and eluted using an organic solvent (non-polar). The stationary phase usually contains silica beads bonded to non-polar linear octadecane groups (C18), these groups can bind polar molecules to polar solvents. In normal phase chromatography, separation is achieved by the direct interaction of molecules with the polar matrix, which consists of silica beads without octadecane groups, in the presence of a non-polar solvent.

In these studies, HPLC analysis was performed using a C18 8 μ m, 300 × 7.7 mm column packed with silica. A mixture of 80% acetonitrile (HPLC grade, obtained from Sigma Aldrich) and 20% distilled, de-ionised and triple-filtered water (2 μ m nylon membrane

filters (Millipore)) was used as an eluent. The column was operated at room temperature at an eluent flow rate of 0.60 ml min⁻¹. A Varian Prostar pump system was used, at a column operating pressure ranging between 450 and 500 psi. A Varian Prostar 410 auto sampler was also used. The detector used for analysis was a Varian Prostar UV-Visible detector, which is capable of measuring absorbance between 200-400 nm. The output data is a chromatogram showing signals of the existing compounds with different intensities. In order to quantify the conversion rate properly, response factors were determined through calibration curves of each reactant and product using pure standards with known concentrations.

Liquid Chromatography - Mass Spectrometry (LC-MS)

LC-MS is a powerful analytical technique that combines the physical separation capabilities of liquid chromatography, as described in the HPLC section, with the mass analysis capabilities of mass spectrometry. It has high sensitivity and selectivity and can be used for general detection and potential identification of chemicals of particular masses in mixtures. The LC-MS analysis method used in these studies utilised an ACE Ultracore 5 Super C18 column with dimensions of 4.6 x 150 mm, and a solvent of 20% acetonitrile in water, flowing in a 1 ml min⁻¹ rate. Absorption was measured at 254 nm. The machine used was an Agilent 1100 HPLC/MSD system with Ion trap and a DAD (diode array) detector.

Gas Chromatography - Mass Spectrometry (GC-MS)

GC-MS is an analytical method that is used to identify different compounds in a sample utilising the powerful features of gas chromatography and mass spectrometry. The instrument is mainly composed of two units: a gas chromatograph and a mass spectrometer. Gas chromatography involves injecting a vaporised sample into a capillary column, where the sample is carried through the column by the flow of the mobile phase, which is usually an inert gas. The column contains a liquid stationary phase, which is adsorbed onto the surface of an inert solid. Molecules are separated inside the column depending on the differences in their chemical properties. Different compounds are retained in the stationary phase for varying times based on their molecular weight. The compounds then elute from the column at different times, allowing the mass spectrometer to collect, ionise, and detect the ionised molecules separately. An illustration of the GC-MS instrument is illustrated in Figure 2-12.

The GC-MS instrument used in our analyses was an Agilent 7980A GC /5975C mass spectrometer, equipped with a Zebron Capillary GC Column, with ZB-SemiVolatiles column 30 m (L) x 0.25 mm (ID) x 0.25 μ m (film thickness).



Figure 2-12: Illustration of GC-MS

2.3 Materials

The catalyst was prepared according an adaptation of the deposition-precipitation method using HAuCl₄ (49+ % Au) obtained from Fluka, and (P25 TiO₂) from Degussa. NH₄OH (35% reagent grade) from Fluka was used for the precipitation step.

For the study of the catalytic oxidation over Au/TiO₂, solutions of lignin-derived model compounds were prepared in distilled, de-ionised water, and the following materials: 3-(4-hydroxy-3-methoxy-phenyl) propenoic acid (ferulic acid) and 2,6-dimethoxybenzoic acid (syringic acid) (\geq 95%) purchased from Sigma, methoxybenzene (anisole) (\geq 99% GC grade), 4-Hydroxy-3-methoxybenzoic acid (vanillic acid) (97% HPLC grade), purchased from Fluka Analytical, 2, methoxy phenol (guaiacol) (+99%), 3,5-dimethoxybenzoic acid (DMBA) (99%) from Acros Organics, p-hydroxybenzoic acid (PHBA) (+99%), 4-allyl-2-methyoxyphenol (eugenol) (99% reagent plus), 2,6-dimethoxybenzo quinone (DMBQ) (97%) purchased from Aldrich.

Samples were filtered to remove any catalyst particles using syringe filters with pore sizes of 0.45 μ and 25 mm diameter, from Thermo Scientific.

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3. Preparation and characterisation of a highly active Au/TiO₂ catalyst for oxidative transformations

This chapter will provide an overview of the methodology for the preparation and characterisation of a highly active Au/TiO_2 catalyst developed by the host research group, its limitations, the characteristics and performance of the prepared gold catalysts, and the effects of different pre-treatment procedures on the catalyst's stability and activity.

3.1 Introduction

Numerous researchers have outlined the preparation procedures of supported catalysts, which are claimed to be highly active and efficient. However, there is still no standardised procedure for preparing catalysts or for testing catalytic activity [72, 79]. Thus, researchers have to develop their own procedures for preparation and testing of supported catalysts, which makes comparing catalytic activities across research groups difficult.

Haruta presented evidence that highly dispersed gold on metal oxide support can be prepared using deposition-precipitation and co-precipitation methods, whereas impregnation fails to produce catalysts with high dispersion. Al_2O_3 and TiO_2 are among the metal oxides that Haruta assessed in 1993 and found to lead to high dispersion and high catalytic activity. TiO_2 was found to be a good supporting material, as it is poorly active by itself [69, 72].

3.2 Catalyst Supports

A significant number of studies have been done using carbon supports since Haruta obtained significant catalytic activity using α -Fe₂O₃, Co₃O₄ and NiO [72-74, 79, 90, 154-156]. Other oxides such as Al₂O₃ and SiO₂ have been investigated as supports [67, 75, 157]. However, in this study TiO₂ was used as a support for the gold catalyst for the reasons mentioned in section 1.3.2.

3.3 Catalyst Preparation

3.3.1 Preparation of catalyst by a modified deposition-precipitation method

The catalyst was prepared using a modified deposition-precipitation method using $HAuCl_4$ solution as a source for Au ions. For the purpose of this study, the catalyst preparation procedure was based on a 1% Au/TiO₂ (w/w) loading. Prepared catalysts were characterised and tested for catalytic activity.

First, the Au stock solution was prepared by dissolving 1 g of HAuCl₄.3H₂O (\geq 99.9%, Sigma-Aldrich) in 100 ml of de-ionised water. NH₃ solution (0.6%v/v) was used as a base for the deposition step of Au particles. The NH₃ solutions was prepared using 5 ml NH₃(aq) (\geq 30%, Aldrich) made up to a total of 250 ml. However, NH₃ solution was used in small volumes with caution because the reaction with NH₃ can lead to formation of azides, or what is known as "fulminating gold", which can be explosive if isolated and dried in pure form [158].

To prepare 5 g of 1% Au/TiO₂catalyst, the following procedure was used:

- 1. 500 ml distilled de-ionised water was heated on a magnetically stirred heater in a conical flask to 70°C.
- A specific amount of HAuCl₄.3H₂O was added to the water to obtain 1% catalyst loading (the standard preparation method required 0.0505 g of Au for 5 g of TiO₂, which corresponds to 12.82 ml of HAuCl₄.3H₂O stock solution).
- 3. 5 g of TiO₂ was added to form a slurry, and stirred for 2 hours at 70°C.
- 4. The HAuCl₄.3H₂O solution was carefully neutralised by the gradual addition of NH₃ solution. It was found experimentally that approximately 6 ml of NH₃ solution was required for this neutralisation.
- The slurry was filtered using a Buchner system and filter paper grade QL120 (Fisher Scientific, equivalent to Whatman # 3, pore size 6 μm).
- 6. The resulting residue (the catalyst) was washed with 3 equivalent volumes of de-ionised water. For 5 g TiO₂, this volume corresponded to 1500 ml.
- The washed catalyst was kept in an oven and allowed to dry in air at 70°C overnight.
- 8. The catalyst was gently ground in a mortar and stored in a refrigerator in vials securely covered to avoid direct light.

3.3.2 Observation during Catalyst Preparation

It was observed during step 2 of the catalyst preparation procedure that when the $HAuCl_4.3H_2O$ solution was added to the water, the pH decreased to approximately 2.6 immediately. Then, when the NH₃ solution was first added to neutralise the mixture in step 3, no significant changes in pH were observed until a large amount of NH₃ was added to the mixture. However, when pH crossed 5, the system became highly sensitive to further NH₃ addition.

Another phenomenon was that if the mixture was left to react at the adjusted pH of 7 without further adjustment, the pH decreased gradually. Hence, the pH of the reaction was not stable, and the amount of NH_3 required for neutralisation could depend on the time spent during neutralisation.

To avoid any inconsistencies in catalyst properties and performance, the preparation procedure was scaled up to produce 15 g of catalyst, which allows for about 30 reactions based on 0.4 g of catalyst per reaction. However, 15 g of catalyst was not sufficient for all the planned reactions in addition to the catalyst samples required for characterisation and testing. Therefore, several batches of the catalyst were prepared and tested for activity and catalytic properties to assure reproducibility and consistency in performance in different reactions.

3.4 Results and Discussion

Different batches of 1% Au/TiO₂ gold catalysts were prepared and tested. Catalyst morphology and characteristics were determined using TEM imaging and ICP-OES. CO oxidation reaction was used as the main test to determine catalytic activity.

3.4.1 ICP-OES

ICP-OES was used to determine the elemental composition of the prepared catalysts. Samples of gold catalyst with 1% and 2% Au loading were compared to confirm the accurate deposition of the required amount of gold. A sample of 1% Au/TiO₂ used for the gas phase oxidation of CO was analysed in order to detect any changes that might happen to the catalyst when spent in a reaction. However, ICP requires the samples to be in a liquid form in order to be analysed, while the catalyst samples were in the solid phase.

Samples were prepared for ICP-OES analysis according to the procedure outlined in section 2.1.4.

Sample	Expected Au	Reported Au	Ti content	
	content (wt. %)	content (wt. %)	(wt. %)	
Fresh 1% Au/TiO ₂	1.0	0.9	99.1	
Fresh 2% Au/TiO ₂	2.0	1.9	98.1	
Spent 1% Au/TiO ₂	1.0	1.09	98.91	

Table 3-1: ICP-OES analyses for fresh and spent 1%Au/TiO2 catalysts

The results in Table 3-1 show that the obtained gold content of fresh and spent catalyst was within the error limits of the analytical method (\pm 0.1 mg). This means that the method used for the preparation of the supported gold catalyst is adequate in producing a catalyst that contains gold in the desired loading percentage. The stability of the catalyst was confirmed by the fact that the gold content remained unchanged before and after the carbon monoxide oxidation reaction.

3.4.2 Environmental Scanning electron microscopy (ESEM)

A sample of 1% Au/TiO₂ catalyst was imaged using ESEM. Image in Figure 3-1 shows the TiO₂ particles with some light coloured gold particles. However, ESEM resolution does not go as low as 5 nm, which is the expected size range for the gold particles. Hence, TEM is expected to provide better images of the catalyst.



Figure 3-1: ESEM image of 1% Au/TiO2 magnified 1000 times

3.4.3 TEM imaging

Catalysts at different states were imaged using a transmission electron microscope (TEM) in order to understand how the catalyst works and the changes that occur to the catalyst's structure after it has been used in a reaction, as well as to evaluate the effect of different pre-treatment procedures on the catalyst's properties and performance.

Catalysts with different gold loadings were prepared and tested. Particle number and size were determined manually by counting the particles and measuring the dimensions of each. The average of sizes from two images is reported for each tested catalyst. Figure 3-2 and 3-3 show that in the catalysts with 1% and 2% gold loading, the majority of the particles are within the range of 2-5 nm, whereas in the catalyst with 5% gold loading, particles were smaller in size, with approximately 38% of gold particles in the range of 1-3 nm (Figure 3-4), compared to less than 30 % in that range for catalysts with 1 and 2 % gold loadings. It is also noted that the particle count results correspond to the gold loading; the image of the 5% gold loading shows an increased number of gold particles.



Figure 3-2: TEM image and particle distribution of 1% Au/TiO₂



Figure 3-3: TEM image and particle distribution of 2% Au/TiO2



Figure 3-4: TEM image and particle distribution of 5% Au/TiO₂

3.4.4 CO oxidation performance

The CO oxidation reaction was used as a standard test to determine the activity of the gold catalyst prepared using the previously outlined method. The reaction was performed in a plug-flow reactor (PFR) and monitored using a quadrupole mass spectrometer. The following procedure was applied for the testing of prepared catalysts in the CO reactor:

1. The gas cylinders were set at 2 bar outlet pressure, and reactor gases flow rates adjusted to:

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CO = 2 \text{ ml min}^{-1}O_2 = 20 \text{ ml min}^{-1}He = 78 \text{ ml min}^{-1}
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- 2. The reactor was run with the gas mixture bypassing to establish a stable baseline for no reaction.
- 3. A known amount (approx. 30 mg) of the catalyst was packed in the glass reaction tube, and loaded in the reaction chamber.
- 4. The gas flow was switched from bypass to reactor, allowing gases to interact with the catalyst bed.
- 5. The reaction temperature and mass spectrometer readings were monitored until they stabilised.
- 6. The temperature of the heating jacket was then increased gradually, and the temperature and the spectrometer were allowed to stabilise.
- 7. Step 6 was repeated until no difference in the spectrometer reading was observed, in order to facilitate a better understanding of the effect of increasing temperature on the catalyst activity.

The bypass function allows all gasses to flow without coming in contact with the catalyst inside the reaction tube. This function is usually run to provide a reference point for the partial pressure of each gas in the system before and after the reaction over the packed catalyst.

The typical output data of the mass spectrometer for the reaction is illustrated in Figure 3-5. The helium trace was omitted to allow the other components to fit into a larger scale to be clearly seen. Other components traces were omitted too for the same reason. The

conversion rate of CO to CO_2 over 1% Au/TiO₂ was calculated using initial and final pressure of CO.



Figure 3-5: CO oxidation using 1% Au/TiO₂

Comparison of catalyst activities

The reaction rates of heterogeneous catalytic reactions can be used as a basic tool for the comparison of catalyst performances, instead of comparing overall products yields or conversions [159, 160]. A common way to compare the activity of different samples of different catalysts in different laboratories is expressing reaction rates in terms of turnover frequencies (TOF). TOF is determined by normalising a reaction rate to the number of active sites in the reactor. Thus, TOF is based on the number of active sites, not on the amount material loaded in the reactor, or the amount or metal loaded onto the support [160]. Active sites are the sites on the surface of the catalyst where the adsorption of a reactant and the reaction takes place. The properties of a catalyst are linked to the surface of the catalyst. Active sites are usually assumed to be equal to all surface sites because the nature of each active site is not known. The number of catalyst active sites is commonly estimated through the titration of the surface metal atoms, for example with H₂ [161, 162].

The capability of H_2 to adsorb on a gold surface is limited, which means that counting the active sites of gold by hydrogen chemisorption measurements is difficult. A sufficient

alternative for estimating the number of active surface sites in a gold catalyst is using the mean particle size to calculate the total number of metal atoms of the metal particle, and then correlating this number to the reaction rate. Assuming that the particles are spherical, standard methods such as TEM, ETEM or XRD are usually used to determine the metal particle size and size distribution [161-163].

Quantifying the number of active sites on a surface can be difficult. With metals and metal oxides, one of the best ways to calculate the number of active sites is to count the number of exposed surface atoms per the unit surface area. This will be an approximation that can be used to calculate the turnover frequency by dividing the reaction rate by the number of exposed surface atoms [164-166].

Using this method, the value of the TOF will be an average value of the catalyst activity because in real catalysts, surface atoms reside in various coordination environments and exhibit different catalytic activities in a given reaction. In fact, the calculated value of TOF would probably be lower than the actual activity of the catalyst, because not all surface atoms contribute to the reaction. Nevertheless, this approach of assessing turnover frequency on a uniform catalyst surface is helpful in comparing reaction rates on metal catalysts, specially supported metal particles [164, 165].

The conversion rates of the CO oxidation reaction using the tested catalysts were calculated to compare the activities of different batches of the prepared Au/TiO_2 . TOFs provided a preliminary measure of catalyst activity, although they may not be an exactly accurate measure of catalyst activity.

Three batches of catalyst were prepared and tested for their activity in the oxidation of CO. The main purpose of these tests was to determine the activity of the prepared catalysts, and to confirm the precision of the preparation procedure in preparing catalyst with comparable performance. The catalyst performances were compared based on the conversion rate calculation. The CO oxidation reactions were carried out in a plug flow reactor (PFR). Hence, the calculations could be performed using the PFR general design equation:

$$r_A = \frac{dF_A}{dV} \tag{3-1}$$

Where:

 V_{PFR} = Volume of plug flow reactor (m³)

 F_{A0} = Initial flow rate of component A (mol s⁻¹)

X = Conversion of component A

 r_A = Rate of reaction with respect to component A (mol m⁻³ s⁻¹)

Since the volume of the catalyst bed can be measured (typically 15 mm high in a circular 4 mm diameter glass tube), the equation can be manipulated to obtain the rate of reaction in terms of reactor volume and conversion.

