SOLVENT FREE BENZYL ALCOHOL OXIDATION BY AuPd/TiO2 CATALYSTS

NORASIDAH BINTI MOHD JAMJAM

FS 2019 78

SOLVENT FREE BENZYL ALCOHOL OXIDATION BY AuPd/TiO_2 CATALYSTS

By

NORASIDAH BINTI MOHD JAMJAM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

September 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

SOLVENT FREE BENZYL ALCOHOL OXIDATION BY AuPd/TiO_2 CATALYSTS

By

NORASIDAH BINTI MOHD JAMJAM

September 2017

Chair : **Mohd Izham Saiman, PhD**
Faculty : **Science**

The development of gold and palladium as heterogeneous catalyst is widely investigated for many oxidation process. In this respect, the main goal of the research is modification of Au-Pd catalyst to achieve highest potential to obtain more benzaldehyde. The monometallic and bimetallic catalysts are synthesized via impregnation and sol-immobalization methods. The physico-chemical properties of the nanoparticle catalysts are characterized by using X-Ray Diffraction (XRD), X-ray Fluorescene (XRF), Brunauer-Emmett-Teller (BET), Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). In addition, the catalytic activity of all synthesized catalysts for the production benzaldehyde by benzyl alcohol with tert-Butyl hydroperoxide (TBHP) as an oxidant and the effect of variables, such as reaction temperature, reaction time, catalyst loading have been evaluated. On the other hand, an examination of the reusability and leaching of gold and palladium into benzyl alcohol is carried out. Among the variables test, the results are discussed with regard to structure activity relationship. The preparation method was shown to be very important in the formation of highly active catalysts. The impregnation method produced catalysts with large Au particles when supported on TiO_2 due to large particle size. Preparation of sol-immobilisation methods produced stable catalysts, highly active density of both metal, highest strength, large surface area and selective for the oxidation benzyl alcohol. According to the extensive modification on the catalyst loading on the Au-Pd, the result revealed that 0.5 wt% Au 0.5 wt% Pd/TiO_2 catalyst prepared by sol-immobilisation methods showed the best catalytic activity in the oxidation of benzyl alcohol at temperature of 80℃ for 4 hours. A synergistic effects of Au-Pd alloys occur on the benzyl alcohol oxidation. It was found that the longer the reaction time, the selectivity of benzaldehyde decrementing and the same was true of highest reaction temperatures (up to 120℃).

A good reusability of the catalysts with leaching of gold into the product has also been obtained. Overall, the oxidation of benzyl alcohol was successfully studied by using

Au-Pd/TiO_2 and the importance of the TBHP as an oxidant is proven in the processes. Moreover, the Au-Pd ratio was the main focus in this study which it is innovated to be a flexible on the current reaction condition with a great performance. These results highlight the advanced of the fundamental understandings of Au-Pd alloys comparing with traditional method in catalyzing benzyl alcohol oxidation.
.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai
memenuhi keperluan untuk ijazah Sarjana Sains

PENGOKSIDAAN BENZIL ALKOHOL MENGGUNAKAN AuPd/TiO_2 PEMANGKIN

Oleh

NORASIDAH BINTI MOHD JAMJAM

September 2017

Pengerusi : Mohd Izham Saiman PhD
Fakulti : Sains

Kini, perkembangan emas dan palladium sebagai medium bagi pemangkinan heterogen di dalam pelbagai proses pengoksidaan telah digunakan secara meluas. Oleh kerana penggunaannya yang menjadi sinonim dalam pemangkin, matlamat kajian perlu dipertingkat dengan pengubahsuaian Au-Pd supaya potensi untuk menghasilkan lebih banyak benzaldehyde berjaya di peroleh.

Justeru itu, pemangkin monometal dan bimetal Au-Pd telah di sintesis melalui kaedah kaedah impregnasi dan sol-immobalisasi. Sifat-sifat fiziko-kimia pemangkin nanopartikel dicirikan dengan menggunakan X-Ray Diffraction (XRD), X-ray Fluorescene (XRF), Brunauer-Emmett-Teller (BET), Transmisi Electron Microscope (TEM)) dan Spektroskopi Penyebaran Tenaga (EDS). Setelah itu, aktiviti pemankin yang telah disentesis perlu melalui proses pengoksidasi menggunakan benzil alkohol sebagai subsrat dan tert-Butyl Hydroperoksida (TBHP) sebagai oksidan. Manakala, proses pengoksidaan turut melalui pengubahsuaian kesan pemboleh ubah seperti suhu, masa dan muatan pemangkin.

Kebolehgunaan berulang dan larut lesap bagi metal Au dan Pd di dalam benzil alkohol dijalankan bagi menguji tahap keupayaan untuk di adaptasi untuk proses pengoksidaan. Seterusnya, perbincangan mengenai hubungan aktiviti dan struktur pemangkin. Melalui perbincangan, faktor yang paling penting dalam pembentukan pemangkin yang sangat aktif adalah kaedah penyediaan. Kaedah impregnasi menghasilkan pemangkin dengan zarah Au yang besar. Manakala, penyediaan kaedah sol-immobilisasi menghasilkan pemangkin yang stabil, ketumpatan yang sangat aktif kedua-dua logam, kekuatan tertinggi, luas permukaan yang besar dan selektif untuk pengoksidaan benzil alkohol. Pengubahsuaian yang meluas pada pemangkin pemangkin pada Au-Pd, hasilnya menunjukkan bahawa 0.5 wt% Au 0.5 wt% Pd / TiO_2 pemangkin yang disediakan oleh kaedah sol-immobilisation menunjukkan aktiviti katalitik terbaik dalam pengoksidaan benzil alkohol pada suhu daripada 80℃ selama 4 jam.

Au yang besar apabila disokong pada TiO_2 kerana saiz zarah yang besar. Penyediaan kaedah sol-immobilisation menghasilkan pemangkin yang stabil, ketumpatan yang sangat aktif kedua-dua logam, kekuatan tertinggi, luas permukaan yang besar dan selektif untuk pengoksidaan benzil alkohol. Melalui pengubasuaian yang banyak,pada pemangkin Au-Pd, menunjukkan bahawa 0.5 wt% Au 0.5 wt% Pd / TiO_2 yang disediakan menggunakan kaedah sol-immobilisation menunjukkan aktiviti pemangkinan terbaik dalam pengoksidaan benzil alkohol pada suhu daripada 80℃ selama 4 jam.

Berdasarkan kajian hubungan struktur dan aktivi ini turut menunujukkan penglibatan kesan sinergi pada Au-Pd aloi semasa proses pengoksidaan. Bagi proses pengoksidaan pemboleh ubah yang bertindak balas masa tindak balas yang lebih panjang menunjukkan penurunan ketara selektif benzaldehid. Hal ini turut memberi kesan yang sama pada suhu tertinggi iaitu 120° C. Selain daripada itu, ujian larut lesap Au dan Pd ke dalam benzil alkohol menunjukkan pemangkin ini secara strukturnya adalah sangat kuat. Secara keseluruhannya, pengoksidaan benzil alkohol telah berjaya dikaji dalam proses dengan menggunakan Au-Pd/TiO_2 dan kepentingan TBHP sebagai oksidan terbukti. Selain itu, nisbah Au-Pd adalah tumpuan utama dalam kajian ini yang ditransformasikan untuk menjadi fleksibel pada pelbagai keadaan dengan prestasi yang hebat. Keputusan ini pemperincikan pemahaman asas aloi Au-Pd yang nilai nya lebih tinggi berbanding kaedah tradisional dalam pemangkin pengoksidaan benzil alkohol.

ACKNOWLEDGEMENTS

بسم الله الرحمن الرحيم

First and foremost, praise be to Allah, I am grateful for His blessing, guidance, chance and strength to complete this research project.

