UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF MOLYBDENUM -VANADIUM OXIDE CATALYST PREPARED BY HOMOGENEOUS PRECIPITATION METHOD USING UREA HYDROLYSIS

WOI PEI MENG

FS 2007 16

CHARACTERIZATION OF MOLYBDENUM - VANADIUM OXIDE CATALYST PREPARED BY HOMOGENEOUS PRECIPITATION METHOD USING UREA HYDROLYSIS

WOI PEI MENG

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2007

CHARACTERIZATION OF MOLYBDENUM-VANADIUM OXIDE CATALYST PREPARED BY HOMOGENEOUS PRECIPITATION METHOD USING UREA HYDROLYSIS

By

WOI PEI MENG

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

May 2007

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGEMENTS	vi
APPROVAL	vii
DECLARATION	ix
LIST OF TABLES	x
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xiv
CHAPTER	
1 INTRODUCTION	
1.1 The Catalysis Phenomenon	1
1.2 Functionality of Alkane in Selective Oxidation	3
1.3 Acrylic Acid and its Current Manufacturing Process	4
1.4 Selective Oxidation of Propane to Acrylic Acid	5
1.5 Significant of the Study	7
1.6 Scope of the Study	8
1.7 Objectives of the Study	8
2 LITERATURE REVIEW	
2.1 Introduction	9
2.2 Molybdenum-Vanadium (Mo-V) Oxide as Catalysts	9
2.3 Other Major Industrial Application of Mo-V Oxides	13
2.4 Preparation of Mo-V Oxides Catalyst	15
2.4.1 Hydrothermal Method	15
2.4.2 Slurry Method	16
2.4.3 Spray Drying	16
2.4.4 Crystallization Method	17
2.5 Precipitation and Homogeneous Precipitation	18
2.6 Influence of Additives	24
2.7 Influence of Calcination Temperature	25
3 EXPERIMENTAL	
3.1 Introduction	27
3.2 Materials and Gases	27
3.3 Preparation of Molybdenum-Vanadium Oxide Catalysts	28
3.3.1 Synthesis of Precursor	28
3.3.2 Calcination of Precursor	31
3.4 Studied Process Parameter	31

3.4.1 Influence of Additives 31
3.4.2 Influence of Calcination Temperature 32
3.5 Catalyst Characterization 33
3.5.1 Thermogravimetric Analysis (TGA) 33
3.5.2 X-ray Diffraction (XRD) Analysis 34
3.5.3 Photon Cross Correlation Spectroscopy (PCCS) Analysis 35
3.5.4 Elemental Analysis 36
3.5.5 Brunauer-Emmet-Teller Surface Area Measurements (S_{BET}) 37
3.5.6 Scanning Electron Microscopy (SEM) Analysis 37
3.5.7 Hydrogen-Temperature Programmed Reduction (H_2-TPR) Analysis 38
3.6 Catalytic Tests 39

4 SURFACE AND BULK CHARACTERIZATION OF $MoVO_x$ CATALYSTS
4.1 Introduction 41
4.2 Influence of Calcination Temperature 41
4.2.1 MoV*cont*$_{pre}$ 42
4.3 Influence of Additives 60
4.3.1 Physicochemical properties of $MoVO_x$-AA added samples calcined at different temperatures 60
4.3.2 Physicochemical properties of $MoVO_x$-MA added samples calcined at different temperatures 71
4.3.3 Physicochemical properties of $MoVO_x$-PVA added samples calcined at different temperatures 84
4.4 Comparative study of the characteristic of $MoVO_x$ catalysts added with additives 96
4.4.1 X-ray Diffraction (XRD) Analysis 97
4.4.2 Elemental Analysis 100
4.4.3 Brunauer-Emmet-Teller Surface Area Measurements (S_{BET}) 101
4.4.4 Scanning Electron Microscopy (SEM) Analysis 103
4.4.5 Hydrogen-Temperature Programmed Reduction (H_2-TPR) Analysis 104
4.5 Catalytic Testing 106
4.5.1 Introduction 106
4.5.2 Catalytic Performance of $MoVO_x$ in Propane Oxidation to Acrylic Acid 107
4.6 Conclusion 111

