



UNIVERSITI PUTRA MALAYSIA

**THE EFFECTS OF DOPANTS ON THE PHYSICO-CHEMICAL
PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS**

TAN KIAN PENG

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**DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA**

2003



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By

TAN KIAN PENG

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS**

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Vanadium phosphorus oxide (VPO), is a commercial catalyst for selective oxidation of butane to maleic anhydride. The nature of the oxidant of the doped and undoped $(VO)_2P_2O_7$ catalysts derived from (i) VPO, reaction of V_2O_5 with H_3PO_4 in isobutanol and (ii) VPD, reaction of $VOPO_4 \cdot 2H_2O$ with isobutanol were investigated. Metal cations, namely of sodium, potassium, magnesium and bismuth, were added as dopants into $(VO)_2P_2O_7$ lattice.

From the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis, the catalysts which have gone through a series of redox reaction do not produce the original morphology of $(VO)_2P_2O_7$.

The results indicated that the addition of dopants lowered the Brunauer-Emmet-Teller (BET) surface area of vanadyl pyrophosphate catalysts, except Bi-doped VPD catalysts. All the doped VPO and VPD catalysts have been shown a vanadyl pyrophosphate phase with three distinct peaks at 22.9° , 28.4° and 29.3° in X-ray Diffraction (XRD) analysis. The Bi-doped VPO and VPD catalysts had significantly



shifted the first reduction peak to a lower temperature in H₂-TPR analysis. The introduction of Bi have modified the (VO)₂P₂O₇ matrix and mobility of these catalyst increased. It can be seen from TPRn analysis where VPDBi1 increased the selectivity of butene and butadiene (selective products) and decreased the selectivity of CO and CO₂ (unselective products).



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**KESAN DOPANT TERHADAP PENCIRIAN FIZIKO-KIMIA MANGKIN
VANADIL PIROFOSFAT**

Oleh

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Vanadium fosforus oksida (VPO), adalah mangkin komersial untuk pengoksidaan selektif butana kepada maleik anhidrida. Sifat pengoksidaan bagi mangkin $(VO)_2P_2O_7$ yang dimodifikasi dan tidak dimodifikasi disediakan melalui (i) VPO, tindak balas V_2O_5 dengan H_3PO_4 dalam isobutanol dan (ii) VPD, tindak balas $VOPO_4 \cdot 2H_2O$ dengan isobutanol telah dikaji. Kation logam, seperti natrium, kalium, magnesium and bismuth telah ditambahkan sebagai dopant dalam kekisi $(VO)_2P_2O_7$.

Daripada analisis mikroskop elektron imbasan (SEM) and mikroskop elektron transmisi (TEM), mangkin di mana telah melalui satu siri keadaan tindakan redoks tidak lagi menghasilkan morfologi $(VO)_2P_2O_7$ yang asal.

Keputusan menunjukkan bahawa penambahan dopant telah menurunkan luas permukaan Brunauer-Emmet-Teller (BET) bagi mangkin vanadil pirofosfat kecuali mangkin VPD yang dimodifikasi dengan Bi. Semua mangkin VPO dan VPD yang dimodifikasi menunjukkan fasa vanadil pirofosfat dengan tiga puncak ketara iaitu 22.9° , 28.4° and 29.3° dalam pembelauan sinar-X (XRD). Mangkin VPO dan VPD



yang dimodifikasi dengan Bi telah mengalihkan puncak penurunan pertama kepada suhu yang lebih rendah secara ketara dalam analisis H₂-TPR. Kehadiran Bi telah memodifikasikan matriks (VO)₂P₂O₇ dan menambahkan mobiliti mangkin tersebut. Ini dapat dilihat daripada analisis TPRn di mana VPDBi1 telah meningkatkan selektiviti butena dan butadiena (produk selektif) dan mengurangkan selektiviti CO dan CO₂ (produk tidak selektif).

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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.



