



UNIVERSITI PUTRA MALAYSIA

**MODIFICATION OF VANADIUM PHOSPHATE CATALYSTS
SYNTHESIZED VIA THE HYDROTHERMAL METHOD**

THEAM KOK LEONG

FS 2008 22



**MODIFICATION OF VANADIUM PHOSPHATE
CATALYSTS SYNTHESIZED VIA THE
HYDROTHERMAL METHOD**

THEAM KOK LEONG

**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

2008



**MODIFICATION OF VANADIUM PHOSPHATE CATALYSTS
SYNTHESIZED VIA THE HYDROTHERMAL METHOD**

By

THEAM KOK LEONG

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

July 2008



Especially Dedicated To

My Dearest Father & Mother

**Theam Lam Seng
Wong Yoke Ngoh**

My Beloved Women

Lim Ai Sun

My Dear Brother

Theam Kok Ming

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



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

**MODIFICATION OF VANADIUM PHOSPHATE CATALYSTS
SYNTHESIZED VIA THE HYDROTHERMAL METHOD**

By

THEAM KOK LEONG

July 2008

Chairman: Professor Taufiq Yap Yun Hin, PhD

Faculty: Science

Vanadium phosphorus oxide (VPO) catalysts synthesized via hydrothermal method were investigated. Some different dopants, Cr, Ni, Fe and Mn were used in the preparation of catalyst precursors, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. Besides, the mechanochemical treatments were introduced to the catalyst precursor with different milling durations in cyclohexane. All these modified precursors were subsequently transformed under reaction condition to give the active phase of VPO catalysts, $(\text{VO})_2\text{P}_2\text{O}_7$. Several techniques were used to characterize the physico-chemical properties of the catalysts such as XRD, BET, H_2 -TPR, redox titration, Laser Raman Spectroscopy and ICP-AES. The catalytic performance of the catalysts for selective oxidation of *n*-butane to maleic anhydride has been carried out by using a fixed bed microreactor (673 K, $\text{GHSV}=2400 \text{ h}^{-1}$). The results showed that the addition of dopants into the VPO catalysts had increased the surface area of the catalysts. Introduction of dopants had also induced the formation of V^{5+} phases as shown in XRD and Raman Spectra. However, a further extraction step with water at reflux temperature gave only catalysts with $(\text{VO})_2\text{P}_2\text{O}_7$. Interestingly, the doped samples showed a higher total amount of O_2 removed from the oxygen lattice of the catalyst. The doping and water



reflux treatment had affected the morphologies of the catalysts. The introduction of mechanochemical treatment produced materials with a mixture of V^{4+} and V^{5+} phases. SEM micrographs showed that the morphology of catalysts which milled in cyclohexane was in smaller platelet compared to the unmilled material. A significant high surface area was obtained for catalysts milled for 30 minutes ($40 \text{ m}^2\text{g}^{-1}$) and 60 minutes ($36 \text{ m}^2\text{g}^{-1}$). However, a longer milling duration drastically lowered the surface area due to the agglomeration of the particles as observed in the SEM micrographs. H_2 -TPR revealed two type of oxygen species removed for all the catalysts associated with V^{5+} and V^{4+} . The amount of active oxygen species removed associated with V^{4+} was significantly increased for 30 min mechano-treated. An increase of the oxygen species associated with V^{4+} phase which was correlated to the catalytic activity and a higher amount of oxygen species released associated to V^{5+} phase also contributed to the activity of the catalysts.