This procedure was repeated with each batch of the catalyst:

$$-r_A = A e^{\frac{-E_A}{RT}} C_A$$

Applying logs:

$$-\ln r_A = \ln[C_A A] - \frac{E_A}{RT}$$

$$\therefore \ln\left(\frac{1}{r_A}\right) = \left(\frac{-E_A}{R}\right) \frac{1}{T} + \ln[C_A A]$$
(3-2)

$$K = \frac{-r_A}{c_A} \tag{3-3}$$

Where:

A = Pre-exponential factor (for 1st order reaction, units = s⁻¹)

 E_A = Activation energy (J mol⁻¹)

R =Universal gas constant (J mol⁻¹ K⁻¹)

T = Temperature (K)

 C_A = Concentration of reactant A (mol)

Equation 3-2 can then be used to characterise the catalyst behaviour in the CO oxidation rig, where the flow rates were 1 ml s⁻¹ for CO and 100 ml s⁻¹ for the total gases, the inner pressure of the reactor was 1.5×10^{-7} mbar and the catalyst bed volume was 0.7543×10^{-6} m³. The constant K was calculated using equation 3-3.

The reaction rates were found to be as follows:

Table 3-2: Calculated	conversion r	ates for t	he CO	reaction	test fo	r different	prepared	batches	of cata	lyst

	1 st Batch	2 nd Batch	3 rd Batch
Conversion (X)	0.35	0.33	0.39
CO concentration (mol m ⁻³)	0.567	0.567	0.567
Reaction rate (mol m ³ s ⁻¹)	0.438	0.4134	0.4885

Previous results had shown that 100% conversion of CO can be achieved at room temperature when 1% Au/TiO₂ is used for the oxidation of CO using a plug flow reactor (PFR). The above results demonstrate that a highly active gold catalyst supported by TiO_2 could be produced using the method outlined in section 3.3.1.

In order to determine the TOF of the catalyst, the active sites of gold were calculated based on a mean diameter of gold nanoparticles of 3 nm. Table 3-3 suggests that satisfactory TOFs were achieved using different ratios of the prepared gold catalyst at room temperature.

CO flow rate (ml min ⁻¹)	Gold weight (mg)	Gold active sites (surface atom mol)	Conversion	Temperature (K)	TOF (s ⁻¹)
4	0.1	1.77 *10 ⁻⁶	47%	298	0.15
10	0.1	1.77 * 10 ⁻⁶	45%	298	0.17

Table 3-3: TOFs of CO oxidation reaction test using reactant flow rates

Utilising the average particle diameter to determine the active sites of Au, Hutchings achieved a TOF of approximately 2×10^{-3} (per Au site per second), using Au/Fe₂O₃ and O₂ for the oxidation of 0.5 ml min⁻¹ of CO [91, 167-170]. Gates reported a CO oxidation rate of approximately 0.1 CO₂ molecules per Au site per second using Au/TiO₂ doped with FeO_x. The rate achieved by Gates is comparable to the rates reported for other oxide supported Au catalysts [72, 91, 146, 169, 170].

Valden suggested that the catalytic activity of Au depends on the method used to prepare the catalyst and on the support, but that the catalyst activity is linked mainly to the size of Au clusters. He found that for low-temperature oxidation of CO on supported Au clusters, TOFs increased from about 0.05 to 0.3 molecule per atom per second as the diameter of the Au clusters was decreased to about 3.5 nm [94].

For the purpose of comparing the different batches of the prepared catalysts, the previous procedure of determining TOFs of prepared Au/TiO₂ catalyst was used with many assumptions that might not be strictly applicable to heterogeneous catalysts. The calculations are based on a first-order reaction, although this type of catalysis could be more complex than first order [171-174]. Equation 3-2 for the determination of activation energy was not used in the current work, as temperature dependency was not assessed in this work. The calculations are provided as estimates only, as the work to accurately determine activation energies and conversions would extend beyond the scope of this work.
3.5 Spent catalyst characterisation

The properties and performance of catalysts used for gas phase and liquid phase reactions were analysed and tested to assess the efficiency of the preparation method in producing active stable catalysts. The catalyst used for the gas phase oxidation of CO was retrieved and used for another cycle of the reaction using the PFR reactor. Figure 3-6 shows that the catalyst reduced by CO was still active for further oxidation. Full conversion could be achieved at room temperature using a catalyst previously spent in a gas phase reaction.



Figure 3-6: Mass spectrometer gas traces of CO oxidation reaction using 1% Au/TiO₂ spent in gas phase reaction

The catalyst spent in the gas or liquid phase oxidation was also retrieved and analysed using TEM. After use in the liquid phase oxidation of one of the lignin-derived compounds, the catalyst was filtered and washed with deionised water and dried in preparation for further analysis.

Figure 3-7 shows the TEM images of the catalyst after it had been used in the liquid phase reaction. The images of the spent catalysts show that there are no gold particles on the catalysts, which suggests that gold may have leached out of the catalyst into the liquid phase.



Figure 3-7: TEM image of spent 1%, 2% and 5% Au/TiO₂

The EDX-SEM elemental analysis of the fresh and spent gold catalyst is shown in Figure 3-8. The spectrum of the spent catalyst shows no evidence of the presence of gold in the analysed sample, which indicates that gold was dissociated from the supporting material.



Figure 3-8: EDX-SEM spectra of fresh and spent 1%Au/TiO2- with no pretreatment

Moreover, XRD analysis of the spent catalyst showed that the analysed sampled consisted mainly of TiO_2 in anatase form, with minor amount of rutile. No evidence of the existence of gold in the sample was found (Figure 3-9).



Figure 3-9: XRD analysis of spent 1% Au/TiO2 with no pre-treatment

The spent non pre-treated catalysts were tested for their activity in oxidising CO in the PFR reactor. Figure 3-10 shows that no reaction occurred with the non-calcined spent catalyst, which supports the TEM suggestion that gold leached out of the catalyst, deactivating the catalyst, which then had no effect in catalysing CO oxidation into CO_2 .



Figure 3-10: Mass spectrometer gas traces of CO oxidation using spent non-calcined 1% Au/TiO₂

All the above experimental findings support the conclusion that gold has leached out of the catalyst causing deactivation. Generally, catalysts can be deactivated through three common causes: fouling, poisoning, thermal degradation and sintering (Figure 3-11). Fouling occurs when the surface of the heterogeneous catalyst is covered with a deposit (known as coke formation), resulting in reducing the active surface area of the catalyst. Poisoning happens when impurities or products have strong interactions with the active sites on the catalyst [175]. One of the most common poisoning agents is sulphur. Sintering or agglomeration of a catalyst occurs when the catalyst is rearranged to reduce the large surface area, and thus causes a decrease in the availability of active sites on a catalyst [176].

Leaching essentially occurs with metal catalysts in the liquid phase reactions of organic molecules, due to the presence of a highly polar medium, which promotes the dissolution of the active components of the catalyst [177].



Figure 3-11: Illustration of catalyst deactivation methods [175]

Therefore, it is thought the experimental data of the spent catalyst when no pre-treatment method was used to condition the catalyst prior to using the catalyst in the liquid phase reaction indicate that catalyst deactivation was due to gold atoms leaching to the reaction solution.

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3.6 Catalyst pre-treatment

The current catalyst preparation method followed to prepare the supported gold catalyst does not include a pre-treatment step. Various studies have suggested that pre-treatment of the catalyst or the support might increase the stability of metal-supported catalysts. Calcination at 300°C under air flow for six hours was found to increase catalyst stability and performance [42, 178, 179]. Research shows that gold catalysts supported on different oxides, including TiO₂, and prepared by the deposition–precipitation method, show increasing activity with calcination temperature up to a maximum temperature of 500°C [180]. However, it is thought that calcining the catalyst under high temperatures would lead to particle size growth, which would reduce the catalyst's activity [181-183]. A very recent study suggested that washing the catalyst under the reaction conditions prior to calcining would eliminate any organics from the catalyst, and would prevent particle growth upon calcination [184].

The effect of a pre-treatment was assessed using two different pre-treatment methods prior to using the catalyst for the liquid phase oxidation. The results were compared to the prepared gold catalyst with no pre-treatment step. The first pre-treatment method included calcining the catalyst at 300°C under a 10 ml min⁻¹ air flow following the preparation method outlined in section 3.3.1. The second method included a washing step before calcining at the same conditions. Washing was carried out under reaction conditions, i.e., using the reaction set up for washing at 70°C and continuous air flow. The catalysts were imaged using TEM in order to determine the particle size distribution and the existence and growth of gold particles in spent catalysts.

Figure 3-12 shows the TEM image and particle size of the catalyst that underwent calcinations only. Most of the particles are within the range of 2-5 nm, which is the ideal size for optimal conversion [185, 186]. Compared to Figure 3-2, which represents the 1% gold on titania, Figure 3-12 shows that there is a slight growth in the gold particle size (4-7 nm range), which indicates that calcination promotes the growth of gold particles. However, when the calcined catalyst is used for the liquid phase reaction, TEM images show that gold particles still exist in the catalyst with a reasonably narrow particle size distribution that indicates further growth in size (Figure 3-13).



Figure 3-12: TEM image and particle distribution of calcined 1% Au/TiO₂



Figure 3-13: TEM image and particle distribution of calcined 1% Au/TiO₂ spent in the liquid phase reaction

For the washing pre-treatment procedure, the deposition-precipitation method was used to prepare 1% Au/TiO₂, after which the catalyst was washed at 70°C, and then calcined at 300°C. TEM images of the fresh and spent catalyst were taken. The particle count and size distribution obtained with TEM suggest that gold particles tend to form in smaller sizes when the catalyst is washed before calcination. More than 50% of the gold particles were in the range of 1-3 nm, which is the ideal size for maximum catalytic activity (Figure 3-14).



Figure 3-14: TEM image and particle distribution of washed/calcined 1% Au/TiO_2

The spent catalyst that was pre-treated using washing/ calcination was found to retain the dispersed gold particles, although using the catalyst in the liquid phase reaction was found to lead to gold particle growth, as shown in Figure 3-15. It was found previously in section 3.5 that the catalyst prepared using the same preparation method without including any pre-treatment procedure prior to using in the liquid phase oxidation was deactivated as gold leached into the solution and no gold was found in the catalyst when it was imaged using TEM.



Figure 3-15: TEM image of washed/calcined 1%Au/TiO2 spent in liquid phase reaction

Upon testing the first of the two pre-treatment methods, it was found that calcination improves the stability of the catalyst, although it leads to particle size growth, and therefore reduces catalyst activity. The pre-treatment procedure according to the second method led to a more stable catalyst, with a larger amount of gold particles remaining in

the spent catalyst and limited particle size growth, in which the majority of the gold particles remained in the range of 2-5 nm, which is the most active range for catalytic reactions [187, 188].



Figure 3-16: Overall catalyst pre-treatment effect on gold particle size

Figure 3-16 shows that when the catalyst was washed under reaction conditions prior to calcination, more than 30% of the gold particles dispersed on the catalyst surface were in the range of 1-2 nm in size. Research has shown that gold particles can achieve maximum activity for gas phase oxidation when they are 1-3 nm in size. Similarly, the catalyst pre-treated only by calcination shows better size distribution of the gold particles than the catalyst with no pre-treatment. The lack of pre-treatment can lead to the production of gold particles larger than 10 nm, which have lower activity. Figure 3-17 shows that when the catalyst was pre-treated by washing and calcination, the majority of the Au particles were on the lower side of the size scale with 57% of Au particles in the range of 1-3 nm in diameter. However, although some growth in the particle size was observed in the spent catalyst that had been washed prior to calcination (Figure 3-18), the majority of the Au particles were in the range of 1-5 nm, which is within the size range of highly active gold catalysts.



Figure 3-17: Effect of washing prior to calcination on the gold particle size



Figure 3-18: Particle size distribution of fresh vs. spent washed/calcined catalyst

3.7 Conclusions

Supported gold catalysts were prepared for use in the oxidation of lignin-derived compounds. Various methods can be used to prepare such catalysts. However, previous studies have shown that highly active supported gold catalysts can be synthesised using

the deposition-precipitation method. An adaptation of the deposition-precipitation method was used to prepare catalysts used for this work. The performance of the catalyst was tested using the carbon monoxide oxidation reaction as an initial test to determine the catalyst activity. CO oxidation was chosen because of abundant data in the literature for comparison.

The experimental data showed that the outlined method was adequate in producing highly active catalysts for gas phase oxidations. ICP-OES confirmed the successful preparation of the correct Au loading supported on TiO₂. Other catalyst features appeared to be in the suitable range for gas and liquid phase reactions. CO oxidation conversion rates comparable to those of previously reported highly active catalysts were achieved using 1% Au/TiO₂. Turn-over-frequencies of up to 0.17 s⁻¹ could be achieved, and full conversion of CO was accomplished at room temperatures.

However, the experimental results of the liquid phase reaction (discussed in more detail in section 4.3) provided evidence that gold leaching out of the catalyst in the liquid phase reaction may occur. It was thought that the instability of the catalyst could be due to the lack of a pre-treatment step for the catalyst/support in the preparation method used for the catalyst.

The effect of catalyst pre-treatment was assessed, by performing calcinations at 300°C under 10 ml/min air flow for six hours, with one method including a washing step, whereby the catalyst is washed under reaction conditions prior to calcination. It was found that catalyst pre-treatment by calcination contributes to the stability of the catalyst, and therefore to the possibility of catalyst re-use in further reactions. Moreover, it was found that the washing step has the effect of controlling the particle size by mitigating the particle growth observed with calcination alone. These results are in line with previous studies that have demonstrated that gold catalysts develop increasing activity with temperature up to a maximum calcination temperature of 500°C [180].

4. Catalytic oxidation of syringic acid

This section will present the catalytic oxidation reaction of syringic acid, which is one of the main components of lignin pyrolysis, over supported gold catalyst. Data obtained with 1% Au/TiO₂ (w/w) catalyst and different concentrations of syringic acid at different conditions will be presented. The analyses to identify the reaction products along with proposed mechanisms will be discussed.

4.1 Introduction

As discussed in chapter 1, lignin processing yields a number of phenolic decomposition products in high yields. Syringic acid (SA) is one of the major products of lignin pyrolysis. It is an O-methylated trihydroxybenzoic acid ($C_9H_{10}O_5$) that is crystalline at room temperature, in the form of a light-brown powder. The solubility of SA is a moderate 5780 mg/L (25°C) in water, limiting the concentration range available to aqueous oxidation reactions. Because syringic acid is produced in high yields, identification of a route by which to upgrade and utilise this compound would have significant benefits.



Figure 4-1: Chemical formula of syringic acid

This chapter will present evidences that the aerobic oxidation of SA over Au/TiO_2 leads to the formation of DMBQ Figure 4-2 is an illustration of the catalytic reaction of syringic acid studied in this chapter.



Figure 4-2: schematic of the syringic acid reaction over Au/TiO2 to produce dimethoxybenzo quinone

4.2 Experimental

4.2.1 Catalyst Variations and Controls

Catalyst pre-treatment and loading conditions were assessed in order to study the effect of each variable on the reaction rate. Control experiments were carried out to verify that the compound was not converted to products simply as a result of heating in the presence of atmospheric oxygen. The effect of temperature on SA was therefore assessed by heating the solution in the absence of the catalyst. Moreover, the possibility of the support material, TiO₂, to catalyse the oxidation reaction by itself was studied using TiO₂ that had undergone the identical preparation route as the Au/TiO₂ catalyst, but without adding any gold. Other parameters such as the reaction temperature, pH, and effect of gold ions in solution were assessed through adding aqueous HAuCl₄.3H₂O.

4.2.2 Reaction parameters

The open flow systems and the pressurisable closed reactor described in chapter 2 were used to examine the transformations of SA in the presence of the Au/TiO₂ catalyst. To examine the possibility that a higher reactant-to-gold ratio would enhance the oxidation reaction of lignin-derived chemicals and yield alkanes in the molecular weight range of fuels. It was therefore decided to assess three different SA:Au reactant ratios: 300:1, 100:1, and 20:1 (mol:mol) for the liquid phase oxidation. The reactions were carried out under atmospheric pressure and near-ambient temperatures up to 70°C, and using a 3 mM concentration of syringic acid. The reactions were monitored over time by regularly taking samples for analysis, using the analytical techniques described in chapter 2. Quick assessments whether any reaction took place were made by UV-vis analysis of the

solutions. When UV-vis indicated significant conversion of SA other techniques were employed to identify products. Other variables such as air pressure, reactant concentration and temperature were also examined in order to determine the optimum conditions for this reaction [189-191].

4.3 Results

4.3.1 Control experiments

Control experiments were carried out as described in section 2.2.2.

Temperature effect on SA solution

To find the effect of temperature on SA, a 3 mM solution was heated at 70°C under continuous air flow at atmospheric pressure using the open reaction system. UV-visible results presented in Figure 4-3 shows that SA did not undergo any changes as a result of heating. This suggests that SA does not yield any products as a result of heating at temperatures up to 70°C.



