



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CHARACTERISATION OF BISMUTH OXIDE
POWDERS**

NOORFARIZAN NASRIAH BINTI MHAMAT NASUDIN.

FS 2005 39



SYNTHESIS AND CHARACTERISATION OF BISMUTH OXIDE POWDERS

By

NOORFARIZAN NASRIAH BINTI MHAMAT NASUDIN

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

JUNE 2005



Especially Dedicated To

My Dearest Mama & Abah

*Noorsiah Morat
Mhamat Nasudin Ismail*

My Dear Sisters & Brother

*Noordianiwati Nasriah
Noorhidayati Nasriah
Noorhafiza Nasriah
Mohd Ismadi Nasri*

My Dear Brother-in-law

Khairul Anwar Ismail

My Beloved Nephew & Niece

*Nurina Maisara
Muhammad Nazril Hadani*

Without whose love and continued support, this thesis would not have been possible.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Master of Science

SYNTHESIS AND CHARACTERISATION OF BISMUTH OXIDE POWDERS

By

NOORFARIZAN NASRIAH BINTI MHAMAT NASUDIN

June 2005

Chairman: Associate Professor Irmawati Ramli, PhD
Faculty : Science

Bismuth oxide has found application in various areas including medicine, material synthesis, organic synthesis and catalysis. In catalysis, this single oxide found important role in providing oxygen for the α -hydrogen abstraction of propene to produce acrolein and acrylonitrile via oxidation and ammoxidation process. This study investigates the influence of multitude of synthesis parameters (precipitating agent, concentration and aging process) on the formation of bismuth oxide powders. The samples microstructural properties were determined using a variety of techniques such as X-Ray Diffraction (XRD), BET Surface Area Measurement, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy. Extend of reduction of the oxide was also investigated by employing Temperature Programmed Reduction (TPR) technique. Finally, a Temperature Programmed Reaction (TPRn) was conducted on selected samples to determine the surface intermediates.



On the influence of precipitating agent, α - Bi_2O_3 that were produced via NaOH as a precipitating agent and calcined in air were discerned to exhibit higher surface areas and higher intrinsic activity as compared to β - Bi_2O_3 which is produced by using NH_4OH as a precipitating agent. However, increment in NaOH concentration has induced the formation of low surface area material.

Investigation on the influence of bismuth concentration on the formation of final products gave high surface area powders with high oxide reducibility when using low concentration of bismuth. The sample high surface area property with its corresponding small particle size has been evidenced to be an induction factor to enhance the oxygen reducibility of the samples. Study on the effect of aging process showed that the parameters controlled the powders particle size.

Temperature programmed reaction studies of propane oxidation showed that α - Bi_2O_3 gave the higher percentage of selectivity to propene and acrolein when compared to β - Bi_2O_3 . The reaction was found to be in step-wise mechanism through the formation of propene intermediate. On the other hand, β - Bi_2O_3 revealed a direct propane conversion into acrolein without having to go through propene route.



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

SINTESIS DAN PENCIRIAN SERBUK BISMUT OKSIDA

Oleh

NOORFARIZAN NASRIAH BINTI MHAMAT NASUDIN

June 2005

Pengerusi: Professor Madya Irmawati Ramli, PhD

Fakulti : Sains

Bismut oksida mempunyai aplikasi dalam pelbagai bidang termasuk perubatan, sintesis bahan, sintesis organik dan pemangkinan. Di dalam pemangkinan, oksida tunggal ini di dapati mempunyai peranan penting di dalam menyediakan oksigen untuk penyingkiran hidrogen α propena bagi menghasilkan akrolin atau akrilonitril. Pembelajaran ini mengkaji kesan daripada pelbagai parameter melalui proses sintesis (agen pemendakan, kepekatan dan proses penglewatan) ke atas pembentukan serbuk bismut oksida. Ciri-ciri struktur mikro sampel-sampel telah ditentukan menggunakan pelbagai teknik seperti Pembelauan X-Ray (XRD), Pengukuran Luas Permukaan dengan kaedah BET, Mikroskopi Pengimbas Elektron (SEM) dan Spektroskopi Inframerah (FTIR). Pemanjangan penurunan oksida telah dikaji dengan menggunakan teknik Penurunan Berprogram Suhu (TPR). Akhirnya, Tindakbalas Berprogram Suhu (TPRn) telah dijalankan ke atas sampel-sampel terpilih untuk menentukan perantara permukaan.