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

**MODIFIKASI TERHADAP MANGKIN VANADIUM FOSFAT DISEDIAKAN
DENGAN MENGGUNAKAN KAEDAH HIDROTERMA**

Oleh

THEAM KOK LEONG

Julai 2008

Pengerusi: Profesor Taufiq Yap Yun Hin, PhD

Fakulti: Sains

Vanadium fosforus oksida (VPO) yang dihasilkan dengan menggunakan kaedah hidroterma telah dikaji. Dopan yang berlainan seperti Cr, Ni, Fe dan Mn telah digunakan dalam penyediaan prekursor, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. Di samping itu, rawatan secara mekanokimia juga diberikan kepada prekursor mangkin dengan masa kisaran yang berlainan dalam siklohexana. Semua prekursor mangkin yang telah dimodifikasikan telah ditukar kepada mangkin VPO dalam keadaan reaksi untuk menghasilkan fasa yang aktif bagi mangkin VPO iaitu $(\text{VO})_2\text{P}_2\text{O}_7$. Beberapa teknik telah digunakan untuk mencirikan mangkin-mangkin yang dihasilkan seperti XRD, BET, H_2 -TPR, titratan redoks, Laser Raman Spektroskopi dan ICP-AES. Kecekapan mangkin-mangkin untuk pengoksidaan terpilih *n*-butana ke malik anhidrida juga telah dibuat dengan menggunakan mikroreaktor (673 K, GHSV=2400 h^{-1}). Keputusan eksperimen telah menunjukkan tambahan dopan-dopan ke dalam mangkin-mangkin VPO telah meningkatkan luas permukaan mangkin-mangkin tersebut. Penambahan dopan-dopan telah mengakibatkan penghasilan fasa-fasa V^{5+} . Walau demikian, langkah pengekstrakan pada suhu penyulingan hanya menghasilkan mangkin-mangkin yang mempunyai fasa $(\text{VO})_2\text{P}_2\text{O}_7$ sahaja. Menariknya, sampel-



sampel yang mempunyai dopan menghasilkan lebih banyak jumlah oksigen yang terlepas dari kekisi oksigen mangkin. Penedopan dan rawatan penyulingan air telah mempengaruhi morfologi mangkin-mangkin. Rawatan mekanokimia telah menghasilkan bahan-bahan yang mempunyai campuran fasa V^{4+} dan V^{5+} . Mikrograf SEM menunjukkan morfologi mangkin-mangkin yang dikisar dalam siklohexana menghasilkan kepingan yang lebih kecil berbanding dengan bahan yang tidak kisar. Luas permukaan yang tinggi telah diperolehi bagi mangkin-mangkin yang dikisar pada 30 minit ($40 \text{ m}^2 \text{ g}^{-1}$) dan 60 minit ($36 \text{ m}^2 \text{ g}^{-1}$). Walau demikian, masa kisanan yang lebih panjang megurangkan luas permukaan mangkin secara mendadak disebabkan oleh timbunan kepingan kecil yang dapat dilihat dalam mikrograf SEM. H_2 -TPR menunjukkan dua jenis oksigen dilepaskan bagi semua mangkin berkaitan dengan V^{5+} dan V^{4+} . Jumlah oksigen yang aktif yang telah dilepaskan berkaitan dengan V^{4+} telah bertambah bagi sampel yang dikisar 30 minit. Penambahan oksigen dari fasa V^{4+} akan meningkatkan aktiviti mangkin dan oksigen dari V^{5+} juga menyumbang kepada aktiviti mangkin-mangkin yang dihasilkan.

ACKNOWLEDGEMENTS

I would like to express my appreciation to Professor Dr. Taufiq Yap Yun Hin for all his generous guidance, dedicated supervision and precious suggestion throughout my Master degree journey. Without the help from Professor Taufiq-Yap, I will not be able to complete my Master research. It has been a wonderful experience to work under a professional researcher. This has enabled me to gather enough experience and knowledge about the research that I have been handling for four semesters. My pleasure thanks also to my co-supervisor Professor Dr. Mohd Zobir Hussein for his supervision and in valuable advice throughout this study.

Great appreciation and sincere thanks to all the laboratory assistant in Chemistry Department, especially Madam Choo Chai Syam for her help and advice in running the ICP-AES analysis. I also need to appreciate Mr. Tang Wen Jiuun, Mr Lee Kian Mun and other lab mates for their help and suggestions.

Last but not least, I would like to thank to my parents, my beloved women Miss Lim Ai Sun and my brother who given me tremendous support both financially and emotionally. Without their encouragement, I would not be able to carry on with this study.

Financial support from the Ministry of Science, Technology and Innovation (MOSTI) in the form of National Science Fellowship (NSF) is gratefully acknowledged.