5 CONCLUSION AND SUGGESTION
5.1 Conclusion 112
5.2 Suggestions and Recommendations for further research 114

REFERENCES 115
APPENDICES 121
BIODATA OF THE AUTHOR 128

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

CHARACTERIZATION OF MOLYBDENUM-VANADIUM OXIDE CATALYST PREPARED BY HOMOGENEOUS PRECIPITATION METHOD USING UREA HYDROLYSIS

By

WOI PEI MENG

May 2007

Chairman: Irmawati Ramli, PhD

Faculty: Science

Molybdenum-vanadium oxide (Mo-V-O) has been constantly reported as an active and selective catalyst for the direct propane transformation to acrylic acid. In this study, crystalline molybdenum-vanadium oxide catalysts have been successfully synthesized by homogeneous precipitation method using urea hydrolysis. A new approach was taken whereby the solid obtained were further refluxed in the presence of additives which are adipic acid (AA), maleic acid (MA) and polyvinyl alcohol (PVA). The precursors which upon drying were subjected to various calcination temperatures.

The effect of additives and calcination temperatures on the formation and properties of Mo-V-O characteristics were monitored by Thermogravimetric Analysis (TGA), Powder X-ray diffraction (XRD), Photon Cross Correlation Spectroscopy (PCCS), Inductively Couple Plasma-Atomic Emission Spectroscopy

(ICP-AES), BET Surface Area Measurements (S_{BET}), Scanning Electron Microscopy (SEM) and Hydrogen-Temperature Programmed Reduction (H_2-TPR).

It was found that without the presence of additives, the precursor was in a semicrystalline form of ammonium molybdate anorthic phase. However, in the presence of additives, the precursors were highly crystalline with the presence of desirable orthorhombic, monoclinic and tetragonal $MoVO_x$ species. Heat treatment that imposed on the materials has successfully transformed the precursor into a more stable phase. The desirable orthorhombic phase was found to be achieved when sample was calcined at 873 K in nitrogen atmosphere.

SEM analysis showed a rather randomly distributed particle with defined size and shape. Total surface area, S_{BET} for sample prepared by complexing MoV salts with PVA (MoV*PVA*$_{873}$) was found to be the highest, *i.e.* 20.5 m^2 g^{-1}. This property consequently contributed to the highest total amount of oxygen species removed from the oxide, hence an indication of the highly active and selective characteristics borne by the oxide. This is further confirmed by catalytic test of propane oxidation to acrylic acid which done on the sample. The test showed that samples treated with organic species (AA, MA, PVA) give better acrylic acid selectivity and yield.

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

PENCIRIAN MOLIBDENUM VANADIUM OKSIDA MELALUI KAEDAH PEMENDAKAN HOMOGEN MENGGUNAKAN HIDROLISIS UREA

Oleh

WOI PEI MENG

Mei 2007

Pengerusi: Irmawati Ramli, PhD

Fakulti: Sains

Molibdenum-vanadium oksida (Mo-V-O) telah dilaporkan pengunaannya sebagai mangkin yang aktif dan memilih dalam proses tindak balas pertukaran propana secara terus kepada asid akrilik. Dalam kajian ini, mangkin molibdenum-vanadium oksida hablur telah berjaya disintesiskan melalui kaedah pemendakan homogen secara hidrolisis urea. Satu pendekatan baru telah diambil dimana pepejal prekursor yang diperolehi akan direflukskan dengan kehadiran bahan tambah seperti asid adipik (AA), asid maleik (MA) dan polivinil alkohol (PVA). Prekursor yang diperolehi selepas pengeringan akan dikalsinkan pada pelbagai suhu.

Kesan bahan tambah dan suhu pengkalsinan ke atas pembentukan dan sifat-sifat Mo-V-O telah diperhatikan melalui analisis gravimetri terma (TGA), pembelauan sinar-X (XRD), spektroskopi korelasi silang foton (PCCS), spektroskopi pengandingan plasma teraruh-pancaran atom (ICP-AES), pengukuran luas

permukaan BET (S_{BET}), mikroskopi pengimbasan elektron (SEM) dan penurunan berprogramkan suhu hidrogen (H_2-TPR).

