

UNIVERSITI PUTRA MALAYSIA

SOLVENT FREE OXIDATION OF BENZYL ALCOHOL TO PRODUCE BENZALDEHYDE USING BIMETALLIC Au-Pd SUPPORTED CATALYSTS

SANAA TAREQ SARHAN

FS 2018 73



SOLVENT FREE OXIDATION OF BENZYL ALCOHOL TO PRODUCE BENZALDEHYDE USING BIMETALLIC Au-Pd SUPPORTED CATALYSTS



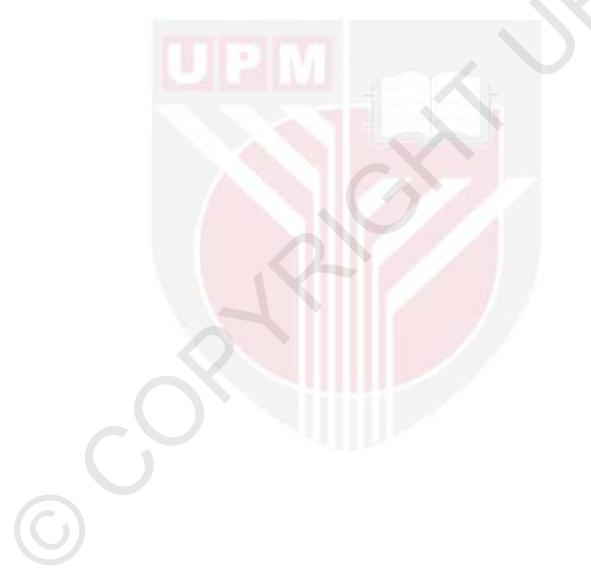
Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2018

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs, and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

SOLVENT FREE OXIDATION OF BENZYL ALCOHOL TO PRODUCE BENZALDEHYDE USING BIMETALLIC Au-Pd SUPPORTED CATALYSTS

By

SANAA TAREQ SARHAN

May 2018

Chairman : Mohd Izham bin Saiman, PhD Faculty : Science

The study of using a gold and palladium as heterogeneous catalyst is commonly investigated for many oxidation process now days especially in benzyl alcohol oxidation. In this respect, the main goal of this research is to study the influence of oxidant with Au-Pd bimetallic catalyst to achieve highest potential to obtain more benzaldehyde. The monometallic and bimetallic catalysts are synthesized via impregnation and sol-immobilization methods. The structural, texturalphysicochemical, morphological, and thermal characteristics of the synthesized catalysts hav investigated by using X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Transmission Electron Microscope (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Brunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy (FESEM) and Temperature Programmed Desorption (TPD-NH₃).On the other hand, an examination of the reusability and leaching of gold and palladium into benzyl alcohol also was carried out. As a result, sol-immobilization methods was shown produced stable catalysts, highly active density of both metal loading, highest strength, large surface area and more selective for the oxidation benzyl alcohol. The result also revealed that 1wt%Au-Pd/C catalyst prepared by solimmobilizations methods showed the best catalytic activity in the oxidation of benzyl alcohol at temperature of 80 °C for 4hours. Comparing with mono Au or Pd catalyst, bimetallic Au-Pd gave alloy formation that contribute a synergy effects and showed an improvement for conversion and selectivity on the benzyl alcohol oxidation. In addition, the effect of variable parameters, such as reaction temperature, effect of different support, heat treatment conditions, oxidant ratio, reaction time and metal loading ratio have been evaluated for optimization to produce more benzaldehyde. It was found that the activity and selectivity of the oxidation benzyl alcohol was highly dependent on these variables. A good reusability of the catalysts with less of leaching gold into the product has obtained also.



As a conclusion, the oxidation of benzyl alcohol was successfully studied and the best catalyst was Au-Pd/C that synthesized by using sol-immobilization. This catalyst was found had a good distribution of narrowed small particles (2.79nm). Furthermore, the importance of the H_2O_2 as an oxidant have been proven in this research.



Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGOKSIDAAN BENZIL ALKOHOL TANPA PELARUT UNTUK MENGHASILKAN BENZALDEHID MENGGUNAKAN MANGKIN BERPENYOKONG DWILOGAM Au-Pd

By

SANAA TAREQ SARHAN

Mei 2018

Pengerusi: Mohd Izham bin Saiman, PhDFakulti: Sains

Hasil kajian menggunakan emas dan paladium sebagai mangkin heterogen biasanya disiasat dalam banyak proses pengoksidaan sekarang ini terutama peengoksidaan bagi benzil alkohol. Dalam hal ini, matlamat utama penyelidikan adalah untuk kajian kesan bahan pengoksidaan dengan mangkin Au-Pd untuk mencapai potensi tertinggi bagi menghasilkan lebih benzaldehid. Mangkin monologam dan dwilogam disintesis melalui kaedah pemendakan dan sol-immobilisasi. Ciri-ciri struktur, tekstur fizikokimia, morfologi, dan ciri-ciri terma mangkin yang disintesis telah dicirikan dengan menggunakan kaedah Pembelauan Sinar-X (XRD), Analisis Terma Gravimetri (TGA), Mikroskop Transmisi Elektron (TEM), Mikroskop Transmisi Elektron Beresolusi Tinggi (HRTEM), Brunauer-Emmett-Teller (BET), Mikroskop Imbasan Elekron (FESEM) dan Program-Suhu-Nyahjerapan Ammonia (TPD-NH₃). Tambahan lagi, penelitian terhadap keupayaan kebolehgunaan dan keterlarutan emas dan palladium dalam benzil alkohol juga telah dijalankan. Keputusannya, teknik sol immobilisasi menunjukkan penghasilan mangkin yang stabil, ketumpatan yang aktif bagi kemuatan kedua-dua logam, kekuatan yang tinggi, luas permukaan yang besar dan kepilihan yang tinggi bagi pengoksidaan benzil alkohol. Hasil kajian ini juga menunjukkan bahawa mangkin 1wt% Au-Pd/C yang disediakan menggunakan kaedah sol-immobilisasi mempamerkan aktiviti pemangkinan terbaik dalam proses pengoksidaan benzil alkohol pada suhu 80°C selama 4 jam. Perbandingan dengan mono mangkin Au atau Pd, dwilogam Au-Pd memberikan pembentukan aloi yang menyumbang kepada kesan sinergi dan menunjukkan peningkatan terhadap penukaran dan kepilihan terhadap pengoksidaan benzil alkohol. Tambahan lagi, kesan pelbagai pembolehubah seperti suhu tindak balas, kesan sokongan yang berbeza, keadaan rawatan haba, nisbah bahan pengoksidaan, masa tindak balas dan nisbah pemuatan logam telah pun dikaji untuk mengoptimumkan penghasilan lebih benzaldehid. Ia telah mendapati penukaran dan kepilihan oleh pengoksidaan benzil



alkohol adalah bergantung kepada pembolehubah tersebut. Sebagai kesimpulannya, pengoksidaan benzil alkohol telah berjaya dikaji dan mangkin terbaik adalah Au-Pd / C yang disintesis melalui kaedah sol-immobilisasi. Mangkin ini didapati mempunyai sebaran zarah-zarah kecil sempit yang bagus (2.79 nm). Tambahan pula, kepentingan H_2O_2 sebagai bahan pengoksidaan telah terbukti dalam kajian ini.



ACKNOWLEDGEMENTS

First and foremost, I would like to express my praise and gratitude to God Almighty for giving me the chance to successfully completing this piece of research work. Surely this knowledge that I have is only a tiny piece of His many other undiscovered knowledge. I wish to thank my supervisor Dr. Mohd Izham for the useful comments and remarks, His guidance helped me in all the time of research and writing of this thesis and giving me the possibility to involve in this research project in UPM and for the chance to explore field of chemistry during my time spent working on this PhD study. Moreover, I would like to thank Prof. Yun Hin Taufiq-Yap for his assistance in supervising and to have patiently contributed to the corrections of this thesis as well as Dr. A.H. Abdullah and Dr. Umer Rashid.

My PhD study also would not have been possible without the help of other people. Therefore, I express my deepest gratitude to my family for their unflagging love and unconditional support throughout my life and studies. Special thanks also goes to my father and my mother, thank you for being a loving parent for me and your Doa' for my success.

Deepest gratitude to my husband khalid, for being supportive, wonderful memories in our life, your advices, Also, special gratitude to my daughter Gadgha

and my sons, Yasser, Sadeq for being here with me during my study period. Special gratitude also goes to my brother and my sisters . Special gratitude also goes for Professor Ahlam Mohamad Farhan the dean of faculity of science for women Special gratitude also my best freind Anwar Ali for her supporting .Nor forgotten, thanks to all my colleagues and friends, especially from Catalysis Science and Technology Research Centre (PutraCAT), staffs and technicians at the Chemistry Department, Faculty of Science. Finally, I also would like to thank Iraqi Government for the financial support.

-Alhamdulillah-

I certify that a Thesis Examination Committee has met on 14 May 2018 to conduct the final examination of Sanaa Tareq Sarhan on her thesis entitled "Solvent Free Oxidation of Benzyl Alcohol to Produce Benzaldehyde Using Bimetallic Au-Pd Supported Catalysts" 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 Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Tan Yen Ping, PhD Senior Lecturer Faculty of Science Universiti Putra Malaysia (Chairman)

Jaafar bin Abdullah, PhD Senior Lecturer Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Lim Hong Ngee, Janet, PhD Associate Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Didik Prasetyoko, PhD

Professor Sepuluh Nopember Institute of Technology Indonesia (External Examiner)

RUSLI HAJI ÅBDULLAH, PhD Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date: 30 July 2018

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

Mohd Izham Saiman, PhD

Senior Lecturer Faculty of Science Universiti Putra Malaysia (Chairman)

Taufiq Yap Yun Hin, FASc, PhD

Professor Faculty of Science Universiti Putra Malaysia (Member)

Abdul Halim Abdullah, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Member)

Umer Rashid, PhD

Associate Professor Institute of Advance Technology 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 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: Sanaa Tareq Sarhan, GS39707

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) were adhered to.

DR. MOHD IZHAM SAIMAN SENIOR LECTURER DEPARTMENT OF CHEMISTRY Signature: ERSITI PUTRA MALAYSIA Name of Chairman 43400 UPM SERDANG SELANGOR DARUL EHSAN. of Supervisory Dr. Mohd Izham Saiman Committee: ROFESSOR DR. TAUFIQ YAP YUN HIN FASc, FMIC (M'sia), CChem, FRSC, AMIChemE (UK) Putra Laboratory for Sustainable Bioenergy and Chemicals Signature: Department of Chemistry Name of Member Faculty of Science of Supervisory Professor Dr. Taufiq Yap Yun Hin, FASkiversiti Putra Malaysia Committee: 43400 UPM Serdang Selangor, MALAYSIA PROF. MADYA DR. ABDUL HALIM ABDULLAH Signature: JABATAN KIMIA FAKULTT SAINS Name of Member UNIVERSITI PUTRA MALAYSIA 43400 UPN SERDANG, SELANGOR of Supervisory Associate Professor Dr. Abdul Halim Abdullah Committee: DR. UMER RASHID Fellow Researcher Material Processing and Technology Laboratory Signature: Institute of Advanced Technology (ITMA) Name of Member Universiti Putra Malaysia of Supervisory 43400 UPM Serdang, Selangor Associate Professor Dr. Umer Rashid Committee:

TABLE OF CONTENTS

Page

ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xiv
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS	xxiii
CHAPTER	

1	INTR	RODUCTION	1
	1.1	Uses of benzyl alcohol	1
	1.2	Methods of Manufacturing benzyl alcohol	1
	1.3	Possible mechanisms for benzyl alcohol oxidation reaction	2
	1.4	Benzaldehyde	4
	1.1	1.4.1 Chemical and physical properties of benzaldehyde	5
		1.4.2 Uses of benzaldehyde	6
		1.4.3 Manufacture benzaldehyde	6
	1.5	Catalysis	7
	1.6	Gold history	8
	1.7	Problem statement	9
		1.7.1 Scope of the study	10
	1.8	Objectives of the research	11
2	LITE	CRATURE REVIEW	12
	2.1	Oxidation Reaction	12
	2.2	Homogeneous and heterogeneous catalysts in oxidation reaction	13
		2.2.1 Mono Gold supported catalyst for oxidation reaction	15
		2.2.2 Mono Palladium supported catalyst for oxidation reaction	17
		2.2.3 Bimetallic Au-Pd supported catalyst for oxidation reaction	17
	2.3	Hydrogen peroxide as an oxidant for selective oxidation of alcohol	
		2.3.1 Hydrogen Peroxide	20
		2.3.2 Synthesis of hydrogen peroxide	21