Berdasarkan kesan oleh agen pemendakan, α - Bi_2O_3 yang terhasil melalui NaOH sebagai agen pemendakan dan dikalsin dalam udara jelas menunjukkan luas permukaan dan aktiviti intrinsik yang lebih tinggi berbanding β - Bi_2O_3 yang terhasil dengan menggunakan NH_4OH sebagai agen pemendakan. Walau bagaimanapun, peningkatan dalam kepekatan NaOH telah menggalakkan pembentukan bahan berluas permukaan yang rendah.

Kajian ke atas kesan kepekatan bismut ke atas pembentukan produk-produk terakhir memberikan serbuk berluas permukaan tinggi dan pembebasan oksigen yang tinggi apabila menggunakan kepekatan bismut yang rendah. Ciri-ciri sampel berluas permukaan tinggi dan saiz partikel kecil telah dibuktikan menjadi satu faktor dorongan untuk meningkatkan pembebasan oksigen sesuatu sampel. Kajian ke atas kesan proses penglewatan menunjukkan bahawa parameter ini mengawal saiz partikel serbuk.

Kajian Tindakbalas Berprogram Suhu bagi pengoksidaan propena menunjukkan bahawa α - Bi_2O_3 memberikan peratus lebih tinggi bagi pemilihan kepada propena dan akrolin jika dibandingkan dengan β - Bi_2O_3 . Tindakbalas di dapati merupakan mekanisma langkah tersusun melalui pembentukan perantara propena. Sebaliknya, β - Bi_2O_3 menunjukkan penukaran propena secara menerus kepada akrolin tanpa perlu melalui laluan propena.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere and deepest appreciation to my supervisor, Assoc. Professor Dr. Irmawati Ramli and co-supervisors Assoc. Professor Dr. Taufiq-Yap Yun Hin and Assoc. Professor Dr. Sharifah Bee Abdul Hamid for their supervision, invaluable guidance, unfailing help and superb tolerance throughout the course of this work. Heartfelt thanks are extended to all the laboratory assistants in Department of Chemistry especially Mr. Zulhisham and Mrs. Rusnani and also to Mrs. Faridah from Institute of Bioscience for their favourable help and advice.

I am also very grateful to all my lab mates (Hidayaty, Yati, Raslan, Izham, Asri, Siti Fatimah, Hasbi, Hairul, Murni, Ernee, Saw, Hooi Hong and Chee Keong) and our Science Officer Mrs. Zaidina, whose help, suggestions, encouragement and companion are of great help in sustaining the morale and enthusiasm.

Last but not least, I would like to thank all those who had contributed to the success of this work in one way or another especially my parents, sisters, brother, brother in-law, COMBICAT's lecturers and friends for their deep support and understanding.

Financial support from the Universiti Putra Malaysia and the Ministry of Science, Technology and Innovation in the form of PASCA Graduate Scheme is gratefully acknowledged.



TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	x
LIST OF TABLES	xiv
LIST OF FIGURES	xv
LIST OF ABBREVIATION	xviii
CHAPTER	
1 INTRODUCTION	1
1.1 General Introduction to Catalysis and Catalyst	1
1.2 The Catalytic Cycle	2
1.3 Classification of Catalytic System	4
1.4 The Importance of Catalyst	6
1.5 Catalysts for Industrial Processes: General Requirements	7
1.6 Bismuth Oxide as Catalyst in Industrial Processes	7
2 LITERATURE REVIEW	10
2.1 Selective Catalytic Oxidation	10
2.2 Selective Oxidation Reaction	11
2.3 Alkanes as Raw Materials for Selective Oxidation Reaction	13
2.3.1 Processes of Industrial Interest Using an Alkane Feedstock	14
2.4 Acrolein	15
2.4.1 Development of Acrolein Synthesis	16
2.5 Catalysts for Propane Oxidation	17
2.6 Bismuth oxide, Bi ₂ O ₃ as Proposed Catalyst for Propane Oxidation	19
2.7 Bi ₂ O ₃ as a Catalyst	21
2.8 Other Major Industrial Application of Bi ₂ O ₃	24
2.8.1 Electrolyte	24
2.8.2 Smoke Sensor	26
2.8.3 Thin Film	27
2.9 Preparation of Bismuth Oxide	28
2.9.1 Preparation Methods	28
2.9.2 Effects of Preparation Parameters	29
2.10 Objectives of This Thesis	33
3 SAMPLES SYNTHESIS AND CHARACTERISATIONS	34
3.1 Preparation of Bismuth Oxide via Different Precipitation Parameters	34



3.1.1	Influence of Bismuth Concentration	34
3.1.2	Influence of Precipitating Agent (NaOH/NH ₄ OH) Concentration	35
3.1.3	Influence of Aging Process	35
3.2	Materials and Gases	36
3.3	Catalysts Characterisations	36
3.3.1	X-ray Diffraction (XRD)	36
3.3.2	Fourier Transform Infrared (FTIR) Spectroscopy	38
3.3.3	BET Surface Area Measurements	39
3.3.4	Scanning Electron Microscopy (SEM)	40
3.3.5	Temperature-Programmed Reduction (TPR) by Hydrogen	42
3.3.6	Temperature Programmed Reaction (TPR _n) of Propane	43
4	INFLUENCE OF BISMUTH CONCENTRATION ON THE PHYSICO-CHEMICAL PROPERTIES OF BISMUTH OXIDE	44
4.1	Introduction	44
4.2	Influence of Bismuth Concentration by Using NaOH as a Precipitating Agent	44
4.2.1	Titration Curves	44
4.2.2	Thermogravimetric Analysis (TGA)	47
4.2.3	Phase Identification using Powder XRD Technique	48
4.2.4	BET Surface Area Measurements	54
4.2.5	Scanning Electron Microscopy	55
4.2.6	Fourier Transform Infrared (FTIR) Spectroscopy	59
4.2.7	Temperature Programmed Reduction (TPR in H ₂)	61
4.3	Influence of Bismuth Concentration by using NH ₄ OH as a Precipitating Agent	66
4.3.1	Titration Curves	66
4.3.2	Phase Identification using Powder XRD Technique	68
4.3.3	BET Surface Area Measurements	73
4.3.4	Scanning Electron Microscopy	74
4.3.5	Fourier Transform Infrared (FTIR) Spectroscopy	78
4.3.6	Temperature Programmed Reduction (TPR in H ₂)	79
4.4	Conclusion	80
5	INFLUENCE OF PRECIPITATING AGENT CONCENTRATION ON THE PHYSICO-CHEMICAL PROPERTIES OF BISMUTH OXIDE	83
5.1	Introduction	83
5.2	Influence of Precipitating Agent Concentration by using NaOH as a Precipitating Agent	83
5.2.1	Titration Curves	83
5.2.2	Phase Identification using Powder XRD Technique	85
5.2.3	BET Surface Area Measurements	87
5.2.4	Scanning Electron Microscopy	91
5.2.5	Fourier Transform Infrared (FTIR) Spectroscopy	93