Prekursor tanpa kehadiran bahan tambah didapati berada dalam bentuk semikristal ammonia molibdat fasa anortik. Walau bagaimanapun, dengan kehadiran spesies organik, prekursor berada dalam keadaan kehabluran tinggi dengan kehadiran fasa ortorombik, monoklinik dan tetragon spesis Mo-V-O_x yang dikehendaki. Rawatan haba ke atas sampel berjaya menukarkan prekursor kepada fasa yang lebih stabil. Fasa ortorombik yang diingini berjaya dicapai apabila sampel dikalsinkan pada suhu 873 K dalam atmosfera nitrogen.

Analisis SEM menunjukkan penaburan partikel yang agak berselerak tetapi dengan saiz dan bentuk yang jelas. Luas permukaan (S_{BET}) bagi sampel MoV yang dirawat dengan PVA (MoV*PVA*$_{873}$) memberikan nilai yang tertinggi iaitu 20.5 $m^2 g^{-1}$. Ciri ini menyumbangkan kepada jumlah oksigen tertinggi yang disingkirkan dari oksida, maka menandakan oksida mempunyai ciri kepilihan yang tinggi. Ujian pemangkinan untuk pertukaran propana ke asid akrilik yang dijalankan ke atas sampel telah mengesahkan hal tersebut. Ujian ini menunjukkan bahawa sampel yang dirawat dengan spesies organik (AA, MA, PVA) memberikan kepilihan dan hasil kepada asid akrilik yang lebih baik.

ACKNOWLEDGEMENTS

I am particularly grateful to my supervisor; Assoc. Prof. Dr. Irmawati Ramli and my co-supervisor, Assoc. Prof. Dr. Taufiq Yap Yun Hin for their assistance, direction and guidance which have been invaluable for the project improvement and accomplishment. Their support has made this work possible and the quality of this experiment was also greatly enhanced by the gracious collaboration from both of them.

I would like to extend my sincere thanks to Assoc. Prof. Dr. Fauziah Othman, Mr. Ho and Mdm. Faridah from Electron Microscopy Laboratory, Institute of Bioscience, UPM for their technical help and advice in running SEM analysis. I also wish to express my thanks to the Department of Chemistry, UPM, for the analytical instrumentation and funding the fees for certain characterization process.

I also wish to express my gratitude to my father, mother and the rest of my family members for their unending support and encouragement throughout the years.

Finally, words alone cannot express the thanks I owe to my lab-mates and friends who have given their help unselfishly in one way or another. Thank you for your valuable friendship.

I certify that an Examination Committee met on 23th May 2007 to conduct the final examination of Woi Pei Meng on her Master of Science thesis entitled "Characterization of Molybdenum-Vanadium Oxide Catalyst prepared by Homogeneous Precipitation Method using Urea Hydrolysis" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Mohd. Basyaruddin Abdul Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairperson)

Mohd Zaizi B. Desa, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Halim Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Zainab Ramli, PhD
Associate Professor
Faculty of Science
Universiti Teknologi Malaysia
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21th June 2007

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

Irmawati Ramli, Phd
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Taufiq Yap Yun Hin, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____

AINI IDERIS, PhD
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 17th JULY 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