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TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGEMENTS	vi
APPROVAL	vii
DECLARATION FORM	ix
LIST OF TABLES	xiii
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xviii
 CHAPTER	
1	INTRODUCTION
1.1	Definition of Catalysis and Catalyst 1
1.1.1	Classification of Catalytic Systems 3
1.1.2	Catalysts for Industrial Processes: General Requirements 4
1.2	Catalytic Oxidation Processes 5
1.3	Selectivity: A Special Requirement in Oxidation Catalysts 7
2	LITERATURE REVIEW
2.1	Maleic Anhydride 10
2.2	Historical Development of Maleic Anhydride Synthesis 12
2.3	Processes For the Production of Maleic Anhydride from <i>n</i> -Butane 14
2.4	Vanadium Phosphorus Oxide Catalyst 20
2.5	Preparation of Vanadium Phosphorus Oxide Catalyst 27
2.5.1	Influence of Reducing Agent and Solvent 28
2.5.2	Influence of P:V Ratio 30
2.5.3	Activation 32
2.6	Physical and Chemical Properties of Vanadium Phosphorus Oxide Catalyst 37
2.7	Doped Vanadium Phosphorus Oxide Catalyst 38
2.8	Catalyst Characterisation 45
2.9	Scope of Study 53
3	METHODOLOGY
3.1	Preparation of Bulk Vanadyl Pyrophosphate Catalyst 55
3.1.1	VPO Route via $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ Precursor 55
3.1.2	VPD Route via $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ Precursor 56



3.2	Physical and Chemical Properties of Vanadyl Pyrophosphate Catalysts	57
3.2.1	Reduction in N ₂	57
3.2.2	Reduction-Oxidation-Reduction Pretreatment	57
3.3	Preparation of Doped Vanadyl Pyrophosphate Catalysts	58
3.3.1	VPO Route via VOHPO ₄ ·0.5H ₂ O Precursor	58
3.3.2	VPD Route via VOPO ₄ ·2H ₂ O Precursor	59
3.4	Materials and Gases	60
3.5	Catalysts Characterisation	61
3.5.1	Surface Area Measurement	61
3.5.2	Elemental Analysis	61
3.5.3	Redox Titration Method	61
3.5.4	X-Ray Diffraction (XRD) Analysis	62
3.5.5	Scanning Electron Microscopy (SEM)	62
3.5.6	Transmission Electron Microscopy (TEM)	63
3.5.7	Temperature Programmed Techniques	63
	3.5.7.1 Temperature Programmed Desorption (TPD) of Oxygen	63
	3.5.7.2 Temperature Programmed Reduction (TPR) in H ₂ /Ar	64
	3.5.7.3 Temperature Programmed Reaction (TPRn)	64
4	PHYSICAL AND CHEMICAL PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS	
4.1	Introduction	65
4.2	BET surface area measurement	66
4.3	Chemical Analysis and Redox Titration	67
4.4	Phases Identification	68
4.5	Microstructure of the Catalysts	70
	4.5.1 Scanning Electron Microscopy (SEM)	73
	4.5.2 Transmission Electron Microscopy (TEM)	78
5	EFFECT OF DOPANTS TO VANADYL PYROPHOSPHATE CATALYSTS	
5.1	Introduction	84
5.2	BET surface area measurement	84
5.3	Chemical Analysis and Redox Titration	86
5.4	Phases Identification and Plate Thickness	88
5.5	Surface Morphology	103
5.6	Oxygen Desorption	109
	5.6.1 Na-doped VPO and VPD Catalysts	114
	5.6.2 K-doped VPO and VPD Catalysts	116
	5.6.3 Mg-doped VPO and VPD Catalysts	117
	5.6.4 Bi-doped VPO and VPD Catalysts	118
5.7	Temperature Programmed Reduction (TPR)	119
	5.7.1 Na-doped VPO and VPD Catalysts	128
	5.7.2 K-doped VPO and VPD Catalysts	129
	5.7.3 Mg-doped VPO and VPD Catalysts	130



5.7.4	Bi-doped VPO and VPD Catalysts	131
5.8	Temperature Programmed Reaction (TPRn)	132
5.9	Conclusions	140
6	SUMMARY AND CONCLUDING REMARKS	
6.1	Introduction	142
6.2	Summary	142
	REFERENCES	144
	APPENDICES	154
	BIODATA OF THE AUTHOR	157