5.2.6	Temperature Programmed Reduction (TPR in H ₂)	94
5.3	Influence of Precipitating Agent Concentration by using NH ₄ OH as a Precipitating Agent	98
5.3.1	Titration Curves	98
5.3.2	Phase Identification using Powder XRD Technique	100
5.3.3	BET Surface Area Measurements	105
5.3.4	Scanning Electron Microscopy	106
5.3.5	Fourier Transform Infrared (FTIR) Spectroscopy	108
5.3.6	Temperature Programmed Reduction (TPR in H ₂)	110
5.4	Conclusion	113
6	INFLUENCE OF AGING PROCESS ON THE PHYSICO-CHEMICAL PROPERTIES OF BISMUTH OXIDE	114
6.1	Introduction	114
6.2	Influence of Aging by using NaOH as a Precipitating Agent	115
6.2.1	Phase Identification using Powder XRD Technique	115
6.2.2	BET Surface Area Measurements	119
6.2.3	Scanning Electron Microscopy	120
6.2.4	Fourier Transform Infrared (FTIR) Spectroscopy	124
6.2.5	Temperature Programmed Reduction (TPR in H ₂)	124
6.3	Influence of Aging Concentration by using NH ₄ OH as a Precipitating Agent	129
6.3.1	Phase Identification using Powder XRD Technique	129
6.3.2	BET Surface Area Measurements	130
6.3.3	Scanning Electron Microscopy	134
6.3.4	Fourier Transform Infrared (FTIR) Spectroscopy	137
6.3.5	Temperature Programmed Reduction (TPR in H ₂)	139
6.4	Conclusion	142
7	CATALYTIC TESTING OF α -Bi ₂ O ₃ and β -Bi ₂ O ₃	143
7.1	Introduction	143
7.2	Anaerobic Temperature-Programmed Reaction (TPR _n) of the Propane/He (5 % Propane) over the α -Bi ₂ O ₃ and β -Bi ₂ O ₃ samples	144
7.3	Conclusion	149
8	CONCLUSIONS & SUGGESTIONS	150
8.1	Introduction	150
8.2	Summary	150
	REFERENCES	153
	APPENDICES	159
	BIODATA OF THE AUTHOR	163



LIST OF TABLES

Table		Page
1.1	Industrial processes and type of catalyst applied	5
2.1	Some common oxide catalysed selective oxidation reactions	12
2.2	Industrial processes and processes under study or development for the oxidative transformation of light alkanes (C ₁ -C ₆)	14
2.3	Several types of catalysts for the propane oxidation to acrylic acid	19
4.1	Variation of crystallite size of (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	53
4.2	Total amounts of oxygen atoms removed from (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	65
4.3	Variation of crystallite size of (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	72
4.4	Total amounts of oxygen atoms removed from (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	82
5.1	Variation of crystallite size of (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N	89
5.2	Total amounts of oxygen atoms removed from (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N	97
5.3	Variation of crystallite size of (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H	104
5.4	Total amounts of oxygen atoms removed from (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H	112
6.1	Variation of crystallite size of (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and 1BN168J samples	118
6.2	Total amounts of oxygen atoms removed from (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and 1BN168J samples	128
6.3	Variation of crystallite size of (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and 1BH168J samples	133
6.4	Total amounts of oxygen atoms removed from (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and 1BH168J samples	141
7.1	The m/z ratios followed to identify the compounds cited	144
7.2	The catalytic performance of the anaerobic reaction of propane over fresh oxide catalysts.	148