_____

WOI PEI MENG

Date: 13th JUNE 2007

LIST OF TABLES

Table		Page
4.1	Summary of percentage weight loss for MoV*cont*$_{pre}$.	44
4.2	Particle size measurements for $MoVO_x$ calcined samples from PCCS analysis.	47
4.3	Calculated crystallite size, D of $MoVO_x$ calcined samples based on XRD data.	48
4.4	Bulk composition for the $MoVO_x$ calcined samples.	50
4.5	BET surface area for $MoVO_x$ calcined samples.	51
4.6	The values of reduction activation energies and the total amount of oxygen removed obtained by H_2-TPR.	58
4.7	Summary of percentage weight loss for MoV*MA*$_{pre}$.	62
4.8	Calculated crystallite size, D of $MoVO_x$-MA calcined samples based on XRD data.	65
4.9	Bulk composition for $MoVO_x$-MA calcined samples.	66
4.10	BET surface area for $MoVO_x$-MA calcined samples.	67
4.11	The values of reduction activation energies and the total amount of oxygen removed obtained by H_2-TPR.	71
4.12	Summary of percentage weight loss for MoV*AA*$_{pre}$.	73
4.13	Calculated crystallite size, D of $MoVO_x$-AA calcined samples based on XRD data.	77
4.14	Bulk composition for $MoVO_x$-AA calcined samples.	78
4.15	BET surface area for $MoVO_x$-AA calcined samples.	79
4.16	The values of reduction activation energies and the total amount of oxygen removed obtained by H_2-TPR.	84
4.17	Summary of percentage weight loss for MoV*PVA*$_{pre}$.	86
4.18	Calculated crystallite size, D of $MoVO_x$-PVA calcined samples based on XRD data.	89

4.19	Bulk composition for $MoVO_x$-PVA calcined samples.	90
4.20	BET surface area for $MoVO_x$-PVA calcined samples.	91
4.21	The values of reduction activation energies and the total amount of oxygen removed obtained by H_2-TPR.	95
4.22	Calculated crystallite size, D of samples calcined at 873 K based on XRD data.	100
4.23	Bulk composition for the samples calcined at 873 K.	101
4.24	BET surface area for the samples calcined at 873 K.	101
4.25	The values of reduction activation energies and the total amount of oxygen removed obtained by H_2-TPR.	106
4.26	The performance of MoVO catalysts for propane oxidation with feed compositions of $C_3H_8/O_2/N_2/H_2O$ = 8/10/37/45.	109

LIST OF FIGURES

Figure		Page
1.1	Catalytic cycle.	2
1.2	Structure of acrylic acid.	4
2.1	Structural model of the orthorhombic phase along [001] and [010] directions for Mo-V-O catalysts.	11
3.1	Flow chart for the preparation and characterization of Mo-V oxides.	30
4.1	TGA-DTG thermogram for MoV*cont*$_{pre}$	42
4.2	XRD diffractogram for MoV*cont*$_{pre}$	46
4.3	XRD diffractograms for a) MoV*cont*$_{553}$, b) MoV*cont*$_{658}$, c) MoV*cont*$_{703}$ and d) MoV*cont*$_{873}$	46
4.4	SEM micrographs for MoV*cont*$_{pre}$ at a) 5000 x and b) 15000 x magnification.	52
4.5	SEM micrographs for a) MoV*cont*$_{553}$, b) MoV*cont*$_{658}$, c) MoV*cont*$_{703}$ and d) MoV*cont*$_{873}$ taken at 15000 x magnification.	53
4.6	H_2-TPR profiles for a) MoV*cont*$_{553}$, b) MoV*cont*$_{658}$, c) MoV*cont*$_{703}$ and d) MoV*cont*$_{873}$.	56
4.7	Schematic of H_2 interaction with surface oxygen.	57
4.8	TGA-DTG thermogram for MoV*MA*$_{pre}$.	61
4.9	XRD diffractogram for MoV*MA*$_{pre}$.	63
4.10	XRD diffractograms for a) MoV*MA*$_{523}$, b) MoV*MA*$_{623}$ and c) MoV*MA*$_{873}$.	64
4.11	SEM micrographs for MoV*MA*$_{pre}$ at a) 5000 x and b) 15000 x magnification.	67
4.12	SEM micrographs for a) MoV*MA*$_{523}$, b) MoV*MA*$_{623}$ and c) MoV*MA*$_{873}$ taken at 15000 x magnification.	68
4.13	H_2-TPR profiles for a) MoV*MA*$_{523}$, b) MoV*MA*$_{623}$ and c) MoV*MA*$_{873}$.	69