2.2.3	Binetanic Au-ru supported cataryst for oxidation reaction	1/
Hydrog	gen peroxide as an oxidant for selective oxidation of alcohol	20
2.3.1	Hydrogen Peroxide	20
2.3.2	Synthesis of hydrogen peroxide	21
2.3.3	Non solvent oxidation of alcohols	22
2.3.4	Hydrogen peroxide as effective oxidant for the synthesis	
	of benzaldehyde	23
Prepara	ation techniques of gold based catalysts	25
2.4.1	Generic impregnation techniques	26

2.4.2Sol immobilisation techniques262.4.2Sol immobilisation techniques26

2.4

3	METI	HODOI	LOGY		28
	3.1	Materi	als		28
	3.2	Gases			29
	3.3	Cataly	st prepara	tion	30
		-		ation technique	30
			3.3.1.1	Preparation mono Au or Pd support catalysts	30
			3.3.1.2	Preparation of bimetallic Au-Pd supported	
				catalyst	30
		3.3.2	Sol immo	bilization method	31
		0.0.2	3.3.2.1	Preparation of mono Au or Pd supported catalyst	
			3.3.2.2	Preparation of bimetallic Au-Pd supported	
			5.5.2.2	catalyst	31
	3.4	Cataly	sts Reacti	•	32
	3.5		st Reusabi		33
	3.6		st characte		33
·	5.0			ravimetric analysis (TGA)	34
		3.6.2		ble spectroscopy	35
				ffraction Analysis (XRD)	35
		3.6.4	-	surface area measurement (BET)	36
		3.6.5		sion electronic microscopy (TEM)	37
		3.6.6			57
		5.0.0	0	plution transmission electron microscopy	37
		267	(HRTEM		
		3.6.7		ission Scanning Electron Microscopy (FESEM)	38
		3.6.8	-	ture-Programmed Desorption Analysis (TPD)	38
		3.6.9		products analysis	39
			Internal s		41
		3.6.11	Gas Chro	omatography - Mass Spectrometry (GC-MS)	41
4	СПАТ	ACTE	DISATIC	ON OF THE CATALYSTS	43
4	4 .1	Introdu		IN OF THE CATALISTS	43 43
	4.1			ria analyzia (TCA)	43 43
				ric analysis (TGA)	45 45
	4.3	-		on (XRD) analysis	43
		4.3.1		d bimetallic 5wt%(Au-Pd)/TiO ₂ catalysts	45
		122		e by impregnation method	45
		4.3.2	· · · ·	u-Pd) catalysts supported various support	50
		4 2 2		synthesized by impregnation technique	50
		4.3.3	· ·	u-Pd)/TiO ₂ catalysts prepared by the sol-	
		F ! 11		sation method	52
	4.4			canning electron microscopy (FESEM)	53
	4.5			ectron microscopy (TEM)	56
	4.6			a measurements	68
	4.7		-	erature-Programmed Desorption (TPD)	71
	4.8	UV- V	isible spe	ctroscopy	77

UV- Visible spectroscopy 4.8

5 RESULT	TS AI	ND DISCU	USSION	78
5.1 II	mpreg	nation Teo	chnique	78
5	.1.1	Blank be	nzyl alcohol oxidation	78
		5.1.1.1	Effect of different temperature	78
		5.1.1.2	Effect of support only on benzyl alcohol	
			oxidation	79
		5.1.1.3	Effect of different supports on catalytic activity	
			of 5wt% Au-Pd catalyst prepared via the	
			impregnation method	80
5	.1.2	Catalyst u	using TiO_2 as support	81
		5.1.2.1	Effect of mono 5wt% Au or 5wt% Pd and	
			bimetallic catalyst 5wt% Au-Pd supported TiO ₂	
			prepared using the impregnation technique	81
		5.1.2.2	Effect of prolonged reaction time on benzyl	
			alcohol oxidation using 5wt% (Au-Pd)/TiO ₂	
			catalyst prepared by impregnation technique	83
		5.1.2.3	Effect of catalyst pre-treatment on benzyl	
			alcohol oxidation using 5wt% (Au-Pd)/TiO ₂	~ -
			prepared by impregnation method	85
		5.1.2.4	Reusing the bimetallic Au-Pd catalyst supported	
		5105	on TiO ₂ prepared using impregnation	87
		5.1.2.5	Effect on He condition	89
		5.1.2.6	Catalyst using Carbon as support	90
		5.1.2.7	Effect of mono 5wt% Au/C, 5wt%Pd/C and	
			bimetallic 5wt%Au-Pd / C catalysts prepared	
			by using impregnation method on benzyl	0.0
		5100	alcohol oxidation	90
		5.1.2.8	Reaction of Benzyl Alcohol Oxidation using	
			Recycled 5wt% (Au-Pd) catalyst supported on	00
	10	C I I	carbon	92
5	.1.3	Catalyst s		93
		5.1.3.1	Benzyl alcohol oxidation in He and H_2	
			conditions using 5wt% (Au-Pd)/C prepared via	0.4
5.0	1.1.7	1	the impregnation method	94
			on Technique	95
5	.2.1	TiO_2 as su		95
		5.2.1.1	Effect of sol-immobilization preparation	
			technique of mono 1wt %Au or 1wt % Pd and	
			bimetallic 1wt%Au-Pd catalyst supported TiO ₂	05
		5 2 1 2	catalysts	95
		5.2.1.2	Time-online of benzyl alcohol oxidation for	
			1wt%(Au-Pd)/ TiO ₂ synthesized via sol-	00
		5 2 1 2	immobilisation technique	98
		5.2.1.3	Effect of catalyst pretreatment on benzyl	
			alcohol oxidation using 1wt% (Au-Pd)/TiO ₂	99
		5 2 1 4	prepared via sol immobilization	99
		5.2.1.4	Reusing the bimetallic 1 wt% Au-Pd catalyst	102
			supported on TiO ₂	102

		5.2.2	Carbon as	support	104
			5.2.2.1	Benzyl alcohol oxidation on mono 1wt %Au,	
				1wt %Pd and bimetallic catalyst 1wt%Au-Pd	
				supported carbon prepared via sol	104
			5 2 2 2	immobilization method	104
			5.2.2.2	Effect of Au:Pd/C metal ratio of of Au-Pd	
				bimetallic sol- catalyst on benzyl alcohol oxidation	105
			5 2 2 2		105
			5.2.2.3	Time on-line plot of benzyl alcohol oxidation for catalyst 1wt%Au-Pd supported carbon	
				prepared via sol immobilization method	107
			5.2.2.4	Reused the bimetallic catalyst 1 wt%Au-Pd	
				catalyst supported on carbon prepared via sol- immobilization method	100
	5.3	Onting	Tation Ta		109 111
	5.5	5.3.1		Produce More Benzaldehyde Product ent of Catalytic performance for conversion of	111
		5.5.1	-	ohol using 1wt%AuPd catalyst	
				carbon prepared via sol immobilization	
			technique	carbon prepared via sor miniounization	111
		5.3.2	Effect of o	vidante	111
		5.5.2	5.3.2.1	Effect of catalyst amount	112
			5.3.2.2	Effect of H_2O_2 ratio to benzyl alcohol	112
			5.5.2.2	oxidation using Au-Pd catalyst supported	
				carbon prepared by sol immobilization	
				technique	114
			5.3.2.3	Effect of temperature	115
			0101210		110
6	CON	TUSIC	N AND R	RECOMMENDATION	117
U	6.1	Conclu			117
	6.2			for future work	120
		Recom			120
REFE	RENC	ES			121
	NDICE				139
		F STUI	DENT		144
2100		- ~ • • •			

 \bigcirc

LIST OF TABLES

Table		Page
1.1	Chemical properties of benzaldehyde Chemical Properties http://en.wikipedia.org/wiki/Toluene)	6
2.1	Special features, advantages, and disadvantages of homo- and heterogeneous catalysts	15
2.2	Gold based catalysts supported on various supports for different chemical reactions	20
3.1	Chemicals brands and their purity	29
3.2	List of the gases used for the experimental works	30
3.3	GC-MS Column condition	40
3.4	Order of elution and retention for each product for benzyl alcohol reaction in liquid phase GC	41
3.5	GC-MS column method	42
4.1	Crystallite size of mono Au and bimetallic 5wt %(Au-Pd)/TiO ₂ catalysts synthesize by impregnation technique with various treatments	48
4.2	Crystallite sizes of 5wt% (Au-Pd) nanoparticle catalysts supported on different materials. All the catalysts were synthesized utilizing the impregnation technique and calcined in static air at 400 °C for 3 hours	52
4.3	EDX of (Au-Pd) catalyst prepared by sol-immobilisation and impregnation techniques supported TiO_2	56
4.4	EDX of (Au-Pd) catalyst prepared by sol-immobilisation and impregnation techniques supported carbon	56
4.5	The average particle sizes of the 1wt% (Au-Pd) catalysts supported by carbon prepared by sol immobilization.using different metal ratios of Au:Pd	68
4.6	BET analysis of 5wt% (Au-Pd) with various supports prepared using the impregnation technique, calcined in static air at 400 °C for 3 hrs	68
4.7	BET analysis of the $5wt\%$ (Au- Pd) /TiO ₂ catalyst prepared using the impregnation technique using various pretreatment processes	69

4.8	BET analysis of the 5wt% (Au-Pd)/ C catalyst prepared using the impregnation technique	69
4.9	BET analyses of 1wt% (Au-Pd) with titania and carbon supports prepared using the sol-immobilization technique and dried in air at 120 $^{\circ}\mathrm{C}$	70
4.1	0 The particle sizes and surface area of the 1wt%(Au-Pd) /C _{SI} catalyst prepared by sol immobilization at different metal ratios of Au:Pd	71
4.1	1 TPD-NH ₃ values of the different catalysts synthesized using the impregnation method	74
4.1	2 TPD-NH ₃ values of the different catalysts synthesized by sol immobilization method	76
5.1	Effect of temperature for blank reaction on benzyl alcohol at mild conditions (80 °C) using H_2O_2 as an oxidant, with a stirring rate of - 300 rpm for 4 hours	79
5.2	Oxidation of benzyl alcohol using only support at mild conditions (80 °C) with H_2O_2 as an oxidant, and a stirring rate of 300 rpm for 4 hours	79
5.3	Oxidation of benzyl alcohol utilizing $5wt\%$ AuPd of different supported catalyst prepared using the impregnation technique and H_2O_2 as an oxidant at 80°C, with a stirring rate of 300 rpm, for 4 hours	80
5.4	Oxidation of benzyl alcohol of mono and bimetallic $5wt\%$ (Au-Pd)/TiO ₂ catalysts synthesized using an impregnation method at mild conditions (80 °C) and H ₂ O ₂ as an oxidant with a stirring rate of 300 rpm	82
5.5	Time on-line profile for oxidation of benzyl alcohol using Au-Pd catalyst supported on TiO ₂ prepared by impregnation method at mild conditions (80 °C) utilizing H_2O_2 as an oxidant with a stirring rate of 300 rpm for 4 hours	84
5.6	Reaction of Benzyl Alcohol Oxidation using Recycled Catalyst $5wt\%(Au-Pd)/TiO_2$ prepared using the impregnation technique at mild conditions (80 °C) using H ₂ O ₂ as an oxidant, with a stirring rate of 300 rpm, for 4 hours	88
5.7	Oxidation of benzyl alcohol using 5wt% (Au-Pd)/TiO ₂ , prepared by	89

impregnation method, utilizing H_2O_2 as an oxidant at 80 °C, stirring rate -300 rpm, for 4 hrs