LIST OF FIGURES

Figure		Page
1.1	Molecular and atomic events during a catalytic reaction	2
1.2	Energy diagram in the presence of a catalyst	3
1.3	The stable and metastable regions found in Bi_2O_3	9
2.1	Molecule of acrolein	15
2.2	The chemical routes of propane	17
2.3	Parameters affecting the properties of the precipitate and main properties influenced	31
3.1	The four types of adsorption isotherm usually found by nitrogen adsorption	39
4.1	Titration curves of (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	46
4.2	Thermogram of 0.1BN and 0.3BNH	47
4.3	XRD diffractogram of uncalcined (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	50
4.4	XRD diffractogram of calcined (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	52
4.5	BET surface area measurement of calcined (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	55
4.6 (a)	SEM micrographs of 0.1BN	56
4.6 (b)	SEM micrographs of 0.2BN	57
4.6 (c)	SEM micrographs of 0.3BN	57
4.6 (d)	SEM micrographs of 0.4BN	58
4.6 (e)	SEM micrographs of 0.5BN	58
4.7	FTIR spectrums of (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	60
4.8	H_2 -TPR spectra of (a) 0.1BN, (b) 0.2BN, (c) 0.3BN, (d) 0.4BN and (e) 0.5BN samples	64
4.9	Titration curves of (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	67
4.10	XRD diffractogram of uncalcined (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	70
4.11	XRD diffractogram of calcined (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	71
4.12	BET surface area measurement of calcined (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	74
4.13 (a)	SEM micrographs of 0.1BNH	75
4.13 (b)	SEM micrographs of 0.2BNH	76
4.13 (c)	SEM micrographs of 0.3BNH	76
4.13 (d)	SEM micrographs of 0.4BNH	77
4.13 (e)	SEM micrographs of 0.5BNH	77
4.14	FTIR spectrums of (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d)	78



0.4BNH and (e) 0.5BNH samples

4.15	H ₂ -TPR spectra of (a) 0.1BNH, (b) 0.2BNH, (c) 0.3BNH, (d) 0.4BNH and (e) 0.5BNH samples	81
5.1	Titration curves of (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	84
5.2	XRD diffractogram of uncalcined (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	86
5.3	XRD diffractogram of calcined (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	88
5.4	BET surface area measurement of calcined (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	90
5.5 (a)	SEM micrograph of 0.2BN	91
5.5 (b)	SEM micrograph of 0.2B1N	92
5.5 (c)	SEM micrograph of 0.2B2N	92
5.5 (d)	SEM micrograph of 0.2B3N	93
5.6	FTIR spectrums of (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	94
5.7	H ₂ -TPR spectra of (a) 0.2BN, (b) 0.2B1N, (c) 0.2B2N and (d) 0.2B3N samples	96
5.8	Titration curves of (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	99
5.9	XRD diffractogram of uncalcined (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	102
5.10	XRD diffractogram of calcined (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	103
5.11	BET surface area measurement of calcined (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	105
5.12 (a)	SEM micrographs of 0.2BH	106
5.12 (b)	SEM micrographs of 0.2B1H	107
5.12 (c)	SEM micrographs of 0.2B2H	107
5.12 (d)	SEM micrographs of 0.2B3H	108
5.13	FTIR spectrums of (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	109
5.14	H ₂ -TPR spectra of (a) 0.2BH, (b) 0.2B1H, (c) 0.2B2H and (d) 0.2B3H samples	111
6.1	XRD diffractogram of uncalcined (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and (e) 1BN168J samples	116
6.2	XRD diffractogram of calcined (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and (e) 1BN168J samples	117
6.3	BET surface area measurement of calcined (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and (e) 1BN168J samples	120
6.4 (a)	SEM micrographs of 1BN0J	121
6.4 (b)	SEM micrographs of 1BN3J	122
6.4 (c)	SEM micrographs of 1BN024J	122



6.4 (d)	SEM micrographs of 1BN96J	123
6.4 (e)	SEM micrographs of 1BN168J	123
6.5	FTIR spectrums of (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and (e) 1BN168J samples	125
6.6	H ₂ -TPR spectra of (a) 1BN0J, (b) 1BN3J, (c) 1BN24J, (d) 1BN96J and (e) 1BN168J samples	127
6.7	XRD diffractogram of uncalcined (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples	131
6.8	XRD diffractogram of calcined (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples	132
6.9	BET surface area measurement of calcined (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples	134
6.10 (a)	SEM micrograph of 1BH0J	135
6.10 (b)	SEM micrograph of 1BH3J	135
6.10 (c)	SEM micrograph of 1BH24J	136
6.10 (d)	SEM micrograph of 1BH96J	136
6.10 (e)	SEM micrograph of 1BH168J	137
6.11	FTIR spectrums of (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples	138
6.12	H ₂ -TPR spectra of (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples	140
7.1	TPR _n profile of α -Bi ₂ O ₃	145
7.2	TPR _n profile of β -Bi ₂ O ₃	146