LIST OF TABLES

Table		Page
1.1	Classification of heterogeneous catalysts (less important functions in parentheses) (Bond, 1987)	4
1.2	Some Common Oxide Catalysed Selective Oxidation Reactions (Kung, 1986)	9
2.1	Uses of Maleic Anhydride in the United States, 2000 (Felthouse <i>et al.</i> , 2001).	11
2.2	Total world production and consumption of maleic anhydride (x 1000 metric tons) (Ruitenbeek, 1999)	11
2.3	World maleic anhydride capacity by reactor type (Felthouse <i>et al.</i> , 2001).	19
2.4	Typical applications of X-ray diffraction methods.	50
4.1	BET data for vanadyl pyrophosphate catalysts after undergoing a series of redox reaction.	66
4.2	Chemical properties, average vanadium valence and percentages of V ⁴⁺ and V ⁵⁺ oxidation states present in vanadyl pyrophosphate catalysts after a series of redox reaction with fresh VPO and VPD catalysts.	68
5.1	BET data for undoped and doped VPO and VPD catalysts.	85
5.2	Chemical properties, average vanadium valence and percentages of V ⁴⁺ and V ⁵⁺ oxidation states present in undoped and doped VPO and VPD catalysts.	88
5.3	XRD data of undoped and doped VPO and VPD precursors.	94
5.4	XRD data of doped VPO and VPD catalysts with the undoped catalyst.	96
5.5	Amount of Oxygen Desorbed and Desorption Activation Energies Obtained by Temperature Programmed Desorption from undoped and doped VPO catalysts.	112
5.6	Amount of Oxygen Desorbed and Desorption Activation Energies Obtained by Temperature Programmed Desorption from undoped and doped VPD catalysts.	113



5.7	Total Number of Oxygen Atoms Removed from the undoped VPO and VPD Catalysts by Reduction in H ₂ /Ar.	121
5.8	Total Number of Oxygen Atoms Removed from the Na-doped VPO and VPD Catalysts by Reduction in H ₂ /Ar.	124
5.9	Total Number of Oxygen Atoms Removed from the K-doped VPO and VPD Catalysts by Reduction in H ₂ /Ar.	125
5.10	Total Number of Oxygen Atoms Removed from the Mg-doped VPO and VPD Catalysts by Reduction in H ₂ /Ar.	126
5.11	Total Number of Oxygen Atoms Removed from the Bi-doped VPO and VPD Catalysts by Reduction in H ₂ /Ar.	127
5.12	The <i>m/z</i> ratios followed to identify the compounds cited.	132
5.13	Selectivity of products from TPRn of <i>n</i> -butane over VPD, VPDMg1 and VPDBi1.	138



LIST OF FIGURES

Figure	Page
2.1 Structure of maleic anhydride.	10
2.2 Schematic flow diagram of the Huntsman fixed-bed maleic anhydride process (MA = maleic anhydride) (Felthouse <i>et al.</i> , 2001).	16
2.3 DuPont recirculating-solids process for the production of THF (tetrahydrofuran) from <i>n</i> -butane via maleic anhydride (Lerou and Mills, 1993).	18
2.4 Layered structure of $(VO)_2P_2O_7$	21
2.5 Idealized vanadyl pyrophosphate structure in (100) plane. (Cavani <i>et al.</i> , 1985a).	22
2.6 Diagram of phase transformations among vanadium phosphorus oxide catalysts and precursors (Zhi-Yang and Schrader, 1999).	23
2.7 Scheme of proposed evolution of the VPO catalyst with activation time (Abon <i>et al.</i> , 1995)	24
2.8 The four types of adsorption isotherm usually found by nitrogen adsorption (Leofanti <i>et al.</i> , 1998).	47
2.9 The four hysteresis shapes of adsorption isotherm usually found by nitrogen adsorption (Leofanti <i>et al.</i> , 1998).	47
4.1 XRD diffractogram for VPO_{redN} and VPD_{redN} with fresh VPO and VPD catalysts.	69
4.2 XRD diffractogram for VPO_{redH1} , VPO_{ox} and VPO_{redH2} with VPO fresh catalyst.	71
4.3 XRD diffractogram for VPD_{redH1} , VPD_{ox} and VPD_{redH2} with VPD fresh catalyst.	72
4.4 SEM micrographs of (a) VPO and (b) VPD catalysts.	74
4.5 SEM micrographs of (a) VPO_{redN} and (b) VPD_{redN} catalysts.	75
4.6 SEM micrographs of (a) VPO_{redH1} , (b) VPO_{ox} and (c) VPO_{redH2} catalysts.	76
4.7 SEM micrographs of (a) VPD_{redH1} , (b) VPD_{ox} and (c) VPD_{redH2} catalysts.	77