- Oxidation of benzyl alcohol using 5wt% (Au-Pd)/C prepared by 5.8 91 impregnation method at mild conditions (80 °C) using H_2O_2 as an oxidant, and a stirring rate of 300 rpm, for 4 hours 5.9 Reaction of Benzyl Alcohol Oxidation using Recycled Catalyst 5wt% 92 (Au-Pd)/C prepared using the impregnation technique with H_2O_2 as an oxidant at mild conditions (80 °C), and a stirring rate of 300 rpm, for 4 hours 5.10 Influence of the calcination temperature on leaching of gold and 94 palladium in 5wt% (Au-Pd) catalysts after reaction 5.11 Oxidation of benzyl alcohol using bimetallic 5wt% Au-Pd catalysts 95 supported on carbon prepared by impregnation utilizing H₂O₂ as an oxidant at 80 °C, and with a stirring rate of 300 rpm, for 4 hours Oxidation of benzyl alcohol using mono 1wt%Au/TiO2 5.12 97 ,1wt%Pd/TiO2, and 1wt%Au-Pd/TiO2 catalysts prepared by solimmobilization utilizing H_2O_2 as an oxidant, stirring rate -300 rpm,4 hours 5.13 Oxidation of benzyl alcohol using 1 wt%(Au-Pd)/TiO₂ synthesized 100 by the sol-immobilisation technique .Reaction conditions: $T = 80 \text{ }^{\circ}\text{C}$, , stirring rate -300 rpm for 4 hrs with various treatments at 250 °C, in H_2 , N_2 and air flow 5.14 Oxidation of benzyl alcohol for reused 1wt%AuPd / TiO₂ catalyst 103 synthesized by the sol-immobilization utilizing H₂O₂ as an at mild condition (80 °C), oxidant stirring rate-300 rpm for 4 hrs 5.15 Oxidation of benzyl alcohol on mono 1wt% Au, 1wt% Pd, and 105 bimetallic catalyst 1wt% Au-Pd supported on carbon prepared via the sol immobilization method using H_2O_2 as an oxidant at 80 °C, with a stirring rate of 300 rpm for 4 hours Oxidation of benzyl alcohol Au:Pd/C metal ratio 106 5.16of Au-Pd bimetallic sol- catalyst utilizing H₂O₂ as an oxidant at mild condition (80 °C), oxidant stirring rate -300 rpm for 4 hrs Time on-line profile, oxidation of benzyl alcohol using catalyst 1wt% 5.17 108 Au-Pd supported on carbon prepared by sol-immobilization method, utilizing H₂O₂ as an oxidant at mild conditions (80 °C), at an oxidant
 - 5.18 Reaction of Benzyl Alcohol Oxidation using Recycled 1wt%AuPd 110 catalyst supported on carbon prepared by the sol-immobilization at mild conditions (80 °C) using H2O2 as an oxidant with a stirring rate of 300 rpm for 4 hours

stirring rate of 300 rpm for 4 hours

5.19 Oxidation of benzyl alcohol 1wt%Au-Pd supported carbon 114 synthesized by sol-immobilization utilizing H₂O₂ as an oxidant at mild condition (80 °C). Reaction conditions T=80 °C, stirring rate - 300 rpm, 0.3g for 6 hrs



LIST OF FIGURES

Figure		Page
1.1	Oxidation reactions of benzyl alcohol (Li, 2006)	2
1.2	Condensation reaction between benzaldehyde and benzyl alcohol	3
1.3	Hemiacetal oxidation to the corresponding ester (Li G. a., 2006)	3
1.4	Formation of dibenzyl ether mechanism (Li G. a., 2006)	4
2.1	Particle size distributions for Au-Pd/TiO ₂ and Au-Pd/C catalysts prepared by standard wet impregnation, air dried (110 °C, 16 h) and calcined in static air (400 °C, 3 h) (Edwards J. K., 2008)	18
3.1	Stages of the impregnation preparation method for Au-Pd supported catalyst	31
3.2	Stages of the sol-immobilisation preparation method for1wt% (Au- Pd) supported catalys	32
3.3	Glass stirred round bottom flask	33
4.1	TGA profile recorded for 5wt% Pd /TiO ₂ , 5wt% Au /TiO ₂ and 5wt% (Au-Pd)/TiO ₂ prepared by impregnation technique, (dried at 110 °C)	44
4.2	TGA profile recorded for $1wt\%$ (Au-Pd)/TiO _{2 IM} (dried at 120 °C) prepared by sol immobilization techniques	45
4.3	X-ray diffraction patterns of mono and bimetallic $5wt\%$ (Au-Pd)/TiO _{2 IM} catalyst calcined in air at 400 °C. Key: a) $5wt\%$ Au, b) $5wt\%$ Au-Pd/TiO _{2 IM} , c) $5wt\%$ Pd	46
4.4	An enlargement of the X-ray diffraction pattern from Figure 4.3 revealed Au metallic and Au-Pd alloy peaks	46
4.5	X-ray diffractogram of the $5wt\%$ (Au-Pd)TiO ₂ catalysts synthesize by impregnation technique. Key: a) uncalcined, b) calcined at 400 °C for 4 hours, c) reduced in 5% hydrogen in argon at 400 °C for 3 hours	49
4.6	An enlargement of the XRD diffractogram for the: a) $5wt\%$ (Au-Pd)/TiO _{2 (IM)} catalyst synthesize by impregnation technique, dried at 110 °C for 16 hours, b) calcined at 400 °C for 3 hours, and c) reduced in 5% hydrogen in argon at 400 °C for 3 hours	50

	4.7	X-ray diffractogram of $5wt\%$ (Au-Pd) with various catalyst supports, calcined in static air at 400 °C for hours. Key: a) TiO ₂ , b) Carbon (G-60), c) ZrO ₂ , d) graphite	51
	4.8	X-ray diffractogram of the mono and bimetallic 1wt%Au/TiO ₂ , 1wt%Pd/TiO ₂ , 1wt%(Au-Pd)/TiO ₂ synthesized by the sol- immobilisation technique, dried at 120 °C for hours	53
	4.9	FESEM-EDX of the 5 wt% (Au-Pd) catalyst prepared by impregnation supported with a) TiO_2 and b) Carbon	54
	4.10	FESEM-EDX of the $5wt\%$ (Au-Pd) catalyst prepared by sol- immobilisation supported with; a) TiO ₂ and b) Carbon	55
	4.11	TEM images of the $5wt$ %Au/TiO _{2 IM} catalyst prepared by impregnation technique, dried at 110 °C	57
	4.12	TEM images of the 5wt%Au/TiO _{2 IM} catalyst prepared by impregnation technique, calcined at 400 °C	58
	4.13	TEM images of the 5wt%Pd/TiO ₂ catalyst prepared by impregnation technique, dried at 110 °C and calcined at 400 °C	58
	4.14	TEM images of the 5wt%(Au-Pd)/TiO ₂ catalyst prepared by the impregnation technique dried at 110 °C for 16 hrs	60
	4.15	TEM images of the 5wt%(Au-Pd)/TiO _{2 IM} catalyst prepared using the impregnation technique with calcination in air at 400 $^{\circ}$ C	61
	4.16	TEM images of the $5wt\%$ (Au-Pd)/TiO _{2 IM} catalyst prepared using the impregnation technique, reduced in 5% H ₂ /Ar at 400 °C	61
	4.17	TEM images of the 5 wt%(Au-Pd)/TiO _{2 IM} catalyst prepared by the impregnation technique, calcined at 400 °C after use	62
	4.18	TEM images of the 1wt%(Au-Pd)/TiO ₂ catalyst prepared by the sol- immobilization technique dried at 120 °C for 16 h	63
	4.19	TEM images of the $1wt\%(Au-Pd)/TiO_2$ catalyst prepared by the sol- immobilization technique reduced in $5\%H_2/Ar$ at 250 °C	64
	4.20	HRTEM micrograph and particle size distribution of the 1wt% Au metal prepared by sol immobilization	65
	4.21	HRTEM micrographs and particle size distribution of the colloidal metals prepared by sol immobilization using different metal ratios, Au:Pd (1:1, 1:2, 1:3, 1:7)	66

- 4.22 HRTEM micrographs and particle size distribution of the colloidal 67 metal prepared by sol immobilization using different metal ratios, Au:Pd (Pd only 2:1, 3:1, 7:1)
- 4.23 TPD-NH₃ profiles of the mono and bimetallic catalysts after 73 calcination in air for 4 hrs at 400 °C: (a) 5wt%Au/TiO_{2 IM}, (b) 5 wt%Pd/TiO_{2 IM}, (c) 5 wt% (Au-Pd)/TiO_{2 IM}
- 4.24 TPD-NH3 profiles of the mono and bimetallic catalysts after 73 calcination in air for 4 h at 400 °C: (a) 5 wt%Au/C IM, (b) 5wt%Pd/C IM, (c) 5wt%(Au-Pd)/C IM
- 4.25 TPD-NH₃ profiles of the mono and bimetallic catalysts: (a) 1wt% 75 Au/TiO_{2 SI}, (b) 1wt%Pd/TiO_{2 SI}, (c) 1wt%(Au-Pd)/TiO_{2 SI}
- 4.26 TPD-NH₃ profiles of the mono and bimetallic catalysts synthesized 75 by sol immobilization method: (a) 1wt% Au/C_{SI}, (b) 1wt%Pd/C_{SI}, (c) 1wt%(Au-Pd)/C_{SI}
- 4.27 TPD-NH₃ profiles of the bimetallic catalysts prepared by 76 impregnation and sol immobilization methods: (a) 5 wt%(Au-Pd)/C_{IM}, and (b) 1wt%(Au-Pd)/C_{SI}
- 4.28 UV-vis spectra of Au and the 1wt%(Au-Pd)/ TiO_{2 SI} catalyst 77 prepared by sol immobilization
- 5.1 Oxidation of benzyl alcohol using mono 5wt% Au/TiO₂, 5wt% 83 Pd/TiO₂, and bimetallic 5wt% AuPd supported catalysts prepared using impregnation method at mild conditions (80°C) with H₂O₂ as an oxidant and a stirring rate of 300 rpm for 4 hours
- 5.2 Time on-line plot of benzyl alcohol oxidation of 5wt% (Au-Pd)/TiO₂ catalyst prepared using the impregnation method. Reaction conditions: T = 80°C, ratio of benzyl alcohol:H₂O₂ (mol) = 1:0.1 with a stirring rate of 300 rpm, for 4 hours
- 5.3 Time-online plot of benzyl alcohol oxidation using 5wt% (Au-Pd)/TiO₂ catalyst prepared by the impregnation technique with flowing 5% H₂/Ar heat treatment. Reaction conditions: T = 80°C, ratio of benzyl alcohol (mol):H₂O₂ (mol) = 1:0.1 with a stirring rate of 300 rpm, for 4 hour
- 5.4 Reaction of benzyl alcohol oxidation using recycle catalyst 88 5wt%(Au-Pd)/TiO₂prepared by using eimpergnation technique at mild condition (80 ° C) using H₂O₂ as an oxidant, stirring rate -300 rpm, for 4 hrs

5.5	Oxidation of benzyl alcohol using 5 wt% (Au-Pd)/C prepared by impregnation method using H ₂ O ₂ as an oxidant at mild conditions (80°C), with a stirring rate of 300 rpm, for 4 hours	91
5.6	Reaction of Benzyl Alcohol Oxidation using Recycle Catalyst $5wt\%(Au-Pd)/C$ prepared using the impergnation technique using H_2O_2 as an oxidant at mild conditions (80°C), and a stirring rate of 300 rpm, for 4 hours	93
5.7	Oxidation of benzyl alcohol using mono $1wt\%Au/TiO_2$, $1wt\%Pd/TiO_2$ and $1wt\%Au-Pd/TiO_2$ catalysts synthesized via solimmobilisation technique using H_2O_2 as an oxidant. Reaction conditions: $T=80$ °°C, stirring rate -300 rpm for 4 hrs	98
5.8	Time-online plot of benzyl alcohol oxidation for $(1wt\%(Au-Pd)/TiO_2 \text{ prepared using sol immobilisationusing } H_2O_2 \text{ as oxidant.} Reaction conditions: T= 80 °C, stirring rate -300 rpm for 4 hrs$	99
5.9	(a) Conversion versus reaction time and (b) TOF vs. reaction time	102
5.10	Oxidation of benzyl alcohol using reused $1wt\%$ Au-Pd/TiO ₂ catalysts prepared by sol-immobilization using H ₂ O ₂ as an oxidant in mild conditions (80°C) at a stirring rate of 300 rpm, for 4 hours	104
5.11	Time on-line plot of benzyl alcohol oxidation using the bimetallic $(1wt\% (Au-Pd)/C_{SI})$ catalyst. Reaction conditions: benzyl alcohol 10 mL, T = 80°C, ratio of benzyl alcohol (mol): H ₂ O ₂ (mol) = 10:1	108
5.12	Time on-line profile, oxidation of benzyl alcohol using 1wt% Au-Pd catalyst supported on carbon prepared by sol-immobilization method, utilizing H_2O_2 as an oxidant at mild conditions (80°C), with an oxidant stirring rate of 300 rpm for 4 hours	109
5.13	Reaction of Benzyl Alcohol Oxidation using Recycled 1wt% AuPd catalyst supported on carbon prepared by the sol-immobilization using H_2O_2 as an oxidant at mild conditions (80 °C), with a stirring rate of 300 rpm for 4 hours	110
5.14	The effect of various oxidant on the conversion and selectivity of $1wt\%$ (Au- Pd/C _{SI}) catalyst using sol immobilization for benzyl alcohol oxidation reaction, as an oxidant at mild condition (80 °C), stirring rate -300 rpm for 6hrshrs	112
5.15	Effect of catalyst amount on the benzyl alcohol oxidation reaction, using $(1wt\% (Au-Pd)/C)$ catalyst synthesized using sol immobilization, H ₂ O ₂ as an oxidant at mild conditions. Reaction conditions: stirring rate of 300 rpm and T = 80°C	113