LIST OF ABBREVIATIONS

BET	Brunauer-Emmer-Teller
Bi	Bismuth
Bi ₂ O ₃	Bismuth Trioxide
CO	Carbon Monoxide
Dy ₂ O ₃	Dysprosium Trioxide
<i>fcc</i>	Face Centered Cubic
FWHM	Full-Width at Half Maximum
HPC	Heteropoly Acids and Salts
JCPDS	Joint Committee on Powder Diffraction Standards
MoO ₃	Molybdenum Trioxide
NO	Nitrogen Monoxide
O	Oxygen
SEM	Scanning Electron Microscopy
SOHIO	Standard Oil Company of Ohio
T max	Temperature at peak maximum
TCD	Thermal Conductivity Detector
TPR	Temperature Programmed Reduction
VPO	Vanadium Phosphorus Oxide
WO ₃	Tungsten Trioxide
XRD	X-Ray Diffraction



CHAPTER 1

INTRODUCTION

1.1 General Introduction to Catalysis and Catalyst

Catalysis is an extremely important phenomenon for our modern industrial economy. Generally, catalysis is a process whereby a reaction occurs faster than the uncatalysed reaction, with the presence of a catalyst (Bowker, 1998) [1]. The term “catalysis” was coined by Berzelius in 1835 in his renowned appraisal of the researches by Edmund Davy (1820), J.W. Döbereiner (1822) and others (Thomas and Thomas, 1967) [2]. The word catalysis comes from two Greek words, the prefix *cata-*, meaning down and the verb *lysein*, meaning to split or break.

Later, in 1895, William Ostwald was the first to write down a definition of a catalyst: ‘a catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products’. A catalyst enters into the reaction process, accelerating the rate of a reaction, without going through any permanent chemical change itself (Burton, 1996) [3]. A catalyst does not appear in the stoichiometric equation for an overall reaction, but it is nevertheless directly involved in the conversion and appears both in individual mechanistic steps, and in the kinetic rate law (Bowker, 1998) [1]. The catalyst remains, in general, unaltered at the end of the catalytic process.



1.2 The Catalytic Cycle

From a molecular point of view, the catalyst provides a surface for the reactant molecules to position themselves with one another so that when they do collide they will do so much more effectively. Figure 1.1 shows the crucial part of a supported metal catalyst, where all the chemical action takes place on the surface.