Figure 4-3: UV-Visible spectra of SA heated at 70°C

Effect of TiO₂ on SA Solution

Another control experiment was carried out to exclude any potential for TiO_2 itself to catalyse the reaction. TiO_2 equivalent in weight to the planned weight of catalyst when

employing a 20:1 reactant to gold ratio was added to the SA solution. The mixture was the heated at 70°C and atmospheric pressure for 24 hours in the open reaction system. The reaction was monitored using a UV-visible spectrometer. The results in Figure 4-4 shows that no reaction occurred over the reaction time, as SA spectra remained unchanged throughout the experiment. This suggests that TiO_2 causes no catalytic transformation reaction of SA.



Figure 4-4: UV-Visible spectra of SA heated with unloaded TiO₂

Effect of Dissolved Au Ions

This control experiment was probably the most important one, as it would help determine the actual form of Au that catalyses the reaction. Ideally, the reaction should be catalysed by the supported gold particles in the form of catalyst rather than by Au ions leached into the solution. HAuCl₄ solution was added to SA solution at a reactant:Au ratio of 20:1. The solution was heated to 70°C for 24 hours under continuous air flow. The UV-Visible spectra of the reaction progression are shown in Figure 4-5.



Figure 4-5:UV-Visible spectra of SA heated with HAuCl₄

The data show that SA remained unchanged even after 24 hours. This indicates that dissolved gold ions have no catalysing effect on the SA transformation reaction.

4.3.2 Optimising reaction conditions

Reaction temperatures

The effect of temperature on the catalytic reaction was assessed by varying the reaction temperature and comparing the reaction progression to the reaction performed at 70°C. The oxidation reaction of SA was performed at room temperature and at 100°C. It was found that the optimum temperature to achieve the maximum conversion was 70°C, showing a conversion of 80% after 24 hours of reaction; in contrast, only 60% conversion was attained when the oxidation reaction was performed at 100°C. This could be attributed to the fact that the solubility of oxygen at 100°C is less than at 70°C [192]. When the reaction was carried out at room temperature, the conversion was less than 20%, indicating that moderate heating accelerated the reaction significantly. See Figure 4-6 to Figure 4-10.



Figure 4-6: SA oxidation to DMBQ (2,6-dimethoxybenzo quinone) using 1%Au/TiO₂ at room temperature monitored by HPLC





Figure 4-8: SA oxidation to DMBQ (2,6-dimethoxybenzo quinone) using 1%Au/TiO₂ at 100°C monitored by HPLC



Figure 4-9: Reduction of SA concentration as a function of reaction temperature based on HPLC signal intensity



Figure 4-10: Product formation as a function of reaction temperature based on HPLC signal intensity

Influence of Reactant: Catalyst ratio on the reaction rate

No previous studies were found on the required reactant:Au ratio for the oxidation of lignin-derived compounds, as gold has not been studied previously for this purpose. However, studies using zeolite and other metal oxides catalysts proposed utilising a ratio of 20:1 of lignin products to the catalyst, whereas other studies on similar compounds showed that the reaction can be carried out using a 500:1 reactant: catalyst ratio with other supported metal catalysts. Hence, it was decided to assess different ratios of SA:Au in order to determine the optimum ratio required to achieve maximum conversion rate and to aid in understanding the activity of the catalyst. SA:Au ratios of 300:1, 100:1, and 20:1 using 1% Au/TiO₂ catalyst were assessed. The reactions were again carried out using a 3 mM solution of SA under the outlined conditions, using continuous air bubbling and 70°C in an open reaction system. The reactions were monitored using HPLC to detect and quantify any reaction products.



Figure 4-11: Reaction progression based on HPLC measurements of the SA reaction over 1% Au/TiO₂ with reactant:Au ratio of: a. 300:1, b, 100:1, c. 20:1

Figure 4-11 shows that when a ratio of 300:1 reactant:Au was used for the oxidation of SA under the reaction conditions, a low conversion of 8% was achieved after 48 hours of reaction. Decreasing the ratio to 100:1 increased the conversion to almost 30%. The highest conversion rate was achieved when a ratio of 20:1 was utilised for the SA reaction.

The approximately linear relationship in Figure 4-12 indicates that the reaction rate is mostly limited by available catalyst, so that measured reaction rates for one SA:Au catalyst ratio may be extrapolated to other ratios. Under the reaction conditions of 70°C and atmospheric pressure, with air as the oxidant, the maximum conversion rate was achieved when the reactant:Au ratio of 20:1 was used And this ratio was selected for further studies to achieve a quick evaluation of the oxidation performance. Furthermore, this ratio was subsequently used for assessing the reactivity of other lignin-derived compounds (see subsequent chapters).



 $\frac{Figure \ 4-12: Relation \ between \ reactant: Au \ ratio \ and \ conversion \ of \ SA \ after \ 48 \ hours \ of \ reaction \ over \ \underline{1\%Au/TiO_2}$

4.3.3 Reaction profiles

Syringic acid transformation using 1% Au/TiO₂

The oxidation reaction performed at 70°C with a continuous air flow of 1 ml min⁻¹ in an open glass reaction system was monitored mainly by UV-visible spectrometer and HPLC. Figure 4-13, below, represents the progression of the reaction over 48 hours, as monitored by HPLC. The data in blue indicate that the concentration of syringic acid decreased as the reaction progressed. The product (dimethoxy benzoquinone, DMBQ, see below) formation almost quantitatively mirrored the SA decomposition curve until approximately 80% conversion to product was achieved after 24 hours of reaction.



Figure 4-13: HPLC analysis of the reaction progression of SA oxidation using 1%Au/TiO₂

However, the figure also shows that the reaction stopped after 24 hours, when 80% conversion was reached. This may be attributed to achieving some equilibrium, or to deactivation of the catalyst by leaching or by poisoning with the product.

This experiment therefore prompted investigation of catalyst deactivation, as described in chapter 3. The results showed that the reason for catalyst deactivation was gold leaching into the aqueous phase when the preparation method of the catalyst did not include a pre-treatment step.

The stability of the catalyst was improved by the inclusion of a pre-treatment procedure, as described in section 3.6, and only pre-treated catalysts were subsequently used for liquid phase oxidations.

The product analysis was performed using several analytical techniques in order to identify and confirm the structure of the resulting oxidation products. Proton NMR, GC-MS and FT-ICR-MS were used for this analysis.



Figure 4-14: FT-ICR-MS spectra of the progression of SA oxidation reaction using 1% Au/TiO2

FT-ICR-MS showed that a product started forming after 2 hours for the reaction over 1% Au/TiO₂. The product had the molecular formula of $C_8H_8O_4$ and a molecular weight of 168 g mol⁻¹. The reaction was monitored for 24 hours, the concentration of this product was found to increase over time (Figure 4-14). The figure shows the presence of minor by products that could not be identified due to the small concentrations that are undetectable by most analytical methods. The existence of bi products might explain the lack of isosbestic points in the UV-Visible spectra of the reaction solution.

GC-MS was used in order to determine the structure of the compound detected by FT-ICR-MS. The results showed that the reaction of SA over Au/TiO₂ catalyst yields a product with the molecular weight of 168 g mol⁻¹, and a chromatogram that matches that of the 2,6-dimethoxy benzoquinone structure (Figure 4-15- Figure 4-17).



Figure 4-15: GC-MS chromatogram of SA oxidation reaction solution



Figure 4-16: MS chromatogram of SA catalytic oxidation product



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 4-17: Reference mass spectrum of 2,6-DMBQ



Figure 4-18: ¹H NMR signals assignment for syringic acid and 2,6-Dimethoxy benzoquinone

Proton NMR was used in order to confirm the suggested structure of the resulting product. The SA reference solution using MeOD gives ¹H NMR signals at 3.90 ppm (s, 6 H, $-OCH_3$) and 7.3 ppm (s, 2 H, =CH-).

Proton NMR analysis of the reaction solution showed that the compound produced by the reaction of SA over 1% Au/TiO₂ has two single peaks at 3.86 ppm (s, 6 H, $-OCH_3$) and 5.8 ppm (s, 2 H, =CH-) (Figure 4-18), in addition to the signals attributed to SA (Figure 4-19 and Figure 4-20).

The oxidation of SA to DMBQ is well known to proceed by other transformation routes, such as biochemical transformation [136, 193] or homogenous catalysis [194], but has never been reported as a heterogeneously catalysed route.

Figure 4-19 represents the obtained proton NMR spectra of the SA reaction solution. It was found that the dominating water signal makes it difficult to detect and quantify other signals of existing compounds. Hence, it was necessary to magnify the spectra and zoom into areas of chemical shifts where signals where found.



Figure 4-19: ¹H NMR spectra of SA reaction solution using MeOD as a solvent and 400 MHz magnet



Figure 4-20: Proton NMR of SA oxidation using 1%Au/TiO₂ using MeOD as a solvent and 400 MHZ magnet

The reported chemical shifts for the product were found to match the signals of 2,6dimethoxybenzoquinone and as reported in the literature [195-197].



Figure 4-21: ¹H NMR analysis for the reaction progression of SA oxidation using 1% Au/TiO₂

Figure 4-21 shows the SA oxidation reaction over supported gold catalyst carried out and monitored using ¹H NMR analysis for 6 days. The results support the HPLC finding of formation of DMBQ as a product of SA oxidation. However, the reaction appears to level out after 28 hours of reaction due to use of a non-calcined catalyst, which likely underwent gold leaching, and therefore deactivation. Moreover, although the NMR absolute is difficult to obtain, the results in the above figure shows more than 60% conversion of SA after 48 hours of reaction over Au/TiO₂, which provides further support to the HPLC findings.

The FT-MS analyses also suggested that there were trace by-products during the oxidation of SA to DMBQ. However, repeated analyses using GC-MS, LC-MS, and ¹H NMR failed to detect sufficient by-product concentrations besides DMBQ to permit determination of their nature. FT-ICR-MS is a very sensitive analytical technique, and these by-products are probably produced at negligible low concentrations.

An attempt was made to extract the organic compounds from the aqueous solution to another solvent in order to eliminate the water signal and enable better detection of products via NMR. Samples were concentrated, and dissolved in MeOH in order to be analysed by GC-MS to identify the structure of the products. Results suggested the presence of DMBQ (M.W. 168) and another product with the M.W. of 212. The mass spectrum of the second product (Figure 4-22) suggested the formation of methoxylated compounds, probably as a result of a radical reaction where a methyl group is added to the SA structure. These methoxylated compounds (Figure 4-23) are expected to be produced as a result of the extraction procedure using methanol. Hence, extraction was abandoned as it might jeopardise the integrity of the sample structure.



Figure 4-22: Mass spectrum of the methoxylated SA oxidation product extracted by MeOH



Figure 4-23: Possible structures of the methoxylated SA oxidation product resulting from extraction by <u>MeOH</u>

Oxidation by O_2 or by H_2O ?

In another control experiment, the reaction was run in the absence of O_2 , using a pure N_2 stream. To ensure saturation with N_2 , the reactant solution was kept under 10 ml min⁻¹ N_2 for an hour prior to adding the catalyst. When the N_2 flow was kept and the catalyst added the reaction solution did not turn yellow, which indicates that production of DMBQ did not occur. More importantly, the UV-vis analysis (Figure 4-25) confirmed that in an N_2 -saturated atmosphere, no reaction of SA occurred. The spectra remained unchanged after 24 hours of heating at 70°C in the presence of 1% Au/TiO₂ at a reactant: Au ratio of 1:20.



Figure 4-24: Full UV-Vis spectra of SA reaction over Au/TiO2 in the absence of O2



Figure 4-25: Magnified UV-Visible spectra of SA reaction over 1% Au/TiO₂ in the absence of O₂

Influence of Au loading on catalyst performance

Different catalysts were prepared using various loadings of Au in order to understand the effect of Au loading on the activity of the catalyst and, therefore, the oxidation reaction rate. Catalysts with gold loadings of 1%, 2% and 5% were prepared, tested and used in the liquid phase oxidation reaction of SA. Figure 4-26 shows that the gold loading has no effect on the reaction rate. Therefore, there is no need to work with catalysts with high gold loadings. One possible explanation for this result is that the rate determining step may be adsorption of SA on the TiO₂ surface, rather than the oxidation reaction at the Au nanoparticles on the TiO₂ surface. Future work should therefore examine whether variations in TiO₂ surface area have an effect on SA conversion.



Figure 4-26: Influence of Au loading on the conversion rate of SA oxidation to DMBQ based on HPLC signal intensity

Catalytic or stoichiometric?

It was decided to explicitly address the question whether the reaction was catalytic or stoichiometric. Another experiment was performed in which SA was oxidised using 1% Au/TiO₂ for 72 hours to ensure that all SA was used in the reaction prior to adding another equivalent amount of SA to the reaction mixture. This was done in order to confirm that the catalyst was still active and could catalyse the reaction at the same rate, which would mean that the gold in the catalyst was not used up as a reactant in a stoichiometric reaction.

The first part of the experiment conformed to the pattern of a normal SA oxidation reaction using 1% Au/TiO₂. UV-visible spectra showed that the reaction resulted in the production of DMBQ (increased absorbance at 290 nm) as the concentration of SA was decreased (265 nm) (Figure 4-27). After 48 hours of reaction, the absorbance of DMBQ remained unchanged with no further increase, indicating that the reaction had stopped, with no additional formation of the oxidation product.



Figure 4-27: UV-Visible spectra of the SA oxidation reaction progression with 1%Au/TiO2

After 72 hours, more SA was added to the reaction solution under the same reaction parameters, at a 1:20 gold-to-SA ratio. Figure 4-28 below shows that the formation of DMBQ resumed as the reactant concentration was restored. The absorbance of DMBQ increased, indicating increased concentration of the product in the solution. The absorption almost doubled compared to the first cycle of the reaction (Figure 4-29). This might indicate that all SA existing in the reaction mixture is converted into DMBQ in a catalytic reaction using Au/TiO₂.



Figure 4-28: UV-Visible spectra of the SA oxidation reaction progression over 1% Au/TiO₂ after the addition of an equivalent amount of SA after 48 hours of reaction



Figure 4-29: Reaction progression of two cycles of SA oxidation over 1% Au/TiO₂ monitored with a UV-<u>Visible spectrometer</u>

Influence of air pressure on the catalytic reaction rate

The oxidation reaction was carried under different conditions, but all experiments were carried under ambient pressure. Previous studies have suggested that lignin-derived chemicals undergo oxidation under such severe reaction conditions as 170°C and 20 bar to produce alkanes in the range of gasoline streams [37, 141]. However, the aim of this study was to find a conversion route for lignin-derived products that can be performed on a large scale at a cost that would be economically viable for industrial applications. Hence, it was decided to carry out the reaction under less severe conditions, at a pressure lower than 20 bar, to test the effect of pressure on the catalytic reaction rate. The oxidation reaction of SA was carried out in a closed stainless steel Teflon-coated micro-reactor under 10 bar pressure. All other parameters remained unchanged.



Figure 4-30: Influence of pressure on the reduction rate of SA



Figure 4-31: Influence of pressure on the formation rate of DMBQ as oxidation product of SA

The reaction was again monitored by taking samples from the liquid phase, but additionally, utilising a closed reactor allowed the capture of products in the gas phase. Gaseous samples were collected through a sampling valve connected to a previously evacuated stainless steel vessel. These gas samples were then analysed using a quadrupole mass spectrometer. No products were identified in the gas phase as a result of SA oxidation over supported gold catalyst.

Figure 4-30 and Figure 4-31 show the rate of SA consumption and DMBQ formation when SA was oxidised under ambient (red trace) and high pressure (blue trace). The

results suggest that 90% conversion is achieved in less than 4 hours when the reaction is carried under elevated pressure. This high conversion rate was seen under ambient pressure only after 24 hours of reaction. This confirms the hypothesis that carrying out the reaction under higher pressure would increase the SA conversion rate and significantly reduce the time required to obtain this result (Figure 4-32).



Figure 4-32: Comparison between the reaction rate of SA oxidation over 1% Au/TiO₂ under ambient and high pressure monitored by HPLC

H_2O_2 formation?

The industrial route to form H_2O_2 involves the use of a hydroquinone/quinone equilibrium to convert O_2 into H_2O_2 [198, 199]. The formation of a quinone in a catalysed aerobic oxidation immediately raises the question whether an intermediate formation of H_2O_2 is the cause of the observed oxidation. It is thought that SA oxidises to DMBQ, so such a mechanism would have to involve dimethoxyhydroquinone (DMHQ) and the production of H_2O_2 [195, 200-203]. It was therefore decided to test the reaction solution to detect the presence of H_2O_2 , which might be formed during the catalytic reaction. The detection procedure was performed in accordance with the method outlined in the study by Prati et al. using TiO(SO₄) with sulfuric acid [113].

SA oxidation using 1% Au/TiO₂ (1:20) at 70°C with air was re-examined whereby samples were treated with the detection solution and analysed using UV-Visible spectroscopy. The spectra of TiOSO₄, SA and DMBQ are included for reference.