I would first like to thank my supervisor Dr. Mohd Izham bin Saiman of the Faculty of science at Universiti Putra Malaysia. He always around whenever I ran into a trouble or had a question about my research or writing. He consistently allowed this project to be my own work, but steered me in the right the direction whenever he thought I needed it. Not to be forgotten, many thanks to my co-supervisor Dr Ernee Noryana Mohamad. I am gratefully indebted to her for her very valuable comments on my research project paper.

I would also like to thank the experts who were involved for this research project include all lecturers and staff of Chemistry Department as well as associates in PUTRACAT for your kind and helpful for the whole time during my years as master student. Without their passionate participation and input, the research project could not have been successfully conducted. Many thanks to all of my friend for being such a nice and considered people around me and looking after me with such a troublemaker character after all this time we were together.

Finally, I must express my very profound gratitude to my beloved family especially my parents, Mohd Jam Jam bin Rasid and Yusni Binti Osman and also my sisters, Norasikin and Noratikah for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

Anas (May Allah be pleased with him) reported: The Messenger of Allah (sallallaahu ’alayhi wa sallam) said, “He who goes forth in search of knowledge is considered as struggling in the Cause of Allah until he returns”. [At-Tirmidhi].

Wallahu’alam bissawab

I certify that a Thesis Examination Committee has met on (date of viva voce) to conduct the final examination of (student's name) on his (her) thesis entitled ("Title of Thesis") in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the (insert the name of relevant degree).

Members of the Thesis Examination Committee were as follows:

Name of Chairperson, PhD
Title (e.g., Professor/Associate Professor/Ir; omit if irrelevant)
Name of Faculty
Universiti Putra Malaysia
(Chairman)

Name of Examiner 1, PhD
Title (e.g., Professor/Associate Professor/Ir; omit if irrelevant)
Name of Faculty
Universiti Putra Malaysia
(Internal Examiner)

Name of Examiner 2, PhD
Title (e.g., Professor/Associate Professor/Ir; omit if irrelevant)
Name of Faculty
Universiti Putra Malaysia
(Internal Examiner)

Name of External Examiner, PhD
Title (e.g., Professor/Associate Professor/Ir; omit if irrelevant)
Name of Department and/or Faculty
Name of Organisation (University/Institute)
Country
(External Examiner)

(Insert name of current Deputy Dean)
(E.g. XXXXX XXXX, PhD)
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Mohd Izham Saiman, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Ernee Noryana Muhamad, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ________________________ Date: __________________

Name and Matric No.: Norasidah Binti Mohd Jamjam, GS40657

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ______________________________
Name of Chairman of
Supervisory Committee: Mohd Izham Saiman

Signature: ______________________________
Name of Member of
Supervisory Committee: Ernee Noryana Muhamad

TABLE OF CONTENTS

Page

CHAPTER

1 INTRODUCTION

2 LITERATURE REVIEW

3 METHODOLOGY

4 **CHARACTERIZATION**

5 **REACTION OPTIMIZATION STUDIES**

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

TOF	Turn Over Frequency
FCC	Food Chemica Codex
LHSV	Liquid Hourly Space Velocity
XRF	Xray Fluorescence
XRD	Xray Diffraction
SEM	Scanning Electron Microscopy
FWHM	Full Width Half Maximum
TEM	Transmission Electron Microscopic
AAS	Atomic Absorption Spectroscopy
EDX	Energy Dispersive Xray
GCFID	Gas Chromatography Flame Ionisation Detector
GCMS	Gas Chromatography Mass Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Catalysis is of vital importance for both industrial and chemical manufacturing processes. With the current desire for green technology and processes, the demand for new catalysts and catalytic processes has led to significant research into the field. Basically, catalysis is a process that lowers the activation energy of the reaction as shown in figure 1.1. The catalyst was able to alter the rate of chemical reaction. Even now the transformation of catalyst may occur simultaneously during the reaction. However the thermodynamics and the products of the reaction remain the same.

Basically, the catalyst is divided into two categories which are homogenous catalyst and heterogeneous catalyst. If the catalyst has the same phase with the reactant, it is called as homogeneous catalyst. While the different phase of reactant and catalyst are heterogeneous catalyst.

During the early century, the main focus of research is to establish the productivity of catalyst. After more years, the concept of sustainable growth and green chemistry has given a good response among the researcher. Not only that, the high selectivity has becomes the driving force of the chemical activity to develop all new catalytic process. Thus today, the new generation of catalyst must associate with high activity, high selectivity and stability. In economic viewpoint along with the society need, heterogeneous catalyst is a key process in the three aspect above when compare with homogeneous catalyst. There is intense and broad interest in the design of new catalysts as well as seeking to understand how these materials function as catalysts.

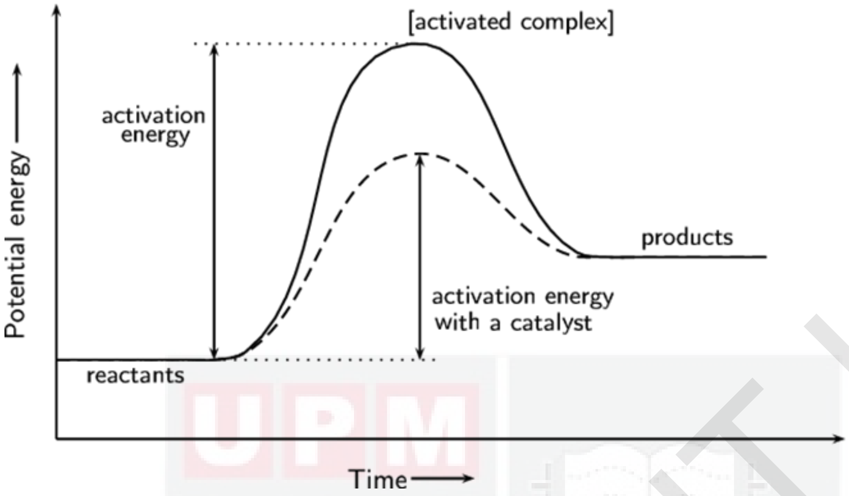


Figure 1.1. A Potential Energy Diagram Showing an Exothermic Reaction Reactant to Give Product. The Peaks on The Diagram Represent Transition States, by Forming One or More Lower Energy Transition State The Catalyst.

In oxidation processes, the aldehyde as intermediate product is fundamental and important reaction in organic synthesis. It is very useful for perfumery, pharmaceuticals, cosmetics, dyestuff, and agrochemical industries. Due to this reason, the use of catalyst in the oxidation process has been of growing interest because of the conventional method of oxidation process has brought risk to environment. As an example, lots of solvent and inorganic oxidant has been used before this which leads increment production quantity of toxicity waste. This is the main reason for all the new catalytic design using heterogeneous catalyst in oxidation processes.

Compared to other heterogeneous catalyst, gold is one of the well-known catalysts for an ideal green oxidation process which exhibit superior catalytic performances. The success of gold as the active metal in catalysis has been mainly due to the development of appropriate methods. The research was continued for seeking a better performance of the catalytic abilities of gold catalyst to keep enhancing the oxidation alcohol to produce aldehyde. This includes the design of electronic structure by changing the composition material such as modifying the gold using a second metal. Some progress have been accomplished that bimetallic catalyst study focuses on the control of active site and different nanostructure such as core-shell, alloy and size particle. For supported catalyst, both metal and support play an important part in controlling the product of oxidation. On the other hand, in the reaction aspect, the utilization of oxidant that have high oxygen availability as initiator for oxidation is important remarks in maintaining high activity of oxidation process.