4.14	TGA-DTG thermogram for MoV*AA*$_{pre}$.	72
4.15	XRD diffractogram for MoV*AA*$_{pre}$.	74
4.16	XRD diffractograms for a) MoV*AA*$_{523}$, b) MoV*AA*$_{673}$, c) MoV*AA*$_{773}$ and d) MoV*AA*$_{873}$.	75
4.17	SEM micrographs for MoV*AA*$_{pre}$ at a) 5000 x and b) 15000 x magnification.	80
4.18	SEM micrographs of a) MoV*AA*$_{523}$, b) MoV*AA*$_{673}$, c) MoV*AA*$_{773}$ and d) MoV*AA*$_{873}$ taken at 15000 x magnification.	81
4.19	H_2-TPR profiles for a) MoV*AA*$_{523}$, b) MoV*AA*$_{673}$, c) MoV*AA*$_{773}$ and d) MoV*AA*$_{873}$.	82
4.20	TGA-DTG thermogram for MoV*PVA*$_{pre}$.	85
4.21	XRD diffractogram for MoV*PVA*$_{pre}$.	87
4.22	XRD diffractograms for a) MoV*PVA*$_{523}$, b) MoV*PVA*$_{623}$ and MoV*PVA*$_{873}$.	88
4.23	SEM micrographs for MoV*PVA*$_{pre}$ at a) 5000 x and b) 15000 x magnification.	92
4.24	SEM micrographs for a) MoV*PVA*$_{523}$, b) MoV*PVA*$_{623}$ and c) MoV*PVA*$_{873}$ taken at 15000 x magnification.	93
4.25	H_2-TPR profiles for a) MoV*PVA*$_{523}$, b) MoV*PVA*$_{623}$ and c) MoV*PVA*$_{873}$.	94
4.26	XRD diffractograms for a) MoV*cont*$_{pre}$, b) MoV*AA*$_{pre}$, c) MoV*MA*$_{pre}$ and d) MoV*PVA*$_{pre}$.	97
4.27	XRD diffractograms for a) MoV*cont*$_{873}$, b) MoV*AA*$_{873}$, c) MoV*MA*$_{873}$ and d) MoV*PVA*$_{873}$.	99
4.28	Concept diagram on removal of organic species from precursor.	102
4.29	SEM micrographs for a) MoV*cont*$_{873}$, b) MoV*AA*$_{873}$, c) MoV*MA*$_{873}$ and d) MoV*PVA*$_{873}$ taken at 15000 x magnification.	103
4.30	H_2-TPR profiles for a) MoV*cont*$_{873}$, b) MoV*AA*$_{873}$, c) MoV*MA*$_{873}$ and d) MoV*PVA*$_{873}$.	105
4.31	Changes of propane conversion and acrylic acid selectivity for the catalysts with feed compositions of $C_3H_8/O_2/N_2/H_2O$ = 8/10/37/45.	110

LIST OF ABBREVIATIONS

2θ	2 Theta
Å	Angstrom
AA	Adipic acid
BET	Brunauer-Emmett-Teller
E_r	Reduction activation energy
ICP-AES	Inductively Couple Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
MA	Maleic acid
Mo-V-O	Molybdenum-vanadium oxide
PCCS	Photon Cross Correlation Spectroscopy Analysis
PVA	Polyvinyl alcohol
SEM	Scanning Electron Microscopy
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TGA-DTG	Thermogravimetric analysis-derivative thermal gravimetric
TPR	Temperature-programmed reduction
XRD	X-ray diffraction

Table 4.26: The performance of $MoVO_x$ catalysts for propane oxidation with feed compositions of $C_3H_8/O_2/N_2/H_2O$ = 8/10/37/45.

Catalysts	Propane Conversion (%)	Acrylic Acid Selectivity (%)	Acrylic Acid yield (%)	Acetic Acid Selectivity (%)	CO_2 Selectivity (%)	CO Selectivity (%)
MoV*cont*$_{873}$	8.3	72.4	6.0	7.8	2.0	0.0
MoV*AA*$_{873}$	10.6	78.8	8.4	6.3	6.9	0.0
MoV*MA*$_{873}$	9.6	85.0	8.2	5.1	4.2	0.0
MoV*PVA*$_{873}$	7.2	90.1	6.5	1.7	4.2	0.0