Figure 4-33: UV-Visible spectra of SA oxidation over 1% Au/TiO₂ treated to detect H₂O₂ formation

As the reaction progressed, the formation of DMBQ became apparent, but there was no evidence that H_2O_2 was produced in the process. A possible explanation would be that the concentration of the produced H_2O_2 is below the detection limit, and/or that it is consumed at the same rate as it is produced.

To understand the potential role of H_2O_2 in the reaction mechanism, SA was reacted with H_2O_2 in the absence of the catalyst. This would help to determine whether the supported gold activates the reaction by promoting the generation of H_2O_2 , or whether the reaction mechanism does not include peroxide generation.

The figure below (Figure 4-34) shows that no change in the SA spectra occurred over time when SA was heated with H_2O_2 (the slight shift in the spectra is probably irreproducibility due to measuring the samples on different days).

It can be concluded from these results that even if the reaction involves the formation of H_2O_2 as an intermediate at low concentrations, it is not is required for the reaction to be accomplished.



Figure 4-34: UV-Visible spectra of SA reaction with H₂O₂

Reusing spent Au/TiO₂ catalyst for SA oxidation

One of the most important aspects of catalytic performance is the ability to reuse or to recycle a catalyst. In order to determine if the catalyst was deactivated by gold leaching or by any other way, the catalyst used for the oxidation of SA was collected, washed and dried before use in a second oxidation cycle. The results in Figure 4-34 show the HPLC-monitored progression of the SA oxidation reaction using the spent catalyst. The achieved conversion was consistent with the conversion when a fresh catalyst was used.

This result suggests that the prepared catalyst is stable and can be reused for more than one oxidation cycle of SA. It also supports the conclusion that SA oxidation with Au/TiO_2 is a heterogeneous catalytic reaction in which the reactant is activated by the supported gold catalyst and not the free gold that leaches into the solution.


Figure 4-35: SA oxidation reaction using spent 1% Au/TiO2 catalyst

4.4 Discussion

It was found that syringic acid oxidation over supported gold catalyst results in the formation of 2,6-dimethoxybenzoquinone. The mechanism of the reaction is thought to include an oxygen activation step in order to provide the active form of the oxidant to the reaction mixture [87-89]. So far, it has been found that the oxidation reaction of SA over supported gold catalyst involves oxygen, although the mechanism is not yet clear. It has been proposed that the mechanism of oxidation of phenols under gold catalysis begins by cleavage of the C-H bonds in the phenol molecule to form Au-H species. To restore the catalytic activity, hydrogen needs to be removed from the Au surface, and this is thought to be via O_2 reacting with hydrogen to form H_2O , or H_2O_2 that decomposes to form H_2O . The extra hydrogen comes from the -OH bond, which is broken to form a carboxyl group [83, 84, 204-206].

2,6-Dimethoxybenzoquinone is known to be an oxidation product of syringic acid [136, 194]. It can be produced non-catalytically from the oxidation of syringic acid in aqueous solution using dilute H_2SO_4 and $Na_2Cr_2O_7$. A possible reaction mechanism could be that syringic acid undergoes an electron transfer to form a phenoxy radical, at which point a second electron transfer takes place to produce 2,6-dimethoxybenzoquinone (DMBQ)

[207]. The measured minimal changes in pH of the reaction mixture suggest that this mechanism is plausible (Figure 4-36).



Figure 4-36: Proposed mechanism of syringic acid oxidation over supported gold catalyst

The pH values of the reactions solution changed from 3.2 to 4.4 at the end of the reaction. The minor increase in the pH value of the solution shows that the formed compound have less acidity compared to the reacting compound, which might further support the proposed mechanism involving proton transfers. It was found that SA oxidation over a supported gold catalyst resulted in the formation of DMBQ. The reaction was carried out at 70°C and continuous air flow using a 1:20 gold to SA ratio. A conversion of 80% was achieved using these conditions after 24 hours of reaction. However, a higher conversion rate was obtained in less than 5 hours when the reaction was performed under pressure (10 bar).

4.5 Conclusions

An important product of lignin decomposition is syringic acid (SA). It has been suggested that syringic acid should be upgraded into other valuable chemicals using different routes, one of which is catalytic oxidation. It has been found that 1% Au/TiO₂ catalysts facilitate the aerobic oxidation of syringic acid 2,6-dimethoxybenzoquinone (DMBQ) under ambient and near-ambient conditions. Employing a 20:1 syringic acid to gold ratio and a temperature of 70°C under continuous air flow, an 80% conversion rate of SA to DMBQ can be achieved after 24 hours of reaction. The results suggest that the best reaction rate occurred when the reaction was carried out at 70°C. However, it was found that the reaction rate could be improved by using a high pressure (10 bar) in a closed reaction system.

5. Catalytic oxidation of vanillic acid

The catalytic transformation of vanillic acid (VA) over supported gold catalyst will be discussed in this section. Results of experimental work using 1% Au/TiO₂ (w/w) catalyst will be presented along with the product analysis and proposed mechanism.

5.1 Introduction

The significance of processing lignin-derived organic building blocks to either valueadded products or to chemicals with potential as feeds for other platform processes has been discussed in Chapter 1. Depending on the plant species, vanillic acid (VA) is a major product of pyrolytic lignin processing [208, 209]. VA is a dihydroxy benzoic acid derivative that is isolated at room temperature as a light yellow powder that has the molecular formula of $C_8H_8O_4$ and a molecular weight of 168 g mol⁻¹. It is the oxidised form of vanillin, which is the aldehydic form widely used as a flavouring agent. It is produced as an intermediate in vanillin production from ferulic acid, and has a solubility of 1.5 mg/ml at 14 °C.



Figure 5-1: Molecular structures of vanillic acid (left) and syringic acid (right)

SA and VA (Figure 5-1) are representative compounds of the phenolic carboxylic acids that result from lignin transformation. Various studies have been conducted to understand the degradation reaction of these compounds. However, most of these studies were focused on the biochemical reactions by microorganisms [210-213]. The structure of vanillic acid (VA) is similar to that of syringic acid (SA, chapter 4) - the only difference is the absence of one of the methoxy groups on the ring (Figure 5-1). Understanding how

VA reacts over supported gold catalyst might therefore contribute to the overall understanding of the reaction mechanisms and networks of similar lignin-derived compounds, including understanding the influence of the methoxy groups on the oxidation of SA (see chapter 4).

As one of the most important chemicals resulting from the metabolism of lignin by white-rot fungi, the transformation of vanillic acid has attracted a lot of interest. The bio chemical degradation of vanillic acid and its effect on the human body has been extensively studied as well [211, 214, 215]. Research has concluded that through the biochemical transformation route, VA either undergoes oxidative decarboxylation to produce a hydroquinone or is reduced to vanillin [216]. Other studies using enzymatic conversion reported the production of 2-methoxyphenol (guaiacol) as a result of vanillic acid transformation [210, 217-219].

5.2 Experiment

5.2.1. Reaction conditions

The transformation reaction of VA was carried out using the reaction conditions optimised with SA. The VA reaction over 1% Au/TiO₂ was performed using a reactant to Au ratio of 20:1 and a VA solution concentration of 3 mM under atmospheric as well as elevated air pressure. The aim of these studies was to compare the difference in the reaction rate of VA oxidation with that of SA oxidation. Performing the reaction in the closed reactor would also help with trapping and identifying products in the gas phase. Other parameters, including reactant:Au ratio and reaction temperature remain unchanged. The progress of reactions was monitored through regular sampling and analyses using the methods described in chapter 3.

5.3 Results

5.3.1 Control experiments

Temperature effect on VA solution

VA solution was heated at 70°C under continuous air flow and atmospheric pressure using the open reaction system. Figure 5-2 shows that no change occurred to the UV-visible absorption of the VA solution over time as the solution was heated with no added catalyst. The results indicate that VA was not affected by heating and that no products resulted from heating VA in the absence of a catalyst.



Figure 5-2: UV-visible spectra of vanillic acid heated at 70°C

Au-free TiO₂

Unloaded TiO_2 was added to the VA solution and heated at 70°C at atmospheric pressure. The UV-visible spectroscopy analysis of the reaction mixture showed that no change occurred over time. TiO_2 does not have a catalytic effect on VA oxidation (Figure 5-3).



Figure 5-3: UV-visible spectra of vanillic acid heated in the presence of TiO₂

Homogeneous Ionic Au

HAuCl₄ solution was added to VA to a ratio of 20:1. The mixture was heated under ambient pressure and 70°C. Figure 5-4 shows the UV-visible spectra of the VA solution over 24 hours. The results suggest that free gold ions have no effect on VA spectra, as no reaction was detected in the presence of Au solution. Minimal changes could be attributed to evaporation and instrument drift.



Figure 5-4: UV-visible spectra of vanillic acid heated in the presence of HAuCl₄

5.3.2 Reaction profiles

Catalytic oxidation of VA over 1% Au/TiO₂

The transformation of VA over the Au/TiO₂ was studied by performing the reaction under the same conditions used for the SA oxidation (chapter 4). A 3 mM concentration of VA solution of was placed in the open reaction system, to which a specific weight (440 mg) of 1% Au/TiO₂ catalyst, prepared according to the deposition-precipitation method outlined earlier was added. The reaction was performed under atmospheric pressure and a temperature of 70°C with continuous air flow (1 ml min⁻¹). The progress of the reaction was monitored using UV-visible spectroscopy as preliminary test to detect any changes in the solution spectra that might indicate consumption of the reactant and/or formation of a product.



Figure 5-5: UV-visible spectra of the vanillic acid reaction over Au/TiO₂

The UV-visible spectra show that the concentration of VA decreased as the reaction progressed, which might indicate that VA is consumed in a transformation reaction. No products were detected by UV-Visible spectrometry (Figure 5-5).

Samples were analysed using HPLC in order to separate and distinguish any products that were not detected by UV-visible spectrometry. Figure 5-6 shows the progression of

the VA reaction over Au/TiO₂ monitored by HPLC. HPLC results showed that VA has a retention time of 5.4 minutes, and a reaction product with a retention time of 5.9 minutes was detected.



Figure 5-6: HPLC chromatogram of VA reaction solution over 1% Au/TiO2

Monitoring the reaction progression by HPLC (Figure 5-7) shows that 50% of VA was converted into a product after 48 hours of reaction.



Figure 5-7: Reaction progression of vanillic acid catalytic transformation over Au/TiO₂ using HPLC signals relative intensity

The product was analysed using GC-MS, which showed that VA oxidation resulted in the formation of a product with a molecular weight of 124 g mol⁻¹, corresponding to a formula $C_7H_8O_2$ whose chromatogram matched that of 2-methoxyphenol (guaiacol) (Figure 5-8 and Figure 5-9).



Figure 5-8: GC-MS chromatogram of the reaction solution of VA over 1%Au/TiO₂



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 5-9: Reference mass spectrum of guaiacol

¹H NMR analysis was performed in order to confirm the structure of the resulting product. VA gives a ¹H NMR signals as follows: (MeOD) ppm 3.90 (s, 3 H, 3-OCH₃), 7.45 (d, J=8.7 Hz, 1 H, 6-H), 6.84 (d, J=8.7 Hz, 1 H, 5-H), 7.43 (s, 1 H, 2-H) [167, 220]. The resulting product gave signals at ppm 3.90 (s, 3 H, -OCH₃), 6.84 - 6.90 (m, 3 H, H-3, H-4, H-6), 6.91-6.95 (m, 1 H, H-5) (Figure 5-10). These signals correspond to guaiacol NMR signals found in previous studies [219, 221], and found experimentally as shown in Figure 5-10. Note that ¹H NMR signals for both VA and guaiacol are similar and have closely related chemical shifts.



Figure 5-10: ¹H NMR signals assignment of vanillic acid and guaiacol



Figure 5-11: ¹H NMR spectra of the reaction progression on vanillic acid over 1% Au/TiO₂

Figure 5-11 shows the progress of guaiacol formation as the concentration of VA decreased, monitored by ¹H NMR. Analysing the reaction solution by FT-MS showed the presence of vanillic acid ($C_8H_8O_4$), in addition to a compound that has the molecular weight of 124, and the formula of $C_7H_8O_2$, which matches that of guaiacol (Figure 5-12).



Figure 5-12: FT-MS chromatogram of the reaction solution of vanillic acid over 1%Au/TiO₂

The UV-visible spectrum of guaiacol solution with a concentration of 3 mM was obtained and compared to the reaction solution spectrum (Figure 5-13).



Figure 5-13: UV-visible spectra showing the reaction progression of vanillic acid over 1% Au/TiO₂

As seen in the figure above, there is significant overlap between all electronic transitions evident in the UV-vis spectrum, making it difficult to establish the guaiacol concentration. It was noticed that the yellow colour of the vanillic acid faded out, and that the solution remained colourless with no further formation of the coloured product resulting from the possible oxidation of guaiacol. The lack or isosbestic point in the spectra might have resulted from the spectral overlap, in addition to possible evaporation of the product, which is found to evaporate rapidly under the reaction conditions (section 7.3.1)

Pressure effect on the reaction rate

When ambient pressure was used for the catalytic transformation of VA, only 50% conversion was achieved after 48 hours of reaction. It was found that elevated pressure had a significant effect on increasing the oxidation rate for syringic acid (chapter 4), so the effect of pressure on the VA reaction over Au/TiO₂ was assessed in the closed pressure reactor at 10 bar pressure, with all other parameters remaining unchanged. Samples of the gas phase stream were again analysed using a quadrupole mass spectrometer, but no evidence was found of any products in the gas phase. UV-visible spectra showed a decrease in the VA concentration (Figure 5-14). However, there was no

clear evidence for the formation of guaiacol as a resulting product. This might be due to the low conversion rate and the overlap between the UV-visible spectra of VA and guaiacol.



Figure 5-14: UV-visible spectra of the progression of vanillic acid reaction over 1% Au/TiO₂ under 10 bar pressure

Analysing the reaction solution by HPLC confirmed again that guaiacol was eluted. Figure 5-15 illustrates the reaction progression for VA. The relative intensity of signals shows a conversion to 80% after only 6 h of reaction over Au/TiO₂, confirming the expectation that higher O_2 partial pressures accelerated the reaction.



Figure 5-15: Progression of the vanillic acid catalytic oxidation reaction under 10 bar pressure monitored by HPLC

In summary, the above result shows that VA is converted to guaiacol over Au/TiO₂ with a reactant:Au ratio of 20:1. The conversion rate was found to be 50% after 48 hours of reaction at atmospheric pressure, and it increased to 80% in just 6 hours when the reaction was carried out at 10 bar air pressure. When the reaction was performed at room temperature, only 20% of VA had reacted after 72 hours (Figure 5-16).



Figure 5-16: Progression of the vanillic acid catalytic reaction over Au/TiO₂ at room temperature

Role of O_2

In order to understand the reaction of VA over gold catalyst and propose a mechanism through which VA is converted to guaiacol, it is crucial to determine the significance of air/O₂ and the role it plays in the reaction. Therefore, a control experiment was carried out in which the reaction system was purged with N₂ to eliminate any O₂. After 1 hour of flushing the system with 5 ml min⁻¹ of N₂, the gold catalyst was added under continuous N₂ flow, and the composition of the reaction mixture sampled as a function of time, using UV-visible spectrometry. The results in Figure 5-17 shows that after 24 hours of reaction, the VA concentration remained unchanged, except for some minimal instrumental drift in the spectra because samples were measured on different days.



Figure 5-17: UV-visible spectra of vanillic acid reaction over Au/TiO2 in the absence of O2

5.4 Discussion

Vanillic acid is one of the most important lignin decomposition products. Its similarity with SA increases the significance of understanding how it reacts in the presence of supported gold catalyst. Experimental results suggest that VA is not affected by heating it to 70°C with no added catalyst. Unloaded TiO₂ and non-supported Au were found to have no catalytic effect on VA.

Performing the catalytic reaction over 1% Au/TiO₂ at ambient and near-ambient conditions resulted in the formation of 2-methoxyphenol (guaiacol) as a transformation product. Guaiacol is more useful as a base chemical due to its broader application range, for example as an intermediate in the synthesis of active pharmaceutical materials, perfumery and food flavourings.

Interestingly, it has previously been suggested that lignin-derived VA is the most likely precursor for guaiacol synthesis [218, 222]. In fact, the transformation of vanillic acid to guaiacol is a well-known bio-catalytic route in microorganisms that metabolise vanillic acid to produce guaiacol through non-oxidative decarboxylation. In many of these studies, vanillic acid was transformed into guaiacol exclusively, with no other products formed to detectable limits [217, 218, 223-225].

It appears that aqueous VA equally undergoes an overall non-oxidative decarboxylation to guaiacol [226-229]. However, performing the reaction in the absence of O_2 did not yield any products, which indicates that O_2 has a role in activating VA for decarboxylation to produce CO_2 and guaiacol (<u>Scheme 5-18</u>). As discussed in chapter 4 for SA, this step likely involving OH radicals produced by reaction of O_2 on the catalyst surface. No H_2O_2 or other peroxides were detected throughout the VA reaction experiments, which suggest that any peroxide species formed, are almost instantly consumed in the reaction with VA. The overall reaction rate appears to be slow and the product is formed in a small concentration, hence the amounts of H_2O_2 present at any time may well be below detection limits.