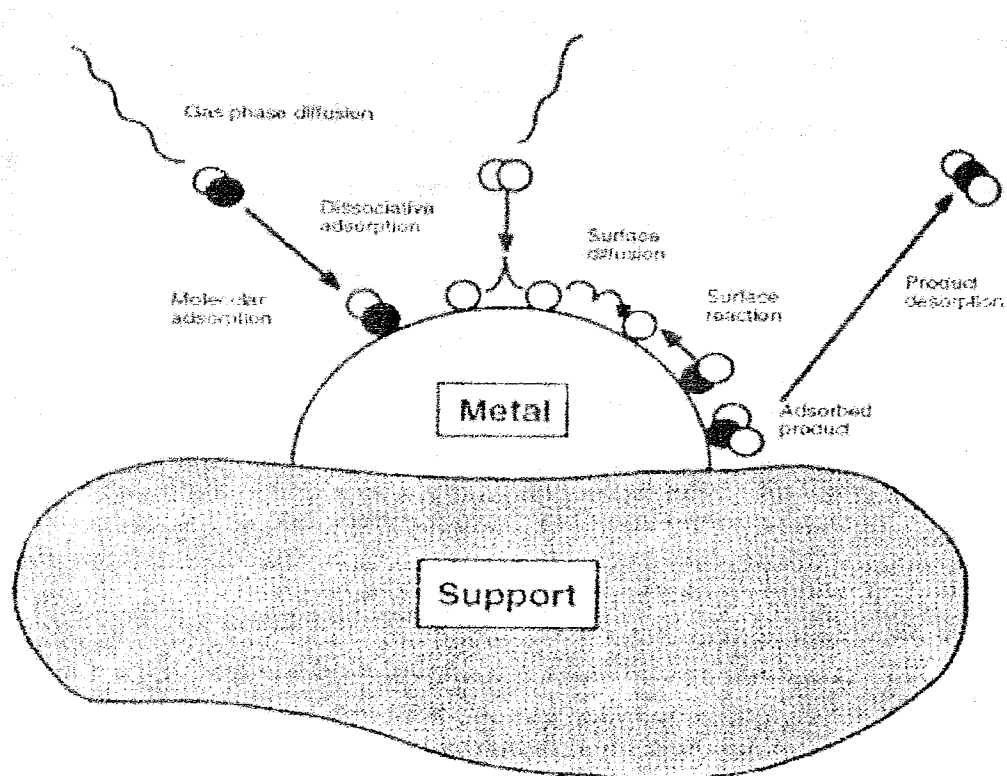


Figure 1.1 Molecular and atomic events during a catalytic reaction [1]

The first step is diffusion of the molecules through the gas phase to the metal surface where the molecules may bond (adsorption) in a molecular form. Surface diffusion may then occur and the molecule may dissociate into atoms. The next step is a

surface reaction whereby the adsorbed product was formed. The surface reaction step is often the rate-determining step in a catalytic reaction. Finally, product desorption occurs, where the adsorbed product enters the gas phase and diffuses down the catalyst pores to emerge finally at the end of the reactor.

Catalysts provide a different pathway for the reaction, which has lower activation energy than before (Logan, 1997) [4]. Figure 1.2 shows the energy diagram in the presence of a catalyst. Because the energy barrier is now lower, the reaction proceeds with greater speed. Catalysts generally reduce the energy of activation so that product might be formed at a lower temperature.

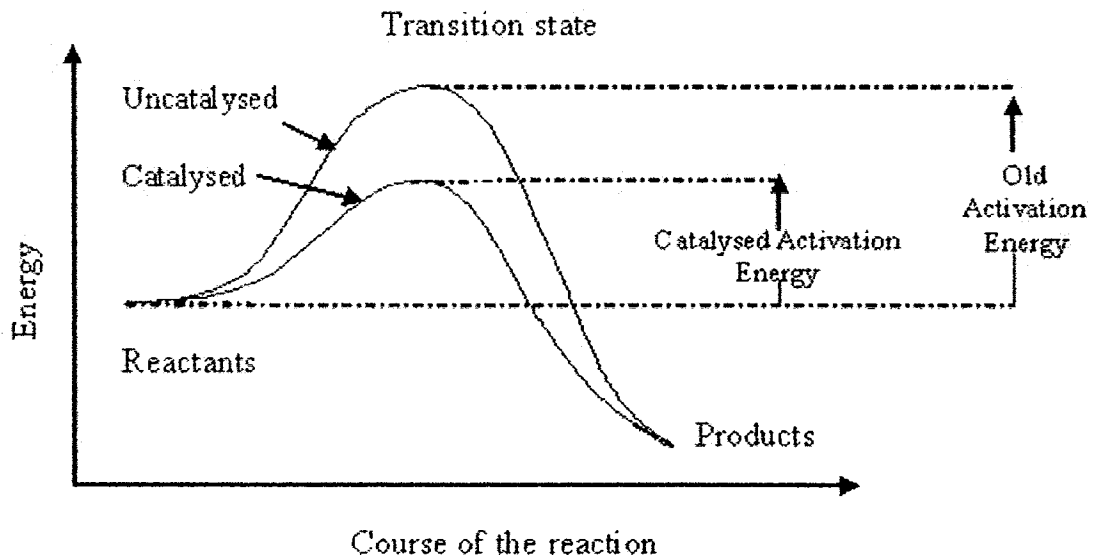


Figure 1.2 Energy diagram in the presence of a catalyst [1]