CHAPTER 1

INTRODUCTION

1.1 The Catalysis Phenomenon

Humans have known about catalysis for many centuries, even though they knew nothing about the chemical process that was involved. The making of soap, the fermentation of wine to vinegar, and the leavening of bread are all processes involving catalysis. It was until 1836, a Swedish chemist Jöns Jakob Berzelius introduced the term ‘catalysis’. This word comes from two Greek terms, *kata* which stands for down, and *lysein*, which means to split or break. Berzelius assumed that catalysts possess special powers that can influence the affinity of chemical substances (Thomas and Thomas, 1996). In 1895, William Ostwald comes out with a definition of catalyst that still valid today: ‘A catalyst accelerates a chemical reaction without affecting the position of equilibrium’(Gates, 1992).

While it was formerly assumed that the catalyst remained unchanged in the course of reaction, it is now known that the catalyst is involved in chemical bonding with the reactants during the catalytic process (Hagen, 1999). Thus, catalysis is a cyclic process (Figure 1.1). The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give product, P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle

in its original state. Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle (Chorkendorff and Niemantsverdriet, 2003).

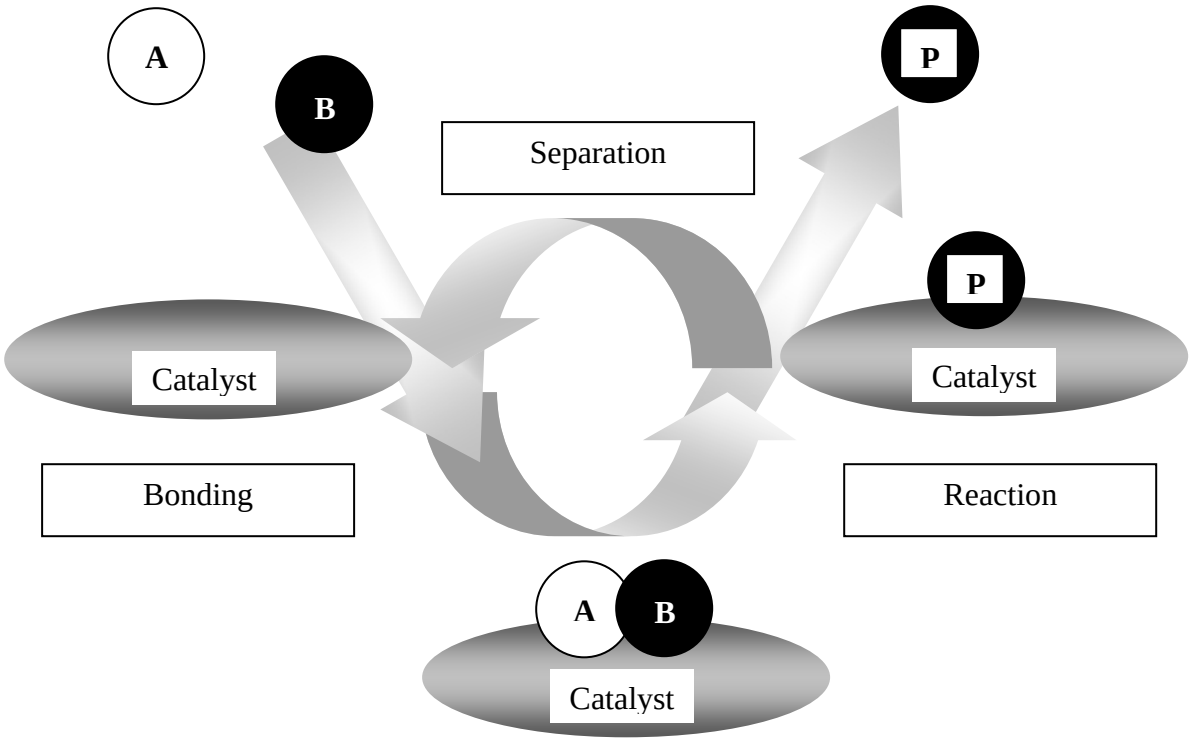

Figure 1.1: Catalytic cycle (Chorkendorff and Niemantsverdriet, 2003).