Scheme 5-18: Proposed mechanism of the oxidation of vanillic acid to guaiacol

The hypothesis of OH, H_2O_2 or any other peroxide production that would provide an oxidant for the activation of VA could not be confirmed with the techniques available for this product. Voltammetric analysis might be able to detect radicals or peroxo-

intermediates [227, 230, 231]. Another method of free radical detection could be the scavenger methods using radical quenchers such as diphenyl picrylhydrazyl (DPPH) [232].

5.5 Conclusions

VA undergoes catalytic decarboxylation to produce 2-methoxyphenol (guaiacol) in the presence of O_2 and Au/TiO₂. It appears that oxygen is activated over the supported gold catalyst, likely forming OH radicals that reacts with VA and leads to decarboxylation to guaiacol, releasing CO₂. With air at atmospheric pressure the reaction rate was low and resulted in the conversion of only 50% of VA after 48 hours of reaction. The conversion was significantly increased to 80% in just 6 hours by using 10 bar of air pressure.

6. Catalytic Oxidation of Ferulic Acid

This section will present the findings of the aerobic oxidation of 3-(4-hydroxy-3methoxy-phenyl) propenoic acid (ferulic acid), another lignin-derived building block, over Au/TiO₂. Ferulic acid has the same functional groups as vanillic acid, but the carboxylic acid group is sterically separated from the aromatic ring by a C=C unit (Figure 6-1).

6.1 Introduction



Figure 6-1: Molecular structures of ferulic acid (left) and vanillic acid (right)

Ferulic acid (FA) is a naturally occurring chemical that is found in plants and has antioxidant properties. It can be found in the form of a crystalline powder that has a molecular formula of $C_{10}H_{10}O_4$, and molecular weight of 194 g mol⁻¹. FA is one of the major non-core lignin monomers that is used as a precursor to synthesise other aromatic compounds [227, 228].

Some plants and grasses such as corn contain an abundance of FA [227, 228, 233], which has led to increasing attention towards investigating FA behaviour and reactions [234]. Some studies suggest that FA might represent a platform for producing value added chemicals such as diols or ketones, similar to other carboxylic acids [26, 235].

As an important precursor for vanillin, a widely used food flavouring, the reactions of FA have been studied extensively [236, 237]. Researchers have studied different reaction

pathways for the oxidation of FA. During enzymatic oxidation with laccase, FA goes through three intermediate radical product isomers, which results in the formation of two major products with dimeric structures. The chemical oxidation of FA has been studied with Fenton's reagent and ozonation. They lead to the formation of vanillin and vanillic acid, respectively, with an oxalic acid intermediate. The electrochemical oxidation of FA was studied by cyclic voltammetry using carbon and gold electrodes. A one electron transfer occurs, which is followed by irreversible coupling of two phenoxy radicals [238].

In 2007, Bhargava et al. studied the effect of a heterogeneous copper catalyst on ferulic acid, and found that under severe conditions, FA completely degraded as a result of a combination of decarboxylation and oxidation over the catalyst [82].

6.2 Experiment

The transformation reaction of FA over supported gold catalyst was assessed using the same reaction conditions employed for other lignin-derived compounds in this study (see chapters 4 and 5). Control experiments were carried out to ensure FA reactivity was associated with the Au/TiO₂ catalyst. The transformation reaction was performed with a 3 mM solution of FA and 1% Au/TiO₂ in a reactant:Au ratio of 20:1.

6.2.1 Control experiment

Control experiments were performed according to the procedure described in section 2.2.2, in order to determine the effect of each parameter on the reaction progression of ferulic acid oxidation.

Thermally Induced Non-Catalytic Reaction

The aqueous FA solution was heated at 70°C for 24 hours to determine the effect of this temperature on the solution, and whether FA would evaporate, or be turned into another compound by simply heating it with no added catalyst.

The UV-visible spectra of samples taken during the course of the experiment show that FA remained unchanged throughout the time it was heated (Figure 6-2). This suggests that heating FA at 70°C does not have any effects on the molecular structure.



Figure 6-2: UV-visible spectra of ferulic acid solution heated at 70°C with no added catalyst

Effect of HAuCl₄ Solutions on FA

This experiment was performed to eliminate any uncertainties regarding whether FA ionic Au (III) that may leach from a heterogeneous catalyst. HAuCl₄ solution was added to the FA solution to result in a 20:1 reactant:Au ratio. The solution was heated for 24 h under 70°C and continuous air supply. The results in Figure 6-3 suggest that FA does not react in the presence of Au³⁺ ions.



Figure 6-3: UV-visible spectra of ferulic acid heated at 70°C in the presence of gold in the form of a solution

6.2.2 Reaction profiles

The transformation reaction of FA over gold catalyst was assessed by adding 440 mg of 1% Au/TiO₂ to a 3 mM solution of FA. The reaction was performed in the open reaction system at atmospheric pressure and 70°C. Air was supplied at a rate of 1 ml min⁻¹.

FA has a UV-vis absorbance maximum at 321 nm and a shoulder at 278 nm (Figure 6-4), and shows a reduction in FA absorbance as the reaction progressed, which indicates that FA is consumed in the reaction. Moreover, a different signal with maximum absorbance of 200 nm becomes evident as the reaction progresses. After 48 h of reaction the formation of a product as a result of the FA reaction over Au/TiO₂ is clear.



Figure 6-4: UV-visible spectra of ferulic acid catalytic oxidation over 1%Au/TiO2

Analysing the reaction solution using HPLC revealed the separation of two compounds, one of which had a retention time that corresponded to that of the FA reference solution at 5.45 minutes, and a new product forming that eluted after 5.91 minutes. After 24 hours of reaction, another compound eluted at 3.2 minutes (Figure 6-5).



Figure 6-5: HPLC chromatogram of the FA reaction progression

By following the reaction progression by HPLC and plotting the relative intensity of the two signals, it was found that FA was converted to just 20% at the ambient conditions employed (Figure 6-6).



Figure 6-6: Reaction progression of ferulic acid catalytic oxidation over 1%Au/TiO2 monitored via HPLC

It should be noted that the lack of Isosbestic point could be attributed to spectral deficiencies and evaporation and possible formation of bi products.

Attempts were made to identify the structure of the product using GC-MS, ¹H NMR, and FT-MS. Analysis by GC-MS showed that a compound with the molecular weight of 152 g mol⁻¹ and formula of C₈H₈O₃ was present in the reaction mixture, in addition to the original FA (196 g mol⁻¹) (Figure 6-7). The mass spectrum of this product matches that of vanillin (4-Hydroxy-3-methoxybenzaldehyde), which is a known decarboxylation product of ferulic acid (Figure 6-8) [239-243].



Figure 6-7: GC-MS chromatogram and mass spectrum of the product of ferulic acid oxidation over <u>Au/TiO2</u>



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 6-8: Reference UV-Vis spectrum of vanillin

Further testing with FT-MS enabled the identification of a compound with the molecular weight of 152 g mol⁻¹ that matches the molecular weight of vanillin identified by GC-MS. Mass analysis of the reaction solution after 24 of reaction over Au/TiO₂ showed another signal from a compound with a molecular weight of 150 g mol⁻¹ (Figure 6-9). A well-known reaction of FA is the oxidation to form vanillin (C₈H₈O₃), which has a molecular weight of 152 g mol⁻¹, through the formation of 4-vinyl guaiacol (C₉H₁₀O₂ - 150 g mol⁻¹) as an intermediate.



Figure 6-9: LC-MS chromatogram of ferulic acid oxidation products - MS by positive electrospray

Proton NMR analysis was performed to confirm the structure of the transformation product of FA. FA was analysed in MeOD (Figure 6-10); the ¹H NMR spectrum indicated a methoxyl group at ppm 3.88 (s, 3 H), aromatic protons at 7.28 (d, J= 2.1 Hz 1 H), 6.84 (d, J= 8.3 Hz, 1 H) and 7.11 (dd, J= 8.3, 2.1 Hz, 1H), and the olefinic protons 6.35 (d, J= 15.6 Hz, 1 H) 7.58 (d, J= 15.6 Hz, 1 H). The ¹H NMR spectra of the reaction mixture indicated chemical shifts expected for vanillin, for which an aldehydic proton appears around 9.8 ppm (s, 1 H), alongside a methoxy group (s, 3 H) at 3.9 ppm, and aromatic protons at 7.43 ppm and 7.45 (d, 1 H), and 7 ppm (d, 1H) (Figure 6-11) [244].



Figure 6-10: ¹H NMR spectra of the progression of ferulic acid oxidation reaction over Au/TiO₂



Figure 6-11: ¹H proton signal assignment

The NMR data may indicate the presence of vanillin in the reaction solution, but it needs to be kept in mind that the signals of ¹H NMR spectrum of 4-vinylguaiacol arise almost in the same range of that of vanillin and ferulic acid. These signals arise as follows:

6.8 (d, 1 H), 6.89 (d, 1 H), 7.6 (s, 1 H), 6.6 (dd, 1 H), 5.6 (d, 1H), 5.3 (d, 1H), 3.91 (s, 3 H), 4-vinyle guaiacol at 6.63 (dd, J=10.7, 17.8, 1 H), 5.61 (s, 1 H), 6.88 (m, 3 H), 5.88 (d, J=17.8 Hz, 1H), 5.12 (d, J=10.7 Hz, 1H), 3.91 (s, 3 H) [241, 245].

The presence of 4-vinylguaiacol as an intermediate was confirmed by a very weak ¹H NMR signal at ~6.60 ppm (1H, dd, -CH=CH) observed after 2 hours of FA reaction over Au/TiO₂ and disappeared after 8 hours of reaction (Figure 6-12).



Figure 6-12: ¹H NMR spectra during FA oxidation over Au/TiO₂, showing vinylguaiacol signals at 6.3 ppm

It could be concluded that ferulic acid is decarboxilated to 4-vinylguaiacol, which is converted immediately to vanillin through further oxidation. This is a well-known mechanism of ferulic acid microbial metabolism to form vanillic acid through the same reaction steps [241].

6.3 Discussion

Ferulic acid continues the pattern of aerobic oxidation reactivity set up by the studies of aqueous syringic acid (chapter 4) and vanillic acid (chapter 5) solutions. As in these two systems, decarboxylation is the first step of the aerobic oxidation process in the presence of a heterogeneous Au/TiO₂ catalyst. As such, the results show that the oxidation of ferulic acid over Au/TiO₂ leads initially to the formation of 4-vinyl guaiacol, which then reacts further to form vanillin (Scheme 6-13). A plausible mechanistic scenario is that FA undergoes a non-oxidative decarboxylation to form 4-vinyl guaiacol, which is then converted to vanillin through further oxidation [144]. This reaction mimics the sequence of events in microbial metabolic processing of FA, for which 99% pure 4-vinylguaiacol and vanillin could be isolated after 4 hours of incubation [241]:



Ferulic acid

Scheme 6-13: Proposed mechanism for the oxidation reaction of ferulic acid over Au/TiO₂

6.4 Conclusions

Just like syringic and vanillic acid, ferulic acid undergoes an aerobic catalytic transformation in the presence of Au/TiO_2 catalyst under near-ambient reaction conditions. It is decarboxylated to produce 4-vinylguaiacol, which undergoes further oxidation to form vanillin. The conversion achieved after 72 h was 20%, which is lower than for SA and VA, indicating that activation of the carboxylic acid group bound to the vinyl group is more difficult than that for the carboxylic acid group in the benzoic acid derivatives.

7. Catalytic oxidation of Guaiacol

7.1 Introduction

Guaiacol (2-methoxyphenol, Figure 7-1) represents the fundamental structural motif common to all three previously examined lignin-derived carboxylic acid compounds (syringic, vanillic and ferulic acid) in this thesis. Guaiacol itself is one of the structurally most simple lignin-derived building block, representing one of the most abundant products of lignin degradation, with yields depending on the plant species [246, 247].

Guaiacol is a yellowish oil at room temperature. It has the molecular formula $C_7H_8O_2$ and molecular weight of 124 g mol⁻¹. It has a boiling point of 205°C and a vapour pressure of 0.08 mbar at 25°C. It contributes to flavours and is used as a precursor for other flavouring agents such as eugenol and vanillin. Guaiacol is used in pharmaceutical synthesis [248, 249] and as an indicator of oxygen production in chemical reactions [250-253]



Figure 7-1: Molecular structure of guaiacol

Various studies were conducted on the degradation and transformation of guaiacol as a model aromatic compound of lignin. Two of the most important reactions of guaiacol and other methoxy-substituted compounds are radical rearrangement of the methoxy group, and the cleavage of the O–CH₃ bond to form methyl radicals [254].

Guaiacol oxidation has been the subject of many studies, mostly examining reactions with peroxides [51, 53, 54, 221, 247, 254-257]. In recent studies, the conversion of guaiacol over supported metal catalysts has been assessed [3, 52-55]. Pt/Al₂O₃ catalyst and zeolite were used for the conversion, which resulted in the cleavage of C-O bonds, and methyl group transfer. The reactions produced various products in different yields, with catechol, phenol, and dimethoxybenzene being the major products. However, this

work did not include oxidation reactions, and utilised relatively high temperatures and H_2 as a reactant, which both increase the cost of the process.

This section will describe the transformation of guaiacol as one of the major lignin decomposition products over the supported gold catalyst prepared and tested as outlined in chapter 3.

7.2 Experiment

The guaiacol transformation reaction over 1% Au/TiO₂ was assessed using a guaiacol:Au ratio of 20:1, according to the experimental procedure described in section 2.2.2.

7.3 Results

7.3.1 Control experiments

Heating of guaiacol solutions

UV-Visible monitoring (Figure 7-2) revealed a significant loss of guaiacol when the solution was heated at 70°C under continuous air flow at atmospheric pressure in the open reaction system, but HPLC analysis of these solutions showed no evidence of the presence of any other compound besides the original reactant. This result suggests that heating guaiacol at 70°C under air flow led to its evaporation.

Indeed, guaiacol has a vapour pressure of 0.08 mbar at 25°C and it boils at 205°C. It appears that the vapour pressure of guaiacol at 70°C is sufficient to permit its evaporation at a significant rate.

Subsequent experiments adding a cooling condenser to the outlet stream of the reactor during catalytic oxidative transformation (see section 7.3.2 below) confirmed further that unreacted guaiacol was removed from the system by evaporation.



Figure 7-2: UV-visible spectra of guaiacol solution heated at 70°C with no added catalyst

Reaction in the presence of TiO_2

Figure 7-3 shows the UV-visible absorption of guaiacol solution heated in the presence of gold-free TiO_2 under the reaction conditions. The results suggest that guaiacol is removed from the solution by evaporation at approximately the same rate as for its pure aqueous solution, in the absence of any catalyst. No evidence of the formation of a product was observed.



Figure 7-3: UV-visible spectra of guaiacol solution heated with unloaded TiO2

Effect of ionic Au in solution

HAuCl₄ solution was added to the guaiacol solution to provide a source of Au^{3+} . The solution was heated for 24 h at 70°C and under air flow at atmospheric pressure. Again, concentration of guaiacol was found to decrease, but as a result of evaporation, as no products were detected in the liquid phase (Figure 7-4).



Figure 7-4: UV-visible spectra of guaiacol solution heated in the presence of Au in the form of HAuCl₄

7.3.2 Reactions

The observed evaporative losses of guaiacol in an open system make the determination of reactions rates difficult, as any chemical process competes with the physical evaporation process. Therefore, only a qualitative analysis of reactivity in the open system at atmospheric pressure was conducted.

Guaiacol reaction over 1% Au/TiO₂

Reaction conditions similar to those used for other lignin-derived compounds were employed for the catalytic transformation of guaiacol over the supported Au/TiO_2 catalyst. A guaiacol:Au ratio of 20:1 was employed, while the temperature was 70°C and continuous air flow was maintained at atmospheric pressure.



Figure 7-5: UV-visible spectra of the oxidation reaction of guaiacol over 1% Au/TiO2

UV-vis analysis indicates a faster removal of guaiacol as compared to the system with no catalyst (Figure 7-5). It was also observed that the colourless guaiacol solution had assumed a deep amber colour already after 3 h of reaction (Figure 7-6). The presence of the coloured product allowed the reaction to be followed using the visible range of the electromagnetic spectrum. For this, samples could not be prepared using the usual dilution factor of 100 used for UV-vis sampling elsewhere in this dissertation, as the change in the visible absorbance became undetectable with this dilution. Instead, samples without dilution were analysed. This resulted in saturating the detector in the range of 190-290 nm, but led to the detection of the product signal at 390- 490 nm range, which was undetectable when samples were diluted.

It needs to be mentioned that it was also observed that the amber colour faded slowly over a period of a few hours. Even amber-coloured material stored at refrigerator temperatures around 3-5°C lost the colour and turned back to colourless within 24 hours. This indicates that the resulting amber-colour material converts into another product.