1.2 Problem Statement

Over the past century, oxidation remain one of the main synthetic steps for the activation of a broad range of substrates for the production of either finished products or intermediates to be used widely in preparation of pharmaceutical, agrochemicals as well as commodity chemicals. However, most of the earlier research used conventional method where the oxidation are performed with stoichiometric amounts of inorganic oxidants and notably chromium (VI) reagents (Cainelli, Gianfranco, & Cardillo, 2012; Pillai & Sahle-demessie, 2003). One of the greatest challenges, these oxidants are not only relatively expensive, but they also generate copious amounts of heavy-metal waste. Moreover, these reactions have been shown to perform with existence of the environmentally undesirable solvents, typically chlorinated hydrocarbons which led to more consumption of toxic.

There are relatively few selective oxidation reaction that are using molecular oxygen as an oxygen sources (Abad, Corma, & García, 2007; Parreira *et al*., 2011; Wu, Chen, & Xu, 2005). However, the selectivity was poor and these processes can only be achieved if stoichiometric oxygen donor such as manganates or any activated form of oxygen like tert-butyl hydroperoxide to make use in the reaction. As the effect, the cost of production is increases, as well as significantly decreasing the atom efficiency of the overall process. There is, therefore, a real need for new catalytic process using other oxidants such TBHP, especially since environmental factors are of paramount importance and urgent need to develop efficient green process

In constant search of cleaner technologies, high activity and selectivity, various oxidation reactions in the gas or liquid phases have been studied to synthesize valuable intermediate products or fine chemicals (Pillai & Sahle-demessie, 2003). Many of these type of product carried out using catalytic partial oxidation of alcohols such as benzyl alcohol for the preparation of aldehydes and ketones (Schultz, Adler, Zierkiewicz, Privalov, & Sigman, 2005). In the literature on the homogenous catalyst, it has been good in activity when use it for oxidation of alcohol (Burch *et al.*, 2003; Dijksman et al., 2001; Samec *et al*., 2005). But there is disadvantages of using it such as, requiring more work to separate the product and poor selectivity of desired product.

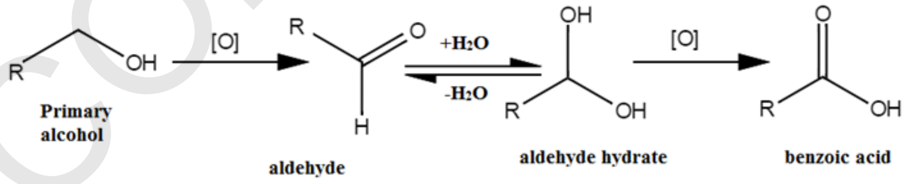
Indeed, the major advances in oxidation using heterogeneous catalyst were marked out over 10 years ago, since then there have been the remarkable development of the many type of metal catalyst especially for the oxidation alcohol to aldehyde. Among the all the transition metal, the preliminary studies over gold catalyst have superior catalyst (G. Bond & Thompson, 2000) for carbon monoxide oxidation and palladium metal in catalyzing aerobic oxidation of alcohol (Blackburn & Schwartz, 1977). Both of these metal use activated forms of oxygen had eluded many talented researchers. Bimetallic catalyst usually exhibit a superior catalytic performance compared with monometallic components Au-Pd bimetallic system have shown its synergistic effect in direct synthesis of H_2O_2 (Edwards, Edwin, et al., 2009; Edwards, Solsona, *et al*., 2009), selective oxidation of alcohol (Balcha, Strobl, Fowler, Dash, & Scott, 2011; D I Enache *et al*., 2006), C-C coupling (Zhang *et al*., 2014), and selective hydrogenation of unsaturated hydrocarbon (Kolli, Delannoy, & Louis, 2013b; Yu, Mullen, Flaherty, &

Mullins, 2014) The catalytic performance of these catalyst is still in search of either depends on the particle size or their surface structure. There is a report on surface structure for Pd which is isolate by Au atoms to promote hydrogenation reaction (Kolli *et al*., 2013b) while Au atom isolated by Pd atom to improve low-temperature CO (Gao *et al.*, 2017). However, there is less report on the benzyl alcohol oxidation on Au-Pd system performance in related to the particle size and its surface structure. Thus in this research, the TiO_2 is applied as the support to synthesis a series of Au-Pd/TiO_2 catalyst with Au-Pd ratios. The components of the structure were characterized in detail and the catalysts were probed by benzyl alcohol oxidation.

It is against this background and problem that recent developments in selective oxidation reaction using supported gold-palladium nanoparticle are beginning to make impact, a substantial investigation using a combination of experiment and theory was in need to improve the catalytic oxidation and it would seem to be a worthwhile problem to be addressed by our study.

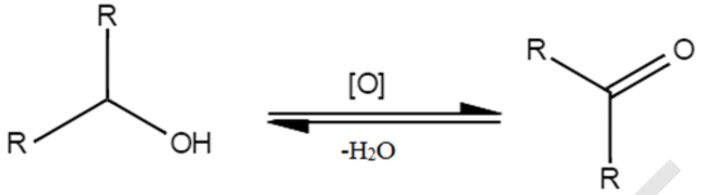
1.3 Oxidation of Alcohols

Oxidation of alcohol is one of the important organic reactions. By oxidizing different type of alcohol will give different product. Primary alcohol oxidation will produce either aldehyde group or carboxylic acid group. This is depending on reaction condition that will be conducted. Further oxidation of aldehyde to carboxylic acid which in this case, the aldehyde is only act as an intermediate as it is form only when there is the excessive of alcohol during oxidation process. The excessive of alcohols means that the oxidants have used enough to proceed with the second oxidation. This is half full oxidation where only aldehyde form immediately. In order to complete the reaction, the carboxylic is formed if only the aldehyde maintain in the mixture. With the excessive amount of oxidant, the process is carried out from aldehyde to carboxylic acid. From scheme 1.1, the simple equation is used to simplify the reaction order.

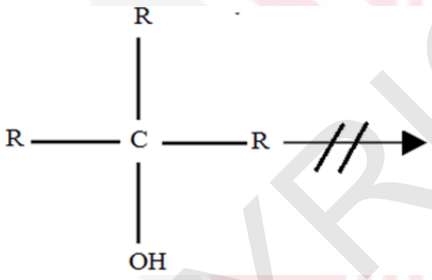


Scheme 1.1. The Equation of Alcohol Oxidation

Secondary alcohol will form ketone as it the only major product. Even the reaction is adjusted and changes, there is no different to the product (Scheme 1.2). The reason is secondary alcohol has no β-Hydrogen cause it to have no further conversion to any other product (Scheme 1.3). The situation mostly like tertiary alcohol as for it has no conversion to any product due to absence of any hydrogen attached to the carbon for hydroxyl group.



Scheme 1.2. **The Equation of Secondary Alcohol Oxidation**



Scheme 1.3. **The Equation of Tertiary Alcohol Oxidation**

1.3.1 Benzyl Alcohol Oxidation

The general idea concerning this oxidation is oxygen-activating components and substrate-selective catalyst to obtain high selectivity as well as high reactivity. In many cases, aldehydes are obtained from the activated alcohols in which the carbon bears a phenyl group which is benzyl alcohol (Markó, Giles, Tsukazaki, Brown, & Urch, 1996; Schultz *et al.,* 2005). Selective oxidation of benzyl alcohol is a model substrate in activating raw materials to form intermediates for use in the chemical, pharmaceutical and agricultural business sector (Sheldon, Arends, & Dijksman, 2000). One class of raw materials is toluene and benzaldehyde. The simplest member of this class can be oxidized to benzoic acid and benzyl benzoate. These products are commercially significant as versatile intermediates in the manufacture of pharmaceuticals, dyes, solvents, perfumes, plasticizer, dyestuffs, preservatives, and flames retardants.