- 5.16 Effect of catalyst amount on benzyl alcohol oxidation reaction, using 113 $(1wt\%(Au-Pd)/C_{SI})$. Reaction conditions: T = 80°C, stirring rate of 300 rpm, 0.3 g catalyst for 6 hours
- 5.17 Effect of H_2O_2 ratio for benzyl alcohol oxidation using (1wt%Au-Pd/C_{SI}), synthesized by sol-immobilization utilizing H_2O_2 as an oxidant at mild condition (80 °C). Reaction conditions T=80 °C, stirring rate-300 rpm ,0.3g for 6 hrs
- 5.18 Effect of temperature on benzyl alcohol oxidation reaction using 116 $1wt\%(1Au-3Pd/C_{SI})$ synthesized by sol-immobilization utilizing H_2O_2 as an oxidant, reaction codition: ratio of benzyl alcohol (mol): H_2O_2 (mol) = 1:0.3 mL, catalyst amount=0.3 g ,stirring rate-300 rpm , reaction time= 6 hrs

LIST OF ABBREVIATIONS

H_2O_2	Hydrogen peroxide
HAuCl ₄	Chloroauric acid
PVA	Poly vinyl alcohol
NaBH ₄	Sodium tetrahydridoborate
STEM	Scanning transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
PdCl ₂	Palladium chlorid
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionisation detector
GC-MS	Gas chromatography mass spectrometry
XRD	X-ray diffraction analysis
HRTEM	High resolution transmission electron microscopy
BET	Brunauer–Emmett–Teller surface area measurement technique
AAS	Atomic absorption spectrophotometer
UV	UV- Visible spectroscopy
FESEM-EDS	Field emission scanning electron microscope-energy dispersive X-ray spectroscopy
TPD	Temperature-programmed desorption
TGA	Thermogravimetric analysis
TPDRO	Temperature programed desportion reduction- oxidation.

- TEM Transmission electron microscopy
- TBHP Tert-butyl hydroperoxide
- IM Impregnation preparation technique
- SI Sol-immobilization preparation technique



CHAPTER 1

INTRODUCTION

Benzyl Alcohol is an aromatic alcohol, of molecular formula $C_6H_5CH_2OH$ is a colourless liquid with а sharp burning taste and slight odor flavouring. The benzyl group is often abbreviated "Bn" (not to be confused with "Bz" which is used for benzoyl), thus benzyl alcohol is denoted as BnOH. Benzyl alcohol is a colorless liquid with a mild pleasant aromatic odor. It is a useful solvent due to its polarity. and low low toxicity, vapor pressure. Benzyl alcohol has moderate solubility in water (4 g/100 mL) and is miscible in alcohols and diethyl ether. The anion produced by deprotonation of the alcohol group is known as benzylate or benzyloxide.

1.1 Uses of benzyl alcohol

Several of its natural and synthetic esters have long been used in perfumery; the alcohol itself has become important in the second half of the 20th century as a developer booster in the processing of colour motion-picture film and as a dyeing assistant for filament nylons. Benzyl alcohol is manufactured by the hydrolysis of benzyl chloride in the presence of soda ash.

It is a precursor to a variety of esters used in the manufacture of soap, perfume, flavors & fragrances, and food additives. Benzyl alcohol is also useful as a degreasing agent, dyeing polyamide, and as a bonding aid. Pharmaceutical grade benzyl alcohol is used as a bacteriostatic and as a local anesthetic.

Benzyl alcohol used in a wide variety of cosmetic formulations as a fragrance component, preservative, solvent, and viscosity-decreasing agent. It is used as a local anesthetic and to reduce pain associated with Lidocaine injection. Also, it is used in the manufacture of other benzyl compounds, as a pharmaceutical aid, and in perfumery and flavoring.

1.2 Methods of Manufacturing benzyl alcohol

Firdt method by hydrolysis of benzyl chloride; second method from benzaldehyde by catalytic reduction or Cannizzaro reaction (Lewis, 2007).

Other processes for the production of benzyl alcohol include the hydrogenation of benzoic acid, the electrochemical reduction of benzoic acid, the hydrolysis of benzyl sulfonic acid, and the decarboxylation of benzyl formate. These processes have no importance in the industrial production of benzyl alcohol, but they may be used to produce derivatives substituted on the aromatic nucleus (In, 2003).

1.3 Possible mechanisms for benzyl alcohol oxidation reaction

Oxidation of benzyl alchohol leads to form various products (Li G. a., 2006). Benzaldehyde is formed at the beginning of the oxidation reaction, which is the main product in most oxidation reactions of benzyl alcohol. Continuing the oxidation reaction leads to the forming of benzoic acid (**Figure 1.1**) (Li, 2006).

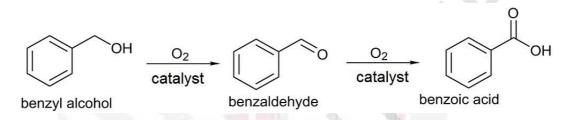


Figure 1.1 : Oxidation reactions of benzyl alcohol (Li, 2006)

According to Li et al. other by-products formed from the side reactions, where any of those by-products can be produce on the reaction settings and they used metal catalyst. Among the possible routes of the side reactions, the decarbonylation reaction leads to produce benzane. An additional possible route of the side reaction is the condensation reaction between benzyl alcohol and benzaldehyde, this reaction forms a hemiacetal, which is unsteady under the reaction conditions and is thereafter either oxidised to the corresponding ester (Figure 1.2) or, tracking the next condensation with a second molecule of alcohol, where that reaction also catalysed by the acid–basic sites of the catalysts, the latest condensation reaction leads to the formation of the corresponding dibenzyl acetal (Figure 1.2), (Figure 1.3) and (Figure 1.4) (Li G. a., 2006).

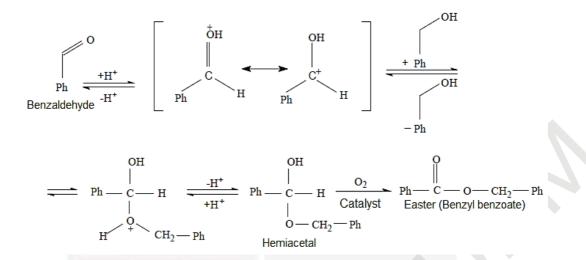


Figure 1.2 : Condensation reaction between benzaldehyde and benzyl alcohol

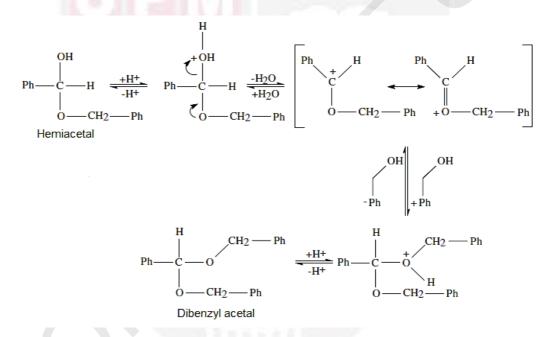


Figure 1.3 : Hemiacetal oxidation to the corresponding ester (Li G. a., 2006)

Another catalysed reaction by the acid–basic sites of the catalyst leads to generate dibenzylether (Figure 1.4).

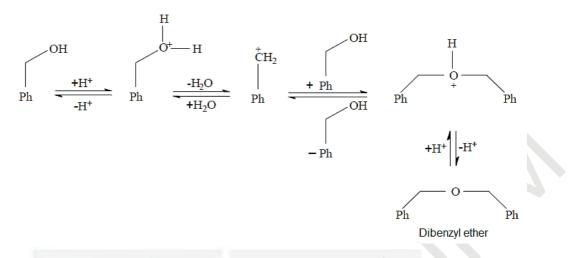


Figure 1.4 : Formation of dibenzyl ether mechanism (Li G. a., 2006)

1.4 Benzaldehyde

Raw materials are essential in the production or synthesis of other chemical compounds at commercial quantity. Chemical compounds such as benzene, alcohols, aldehydes and benzaldehyde are utilized in food, flavour and perfume industries. Some of these compounds are naturally occurring in nature. Nevertheless, the demand of these compounds as raw materials for the production various products at commercial scale supersedes the amount that occur naturally, and therefore, it is necessary to device sustainable techniques for their production. A number of techniques using catalytic process have so far been adopted for the production of various organic compounds such as toluene, alcohol and benzaldehyde.

Selective oxidation is one of the essential techniques employed for the production of various fine chemicals needed at commercial scale in food and beverage industry. Aldehydes are produced by the oxidation of primary alcohol in both laboratory and industrial scale (Enache D. I., 2006). Aldehydes are known as mutually valued as intermediary or high-valued component of the pharmaceutical and medical industries and in perfume production. The preparation of this type of oxidation usually employed oxygen providers such as chromate or permanganate. However, these reagents are not only costly but also dangerous toxic materials, which are harmful to the environment. Typically, aldehydes are obtained from activated alcohols in which the carbon bears a phenyl group, such as benzyl alcohol (Sheldon, 1981; Pillai U. R.-D., 2003; Griffith, 1991). In many previous interactions aldehydes were obtained only from the activation of alcohol in which the carbon carries a vinyl group. The common example of such alcohol is benzyl alcohol (Markó, 1996; Schultz, 2005).

Catalytic dual-phase system was used to convert pentan-1-ol to aldehyde in the first place and later results to the formation of acid when hexan-1-ol was utilized.

The production of such chemicals has faced many restrictions as a result of longer reaction period and low product yield. The development of heterogeneous catalysts using either O_2 or H_2O_2 as oxidants has reduced much of such drawbacks (Neumann, 1995).

Recent studies have proved that nanoparticles of metal support showed high effectiveness as catalysts for the oxidation of alcohol to aldehydes when oxygen is utilized under relatively mild reaction conditions. According to Kaneda and his work team (Mori, 2004) the hydroxyapatite-supported by palladium Nano-clusters (Pd / HAP) showed higher turnover frequencies (TOFs) for phenyl-ethanol and alcohols oxidation such as octan-1-ol oxidation. Coma and his work team (Abad A. C., 2005), revealed that it is possible to convert the CeO₂ oxide from a stoichiometry oxidant to a catalytic system when Au Nano crystals is added, thereby promoting the earlier findings of Kaneda and co-workers (Mori, 2004), with similar TOFs.

1.4.1 Chemical and physical properties of benzaldehyde

Selective oxidation reaction process of aromatic hydrocarbon compounds to produce important chemicals at commercial scale maintains to be a major task for the chemical industries to date (Thomas J. M., 1999; Stahl, 2004; Limberg, 2003; Sadow, 2003). Recently, researchers all over the world have focussed their researcher work in developing new catalysts that are capable of catalysing the oxidation process of such hydrocarbon compounds to obtain their corresponding by-products. Benzaldehyde is one of the most important substrates currently attracting research interest in industry and academia. Benzaldehyde is one of the organic compounds made up of a benzene ring and a substituent. Benzaldehyde is considered as the simplest aromatic compound (aldehyde) and one of the most useful industrially. Benzaldehyde also known as benzene carbaldehyde, phenyl methanol or Benzoic aldehyde is a mono substituted benzene derivative in which the single hydrogen atom from benzene is replaced by – COH (RA Sheldon and H. van Bekkum, 2001).

Benzaldehyde is also a representative of aromatic hydrocarbons categorized as hazardous material (U.S E Protection, 1999). Therefore, the development of better methods for the oxidation of aromatics such as benzaldehyde is necessary for environmental reasons.

5

Molecular formula	C7H6O or C6H5CHO	
Molar Mass	106.124 g/mol	
Appearances	Colourless liquid and strongly refractive	
Density	1.044 g/mL, Liquid	
Melting points	-57.12 °C	
Boiling Points	178.1 °C	
Solubility in water	3 g/L (20 °C)	

Table 1.1 : Chemical properties of benzaldehyde Chemical Propertieshttp://en.wikipedia.org/wiki/Toluene)

1.4.2 Uses of benzaldehyde

Benzaldehyde is usually used to confer almond flavours to food and other related scented products. Benzaldehyde like many aromatic compounds is employed in the production of cosmetics (Andersen, 2006). Industrially, benzaldehyde is utilized chiefly as a precursor to various organic compounds such as chemical intermediate in the manufacture of dyes, pharmaceuticals, perfumes and flavouring chemicals. Others include plastic additives, precursor in the preparation of aniline dye malachite green, cinnamaldehyde and styrene.