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

Taufiq Yap Yun Hin, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zobir Hussein, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 11 September 2008



DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

THEAM KOK LEONG

Date: 25 August 2008



TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	ix
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xvi
CHAPTER	
1 INTRODUCTION	1
1.1 General Introduction to Catalysis	1
1.2 The Importance of Catalysis In Chemical Industries	2
1.3 Types of Catalysts	3
1.3.1 Homogeneous Catalyst	3
1.3.2 Heterogeneous Catalyst	4
1.3.3 General Principles of Heterogeneous Catalysis	5
1.4 Selective Oxidation	6
1.4.1 Dehydrogenation Reactions	7
1.4.2 Dehydrogenation and Oxygen Insertion	8
1.4.3 Fundamental Principles of Selective Heterogeneous Oxidation Catalysis	10
1.4.4 Applications of Selective Oxidation Catalysis	13
1.4.5 Key Factors in Selective Oxidation of Light Alkanes	14
1.5 Objectives of Research	16
2 LITERATURE REVIEW	17
2.1 Production of Maleic Anhydride	17
2.2 The Different Routes to Maleic Anhydride	18
2.2.1 Oxidation of Benzene	19
2.2.2 Oxidation of <i>n</i> -Butane	20
2.3 Technologies for the Production of Maleic Anhydride	20
2.4 Vanadium Phosphorus Oxide (VPO) Catalysts	26
2.4.1 Structure of Vanadium Phosphorus Oxide Phases	28
2.4.2 Reactivity Characteristics of the Vanadyl Pyrophosphate, (VO) ₂ P ₂ O ₇	29
2.5 Preparation of Vanadium Phosphorus Oxide Catalyst	31
2.6 Factor Affecting the Performance of Vanadium Phosphorus Oxide Catalyst	38
2.6.1 Influence of P : V Ratio on Catalysts Performance	38
2.6.2 Promoters	39
2.6.3 Mechanochemical Treatment	46
2.6.4 Activation and Conditioning Procedure	49



3	MATERIALS AND METHODS	52
3.1	Materials and Gases	52
3.2	Preparation of Vanadium Phosphorus Oxide Catalyst via Hydrothermal Method	53
3.3	Preparation of Doped Vanadium Phosphorus Oxide Catalysts	54
3.4	Mechanochemical Treatment to VOHPO ₄ ·0.5H ₂ O	55
3.5	Catalysts Characterization	56
3.5.1	X-Ray Diffraction (XRD) Analysis	56
3.5.2	Laser Raman Spectroscopy (LRS)	57
3.5.3	Chemical Analysis	57
3.5.4	Redox Titration	58
3.5.5	Scanning Electron Microscopy (SEM)	60
3.5.6	BET Surface Area Measurement	60
3.5.7	Temperature Programmed Reduction (TPR in H ₂ /Ar)	61
3.5.8	Catalytic Test	62
4	PHYSICO-CHEMICAL CHARACTERIZATION AND CATALYTIC TEST	64
4.1	Effect of Dopants on the Physico-chemical Properties of Vanadium Phosphorus Oxide Catalysts Synthesized via Hydrothermal Method	64
4.1.1	Phase Identification Using X-Ray Diffraction (XRD) Technique	65
4.1.2	BET Surface Area Measurement	74
4.1.3	Chemical Analysis	77
4.1.4	Laser Raman Spectroscopy (LRS)	80
4.1.5	Surface Morphology	83
4.1.6	Temperature Programmed Reduction (TPR in H ₂)	91
4.1.7	Selective Oxidation <i>n</i> -Butane Oxidation to Maleic Anhydride	100
4.2	Effect of Mechanochemical Treatment	104
4.2.1	Phase Identification Using X-Ray Diffraction (XRD) Technique	104
4.2.2	BET Surface Area Measurement	108
4.2.3	Chemical Analysis	109
4.2.4	Surface Morphology	110
4.2.5	Temperature Programmed Reduction (TPR in H ₂)	113
4.2.6	Selective Oxidation <i>n</i> -Butane Oxidation to Maleic Anhydride	117
5	CONCLUSIONS	123
	RECOMMENDATIONS AND SUGGESTIONS	126
	REFERENCES	127
	APPENDICES	137
	BIODATA OF STUDENT	142