In early research, Herriot and Picker (1974) using permanganate as oxidant to oxidize the benzyl alcohol in the presence of a phase transfer catalyst (Herriott et al., 1974). However, after reaction, no benzaldehyde was observed and the higher amount of benzoic acid was form. In addition, the copious amount of heavy-metal waste forms. Ishii and Kishi (1980) was employing the aqueous sodium hypochlorite under phase-transfer-catalysis and other researcher also proceeding the use of hypochlorite ion as oxidants for oxidation of alcohol (Ishii *et al*., 1980). Unfortunately, it has been reported that the rate of conversion was slow and low. Choudhary et al., (2004) was reported the oxidation of benzyl alcohol to benzaldehyde over MNO^{4-} exchanged hydrotalcite and transition metal containing layered double hydroxides and/or mixed hydroxides leave Tert-butanol as co-product and hence it is not a clean oxidizing agent (V R Choudhary *et al*., 2004). All the catalyst discuss above is the earliest studies on the oxidation of benzyl alcohol and show the low activity and selectivity even at highest temperature applies in the reaction.

Further investigations of benzyl alcohol as the substrate are being concern from the use of heterogeneous catalyst. Many studies have been reported from the use of benzyl alcohol. The production is either finishes product or intermediates. Previously, benzyl alcohol oxidation in gas phase has been study but the formation of excessive carbon dioxide (Hirofumi, Nishiyama, Tsuruya, & Masai, 1995). Choudhary and coworkers have investigated using non-noble transition containing metal hydrotalcite-like solid catalyst under solvent free conditions. Even though all of the catalyst has shown the conversion but the condition of reaction was at high temperature (210℃). The catalyst containing Mn or Cu catalyst was high in conversion but less selectivity towards benzaldehyde (Choudhary *et al.,* 2003). This is clearly a need to develop heterogeneous catalysts for benzyl alcohol oxidation that have greatly improved activity while retaining activity.

1.4 Gold Catalyst

From chemistry perspective, gold is well known as noble of metals that exist in bulk form which led to limited chemistry. Around 1980s, researcher discovered when subdivide gold into nano size can be highly reactive and activate small molecules (Haruta, 1997). The interest grows and focuses on the synthesis and use of small gold-containing nanoparticles as redox catalysts. There are several general reasons that explain this interest that has been well explained by Corma A. and Garcia H. (Corma & Garcia, 2008). The particle size of the gold is important properties of gold that in needs of observations as their ability as catalyst will disappear if the size grows into micrometric scale. Considering the current great response of nanoscience, it is understandable that all the aspects related to the preparation of small nanoparticles of narrow size distribution, their stabilization and their unique properties compared to larger particle size are appealing to a large community of researchers from material science, computational chemistry and catalysis (Haruta, 1997). The interest in gold nanoparticles as catalysts can be quantitatively ascertained by the exponential growth in the number of publication in this subject as in Figure 1.2.

Although the surface of gold is intrinsically inert, the catalytic nature of gold has been found to be tunable the control of its size, the suitable selection of support materials, and the architecture of the metal-support interaction. This increase the interest amongst the researchers to explore and study more for better understanding on the role of Au in the catalytic activity. The feature promises two important opportunities for gold in the science and technology of catalysis. The markedly large structure sensitivity of activity and selectivity will offer interesting topics for fundamental research at an atomic scale. The wide range in tuneability of catalytic properties from oxidation to hydrogenation presents future opportunities for industrial and environmental applications. In particular since supported gold catalysts are especially active at low temperatures, it will be a significant contribution of gold catalyst especially for environmental maintenance. Thus, understanding the reasons of this catalytic activity, expanding the scope to other reactions, optimizing and finding the reaction mechanisms for gold catalysed reactions is a new field in heterogeneous catalysis.

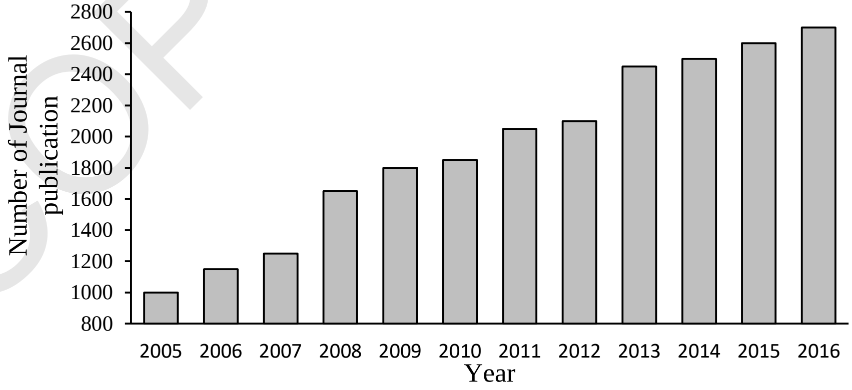


Figure 1.2. Graph of Exponential Growth in Growth in Journal Papers on Catalysis with Gold

1.5 Objective of Research

The objectives of the investigation are related to the catalyst design for gold palladium bimetallic catalysts and the application of these catalysts to develop widely green oxidation systems for various industrially useful oxidation targets. This study embarks on the following objectives:

1. To synthesize and characterize the gold-palladium supported titanium oxide via different technique preparation (i.e: impregnation and sol immobilisation).

2. To study the oxidation of benzyl alcohol under free solvent condition using prepared catalyst and TBHP as an oxidant.

3. To determine the optimum reaction conditions that can enhance the conversion and selectivities.

REFERENCES

Abad, A., Concepción, P., Corma, A., & García, H. (2005). A collaborative effect between gold and a support induces the selective oxidation of alcohols. *Angewandte Chemie - International Edition*, *44*, 4066.

Abad, A., Corma, A., & García, H. (2007). Supported gold nanoparticles for aerobic, solventless oxidation of allylic alcohols. *Pure and Applied Chemistry*, *79*, 1847–1854.

Arts, S. J. H. F., Rantwijk, F. van, & Sheldon, R. A. (1994). Oxidation of methyl 4, 6-o-isopropylidene-α-d-glucopyranoside as a model compound for starch. *Journal of Carbohydrate Chemistry*, *13*(6), 851–857. http://doi.org/10.1080/07328309408011685

Baatz, C., Decker, N., & Prüße, U. (2008). New innovative gold catalysts prepared by an improved incipient wetness method. *Journal of Catalysis*, *258*, 165–169.

Balcha, T., Strobl, J. R., Fowler, C., Dash, P., & Scott, R. W. J. (2011). Selective aerobic oxidation of crotyl alcohol using aupd core-shell nanoparticles. *ACS Catalysis*, *1*(5), 425–436. http://doi.org/10.1021/cs200040a

Bennett, R. A., Stone, P., & Bowker, M. (1999). Pd nanoparticle enhanced re-oxidation of non-stoichiometric TiO2: STM imaging of spillover and a new form of SMSI. *Catalysis Letters*, *59*, 99–105. http://doi.org/0

Bianchi, C., Porta, F., Prati, L., & Rossi, M. (2000). Selective liquid phase oxidation using gold catalysts. *Topics in Catalysis*, *13*(3), 231–236.

Biella, S., Castiglionib, G. L., Fumagallib, C., Prati, L., & Rossi, M. (2002). Application of gold catalysts to selective liquid phase oxidation. *Catalysis Today*, *72*(1–2), 43–49.

Biella, S., & Rossi, M. (2003). Gas phase oxidation of alcohols to aldehydes or ketones catalysed by supported gold. *Chemical Communications*, 378–379.

Blackburn, T. F., & Schwartz, J. (1977). Homogeneous Catalytic Oxidation of Secondary Alcohols to ketones by molecular oxygen under Mild Conditions. *Journal of the Chemical Society, Chemical Communications*, 157–158.

Bond, G. C., C.L., D., & Thompson, T. (2006). *Catalysis by Gold*. Imperial College Press.

Bond, G., & Thompson, D. (2000). Gold-Catalysed Oxidation of carbon monoxide. *Gold Bulletin*, *33*(2), 41–50.