4.8	TEM micrographs for undoped catalysts, (a) VPO and (b) VPD.	79
4.9	Scheme of morphology change.	80
4.10	TEM micrographs of (a) VPO _{redN} and (b) VPD _{redN} catalysts.	81
4.11	TEM micrographs of (a) VPO _{redH1} , (b) VPO _{ox} and (c) VPO _{redH2} catalysts.	82
4.12	TEM micrographs of (a) VPD _{redH1} , (b) VPD _{ox} and (c) VPD _{redH2} catalysts.	83
5.1	Undoped precursors prepared by VPO and VPD routes with JCPDS reference.	90
5.2	XRD diffractograms of doped VPO precursors.	91
5.3	XRD diffractograms of doped VPD precursors.	92
5.4	Undoped catalysts prepared by VPO and VPD routes with JCPDS reference.	98
5.5	XRD diffractograms of doped VPO catalysts.	99
5.6	XRD diffractograms of doped VPD catalysts.	100
5.7	SEM micrographs for Na-doped catalysts, (a) VPONa1, (b) VPONa3, (c) VPDNa1 and (d) VPDNa3.	104
5.8	SEM micrographs for K-doped catalysts, (a) VPOK1, (b) VPOK3, (c) VPDK1 and (d) VPDK3.	105
5.9	SEM micrographs for Mg-doped catalysts, (a) VPOMg1, (b) VPOMg3, (c) VPDMg1 and (d) VPDMg3.	106
5.10	SEM micrographs for Bi-doped catalysts, (a) VPOBi1, (b) VPOBi3, (c) VPDBi1 and (d) VPDBi3.	107
5.11	O ₂ -TPD profiles for doped VPO catalysts with undoped catalyst.	110
5.12	O ₂ -TPD profiles for doped VPD catalysts with undoped catalyst.	111
5.13	TPR profiles for doped VPO catalysts with undoped catalyst.	122
5.14	TPR profiles for doped VPD catalysts with undoped catalyst.	123
5.15	Production of but-1-ene by TPR _n of <i>n</i> -butane over the VPD, VPDMg1 and VPDBi1	133



5.16	Production of but-1,3-diene by TPRn of <i>n</i> -butane over the VPD, VPDMg1 and VPDBi1	134
5.17	Production of furan by TPRn of <i>n</i> -butane over the VPD, VPDMg1 and VPDBi1	135
5.18	Production of CO by TPRn of <i>n</i> -butane over the VPD, VPDMg1 and VPDBi1	136
5.19	Production of CO ₂ by TPRn of <i>n</i> -butane over the VPD, VPDMg1 and VPDBi1	137



LIST OF ABBREVIATIONS

ASAP	Analysis of Surface Area and Porosity
BET	Brunauer-Emmet-Teller
CCD	Charge Coupled Device
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
FWHM	Full Width of Half Maximum
ICP-AES	Inductively Coupled Plasma-Absorption Emission Spectroscopy
JEOL	Japan Electron Optics Laboratory
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee Powder Diffraction Standards
MA	Maleic Anhydride
MS	Mass Spectrometer
TCD	Thermal Conductivity Detector
THF	Tetrahydrofuran
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
TPR _n	Temperature Programmed Reaction
XRD	X-ray Diffraction



CHAPTER 1

INTRODUCTION

1.1 Definition of Catalysis and Catalyst

Although nowadays catalytic processes have already been applied for a long period of time, it was not until 1836 that Berzelius introduced the term 'catalysis' (Bond, 1987). The word catalysis comes from two Greek words, the prefix *cata-*, meaning down, and the verb *lysein*, meaning to split or break. By 'awaking affinities which are asleep', a catalyst breaks down the normal forces which inhibit the reactions of molecules.

Later, in 1895, William Ostwald was the first to write down a definition of a catalyst: 'A catalyst is a substance that change the rate of a chemical reaction without itself appearing in the products'. A material scientist might describe a catalyst as a device for chemical transformation (Gates, 1995): Reactant molecules flow into the device and are transformed into product molecules that flow out; energy may be consumed or liberated. It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald's description: 'A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed'.



Catalysts are among the most important technological materials, being used in the manufacture of chemicals, fuels, foods, clothing, pharmaceuticals, and materials such as organic polymers (Gates, 1992). The value of the goods manufactured in the United States in processes that at some stage involve catalysis is about \$1 trillion annually; the catalysts used in these processes cost only a few tenths of a percent of the value of the products.