LIST OF TABLES

Table		Page
1.1	Comparison of homogeneous and heterogeneous catalysts	5
1.2	Common oxide-catalysed selective oxidation reactions	7
1.3	Typical oxidation reactions catalyzed by heterogeneous catalysts	9
1.4	Major Catalytic Oxidation Process for the Synthesis of Monomers	14
2.1	Phases detected in VPO catalysts	34
4.1	XRD Data of undoped and doped catalysts	69
4.2	XRD Data of undoped and doped catalysts with water reflux treatment	73
4.3	BET surface area of undoped and doped catalysts	75
4.4	BET surface area of undoped and doped catalysts with water reflux treatment	76
4.5	Bulk composition, average oxidation states and percentage of V ⁴⁺ and V ⁵⁺ oxidation states present in undoped and doped catalysts	78
4.6	Bulk composition, average oxidation states and percentage of V ⁴⁺ and V ⁵⁺ oxidation states present in undoped and doped catalysts with water reflux treatment	79
4.7	Total number of oxygen atoms removed from the undoped and doped catalysts by reduction in H ₂ /Ar	95
4.8	Total number of oxygen atoms removed from the undoped and doped catalysts with water reflux treatment by reduction in H ₂ /Ar	99
4.9	The catalytic performance of undoped catalyst and catalysts doped with 0.5 % of Cr, Ni, Fe and Mn	100
4.10	The catalytic performance of undoped catalyst and doped catalyst with water reflux treatment	100



4.11	XRD data of unmilled and milled catalysts	108
4.12	BET surface area of unmilled and milled catalysts	109
4.13	Bulk composition, average oxidation states and percentage of V ⁴⁺ and V ⁵⁺ oxidation states present in undoped and doped catalysts	109
4.14	Total number of oxygen atoms removed from the unmilled and milled catalysts by reduction in H ₂ /Ar	115
4.15	Catalyst performance of unmilled and milled catalysts for the oxidation of <i>n</i> -butane	117

LIST OF FIGURES

Figure		Page
2.1	Maleic Anhydride process flowsheet: fixed bed reactor with Monsanto solvent collection system	24
2.2	ALMA fluidized bed process for the production of maleic anhydride	25
2.3	DuPont's circulating solids riser reactor	25
2.4	Geometrical structure of the $(VO)_2P_2O_7$ (1 0 0) surface	27
3.1	Scheme of fixed-bed microreactor for catalyst testing	63
4.1	X-ray diffraction patterns of undoped and doped precursors	66
4.2	X-ray diffraction patterns of undoped and doped catalysts	67
4.3	XRD patterns for undoped and doped precursors with water reflux treatment	71
4.4	XRD patterns for water reflux treated undoped and doped catalysts	72
4.5	LRS spectra of VPH and VPHR	80
4.6	LRS spectra of VPHCr1 and VPHCr1R	81
4.7	LRS spectra of VPHNi1 and VPHNi1R	82
4.8	LRS spectra of VPHMn0.5 and VPHMn0.5R	83
4.9	SEM micrograph of VPH	84
4.10	SEM micrograph of VPHR	84
4.11	SEM micrograph of VPHCr1	85
4.12	SEM micrograph of VPHCr1R	85
4.13	SEM micrograph of VPHNi1	86
4.14	SEM micrograph of VPHNi1R	86
4.15	SEM micrograph of VPHCr0.5	87
4.16	SEM micrograph of VPHCr0.5R	87

4.17	SEM micrograph of VPHNi0.5	88
4.18	SEM micrograph of VPHNi0.5R	88
4.19	SEM micrograph of VPHFe0.5	89
4.20	SEM micrograph of VPHFe0.5R	89
4.21	SEM micrograph of VPHMn0.5	90
4.22	SEM micrograph of VPHMn0.5R	90
4.23	TPR Profiles for undoped and doped catalysts	93
4.24	TPR Profiles for undoped and doped catalysts with water reflux treatment	98
4.25	Catalytic performance of the undoped and doped catalysts	101
4.26	Catalytic performance of undoped and doped catalysts with water reflux treatment	101
4.27	XRD patterns of unmilled and milled precursors	105
4.28	XRD patterns of unmilled and milled catalysts	106
4.29	SEM micrograph of VPH	111
4.30	SEM micrograph of VPH30C	111
4.31	SEM micrograph of VPH60C	112
4.32	SEM micrograph of VPH90C	112
4.33	SEM micrograph of VPH120C	113
4.34	TPR Profiles for unmilled and milled catalysts	114
4.35	<i>n</i> -Butane conversion as a function of surface area	118
4.36	<i>n</i> -Butane conversion as a function of amount of oxygen removed associated with V ⁴⁺	119
4.37	MA selectivity as a function of amount of oxygen removed associated with V ⁵⁺	120
4.38	MA selectivity as a function of V ⁵⁺ phases	121
4.39	<i>n</i> -Butane conversion as a function of V ⁵⁺ phases	123