Bond, Geoffrey C., & Thompson, D. T. (1999). Catalysis Reviews 41. In *Catalysis by gold* (pp. 319–388).

Brink, G., Arends, I. W. C. E., & Sheldon, R. a. (2004). The Baeyer − Villiger Reaction : New Developments toward Greener Procedures. *Chem. Rev.*, *104*, 4105.

Burch, R., & Ellis, P. R. (2003). An investigation of alternative catalytic approaches for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. *Applied Catalysis B: Environmental*, *42*, 203–211.

Cainelli, Gianfranco, & Cardillo, G. (2012). Chromium oxidations in organic chemistry. *Springer Science& Business Media*, *19*.

Carlson, T. . (1978). *X-ray photoelectron spectroscopy (Vol. 2)*. Dowden, Hutchinson & Ross.

Chen, M., Kumar, D., Yi, C.-W., & Goodman, D. W. (2005). The Promotional Effect of Gold in Catalysis by Palladium-Gold. *Science*, *310*, 291.

Chen, Y., Lim, H., Tang, Q., Gao, Y., Sun, T., Yan, Q., … Ray, A. K. (2010). Solvent-free aerobic oxidation of benzyl alcohol over Pd monometallic and Au-Pd bimetallic catalysts supported on SBA-16 mesoporous molecular sieves. *Applied Catalysis A: General*, *380*, 55–65.

Chen, Y., Zheng, H., Guo, Z., Zhou, C., Wang, C., Borgna, A., & Yang, Y. (2011). Pd catalysts supported on MnCeOx mixed oxides and their catalytic application in solvent-free aerobic oxidation of benzyl alcohol: Support composition and structure sensitivity. *Journal of Catalysis*, *283*, 34.

Choudary, B. M., Kantam, M. L., Rahman, A., Reddy, C. V., & Rao, K. K. (2001). The first example of activation of molecular oxygen by nickel in ni-al hydrotalcite: A novel protocol for the selective oxidation of alcohols. *Angewandte Chemie - International Edition*, *40*(4), 763–766. http://doi.org/10.1002/1521-3773(20010216)40:4<763::AID-ANIE7630>3.0.CO;2-T

Choudhary, V. R., Chaudhari, P. A., & Narkhede, V. S. (2003). Solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen using non-noble transition metal containing hydrotalcite-like solid catalysts. *Catalysis Communications*, *4*, 171–175.

Choudhary, V. R., Dumbre, D. K., Uphade, B. S., & Narkhede, V. S. (2004). Solvent-free oxidation of benzyl alcohol to benzaldehyde by tert -butyl hydroperoxide using transition metal containing layered double hydroxides and / or mixed hydroxides. *Journal of Molecular Catalysis A: Chemical*, *215*, 129–135.

Choudhary, V. R., Samanta, C., & Gaikwad, a G. (2004). Drastic increase of selectivity for H2O2 formation in direct oxidation of H2 to H2O2 over supported Pd catalysts due to their bromination. *Chemical Communications (Cambridge, England)*, 2054–2055.

Comotti, M., Della Pina, C., Falletta, E., & Rossi, M. (2006). Aerobic oxidation of glucose with gold catalyst: Hydrogen peroxide as intermediate and reagent. *Advanced Synthesis and Catalysis*, *348*, 313–316.

Corma, A., & Garcia, H. (2008). Supported gold nanoparticles as catalysts for organic reactions. *Chemical Society Reviews*, *37*, 2096–2126.

Crdenas-Lizana, F., Gmez-Quero, S., Hugon, A., Delannoy, L., Louis, C., & Keane, M. A. (2009). Pd-promoted selective gas phase hydrogenation of p-chloronitrobenzene over alumina supported Au. *Journal of Catalysis*, *262*, 235–243.

Cui, X., Zhang, C., Shi, F., & Deng, Y. (2012). Au/Ag-Mo nano-rods catalyzed reductive coupling of nitrobenzenes and alcohols using glycerol as the hydrogen source. *Chemical Communications (Cambridge, England)*, *48*, 9391–3.

Daniel, M. C., & Astruc, D. (2004). Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications Toward Biology, Catalysis, and Nanotechnology. *Chemical Reviews*, *104*, 293–346.

Della Pina, C., Falletta, E., Prati, L., & Rossi, M. (2008). Selective oxidation using gold. *Chemical Society Reviews*, *37*, 2077.

Dhakshinamoorthy, A., Alvaro, M., & Garcia, H. (2011). Metal–organic frameworks as heterogeneous catalysts for oxidation reactions. *Catalysis Science & Technology*, *1*(6), 856. http://doi.org/10.1039/c1cy00068c

Dijksman, A., Marino-González, A., Mairata I Payeras, A., Arends, I. W., & Sheldon, R. a. (2001). Efficient and selective aerobic oxidation of alcohols into aldehydes and ketones using ruthenium/TEMPO as the catalytic system. *Journal of the American Chemical Society*, *123*, 6826–6833.

Dimitratos, N., Lopez-Sanchez, J. A., Morgan, D., Carley, A. F., Tiruvalam, R., Kiely, C. J., … Hutchings, G. J. (2009). Solvent-free oxidation of benzyl alcohol using Au-Pd catalysts prepared by sol immobilisation. *Physical Chemistry Chemical*

Physics : PCCP, *11*(25), 5142–5153.

Dimitratos, N., Lopez-Sanchez, J. A., Morgan, D., Carley, A., Prati, L., & Hutchings, G. J. (2007). Solvent free liquid phase oxidation of benzyl alcohol using Au supported catalysts prepared using a sol immobilization technique. *Catalysis Today*, *122*, 317–324.

Dissanayake, D. P., & Lunsford, J. H. (2002). Evidence for the Role of Colloidal Palladium in the Catalytic Formation of H 2 O 2 from H 2 and O 2. *Journal of Catalysis*, *176*, 173–176.

Dissanayake, D. P., & Lunsford, J. H. (2003). The direct formation of H2O2 from H2 and O2 over colloidal palladium. *Journal of Catalysis*, *214*(1), 113–120.

Duff, D. G., Baiker, A., & Edwards, P. P. (1993). A new hydrosol of gold clusters. *Journal of the Chemical Society, Chemical Communications*, *272*, 96.

Dulub, O., Hebenstreit, W., & Diebold, U. (2000). Imaging Cluster Surfaces with Atomic Resolution: The Strong Metal-Support Interaction State of Pt Supported on TiO2(110). *Physical Review Letters*, *84*, 3646–3649.

E.G, R., S.A, C., Delgado, J. J., Chen, X., M.F, P., & Orfao J.J. (2012). Corrigendum to "Gold supported on carbon nanotubes for the selective oxidation of glycerol." *Journal of Catalysis*, *292*, 246–247.

Edwards, J. K., Edwin, N. N., Carley, A. F., Herzing, A. A., Kiely, C. J., & Hutchings, G. J. (2009). Direct synthesis of H2O2 from H2 and O2 over gold, palladium, and gold-palladium catalysts supported on acid-pretreated TiO2. *Angewandte Chemie - International Edition*, *48*(45), 8512–8515. http://doi.org/10.1002/anie.200904115

Edwards, J. K., Solsona, B. E., Landon, P., Carley, A. F., Herzing, A., Kiely, C. J., & Hutchings, G. J. (2005). Direct synthesis of hydrogen peroxide from H2 and O2 using TiO2-supported Au-Pd catalysts. *Journal of Catalysis*, *236*, 69.

Edwards, J. K., Solsona, B., N, E. N., Carley, A. F., Herzing, A. a, Kiely, C. J., & Hutchings, G. J. (2009). Switching off hydrogen peroxide hydrogenation in the direct synthesis process. *Science (New York, N.Y.)*, *323*, 1037–41.