In theory, an ideal catalyst would not be consumed, but this is not the case in practise. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Hence, catalysts must be regenerated. Apart from accelerating reactions, catalysts have another important property: they can influence the selectivity of chemical reactions. This means that completely different

products can be obtained from a given starting material by using different catalyst systems (Hagen, 1999).

Catalysts can be in the form of gases, liquids or solids. Most industrial catalysts are liquids or solids, whereby the latter react only via their surface. The importance of catalysis in the chemical industry is shown by the fact that 75% of all chemicals are produced with the aid of catalysts; in newly developed processes, the figure is over 90%. Numerous organic intermediate products, required for the production of plastics, synthetic fibres, pharmaceuticals, dyes, resins and pigments, can only be produced by catalytic processes. Most of the processes involved in crude-oil processing and petrochemistry, such as purification stages, refining and chemical transformations, are also require catalysts (Hagen, 1999).

1.2 Functionality of Alkane in Selective Oxidation

Short chain alkanes (C_1–C_5) are considered as cheap raw material for petrochemical catalytic processes, in particular for the production of olefins, alcohols, aldehydes, anhydrides or acids. The selective oxidation of alkane has been largely studied in the past 20 years for two main reasons. The first one is economical since alkanes are much cheaper and more abundant than the corresponding olefins. The second one is fundamental since the way by which the alkane is activated and functionalised into an oxygenate remains unclear and challenging (Védrine *et al.*, 2003). Moreover, the only process based on alkanes that met industrial applications at this moment, is the

oxidation of *n*-butane to maleic anhydride on vanadylpyrophosphate, $(VO)_2P_2O_7$ based catalysts (Centi *et al.,* 1988). Therefore, the developments of new catalytic systems for the gas phase oxidation of short chain alkanes have special interest from both fundamental and industrial point of view.

Alkanes are characterized by the absence of reactive sites such as hydrogen atoms, which can be easily abstracted and double bonds. Therefore, they are largely less reactive than most of the possible reaction products. Thus the solid catalysts used in the selective activation and transformation of alkanes must have very special surface properties in order to control the reactivity, bulk catalyst properties, and structural characteristics of the catalyst (Centi *et al.*, 2001).

1.3 Acrylic Acid and its Current Manufacturing Process

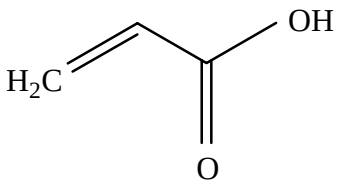

Figure 1.2: Structure of acrylic acid

Acrylic acid, CH_2=CHCOOH (Figure 1.2) which also known as propenoic acid, ethylene carboxylic acid, 2-propenoic acid or acroleic acid is a colourless liquid or solid, with an irritating odour at room temperature and pressure. It is miscible with water and most organic solvents (Mamedov, 1995).

Acrylic acid is the main precursor in the production of super absorbent polymers, materials which absorb many times their own weight in liquid and are mainly used in diapers or other hygienic products. In addition, acrylic acid has also been used in the manufacturing of plastics, bonding and hydrogels used for contact lenses (Mamedov, 1995).

The acrylic acid demand in the global market grows at 4.0 percent per year through 2004, to 2.554 billion pounds. In Malaysia, a large-scale acrylic acid facility has been built in Gebeng, Pahang by Petronas/BASF. This acrylic acid plant produces 1600,000 t/y of acrylic acid (http://www.petronas.com/).

This desirable product is synthesized using the most widely accepted process which is the vapour phase oxidation of propylene. This two-step process starts with propylene and goes through acrolein as intermediate to make acrylic acid. The involved reactions are shown as follow:

$$H_2C{=}CHCH_3 + O_2 \longrightarrow H_2C{=}CHCHO + H_2O \qquad \text{(Eq. 1.1)}$$

$$H_2C{=}CHCHO + \tfrac{1}{2}\, O_2 \longrightarrow H_2C{=}CHCOOH \qquad \text{(Eq. 1.2)}$$

1.4 Selective Oxidation of Propane to Acrylic Acid

In the coming century, the petrochemical industry will have to move to the direct use of natural gas as feedstock to fulfil the increasing demand in the intermediate