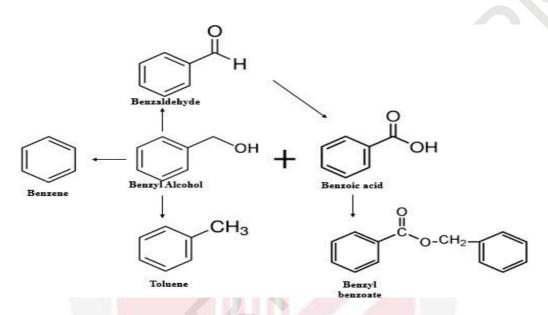
1.4.3 Manufacture benzaldehyde

Benzaldehyde is the major product of interest in this study, as a result of its high demand in the present chemical industries practices. Benzaldehyde is found to be one of the most needed chemical compounds used as raw materials for the preparation of many useful compounds at industrial scale. Benzaldehyde is currently produced by various chemical processes both at laboratory and industrial scale. The main routes used for its preparation are oxidation of toluene and liquid phase chlorination. Other routes that were developed include partial oxidation of benzyl alcohol, alkali hydrolysis of benzyl chloride and the carbonylation of benzene (Brühne, F., & Wright, E., 2002).



About 7000 tonnes of synthetic benzaldehyde and 100 tonnes of natural benzaldehyde were reported to be produced annually as of 1999. The significant amount of natural benzaldehyde is synthesized from cinnamaldehyde obtained from cassia oil using retro-aldol reaction (Passos, Maria Laura.,et. al, 2009). During the reaction process, the cinnamaldehyde is subjected to heating in aqueous/alcoholic solution at a temperature of 90 and 150 °C with base for a period of 5 to 80 h (Wiener & Charles & Alan , 1986) and the produced benzaldehyde will undergo distillation process.

In gas phase oxidation process of toluene, the contact time might be decreased and therefore the oxidation of benzaldehyde might be reduced so that high selectivity to benzaldehyde may be achieved (Centi & et. al, 2000; Larrondo & et. al, 2001). Nevertheless, there is no commercial plants for the production of benzaldehyde from the oxidation of toluene by air in gas phase that are currently available due to the low activity/ and or selectivity. Studies are currently on-going to develop proper catalysts for the improved catalytic behaviour towards benzaldehyde production (Xue & et. al, 2009). The main mechanism for the production of benzaldehyde is depicted in scheme 1.1



Scheme 1.1 : Mechanism for the production of benzaldehyde and other compounds

1.5 Catalysis

Catalysis can be defined as an important technology for accelerating rate of chemical reactions/conversions. It recognises the environmentally benign and commercially feasible chemical reactions that are used to transform energy carriers to more useful energy form. Moreover, Nano-catalysts, besides decreasing the activation energy of the reaction, which eventually reduce the total input energy required for reaction processes but also advances two major considerable catalysts properties i.e thermal stability and selectivity and therefore, resulting to ecologically friendly catalytic system.

Recently, Nano-materials are reported to be used as Nano-catalysts, which are used in the range of liquid and solid catalysis applications. Meanwhile, solid catalysts are classified as one of the previously used catalysts at industrial scale for main chemical processes (Serrano *et al.*, 2009; Zäch*et al.*, 2006). Thus *catalysis play a fundamental role in the improvement of sustainable reactions, which are principal to allow the*

present and future, universal production of energy and chemicals while avoiding harmful consequences to the surrounding environment and has demonstrated the meaning of the key technology. Synthesis of ammonia and methyl alcohol are some of the few industrial operations that currently employ catalysis technology.

Both ammonia and methyl alcohol synthesis at commercial scale attain the development of the water-gas shift process and solid catalysis. About \$900 billion dollars were reported to be generated through the chemical products manufacturing world-wide, which account for about 85-90% of the out-put (Robertson, 1970).

1.6 Gold history

The earliest discovering was done by Dulong and Thenard in 1823, who they discovered gold as one of the metals that have the ability to catalysed the ammonia decomposition; this could possibly be the earliest mention to the fact which is gold not all the time showing weak activities. Michael Faraday In 1834, made the reaction of hydrogen with oxygen by using gold catalysed at room temperature. In 1861, for the first time Thomas Graham noticed through investigations the gold effects on the solubility of hydrogen in palladium.

In 1906 Faraday reaction was carried out again to study of the oxidation of hydrogen using gold gauze (Nikolaeva, 2014). In 1925, gold powder approved as an effective catalyst (Chapman, 1925). Later, the first report was published explaining the CO oxidation using gold gauze. Also, at that time it had been noted that gold have minor action for ethane hydrogenation (Benton, 1927). In 1973, Bond and the research team were able successfully in catalyse the process of hydrogenation of alkenes and alkynes using gold in small particles scattered on SiO₂ or Al₂O₃. So they approved for the first time that gold has the ability to be a remarkable active catalyst when dispersed in the form of nanoparticles (Bond G. C., 1973).

The practical proof of the fact that nano-particulate gold could be the optimal catalyst for some reactions came from Hutchings and his team, who they estimated that gold could be the highest active catalyst for etheylene hydrochlorination proscess (Hutchings G. J., Vapor Phase l-lydrochlorination of Acetylene: Correlation of Catalytic Activity of Supported Metal Chloride Catalysts, 1985), and Haruta found also, the full activity of catalysts when supported by gold, especially for CO oxidation process at low temperature. Thereafter, the nanoparticles of gold catalysts had attracted considerable interest because of the amazing characteristics (Haruta M. a., 1989).



A unique work has been developed in many studies on improving the catalysis with gold. Only in the late 1990's Prati discovered that gold could be a catalyst for alcohol oxidation (Prati L. a., 1998). It was proved that, unlike Pt/C and Pd/C that can oxidise alcohol independently of the solution pH, a base was required for activity with Au/C.

1.7 Problem statement

Organic compounds such as toluene, benzoic acid and benzaldehyde are among the most important fine chemicals needed as either a raw materials or intermediates in the production process of many flavours, food, beverages and cosmetics. Although such organic compounds/materials can occur naturally, yet their production in commercial scale is necessary for varieties of industrial applications. Oxidation of alcohols, particularly primary alcohols is considered as one of the important methods for the conversion of such organic compounds to their corresponding carbonyl carbon compounds. A lot of techniques have been proven positive for such transformations. However, most of the reported earlier research employed conservative technique, which adopted the oxidation process performed with stoichiometric amounts of inorganic oxidants and notably chromium (VI) reagents (Cardillo, 2012; Pillai U. R.-D., 2003).

One of the major drawbacks of such oxidants is that apart from being relatively expensive, the oxidants also generate plentiful amounts of heavy-metal waste product. Moreover, the oxidation reaction process has demonstrated to be carried out using some environmentally unwanted solvents, typically chlorinated hydrocarbons, which led to production of more toxic waste. A wide variety of metal and non-metal-based stoichiometric reagents have been reported to be employed for the oxidation of primary alcohols to their corresponding aldehydes.

Considering the environmental effects of the utilization of conventional techniques, oxidants, solvents and catalysts for the oxidation/selective oxidation of alcohols to corresponding aldehydes, it has become necessary to device more environmental benign methods for such processes. Thus, the development of greener oxidation systems using less poisonous catalysts, less toxic oxidants and solvents become a vital aim for this study. Hydrogen peroxide is considered as one of the most perfect candidates as an environmentally friendly oxidant for selective oxidation reaction of alcohol. There are some few selective oxidation reactions that were reported to utilize molecular oxygen as an oxidant. Nevertheless, the selectivity of the reaction was found to be poor and therefore, the process can only be achieved if the stoichiometric oxygen donor such as manganates or any activated form of oxygen such as tert-butyl hydro peroxide is employed. As a result of the aforementioned problems associated to conservative oxidation reaction processes, there is need for the new catalytic routes that utilize less harmful oxidants especially H_2O_2 , which produces only water as the reaction by-products and therefore harmless to the environment.

Homogeneous catalysts were reported to have excellent activity in the oxidation reaction of alcohols and many other reaction processes. However, such catalysts have displayed many disadvantages, which include difficulty in separation after use and polluting the environment during water washing. Heterogeneous catalysts system was recently reported to be excellent in the oxidation reaction of alcohols to their corresponding carbonyl compounds. This study will employ metal oxides in mono and bimetallic form supported on transition metal oxides and carbon based supports for the selective oxidation of primary alcohol to benzaldehyde using hydrogen peroxide as an oxidant under mild reaction conditions. Typically, gold-palladium nanoparticle supported on titanium oxide and carbon catalysts are employed for this study.

1.7.1 Scope of the study

The scope of research is limited to the synthesise of mono Au,Pd and bimetallic Au-Pd catalyst using sol immobilization and impregnation methods by utilizing different supports of TiO_2 and activated carbon and characterization of the catalyst. Moreover, attention has been paid to the preparation of gold based catalysts in order to assess the relation between support/active metal, preparation method the catalysts characterisation (XRD, TEM, HRTEM, TGA, BET, and TPD).

The catalysts characterizations will help to study the composition, acidity/basicity and surface morphology of the synthesised gold Nano-particles catalyst. The studies will help to greatly modify the activity and/or the selectivity of the whole catalyst. The aim of this study is to produce benzaldehyde from benzyl alcohol using suitable gold base catalysts synthesized from a suitable preparation technique. The synthesized catalysts were examined in the oxidation reaction of benzyl alcohol in the presence of hydrogen peroxides as the oxidant.

The contribution of this study is that the hydrogen peroxide was employed as an oxidant for the benzyl alcohol oxidation. This is because of its environmental benign, water being the only chemical by-product; on the other hand, the water is actually used as a process solvent, so the reactions are of general interest due to their potential in combinational chemistry, simple processes, easy work-up, low cost and reduction in harmful waste materials. This study mainly focuses on the selective oxidation of benzyl alcohol to benzaldehyde by using hydrogen peroxide as a green oxidant.

1.8 Objectives of the research

The main objectives of the study are:

- To synthesize mono gold, palladium and bimetallic gold-palladium supported titanium oxide and carbon via different impregnation and sol immobilization.
- To characterize the catalysts using Thermogravimetry Analysis (TGA), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), High-Resolution Transmission Electron Microscope (HRTEM) and Temperature Programmed Desorption (TPD)
- To study the oxidation of benzyl alcohol using prepared catalyst and H_2O_2 as an oxidant for the conversion and selectivity to benzaldehyde.
- To optimize the conditions based on effect of the oxidants, amount of the catalyst, different loading H₂O₂ as an oxidant and different temperature) towards enhance conversation and selectivity of benzyl alcohol oxidation.



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(26), 4066-4069.
- Abdelrazek, E., Elashmawi, I., El-Khodary, A., & Yassin, A. (2010). Structural, optical, thermal and electrical studies on PVA/PVP blends filled with lithium bromide. *Current Applied Physics*, 10(2), 607-613.
- Aldbea, F. W., Ibrahim, N., Abdullah, M. H., & Shaiboub, R. E. (2012). Structural and magnetic properties of Tb x Y 3-x Fe 5 O 12 ($0 \le x \le 0.8$) thin film prepared via sol-gel method. *Journal of sol-gel science and technology*, 62(3), 483-489.
- Amenomiya, Y., & Cvetanovic, R. (1963). Application of flash-desorption method to catalyst studies. I. Ethylene—alumina system1. *The Journal of Physical Chemistry*, 67(1), 144-147.
- Astruc, D., Lu, F., & Aranzaes, J. R. (2005). Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. *Angewandte Chemie International Edition*, 44(48), 7852-7872.
- Auer, E., Freund, A., Pietsch, J., & Tacke, T. (1998). Carbons as supports for industrial precious metal catalysts. *Applied Catalysis A: General*, 173(2), 259-271.
- Bagheri, S., Muhd Julkapli, N., & Bee Abd Hamid, S. (2014). Titanium dioxide as a catalyst support in heterogeneous catalysis. *The Scientific World Journal*, 2014.
- Behera, G. C., & Parida, K. (2012). Liquid phase catalytic oxidation of benzyl alcohol to benzaldehyde over vanadium phosphate catalyst. *Applied Catalysis A: General, 413,* 245-253.

Berzelius J.J. (1836). Edinburgh New Philosophical Journa, 21..