LIST OF ABBREVIATIONS

BET	Brunauer Emmett Teller
FWHM	Full-Width at Half Maximum
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
ICP-AES	Inductive Couple Plasma – Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
LRS	Laser Raman Spectroscopy
MA	Maleic Anhydride
M/V	Metal dopant / Vanadium
P/V	Phosphorus / Vanadium
SEM	Scanning Electron Microscopy
T _{max}	Temperature at peak maximum
TCD	Thermal Conductivity Detector
TPR	Temperature Programmed Reduction
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy



CHAPTER 1

INTRODUCTION

1.1 General Introduction to Catalysis

The term “catalysis” was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions. A definition that is still valid today is due to Ostwald (1895): “A catalysts accelerates a chemical reaction without affecting the position of the equilibrium” (Hagen, 1999). Catalysis occurs when there is a chemical interaction between catalyst and the reactant-product system without changing the chemical nature of the catalyst except at the surface. This means that there is a surface interaction and does not penetrate into the interior of the catalyst (Bond, 1987). A catalyst usually works by forming chemical bonds to one or more reactants and thereby facilitating their conversion. Catalysis always involves a cycle of reaction steps, and the catalyst is converted from one form to the next, ideally without being consumed in the overall process (Gates, 1992).

In theory, an ideal catalyst would not be consumed, but this is not the case in practice. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalysts deactivation). Thus, catalyst must be regenerated or eventually replaced. 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. Industrially, this targeted reaction control is often even more important than the catalytic activity (Hagen, 1999).

1.2 The Importance of Catalysis in Chemical Industries

Catalysis is a multidisciplinary science. It is a combination of fundamental and applied science with major contributions from chemistry, physics and material science. Its technological importance lies in the tremendous achievements of this science to give humanity some cheap, highly convenient and outstanding materials (Gai, 2003) .

Catalysis is of crucial importance for the chemical industry, the number of catalysts applied in industry is very large and catalysts come in many forms, from heterogeneous catalysts in the form of porous solids over homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. Today, almost 70 % of all chemicals that are produced have been in contact with a catalyst, somewhere in their synthesis process. This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform. In principal, catalysis can be used to abate environmental pollution (Ruitenbeek, 1999).

Catalysts can be gases, liquids, or solids. Most industrial catalysts are in 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 development processes, the figure is over 90%.

Numerous organic intermediate products, required for the production of plastics, synthetic fibers, pharmaceuticals, dyes, crop-protection agents, resins, and pigments, can only be produced by catalytic processes (Hagen, 1999).

It is fascinating to note that many of these processes start out in the laboratory with a handful of research scientists experimenting with ideas. These are then transferred to a pilot plant and, if successful, to a full plant. The long-term advantage of this approach is that a new fundamental scientific knowledge base associated with a catalytic process is often developed (Gai, 2003). Catalysts have been successfully used in the chemical industry for more than 100 years, examples being the synthesis of sulfuric acid, the conversion of ammonia to nitric acid, and catalytic hydrogenation. Later developments include new highly selective multicomponent oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry. This was supplemented by new high-performance techniques for probing catalyst and elucidating the mechanisms of heterogeneous and homogeneous catalysis (Hagen, 1999).

1.3 Types of Catalysts

1.3.1 Homogeneous Catalysts

Catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysis. Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which, together with reactants, are molecularly dispersed in the reaction medium. Examples of homogeneous catalysts

include mineral acids and transition metal compounds (e.g., rhodium carbonyl complexes in oxo synthesis) (Hagen, 1999).

1.3.2 Heterogeneous Catalysts

Catalysis occurring in the presence of more than one phase is called heterogeneous catalysis. Most practically important examples of heterogeneous catalysis involved solid catalysts and gas phase reactants (Gates, 1992). Heterogeneous catalysts are frequently defined as solids or mixtures of solids which accelerate chemical reaction without themselves undergoing changes. This definition however is too limited in scope, considering that the properties of catalysts can change significantly with use, with service lives that vary from minutes to years. Hence, the overall chemical reactions concern the gas-phase species. The solid is involved in the formation of intermediate species and the influence of the solid does not effectively extend more than an atomic diameter into the gas phase. The direct involvement of atoms below the topmost layers is not usually possible (Campanati *et al.*, 2003). Examples of heterogeneous catalyst are Pt/Rh nets for the oxidation of ammonia to nitrous gases (Ostwald process) and amorphous or crystalline aluminosilicates for cracking petroleum fraction (Hagen, 1999). Table 1.1 summarizes the advantages and disadvantages of the two classes of catalyst.