Figure 7-6: Original guaiacol solution and after reaction, showing amber-coloured product



Figure 7-7: UV-visible spectra of the oxidation reaction of guaiacol over 1% Au/TiO₂ - using non-diluted samples

This is illustrated best by following the absorbance at 470 nm in the visible range, which initially increased as the reaction progressed (Figure 7-7). The inset in Figure 7-7 as well as Figure 7-8 shows that the maximum absorbance was observed after 7 hours of reaction. Subsequently, the colour of the mixture, and therefore the absorbance signal of the product were found to decrease and fade over 24 hours. The grey dashed lines in Figure 7-8 represent the reduction in the absorbance of the product, which corresponded to the observed decline in the colour intensity of the reaction mixture.



Figure 7-8: UV-visible spectra of the formation/reduction of a product as a result of guaiacol reaction over <u>Au/TiO2</u>

The UV-vis spectrum of the product in Figure 7-9 matches that of tetraguaiacol found in previous studies (Figure 7-9, A [255], B [258]).



Figure 7-9: Reference UV-visible spectrum of tetraguaiacol as a result of guaiacol oxidation using H₂O₂ and peroxidase, with figure B showing the change of the reaction solution as a result of tetraguacol formation

Various previous studies of guaiacol transformations have shown that guaiacol oxidation using peroxidase in the presence of H_2O_2 results in an amber coloured product, tetraguaiacol, which gives the distinctive UV–vis absorption at 470 nm [136, 221, 255, 256, 259, 260]. The reaction can be summarised as follows:


Scheme 7-10: Guaiacol oxidation using H2O2 to form tetraguaiacol

In fact, a common colorimetric assay of guaiacol is based on this formation of tetraguaiacol by peroxidases in the presence of H_2O_2 [255, 256].

Samples of the reaction mixture were analysed using HLPC and GC-MS. However, due to the time between sampling and analysing samples, degradation of the samples had occurred, so no meaningful results could be obtained.



Figure 7-11: GC-MS chromatogram of guaiacol oxidation over Au/TiO₂ after 3 hours of reaction compared to the chromatogram of guaiacol solution

To assess the evaporation rate and to collect any products carried away in the gas phase, a distillation column was attached to the reaction system. The distillation column was connected to a condenser to collect and analyse the condensate streams. The reaction was performed using the same reaction parameters used for the oxidation of guaiacol in the open reaction system. The collected condensate was analysed using UV-visible spectroscopy and GC-MS. It was found that only guaiacol, the original reactant, existed in the condensate stream (Figure 7-12). This implies that the catalytic transformation of guaiacol over Au/TiO_2 does not lead to any condensable products removed through the gas phase. Moreover, condensing and collecting guaiacol is further evidence for purely evaporative guaiacol losses, as discussed earlier in section 7.3.1.



Figure 7-12: UV-visible spectra of the condensate stream resulting from guaiacol oxidation over Au/TiO2

Reaction with H₂O₂

As discussed in previous chapters, it seems likely that the formation of OH radicals or possibly H_2O_2 by O_2 activation on the Au/TiO₂ catalyst may be responsible for any oxidative transformations of the organic substrate. It was examined whether simply adding H_2O_2 to the guaiacol solution would result in the formation of oxidation products. It was found that the presence of H_2O_2 alone does not result in the formation of the coloured product. It appears that the Au/TiO₂ catalyst assumes the role of the peroxidase in the above mentioned colorimetric assay based on the detection of tetraguaiacol. Indeed, a previous study showed that metals are able to catalyse the oxidation of guaiacol to tetraguaiacol in the presence of H_2O_2 [261]. The experimental procedure described in section 4.3.3 for H_2O_2 detection in syringic acid oxidation was used to detect potential peroxide formation. Samples were treated and analysed using UV-Visible spectroscopy. No evidence was found for the formation of free H_2O_2 during guaiacol oxidation over Au/TiO₂ (Figure 7-13). A possible explanation would be that H_2O_2 was formed and consumed instantly in the oxidation process of guaiacol, and that the amounts of H_2O_2 produced were below detection limits.



Figure 7-13: UV-visible spectra of guaiacol reaction with H2O2

Another experiment was performed in order to understand the possible role of potentially produced H_2O_2 on the reaction in the presence of the active gold catalyst. H_2O_2 was added to the guaiacol in the presence of the gold catalyst. H_2O_2 was added to the guaiacol in the presence of the gold catalyst. H_2O_2 was added to the guaiacol solution in a ratio of 1:1 H_2O_2 to guaiacol, while employing a 20:1 guaiacol to Au catalyst ratio. It was found that the reaction rate increased significantly when H_2O_2 was added to the reaction mixture, compared to the reaction in the presence of the gold catalyst alone.



Figure 7-14: UV-vis spectra of guaiacol oxidation solution over AulTiO₂ in the presence of H₂O₂

Furthermore, one experiment was performed where H_2O_2 was added to guaiacol in the presence of unloaded TiO₂ in order to determine the role of the catalyst in the reaction, and whether the reaction is initiated by TiO₂ to produce H_2O_2 .



Figure 7-15: UV-vis spectra of guaiacol oxidation solution over unloaded TiO2 in the presence of H2O2

Figure 7-16 shows that the maximum UV-Vis absorbance of the reaction solution of three experiments: Guaiacol oxidation over Au/TiO₂, Guaiacol oxidation over Au/TiO₂ in the presence of an equal amount of H_2O_2 , and guaiacol reaction in the presence of unloaded TiO₂ and equal amount of H_2O_2 . The figure shows that the absorbance of the product (tetraguaiacol) at 470 nm doubled after 3 hours of reaction when H_2O_2 is added to the solution in the presence of active catalyst. The red trace shows that when unloaded TiO₂ is added to the solution, no reaction of guaiacol occurs in the absence of gold.



Figure 7-16: Maximum UV-Vis absorbance of guaiacol reaction solution with different catalyzing agents

Role of O_2 in the catalytic reaction of guaiacol

Having established that H_2O_2 formation is unlikely to be responsible for the production of tetraguaiacol leaves the presence of OH or peroxo radicals as a result of O_2 activation over Au/TiO₂ as the most likely mechanistic scenario.

To ascertain the active role of O_2 in the reaction, the guaiacol solution was examined using N_2 flow, first purging the aqueous solution of O_2 by flowing N_2 before the addition of the catalyst, and then keeping the mixture under N_2 throughout the reaction. UVvisible spectra of the reaction progression in Figure 7-17 show a decrease in guaiacol concentration in line with the evaporative losses described above, but no evidence for tetraguaiacol formation was detected. The absence of reaction implies that O_2 is vital for the oxidation of guaiacol to tetraguaiacol.



Figure 7-17: UV-visible of guaiacol reaction over Au/TiO2 in the absence of O2

7.4 Discussion

The results of this study suggest that the combination of air flow and a heterogeneous 1% Au/TiO₂ catalyst achieves the oxidative transformation into tetraguaiacol (Scheme 7-18) under mild and purely aerobic conditions, mimicking the well-known peroxidase-catalysed transformation of guaiacol through a non-biochemical pathway. With similarly high selectivity as the biochemical oxidation of guaiacol to tetraguaiacol [262].



Scheme 7-18: Mechanism of guaiacol oxidation to tetraguaiacol

It is currently not possible to decide whether the formation of tetraguaiacol is caused by forming a peroxide intermediate compound (including H_2O_2) by the Au catalyst, or

whether reactive species such as OH radicals are involved. It can be then assumed that the reaction mechanism of guaiacol oxidation into tetraguaiacol might involve the production of very low, undetectable concentrations of H_2O_2 as a result of O_2 activation. A possible explanation could be that O_2 is activated on the surface of Au, where it binds with water to form a peroxide molecule. The peroxide molecule then reacts with guaiacol as a donor molecule oxidising guaiacol and forming a peroxide bond between guaiacol units.

Alternatively, more recent studies of the biochemical system determined that the reaction product tetraguaiacol is actually a dimer of guaiacol, 3,3'-dimethoxy-4,4'-dihydoxybiphenyl (DHBP). DHBP, which is a biphenyl compound, is formed by a radical mechanism. It is further oxidised to the corresponding biphenoquinone, i.e., 3,3'-dimethoxy-4,4'-biphenoquinone (DBPQ), which is responsible for the absorption at 470 nm [255, 257, 262]. It may be the case that this pathway accounts for the reaction catalysed by Au/TiO₂ – a plausible mechanistic sequence is shown in

Scheme 7-19. The reaction of guaiacol then might involve the activation of the reactants on the surface of the Au particles, where guaiacol functions as a hydrogen donor (where guaiacol loses H and changes colour). It is thought that H_2O_2 is produced and acts as a hydrogen acceptor, whereby two guaiacol molecules bind to form the hydroxybiphenyl, which is oxidised into dimethoxybiphenoquinone [262]. Tetraguaiacol is thought to degrade rapidly as the coloration of the solution faded out as reported by many studies. However, no information on the degradation products was found.



Scheme 7-19: Proposed mechanism for the formation of 3,3'-dimethoxy-4,4'-dihydoxybiphenyl as an oxidation product of guaiacol over Au/TiO₂

The overall oxidation of guaiacol in the presence of H_2O_2 to produce tetraguaiacol in the form of 3,3'-dimethoxy-4,4'-biphenoquinone (Figure 7-20) could then be represented by equation 7-1:

2 guaiacol + 2
$$H_2O_2 \rightarrow$$
 tetraguaiacol + 4 H_2O (7-1)



Figure 7-20: molecular structure of dimethoxy dihydroxy biphenyl (tetraguaiacol)

7.5 Conclusions

In conclusion, the oxidation reaction of guaiacol over supported gold catalyst was assessed under ambient conditions. Guaiacol was found to evaporate under the planned experimental temperature, which made quantifying the reaction and measuring the conversion rate difficult. Moreover, the transformation product was found to decompose rapidly, which added to the difficulty of any attempt to monitor the reaction quantitatively.

Guaiacol was found to form an amber-coloured product as a result of the reaction over Au/TiO_2 in the presence of O_2 . The resulting product had a prominent UV-visible signal at 470 nm, which is distinct to tetraguaiacol. The oxidation of guaiacol to form tetraguaiacol is a well-known reaction that is catalysed by peroxidase in a biochemical transformation. As have been found by numerous studies, the amber colour fades out after few hours of reaction indicating the degradation of produced tetraguaiacol. No references have been found on the resulting degradation material, nor could it be identified experimentally.

The formation of tetraguaiacol from guaiacol requires H_2O_2 in order to form the intermolecular linkage. When H_2O_2 solution was added to guaiacol in the absence of a catalyst, no reaction was detected, and no change in the colour of the solution indicating formation of an oxidation product was observed. This might confirm the role of the supported gold catalyst in activating reactants to form tetraguaiacol. However, there was no evidence of the formation of H_2O_2 during the oxidation reaction of guaiacol, although the actual formation of a product that contains the peroxide link might be a sufficient proof of the formation of H_2O_2 , which is probably consumed at the same rate at which it is produced.

An alternative to the direct H_2O_2 -mediated oxidation to tetraguaiacol is radical reaction of guaiacol to form 3,3'-dimethoxy-4,4'-biphenoquinone involving peroxide to form the intermolecular peroxide links between the guaiacol units. Peroxide may have formed from O_2 as an intermediate with low concentration in the reaction. What is clear is that oxygen is essential for the reaction to occur, so any reaction mechanism will involve O_2 activation over Au. A possible mechanism is that O_2 is activated on the surface of Au, where it binds with water to form a peroxide molecule. The peroxide molecule then reacts with guaiacol to remove CO_2 and form a peroxide bond between guaiacol units.

8. Catalytic Oxidation of Eugenol

This section discusses the catalytic transformation of eugenol, another lignin-derived compound without carboxylic acid functionality, over supported gold catalyst. Experimental data and the proposed reaction mechanisms will be presented.

8.1 Introduction

Eugenol (4-allyl-2-methyoxyphenol, Figure 8-1) is a natural material that exists in many plants and plant products such as clove oil, nutmeg, cinnamon, and bay leaf. Eugenol is colourless oil used as flavouring agent in cosmetic and food products. It is also widely used in dentistry as a cement material with zinc oxide or as a sedative agent. Eugenol has the formula $C_{10}H_{12}O_2$ and molecular weight of 164 g mol⁻¹.



Figure 8-1: Molecular formula of eugenol

Eugenol is one of the lignin degradation products that are found in the volatile fraction of lignocellulosic bio-oils at different yields, depending on the plant species from which lignin is derived. It can represent up to 80–90% of the composition of cloves [263]. Several recent investigations have shown that among substituted lignin-derived compounds, eugenol has great potential for catalytic conversion into useful fuel components and chemicals [3, 4, 50, 51, 53, 55, 56, 264].

Eugenol was included in this study because it has several key functional groups that link it to lignin, while having a structural relationship to guaiacol as well as ferulic, vanillic and syringic acid. What sets eugenol apart from these is the lack of carboxylic acid functionality, and the presence of the alkenyl group without

The catalytic conversion of eugenol has been studied in the presence of solid acid (zeolite) as well as supported metals catalysts (Pt/C-Al₂O₃) [2]. The catalytic conversion of eugenol catalysed by zeolite produced guaiacol and two isomers of isoeugenol through deallylation and isomerisation, respectively. Pt/C-Al₂O₃ was found to be highly active for hydrogenation reactions, leading to substantial formation of 4-propylguaiacol. These results highlight the effect of an alkenyl substituent on the catalytic conversion of lignin-derived compounds, and complement data reported for other lignin-derived compounds [2]. The oxidation of eugenol has been assessed extensively from a bio-chemical point of view because of its applications in food and dentistry [265-269]. Eugenol is known to be metabolised by enzymes to a quinone methide intermediate [267, 270]. There does not seem to be any previous work examining the catalytic oxidation of eugenol.

8.2 Experiment

8.2.1 Control experiments

As for the compounds studied in previous chapters, the first control was heating aqueous eugenol solution in the absence of any catalyst but under otherwise identical conditions as for the catalytic oxidative reaction. Aqueous eugenol solution with 3 mM concentration was heated at 70°C for 24 hours. Monitoring the UV-vis absorbance of the solution for 24 hours revealed that in the absence of any added catalyst, the absorbance of the solution decreased over time, but no products are identifiable in the UV-vis spectra (Figure 8-2). This indicates that eugenol, like guaiacol, does not undergo any transformation, but evaporates when the solution is heated.



Figure 8-2: UV-visible of eugenol solution heated at 70°C with no added catalyst

Similarly, the analysis of heating eugenol solution in the presence of un-loaded TiO_2 , and un-supported Au resulted in the same observation on eugenol evaporation. These results suggest that any reaction detectable in the presence of Au/TiO₂ would be a result of a catalytic reaction rather than a stoichiometric reaction with Au or TiO₂.

8.2.2 Aerobic Oxidation in the Presence of Au/TiO₂

The conversion reaction of eugenol was performed in the presence of 1%Au/TiO₂ with a reactant to Au ratio of 20:1. The reaction was carried out under atmospheric pressure and a temperature of 70°C and continuous air flow.

Under these conditions the solution was observed to change colour, from colourless to light yellow, suggesting the formation of a reaction product. Monitoring the reaction via UV-visible spectroscopy revealed the formation of a product with absorption maximum at 350 nm, in addition to the eugenol has absorption peaks at 210, 226 and 282 nm (Figure 8-3). Many previous studies have suggested that an oxidative conversion of eugenol results in the formation of quinone methide, which has a characteristic absorbance maximum at around 350 nm [267, 271-273].



Figure 8-3: UV-visible spectra of the oxidation reaction of eugenol over 1%Au/TiO2

It was observed that the colour intensity of the reaction mixture started fading after 24 h of reaction. Figure 8-4 shows that the absorbance of the reaction product at 350 nm reached its maximum at 24 h of reaction, before it started to decrease at 27 hours of reaction.



Figure 8-4: UV-visible of the progression of eugenol reaction showing reduction in the product absorption after 27 hours of reaction over Au/TiO₂

Further analysis via HPLC showed the formation of peak at 5.4 and 5.9 minutes in addition to the original eugenol retention time at 7.21 minutes (Figure 8-5). However, quantifying the conversion reaction of eugenol would be complex due to its evaporation at the reaction temperature.



Figure 8-5: HPLC chromatogram of reaction solution of eugenol after 24 hours of reaction over Au/TiO2

Because evaporation of eugenol takes place at the same time as the reaction only an estimate of the actual reaction rate can be provided using HPLC analysis. Figure 8-6 shows the apparent conversion that includes the effect of eugenol evaporation. The results show that almost 70% of the eugenol has been converted after 24 h of reaction over Au/TiO₂.



Figure 8-6: Reaction progression of eugenol oxidation over Au/TiO2 indicated by HPLC signal intensity

LC-MS analysis of the reaction mixture after 4 hours of reaction gave results that were consistent with the formation of eugenol quinone methide (EQM), which has the formula $C_{10}H_{10}O_2$ and the molecular weight of 162 g mol⁻¹, as the oxidation product (Figure 8-7).