- Benton, A. F., & Elgin, J. C. (1927). THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC GOLD1. *Journal of the American Chemical Society, 49*(10), 2426-2438.
- Besson, M., & Gallezot, P. (2000). Selective oxidation of alcohols and aldehydes on metal catalysts. *Catalysis today*, *57*(1-2), 127-141.
- Bianchi, C., Porta, F., Prati, L., & Rossi, M. (2000). Selective liquid phase oxidation using gold catalysts. *Topics in Catalysis, 13*(3), 231-236.

- Bianchi, C. L., Canton, P., Dimitratos, N., Porta, F., & Prati, L. (2005). Selective oxidation of glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals. *Catalysis today*, 102, 203-212.
- bin Saiman, M. I., Brett, G. L., Tiruvalam, R., Forde, M. M., Sharples, K., Thetford, A., . . . Murphy, D. M. (2012). Involvement of surface- bound radicals in the oxidation of toluene using supported Au- Pd nanoparticles. *Angewandte Chemie International Edition*, 51(24), 5981-5985.
- Bond, G., Atkins, P., Holker, J., & Holliday, A. (1987). Heterogeneous Catalysis: Principles and Applications, Clarendon: Oxford.
- Bond, G., & Sermon, P. (1973). Gold catalysts for olefin hydrogenation. Gold Bulletin, 6(4), 102-105.
- Bond, G. C., Louis, C., & Thompson, D. T. (2006). *Catalysis by gold* (Vol. 6): World Scientific.
- Bonino, F., Damin, A., Ricchiardi, G., Ricci, M., Spanò, G., D'Aloisio, R., ... Bordiga, S. (2004). Ti-peroxo species in the TS-1/H2O2/H2O system. *The Journal of Physical Chemistry B*, 108(11), 3573-3583.
- Bowker, M. (1998). The basis and applications of heterogeneous catalysis. Oxford Chemistry Primers, 53(1), ALL-ALL.
- Briggs, D. (1990). Practical surface analysis. Auger and X-Ray Photoelecton Spectroscory, 1, 151-152.
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2), 309-319.
- Campanati, M., Fornasari, G., & Vaccari, A. (2003). Fundamentals in the preparation of heterogeneous catalysts. *Catalysis today*, 77(4), 299-314.
- Carlson, T. (1978). X-ray Photoelectron Spectroscopy, Dowden, Hutchinson & Ross. *Inc., Stroudsburg.*
- Carrettin, S., McMorn, P., Johnston, P., Griffin, K., & Hutchings, G. J. (2002). Selective oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide. *Chemical Communications*(7), 696-697.
- Carrettin, S., McMorn, P., Johnston, P., Griffin, K., Kiely, C. J., & Hutchings, G. J. (2003). Oxidation of glycerol using supported Pt, Pd and Au catalysts. *Physical Chemistry Chemical Physics*, 5(6), 1329-1336.

- Centeno, M. A., Ramírez Reina, T., Ivanova, S., Laguna, O. H., & Odriozola, J. A. (2016). Au/CeO2 catalysts: Structure and CO oxidation activity. *Catalysts*, *6*(10), 158.
- Chapman, D., Ramsbottom, J., & CG Trotman, B. (1925). *The union of hydrogen and oxygen in presence of silver and gold*. Paper presented at the Proc. R. Soc. Lond. A.
- Chorkendorff, I., & Niemantsverdriet, J. W. (2017). *Concepts of modern catalysis and kinetics*: John Wiley & Sons.
- Choudhary, V., Dumbre, D., Narkhede, V., & Jana, S. (2003). Solvent-Free Selective Oxidation of Benzyl Alcohol and Benzaldehyde by tert-Butyl Hydroperoxide Using MnO-4-Exchanged Mg–Al–Hydrotalcite Catalysts. *Catalysis letters*, 86(4), 229-233.
- Choudhary, V., Dumbre, D., Uphade, B., & Narkhede, V. (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*(1-2), 129-135.
- Choudhary, V. R., Dhar, A., Jana, P., Jha, R., & Uphade, B. S. (2005). A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst. *Green Chemistry*, 7(11), 768-770.
- Choudhary, V. R., & Dumbre, D. K. (2011). Solvent-free selective oxidation of primary alcohols-to-aldehydes and aldehydes-to-carboxylic acids by molecular oxygen over MgO-supported nano-gold catalyst. *Catalysis Communications, 13*(1), 82-86.
- Choudhary, V. R., Jha, R., & Jana, P. (2007). Solvent-free selective oxidation of benzyl alcohol by molecular oxygen over uranium oxide supported nano-gold catalyst for the production of chlorine-free benzaldehyde. *Green Chemistry*, 9(3), 267-272.
- Comotti, M., Li, W.-C., Spliethoff, B., & Schüth, F. (2006). Support effect in high activity gold catalysts for CO oxidation. *Journal of the American Chemical Society*, 128(3), 917-924.
- Corma, A., Palomares, A., & Márquez, F. (1997). Determining the Nature of the Active Sites of Cu-Beta Zeolites for the Selective Catalytic Reduction (SCR) of NOxby Using a Coupled Reaction-XAES/XPS Study. *Journal of Catalysis*, *170*(1), 132-139.

- Corti, C. W., Holliday, R. J., & Thompson, D. T. (2002). Developing new industrial applications for gold: gold nanotechnology. *Gold Bulletin*, 35(4), 111-117.
- Deki, S., Akamatsu, K., Hatakenaka, Y., Mizuhata, M., & Kajinami, A. (1999). Synthesis and characterization of nano-sized gold-palladium bimetallic particles dispersed in polymer thin film matrix. *Nanostructured materials*, 11(1), 59-65.
- Delannoy, L., El Hassan, N., Musi, A., Le To, N. N., Krafft, J.-M., & Louis, C. (2006). Preparation of supported gold nanoparticles by a modified incipient wetness impregnation method. *The Journal of Physical Chemistry B*, 110(45), 22471-22478.
- Della Pina, C., Falletta, E., & Rossi, M. (2008). Highly selective oxidation of benzyl alcohol to benzaldehyde catalyzed by bimetallic gold–copper catalyst. *Journal of Catalysis, 260*(2), 384-386.
- Demirel, S., Lehnert, K., Lucas, M., & Claus, P. (2007). Use of renewables for the production of chemicals: Glycerol oxidation over carbon supported gold catalysts. *Applied Catalysis B: Environmental*, 70(1-4), 637-643.
- Dimitratos, N., Edwards, J. K., Kiely, C. J., & Hutchings, G. J. (2012). Gold catalysis: helping create a sustainable future. *Applied Petrochemical Research*, 2(1-2), 7-14.
- Dimitratos, N., Lopez-Sanchez, J. A., Anthonykutty, J. M., Brett, G., Carley, A. F., Tiruvalam, R. C., . . . Hutchings, G. J. (2009). Oxidation of glycerol using gold–palladium alloy-supported nanocrystals. *Physical Chemistry Chemical Physics*, 11(25), 4952-4961.
- 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(3-4), 317-324.
- 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*, 11(25), 5142-5153.
- Dimitratos, N., Villa, A., Wang, D., Porta, F., Su, D., & Prati, L. (2006). Pd and Pt catalysts modified by alloying with Au in the selective oxidation of alcohols. *Journal of Catalysis, 244*(1), 113-121.
- D. Kealey P. J. H . (2002). Instant notes: Analytical Chemistry. BIOS Scientific Publishers Limited: Oxford.

- Dobrzeniecka, A., & Kulesza, P. J. (2013). Electrocatalytic Activity toward Oxygen Reduction of RuSxNy Catalysts Supported on Different Nanostructured Carbon Carriers. *ECS Journal of Solid State Science and Technology*, 2(12), M61-M66.
- Duff, D. G., Baiker, A., & Edwards, P. P. (1993). A new hydrosol of gold clusters. Journal of the Chemical Society, Chemical Communications(1), 96-98.
- Edwards, J. K., Carley, A. F., Herzing, A. A., Kiely, C. J., & Hutchings, G. J. (2008). Direct synthesis of hydrogen peroxide from H 2 and O 2 using supported Au– Pd catalysts. *Faraday Discussions*, *138*, 225-239.
- Edwards, J. K., Ntainjua, 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.
- Edwards, J. K., Solsona, B., Ntainjua, E., Carley, A. F., Herzing, A. A., Kiely, C. J., & Hutchings, G. J. (2009). Switching off hydrogen peroxide hydrogenation in the direct synthesis process. *Science*, *323*(5917), 1037-1041.
- 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*(1), 69-79.
- Edwards, J. K., Thomas, A., Solsona, B. E., Landon, P., Carley, A. F., & Hutchings, G. J. (2007). Comparison of supports for the direct synthesis of hydrogen peroxide from H2 and O2 using Au–Pd catalysts. *Catalysis today*, 122(3-4), 397-402.
- Elnashaie, S. S., Danafar, F., & Rafsanjani, H. H. (2015). Nanotechnology for chemical engineers: Springer.
- Enache, D. I., Barker, D., Edwards, J. K., Taylor, S. H., Knight, D. W., Carley, A. F., & Hutchings, G. J. (2007). Solvent-free oxidation of benzyl alcohol using titania-supported gold–palladium catalysts: effect of Au–Pd ratio on catalytic performance. *Catalysis today*, *122*(3-4), 407-411.
- 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*(5759), 362-365.
- 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*(1-2), 43-52.

- Eschemann, T. O., Bitter, J. H., & De Jong, K. P. (2014). Effects of loading and synthesis method of titania-supported cobalt catalysts for Fischer–Tropsch synthesis. *Catalysis today*, 228, 89-95.
- Fang, W., Zhang, Q., Chen, J., Deng, W., & Wang, Y. (2010). Gold nanoparticles on hydrotalcites as efficient catalysts for oxidant-free dehydrogenation of alcohols. *Chemical Communications*, 46(9), 1547-1549.
- Fang, Y.-L., Miller, J. T., Guo, N., Heck, K. N., Alvarez, P. J., & Wong, M. S. (2011). Structural analysis of palladium-decorated gold nanoparticles as colloidal bimetallic catalysts. *Catalysis today*, 160(1), 96-102.
- Ferrari, L., Kaufmann, J., Winnefeld, F., & Plank, J. (2010). Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements. *Journal of Colloid and Interface Science*, 347(1), 15-24.
- Griffith, W., & Jolliffe, J. (1991). Ruthenium and osmium carboxylato oxo complexes as organic oxidants *Studies in Surface Science and Catalysis* (Vol. 66, pp. 395-400): Elsevier.

Grunwald, P. (2014). Industrial biocatalysis (Vol. 1): CRC Press.

- Grunwaldt, J.-D., Kiener, C., Wögerbauer, C., & Baiker, A. (1999). Preparation of supported gold catalysts for low-temperature CO oxidation via "size-controlled" gold colloids. *Journal of Catalysis, 181*(2), 223-232.
- Guczi, L., Beck, A., & Pászti, Z. (2012). Gold catalysis: Effect of particle size on reactivity towards various substrates. *Catalysis today*, 181(1), 26-32.

Hagen, J. (2015). Industrial catalysis: a practical approach: John Wiley & Sons.

- Han, Y.-F., Zhong, Z., Ramesh, K., Chen, F., Chen, L., White, T., ... Wang, Z. (2007).
 Au Promotional Effects on the Synthesis of H2O2 directly from H2 and O2 on supported Pd– Au Alloy Catalysts. *The Journal of Physical Chemistry C*, 111(24), 8410-8413.
- 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., Yamada, N., Kobayashi, T., & Iijima, S. (1989). Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide. *Journal of Catalysis, 115*(2), 301-309.
- He, Y., Ma, X., & Lu, M. (2012). Oxidation of alcohols with hydrogen peroxide in the presence of a new triple-site phosphotungstate. *Arkivoc*, *8*, 187-197.

Henry W. (1825). Philosophical Magazine, 65.