Table 1.1. Comparison of homogeneous and heterogeneous catalysts
(Hagen, 1999)

	Homogeneous	Heterogeneous
<i>Effectivity</i>		
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Diffusion problems	practically absent	present (mass-transfer-controlled reaction)
Reaction conditions	mild (323-473 K)	severe (often >523 K)
Applicability	limited	wide
Activity loss	irreversible reaction with products (cluster formation); poisoning	sintering of the metal crystallites; poisoning
<i>Catalyst properties</i>		
Structure/stichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high
Catalyst separation	sometimes laborious (chemical decomposition, distillation, extraction)	fixed-bed: unnecessary suspension: filtration
Catalyst recycling	possible	unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	high	low

1.3.3 General Principles of Heterogeneous Catalysis

The fundamental processes occurring when a gas mixture is passed through a catalytic reactor may be described as follows:

Step 1: Diffusion of the reactants to the active site. This term covers boundary layer diffusion and pore volume diffusion.

Step 2: Adsorption of at least one reactant on the catalyst surface.

Step 3: Surface reaction.

Step 4: Desorption of the products.

Step 5: Diffusion away from the active site.

The rates for steps 1 and 5 are determined by diffusion coefficients and porosity, whereas steps 2-4 are determined by chemical phenomena occurring at the molecular scale. Any one of these steps can represent the slow step of the overall process (Hodnett, 2000).

1.4 Selective Oxidation

Interest in the transformation of light alkanes to valuable oxygenated compounds and olefins by means of oxidation has been growing in recent years due to the possibility of developing new processes of lower environmental impact and of lower cost. Many papers have been published which analyzed the fundamental aspects related to the oxidative activation and transformation of light alkanes over heterogeneous catalysts. The general picture that can be drawn on the basis of the most important factors which are examined in these reviews clearly shows that the problem of paraffin conversion and selectivity to the desired product has to be solved within a complex framework of inter-related aspects (Cavani and Trifirò, 1999).

Selective oxidation reactions can be divided into two categories, one involves only dehydrogenation and the other involves both dehydrogenation and oxygen insertion into the hydrocarbon molecule. Table 1.2 shows the common oxide-catalyzed selective oxidation reactions and the catalysts (Kung, 1986).

Table 1.2. Common oxide-catalysed selective oxidation reactions (Kung, 1986)

Reaction	Catalyst
Dehydrogenation	
Ethylbenzene → Styrene	Fe-Cr-K-O
Isooctane, Isopentene → Isoprene	Sn-Sb-O
Butane, Butene → Butadiene	Bi-Mo-O, promoted Fe-O, promoted V-O
Methanol → Formaldehyde	Fe-Mo-O, MoO ₃
Dehydrogenation and Oxygen Insertion	
Butane, Butene → Maleic Anhydride	V-P-O
Propene → Acrolein	Bi-Mo-O
Propene and NH ₃ → Acetonitrile	Bi-Mo-O, U-Sb-O, Fe-Sb-O, BI-Sb-Mo-O
propene → acrolein, acrylic acid, acetaldehyde	Co-Mo-Te-O, Sb-V-Mo-O
benzene → maleic anhydride	V-P-O, V-Sb-P-O
<i>o</i> -xylene, naphthalene → phthalic anhydride	promoted V-O
methane → methanol, formaldehyde	Mo-O, V-O
ethylene → ethylene oxide	Fe-Mo-O, promoted Ag
methyl ethyl ketone → biacetyl	Co-O (promoted by Ni, Cu)
methyl ethyl ketone → acetaldehyde, acetic acid	V-Mo-O

1.4.1 Dehydrogenation Reactions

The reactions in which a hydrocarbon molecule is converted into a more unsaturated hydrocarbon by breaking carbon-hydrogen bonds and forming C=C bonds. In the absence of oxidants, hydrogen is a byproduct. In such cases, the reactions are run at rather high temperatures (above 500 °C) because the thermodynamic equilibrium