Edwards, J. K., Thomas, A., Carley, A. F., Herzing, A. a., Kiely, C. J., & Hutchings, G. J. (2008). Au–Pd supported nanocrystals as catalysts for the direct synthesis of hydrogen peroxide from H2 and O2. *Green Chemistry*, *10*, 388.

Enache, D. I., Edwards, J. K., Landon, P., Solsona-Espriu, B., Carley, A. F., Herzing, A. A., … Hutchings, G. J. (2006). Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/TiO2 catalysts. *Science*, *311*, 362.

Enache, D. I., Knight, D. W., & Hutchings, G. J. (2005). Solvent-free oxidation of primary alcohols to aldehydes using supported gold catalysts. *Catalysis Letters*, *103*, 43–52.

Esumi, K., Sato, N., Torigoe, K., & Meguro, K. (1992). Size Control of Gold Particles Using Surfactants. *Journal of Colloid and Interface Science*, *149*, 295.

Gallezot, P. (1997). Selective oxidation with air on metal catalysts. *Catalysis Today*, *37*, 405–418.

Gao, F., Wang, Y., Goodman, D. W., Kolli, N. El, Delannoy, L., Louis, C., … Huang, W. (2017). CO/NO and CO/NO/O2 reactions over a Au-Pd single crystal catalyst. *Catalysis Today*, *280*(1), 253–258. http://doi.org/10.1016/j.jcat.2012.09.022

Grootboom, N., & Nyokong, T. (2002). Iron perchlorophthalocyanine and tetrasulfophthalocyanine catalyzed oxidation of cyclohexane using hydrogen peroxide, chloroperoxybenzoic acid and tert-butylhydroperoxide as oxidants. *Journal of Molecular Catalysis A: Chemical*, *179*, 113–123.

Gu, X., Lu, Z., Jiang, H., Akita, T., & Xu, Q. (2011). Synergistic Catalysis of Metal-Organic Framework-Immobilized AuPd Nanoparticles in Dehydrogenation of

Formic Acid for Chemical Hydrogen Storage. *Journal of the American Chemical Society*, *133*, 11822–11825.

Hackett, S. F. J., Brydson, R. M., Gass, M. H., Harvey, I., Newman, A. D., Wilson, K., & Lee, A. F. (2007). High-Activity , Single-Site Mesoporous Pd / Al2O3 Catalysts for Selective Aerobic Oxidation of Allylic Alcohols. *Angew.Chem., Int.Ed.*, *46*, 8593.

Haruta, M. (1997). Size- and support-dependency in the catalysis of gold. *Catalysis Today*, *36*, 153–166.

Haruta, M. (2004). Gold as a novel catalyst in the 21st century: Preparation, working mechanism and applications. *Gold Bulletin*, *37*(1–2), 27–36.

Haruta, M., Kobayashi, T., Sano, H., & Yamada, N. (1987). Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0 Degree Celcius. *Chemistry Letters*, *16*(2), 405–408.

Herriott, A. W., & Picker, D. (1974). Purple benzene: permanganate oxidations using quaternary ammonium ions. *Tetrahedron Letters*, *15*, 1511–1514.

Herzing, A. a, Watanabe, M., Edwards, J. K., Conte, M., Tang, Z., Hutchings, G. J., & Kiely, C. J. (2008). Energy dispersive X-ray spectroscopy of bimetallic nanoparticles in an aberration corrected scanning transmission electron microscope. *Faraday Discussions*, *138*, 337-351-434.

Hirofumi, H., Nishiyama, S., Tsuruya, S., & Masai, M. (1995). The effect of alkali promoters on Cu-Na-ZSM-5 catalysts in the Oxidation of Benzyl alcohol. *Journal of Catalysis*, *153*, 254–264.

Hutchings, G. J. (2008). Nanocrystalline gold and gold-palladium alloy oxidation catalysts: a personal reflection on the nature of the active sites. *Dalton Transactions (Cambridge, England : 2003)*, *9226*, 5523–5536.

Ishii, F., & Kishi, K. (1980). Oxidation of hydroquinone and Catechols with aqueous sodium hypochlorite under Phase-Transfer catalysis. *Synthesis*, *9*, 706–708.

Jia, C. G., Jing, F. Y., Hu, W. D., Huang, M. Y., & Jiang, Y. Y. (1994). Liquid-phase oxidation of alcohols by dioxygen using oxide-supported platinum catalysts. *Journal of Molecular Catalysis*, *91*(1), 139–147. http://doi.org/10.1016/0304-5102(94)00025-5

Kesavan, L., Tiruvalam, R., Rahim, M. H. A., bin Saiman, M. I., Enache, D. I., Jenkins, R. L., … Hutchings, G. J. (2011). Solvent-Free Oxidation of Primary Carbon-Hydrogen Bonds in Toluene Using Au-Pd Alloy Nanoparticles. *Science*, *331*, 195–199.

Kim, Y. D., Seitsonen, A. P., Wendt, S., Wang, J., Fan, C., Jacobi, K., … Ertl, G. (2001). Characterization of various oxygen species on an oxide surface: RuO2(110). *Journal of Physical Chemistry B*, *105*(18), 3752–3758. http://doi.org/10.1021/jp003213j

Kolli, N. El, Delannoy, L., & Louis, C. (2013a). Bimetallic Au-Pd catalysts for selective hydrogenation of butadiene: Influence of the preparation method on catalytic properties. *Journal of Catalysis*, *297*, 79–92.

Kolli, N. El, Delannoy, L., & Louis, C. (2013b). Bimetallic Au – Pd catalysts for selective hydrogenation of butadiene : Influence of the preparation method on catalytic properties. *Journal of Catalysis*, *297*, 79–92. http://doi.org/10.1016/j.jcat.2012.09.022

Kung, H. H., Kung, M. C., & Costello, C. K. (2003). Supported Au catalysts for low temperature CO oxidation. *Journal of Catalysis*, *216*, 425–432.

Landon, P., Collier, P. J., Papworth, A. J., Kiely, J., & Graham, J. (2002). Direct formation of hydrogen peroxide from H 2 / O 2 using a gold catalyst. *Chemical Communications*, 2058–2059.

Lee, Y. W., Kim, M., Kim, Y., Kang, S. W., Lee, J. H., & Han, S. W. (2010). Synthesis and electrocatalytic activity of Au-Pd alloy nanodendrites for ethanol oxidation. *Journal of Physical Chemistry C*, *114*, 7689–7693.

Liotta, L. ., Venezia, A. ., Deganello, G., Longo, A., Martorana, A., Schay, Z., & Guczi, L. (2001). Liquid phase selective oxidation of benzyl alcohol over Pd–Ag catalysts supported on pumice. *Catalysis Today*, *66*, 271.

Liu, F., Wechsler, D., & Zhang, P. (2008). Alloy-structure-dependent electronic behavior and surface properties of Au-Pd nanoparticles. *Chemical Physics Letters*, *461*, 254.

Liu, H., Li, Y., Jiang, H., Vargas, C., & Luque, R. (2012). Significant promoting effects of Lewis acidity on Au–Pd systems in the selective oxidation of aromatic hydrocarbons. *Chemical Communications*, *48*, 8431–8433.

Liu, J. H., Wang, A. Q., Chi, Y. S., Lin, H. P., & Mou, C. Y. (2005). Synergistic effect in an Au-Ag alloy nanocatalyst: CO oxidation. *Journal of Physical Chemistry B*, *109*(1), 40–43.

Lopez-Sanchez, J. A., Dimitratos, N., Miedziak, P., N, E. N., Edwards, J. K., Morgan, D., … Hutchings, G. J. (2008). Au–Pd supported nanocrystals prepared by a sol immobilisation technique as catalysts for selective chemical synthesis. *Physical Chemistry Chemical Physics : PCCP*, *10*, 1921–1930.