Figure 8-7: Mass spectra EQM by LC-MS, a product of eugenol oxidation

However, although HPLC analysis of the reaction mixture indicated the presence of two peaks in addition to eugenol (Figure 8-5), other analytical techniques including GC-MS, NMR failed to identify any products as a result of the reaction of eugenol over Au/TiO₂.

8.3 Discussion

Eugenol was studied as an important natural fine chemical that is also a model compound for lignin-derived building blocks. The variety of functional groups on eugenol links it to coniferyl alcohol, which is one of the main subunits of lignin; therefore, identifying the possible reactions of eugenol is of relevance.

It was observed that eugenol evaporated at 70°C with a significant rate, although it has a boiling point of 254°C. The fast evaporation rate could be explained by the fact eugenol and water are almost immiscible, so the free energy of mixing is expected to be low [274]. As a result, the eugenol vapour pressure over the solution is probably close to that of its pure form resulting in rapid removal relative to the much larger volume of water.

Eugenol has a similar structure to guaiacol, with an allyl substitution in the para position, and like guaiacol, eugenol in known to be oxidised by peroxidase in the presence of H_2O_2 , resulting in the formation of a quinone methide [267, 269, 275, 276]. Quinone methide (EQM) is a known intermediate of eugenol metabolism by different enzymes [267, 270], and has been found to react rapidly to form an insoluble complex polymeric material. The stoichiometry of the disappearance of eugenol against H_2O_2 to form the quinone methide was found to be 2:1, which may provide evidence that peroxide could not be detected as a product because it is consumed by the reaction as it is produced [267].

The quinone methide of eugenol (2-methoxy-4-allylidene-2,5-cyclohexadien-1-one) was found to have a half-life of approximately 5 min in water [277], which makes it a difficult task to conduct accurate kinetic analysis. Therefore, strategies to perform rapid analyses will be required to provide an opportunity to evaluate the conversion reaction [270].

Experimental results showed that the transformation reaction of eugenol over Au/TiO_2 leads to the formation of a product with a maximum absorbance at 350 nm, which is consistent with findings in the available literature data of quinone methide. The resulting product was found to disappear from the solution after a few hours of reaction, and this is in line with a previous study that showed that EQM has a short half -life in water of almost 5.8 minutes [268].

The oxidation reaction of eugenol is thought to start with O_2 activation on Au surface to form a reactive oxidant species (OH radicals, peroxo species, possibly even hydrogen peroxide). Eugenol may then be oxidised via a one-electron transfer to form a phenoxyl radical, which can change subsequently into a eugenol quinone methide [265].



Scheme 8-8: Proposed mechanism for eugenol oxidation over Au/TiO2

Generally, quinone methides are known to have high reactivity. The radicals and quinone methide are thought to react to form a complex, insoluble polymeric material [267, 270, 277].

8.4 Conclusion

The catalytic transformation of eugenol over the supported gold catalyst was found to lead to the formation of eugenol quinone methide, mimicking a well-known biochemical pathway. Various previous enzymatic studies found that eugenol quinone methide results from the oxidation of eugenol over different enzymes.

The oxidation mechanism is thought to involve the activation of oxygen over the supported gold catalyst, which subsequently reacts with eugenol to form a phenoxyl radical that results in the production of a yellow intermediate identified as quinone methide. However, due to evaporation of eugenol under the reaction temperature, only an estimated conversion could be presented.

9. Catalytic Oxidation of Anisole and Relevant Non-Lignocellulosic Compounds with Lower Functional Complexity

In addition to evaluating the reaction rates of the lignin pyrolysis products discussed in the previous chapters test experiments were performed on three other compounds. These compounds included one lignin-derived compound, anisole, and two non-lignocellulosic chemicals, are p-hydroxybenzoic acid and dimethoxybenzic acid. These lignin compounds were studied to assess the influence of towards Au/TiO₂ under the reaction conditions due to their structural similarity to the lignin-derived compounds evaluated in this study.

9.1 Anisole

Anisole, also known as methoxybenzene, is an organic compound that has the formula C_7H_8O (Figure 9-1). It exists naturally in the form of a colourless liquid that has the distinctive smell of aniseed. Its derivatives are used as flavourings, and it is also used as a precursor for synthesising other fine chemicals.



Figure 9-1: Molecular structure of Anisole

Conversions of anisole have been studied extensively over the past few years, as it has potential for upgrading into fuel chemicals [58, 278-280]. As a model compound for lignin-derived products its conversion over different catalysts, including Pt and zeolite, has also been investigated [281-283]. Zeolite and metal catalysts were found to lead to demethylation, hydrogenation and acylation, to produce phenol, benzene, and 4-acyl anisole, respectively [284, 285]. Conditions required to achieve these reactions were

temperatures above 200°C, while hydrogenations required high pressures [286] of costly H_2 [3]. The catalytic conversion of anisole over Pt leads to transalkylation and hydrodeoxygenation at 300°C under H_2 flow [3]. The oxidation reaction of anisole was also studied and found to require the presence of a substituted hydrocarbon solvent such as methyl acetate to produce methoxy benzyl acetate [287-291].

It is interesting to study the reaction of anisole under the near-ambient aerobic oxidation conditions because it contains an isolated methoxy group on the aromatic ring, which is a common motif across all lignin building blocks whose aerobic oxidations were described in earlier chapter 3 [58]; in fact, the majority of lignin pyrolysis products are methoxy-substituted [292]. Evaluating the reactivity of anisole was thus expected to provide insight into the role of the methoxy functional group.

9.1.1 Experimental results

As for the compounds discussed in previous chapters, initially a 3 mM solution of anisole with no catalyst or reactant added was heated to 70°C for 24 h in an open reaction system with no added catalyst. Results in Figure 9-2 show the UV-visible absorbance of the solution throughout the period of the experiment. The rapid reduction in the absorbance of anisole suggests that within one h of heating, almost all anisole had evaporated, similar to the observations made for guaiacol (chapter 5).



Figure 9-2:UV-visible spectra of anisole solution heated with no added catalyst

The fast evaporation of anisole was also observed when the reaction was carried out in the presence of Au/TiO_2 at 70°C (Figure 9-3). The remaining concentration of anisole in the solution became quickly too low to provide a meaningful detection of products. It was impossible to establish with the open flow reactor system whether the fast evaporation of anisole resulted in insufficient reactant availability to permit a catalytic reaction to take place, or whether anisole was intrinsically inert.



Figure 9-3: UV-visible spectra of anisole reaction over 1% Au/TiO2 at 70°C

To slow down evaporation of anisole, the reaction in the presence of the gold catalyst was performed at room temperature. This approach was successful in slowing down the evaporation significantly (Figure 9-4), so that the decline of the anisole concentration could be monitored as a function of time over several hours.



Figure 9-4: UV-visible spectra of anisole reaction over 1% Au/TiO2 at room temperature

However, no products were detected by UV-visible spectroscopy, and samples analysed using HPLC confirmed the presence of anisole, but no reaction products as a result of the presence of Au/TiO_2 in the solution (Figure 9-5).



Figure 9-5: HPLC traces of initial anisole solution and the solution after contact with Au/TiO₂ for 4 hours.

It appeared that evaporation was the effect dominating the reduction of the anisole concentration. To confirm this, the oxidation was carried out in the closed reaction system (see section 2.2.1) under higher air pressure (10 bar). Using the closed system eliminated the influence of evaporation and preserved the anisole solution at the initial concentration,

The reaction was carried out at 70°C, employing a anisole:Au ratio of 20:1. The UVvisible absorbance analysis of the reaction solution shows that although evaporation was reduced to a minimum, no significant reduction of the anisole concentration could be detected (Figure 9-6). The absorbance of anisole remained unchanged, and no signs of any formed products were observed. The minimal differences in the spectra can be attributed to detector saturation (in the wavelength range below 225 nm) and some material loss caused by gas phase MS sampling.



Figure 9-6: UV-visible of anisole reaction over Au/TiO2 under high pressure

9.1.2 Discussion

It appears that anisole does not undergo any oxidative transformation, even at high air pressure, in difference to all previously examined reactants. In an open system, anisole rapidly evaporates under air flow at atmospheric pressure and at 70°C. These findings suggest that it is not easy to aerobically oxidise the methoxy group or the benzene ring in the presence of Au/TiO₂. In the reactive transformations reported in earlier chapters, the

methoxy group may play a role through its inductive effect on the aromatic ring, but it does not itself appear to offer a site for oxidative attack or activation of the molecule.

9.2 p-Hydroxybenzoic acid

The influence of the methoxy group is further examined by studying the reactivity of phydroxybenzoic acid (PHBA) solutions under the reaction condition over Au/TiO₂. The reaction of PHBA over the supported gold catalyst was studied because its molecular structure resembles that of syringic and vanillic acid less the methoxy functional group(s) on the aromatic ring.

9.2.1 Overview

PHBA is a phenolic derivative of benzoic acid with the formula ($C_7H_6O_3$), which exists in a white crystalline form. It is found naturally in plants and fungi, and is used as a chemical intermediate for the synthesis of pharmaceuticals, antibacterials, dyes and plasticisers. Its most important use is in the production of parabens, which are widely used preservatives in the cosmetic and pharmaceutical industry (<u>Figure 9-7</u>).



Figure 9-7: Molecular structure of PHBA

9.2.2 Experiment

The reaction of PHBA was studied under the same reaction conditions as for the oxidation of lignin-derived compounds in previous chapters. 3 mM aqueous solution, open reaction system, air flow at atmospheric pressure, T = 70°C and a reactant:Au ratio of 20:1.

Control experiment

As a control, a PHBA solution (3 mM) was heated in the absence of a catalyst, in order to determine the temperature effect on the stability of the aqueous solution. The UV-visible spectra in <u>Figure 9-8</u> show that heating PHBA for 24 hours at 70°C did not lead to any change in the absorbance of the solution, and hence no formation of any products.



Figure 9-8: UV-visible spectra of PHBA heated with no added catalyst

Similar UV-visible results were obtained when the PHBA solution was heated in the presence of Au-free TiO_2 and in a mixture with HAuCl₄ solution. These results indicate that PHBA is not affected by the presence of TiO_2 or free Au in the solution, and that they have no effect on catalysing PHBA transformation under the reaction conditions.

Reaction profile

The reaction of PHBA over 1 %Au/TiO₂ was performed using the reaction conditions established in previous chapters, in the open reaction system under air-flow at atmospheric pressure and with a PHBA:Au ratio of 20:1. UV-vis monitoring of the solution (Figure 9-9) showed that after 24 hours of reaction over the supported gold catalyst, the absorbance of PHBA had declined significantly, although no product was identifiable.



Figure 9-9: UV-visible spectra of PHBA reaction progression over Au/TiO2

Performing the reaction in a closed reactor under elevated pressure (10 bar) revealed an increased consumption of PHBA, but with no products identifiable in the liquid phase via UV-vis detection (Figure 9-10), or in the gas phase by use of a quadrupole mass spectrometer. The loss in PHBA appears to be due to a reaction that forms a product with no significant UV-visible absorption or at such low concentration that it could not be distinguished from the unreacted PHBA.



Figure 9-10: UV-visible spectra of PHBA reaction over Au/TiO₂ under high pressure

HPLC successfully separated two compounds from the reaction mixture, with PHBA eluting with a retention time of 5.3 min and a low-concentration component eluting at 3 min after 24 hours of reaction (Figure 9-11).



Figure 9-11: HPLC chromatogram of the reaction progression of PHBA over Au/TiO2

The reaction samples were analysed by GC-MS in order to identify the resulting product present at a low concentration. The GC chromatogram in <u>Figure 9-12</u> showed a product with a molecular weight of 94 g mol⁻¹, which is consistent with the formation of phenol.



Figure 9-12: GC-MS spectrum of phenol as an oxidation product of PHBA over Au/TiO₂

9.2.3 Discussion

The oxidative transformation of PHBA using 1% Au/TiO₂ catalyst proceeds slowly, leading to a small reduction in PHBA concentration as the reaction progressed (<u>Figure</u>

<u>9-13</u>). GC-MS reveals phenol formation, consistent with the decarboxylation reactions already observed for the other benzoic acid derivatives examined in this dissertation. Closer inspection of the UV-visible data in comparison with an aqueous phenol reference spectrum (<u>Figure 9-13</u>) reveals that weak shoulders in the spectra at ~215 nm and ~272 nm stem from the phenol formed in the reaction.



Figure 9-13: The UV-visible spectrum of the PHBA oxidation reaction over Au/TiO₂ compared to the spectrum of phenol



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 9-14: Reference phenol UV-Vis spectrum

As for previous systems, the observation of PHBA decarboxylation required the presence of oxygen, indicating that Au/TiO₂ plays an important role in O₂ activation. This nonoxidative decarboxylation of PHBA again resembles a well-established enzymatic pathway to phenol [222, 293] as well as a previously reported metal-catalysed reaction [294]. Again, it would seem that the mechanism of this reaction involves a step in which O₂ is activated and bonds with the PHBA molecule and the carboxyl group are broken to produce CO₂ and phenol (<u>Scheme 9-15</u>).



Scheme 9-15: Overall PHBA decarboxylation route

It appears that under the reaction conditions, the carboxyl group is the easiest to be attacked by active oxygen, which results in release of CO_2 and formation of a decarboxylated form of the reactant. The resulting phenols are easily oxidised over an oxidising agent (gold catalyst), as phenol could undergo further oxidative transformation through an electron transfer to form phenoxy radicals. Phenoxy radicals can undergo another electron transfer to complete the oxidation reaction and form benzoquinones, which are important intermediates [295, 296].

9.3 3,5-dimethoxybenzoic acid

The reaction of 3,5-dimethoxybenzoic acid (DMBA) was assessed as part of the experiments performed to further elucidate the effect of functional groups on the aerobic reactions of lignin-derived compounds over supported gold catalyst. DMBA has the formula $C_9H_{10}O_4$, which is similar to the structure of SA without the hydroxyl functional group (Figure 9-16).



Figure 9-16: Molecular structure of DMBA

9.3.1 Experimental results

A 3 mM solution of DMBA with was prepared and used for the reaction in the presence of 1% Au/TiO₂ under the same reaction conditions as the lignin-derived compounds described earlier.

First, the control experiment where DMBA was heated to reaction temperature with no added catalyst was performed. No change to the UV-visible absorbance of DMBA occurred over time (Figure 9-17), indicating the absence of evaporation or reaction.



Figure 9-17: UV-visible spectra of DMBA solution heated at 70°C with no added catalyst

The DMBA solution was then reacted in the presence of 1% Au/TiO₂ under the reaction conditions, and samples analysed using UV-visible spectroscopy. Figure 9-18 shows that the absorption of DMBA decreased slightly as the reaction progressed. This suggests

that DMBA is consumed in a reaction, although no products were identifiable with UVvisible spectroscopy.



Figure 9-18: UV-Visible spectra of DMBA reaction over 1% Au/TiO2

The reaction was monitored using GC-MS, ¹H NMR, and LC-MS, with no evidence of the formation of any reaction products of DMBA over Au/TiO₂.

9.3.2 Discussion

No catalytic conversion of DMBA could be observed under the reaction conditions. Given the pattern of decarboxylation observed for the benzoic acid derivatives examined in previous chapters, it would seem likely that DMBA would be oxidized over the supported gold catalyst to form1,3-dimethoxybenzene (dimethylresorcinol), but this could not be confirmed based on the available data. Further investigation of this reaction would be required in the future.

9.4 Conclusion

Transformation reactions of three compounds have been described. The behaviour of these compounds over gold as a catalyst fits well into the established pattern of reactivity, with decarboxylation observed for the two benzoic acid derivatives. The presence of a phenolic OH appears to stabilise the acid against decarboxylation, while methoxy groups appear to activate the C-C bond to the carboxylic acid group.

Anisole, has only one methoxy substituent attached to the aromatic ring is unreactive, even under elevated air pressure.

PHBA undergoes an oxidative decarboxylation to produce phenol,

Like Anisole, DMBA was unreactive under the reaction conditions, with no identified reaction products. No references were found on the oxidative reactions of DMBA.

10. General discussion and conclusions

Attention towards the chemistry of lignin-derived chemicals is rapidly increasing worldwide, as these chemicals represent an attractive source of renewable resources. The available literature lacks in fundamental information regarding reactions that may convert these compounds inexpensively and effectively into other products. The main aim of this study was to assess whether aqueous solutions of lignin-derived compounds underwent catalytic aerobic oxidations near room temperature, and to establish the main product of these reactions.

The series of syringic acid, vanillic acid, ferulic acid, guaiacol, eugenol, and anisole was examined to establish whether patterns of reactivity could be established as a function of the presence and absence of the phenolic OH group, methoxy group(s) and the carboxylic acid group on the aromatic benzene ring.

One pattern that has emerged from these studies is that all carboxylic acid compounds underwent oxidative decarboxylation. For the benzoic acid derivatives it seems likely that a phenoxy radical is formed in a first step, which is oxidised further to a quinone when a phenolic OH group is present in para position.

Oxidation of SA thus resulted in the formation of 2,6-dimethoxybenzoquinone, which is a reaction with a homogeneous non-catalytic analogue in the system with aqueous $Na_2Cr_2O_7$.