- Hüfner, S. (2013). *Photoelectron spectroscopy: principles and applications*: Springer Science & Business Media.
- Hutchings, G. J. (1985). Vapor phase hydrochlorination of acetylene: Correlation of catalytic activity of supported metal chloride catalysts. *Journal of Catalysis*, *96*(1), 292-295.
- Hutchings, G. J. (2008). Nanocrystalline gold and gold palladium alloy catalysts for chemical synthesis. *Chemical Communications*(10), 1148-1164.
- Hutchings, G. J., & Kiely, C. J. (2013). Strategies for the synthesis of supported gold palladium nanoparticles with controlled morphology and composition. *Accounts of chemical research*, 46(8), 1759-1772.
- Imelik, B., & Vedrine, J. C. (2013). *Catalyst characterization: physical techniques for solid materials*: Springer Science & Business Media.
- Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T., & Ogawa, M. (1988). Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride. Epoxidation of olefins and allylic alcohols, ketonization of alcohols and diols, and oxidative cleavage of 1, 2-diols and olefins. *The Journal of Organic Chemistry*, 53(15), 3587-3593.
- Kakuma, Y., Nosaka, A. Y., & Nosaka, Y. (2015). Difference in TiO 2 photocatalytic mechanism between rutile and anatase studied by the detection of active oxygen and surface species in water. *Physical Chemistry Chemical Physics*, 17(28), 18691-18698.
- Kent, P. D., Mondloch, J. E., & Finke, R. G. (2014). A Four-Step Mechanism for the Formation of Supported-Nanoparticle Heterogenous Catalysts in Contact with Solution: The Conversion of Ir (1, 5-COD) Cl/γ-Al2O3 to Ir (0)~ 170/γ-Al2O3. Journal of the American Chemical Society, 136(5), 1930-1941.
- Kesavan, L., Tiruvalam, R., Ab Rahim, M. H., bin Saiman, M. I., Enache, D. I., Jenkins, R. L., . . . Knight, D. W. (2011). Solvent-free oxidation of primary carbon-hydrogen bonds in toluene using Au-Pd alloy nanoparticles. *Science*, 331(6014), 195-199.
- Kotai, L., Kazinczy, B., Keszler, Á., Holly, S., Gács, I., & Banerji, K. K. (2001). Three reagents in one: Ammonium permanganate in the oxidation of benzyl alcohol. *Zeitschrift für Naturforschung B*, 56(8), 823-825.

- Landers, J., Gor, G. Y., & Neimark, A. V. (2013). Density functional theory methods for characterization of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 437, 3-32.
- Landon, P., Collier, P. J., Papworth, A. J., Kiely, C. J., & Hutchings, G. J. (2002). Direct formation of hydrogen peroxide from H 2/O 2 using a gold catalyst. *Chemical Communications*(18), 2058-2059.
- Lawrence, M., & Jiang, Y. (2017). Porosity, pore size distribution, micro-structure *Bio-aggregates Based Building Materials* (pp. 39-71): Springer.
- Lee, D. G., & Spitzer, U. A. (1970). Aqueous dichromate oxidation of primary alcohols. *The Journal of Organic Chemistry*, 35(10), 3589-3590.
- Li, G., Enache, D. I., Edwards, J., Carley, A. F., Knight, D. W., & Hutchings, G. J. (2006). Solvent-free oxidation of benzyl alcohol with oxygen using zeolitesupported Au an Au–Pd catalysts. *Catalysis letters*, 110(1-2), 7-13.
- Li, J., Staykov, A., Ishihara, d T., & Yoshizawa, K. (2011). Theoretical study of the decomposition and hydrogenation of H2O2 on Pd and Au@ Pd surfaces: understanding toward high selectivity of H2O2 synthesis. *The Journal of Physical Chemistry C*, 115(15), 7392-7398.
- Link, S., & El-Sayed, M. A. (1999). Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles. *The Journal of Physical Chemistry B*, 103(21), 4212-4217.
- L.J. Thénard . (1818). Observation on combinations, new between oxygen and various acids. *Annales de chimie et de physique*, 9.
- Lowell, S., Shields, J. E., Thomas, M. A., & Thommes, M. (2012). *Characterization* of porous solids and powders: surface area, pore size and density (Vol. 16): Springer Science & Business Media.
- Lopez-Sanchez, J. A., Dimitratos, N., Hammond, C., Brett, G. L., Kesavan, L., White, S., . . . Carley, A. F. (2011). Facile removal of stabilizer-ligands from supported gold nanoparticles. *Nature Chemistry*, *3*(7), 551.
- Maksimchuk, N., Melgunov, M., Chesalov, Y. A., Mrowiec-Białoń, J., Jarzębski, A., & Kholdeeva, O. (2007). Aerobic oxidations of α-pinene over cobaltsubstituted polyoxometalate supported on amino-modified mesoporous silicates. *Journal of Catalysis, 246*(2), 241-248.

- Menard, L. D., Xu, F., Nuzzo, R. G., & Yang, J. C. (2006). Preparation of TiO2supported Au nanoparticle catalysts from a Au13 cluster precursor: Ligand removal using ozone exposure versus a rapid thermal treatment. *Journal of Catalysis, 243*(1), 64-73. Mallat, T., & Baiker, A. (1994). Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions. *Catalysis today, 19*(2), 247-283.
- Markó, I. E., Giles, P. R., Tsukazaki, M., Brown, S. M., & Urch, C. J. (1996). Coppercatalyzed oxidation of alcohols to aldehydes and ketones: an efficient, aerobic alternative. *Science*, 274(5295), 2044-2046.
- Martin, S. E., & Garrone, A. (2003). Efficient solvent-free iron (III) catalyzed oxidation of alcohols by hydrogen peroxide. *Tetrahedron Letters*, 44(3), 549-552.
- Matsumoto, T., Ueno, M., Wang, N., & Kobayashi, S. (2008). Recent advances in immobilized metal catalysts for environmentally benign oxidation of alcohols. *Chemistry–An Asian Journal*, 3(2), 196-214.
- Meenakshisundaram, S., Nowicka, E., Miedziak, P. J., Brett, G. L., Jenkins, R. L., Dimitratos, N., . . . Hutchings, G. J. (2010). Oxidation of alcohols using supported gold and gold–palladium nanoparticles. *Faraday Discussions*, 145, 341-356.
- Mellor, J. W. (1903). History of the water problem. *The Journal of Physical Chemistry*, 7(8), 557-567.
- Mercera, P., Van Ommen, J., Doesburg, E., Burggraaf, A., & Ross, J. (1990). Zirconia as a support for catalysts: Evolution of the texture and structure on calcination in air. *Applied catalysis*, 57(1), 127-148.
- Miedziak, P. J., He, Q., Edwards, J. K., Taylor, S. H., Knight, D. W., Tarbit, B., . . . Hutchings, G. J. (2011). Oxidation of benzyl alcohol using supported gold– palladium nanoparticles. *Catalysis today*, *163*(1), 47-54.
- 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(45), 8619-8627.
- Morad, M. (2014). *Development of new highly active nano gold catalysts for selective oxidation reactions*. Cardiff University.

- Mori, K., Hara, T., Mizugaki, T., Ebitani, K., & Kaneda, K. (2004). Hydroxyapatitesupported palladium nanoclusters: a highly active heterogeneous catalyst for selective oxidation of alcohols by use of molecular oxygen. *Journal of the American Chemical Society*, *126*(34), 10657-10666.
- Moulijn, J. A., van Leeuwen, P. W., & van Santen, R. A. (1993). *Catalysis: an integrated approach to homogeneous, heterogeneous and industrial catalysis* (Vol. 79): Elsevier.
- Neumann, R., & Levin-Elad, M. (1995). Vanadium silicate xerogels in hydrogen peroxide catalyzed oxidations. *Applied Catalysis A: General, 122*(2), 85-97.
- Nie, M., Shen, P. K., & Wei, Z. (2007). Nanocrystaline tungsten carbide supported Au-Pd electrocatalyst for oxygen reduction. *Journal of Power Sources*, 167(1), 69-73.
- Nikolaev, S., Golubina, E., Krotova, I., Shilina, M., Chistyakov, A., & Kriventsov, V. (2015). The effect of metal deposition order on the synergistic activity of Au–Cu and Au–Ce metal oxide catalysts for CO oxidation. *Applied Catalysis B: Environmental, 168*, 303-312.
- Ntainjua, 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(11), 1162-1169.

Partington, J. R. (1970). A history of chemistry.

- Patil, N., Jha, R., Uphade, B., Bhargava, S., & Choudhary, V. (2004). Epoxidation of styrene by anhydrous t-butyl hydroperoxide over gold supported on Al2O3, Ga2O3, In2O3 and Tl2O3. *Applied Catalysis A: General*, 275(1-2), 87-93.
- Peter J., Miedziaka Qian Heb, Jennifer K. Edwardsa, Stuart H. Taylora, David W. Knighta, (2011). Catalysis Today. 163..
- Petri, B. G., Watts, R. J., Teel, A. L., Huling, S. G., & Brown, R. A. (2011). Fundamentals of ISCO using hydrogen peroxide *In situ chemical oxidation for groundwater remediation* (pp. 33-88): Springer.
- Pigamo, A., Besson, M., Blanc, B., Gallezot, P., Blackburn, A., Kozynchenko, O., . . . Kapteijn, F. (2002). Effect of oxygen functional groups on synthetic carbons on liquid phase oxidation of cyclohexanone. *Carbon*, 40(8), 1267-1278.
- Pillai, U. R., & Sahle-Demessie, E. (2003). Sn-exchanged hydrotalcites as catalysts for clean and selective Baeyer–Villiger oxidation of ketones using hydrogen peroxide. *Journal of Molecular Catalysis A: Chemical*, 191(1), 93-100.

- Planeix, J., Coustel, N., Coq, B., Brotons, V., Kumbhar, P., Dutartre, R., . . . Ajayan,
 P. (1994). Application of carbon nanotubes as supports in heterogeneous catalysis. *Journal of the American Chemical Society*, *116*(17), 7935-7936.
- Porta, F., & Prati, L. (2003). Pre-formed gold particle immobilized on supports: Preparation and catalytic applications. *Journal of vacuum science & technology. A. Vacuum, surfaces, and films, 4*, 99-110.
- 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(2), 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*(1-4), 165-172.
- Prati, L., & Martra, G. (1999). New gold catalysts for liquid phase oxidation. *Gold Bulletin*, 32(3), 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(2), 552-560.
- Prati, L., & Villa, A. (2011). The art of manufacturing gold catalysts. *Catalysts*, 2(1), 24-37.
- Pritchard, J., Kesavan, L., Piccinini, M., He, Q., Tiruvalam, R., Dimitratos, N., . . . Kiely, C. J. (2010). Direct synthesis of hydrogen peroxide and benzyl alcohol oxidation using Au- Pd catalysts prepared by sol immobilization. *Langmuir*, 26(21), 16568-16577.
- Qiao, J., Fu, J., Lin, R., Ma, J., & Liu, J. (2010). Alkaline solid polymer electrolyte membranes based on structurally modified PVA/PVP with improved alkali stability. *Polymer*, *51*(21), 4850-4859.
- Quintanilla, A., Menéndez, N., Tornero, J., Casas, J. A., & Rodríguez, J. J. (2008). Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: Influence on activity, selectivity and stability. *Applied Catalysis B: Environmental*, 81(1-2), 105-114.
- Robertson, A. J. B. (1970). Catalysis of Gas Reactions by Metals. SPRINGER-VERLAG, NEW YORK. 1970, 182 P.
- Rodriguez-Reinoso, F. (1998). The role of carbon materials in heterogeneous catalysis. *Carbon, 36*(3), 159-175.

- Rodríguez-Reinoso, F., & Sepúlveda-Escribano, A. (2009). Carbon as catalyst support. *Carbon materials for catalysis*, 131-155.
- Ross, J. R. (2011). Heterogeneous catalysis: fundamentals and applications: Elsevier.
- Rothenberg, G. (2008). Catalysis Concepts and Green Applications Wiley-VCH. Verlag GmbH & Co KGaA.
- Campanati, M., Fornasari, G., & Vaccari, A. (2003). Fundamentals in the preparation of heterogeneous catalysts. *Catalysis today*, 77(4), 299-314.
- Eschemann, T. O., Bitter, J. H., & De Jong, K. P. (2014). Effects of loading and synthesis method of titania-supported cobalt catalysts for Fischer–Tropsch synthesis. *Catalysis today, 228*, 89-95.
- Lowell, S., Shields, J. E., Thomas, M. A., & Thommes, M. (2012). *Characterization* of porous solids and powders: surface area, pore size and density (Vol. 16): Springer Science & Business Media.
- Mallat, T., & Baiker, A. (1994). Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions. *Catalysis today*, 19(2), 247-283.
- Markó, I. E., Giles, P. R., Tsukazaki, M., Brown, S. M., & Urch, C. J. (1996). Coppercatalyzed oxidation of alcohols to aldehydes and ketones: an efficient, aerobic alternative. *Science*, 274(5295), 2044-2046.
- Martin, S. E., & Garrone, A. (2003). Efficient solvent-free iron (III) catalyzed oxidation of alcohols by hydrogen peroxide. *Tetrahedron Letters*, 44(3), 549-552.
- Matsumoto, T., Ueno, M., Wang, N., & Kobayashi, S. (2008). Recent advances in immobilized metal catalysts for environmentally benign oxidation of alcohols. *Chemistry–An Asian Journal*, 3(2), 196-214.
- Meenakshisundaram, S., Nowicka, E., Miedziak, P. J., Brett, G. L., Jenkins, R. L., Dimitratos, N., . . . Hutchings, G. J. (2010). Oxidation of alcohols using supported gold and gold–palladium nanoparticles. *Faraday Discussions, 145*, 341-356.
- Mellor, J. W. (1903). History of the water problem. *The Journal of Physical Chemistry*, 7(8), 557-567.
- Mercera, P., Van Ommen, J., Doesburg, E., Burggraaf, A., & Ross, J. (1990). Zirconia as a support for catalysts: Evolution of the texture and structure on calcination in air. *Applied catalysis*, *57*(1), 127-148.