Ma, C. Y., Cheng, J., Wang, H. L., Hu, Q., Tian, H., He, C., & Hao, Z. P. (2010). Characteristics of Au/HMS catalysts for selective oxidation of benzyl alcohol to benzaldehyde. *Catalysis Today*, *158*, 246–251.

Ma, C. Y., Dou, B. J., Li, J. J., Cheng, J., Hu, Q., Hao, Z. P., & Qiao, S. Z. (2009). Catalytic oxidation of benzyl alcohol on Au or Au-Pd nanoparticles confined in mesoporous silica. *Applied Catalysis B: Environmental*, *92*, 202–208.

Mahdavi, V., Mardani, M., & Malekhosseini, M. (2008). Oxidation of alcohols with tert -butylhydroperoxide catalyzed by Mn (II) complexes immobilized in the pore channels of mesoporous hexagonal molecular sieves (HMS). *Catalysis Communications*, *9*, 2201.

Maki, T., & Takeda, K. (1985). Benzoic acid and derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry* (p. 6).

Makwana, V. D., Son, Y.-C., Howell, A. R., & Suib, S. L. (2002). The Role of Lattice Oxygen in Selective Benzyl Alcohol Oxidation Using OMS-2 Catalyst: A Kinetic and Isotope-Labeling Study. *Journal of Catalysis*, *210*, 46.

Mallat, T., & Baikeic, A. (1994). Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions. *Catalysis Today*, *19*(93), 247–284.

Mallat, T., & Baiker, A. (2004). Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chemical Reviews*, *104*, 3037.

Markó, I. E., Giles, P. R., Tsukazaki, M., Brown, S. M., & Urch, C. J. (1996). Copper-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones: An Efficient, Aerobic Alternative. *Science*, *274*, 2044–2046.

Martin, A., Bentrup, U., & Wolf, G. U. (2002). The effect of alkali metal promotion on vanadium-containing catalysts in the vapour phase oxidation of methyl aromatics to the corresponding aldehydes. *Applied Catalysis A: General*, *227*(1–2), 131–142. http://doi.org/10.1016/S0926-860X(01)00930-9

Marx, S., & Baiker, A. (2009). Beneficial Interaction of Gold and Palladium in Bimetallic Catalysts for the Selective Oxidation of Benzyl Alcohol. *The Journal of Physical Chemistry C*, *113*, 6191–6201.

mayer A.B.R, & J.E Mark. (1996). Polymer-protected, colloidal platinum nanocatalysts. *Polymer Bulletin*, *37*, 683–690.

Menegazzo, F., Signoretto, M., Manzoli, M., Boccuzzi, F., Cruciani, G., Pinna, F., &

Strukul, G. (2009). Influence of the preparation method on the morphological and composition properties of Pd-Au/ZrO2 catalysts and their effect on the direct synthesis of hydrogen peroxide from hydrogen and oxygen. *Journal of Catalysis*, *268*, 122–130.

Mertens, P. G. N., Bulut, M., Gevers, L. E. M., Vankelecom, I. F. J., Jacobs, P. A., & De Vos, D. E. (2005). Catalytic oxidation of 1,2-diols to α-hydroxy-carboxylates with stabilized gold nanocolloids combined with a membrane-based catalyst separation. *Catalysis Letters*, *102*, 57–61.

Miedziak, P. (2009). *Selective oxidation reactions catalysed by gold*.

Miedziak, P. J., Tang, Z., Davies, T. E., Enache, D. I., Bartley, J. K., Carley, A. F., … Hutchings, G. J. (2009). Ceria prepared using supercritical antisolvent precipitation: a green support for gold–palladium nanoparticles for the selective catalytic oxidation of alcohols. *Journal of Materials Chemistry*, *19*, 8619.

Miedziak, P., Sankar, M., Dimitratos, N., Lopez-Sanchez, J. A., Carley, A. F., Knight, D. W., … Hutchings, G. J. (2011). Oxidation of benzyl alcohol using supported gold-palladium nanoparticles. *Catalysis Today*, *164*(1), 315–319.

Moreau, F., Bond, G. C., & Taylor, A. O. (2005). Gold on titania catalysts for the oxidation of carbon monoxide: Control of pH during preparation with various gold contents. *Journal of Catalysis*, *231*, 105–114.

Mori, K., Hara, T., Mizugaki, T., Ebitani, K., & Kaneda, K. (2004). Hydroxyapatite-Supported Palladium Nanoclusters : A Highly Active Heterogeneous Catalyst for Selective Oxidation of Alcohols by Use of Molecular Oxygen. *Journal of the Chemical Society*, *126*, 10657.

Nascente, P. A. P., Maluf, S. S., Afonso, C. R. M., Landers, R., Pinheiro, A. N., & Leite, E. R. (2014). Au and Pd nanoparticles supported on CeO2, TiO2, and Mn2O3 oxides. *Applied Surface Science*, *315*(1), 490–498.

Nomiya, K., Hashino, K., Nemoto, Y., & Watanabe, M. (2001). Oxidation of toluene and nitrobenzene with 30% aqueous hydrogen peroxide catalyzed by vanadium(V)-substituted polyoxometalates. *Journal of Molecular Catalysis A: Chemical*, *176*, 79.

Ntainjua N., E., Edwards, J. K., Carley, A. F., Lopez-Sanchez, J. A., Moulijn, J. A., Herzing, A. a., … Hutchings, G. J. (2008). The role of the support in achieving high selectivity in the direct formation of hydrogen peroxide. *Green Chemistry*, *10*, 1162.

Over, H., Kim, Y., Seitsonen, A., Wendt, S., Lundgren, E., Schmid, M., … Ertl, G. (2000). Atomic-scale structure and catalytic reactivity of the RuO2 (110) surface. *Science*, *287*, 1474. http://doi.org/10.1126/science.287.5457.1474

Pan, J. M., & Madey, T. E. (1993). The encapsulation of Fe on TiO2(110). *Catalysis Letters*, *20*(3–4), 269–274.

Parreira, L. A., Bogdanchikova, N., Pestryakov, A., Zepeda, T. A., Tuzovskaya, I., Farias, M. H., & Gusevskaya, E. V. (2011). Nanocrystalline gold supported on Fe-, Ti- and Ce-modified hexagonal mesoporous silica as a catalyst for the aerobic oxidative esterification of benzyl alcohol. *Applied Catalysis A: General*, *397*, 145–152.

Partenheimer, W. (2009). The aerobic oxidative cleavage of lignin to produce hydroxyaromatic benzaldehydes and carboxylic acids via metal/bromide catalysts in acetic acid/water mixtures. *Advanced Synthesis and Catalysis*, *351*, 456–466.

Perego, G. (1998). Characterization of Heterogeneous Catalysts by X-Ray Diffraction Techniques. *Catalysis Today*, *41*(1–3), 251–259.

Pesty, F., Steinrück, H. P., & Madey, T. E. (1995). Thermal stability of Pt films on TiO2(110): evidence for encapsulation. *Surface Science*, *339*(1–2), 83–95.

Pillai, U. R., & Sahle-demessie, E. (2003). Oxidation of alcohols over Fe3+/ montmorillonite-K10 using hydrogen peroxide. *Applied Catalysis*, *245*, 103–109.

Porta, F., & Prati, L. (2004). Selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst: An insight into reaction selectivity. *Journal of Catalysis*, *224*, 397–403.

Porta, F., Prati, L., Rossi, M., Coluccia, S., & Martra, G. (2000). Metal sols as a useful tool for heterogeneous gold catalyst preparation: Reinvestigation of a liquid phase oxidation. *Catalysis Today*, *61*, 165.

Porta, F., Prati, L., Rossi, M., & Scari, G. (2002). New Au(0) sols as precursors for heterogeneous liquid-phase oxidation catalysts. *Journal of Catalysis*, *211*, 464–469.