The vanillic acid reaction over Au/TiO_2 led to decarboxylation, forming 2methoxyphenol (guaiacol) as the product. This transformation of VA to guaiacol is an analogue of a known biotransformation and it appears that the aerobic Au/TiO_2 route can be employed to use VA as a source for guaiacol, which itself is a precursor for pharmaceuticals and flavourings on an industrial scale [217, 218, 222-225].

The results of the control experiments excluding O_2 by replacement with an N_2 stream suggest strongly that O_2 is activated on the Au/TiO₂ catalyst and subsequently reacts with the organic substrates. No peroxide was detected, which may be because any peroxide formed is instantly consumed in the reaction, or peroxo species are firmly bound to the catalyst surface, resulting in concentrations of free peroxide in homogenous phase below the detection limit.

Ferulic acid, FA, was found to undergo a transformation over Au/TiO_2 that led to 4-vinyl guaiacol as an intermediate, which in turn converted oxidatively into vanillin. Again, this sequence of reactions is a non-biochemical analogue of an established enzymatic pathway in microbial metabolism of FA [241].

With regard to non-carboxylic models of lignin-derived building blocks, three compounds were studied: guaiacol, eugenol and anisole.

The oxidation of guaiacol over Au/TiO₂ in the presence of O₂ resulted in the formation of a coloured product that was identified as tetraguaiacol. Again, this is a non-biochemical analogue of an enzymatic reaction with H_2O_2 known since the 1950s, The formation of a coloured product as a result of guaiacol oxidation by peroxidase has been used widely in colorimetric assays of the activity of peroxidases [297]. It seems therefore likely that the Au/TiO₂-catalysed oxidation of guaiacol involves the production of H_2O_2 .

A possible mechanism for the formation of tetraguaiacol as a product of guaiacol oxidation is that O₂ is activated on the surface of Au, where it binds with water to form a peroxide molecule. The peroxide molecule then reacts with guaiacol as a donor molecule, oxidizing guaiacol and forming a peroxide bond between guaiacol units. However, tetraguaiacol was recently determined to be a dimer of guaiacol named 3,3'-dimethoxy-4,4'-dihydoxybiphenyl (DHBP). The structure of DHBP likewise presents a plausible mechanism of guaiacol oxidation over Au/TiO₂.

Eugenol has a similar structure to guaiacol, with an allyl substitution in the para position. Somewhat similar to guaiacol, eugenol is known to oxidise enzymatically to quinone methide in the presence of H_2O_2 and peroxidase [267, 269, 275, 276]. Experimental results showed that the transformation of eugenol over Au/TiO₂ leads to the formation of a yellow-coloured product with a maximum absorbance at 350 nm, which is consistent with the available literature data of quinone methide – again confirming that Au/TiO₂ provides access to a non-biochemical and aerobic analogue to a biochemical pathway with H_2O_2 . The resulting product was found to disappear from the solution after few hours of reaction, in line with previous studies suggesting eugenol oxidation reaction
over Au/TiO_2 again seems to involve O_2 activation on the Au catalyst to form, perhaps, a peroxide species for the reaction with eugenol. This is then oxidised via a one-electron transfer to form a phenoxyl radical, which can subsequently change into a eugenol quinone methide [265].

The attempt to oxidatively transform anisole (methoxy phenol) over supported gold catalyst was unsuccessful. Even the utilisation of high pressure did not yield any anisole transformation products. The same observation was found with DMBA (dimethoxybenzoic acid), which was unreactive under the reaction conditions. This underlines the importance of the OH group and carboxylic acid groups in the observed reactions. The experimental data for the non-lignin molecules (chapter 9) confirm this pattern. PHBA underwent oxidative decarboxylation to form phenol.

It can be concluded that the compounds with carboxyl group besides methoxy and hydroxyl groups undergo non-oxidative decarboxylation, resulting in the release of CO_2 and formation of phenolic compounds that can be further oxidised to quinones. Compounds containing only methoxy and hydroxyl groups such as guaiacol and eugenol undergo a one-electron transfer to form phenoxy radicals that form quinones upon further oxidation.

Utilising the same reaction conditions for all compounds, it was found that the highest conversions were achieved with DMBA and the lowest with PHBA, establishing a reactivity pattern as follows:

SA > eugenol > guaiacol > VA > FA > PHBA

Methoxyl groups adjacent to the hydroxyl group, as in vanillic acid and syringic acid, reduced or prevented decarboxylation. Thus, moderate amounts of guaiacol were formed from vanillic acid, but the further decarboxylation to guaiacol did not occur with syringic acid, in which two methoxyl groups are adjacent to the hydroxyl group in the para position [222].

Taken together these results indicate that the methoxy moieties influence reactivity through both their inductive and resonance effects: leaving of the carboxylic acid group appears to be enhanced through the inductive effect, while further oxidation at the phenolic site (in ortho-position) seems to be activated through the resonance effect.

Studies of hydrozybenzoic acids as intermediate metabolites of many aromatic chemicals have shown that these acids react with different rates. Evidence was provided that the methoxy substitution on the aromatic ring of phenolic acids increased the reaction rate. Moreover, longer carboxyl-containing side chains were found to increase the reaction rate as well. A study by Lehmann showed that the chemical reaction to remove phenolic acids representative to lignin from soil using Fe and Mn involved oxidation of the phenolic acids, coupled with a reduction of Fe and Mn oxides. Syringic and ferulic acid were found to have the highest conversion rate over the metal oxides, with conversion of 0-5, 70, 90, and 100% of *p*-hydroxybenzoic, vanillic, ferulic, syringic, respectively [298].

In general, it was found that apart from syringic acid, the lignin-derived compounds assessed in this study are linked to each other through a set of reactions. Figure 10-1 shows the reaction network of the lignin-derived compounds, with solid arrows representing reactions revealed during the present studies over the gold catalyst, and dotted arrows representing reactions of lignin-derived compounds found by other researchers via different routes.

Guaiacol has been found to be converted to anisole via the hydroxydeoxigenation over Pt to anisole [3]. The catalytic oxidation of syringic acid and eugenol led to the formation two quinones: dimethoxybenzoquinone and quinone methide, respectively. Figure 10-1 shows the reaction network of the lignin-derived compounds, with reactions achieved over the prepared Au/TiO₂ catalyst represented by the solid arrows. Dashed arrows represent transformation reactions via other routs accomplished by other researchers.



Figure 10-1: Reactions network

Remarkably, the reaction network of lignin-derived compounds agrees with known biochemical transformation in microorganisms. The resemblance of the catalytic transformation reactions network to the biochemical network might arise because of the mild, almost biological conditions employed in this work (aqueous phase, aerobic environment, ambient pressure, moderate temperatures).

However, reaction rates of lignin-derived chemicals using the supported gold catalyst prepared for this study appears to be slower than similar reactions using other catalysts, such as zeolite or supported Pt on Al_2O_3 [2, 3, 53-55]. Moreover, the inactivity of DMBA in the presence of the supported gold catalyst could not be explained - due to time restrictions, and would require further investigation.

Conclusions

Highly active supported gold on titania catalysts were successfully produced using a modified deposition-precipitation method. The catalysts produced were shown to be active for gas oxidation using the oxidation reaction of CO as an initial test. Excellent

conversion rates were achieved over the prepared catalyst at room temperature. Pretreatment of the catalyst was found to improve its stability, although calcining at 300°C led to a significant growth in particle size. A different pre-treatment strategy that involved washing the catalyst prior to calcinations proved advantageous in improving the catalyst stability and performance for liquid-phase reactions.

Lignin-derived compounds were assessed for their potential catalytic upgrading over supported gold catalyst. Lignin building blocks were selected based on their potentials for catalytic oxidation and for their structural similarity to each other. The compounds studied were syringic acid, vanillic acid, ferulic acid, guaiacol, eugenol, and anisole. The experimental data presented in this report show that the mentioned compounds undergo oxidative transformation over gold, with the exception of anisole, which remained unaffected under the reaction conditions.

The reactions are thought to involve an oxygen activation step to form hydrogen peroxide, which reacts with the lignin-derived molecule to form decarboxylation or oxidation products, based on the functional groups comprising the compound subject to the transformation reaction.

A correlation between the functional groups and reaction rates was proposed. The reaction rate increased as the number of methoxy substituents increased. Moreover, it was found that phenolic acids first undergo decarboxylation reaction, then the reaction proceeds to further oxidation in the phenolic position, resulting in the formation of quinones. This pattern of reaction likely reflects the combined action of the inductive and resonance effects of the methoxy groups.

The compounds studied were found to be connected in a reaction network that has been reported to be achieved through the metabolism of these compounds by microorganisms. Some of these reactions have previously been found to occur with other catalysts, such as Pt and zeolite

Challenges and Future work

There are various lines of further research that could be pursued to provide deeper understanding of the reactions systems and optimise the performance of the discovered reactions.

1. Catalyst stability vs. performance

Although the method used for the catalyst preparation was adequate for producing active catalysts for the gas phase reaction, the prepared catalyst was deactivated in liquid phase reactions. Calcination led to substantial growth in particle size, which reduced catalyst activity. Finally, a pre-treatment method was adopted in which the catalyst was washed under reaction conditions prior to calcination. This method was successful in improving the catalyst stability and maintaining sufficient catalyst performance.

2. Combination with on-line analytical methods

The availability of on-line analytical methods would allow more readily the detection of low concentrations of materials in the reaction solution, which might lead to better identification of by-products or products in low yields. Moreover, online analysis might help confirm the formation of peroxide and intermediates, as an important step in the reaction activation, and help to provide a deeper understanding of reaction mechanisms over the gold catalyst.

3. Catalytic oxidation of non –lignocellulosic compounds

It might worth investigating the reason for the un-reactivity of anisole and DMBA over Au/TiO_2 under the employed reaction conditions. This would probably provide deeper understanding of the reaction mechanisms and the effect of molecular structures and functional groups on the reaction progression and conversion rates.

4. Study reactions of other lignin-derived compounds

Lignin pyrolysis results in a wide array of compounds that are thought to be potential candidates to be upgraded into valuable chemicals. Knowledge in this field is still developing and there is a need to identify possible routes to upgrade lignin-derived compounds using different chemical transformation pathways.

A. CO Oxidation Data

The CO oxidation reaction was used to determine the activity of the gold catalyst prepared using the outlined method. Three batches of catalyst were tested for their activity in the oxidation of CO. A PFR reactor equipped with a quadrupole mass spectrometer was utilised for the analysis.

An amount of 10 mg of catalyst was used for the reaction. The volume of the catalyst bed can be measured based on the typically 15 mm high and 4 mm diameter glass tube. Three batches of catalyst were tested for their activity in oxidising CO at room temperature, and the conversion rate was calculated using the partial pressure of gasses effluent, using the following equation:

Conversion (X) =
$$\frac{\text{Initial pressure-final pressure}}{\text{initial pressure}}$$
 (A-1)

(Maximum value of X is 1 for irreversible reactions).

The number of CO moles converted per minute can be calculated according to the ideal gas law, at 1 atm and 298 K temperature

$$n = \frac{PV}{RT} \tag{A-2}$$

The CO oxidation analyses were performed using a Plug Flow reactor (PFR). Hence, calculations could be done using the PFR general design equation:

$$r_A = \frac{dF_A}{dV} \tag{A-3}$$

Where:

V = Volume of plug flow reactor (m³)

 F_A = Final flow rate of component A (mol s⁻¹)

 r_A = Rate of reaction with respect to component A (mol m⁻³ s⁻¹)

Since the volume of the catalyst bed can be measured (typically 15 mm high in a circular 4 mm diameter glass tube), the equation can be rearranged to obtain the rate of reaction in terms of reactor volume and conversion.

This procedure was repeated with each batch of the catalyst:

$$-r_A = A e^{\frac{-E_A}{RT}} C_A$$

Applying logs:

$$-\ln r_A = \ln[C_A A] - \frac{E_A}{RT}$$

$$\therefore \ln\left(\frac{1}{r_A}\right) = \left(\frac{-E_A}{R}\right)\frac{1}{T} + \ln[C_A A] \tag{A-4}$$

Where:

- A = Pre-exponential factor (for 1st order reaction, units = s⁻¹)
- E_A = Activation energy (J mol⁻¹)
- R =Universal gas constant (J mol⁻¹ K⁻¹)
- T = Temperature (K)
- C_A = Concentration of reactant A (mols)

Equation A-4 can then be used to characterise the catalyst behaviour in the CO oxidation rig where the flow rate of CO (ml s⁻¹), 100 ml s⁻¹ total gases, Inner Pressure of the reactor 1.5×10^{-7} and catalyst bed volume of 0.7543×10^{-6} m³.

Constant K can be calculated using:

$$K = \frac{-r_A}{c_A} \tag{A-5}$$

 $F_{A0} = 0.0817 x \ 10^{-3} \ mol \ min^{-1}$

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 F_{A0} = Initial flow rate of component A (mol s⁻¹)

Applying the PFR general design equation:

$$r_{A} = \frac{-dF_{A0} dX}{dV}$$

$$F_{A} = F_{A0} (1-X)$$

$$dF_{A} = F_{A0} d(1-X)$$

$$dF_{A} = -F_{A0} dX$$

$$KC_{A} = \frac{-FA0 dX}{dV}$$

$$K C_{A0} dV = -F_{A0} dX$$

$$K \int dV = \frac{-FA0}{CA0} \int dX$$

$$K. V = \frac{-FA0}{CA0} \cdot \ln \frac{1}{1-X}$$

$$K = \frac{-FA0}{V.CA0} \cdot \ln \frac{1}{1-X}$$

And
$$r_A = -K CA \pmod{m^{-3} min^{-1}}$$

	1 st Batch	2 nd Batch	3 rd Batch
Conversion (X)	0.35	0.33	0.39
CO concentration (mol m ⁻³)	0.567	0.567	0.567
Reaction rate (mol m ³ s ⁻¹)	0.438	0.4134	0.4885

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Table A-1: Calculated conversion rates for the CO reaction test for different prepared batches of catalyst

Results can be used to calculate the catalyst Turnover Frequency (TOF) as follows:

$$TOF = \frac{CO \text{ converted molecules}}{Catalyst active sites}$$
(A-6)

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In order to determine the TOF of the catalyst, gold active sites were calculated based on a mean diameter of gold nanoparticles.

Catalyst diluted 1:10 with glass beads to a total of 0.1 g

10 mg of catalyst have 0.1 mg of Au

Number of Au moles
$$= \frac{Au \text{ weight}}{Au \text{ atomic weight}}$$
$$= \frac{1 \times 10^{-4} \text{ g}}{196.966}$$
$$= 5.077 \times 10^{-7} \text{ moles of Au}$$

The gold active sites were determined based on a mean diameter of Au particles of 3 nm, assuming that all surface atoms are active. Hence, the circumference of a 3 nm particle divided by the atomic diameter of the Au atom (0.27 nm)

$$= \pi \times 3 \text{ nm}$$

= 9.42 ÷ 0.27
= 34.88 atom

Therefore,

Gold active sites = $5.077 \times 10^{-7} \times 34.88$ (surface atom.mol)

Table 3 suggests that satisfactory turnover frequencies were achieved using different ratios of the prepared gold catalyst at room temperature.

CO flow rate (ml min ⁻¹)	Gold weight (mg)	Gold active sites (surface atom.mol)	Conversion %	Temperature (K)	TOF (s ⁻ ¹)
4	0.1	1.77 ×10 ⁻⁶	47	298	0.15
10	0.1	1.77 ×10 ⁻⁶	45	298	0.17

Table A-2: TOFs of CO oxidation reaction test using reactant flow rates

B. Catalyst ratio for liquid-phase reactions

The ratio of Au: reactant was calculated as follows:

1 g of 1% Au/TiO₂ has 0.99 g of TiO₂ + 0.01g of Au

0.01g of Au:

$$= \frac{0.01}{196.96655}$$

= 5.077×10⁻⁵ mol of Au

For a Au: reactant ratio of 1:20 using 1% Au/TiO₂ with 150 ml of 3 mM of solution:

For a 1:20 ratio

$$= 20 \times 5.077 \times 10^{-5}$$
$$= 1.0154 \times 10^{-3} mol of SA$$

Stock solution 0.003 mol dm⁻³

$$=\frac{1000}{0.003}\times 1.0154\times 10^{-3}$$

= 338.4 ml of solution 0.01M for each gram of catalyst

For 150 ml of SA (3 mM) = $\frac{150}{101.54}$

$$= 0.44 g of 1\% Au/TiO_2 catalyst$$

For an Au ratio using HAuCl₄.3H₂O (50%W/W of Au) in the reaction with the HAuCl₄ solution:

Au needed = $3 \times 5.077 \times 10^{-5} = 1.5 \times 10^{-4} mol = 0.02954 g of Au$

0.02954 g * 2 (for 50%) = 0.05908 g of HAuCl₄.3H₂O

1 g of HAuCl₄.3H₂O is dissolved in 100 ml of water

0.05908 g Au x 100ml = 5.908 ml of HAuCl₄.3H₂O solution

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