The solid catalysts are far more important than the others in large-scale processes for conversion of chemicals, fuels, and pollutants (Satterfield, 1991). Many solid elements and compounds, including metals, metal oxides, and metal sulfides, are catalysts. A few industrial catalysts are simple in composition, for example, Raney nickel, used for hydrogenation of fats, and γ - Al_2O_3 , used for dehydration of ethanol to make ethylene. However, the typical industrial catalyst consists of a variety of components and phases and is so complex that the structure is not well understood.

The activity of a catalyst is a measure of how fast it catalyses a reaction. The selectivity is a measure of how well the catalyst directs the conversion to desired products; a highly selective catalyst is much more active for the desired reactions. The stability of a catalyst is a measure of how fast it loses activity or selectivity in operation. The regenerability is a measure of how effectively a deactivated catalyst can be brought back to a state of high activity and selectivity (Gates, 1995).



1.1.1 Classification of Catalytic Systems

In fact, it is possible to divide catalytic systems into two distinct categories (Bond, 1987). When the catalyst is of the same phase as the reactants and no phase boundary exists, it is a homogeneous catalysis. This may take place either:

- (i) in the gas phase, as, for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or
- (ii) in the liquid phase, as when acids and bases catalyse the mutarotation of glucose.

When a phase boundary separates the catalyst from the reactants, it is a heterogeneous catalysis. Catalysis is essentially a chemical phenomenon. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. Heterogeneous catalysis are concerned with the specific chemical properties of the surface of the chosen substance. These of course reflect the chemistry of the bulk solid, and some useful insight into the catalytic activities of surfaces is gained from knowledge of the bulk properties of the solid. Table 1.1 shows the classification of heterogeneous catalysts. For catalysis to occur, there must be a chemical interaction between catalyst and the reactant-product system, but this interaction must not change the chemical nature of the catalyst except at the surface.

Table 1.1: Classification of heterogeneous catalysts (less important functions in parentheses) (Bond, 1987)

Class	Functions	Examples
Metals	hydrogenation dehydrogenation hydrogenolysis (oxidation)	Fe, Ni, Pd, Pt, Ag
Semiconducting oxides and sulfides	oxidation dehydrogenation desulfurization (hydrogenation)	NiO, ZnO, MnO ₂ , Cr ₂ O ₃ , Bi ₂ O ₃ -MoO ₃ , WS ₂
Insulator oxides	dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Acids	polymerization isomerization cracking alkylation	H ₃ PO ₄ , H ₂ SO ₄ , SiO ₂ -Al ₂ O ₃ , zeolites

1.1.2 Catalysts for Industrial Processes: General Requirements

The criteria for an industrially successful catalyst are very stringent. First, the catalyst must be able to effect the desired reaction at an acceptable rate under conditions of temperature and pressure that are practicable (Anderson, 1975). Chemical technology has advanced to the point where temperatures as high as 1600 K and pressures up to 350 atm (35 MPa). If however good yields can be obtained at low temperatures and pressures, then there is every incentive to find a catalyst that will operate under the mildest possible conditions, since the use of extreme conditions is very costly. It is

concurrently important that side-reactions are minimal, especially those leading to poisoning or deactivation through carbon deposition on catalyst.

Second, the catalyst must be able to sustain the desired reaction over prolonged periods: in some processes, a catalyst life of several years is not uncommon, and is economically necessary. Clearly the longer it lasts, the smaller will be the contribution that its initial cost makes to the overall cost of the process. Initial cost is rarely of over-riding importance: it is usually cheaper in the long run to use an expensive catalyst that will last a long time than a cheap one that has to be replaced frequently.

1.2 Catalytic Oxidation Processes

It was in the first decades of the 20th century, however, that catalytic processes began to appear in significant numbers, though the first heterogeneously-catalysed process, the "contact process", had begun to render obsolescent the chamber process some twenty years earlier (Chinchen *et al.*, 1987). More than 60 % products by catalytic route in chemical industry are by oxidation and the world market for oxidation catalysts may be estimated as around 200-250 million US dollars, about half of which are in Europe (Centi, 1993a).

Many industrial catalytic direct oxidation processes have been successfully developed and introduced since the "contact" process, mainly with the objective of