Prati, L., & Martra, G. (1999). New Gold Catalysts for Liquid Phase Oxidation. *Gold Bulletin*, *32*, 96–101.

Prati, L., & Rossi, M. (1998). Gold on carbon as a new catalyst for selective liquid phase oxidation of diols. *Journal of Catalysis*, *176*, 552–560.

Prati, L., & Villa, A. (2011). The Art of Manufacturing Gold Catalysts. *Catalysts*, *2*, 24–37.

Ragupathi, C., Judith Vijaya, J., Thinesh Kumar, R., & John Kennedy, L. (2014). Selective liquid phase oxidation of benzyl alcohol catalyzed by copper aluminate nanostructures. *Journal of Molecular Structure*, *1079*, 182–188.

Rao, P. S. N., Rao, K. T. V., Sai Prasad, P. S., & Lingaiah, N. (2011). The role of vanadia for the selective oxidation of benzyl alcohol over heteropolymolybdate supported on alumina. *Cuihua Xuebao/Chinese Journal of Catalysis*, *32*, 1719–1726.

Reidy, D. J., Holmes, J. D., & Morris, M. A. (2006). The critical size mechanism for the anatase to rutile transformation in TiO2 and doped-TiO2. *Journal of the European Ceramic Society*, *26*(9), 1527–1534.

Ruiz, M. W. C. R. P., Delmon, B., & Devillers, M. (1997). On the role of bismuth-based alloys in carbon-supported bimetallic Bi-Pd catalysts for the selective oxidation of glucose to gluconic acid, 391–398.

Saiman, M. I., Brett, G. L., Tiruvalam, R., Forde, M. M., Sharples, K., Thetford, A., … Hutchings, G. J. (2012). Involvement of surface-bound radicals in the oxidation of toluene using supported Au-Pd nanoparticles. *Angewandte Chemie - International Edition*, *51*, 5981.

Saiman, M. I. Bin. (2012). *Heterogeneous gold and palladium based catalysts for solvent-free oxidation of toluene*. Cardiff University.

Samec, J. S. M., Éll, A. H., & Bäckvall, J. E. (2005). Efficient ruthenium-catalyzed aerobic oxidation of amines by using a biomimetic coupled catalytic system. *Chemistry - A European Journal*, *11*, 2327–2334.

Sankar, M., He, Q., Morad, M., Pritchard, J., Freakley, S. J., Edwards, J. K., … Hutchings, G. J. (2012). Synthesis of stable ligand-free gold-palladium nanoparticles using a simple excess anion method. *ACS Nano*, *6*, 6600–6613.

Schultz, M. J., Adler, R. S., Zierkiewicz, W., Privalov, T., & Sigman, M. S. (2005). Using mechanistic and computational studies to explain ligand effects in the palladium-catalyzed aerobic oxidation of alcohols. *Journal of the American Chemical Society*, *127*, 8499–8507.

Sheldon, R. ., Arends, I. W. C. ., & Dijksman, A. (2000). New developments in catalytic alcohol oxidations for fine chemicals synthesis. *Catalysis Today*, *57*, 157.

Subrahmanyam, C., Louis, B., Rainone, F., Viswanathan, B., Renken, A., & Varadarajan, T. K. (2002). Partial oxidation of toluene by O2 over mesoporous

Cr-AlPO. *Catalysis Communications*, *3*(2), 45–50. http://doi.org/10.1016/S1566-7367(01)00070-X

Thomas, J. M., Raja, R., Sankar, G., & Bell, R. G. (1999). Molecular-sieve catalysts for the selective oxidation of linear alkanes by molecular oxygen. *Nature*, *398*, 227.

Tsubota, S., Haruta, M., Kobayashi, T., Ueda, A., & Nakahara, Y. (1991). Preparation of highly dispresed gold on Titanium and Magnesium Oxide. *Studies in Surface Science and Catalysis*, *63*, 695–704.

Venezia, A. M., La Parola, V., Nicolì, V., & Deganello, G. (2002). Effect of Gold on the HDS Activity of Supported Palladium Catalysts. *Journal of Catalysis*, *212*(1), 56–62.

Villa, A., Veith, G. M., Ferri, D., Weidenkaff, A., Perry, K. a., Campisi, S., & Prati, L. (2013). NiO as a peculiar support for metal nanoparticles in polyols oxidation. *Catalysis Science & Technology*, 394–399.

Villa, A., Wang, D., Su, D. S., & Prati, L. (2009). Gold sols as catalysts for glycerol oxidation: The role of stabilizer. *ChemCatChem*, *1*, 510–514.

Villa, A., Wang, D., Su, D., Veith, M., & Prati, L. (2010). Using supported Au nanoparticles as starting material for preparing uniform Au / Pd bimetallic catalysts. *Physical Chemistry Chemical Physics : PCCP*, *12*, 2183–2189.

Wang, F., Xu, J., Li, X., Gao, J., Zhou, L., & Ohnishi, R. (2005). Liquid Phase Oxidation of Toluene to Benzaldehyde with Molecular Oxygen over Copper-Based Heterogeneous Catalysts. *Advanced Synthesis & Catalysis*, *347*(15), 1987–1992.

Wang, H. Y., & Ruckenstein, E. (2001). CO2 reforming of CH4 over Co/MgO solid solution catalysts - effect of calcination temperature and Co loading. *Applied Catalysis A: General*, *209*(1–2), 207–215.

Wang, X. G., Venkataramanan, N. S., Kawanami, H., & Ikushima, Y. (2007). Selective oxidation of styrene to acetophenone over supported Au-Pd catalyst with hydrogen peroxide in supercritical carbon dioxide. *Green Chemistry*, *9*, 1352–1355.

Wu, G., Chen, Y. S., & Xu, B. Q. (2005). Remarkable support effect of SWNTs in Pt catalyst for methanol electrooxidation. *Electrochemistry Communications*, *7*(12), 1237–1243.

Xiang, Y., Meng, Q., Li, X., & Wang, J. (2010). In situ hydrogen from aqueous-methanol for nitroarene reduction and imine formation over an Au-Pd/Al2O3 catalyst. *Chemical Communications (Cambridge, England)*, *46*, 5918–5920.

Yamaguchi, K., & Mizuno, N. (2002). Supported ruthenium catalyst for the heterogeneous oxidation of alcohols with molecular oxygen. *Angewandte Chemie - International Edition*, *41*(23), 4538–4542.

Yao, F. L. (2007). tert-butyl hydroperoxide (TBHP): A versatile oxidizing agent in organic synthesis. *Synlett*, *18*, 2922–2923.

Yu, W. Y., Mullen, G. M., Flaherty, D. W., & Mullins, C. B. (2014). Selective hydrogen production from formic acid decomposition on Pd-Au bimetallic surfaces. *Journal of the American Chemical Society*, *136*(31), 11070–11078. http://doi.org/10.1021/ja505192v

Zhan, G., Hong, Y., Mbah, V. T., Huang, J., Ibrahim, A. R., Du, M., & Li, Q. (2012). Bimetallic Au-Pd/MgO as efficient catalysts for aerobic oxidation of benzyl alcohol: A green bio-reducing preparation method. *Applied Catalysis A: General*, *439*, 179.

Zhang, L., Wang, A., Miller, J. T., Liu, X., Yang, X., Wang, W., … Zhang, T. (2014). Efficient and durable Au alloyed Pd single-atom catalyst for the Ullmann reaction of aryl chlorides in water. *ACS Catalysis*, *4*(5), 1546–1553.

http://doi.org/10.1021/cs500071c

Zhao, P., Li, N., & Astruc, D. (2013). State of the art in gold nanoparticle synthesis. *Coordination Chemistry Reviews*, *257*, 638–665.