1.3 Classification of Catalytic System

Catalytic system can be divided into two categories: homogeneous catalysis and heterogeneous catalysis. According to Cavani and Trifirò (1997) [5], homogeneous catalysis occurred when the reactants, the products and the catalysts are in the same phase, usually the liquid phase. “Homo” means “same” and “geneous” is derived from a Greek word meaning “descent”, so homogeneous means of the “same kind”. Examples of homogeneous catalysts are soluble acids, bases, salts and organometallic compounds. The advantages of homogeneous catalysis are the utilization of almost all the molecules of the catalyst in the catalytic act, the higher selectivity obtained in some reactions, especially in the synthesis of optically-active compounds, the easier control of the temperature for highly exothermic reactions and the higher selectivity achieved due to the fact that it is possible to operate at milder conditions (for instance, in oxidation reactions).

The second category of catalytic system is heterogeneous catalyst. Heterogeneous catalyst is widely utilised in the industrial processes. More than 90% of the chemical manufacturing processes in use throughout the world utilise this type of catalysts. These processes include petroleum refining, petrochemical, inorganic chemical processes, etc. Table 1.1 lists some examples of the industrial processes and types of catalysts employed.



Table 1.1 Industrial processes and type of catalyst applied

Industry		Catalyst
Petroleum Refining Process	Catalytic reforming/ naphtha	Pt/Al ₂ O ₃
	Hydrodesulphurization/ petroleum fraction	Co-Mo/Al ₂ O ₃
	Catalytic cracking large petroleum molecules	Zeolite/silica-alumina
Petrochemical Process	Ethylene, O ₂	Supported Ag
	H ₂ C=CH ₂ , HCl	Supported CuCl ₂
	Benzene, O ₂	V ₂ O ₅ -MoO-H ₃ PO ₄
Inorganic Chemical Process	N ₂ , H ₂	Fe/Al ₂ O ₃ /K ₂ O/CaO
	SO ₂ , O ₂	V ₂ O ₅
	NH ₃ , O ₂	Pt/Rh
	CO, H ₂	ZnO-Cr ₂ O ₃
Pollution-controlled Industries	Reduction of NO _x with ammonia from stationary emissions	DeNO _x
	Oxidation of Volatile Organic Compounds	Supported copper oxide
	Catalytic combustion of methane	Aluminate supported oxide
Food Industry	Hydrogenation of vegetable oil	Ni/silica

The term 'heterogen' means that the catalyst and reactant are present in different phases. Sometimes, it was called surface catalysts because they position the reactant

molecules on their very surface (Burton, 1996) [3]. An example of this would be using nickel (solid) to catalyze the hydrogenation of vegetable oils to make margarine. The heterogeneous catalysts are either inorganic solids, such as metal oxides, sulfides or chlorides, or organic solids, such as modified polymers (Cavani *et al.*, 1997) [5]. In heterogeneous catalysis, products and catalyst can be separated easily (Kawai *et al.*, 1998) [6] because the catalyst and reactant are present in different phases. It is also able to withstand high temperatures. This is why heterogeneous catalytic reaction systems are suitable for large scale processes for high temperature chemicals and refining industries.

1.4 The Importance of Catalyst

Catalysts are used in all sectors of the chemical industry (Cavani *et al.*, 1997) [5]. For examples in basic chemistry for the synthesis of nitric acid, sulphuric acid, ammonia, methanol and aromatics, in petrochemistry for the synthesis of intermediate chemicals and polymers, in refining essentially in reactions of fluid catalytic cracking and hydrotreatments, in technologies for the abatement of pollutants for removal of NO, CO and hydrocarbons in emissions of stationary and mobile combustors, in the production of fine chemicals for the synthesis of intermediates and active compounds. According to Bowker (1998) [1], our present economy is highly geared to the use of catalysis. The fuel for cars was produced by cracking and reforming oil into petrol and diesel using a variety of catalysts. The ethylene and propylene from the cracking of naphtha is used in large-scale polymer production.