- Miedziak, P. J., He, Q., Edwards, J. K., Taylor, S. H., Knight, D. W., Tarbit, B., . . . Hutchings, G. J. (2011). Oxidation of benzyl alcohol using supported gold– palladium nanoparticles. *Catalysis today*, *163*(1), 47-54.
- 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(45), 8619-8627.
- Morad, M. (2014). *Development of new highly active nano gold catalysts for selective oxidation reactions*. Cardiff University.
- Mori, K., Hara, T., Mizugaki, T., Ebitani, K., & Kaneda, K. (2004). Hydroxyapatitesupported palladium nanoclusters: a highly active heterogeneous catalyst for selective oxidation of alcohols by use of molecular oxygen. *Journal of the American Chemical Society*, *126*(34), 10657-10666.
- Moulijn, J. A., van Leeuwen, P. W., & van Santen, R. A. (1993). *Catalysis: an integrated approach to homogeneous, heterogeneous and industrial catalysis* (Vol. 79): Elsevier.
- Neumann, R., & Levin-Elad, M. (1995). Vanadium silicate xerogels in hydrogen peroxide catalyzed oxidations. *Applied Catalysis A: General, 122*(2), 85-97.
- Nie, M., Shen, P. K., & Wei, Z. (2007). Nanocrystaline tungsten carbide supported Au-Pd electrocatalyst for oxygen reduction. *Journal of Power Sources*, 167(1), 69-73.
- Nikolaev, S., Golubina, E., Krotova, I., Shilina, M., Chistyakov, A., & Kriventsov, V. (2015). The effect of metal deposition order on the synergistic activity of Au-Cu and Au-Ce metal oxide catalysts for CO oxidation. *Applied Catalysis B: Environmental, 168,* 303-312.
- Ntainjua, 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*(11), 1162-1169.
- Partington, J. R. (1970). A history of chemistry.
- Patil, N., Jha, R., Uphade, B., Bhargava, S., & Choudhary, V. (2004). Epoxidation of styrene by anhydrous t-butyl hydroperoxide over gold supported on Al2O3, Ga2O3, In2O3 and Tl2O3. *Applied Catalysis A: General, 275*(1-2), 87-93.

- Petri, B. G., Watts, R. J., Teel, A. L., Huling, S. G., & Brown, R. A. (2011). Fundamentals of ISCO using hydrogen peroxide *In situ chemical oxidation for* groundwater remediation (pp. 33-88): Springer.
- Pigamo, A., Besson, M., Blanc, B., Gallezot, P., Blackburn, A., Kozynchenko, O., . .
 . Kapteijn, F. (2002). Effect of oxygen functional groups on synthetic carbons on liquid phase oxidation of cyclohexanone. *Carbon, 40*(8), 1267-1278.
- Pillai, U. R., & Sahle-Demessie, E. (2003). Sn-exchanged hydrotalcites as catalysts for clean and selective Baeyer–Villiger oxidation of ketones using hydrogen peroxide. *Journal of Molecular Catalysis A: Chemical*, 191(1), 93-100.
- Planeix, J., Coustel, N., Coq, B., Brotons, V., Kumbhar, P., Dutartre, R., . . . Ajayan,
 P. (1994). Application of carbon nanotubes as supports in heterogeneous catalysis. *Journal of the American Chemical Society*, *116*(17), 7935-7936.
- Porta, F., & Prati, L. (2003). Pre-formed gold particle immobilized on supports: Preparation and catalytic applications. *JOURNAL OF VACUUM SCIENCE & TECHNOLOGY. A. VACUUM, SURFACES, AND FILMS, 4*, 99-110.
- 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*(2), 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(1-4), 165-172.
- Prati, L., & Martra, G. (1999). New gold catalysts for liquid phase oxidation. *Gold Bulletin*, 32(3), 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(2), 552-560.
- Prati, L., & Villa, A. (2011). The art of manufacturing gold catalysts. *Catalysts*, 2(1), 24-37.
- Pritchard, J., Kesavan, L., Piccinini, M., He, Q., Tiruvalam, R., Dimitratos, N., . . . Kiely, C. J. (2010). Direct synthesis of hydrogen peroxide and benzyl alcohol oxidation using Au– Pd catalysts prepared by sol immobilization. *Langmuir*, 26(21), 16568-16577.
- Qiao, J., Fu, J., Lin, R., Ma, J., & Liu, J. (2010). Alkaline solid polymer electrolyte membranes based on structurally modified PVA/PVP with improved alkali stability. *Polymer*, *51*(21), 4850-4859.

- Quintanilla, A., Menéndez, N., Tornero, J., Casas, J. A., & Rodríguez, J. J. (2008). Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: Influence on activity, selectivity and stability. *Applied Catalysis B: Environmental*, 81(1-2), 105-114.
- Robertson, A. J. B. (1970). Catalysis of Gas Reactions by Metals. SPRINGER-VERLAG, NEW YORK. 1970, 182 P.
- Rodriguez-Reinoso, F. (1998). The role of carbon materials in heterogeneous catalysis. *Carbon, 36*(3), 159-175.
- Rodríguez-Reinoso, F., & Sepúlveda-Escribano, A. (2009). Carbon as catalyst support. *Carbon materials for catalysis*, 131-155.
- Ross, J. R. (2011). Heterogeneous catalysis: fundamentals and applications: Elsevier.
- Rothenberg, G. (2008). Catalysis Concepts and Green Applications Wiley-VCH. Verlag GmbH & Co KGaA.
- Saiman, M. I. B. (2012). *Heterogeneous gold and palladium based catalysts for solvent-free oxidation of toluene*. Cardiff University.
- Sankar, M., Nowicka, E., Tiruvalam, R., He, Q., Taylor, S. H., Kiely, C. J., . . . Hutchings, G. J. (2011). Controlling the Duality of the Mechanism in Liquid-Phase Oxidation of Benzyl Alcohol Catalysed by Supported Au–Pd Nanoparticles. *Chemistry-a European Journal*, *17*(23), 6524-6532.
- 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(23), 8499-8507.
- Sheldon, R. (2012). *Metal-catalyzed oxidations of organic compounds: mechanistic principles and synthetic methodology including biochemical processes:* Elsevier.
- Shi, Y., Yang, H., Zhao, X., Cao, T., Chen, J., Zhu, W., . . . Hou, Z. (2012). Au–Pd nanoparticles on layered double hydroxide: highly active catalyst for aerobic oxidation of alcohols in aqueous phase. *Catalysis Communications, 18*, 142-146.
- Shibasaki-Kitakawa, N., Honda, H., Kuribayashi, H., Toda, T., Fukumura, T., & Yonemoto, T. (2007). Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. *Bioresource technology*, *98*(2), 416-421.

- Shiota, Y., & Yoshizawa, K. (2000). Methane-to-methanol conversion by first-row transition-metal oxide ions: ScO+, TiO+, VO+, CrO+, MnO+, FeO+, CoO+, NiO+, and CuO+. *Journal of the American Chemical Society*, *122*(49), 12317-12326.
- Shylesh, S., & Singh, A. (2004). Synthesis, characterization, and catalytic activity of vanadium-incorporated,-grafted, and-immobilized mesoporous MCM-41 in the oxidation of aromatics. *Journal of Catalysis, 228*(2), 333-346.
- Spence, J. C. (2013). High-resolution electron microscopy: OUP Oxford.
- Strukul, G. (1998). Transition metal catalysis in the Baeyer–Villiger oxidation of ketones. *Angewandte Chemie International Edition*, 37(9), 1198-1209.
- Stüber, F., Font, J., Fortuny, A., Bengoa, C., Eftaxias, A., & Fabregat, A. (2005). Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater. *Topics in Catalysis*, 33(1-4), 3-50.
- Su, F.-Z., Chen, M., Wang, L.-C., Huang, X.-S., Liu, Y.-M., Cao, Y., ... Fan, K.-N. (2008). Aerobic oxidation of alcohols catalyzed by gold nanoparticles supported on gallia polymorphs. *Catalysis Communications*, 9(6), 1027-1032.
- Thetford, A., Hutchings, G. J., Taylor, S. H., & Willock, D. J. (2011). The decomposition of H₂ O₂ over the components of Au/TiO₂ catalysts. *Proceedings: Mathematical, Physical and Engineering Sciences*, 1885-1899.
- Thomas, J. M., & Thomas, W. J. (2014). *Principles and practice of heterogeneous catalysis*: John Wiley & Sons.
- Tsubota, S., Cunningham, D., Bando, Y., & Haruta, M. (1995). Preparation of nanometer gold strongly interacted with TiO₂ and the structure sensitivity in low-temperature oxidation of CO *Studies in Surface Science and Catalysis* (Vol. 91, pp. 227-235): Elsevier.
- Tuel, A., Moussa-Khouzami, S., Taarit, Y. B., & Naccache, C. (1991). Hydroxylation of phenol over TS-1: surface and solvent effects. *Journal of molecular catalysis*, 68(1), 45-52.
- Tukač, V., Vokál, J. í., & Hanika, J. í. (2001). Mass transfer- limited wet oxidation of phenol. *Journal of Chemical Technology and Biotechnology*, *76*(5), 506-510.
- Vaino, A. R. (2000). Sodium percarbonate as an oxygen source for MTO catalyzed epoxidations. *The Journal of Organic Chemistry*, 65(13), 4210-4212.

- Van Vleck, J. H. (1932). *The theory of electric and magnetic susceptibilities*: Oxford University Press.
- Venezia, A., La Parola, V., Nicoli, V., & Deganello, G. (2002). Effect of gold on the HDS activity of supported palladium catalysts. *Journal of Catalysis*, 212(1), 56-62.
- Villa, A., Janjic, N., Spontoni, P., Wang, D., Su, D. S., & Prati, L. (2009). Au–Pd/AC as catalysts for alcohol oxidation: Effect of reaction parameters on catalytic activity and selectivity. *Applied Catalysis A: General, 364*(1-2), 221-228.
- Villa, A., Wang, D., Su, D., Veith, G. M., & Prati, L. (2010). Using supported Au nanoparticles as starting material for preparing uniform Au/Pd bimetallic catalysts. *Physical Chemistry Chemical Physics*, 12(9), 2183-2189.
- Voll, F., Palú, F., & Santos, J. (2011). Influence of catalyst treatments on the decomposition of hydrogen peroxide on supported palladium catalysts. *Latin American applied research*, 41(4), 305-310.
- Wang, L.-C., Liu, Y.-M., Chen, M., Cao, Y., He, H.-Y., & Fan, K.-N. (2008). MnO2 nanorod supported gold nanoparticles with enhanced activity for solvent-free aerobic alcohol oxidation. *The Journal of Physical Chemistry C*, 112(17), 6981-6987.
- Webb, P., & Orr, C. (1997). Surface area and pore structure by gas adsorption. Analytical methods in fine particle technology, 53-153.
- Weng, Z., Liao, G., Wang, J., & Jian, X. (2007). Selective oxidation of benzyl alcohol with hydrogen peroxide over reaction-controlled phase-transfer catalyst. *Catalysis Communications*, 8(10), 1493-1496.
- Wisniak, J. (2010). The history of catalysis. From the beginning to Nobel Prizes. *Educación química, 21*(1), 60-69.
- World gold council . (2011). gold the hidden element , ininnovation , gold industrial information, http://www.gold.org/.
- Yang, C.-C., & Lee, Y.-J. (2009). Preparation of the acidic PVA/MMT nanocomposite polymer membrane for the direct methanol fuel cell (DMFC). *Thin Solid Films*, *517*(17), 4735-4740.
- Yu, R., Xiao, F.-S., Wang, D., Sun, J., Liu, Y., Pang, G., ... Fang, C. (1999). Catalytic performance in phenol hydroxylation by hydrogen peroxide over a catalyst of V–Zr–O complex. *Catalysis today*, 51(1), 39-46.

Zanella, R., & Louis, C. (2005). Influence of the conditions of thermal treatments and of storage on the size of the gold particles in Au/TiO2 samples. *Catalysis today*, *107*, 768-777.

